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Probing the Role of Steric and Electronic Effects on the Synthesis, Properties,
and Reactivity of Low Oxidation State Rare-Earth and Actinide Metal Complexes

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Joseph Quangdai Nguyen

Dissertation Committee:
Distinguished Professor Emeritus William J. Evans, Chair
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2025

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DEDICATION

This dissertation is dedicated to
my parents, Quang and Julie,
my partner, Shirley,
and the friends that I made along the way.

Thank you for your love, support, and encouragement.

“A month in the laboratory can often save an hour in the library.”

Frank Westheimer

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Publications

- 1.) “Cooperative Dinitrogen Capture by a Diboraanthracene/Samarocene Pair” Song Xu, Laura Essex, Joseph Q. Nguyen, Joseph W. Ziller, W. Hill Harman,* and William J. Evans,* *Dalton Trans.* **2021**, 50, 15000–15002. DOI: 10.1039/D1DT03220H.
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- 3.) “Accessing Lanthanide Metallocene Two-Electron Reduction Chemistry Using 2,2'-Bipyridine” Cary R. Stennett, Joseph Q. Nguyen, Joseph W. Ziller, and William J. Evans,* *Organometallics* **2023**, 42, 696–707. DOI: 10.1021/acs.organomet.3c00074.
- 4.) “Replacing Trimethylsilyl with Triisopropylsilyl Provides Crystalline (C₅H₄SiR₃)₃Th Complexes of Th(III) and Th(II)” Joseph Q. Nguyen, Lauren M. Anderson-Sanchez, William N. G. Moore, Joseph W. Ziller, Filipp Furche,* and William J. Evans,* *Organometallics* **2023**, 42, 2927–2937. DOI: 10.1021/acs.organomet.3c00343.
- 5.) “Phenylsilyl-Substituted Tetramethylcyclopentadienide Uranium Chemistry: Magnesocenes vs. Grignard Reagents” Joseph Q. Nguyen,[†] Olaf Nachtigall,[†] Brynn N. Turpin, Joseph W. Ziller, and William J. Evans,* *Organometallics* **2023**, 42, 3474–3482. DOI: 10.1021/acs.organomet.3c00420.
- 6.) “Investigating Steric and Electronic Effects in the Synthesis of Square Planar 6d¹ Th(III) Complexes” Joseph Q. Nguyen, Justin C. Wedal, Joseph W. Ziller, Filipp Furche,* and William J. Evans,* *Inorg. Chem.* **2024**, 63, 6217–6230. DOI: 10.1021/acs.inorgchem.3c04462.
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- 9.) “Synthesis and Structure of Heteroleptic $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{tBu})]^{1-}$ Uranium(III) Compounds” Joseph Q. Nguyen,[†] Olaf Nachtigall,[†] Austin J. Ryan, Brynn N. Turpin, Joseph W. Ziller, and William J. Evans,* *Organometallics* **2024**, 43, 2767–2776. DOI: 10.1039/D4SC03977G.
- 10.) “Synthesis and characterization of borohydride rare-earth complexes supported by 2-pyridinemethanamido ligands and their application in the ring-opening polymerization of cyclic esters” Maxime Beauvois, Frédéric Capet, Joseph Q. Nguyen, Joseph W. Ziller, William J. Evans, Yohan Champouret,* and Marc Visseaux,* Lauren M. Anderson-Sanchez, Joseph W. Ziller, and William J. Evans,* *Dalton Trans.* **2025**, 54, 1433–1455. DOI: 10.1039/D4DT02522A.
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- 12.) “A Linear Metallocene of Sc(II) Supported by $[\text{C}_5\text{Me}_4\text{SiMe}_2\text{tBu}]^{1-}$ Ligands” Joseph Q. Nguyen, Ahmadsreza Rajabi, Anthony Wang, Joseph W. Ziller, Filipp Furche,* and William J. Evans,* *in preparation*.
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- 14.) “Triisopropylsilylcyclopentadienyl Ligands Also Stabilize Non-Traditional +2 Rare-Earth Metal Ions” Joseph Q. Nguyen, Jonah P. Stiel, Joshua D. Queen, Brynn N. Turpin, Joseph W. Ziller, and William J. Evans,* *in preparation*.
- 15.) “Synthesis and Structure of the THF, 2,2'-bipyridine, and 2,2':6',2''-terpyridine Adducts of Bis(trimethylsilyltetramethylcyclopentadienyl) Eu, Sm, and Yb Metallocenes.” Joseph Q. Nguyen, Allison K. Bernardo, Gabija Navickaite, Joseph W. Ziller, and William J. Evans,* *in preparation*.

Presentations

- 1.) ACS National Meeting, San Francisco, California, August 2023, “Importance of Ligand Environment in the Synthesis of New Th(II) Complexes”
- 2.) ACS National Meeting, San Diego, California, March 2022, “Synthesis of Square Planar Th(III) Complexes”

ABSTRACT OF THE DISSERTATION

Probing the Role of Steric and Electronic Effects on the Synthesis, Properties,
and Reactivity of Low Oxidation State Rare-Earth and Actinide Metal Complexes

by

Joseph Quangdai Nguyen

Doctor of Philosophy in Chemistry

University of California, Irvine, 2025

Professor William J. Evans, Chair

This Dissertation details a series of investigations into the factors that influence the isolation, properties, and reactivity of low oxidation state rare-earth and actinide metal coordination complexes through exploratory synthesis. Specifically, the role that both steric and electronic effects play on rare-earth and actinide metal chemistry is explored through subtle variations in the ligands employed. Chapter 1 provides an introduction into the landscape of low oxidation state *f*-element chemistry in the context of this work and describes the importance of a better understanding of how steric and electronic effects influence the isolation and properties of low oxidation state rare-earth and actinide metal coordination complexes. Chapter 2 describes the unusual and unexpected products isolated when the *pentamethylcyclopentadienide* reagent used in the synthesis of $(C_5Me_5)_2Sm(THF)_2$ starting from $SmI_2(THF)_2$ is replaced with the chemically similar *tetramethylcyclopentadienide* reagent. Chapter 3 describes the synthesis of tris(mono-silylcyclopentadienyl) Th(III) and Th(II) complexes not available with the tri-methylsilyl substituted ligand, $(C_5H_4SiMe_3)^{1-}$, that can be synthesized with the tri-isopropylsilyl substituted $(C_5H_4Si^iPr_3)^{1-}$ ligand. The dramatic increase in thermal stability as a result of this substitution

ultimately led to the crystallographic characterization of these rare classes of thorium complexes. Chapter 4 explores a different Th(III) system, specifically the tetrakis(aryloxide) Th(III) complexes, which are unexpectedly square planar. The role that steric and electronic effects play in the isolation of this rare class of 6d¹ square planar Th(III) complexes is probed by varying the *ortho* and *para* substituents of the aryloxide ligands. Chapter 5 details attempts to synthesize Th(II) complexes in the bis(cyclopentadienyl) amidinate ligand environment and an investigation into the synthesis of other low oxidation state bis(cyclopentadienyl) thorium amidinate complexes as candidates for reduction to Th(II). Chapter 6 extends the coordination chemistry of the (C₅H₄Si^{*i*}Pr₃)¹⁻ ligand from thorium as described in Chapter 3 to uranium and the rare-earth metals to evaluate the importance of steric and electronic effects in isolating reduced uranium and rare-earth metal complexes. Chapter 7 examines the effect of switching the tri-methylsilyl substituent in the [C₅Me₄(SiMe₃)]¹⁻ ligand to the phenylsilyl substituents SiMe₂Ph and SiMePh₂ with regards to Mg(II) and U(IV) chemistry. The unusual preference for forming magnesocenes is described. Chapter 8 explores the U(III) and U(IV) coordination chemistry of the [C₅Me₄(SiMe₂^{*t*}Bu)]¹⁻ ligand in efforts to synthesize more soluble organouranium complexes. The complexes generated were found to be more challenging to crystallize and purify and the ligand promoted polymorphism. Chapter 9 surveys the synthesis and characterization of bis(cyclopentadienyl) Sc(III) halide complexes to increase the number of bis(cyclopentadienyl) Sc(III) halide complexes available for reduction to Sc(II) compounds. Chapter 10 applies some of the work described in Chapter 9 and details the reduction studies of the bis(cyclopentadienyl) Sc(III) halide complex [C₅Me₄(SiMe₂^{*t*}Bu)]₂ScI to synthesize the first example of a linear Sc(II) metallocene. The spectroscopy, reactivity, and an investigation into the factors that enforce the linearity are discussed. Appendix A details an investigation into the unusual reaction of (C₅Me₅)₂Y(μ -Ph)₂BPh₂

and $\text{NaC}\equiv\text{CH}$ which has yielded an unusual bridging butatrienyldiene ligand presumably formed from a C–C coupling reaction of two $(\text{C}\equiv\text{CH})^{1-}$ ligands. Appendix B describes a study on the coordination chemistry of the $(\text{C}_5\text{Me}_4\text{SiMe}_3)^{1-}$ ligand with thorium which has led to a rare example of a double tuck-in thorium metallocene. Appendix C extends the coordination chemistry of the $(\text{C}_5\text{Me}_4\text{SiMe}_3)^{1-}$ ligand to Sm, Yb, and Eu and investigates the reactivity of the generated divalent metallocenes with 2,2'-bipyridine and 2,2';6',2''-terpyridine. Finally, Appendix D contains a table of the crystallographic data collected throughout the course of the work described in this Dissertation including information about unit-cell parameters.

Chapter 1:

Introduction

Oxidation States. The concept of the oxidation state refers to the overall formal charge of an element relative to its neutral state and this provides a simple model to track the movement of electrons between the different species involved in reduction and oxidation reactions collectively called redox reactions.¹ The transition metals have a rich redox chemistry because many elements in the *d*-block have several different oxidation states that are synthetically accessible.²⁻⁴ Synthetic access to a wide variety of oxidation states is critical to the development of an extensive redox chemistry for any element.

The Rare-Earth Metals (Sc, Y, and the Lanthanides). Compared to the *d*-block elements, the coordination chemistry of the *f*-block elements has not been heavily explored. In addition, the availability of oxidation states synthetically accessible for molecular species of the rare-earth metals, which include Sc, Y, and the lanthanides ($\text{Ln} = \text{La-Lu}$ excluding radioactive promethium), is much more limited in comparison to the transition metals. In 1971, Pimentel and Spratley briefly stated:⁵

“Lanthanum has only one important oxidation state in aqueous solution, the +3 state. With few exceptions, that statement tells the whole boring story about the other 14 elements.”

At that time, the literature on rare-earth metal chemistry was dominated by studies involving the rare-earth metals in the +3 oxidation state since it is the most stable oxidation state.⁶⁻⁸ Furthermore, studies have shown that the chemistry between these rare-earth metals is similar despite their different $4f^n$ ($n = 0-14$) electron configurations. This fundamental property starkly contrasts the

difference in reactivity observed between different groups within the d -block. For example, while $(C_5H_5)_2Fe$ is stable,^{9,10} the analog of the metal next to Fe, $(C_5H_5)_2Co$, is a reducing agent.¹¹

The similarities in reactivity between the lanthanide elements when compared to each other can be explained by studies that have suggested that the electron density of the $4f$ valence orbitals of the lanthanide elements have a limited radial extension beyond the inert [Xe] core, Figure 1.1 (left).^{12,13} As a result, these $4f$ electrons behave very much like inner core electrons. One important implication of this property is that these orbitals do not engage much in metal–ligand bonding

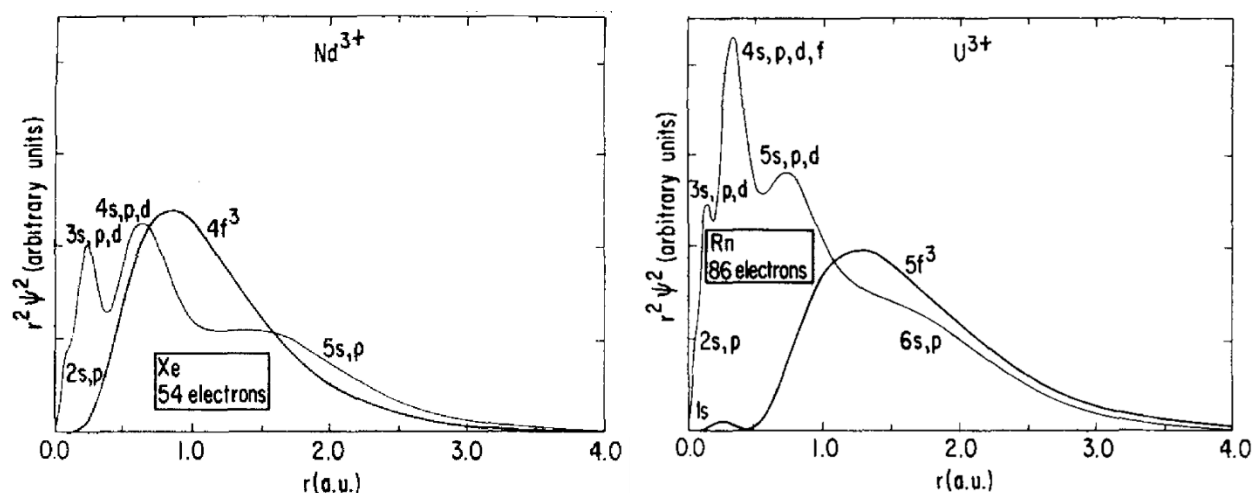


Figure 1.1. Hartree-Fock radial wave functions for the Nd(III) (left) and U(III) ions (right) previously reported by Crosswhite *et al.*¹³

which in turn makes the bonding in lanthanide coordination complexes primarily ionic in character.¹⁴ Another implication is due to the diffuse nature of the $4f$ orbitals, poor shielding of the valence electrons leads to a larger than expected decrease in atomic radii as one traverses through the lanthanide series, also known as the lanthanide contraction, Figure 1.2.¹⁵⁻¹⁷ Therefore, the chemistry of the rare-earth metals is primarily dictated by steric effects from the ligand environment and the differences in the ionic radii of the rare-earth metals. Scandium and yttrium

chemistry are often grouped with the lanthanides despite the lack of f orbitals because their $3d^0$ Sc^{3+} and $4d^0$ Y^{3+} ions have similar reactivities to the other Ln^{3+} ions.

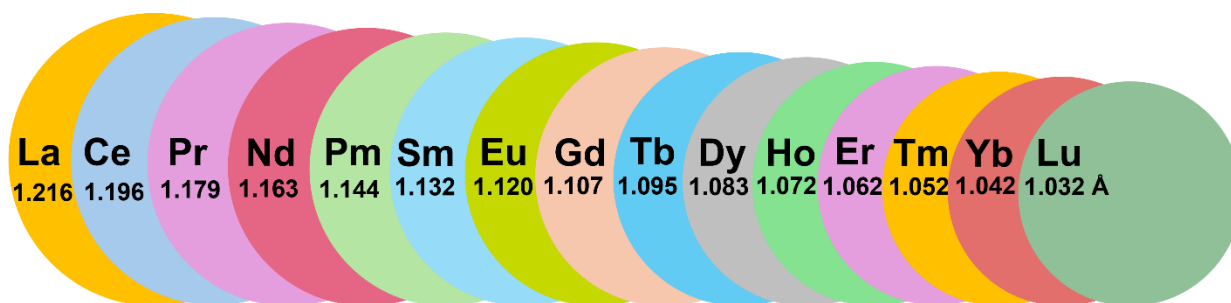


Figure 1.2. Visual representation (drawn not to scale) of the effective nine-coordinate ionic radii of the lanthanide elements (Å) reported by Shannon.¹⁵

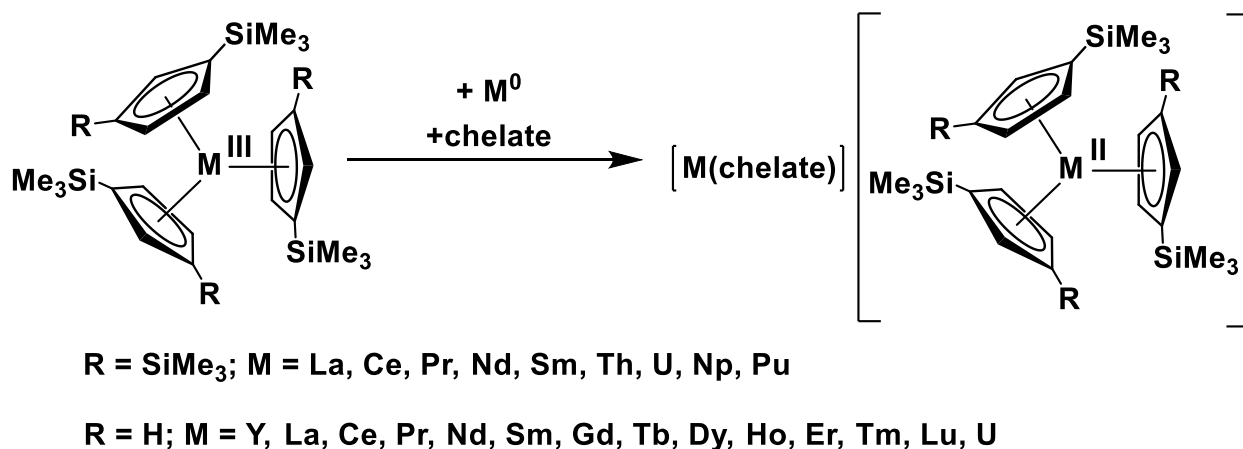
The Actinides Elements. The actinide elements comprise the period right below the lanthanides and display some similarities in coordination chemistry and reactivity with the rare-earth metals. The $5f$ orbitals extend slightly further away from the inert $[\text{Rn}]$ core compared to the $4f$ orbitals of the lanthanides, Figure 1.1 (right),¹³ and this increased radial extension of the $5f$ orbitals leads to a slightly different electronic structure compared to the lanthanides that could allow for some degree of covalency in metal–ligand bonding. The study of the actinide elements is less developed than the lanthanides due to the difficulties of handling radioactive materials and the relatively low supply of suitable starting materials.¹⁸ Consequently, most of the actinide literature focuses mainly on thorium and uranium chemistry due to their relatively low radioactivity and higher natural abundance.¹⁸ Much like the lanthanides, the literature on thorium chemistry is primarily focused on one oxidation state, which for thorium is the closed shell +4 oxidation state. Although uranium has been known to exist in the +3, +4, +5, and +6 oxidation states, access to lower oxidation states were unknown up until 2013.¹⁹

The Importance of the Ligand Environment. For some time, coordination complexes with f -element ions in the +2 oxidation state were limited to Nd, Eu, Sm, Dy, Tm, and Yb. This collection of +2 ions for the lanthanides were coined the “traditional” +2 ions due to the fact that reduction from the +3 to the +2 oxidation state involved a change in electron configuration from $4f^n$ to $4f^{n+1}$.^{14,20} Studies that aimed to estimate the M^{3+}/M^{2+} ($M = \text{La–Lu}$) reduction potentials for a $4f^n$ to $4f^{n+1}$ process for the rare-earth metal series suggested that the $M(\text{II})$ ions would be too unstable and reducing to exist in solution, Table 1.1.²¹⁻²³ Similarly, studies on the M^{3+}/M^{2+} redox potentials for Th and U were estimated to be -4.9 and -4.7 V, respectively.²¹

Table 1.1. Estimated M^{3+}/M^{2+} Standard Reduction Potentials (± 0.2 V) vs SHE of the rare-earth metals, thorium, and uranium.²¹⁻²³

M	Potential (V vs SHE)	M	Potential (V vs SHE)
Eu	-0.35	Pr	-2.7
Yb	-1.15	Y	-2.8
Sm	-1.55	Ho	-2.9
Tm	-2.3	Er	-3.1
Dy	-2.5	La	-3.1
Nd	-2.6	Ce	-3.2
Pm	-2.6	Tb	-3.7
Lu	-2.7	Gd	-3.9
Th	-4.9	U	-4.7

However, that view was challenged in 2008 when Lappert and coworkers spectroscopically and crystallographically characterized the first examples of La(II) and Ce(II) coordination complexes with the tris(*bis*-trimethylsilylcyclopentadienyl) ligand environment.²⁴ After, the Evans group extended the syntheses of rare-earth metal and actinide complexes in the +2 oxidation state to the rest of the rare-earth metals except radioactive promethium and a number of the actinide elements using the tris(cyclopentadienyl) ligand environments shown in Scheme 1.1.^{19,25-30}



Scheme 1.1. General synthesis of tris(cyclopentadienyl) rare-earth metal and actinide complexes in the +2 oxidation state.^{19,24-30}

A combination of spectroscopic and theoretical studies suggested that the reduced metal centers in these tris(cyclopentadienyl) complexes adopt $4f^n 5d^1$ electron configurations upon reduction where the electron is mostly localized in the d_z^2 orbital of the metal.²⁵⁻²⁷ For U, these tris(cyclopentadienyl) complexes tend to adopt $5f^3 6d^1$ configurations¹⁹ while for Th, it is $6d^2$.²⁸ The unusual electron configurations adopted by these +2 rare-earth ions eventually led to them being referred to as the “non-traditional” +2 ions as opposed to the “traditional” +2 ions that adopt $4f^{n+1}$ electron configurations. Population of the d_z^2 orbital of the metal center can be rationalized by the qualitative crystal field splitting diagram shown below in Figure 1.3 previously proposed by theoretical studies on the electronic structures of tris(cyclopentadienyl) metal complexes.^{31,32}

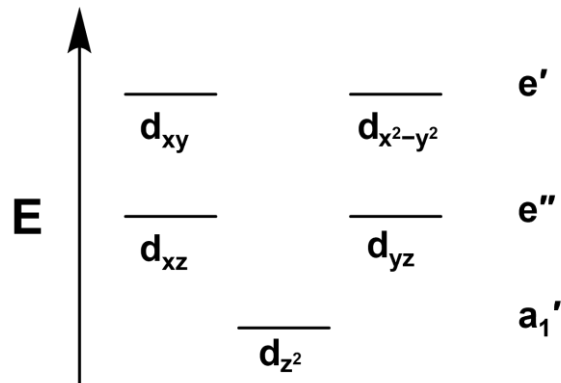


Figure 1.3. Qualitative crystal field splitting diagram of a tris(cyclopentadienyl) metal complex.^{31,32}

Due to the ligand field generated by the three cyclopentadienyl ligands in a trigonal planar coordination environment with D_{3h} symmetry, there is a low-lying d_z^2 orbital that is comparable in energy with the metal's f -orbitals such that reduction populates it with an electron.^{14,31,32} These studies demonstrated the power of using the ligand field to influence the electronic structures of f -element coordination complexes such that isolation of molecular species of the +2 ions was possible.

Since these initial discoveries of the syntheses of complexes containing the non-traditional +2 ions of the rare-earth metals and the actinides, several new examples have been discovered in different ligand environments that include but are not limited to amides,^{33,34} aryloxides,³⁵⁻³⁷ thiolates,³⁸⁻⁴¹ and amidinates.^{42,43} Despite this, cyclopentadienyl ligands are among the most commonly employed class of ligands for the isolation of these reduced complexes.^{19,25-30,44-48}

However, only a limited number of metal ligand combinations can support these relatively reducing ions and their chemical stabilities are heavily dependent on the specific ligands employed. The reasons for these observations are not well understood. Therefore, fundamental studies that probe the factors that affect properties such as the thermal stability, reactivity, and

structure of complexes of these +2 ions are important for developing this largely underdeveloped field of chemistry.

Outline of the Dissertation. The research described in this Dissertation details a series of exploratory synthetic studies aimed at understanding the role that steric and electronic effects play in the isolation and properties of reduced rare-earth metal and actinide metal coordination complexes. Specifically, ancillary ligand effects will be studied through subtle variations in the ligands employed to evaluate how these systematic changes affect the thermal stability, reactivity, and structures of the resulting compounds. The goal of these studies described herein is to further the fundamental chemistry of the rare-earth metals and actinides to help probe periodic trends in the *f*-block and influence design principles for the synthesis of new examples of this rare class of rare-earth metal and actinide coordination complexes.

Chapter 2 explores the chemistry of the reaction between $\text{SmI}_2(\text{THF})_2$ and 2 equiv of $\text{KC}_5\text{Me}_4\text{H}$ in THF to compare with the analogous reaction between $\text{SmI}_2(\text{THF})_2$ and 2 equiv of KC_5Me_5 that was previously reported to generate $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ in good yields. The subtle change of switching from the *pentamethylcyclopentadienyl* ligand, $(\text{C}_5\text{Me}_5)^{1-}$, to the *tetramethylcyclopentadienyl* ligand, $(\text{C}_5\text{Me}_4\text{H})^{1-}$, was observed to yield significantly different reactivity as different and unexpected products were isolated from these reactions.

Chapter 3 describes the synthesis of new examples of tris(mono-silylcyclopentadienyl) low-valent thorium complexes. Replacing the trimethylsilyl substituent in $(\text{C}_5\text{H}_4\text{SiMe}_3)^{1-}$ with the triisopropylsilyl substituent in $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)^{1-}$ was observed to yield a substantial increase in the thermal stabilities of the resulting Th(III) and Th(II) complexes such that crystallographic characterization was possible.

Chapter 4 investigates the role steric and electronic effects have on the isolation and thermal stabilities of rare examples of square planar Th(III) complexes through subtle variations in the aryloxide ligands employed. It was found that the substituents located *ortho* to the oxygen donor atom of the aryloxide ligand play a very important role in isolating these Th(III) square planar complexes and that changes to the electronic natures of the aryloxide ligands play a subtle role in the thermal stabilities of the resulting Th(III) complexes.

Chapter 5 presents attempts to isolate new examples of Th(III) and Th(II) complexes in bis(cyclopentadienyl) amidinate environments. Bis(cyclopentadienyl) thorium metallocene amidinate complexes were synthesized by insertion of carbodiimides into the Th–C bond of bis(cyclopentadienyl) thorium dialkyl complexes and the reduction chemistry of these complexes was examined.

Chapter 6 extends the chemistry of the tri-isopropylsilylcyclopentadienyl ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$)^{1–} ligand to uranium and the rare-earth metals in attempts to synthesize new examples of M(II) ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$)₃M complexes (M = Y, La, Pr, Nd, Gd, Tb, Dy, Ho, U). Reduced metal tris(triisopropylsilylcyclopentadienyl) complexes can be isolated for the larger rare-earth metals and the role that steric and electronic effects play in isolating these ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$)₃M complexes versus other tris(cyclopentadienyl) metal complexes is discussed.

Chapter 7 explores the effect of replacing the trimethylsilyl substituent in the (trimethylsilyl)tetramethylcyclopentadienyl ligand ($\text{C}_5\text{Me}_4\text{SiMe}_3$)^{1–} with phenylsilyl substituents, specifically SiMe₂Ph and SiMePh₂, for use in U(IV) chemistry. Although the reaction between HC₅Me₄SiMe₃ and ⁱPrMgCl cleanly yields the cyclopentadienyl Grignard reagent, ($\text{C}_5\text{Me}_4\text{SiMe}_3$)MgCl(THF), an unexpected preference for forming bis(cyclopentadienyl) Mg(II)

complexes was found in attempts to synthesize cyclopentadienyl Grignard reagents with the $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]^{1-}$ and $[\text{C}_5\text{Me}_4(\text{SiMePh}_2)]^{1-}$ ligands.

Chapter 8 examines the coordination chemistry of the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand with U(III) and U(IV) to explore the synthesis of more soluble organouranium complexes. Salt metathesis reactions between the uranium iodide and chloride salts with different alkali metal cyclopentadienyl reagents were studied. Subtle variations in the alkali metal cyclopentadienyl reagent and uranium halide employed yielded a diversity of reactivity and structural motifs in cyclopentadienyl uranium chemistry with the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand.

Chapter 9 details the synthesis of a series of silyl-substituted bis(cyclopentadienyl) Sc(III) halide complexes in efforts to expand the chemical space of bis(cyclopentadienyl) Sc(III) complexes suitable for reduction to new Sc(II) complexes. It was found that relatively bulky cyclopentadienyl ligands and halides favor the formation of monomeric bis(cyclopentadienyl) Sc(III) complexes, while smaller cyclopentadienyl ligands and halides facilitate dimerization. Over the course of these studies, a rare example of a bimetallic scandium oxide was isolated.

Chapter 10 describes the synthesis, structure, and spectroscopy of the first example of a perfectly linear Sc(II) metallocene supported by $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligands, namely $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Sc}$. The first example of a Sc(II) metallocene, $(\text{C}_5\text{H}_2'\text{Bu}_3)_2\text{Sc}$,⁴⁸ was isolated in 2024, but it has a slightly bent geometry with respect to the cyclopentadienyl rings with a Cnt–Sc–Cnt (Cnt = cyclopentadienyl ring centroid) angle of 170.6°. Hence, it was surprising to find the linear metallocene given the bulkiness of the $(\text{C}_5\text{H}_2'\text{Bu}_3)^{1-}$ ligand compared to the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligands.

Appendix A details an investigation into the unusual reaction of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Ph})_2\text{BPh}_2$ and $\text{NaC}\equiv\text{CH}$ which has yielded an unusual bridging butatrienylidene ligand presumably formed

from a C–C coupling reaction of two $(\text{C}\equiv\text{CH})^{1-}$ ligands. Appendix B describes a study on the coordination chemistry of the $(\text{C}_5\text{Me}_4\text{SiMe}_3)^{1-}$ ligand with thorium which has led to a rare example of a double tuck-in thorium metallocene. Appendix C extends the coordination chemistry of the $(\text{C}_5\text{Me}_4\text{SiMe}_3)^{1-}$ ligand to Sm(II), Yb(II), and Eu(II) and investigates the reactivity of the generated divalent metallocenes with 2,2'-bipyridine and 2,2';6',2''-terpyridine. Appendix D contains a table of the crystallographic data collected throughout the course of the work described in this Dissertation including information about unit-cell parameters.

Taken altogether, these results demonstrate the complexity of factors that allow for the isolation of low oxidation state rare-earth metal and actinide metal complexes. No single factor or trend as of yet explains the variations in structure and stability that have been observed. However, it is clear that careful variations of ancillary ligands can achieve unexpected results in many ways.

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Chapter 2:

Tetramethylcyclopentadienyl Sm(II) Metallocene Chemistry:

Isolation of a Bimetallic Sm(II)/Sm(II) Complex

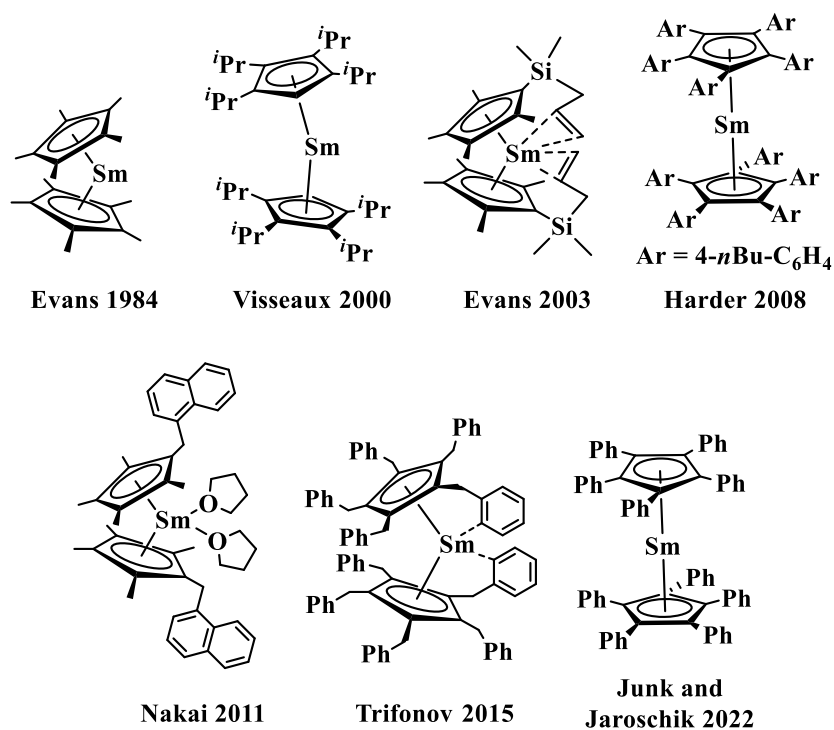
INTRODUCTION[†]

The synthesis and isolation of the first soluble organometallic Sm(II) complexes $(C_5Me_5)_2Sm(THF)_2$ ¹ and $(C_5Me_5)_2Sm$ ² in 1981 and 1984, respectively, propelled progress in organosamarium(II) chemistry by being suitable complexes for a series of reactivity studies that showcased the strong reducing properties of the Sm(II) ion in an organometallic environment. Some early representative examples included the reductive homologation of CO,³ the coupling of alkynes and alkenes with CO,^{4,5} the generation of unusual olefin dianions,^{6,7} and the first example of dinitrogen reduction by an *f*-element.⁸ Subsequently, this system was explored broadly in many other areas.^{9–25}

The pentamethylcyclopentadienyl ligand used in these studies was critical for providing the steric crowding required for isolating monomeric Sm(II) complexes, the solubility of the Sm(II) complexes essential for reactivity, and the crystallinity of the paramagnetic Sm(III) products necessary for characterization using single-crystal X-ray crystallography. The first Sm(II) cyclopentadienyl complex, $[(C_5H_5)_2Sm(THF)_x]_n$,²⁶ was reported much earlier in 1969, but since this unsubstituted cyclopentadienyl complex is insoluble in most solvents including THF, it did not provide access to unusual Sm(II) reactivity. It also did not form single crystals suitable for

[†]Portions of this Chapter have been published: Nguyen, J. Q.; Ziller, J. W.; Evans, W. J. Tetramethylcyclopentadienyl Samarium(II) Metallocene Chemistry: Isolation of a Bimetallic Sm(II)/Sm(II) Complex. *Inorganics* **2023**, *11*, 4. DOI: 10.3990/inorganics11010004

X-ray diffraction. Likewise, $[(C_5MeH_4)_2Sm(THF)_x]_n$ ^{27,28} was observed to display similar behavior. Since then, Sm(II) complexes using various substituted cyclopentadienyl ligands have been reported, including $(C_5H_2^tBu_3)_2Sm$,²⁹ $(C_5^iPr_5)_2Sm$,²⁹ $[C_5(2,5-Ph_2)(3,4-p-tol_2)H]_2Sm(THF)$,³⁰ $(C_5Ph_4H)_2Sm(THF)$,³⁰ $(C_9H_7)_2Sm(THF)$,³¹ $(C_{13}H_9)_2Sm(THF)_2$,³¹ $(C_5Me_4^iPr)_2Sm(THF)$,³² $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]Sm(THF)$,³³ $[C_5Me_4(CH_2C_{10}H_7)]_2Sm(THF)_2$,³⁴ $[C_5Me_4(CH_2C_{10}H_7)]_2Sm$,³⁴ $[(4-^nBu-C_6H_4)_5C_5]_2Sm$,³⁵ $[(4-Et-C_6H_4)_5C_5]_2Sm$,³⁶ $[(4-^iPr-C_6H_4)_5C_5]_2Sm$,³⁶ $[C_5Me_4SiMe_2(CH_2CH=CH_2)]_2Sm$,³⁷ $(C_5^iPr_4H)_2Sm$,^{29,38} $(C_5Ph_5)_2Sm$,^{30,39} and $[C_5(CH_2Ph)_5]_2Sm$,⁴⁰ Scheme 2.1. One commonality between these Sm(II) complexes is the use of sterically bulky and solubilizing substituents on the cyclopentadienyl ligands.⁴¹



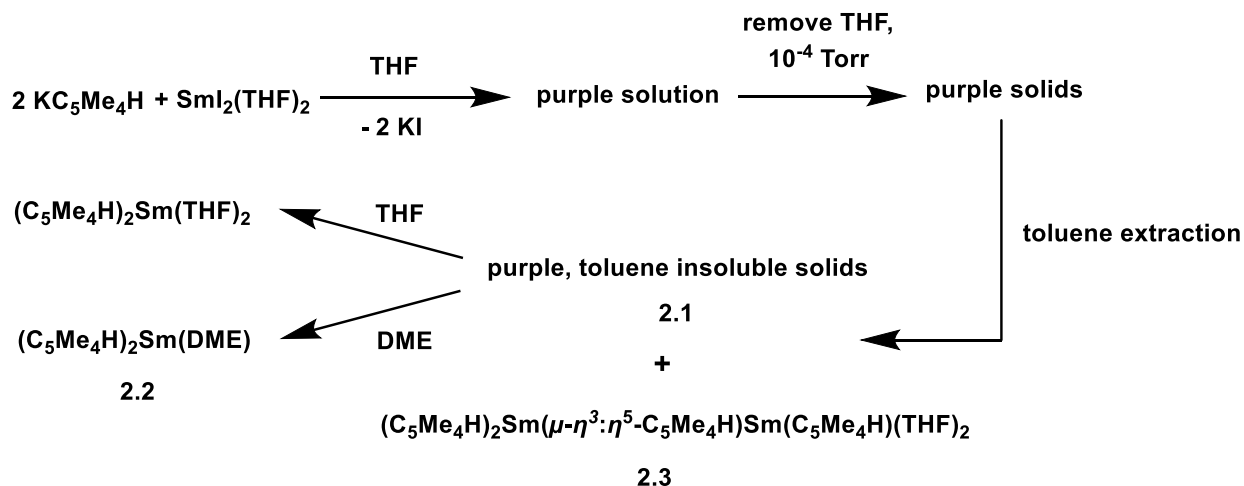
Scheme 2.1. Examples of crystallographically characterized Sm(II) metallocene complexes.

Although many of these Sm(II) metallocenes were characterizable by single-crystal X-ray crystallography, the tetramethylcyclopentadienyl Sm(II) complex, $(C_5Me_4H)_2Sm(THF)_2$,⁴² closely related to $(C_5Me_5)_2Sm(THF)_2$, proved to be challenging to crystallize. Even though spectroscopic

data were reported for the product of the salt metathesis reaction between 1 equiv of $\text{SmI}_2(\text{THF})_2$ and 2 equiv of $\text{NaC}_5\text{Me}_4\text{H}$, no crystallographic characterization of the isolated material was described, presumably due to the presence of complicating impurities.⁴² Given that $(\text{C}_5\text{Me}_4\text{H})_2\text{Yb}$ ⁴³ and $(\text{C}_5\text{Me}_4\text{H})_2\text{Eu}(\text{THF})_2$ ⁴⁴ were previously crystallographically characterized, the Sm(II) chemistry of this ligand as part of a broader study of $(\text{C}_5\text{Me}_4\text{H})^{1-}$ *f*-element chemistry in the Evans laboratory was revisited. Herein, the reaction between $\text{SmI}_2(\text{THF})_2$ and $\text{KC}_5\text{Me}_4\text{H}$ is described which was observed to display unexpectedly different reactivity than when the potassium cyclopentadienide reagent is KC_5Me_5 .⁴⁵ Routes to two different crystallographically characterizable samarocenes involving the $(\text{C}_5\text{Me}_4\text{H})^{1-}$ ligand are reported.

RESULTS

Synthesis and Structure of $(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}(\text{DME})$, 2.2. The reaction between 2 equiv of $\text{KC}_5\text{Me}_4\text{H}$ and 1 equiv of $\text{SmI}_2(\text{THF})_2$ in THF at room temperature immediately produced a purple mixture and a white precipitate. Afterwards, centrifugation and filtration of the purple mixture to remove white insoluble solids, presumably KI, afforded a purple solution. Subsequently, purple solids were obtained from this purple solution upon removal of solvent from the supernatant under reduced pressure at room temperature. The vacuum was applied until the purple solids were dry enough to be a free-flowing powder. About 50–60% of the purple solids by mass were extracted with toluene to give a purple-green solution discussed later. However, about half of the purple solids remained undissolved despite multiple extractions in toluene as shown in Scheme 2.2.



Scheme 2.2. Synthetic and workup procedure for the different products of the reaction between $\text{SmI}_2(\text{THF})_2$ and $2 \text{ KC}_5\text{Me}_4\text{H}$ in THF.

The purple, toluene-insoluble solids, **2.1**, are also insoluble in hydrocarbons, arenes, and diethyl ether. Elemental analysis suggested that compound **2.1** is $[(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}]_n$. However, incomplete combustion, which is commonly observed in organometallic *f*-element chemistry,^{46–50} was observed over multiple runs. In support of this chemical formula, **2.1** is soluble in THF and the ^1H NMR spectrum, taken in $\text{THF-}d_8$, matches the data reported for $(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}(\text{THF})_2$ in 1995,⁴² Scheme 2.2.^{1,2,29–40} Despite multiple attempts, no X-ray quality crystals of this THF-solvated species could be grown which is consistent with the literature.⁴²

The addition of 1,2-dimethoxyethane (DME) to **2.1** at room temperature afforded a dark green solution which has a color similar to that of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{DME})$.⁹ Concentration of the dark green solution and overnight storage at -35°C generated dark green crystals of $(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}(\text{DME})$, **2.2**, which were suitable for study by X-ray diffraction, Figure 2.1, Scheme 2.2.

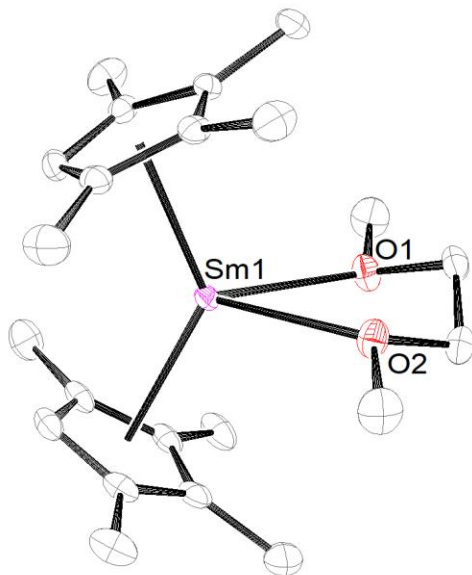


Figure 2.1. Molecular structure of $(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}(\text{DME})$, **2.2**, with selective atom labelling. Ellipsoids are drawn at the 50% probability level. For clarity, hydrogen atoms and the second molecule in the asymmetric unit are not shown.

Complex **2.2** can also be synthesized directly by the reaction between 2 equiv of $\text{KC}_5\text{Me}_4\text{H}$ and $\text{SmI}_2(\text{THF})_2$ in neat DME at room temperature, eq 2.1. The ^1H NMR spectrum of **2.2** taken in $\text{THF-}d_8$ displays resonances corresponding to one type of $(\text{C}_5\text{Me}_4\text{H})^{1-}$ environment as well as one molecule of DME per two $(\text{C}_5\text{Me}_4\text{H})^{1-}$ ligands. Furthermore, the resonances are paramagnetically shifted, which is typical for a Sm(II) complex.^{1,2,29–40}

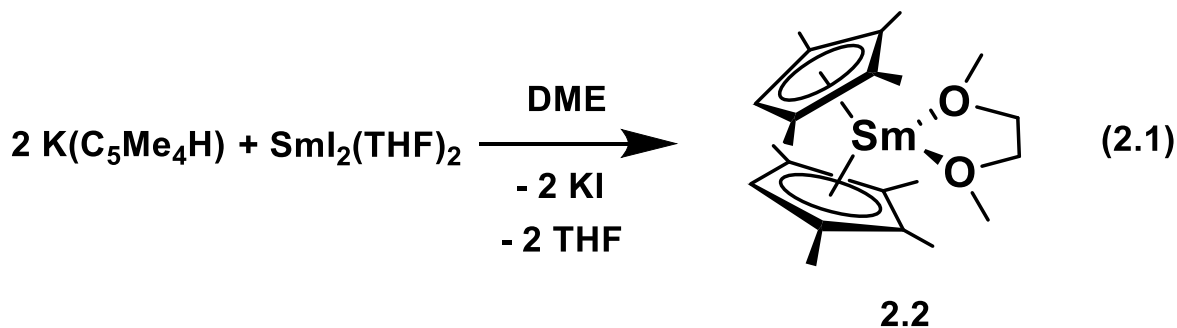


Table 2.1. Selected bond distances (Å) and angles (°) for (C₅Me₄H)₂Sm(DME), **2.2**.

Sm(1)–O(1)	2.591(1)	Sm(2)–O(3)	2.612(1)
Sm(1)–O(2)	2.617(1)	Sm(2)–O(4)	2.601(1)
Sm(1)–C(1)	2.813(2)	Sm(2)–C(23)	2.794(2)
Sm(1)–C(2)	2.821(2)	Sm(2)–C(24)	2.830(2)
Sm(1)–C(3)	2.807(2)	Sm(2)–C(25)	2.824(2)
Sm(1)–C(4)	2.796(2)	Sm(2)–C(26)	2.786(2)
Sm(1)–C(5)	2.787(2)	Sm(2)–C(27)	2.760(2)
Sm(1)–C(10)	2.747(2)	Sm(1)–C(32)	2.810(2)
Sm(1)–C(11)	2.821(2)	Sm(1)–C(33)	2.826(2)
Sm(1)–C(12)	2.867(2)	Sm(1)–C(34)	2.834(2)
Sm(1)–C(13)	2.819(2)	Sm(1)–C(35)	2.819(2)
Sm(1)–C(14)	2.741(2)	Sm(1)–C(36)	2.787(2)
Sm(1)–Cnt(1)	2.534	Sm(2)–Cnt(3)	2.528
Sm(1)–Cnt(2)	2.527	Sm(2)–Cnt(4)	2.544
O(1)–Sm(1)–O(2)	63.92(4)	O(3)–Sm(2)–O(4)	63.21(4)
Cnt(1)–Sm(1)–Cnt(2)	130.3	Cnt(3)–Sm(2)–Cnt(4)	130.3

Complex **2.2** crystallizes in the orthorhombic *Pbca* space group with two crystallographically independent molecules in the asymmetric unit. Selected bond distances and angles for complex **2.2** are summarized in Table 2.1. Each molecule adopts a distorted tetrahedral geometry and is coordinated to two cyclopentadienyl ligands and the two oxygen atoms of a single DME molecule. The two molecules have similar metrical parameters; the Sm–C(C₅Me₄H) distances fall within the range of 2.741(2)–2.867(2) Å and the Cnt–Sm–Cnt (Cnt = ring centroid) angles are 130.3° for both molecules. Furthermore, the 2.591(1)–2.617(1) Å Sm–O(DME) distances are similar to the Sm–O(DME) distances in (C₅Me₅)₂Sm(DME).⁹ However, the average O(DME)–Sm–O(DME) angle in complex **2.2** is 63.57(4)°, which is narrower than the 67.2(9)° seen in (C₅Me₅)₂Sm(DME).

In each molecule of **2.2**, the hydrogen substituted carbon atoms on the cyclopentadienyl rings are located at the back of the wedge where the two rings are closest to each other and have the most steric repulsion. The orientation of the (C₅Me₄H)^{1–} rings with respect to each other is

slightly different in the two molecules, Figure 2.2. One molecule has a $\text{H}(\text{C}_5\text{Me}_4\text{H})\dots\text{H}(\text{C}_5\text{Me}_4\text{H})$ distance of 3.196 Å while the other molecule has an analogous distance of 3.683 Å. The fact that two different orientations with similar metrical parameters form the low energy structure that crystallizes suggests that there is no single preferred orientation. In contrast, $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{DME})$ crystallizes as a single molecule in the asymmetric unit along with one molecule of DME in the lattice.⁹

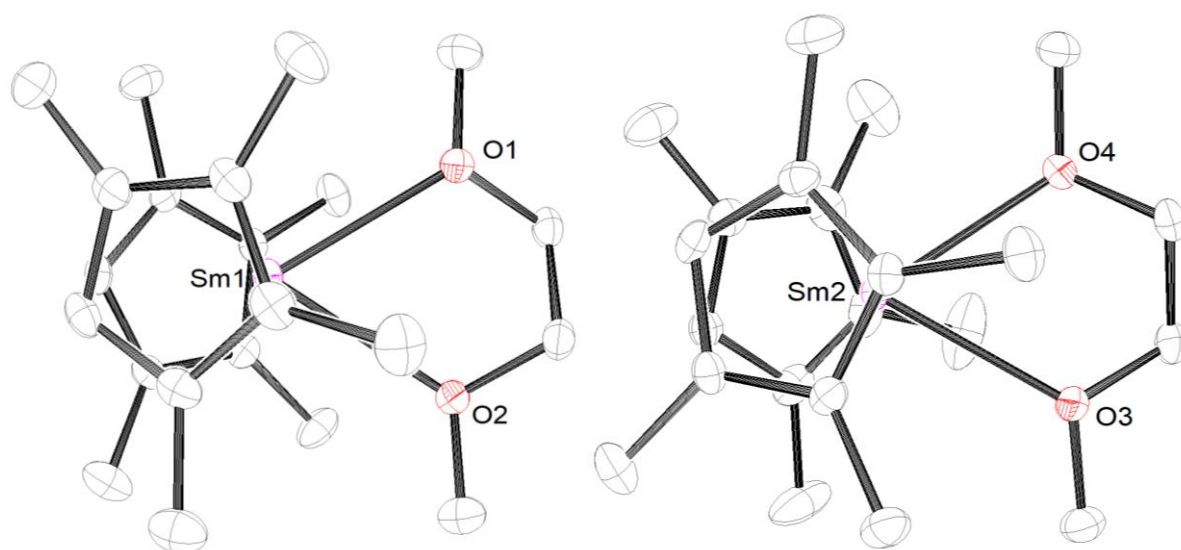


Figure 2.2. Top-down view of both molecules of $(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}(\text{DME})$, **2.2**, in the asymmetric unit. For clarity, hydrogen atoms are not shown.

The metrical parameters of **2.2** are compared to those of other structurally characterized Sm(II) metallocenes in Table 2.2 and are ordered in increasing Cnt–Sm–Cnt angle. The Sm–Cnt distances of complex **2.2** fall within the range typically observed for a Sm(II) metallocene and not for a Sm(III) metallocene.^{1,2,31–40} The Cnt–Sm–Cnt angle of **2.2** is the second smallest observed for a Sm(II) metallocene, behind the 126.4° seen for $(\text{C}_{13}\text{H}_9)_2\text{Sm}(\text{THF})_2$.³¹ However, the more acute angle seen in $(\text{C}_{13}\text{H}_9)_2\text{Sm}(\text{THF})_2$ is possibly a consequence of $(\text{C}_{13}\text{H}_9)_2\text{Sm}(\text{THF})_2$ having a noticeably longer Sm–Cnt distance than the other Sm(II) metallocenes in the literature.

Table 2.2. Comparison of Sm–Cnt (Å) and Sm–O (Å) distances and Cnt–Sm–Cnt angles (°) for various crystallographically characterized Sm(II) metallocenes in order of increasing Cnt–Sm–Cnt angle.

Complex	Sm–Cnt (Å)	Sm–O (Å)	Cnt–Sm–Cnt (°)
(C ₅ Me ₄ H) ₂ Sm(μ - η^3 : η^5 -C ₅ Me ₄ H)Sm(C ₅ Me ₄ H)(THF) ₂ , 2.3^a	2.584, 2.581, 2.537, 2.586	2.577(2), 2.597(2)	122.8, 130.2
(C ₁₃ H ₉) ₂ Sm(THF) ₂ ³¹	2.633, 2.629	2.560(6), 2.540(6)	126.4
(C ₅ Me ₄ H) ₂ Sm(DME), 2.2^a	2.534, 2.527, 2.528, 2.544	2.591(1), 2.617(1), 2.601(1), 2.612(1)	130.3
(C ₅ Me ₅) ₂ Sm(THF) ₂ ¹	2.60	2.63(1)	136.7
[C ₅ H ₂ (SiMe ₃) ₃][C ₅ H ₃ (SiMe ₃) ₂]Sm(THF) ³³	2.559, 2.553	2.547(3)	137.0
[C ₅ Me ₄ (CH ₂ C ₁₀ H ₇)] ₂ Sm ³⁴	2.533, 2.529	---	138.05(6)
(C ₅ Me ₅) ₂ Sm(THF) ³³	2.542, 2.549	2.569(3)	138.5
[C ₅ Me ₄ (CH ₂ C ₁₀ H ₇)] ₂ Sm(THF) ₂ ³⁴	2.576, 2.582	2.646(2), 2.590(2)	138.97(3)
(C ₅ Me ₅) ₂ Sm(DME) ⁹	2.54, 2.57	2.52(1), 2.61(2)	140
(C ₅ Me ₅) ₂ Sm ²	2.53	---	140.1
[C ₅ Me ₄ SiMe ₂ (CH ₂ CH=CH ₂)] ₂ Sm ³⁷	2.551	---	141.2
(C ₅ Me ₄ ^{<i>i</i>} Pr) ₂ Sm(THF) ³²	2.531	2.540(5)	141.6
[C ₅ (CH ₂ Ph) ₅] ₂ Sm ⁴⁰	2.555, 2.565	---	141.8
(C ₅ ^{<i>i</i>} Pr ₄ H) ₂ Sm ^{29,38}	2.51	---	152.0
[(4-Et-C ₆ H ₄) ₅ C ₅] ₂ Sm ³⁶	2.504, 2.521	---	166.9(1), 168.0(1)

^a This work.

Synthesis and Structure of (C₅Me₄H)₂Sm(μ - η^3 : η^5 -C₅Me₄H)Sm(C₅Me₄H)(THF)₂, **2.3.**

The purple-green toluene solution obtained by extraction of the SmI₂(THF)₂/KC₅Me₄H reaction mixture as described above led to the isolation of a different Sm(II) metallocene than **2.1** or **2.2**.

Concentration and subsequent storage of the solution at $-35\text{ }^{\circ}\text{C}$ in the presence of THF generated purple, X-ray quality crystals of the bimetallic complex, $(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}(\mu\text{-}\eta^3\text{:}\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Sm}(\text{C}_5\text{Me}_4\text{H})(\text{THF})_2$, **2.3**, Figure 2.3, Scheme 2.2. Complete removal of the solvent resulted in the formation of green solids. However, these green solids exhibit low solubility in non-coordinating solvents, and no X-ray-quality single crystals were isolated.

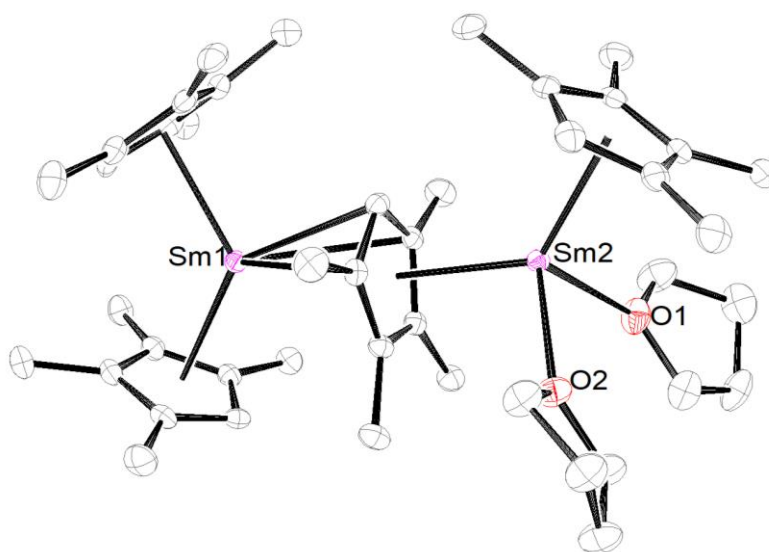


Figure 2.3. Molecular structure of $(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}(\mu\text{-}\eta^3\text{:}\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Sm}(\text{C}_5\text{Me}_4\text{H})(\text{THF})_2$, **2.3**, with selective atom labelling. Ellipsoids are drawn at the 50% probability level. For clarity, hydrogen atoms are not shown.

Complex **2.3** crystallizes in the monoclinic $P2_1/n$ space group with a single molecule in the asymmetric unit. Complex **2.3** is an asymmetric, bimetallic Sm(II)/Sm(II) complex that consists of a desolvated $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Sm}]$ metallocene moiety and a di-solvated $[(\mu\text{-}\eta^3\text{:}\eta^5\text{-C}_5\text{Me}_4\text{H})(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Sm}(\text{THF})_2]$ metallocene moiety bridged by a $(\text{C}_5\text{Me}_4\text{H})^{1-}$ ligand. A cyclopentadienyl-bridged bimetallic samarium complex has been observed previously in the literature. However, it is the mixed-valent Sm(II)/Sm(III) complex, $(\text{C}_5\text{Me}_5)_2\text{Sm}^{\text{II}}(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_5\text{H}_5)\text{Sm}^{\text{III}}(\text{C}_5\text{Me}_5)_2$,⁵¹ which

contains five cyclopentadienyl rings instead of the four in complex **2.3**. Selected metrical parameters for complex **2.3** are summarized in Table 2.3 and are compared with other Sm(II) metallocenes in Table 2.2.

Table 2.3. Selected bond distances (Å) and angles (°) for $(C_5Me_4H)_2Sm(\mu-\eta^3:\eta^5-C_5Me_4H)Sm(C_5Me_4H)(THF)_2$, **2.3**.

Sm(1)–C(1)	2.819(2)	Sm(2)–C(19)	2.814(2)
Sm(1)–C(2)	2.931(2)	Sm(2)–C(20)	2.806(2)
Sm(1)–C(3)	2.932(2)	Sm(2)–C(21)	2.804(2)
Sm(1)–C(4)	2.810(2)	Sm(2)–C(22)	2.811(2)
Sm(1)–C(5)	2.751(2)	Sm(2)–C(23)	2.799(2)
Sm(1)–C(10)	2.831(2)	Sm(2)–C(28)	2.835(2)
Sm(1)–C(11)	2.940(2)	Sm(2)–C(29)	2.872(2)
Sm(1)–C(12)	2.919(2)	Sm(2)–C(30)	2.888(2)
Sm(1)–C(13)	2.791(2)	Sm(2)–C(31)	2.864(2)
Sm(1)–C(14)	2.748(2)	Sm(2)–C(32)	2.807(2)
Sm(1)–C(28)	2.962(2)	Sm(2)–O(1)	2.577(2)
Sm(1)–C(29)	3.160(2)	Sm(2)–O(2)	2.597(2)
Sm(1)–C(30)	3.153(2)		
Sm(1)–C(31)	2.955(2)		
Sm(1)–C(32)	2.842(2)		
Sm(1)–Cnt(1)	2.584	Sm(2)–Cnt(3)	2.537
Sm(1)–Cnt(2)	2.581	Sm(2)–Cnt(4)	2.586
Cnt(1)–Sm(1)–Cnt(2)	122.8	Cnt(3)–Sm(2)–Cnt(4)	130.2

The coordination sphere of Sm(2) in complex **2.3** with two $(\eta^5-C_5Me_4H)^{1-}$ rings and two THF molecules is most similar to that of complex **2.2** and $(C_5Me_5)_2Sm(THF)_2$.¹ The 130.2° Cnt–Sm(2)–Cnt angle in **2.3** is equivalent to those in **2.2** and the 2.537 Å and 2.586 Å Sm(2)–Cnt distances are within a range typical for a Sm(II) metallocene.^{1,2,31–40} Moreover, the Sm(2)–O(THF) distances of 2.577(2) Å and 2.597(2) Å are similar to the Sm–O(THF) distances of other crystallographically characterized Sm(II) metallocenes, as shown in Table 2.2.

Sm(1) has two $(\eta^5-C_5Me_4H)^{1-}$ ligands that have Sm(1)–C(C_5Me_4H) distances ranging from 2.748(2) Å to 2.940(2) Å. The 122.8° Cnt–Sm(1)–Cnt angle for the two $(\eta^5-C_5Me_4H)^{1-}$ ligands is

much more bent than that of complex **2.2** because Sm(1) also has an $(\eta^3\text{-C}_5\text{Me}_4\text{H})^{1-}$ ligand in its coordination sphere. In a sense, the Sm(1) moiety may be considered a Sm(II) analog with $(\text{C}_5\text{Me}_4\text{H})^{1-}$ ligands of the Sm(III) complex, $(\text{C}_5\text{Me}_5)_2\text{Sm}(\eta^3\text{-CH}_2\text{CHCH}_2)$.⁵² However, the Sm(III) metallocene allyl complex has a Cnt–Sm–Cnt angle of 140.3°, presumably because it has Sm–C bond distances that are much shorter due to the metal center having a higher oxidation state than Sm(1) in complex **2.3**. The average Sm(1)–C($\eta^5\text{-C}_5\text{Me}_4\text{H}$) distance in **2.3** is 2.847(2) Å which is longer than the 2.724(30) Å average bond distance observed in $(\text{C}_5\text{Me}_5)_2\text{Sm}(\eta^3\text{-CH}_2\text{CHCH}_2)$.⁵² Similarly, the 2.842(2)–2.962(2) Å Sm(1)–C($\eta^3\text{-C}_5\text{Me}_4\text{H}$) distances in **2.3** for the three closest ring carbon atoms are much longer than the 2.630(15)–2.668(18) Å Sm–C(CH_2CHCH_2) distances in $(\text{C}_5\text{Me}_5)_2\text{Sm}(\eta^3\text{-CH}_2\text{CHCH}_2)$.⁵² This is consistent with the 0.1–0.2 Å differences typically observed between Sm(II)–C and Sm(III)–C distances in complexes featuring cyclopentadienyl or allyl ligands.^{1–8,52} The other Sm(1)–C($\eta^3\text{-C}_5\text{Me}_4\text{H}$) bond lengths in **2.3** for the two more distant carbon atoms in the cyclopentadienyl ligand are noticeably longer and are 3.153 Å and 3.160 Å.

The relatively small 122.8° Cnt–Sm(1)–Cnt angle in **2.3** is reminiscent of the 120° Cnt–Ln–Cnt angle observed in the sterically crowded $(\text{C}_5\text{Me}_5)_3\text{Ln}$ complexes that undergo sterically induced reduction.⁵³ One characteristic of $(\text{C}_5\text{Me}_5)_3\text{Ln}$ complexes that effect sterically induced reduction reactions is that they have at least one methyl substituent that is displaced from the average plane generated by the cyclopentadienyl ring by at least 0.48 Å.⁵³ However, the methyl displacements shown for complex **2.3** in Table 2.4 do not exceed 0.195 Å, and hence it cannot be considered sterically crowded by this criterion even though the Cnt–Sm–Cnt angle is very small.⁵³

The ¹H NMR spectrum of **2.3** in C₆D₆ has resonances that can be attributed to more than one type of $(\text{C}_5\text{Me}_4\text{H})^{1-}$ ligand, but the paramagnetism of the Sm(II) complex precluded a definitive assignment.

Table 2.4. Displacements for the methyl substituents from the average ring carbon plane generated by the $(C_5Me_4H)^{1-}$ ligand (Å) and the (average ring carbon plane)–C(ring)–C(Me) angles (°) for Sm(1) in **2.3**.

Cnt(1)...C(6)	0.032 Å	0.67°	Cnt(2)...C(15)	0.041 Å	0.86°
Cnt(1)...C(7)	0.153 Å	3.25°	Cnt(2)...C(16)	0.146 Å	3.11°
Cnt(1)...C(8)	0.195 Å	4.15°	Cnt(2)...C(17)	0.144 Å	3.04°
Cnt(1)...C(9)	0.044 Å	0.93°	Cnt(2)...C(18)	0.055 Å	1.16°

Infrared Spectroscopy and UV-Visible Spectroscopy. Infrared spectroscopy was used to characterize the purple, toluene-insoluble solids, **2.1**, obtained from the reaction between $SmI_2(THF)_2$ and $K(C_5Me_4H)$ in THF, and to compare to the infrared spectra of **2.2** and **2.3**, Figure 2.4.

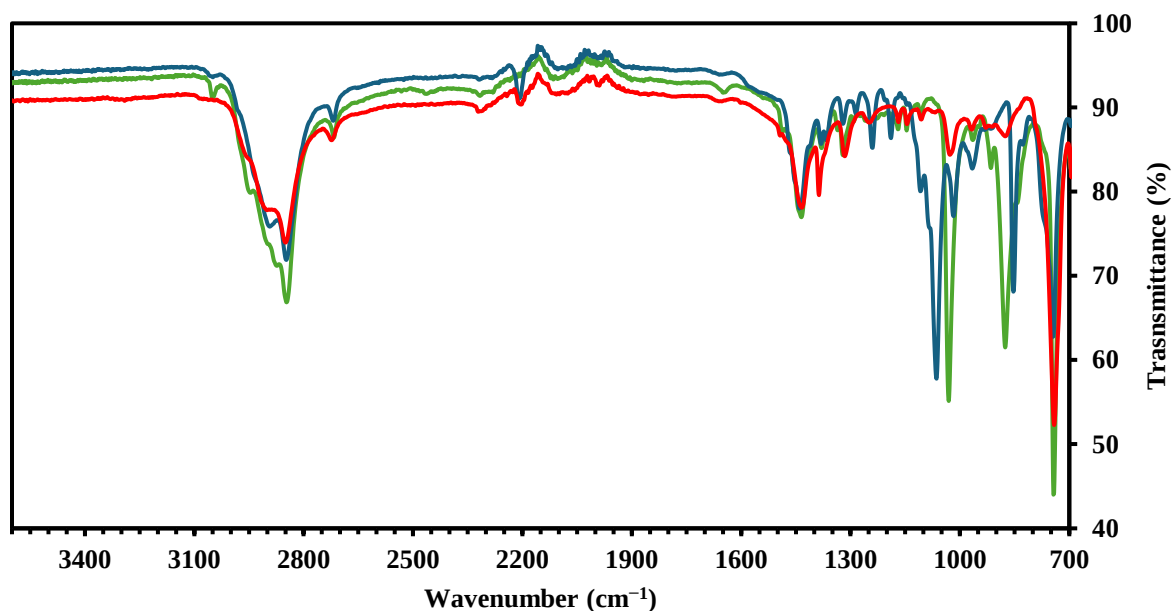


Figure 2.4. Infrared spectra of **2.1** (red), **2.2** (blue), and **2.3** (green).

The infrared spectra of complexes **2.1**, **2.2**, and **2.3** all display absorptions centered around 3000 cm^{-1} and 740 cm^{-1} , which is typical for the C–H stretching vibrations and bending vibrations of the cyclopentadienyl ligands,⁵⁴ respectively. Another band centered around 1440 cm^{-1} is observed and is characteristic of C–C vibrations.⁵⁴ In addition, the infrared spectrum of **2.2** has

two very strong bands at 1060 cm^{-1} and 860 cm^{-1} , diagnostic of coordination of an O-donor ligand on a metal center,^{55–57} which for complex **2.2** is DME. This compares well with the reported infrared data for $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{DME})$, which also has the strong bands associated with coordination of a DME molecule at 1040 cm^{-1} and 860 cm^{-1} .⁹ The infrared spectrum of **2.1** looks very similar to the infrared spectrum of **2.2**, except the bands at 1060 cm^{-1} and 860 cm^{-1} are not present, Figure 2.4. This suggests that these purple, toluene-insoluble solids, **2.1**, are fully desolvated. This notion is further supported by the infrared spectrum of **2.3**, which has a similar spectrum to **2.2**, including the two very strong bands at 1030 cm^{-1} and 876 cm^{-1} corresponding to the THF molecules bound to **2.3**. These bands are similar to the ones found at 1040 cm^{-1} and 895 cm^{-1} in the infrared spectrum of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$, which are absent in $(\text{C}_5\text{Me}_5)_2\text{Sm}$.^{1,2}

The UV-visible spectra of complexes **2.1**, **2.2**, and **2.3** were also collected in THF at room temperature and were compared with the UV-visible spectrum of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$. Despite the differences spectroscopically and structurally between **2.1**, **2.2**, and **2.3**, the UV-visible spectra are identical in THF and display absorptions centered around 390 nm and 550 nm. In comparison to $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$, there are no noticeable differences. Additionally, no differences are observed whether the UV-visible spectrum of **2.3** is taken in THF or toluene.

DISCUSSION

The reaction between $\text{SmI}_2(\text{THF})_2$ and 2 equiv of $\text{KC}_5\text{Me}_4\text{H}$ in DME readily forms single crystals of $(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}(\text{DME})$, **2.2**, amenable to single-crystal X-ray crystallography. This contrasts with the same reaction in THF where X-ray quality crystals of the expected product, $(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}(\text{THF})_2$, have proven elusive. This emphasizes the subtleties that are present in *f*-element organometallic chemistry. Further evidence on this point comes from the isolation of $(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}(\mu\text{-}\eta^3\text{-}\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Sm}(\text{C}_5\text{Me}_4\text{H})(\text{THF})_2$, **2.3**. The isolation of this asymmetric

bimetallic complex that is composed of monometallic $[(C_5Me_4H)_2Sm]$ and $[(C_5Me_4H)_2Sm(THF)_2]$ moieties is most surprising.

Based on the structures of **2.2** and **2.3** and the spectroscopic data obtained in this study, it is likely that removal of solvent under reduced pressure from reactions between $SmI_2(THF)_2$ and KC_5Me_4H generates an insoluble “ $[(C_5Me_4H)_2Sm]_n$ ” species that involves bridging $(C_5Me_4H)^{1-}$ ligands of the type found in **2.3**. If small amounts of THF are present, toluene-soluble compounds such as the bimetallic complex **2.3** can be isolated. In the presence of an excess of coordinating solvents such as THF or DME, $(C_5Me_4H)_2Sm(THF)_2$ and $(C_5Me_4H)_2Sm(DME)$ are likely to exist as monomeric species in solution.

These results with the $(C_5Me_4H)^{1-}$ ligand differ significantly from those of the $(C_5Me_5)^{1-}$ ligand. In the pentamethylcyclopentadienyl case, the unsolvated $(C_5Me_5)_2Sm$ can be isolated and crystallographically characterized. Evidently, the absence of one methyl group on the cyclopentadienyl ring allows bridging structures such as in **2.3** which may not be as energetically accessible as for $(C_5Me_5)_2Sm$. The fact that Sm(1) in **2.3** can achieve a Cnt–Sm–Cnt angle of 122.8° , the smallest observed for a Sm(II) metallocene, is consistent with this.

The structural data of **2.2** and **2.3** present some interesting questions with respect to the locations of the hydrogen substituents on the cyclopentadienyl ring. The existence of two different orientations of the hydrogen substituents in **2.2** is intriguing as well as its possible importance in making **2.2** crystallizable compared to $(C_5Me_4H)_2Sm(THF)_2$. Furthermore, the location of these hydrogen substituents in the back of the wedge would seem to allow for a more acute Cnt–Sm–Cnt angle. This is supported by the fact that the angle in complex **2.2** is 130° whereas the angle is 140° in $(C_5Me_5)_2Sm(DME)$. In complex **2.3**, which has the smallest Sm(II) Cnt–Sm–Cnt angle, 122.8° , only one hydrogen substituent is at the back of the wedge of Sm(1) and the same is true

for Sm(2) which has a coordination environment closest to complex **2.2**. Based on these results, there are clearly subtleties in the packing of tetramethylcyclopentadienyl complexes and these are likely to affect the solubility and crystallinity based on these results.

Given the results obtained with Sm(II) complexes with cyclopentadienyl ligands with one fewer methyl group than $(C_5Me_5)^{1-}$, it seems understandable that the chemistry of Sm(II) complexes of even less substituted cyclopentadienyl ligands is challenging in terms of solubility and crystallinity. Complexes such as $[(C_5H_5)_2Sm(THF)_x]_n$ and $[(C_5H_4Me)_2Sm(THF)_x]_n$ would be expected to oligomerize and could form a variety of bridging motifs.

CONCLUSIONS

In conclusion, synthetic routes to two new crystallographically characterizable Sm(II) metallocenes have been discovered using KC_5Me_4H and $SmI_2(THF)_2$ as starting materials. Although complex **2.2** adopts the typical monomeric Sm(II) bent metallocene structural motif, complex **2.3** is a rare example of an asymmetric bimetallic Sm(II)/Sm(II) complex bridged by a cyclopentadienyl ligand. The isolation of **2.3** provides supporting evidence for the possible oligomerization that may occur during the synthesis of Sm(II) metallocenes with less bulky and less solubilizing cyclopentadienyl ligands. This behavior can interfere with reactivity and can make the isolation and crystallization of reaction products more challenging.

EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP (99.999%) argon and dried by passage through columns containing Q-5 and molecular sieves and stored over activated molecular sieves prior to

use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze–pump–thaw cycles, and vacuum transferred before use. ^1H NMR spectra were recorded on a Bruker AVANCE600 MHz spectrometer at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. UV-visible spectra were collected in THF at 298 K using a Varian Cary 50 Scan UV-visible spectrometer in a 1 mm Schlenk cuvette fitted with a Teflon stopper unless otherwise stated. Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR. Elemental analyses were conducted on a Thermo Scientific FlashSmart CHNS/O Elemental Analyzer at UC Irvine Materials Research Institute’s TEMPR facility in Irvine, California. $\text{KC}_5\text{Me}_4\text{H}$ ⁴⁴ and $\text{SmI}_2(\text{THF})_2$ ⁵⁸ were synthesized according to literature procedures.

Synthesis of 2.1 from $\text{SmI}_2(\text{THF})_2$ and $\text{KC}_5\text{Me}_4\text{H}$ in THF. In a glovebox containing coordinating solvents, solid $\text{KC}_5\text{Me}_4\text{H}$ (486 mg, 3.04 mmol) was added to a stirred dark blue solution of $\text{SmI}_2(\text{THF})_2$ (827 mg, 1.51 mmol) in THF (ca. 5 mL) at room temperature. The mixture immediately turned dark purple with concomitant formation of white, insoluble precipitate. The mixture was stirred at room temperature overnight. After the white solids, presumably KI, were removed via centrifugation and filtration, solvent was removed under reduced pressure to yield purple solids. The purple solids were then washed with toluene ($4 \times$ ca. 2 mL) until the washings were colorless and the toluene extracts and remaining purple solids (237 mg, 0.603 mmol, 40% assuming a $[(\text{C}_5\text{Me}_4\text{H})_2\text{Sm}]_n$ product based on $\text{SmI}_2(\text{THF})_2$) were separated. IR: 2939w, 2870m, 2847s, 2722w, 1435m, 1386m, 1315w, 1025w, 742vs. UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 395 (692), 549 (424). Anal. Calcd. for **2.1**, presumed to be $[\text{C}_{18}\text{H}_{26}\text{Sm}]_n$: C, 55.04; H, 6.67. Found: C, 46.84; H, 5.897. C, 44.30; H, 5.582. C, 46.79; H, 5.876. Low C and H values were found across multiple runs and suggest incomplete combustion.^{46–50} The C to H ratios in the

analytical data give formulas of $C_{18}H_{27}$, $C_{18}H_{27}$, and $C_{18}H_{27}$, respectively, compared to the calculated value of $C_{18}H_{26}$.

Synthesis of $(C_5Me_4H)_2Sm(DME)$, **2.2, from **2.1**.** Compound **2.1** (237 mg) was dissolved in DME (10 mL), which immediately produced a dark green solution. Solvent was removed under reduced pressure to yield green solids [265 mg, 0.549 mmol, 36% based on $SmI_2(THF)_2$]. Dark green crystals of **2.2**, suitable for study by X-ray diffraction, can be grown from a concentrated solution of **2.1** in DME stored at $-35\text{ }^{\circ}C$. ^1H NMR ($THF-d_8$, 600 MHz): δ 15.28 (br s, 2H, C_5Me_4H), 9.21 (br s, 12H, C_5Me_4H), 3.38 (s, 4H, $CH_3OCH_2CH_2OCH_3$), 3.28 (s, 6H, $CH_3OCH_2CH_2OCH_3$), -0.32 (br s, 12H, C_5Me_4H) ppm. IR: 2859s, 2847s, 2715w, 2206w, 1440m, 1239w, 1189w, 1064 vs, 1015m, 853s, 743vs cm^{-1} . UV-vis (THF , room temperature) λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$): 388 (995), 550 (488). Anal. Calcd for **2.2**, $C_{22}H_{36}O_2Sm$: C, 54.72; H, 7.51. Found: C, 33.32; H, 7.51. C, 25.29; H, 3.72. C, 37.86; H, 5.33. Low C and H values were found across multiple runs and suggest incomplete combustion.^{46–50} The C to H ratios in the analytical data give formulas of $C_{22}H_{37}$, $C_{22}H_{38.5}$, and $C_{22}H_{37}$, respectively, compared to the calculated value of $C_{22}H_{36}$.

Synthesis of $(C_5Me_4H)_2Sm(\mu-\eta^3:\eta^5-C_5Me_4H)Sm(C_5Me_4H)(THF)_2$, **2.3.** In a glovebox containing coordinating solvents, the dark purple-green toluene extract obtained from the procedure for the synthesis of **2.1** was concentrated under reduced pressure and stored at $-35\text{ }^{\circ}C$. Over approximately 1 week, purple crystals of **2.3**, suitable for study by X-ray diffraction, were isolated (79 mg, 0.085 mmol, 11% based on $SmI_2(THF)_2$). IR: 2991w, 2926m, 2846s, 2717w, 1435m, 1321w, 1031vs, 876vs, 743vs cm^{-1} . UV-vis (THF , room temperature) λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$): 399 (1320), 552 (809). Anal. Calcd. for **2.3**, $C_{44}H_{68}O_2Sm_2$: C, 56.84; H, 7.37. Found: C, 55.28; H, 7.486. C, 51.53; H, 7.028. Low C and H values were found across multiple runs and

suggest incomplete combustion.^{46–50} The C to H ratios in the analytical data to give formulas of $C_{44}H_{71}$ and $C_{44}H_{71}$, respectively, compared to the calculated value of $C_{44}H_{68}$.

Direct Synthesis of $(C_5Me_4H)_2Sm(DME)$, **2.2.** In a glovebox containing coordinating solvents, solid $SmI_2(THF)_2$ (160 mg, 0.29 mmol) was added to a stirred suspension of $K(C_5Me_4H)$ (94 mg, 0.59 mmol) in 1,2-dimethoxyethane (ca. 5 mL) at room temperature, and the mixture gradually turned dark green over one minute. The mixture was allowed to stir at room temperature overnight. White, insoluble solids, presumably KI, were removed by centrifugation and filtration, and the resulting dark green solution was dried under reduced pressure to yield dark green solids. The solids were triturated with hexane (2 mL) before being dried under reduced pressure to yield **2.2** as a dark green solid (132 mg, 0.273 mmol, 94%). Crystals of **2.2**, suitable for study by X-ray diffraction, were grown from a concentrated solution in DME stored at $-35\text{ }^{\circ}C$ overnight.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_4H)_2Sm(DME)$, **2.2.** A green crystal of approximate dimensions $0.114 \times 0.209 \times 0.481$ mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁹ program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time). The raw frame data was processed using SAINT⁶⁰ and SADABS⁶¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁶² program package. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *Pbca* that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were two molecules of the formula

unit present. Least-squares analysis yielded $wR2 = 0.0470$ and $Goof = 1.039$ for 469 variables refined against 12,415 data ($0.72 \text{ \AA}$), $R1 = 0.0195$ for those 10,938 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_4H)_2Sm(\mu-\eta^3:\eta^5-C_5Me_4H)Sm(C_5Me_4H)(THF)_2$, 2.3. A purple crystal of approximate dimensions $0.170 \times 0.191 \times 0.306 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁹ program package was used to determine the unit-cell parameters and for data collection (20 s/frame scan time). The raw frame data was processed using SAINT⁶⁰ and SADABS⁶¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁶² program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0536$ and $Goof = 1.021$ for 449 variables refined against 12,542 data ($0.70 \text{ \AA}$), $R1 = 0.0239$ for those 10,610 data with $I > 2.0\sigma(I)$.

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Chapter 3:

Replacing Trimethylsilyl with Triisopropylsilyl Provides Crystalline (C₅H₄SiR₃)₃Th Complexes of Th(III) and Th(II)

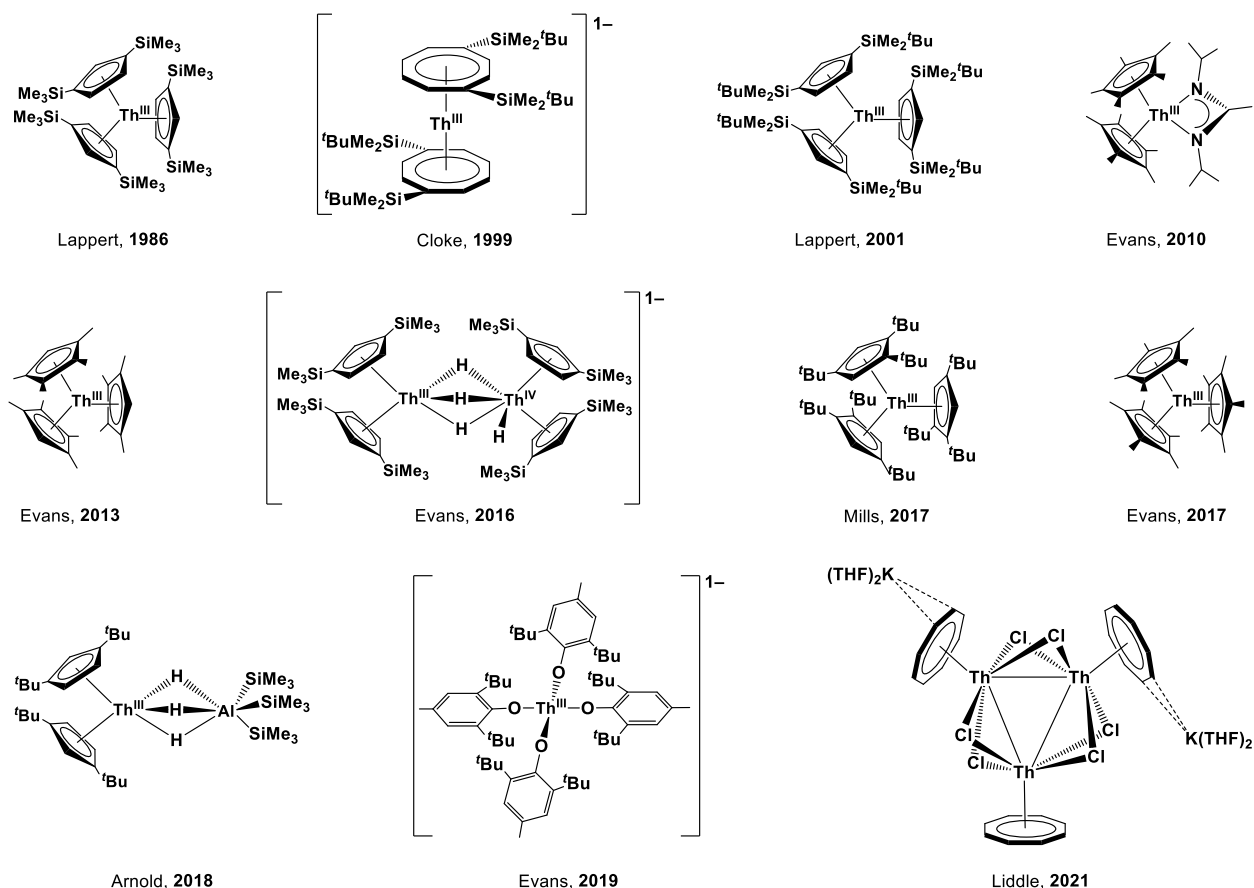
INTRODUCTION[†]

A crucial part of developing the chemistry and reactivity of any element in the periodic table is to have synthetic access to all of the available oxidation states. Generally, isolating coordination complexes containing metals in unusual oxidation states often depends on selecting stabilizing ligands that have suitable steric and electronic profiles. Optimizing the choice of ligands can be achieved by comparing similar metals and similar ligands.

Thorium and uranium chemistry has been advanced through this process since the two metals can display similar features. Despite this, thorium chemistry lags behind uranium chemistry in development, particularly in low oxidation-state chemistry. For example, scores of crystallographically characterized U(III) complexes have been known for several decades,¹⁻⁹ but it was not until 1986 that the first crystal structure of a Th(III) complex of any kind was reported by Lappert and co-workers, namely [C₅H₃(SiMe₃)₂]₃Th (Cp''₃Th).¹⁰ Since then up until 2023, only ten other Th(III) complexes were structurally characterized, Scheme 3.1.¹¹⁻²⁰

The monosilyl-substituted cyclopentadienyl U(III) complex, (C₅H₄SiMe₃)₃U (Cp'₃U), was also reported in 1986,³ but surprisingly, the monosilyl-substituted Th(III) analogue, Cp'₃Th, has never been isolated as it is not thermally stable enough to be crystallographically characterized.²¹

[†]Portions of this Chapter have been published: Nguyen, J. Q.; Anderson-Sanchez, L. M.; Moore, W. N. G.; Ziller, J. W.; Furche, F.; Evans, W. J. Replacing Trimethylsilyl with Triisopropylsilyl Provides Crystalline (C₅H₄SiR₃)₃Th Complexes of Th(III) and Th(II). *Organometallics* **2023**, 42, 2927–2937. DOI: 10.1021/acs.organomet.3c00343



Scheme 3.1. Crystallographically characterized Th(III) Complexes up until 2023.

A similar situation exists in Th(II) and U(II) chemistry. The first example of a crystallographically characterized U(II) complex was reported in 2013 and numerous examples of other U(II) complexes with different ligand systems have been reported since then.²²⁻²⁸ The first example of a molecular Th(II) complex, $(\text{Cp}''_3\text{Th})^{1-}$, was isolated and crystallographically characterized in 2015,²⁹ but up until 2023, no other ligand environments were found to stabilize a new Th(II) complex. This is particularly surprising since the $(\text{Cp}''_3\text{Th})^{1-}$ anion readily forms and has been isolated with five different alkali metal counteranions: $[\text{K}(\text{crypt})]^{1+}$, $[\text{Rb}(\text{crypt})]^{1+}$, $[\text{Cs}(\text{crypt})]^{1+}$, $[\text{Na}(\text{18-crown-6})_2]^{1+}$, and $[\text{K}(\text{18-crown-6})(\text{THF})_2]^{1+}$ (crypt = 2.2.2-cryptand).^{29,30}

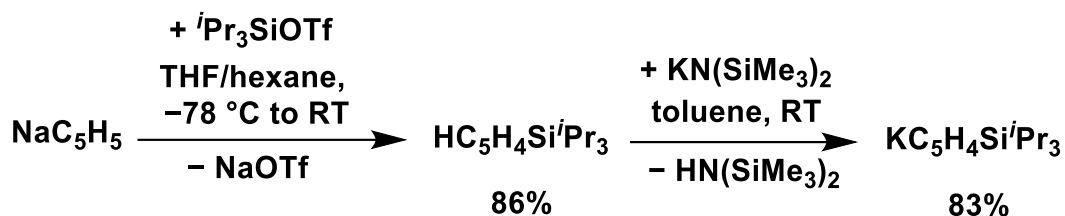
Expanding the small library of low-valent Th(III) and Th(II) complexes is an important goal in understanding fundamental actinide chemistry. However, a major challenge in generating new examples of Th(II) complexes is the dearth of Th(III) precursor complexes. Furthermore, several of the fully characterized Th(III) complexes have polyalkylated cyclopentadienyl ancillary ligands which are less likely to yield stable Th(II) complexes compared to the relatively electron-withdrawing trialkylsilyl-substituted cyclopentadienyl ligands.³¹

Studies on Ln(II) tris(aryloxy) complexes, $[\text{Ln}(\text{OAr}^*)_3]^{1-}$ ($\text{OAr}^* = \text{OC}_6\text{H}_2\text{-Ad}_2\text{-2,6-}^i\text{Bu-4}$, $\text{Ad} = 1\text{-adamantyl}$; $\text{Ln} = \text{Y, La, Ce, Nd, Gd, Dy, Yb, and Lu}$), that highlighted the importance of steric saturation in stabilizing highly reducing Ln(II) ions^{32,33} have provided precedent to explore the capacity of a larger mono(trialkylsilyl)-substituted cyclopentadienyl ligand, namely $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)^{1-}$, $(\text{Cp}^{\text{TIPS}})^{1-}$, to yield new isolable Th(III) and possibly Th(II) complexes. The synthetic, structural, spectroscopic, and electrochemical results from the study are reported here along with density functional theory (DFT) and Guzei Solid Angle calculations³⁴ to evaluate steric trends.

RESULTS AND DISCUSSION

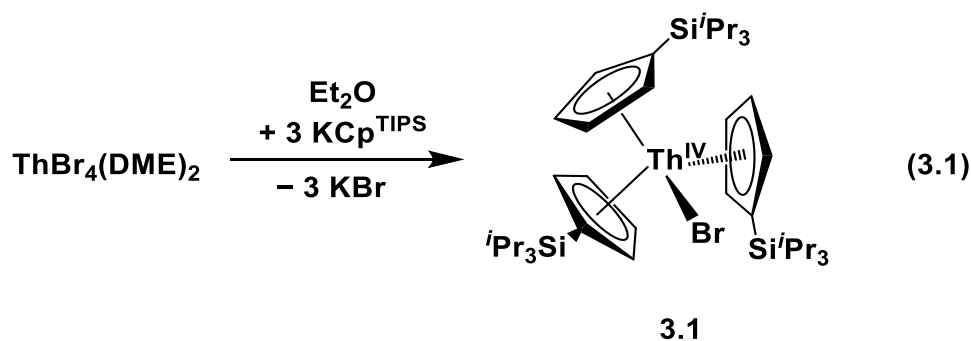
The appropriate alkali metal cyclopentadienyl reagent, $\text{KC}_5\text{H}_4\text{Si}^i\text{Pr}_3$ (KCp^{TIPS}), was synthesized following a modified procedure from that developed by Cloke and coworkers for the synthesis of the disilyl-substituted analog $\text{NaC}_5\text{H}_3(\text{Si}^i\text{Pr}_3)_2$.³⁵ The monosilylcyclopentadienyl reagent was synthesized by slow addition of a solution of $^i\text{Pr}_3\text{SiOTf}$ in hexane to a solution of NaC_5H_5 in THF at $-78\text{ }^\circ\text{C}$ followed by warming to room temperature and stirring for 3 hours before work up, Scheme 3.2. The presence of bis(trialkylsilyl)cyclopentadiene byproducts is commonly observed during the synthesis of mono(trialkylsilyl)cyclopentadienes, so it is necessary to perform the addition slowly at low temperatures.^{36,37} This was crucial for obtaining the

crystalline thorium complexes described below. Extraction into hexane and filtration to remove the NaOTf byproduct yielded a pale-yellow oil that was presumed to be HCp^{TIPS} in 86% yield. HCp^{TIPS} can be treated with either KH in THF or $\text{KN}(\text{SiMe}_3)_2$ in toluene to generate KCp^{TIPS} in 75 and 83% yields, respectively, Scheme 3.2. The potassium salt was identified by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopy.



Scheme 3.2. Synthesis of $\text{KC}_5\text{H}_4\text{Si}^i\text{Pr}_3$ (KCp^{TIPS}) from NaC_5H_5 .

The reaction between 3 equiv of KCp^{TIPS} and 1 equiv of $\text{ThBr}_4(\text{DME})_2$ ($\text{DME} = 1,2$ -dimethoxyethane) in diethyl ether at room temperature generated $\text{Cp}^{\text{TIPS}}_3\text{ThBr}$, **3.1**, eq 3.1, as a white solid in 85% yield. Complex **3.1** was characterized by analytical, spectroscopic, and crystallographic methods.



Initial attempts to crystallize **3.1** were unsuccessful until the methods described above were developed to improve the purity of the HCp^{TIPS} starting material. Once this was done, crystallization was still challenging. Although colorless **3.1** is very soluble in hydrocarbon and

arene solvents as well as diethyl ether, cooling the solutions to $-35\text{ }^{\circ}\text{C}$ usually resulted only in the precipitation of powders. To obtain crystals of **3.1** suitable for study by X-ray diffraction, powders precipitated from a solution in toluene were separated and the more dilute mother liquor was stored at $-35\text{ }^{\circ}\text{C}$ to induce further crystallization. After repeating this procedure several times, a relatively dilute solution of **3.1** in toluene stored at $-35\text{ }^{\circ}\text{C}$ overnight yielded crystals suitable for X-ray diffraction, Figure 3.1.

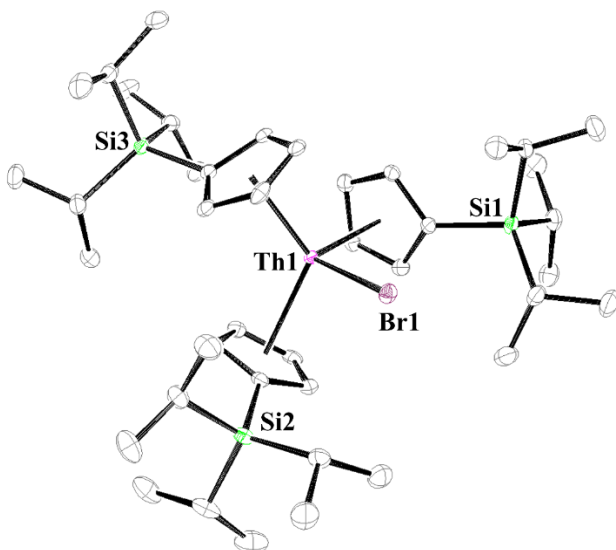
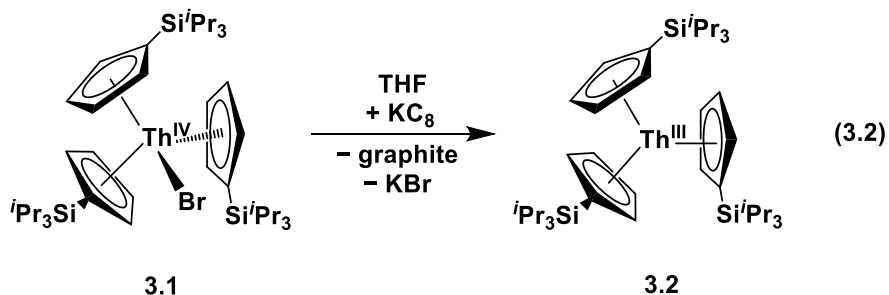


Figure 3.1. Molecular structure of $\text{Cp}^{\text{TIPS}}_3\text{ThBr}$, **3.1**, with selective atom labelling. Ellipsoids are drawn at the 50% probability level and the co-crystallized toluene molecule and hydrogen atoms are not shown for clarity.

Complex **3.1** crystallizes in the $P\bar{1}$ space group with a molecule of toluene in the asymmetric unit. The coordination environment around the thorium metal center is pseudotetrahedral with respect to the bromide ligand and the ring centroids of the three cyclopentadienyl ligands. The degree of distortion from tetrahedral can be evaluated by the sum of the three Cnt–Th–Cnt angles which is 349° instead of the 360° expected for trigonal planar in tris(cyclopentadienyl) Th(III) complexes and 328.5° expected for pure tetrahedral. The $2.55\text{ \AA}$

average Cnt–Th distance of **3.1** falls within a range typically seen for other tris(cyclopentadienyl) Th(IV) complexes with halide ancillary ligands such as $(C_5H_3^tBu)_3ThCl^{38}$ (2.600 Å), $Cp''_2(C_5Me_5)ThCl^{39}$ (2.571 Å), Cp''_3ThCl^{39} (2.565 Å), $[C_5H_3(SiMe_2^tBu)_2]_3ThCl^{39}$ (2.581 Å), $(C_5Me_4H)_3ThBr^{17}$ (2.576 Å), and $(C_5H_4SiMe_3)_3ThBr^{40}$ (2.535 Å). Also, the Th–Br distance of 2.8310(9) Å is comparable with the Th–Br distances of the structurally similar $(C_5Me_4H)_3ThBr^{17}$ [2.8372(8) Å] and $(C_5H_4SiMe_3)_3ThBr^{40}$ [2.8355(8) Å].

Treating complex **3.1** with 1.2 equiv of KC_8 in THF at room temperature immediately generated a dark blue solution similar to that of Cp''_3Th^{10} and a black precipitate, presumably graphite. Upon removal of solvent under reduced pressure, the reduction product was extracted into hexane, dried, and triturated with $SiMe_4$ to yield Cp^{TIPS}_3Th , **3.2**, as a royal blue solid in 98% crude yield, eq 3.2.



The EPR spectrum of a solution of **3.2** in THF at 77 K displays an axial signal with $g_{\parallel} = 1.97$ and $g_{\perp} = 1.88$. At room temperature, that same solution displays an isotropic EPR signal with a $g_{\text{iso}} = 1.90$, Figure 3.2. These values are consistent with other reported crystallographically characterized Th(III) complexes as shown in Table 3.1. Due to the paramagnetism of the Th(III) ion, the ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of **3.2** could not be definitively assigned. However, the $^{29}Si\{^1H\}$ NMR spectrum of **3.2** displays a resonance at -21.8 ppm.

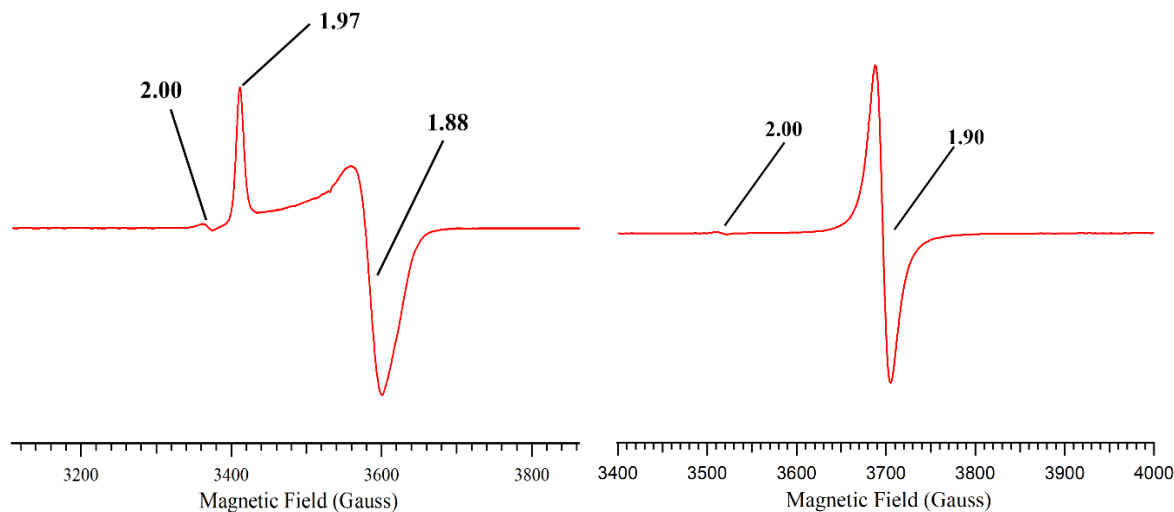


Figure 3.2. X-band EPR of $\text{Cp}^{\text{TIPS}}_3\text{Th}$, **3.2**, in THF at 77 K (left; mode: perpendicular) and at room temperature (right; mode: perpendicular). The feature observed at $g = 2.00$ for both spectra is attributed to electride.⁴¹

Table 3.1. EPR data for Th(III) complexes along with calculated Guzei G values (G) (discussed later) presented in increasing order.

Th(III)/Th(II) Complex	g_{iso}	$g_{\parallel}$	$g_{\perp}$	G (%)
$(\text{C}_5\text{Me}_5)_3\text{Th}^{\text{III}}$ ¹⁴	1.88	1.97	1.85	79
$(\text{C}_5\text{Me}_4\text{H})_3\text{Th}^{\text{III}}$ ¹⁷	1.92	-	-	82
$(\text{C}_5\text{Me}_5)_2\text{Th}^{\text{III}}[\text{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$ ¹⁶	1.871	1.97	1.91	84
$[\text{K}(\text{THF})_5(\text{Et}_2\text{O})][\text{Th}^{\text{III}}(\text{OC}_6\text{H}_2\text{-2,6-}^t\text{Bu}_2\text{-4-Me})_4]$ ¹¹	1.84	1.99	1.79	87
“(C ₅ H ₄ SiMe ₃) ₃ Th ^{III} ” ^{21,a}	1.90	1.98	1.89	87 ^a
$(\text{C}_5\text{H}_3^t\text{Bu}_2)_3\text{Th}^{\text{III}}$ ¹⁹	-	1.974	1.880	88
$[\text{K}(\text{DME})_2][\text{C}_8\text{H}_6(\text{SiMe}_2^t\text{Bu})_2]_2\text{Th}^{\text{III}}$ ¹⁵	1.916	-	-	88
$[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{Th}^{\text{II}}]$, 3.3^b	-	-	-	87 ^c , 88 ^d
$\text{Cp}^{\text{TIPS}}_3\text{Th}^{\text{III}}$, 3.2^b	1.90	1.97	1.88	89

$[\text{K}(\text{crypt})][\text{Cp}''_2\text{Th}^{\text{III}}(\mu\text{-H})_3\text{Th}^{\text{IV}}\text{HCp}''_2]^{13}$	-	-	-	89
$[\text{K}(\text{crypt})][\text{Cp}''_3\text{Th}^{\text{II}}]^{29}$	-	-	-	90
$\text{Cp}''_3\text{Th}^{\text{III}}^{12}$	1.910	1.97	1.88	91
$[\text{K}(\text{crypt})][\text{Cp}''_2\text{Th}^{\text{III}}(\mu\text{-H})_3\text{Th}^{\text{IV}}\text{HCp}''_2]^{13}$	-	-	-	91

^aCalculated from a DFT-calculated structure.

^bThis work.

^c $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{Th}]$ grown from Et_2O .

^d $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{Th}]$ grown from THF/hexane.

The UV–visible spectrum of **3.2** contains absorptions at 504, 582, and 664 nm with extinction coefficients of 1300, 900, and 1100 $\text{M}^{-1}\text{cm}^{-1}$, respectively, and a shoulder at 350 nm with an extinction coefficient of 844 $\text{M}^{-1}\text{cm}^{-1}$, Figure 3.3. As shown, this spectrum is similar to that of the crystallographically characterized Th(III) complex, $\text{Cp}''_3\text{Th}$.¹² In addition, the infrared spectrum of **3.2** is almost identical to that of complex **3.1** since metal–bromide vibrations typically appear below 650 cm^{-1} .⁴²

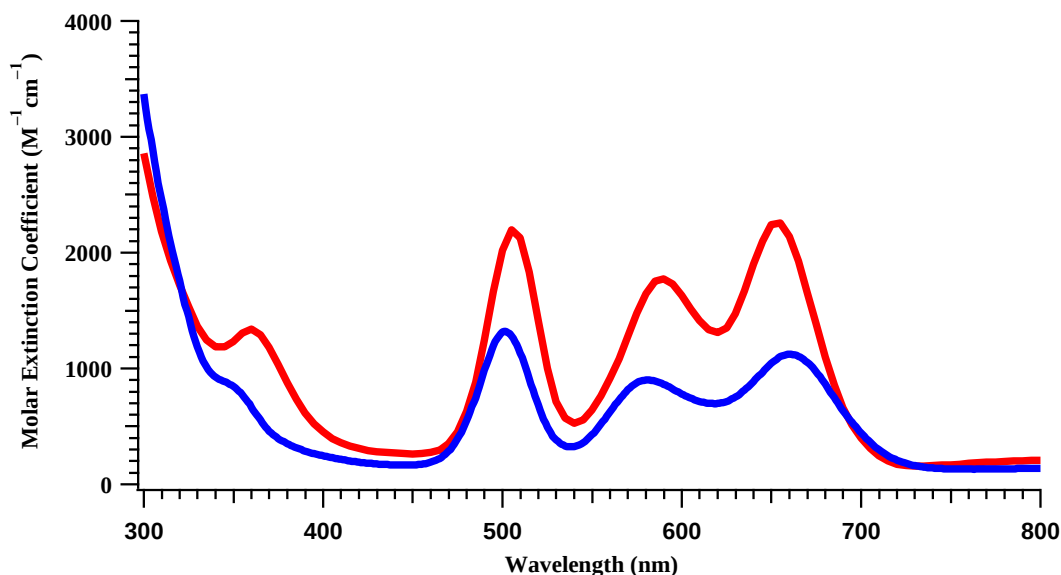


Figure 3.3. UV–visible spectra of **3.2** (blue) and $\text{Cp}''_3\text{Th}$ (red) in THF at room temperature.

Storage of a saturated solution of **3.2** in pentane overnight at $-35\text{ }^{\circ}\text{C}$ generated large dark blue blocks of $\text{Cp}^{\text{TIPS}}_3\text{Th}$, **3.2**, suitable for study by X-ray diffraction, Figure 3.4, in stark contrast to “ $\text{Cp}'_3\text{Th}$,” which has never been isolated.²¹ Complex **3.2** crystallizes in the $P\bar{1}$ space group with a single molecule in the asymmetric unit. Unlike **3.1**, the structure of **3.2** has a trigonal planar arrangement of the three Cp^{TIPS} rings around the thorium metal center with a sum of the Cnt–Th–Cnt (Cnt = ring centroid) angles of 359.4° that matches the 360° sum of angles found for the other tris(cyclopentadienyl) Th(III) complexes.^{10,12,14,17,19} The average Cnt–Th distance of **3.2** is 2.520 Å which is equivalent to that of $\text{Cp}''_3\text{Th}$ ¹⁰ (2.518 Å) and numerically shorter than that of $[\text{C}_5\text{H}_3(\text{SiMe}_2'\text{Bu})_2]_3\text{Th}$ ¹² (2.533 Å), $(\text{C}_5\text{Me}_4\text{H})_3\text{Th}$ ¹⁷ (2.551 Å), $(\text{C}_5\text{H}_3'\text{Bu}_2)_3\text{Th}$ ¹⁹ (2.566 Å), and $(\text{C}_5\text{Me}_5)_3\text{Th}$ ¹⁴ (2.62 Å).

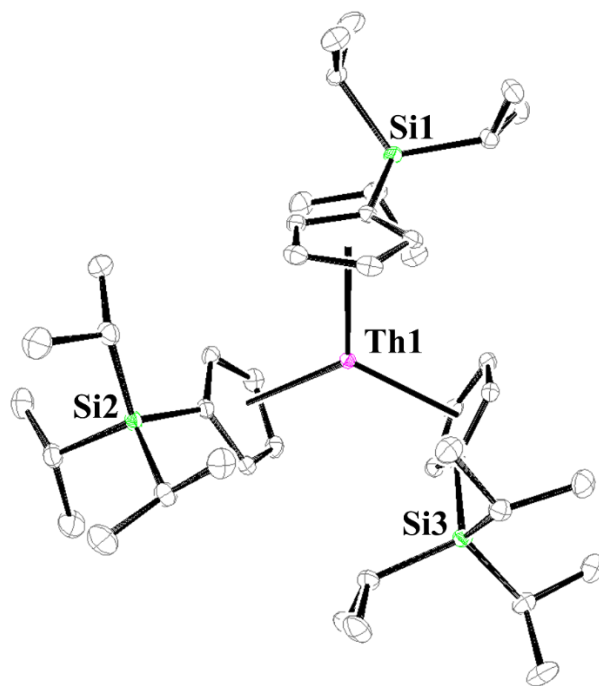
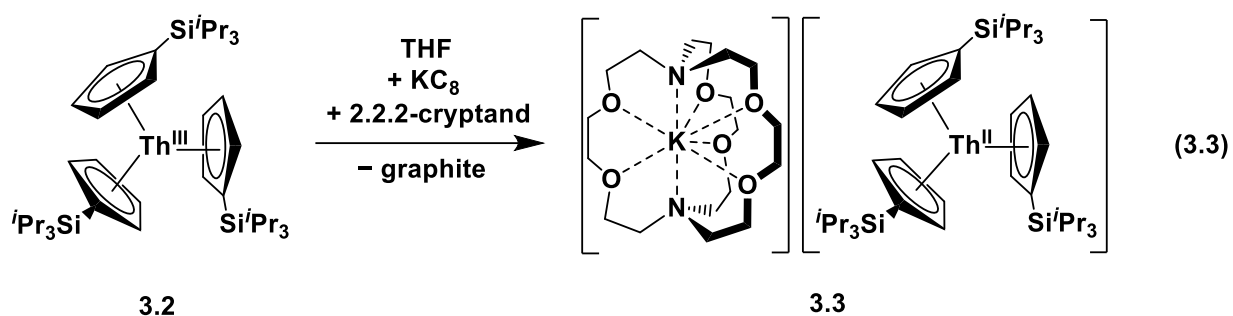


Figure 3.4. Molecular structure of $\text{Cp}^{\text{TIPS}}_3\text{Th}$, **3.2**, with selective atom labelling. Ellipsoids are drawn at the 50% probability level and hydrogen atoms are not shown for clarity.

When a solution of **3.2** and 2.2.2-cryptand (crypt) in THF was treated with 1.2 equiv of KC_8 , an inky dark blue-black color was generated. After filtration to remove insoluble solids, dark blue-black solids were obtained from the filtrate upon removal of the solvent *in vacuo*. Unlike complex **3.2**, these solids are insoluble in hydrocarbon solvents and were washed with hexane to remove unreacted complex **3.2**. Although some attempts to isolate the reduction product by crystallization from diethyl ether or THF/hexane led to the isolation of colorless crystals of the ligand salt, $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}]$, identified by X-ray crystallography, crystallization from either a diethyl ether solution over 2 weeks or from a THF/hexane solution over 2 days at $-35\text{ }^\circ\text{C}$ yielded dark blue-black crystals of $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{Th}]$, **3.3**, identified by X-ray crystallography, Figure 3.5 and eq 3.3.



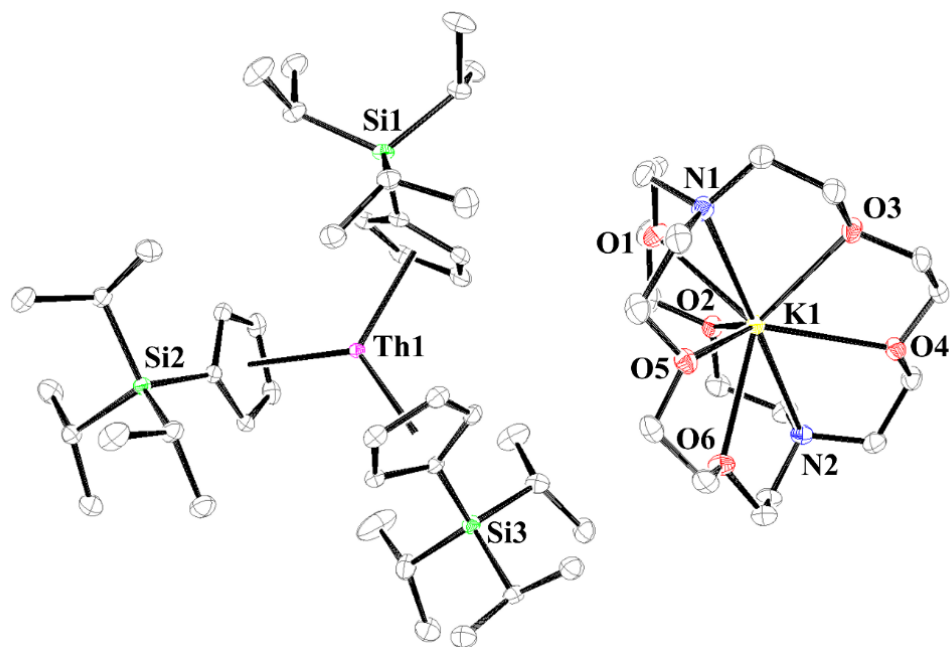


Figure 3.5. Molecular structure of $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{Th}]$, **3.3**, with selective atom labelling. Ellipsoids are drawn at the 50% probability level and hydrogen atoms are not shown for clarity.

Complex **3.3** crystallizes in two different unit cells depending on the crystallization conditions. From a saturated solution of THF/hexane stored at $-35\text{ }^\circ\text{C}$, **3.3** crystallizes in the $P2_1/c$ space group. The structure of **3.3** consists of a $[\text{K}(\text{crypt})]^{1+}$ cation that is well separated from a $(\text{Cp}^{\text{TIPS}}_3\text{Th})^{1-}$ anion. The $(\text{Cp}^{\text{TIPS}}_3\text{Th})^{1-}$ anion in **3.3** has a trigonal planar arrangement of the three Cp^{TIPS} rings around the thorium atom with a sum of 359.5° for the $\text{Cnt}-\text{Th}-\text{Cnt}$ angles, similar to the 360° values reported for the previously characterized structures of the $(\text{Cp}''_3\text{Th})^{1-}$ anion.²⁹ The average $\text{Th}-\text{Cnt}$ distance of $2.521\text{ \AA}$ in complex **3.3** is equivalent to that of $\text{Cp}^{\text{TIPS}}_3\text{Th}$, just as the average $\text{Th}-\text{Cnt}$ distances of $2.521\text{ \AA}$ in $[\text{K}(\text{crypt})][\text{Cp}''_3\text{Th}]$ ²⁹ and $2.525\text{ \AA}$ in $[\text{K}(18\text{-crown-6})(\text{THF})_2][\text{Cp}''_3\text{Th}]$ ²⁹ are equivalent to the average $\text{Th}-\text{Cnt}$ distance in their $\text{Th}(\text{III})$ precursor, $\text{Cp}''_3\text{Th}$.¹⁰ In these $\text{Th}(\text{III})/\text{Th}(\text{II})$ pairs, the bond distance to the ligand does not change significantly upon reduction.^{29,43–46}

When X-ray quality crystals are grown from a saturated diethyl ether solution stored at -35°C , complex **3.3** crystallizes in the $P2_1/n$ space group. The structural parameters of the $P2_1/n$ structure of **3.3** are similar to those of the $P2_1/c$ structure with an average Th–Cnt distance of 2.516 Å and a sum of 359.9° for the Cnt–Th–Cnt angles. However, the relative orientations of the rings and silyl substituents are not equivalent between the two structures of **3.3** and do not superimpose, Figure 3.6. This shows the flexibility of the Cp^{TIPS} ligands to form X-ray quality crystals in more than one orientation.

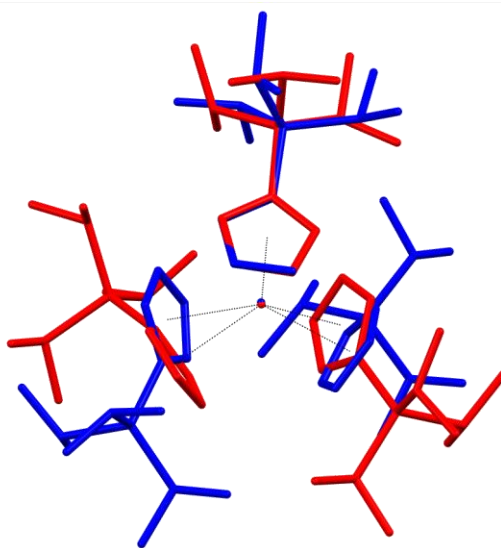


Figure 3.6. Overlay of the $P2_1/n$ (blue) and $P2_1/c$ (red) structures of the anion of $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{Th}]$, **3.3**. Hydrogen atoms are not shown for clarity. Both structures are oriented to have an exact overlay of the thorium metal center and one cyclopentadienyl ring. The two structures are not optical isomers although the orientations of the ligands differ along those lines.

The reduction of $\text{Cp}^{\text{TIPS}}_3\text{Th}$, **3.2**, with KC_8 without the presence of a chelate also generated blue-black solutions similar to those of **3.3**, but once the solvent was removed, the resulting blue-black solids were poorly soluble in THF. Once dissolved, the solutions quickly become colorless. This result highlights the importance of the alkali metal chelate in the successful isolation of **3.3**.

The EPR spectrum of complex **3.3** is silent at 77 K, similar to that of the originally reported EPR spectrum for $(\text{Cp}''_3\text{Th})^{1-}$.²⁹ Indeed, ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra can be collected for complex **3.3** in $\text{THF-}d_8$ and resonances were observed in the diamagnetic region, shifted slightly in comparison to the NMR spectra of KCp^{TIPS} and $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}]$. In comparison to the resonance observed at -6 ppm in the $^{29}\text{Si}\{^1\text{H}\}$ NMR of $[\text{K}(\text{crypt})][\text{Cp}''_3\text{Th}]$,²⁹ complex **3.3** shows a resonance at -5.5 ppm versus SiMe_4 .

Complex **3.3** decomposes faster at room temperature than the previously reported Th(II) complex, $[\text{K}(\text{18-crown-6})(\text{THF})_2][\text{Cp}''_3\text{Th}]$, which decomposes only 8% after 8 days at 298 K in THF.²⁹ In contrast, $\text{THF-}d_8$ solutions of complex **3.3** stored under an argon atmosphere in J. Young NMR tubes at ambient temperature completely lose their color to clear pale-yellow solutions after 4 days. At that point, the ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of the resulting solution showed the presence of a new diamagnetic species which may be a Th(IV) hydride complex based on the resonance observed at 11.83 ppm in the ^1H NMR.¹³ Similar Th(IV) hydride products were observed in attempts to reduce $(\text{C}_5\text{Me}_4\text{H})_3\text{Th}$ with KC_8 in the presence of crypt which led to the identification of $(\text{C}_5\text{Me}_4\text{H})_3\text{ThH}$, $[\text{K}(\text{crypt})]\{(\text{C}_5\text{Me}_4\text{H})_2\text{ThH}[\eta^5:\eta^1\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)]\}$, and $[\text{K}(\text{crypt})][\text{C}_5\text{Me}_4\text{H}]$ as the only isolable products.¹³

The UV–visible spectrum of complex **3.3** is compared to that of **3.2** in Figure 3.7. The measured extinction coefficients of 3900, 4700, and 5200 $\text{M}^{-1} \text{cm}^{-1}$ for the absorptions centered at 424, 585, and 650 nm are likely to be underestimated due to decomposition, but they clearly are more intense than those of complex **3.2**, Figure 3.7. However, the measured extinction coefficients of **3.3** are not as large as the 23,000 $\text{M}^{-1} \text{cm}^{-1}$ value observed for the absorption at 650 nm of $[\text{K}(\text{crypt})][\text{Cp}''_3\text{Th}]$.²⁹

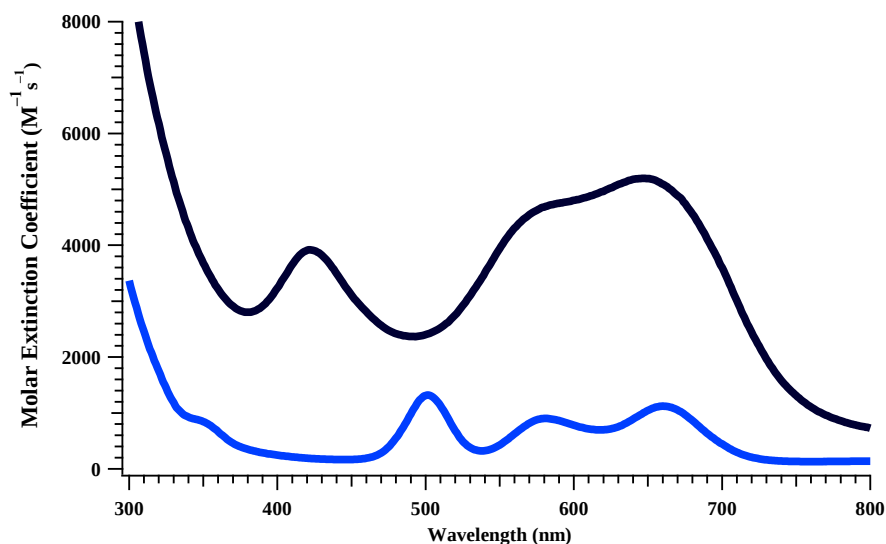


Figure 3.7. UV–visible spectra of **3.2** (blue trace) and **3.3** (blue-black trace) in THF at room temperature.

A key development in the utilization of electrochemistry to characterize *f*-element complexes was the identification of [ⁿBu₄N][BPh₄] as a supporting electrolyte.^{21,30,47,48} Attempts to measure the electrochemical behavior of the dark blue Cp^{TIPS}₃Th, **3.2**, were complicated by the fact that it decomposes to a colorless compound upon addition to electrolyte solutions of [ⁿBu₄N][BPh₄] in THF. Although **3.2** decomposed in the supporting electrolyte solution, the voltammogram of Cp^{TIPS}₃ThBr, **3.1**, could be obtained using approximately 100 mM multiply recrystallized [ⁿBu₄N][BPh₄] supporting electrolyte concentrations in THF. Scanning anodically, a redox process centered at −3.09 V vs Fc⁺/Fc was observed which was assigned as the Th(IV)/Th(III) couple, Figure 3.8. The voltammogram of **3.1** was complicated by redox processes presumed to be ligand-based events, so 20 cycles were performed between −1.92 and −3.82 V to more accurately determine the Th(IV)/Th(III) reduction potential of **3.1**.

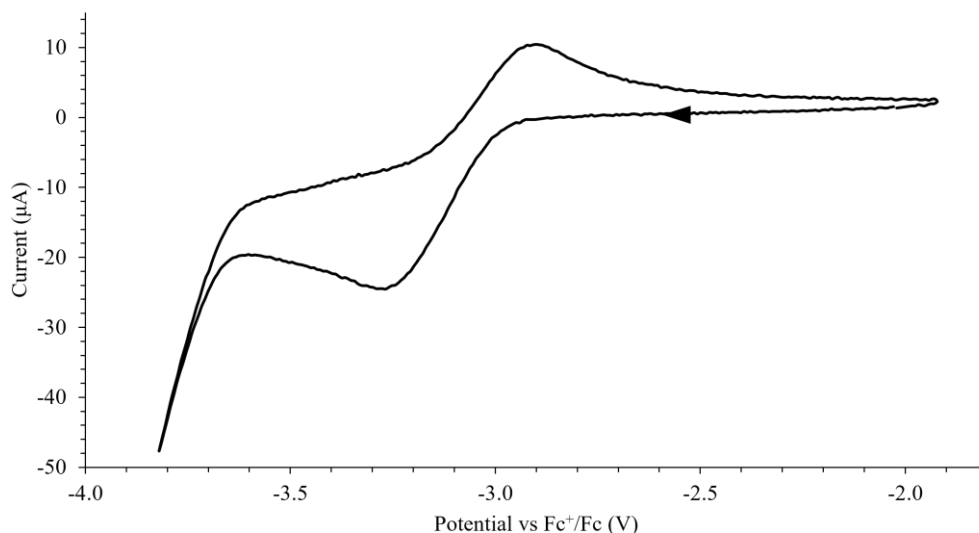


Figure 3.8. Voltammogram of $\text{Cp}^{\text{TIPS}}_3\text{ThBr}$, **3.1**, at $v = 200 \text{ mV s}^{-1}$ in $100 \text{ mM } [\text{nBu}_4\text{N}][\text{BPh}_4]/\text{THF}$ at room temperature after 20 cycles scanned between -1.92 and -3.82 V .

The Th(IV)/Th(III) reduction potential of **3.1** is more negative than that of the $\text{Cp}''_3\text{ThX}$ ($\text{X} = \text{Cl}, \text{Br}$) complexes which contain disilyl-substituted cyclopentadienyl ligands but similar to the redox couple of the Th(IV) complex, $\text{Cp}'_3\text{ThCl}$, which contains monosilyl-substituted cyclopentadienyl ligands, Table 3.2. Furthermore, compared to the Th(IV)/Th(III) reduction potential of $(\text{C}_5\text{Me}_4\text{H})_3\text{ThBr}$ which contains polyalkylated cyclopentadienyl ligands, complex **3.1** and all of the other tris(silylcyclopentadienyl) Th(IV) complexes have noticeably less negative Th(IV)/Th(III) redox potentials. This trend is in line with the electron-withdrawing nature of silyl groups relative to alkyl groups in complexes of this type.³¹ The Th(IV)/Th(III) reduction potential does not change significantly upon substitution of the SiMe_3 substituent with the more sterically encumbering Si^iPr_3 substituent. This suggests that the number of the trialkylsilyl substituents on the cyclopentadienyl ligands has a more significant effect on the Th(IV)/Th(III) redox couple than the specific trialkylsilyl group. Hence, the increased thermal stability of $\text{Cp}^{\text{TIPS}}_3\text{Th}$ compared to

the reduction product of $\text{Cp}'_3\text{ThX}^{21}$ is possibly due to steric saturation about the metal center and not a difference in reduction potentials.

Table 3.2. Reduction Potentials of Tris(cyclopentadienyl)thorium Complexes Versus Ferrocene with 100 mM $[\text{nBu}_4\text{N}][\text{BPh}_4]$ Supporting Electrolyte Concentrations in THF in Increasing Order of $E_{1/2}$.

Th(IV) complex	E_{PC} (V)	E_{PA} (V)	$E_{1/2}$ (V)
$\text{Cp}''_3\text{Th}^{\text{IV}}\text{Br}^{30}$	−3.00	−2.77	−2.89
$\text{Cp}''_3\text{Th}^{\text{IV}}\text{Cl}^{30}$	−3.04	−2.81	−2.93
$\text{Cp}^{\text{TIPS}}_3\text{Th}^{\text{IV}}\text{Br}^{\text{a}}$	−3.27	−2.90	−3.09
$\text{Cp}'_3\text{Th}^{\text{IV}}\text{Cl}^{30}$	−3.38	−2.90	−3.14
$\text{Cp}'_3\text{Th}^{\text{IV}}\text{Br}^{30}$	−3.17	−	−
$(\text{C}_5\text{Me}_4\text{H})_3\text{Th}^{\text{IV}}\text{Br}^{30}$	−3.48	−3.19	−3.34

^a This work.

Electronic structure calculations on both $\text{Cp}^{\text{TIPS}}_3\text{Th}$ and $(\text{Cp}^{\text{TIPS}}_3\text{Th})^{1-}$ were performed using DFT with the TPSSh hybrid meta-generalized gradient density functional⁴⁹ with the D3 dispersion correction^{50,51} and the resolution of the identity (RI-J) approximation.⁵² Scalar relativistic effective core potentials with the def-TZVP basis set⁵³ were used for thorium and the polarized split-valence basis set def2-SV(P) was used for other atoms.⁵⁴ The continuum solvent model COSMO⁵⁵ was used with parameters for THF (dielectric constant $\epsilon = 7.52$ and refractive index $R_{\text{ind}} = 1.41$).⁵⁶ All calculations were performed with the TURBOMOLE package V7.6.^{57,58}

The geometry-optimized structures of the neutral $\text{Cp}^{\text{TIPS}}_3\text{Th}$ and the $(\text{Cp}^{\text{TIPS}}_3\text{Th})^{1-}$ anion have average Th–Cnt distances of 2.501 and 2.489 Å, respectively, which are within 0.03 Å of the experimentally determined Th–Cnt average distances, 2.520 and 2.524 Å, respectively. The

calculated bond angles are also reproduced within a few degrees for both structures. Geometry optimization on the coordinates for both structures yields ground state geometries with C_1 -symmetry.

The electronic structures suggest $(6d_z^2)^1$ and $(6d_z^2)^2$ electron configurations for $\text{Cp}^{\text{TIPS}}_3\text{Th}$ and $(\text{Cp}^{\text{TIPS}}_3\text{Th})^{1-}$, respectively. These are the same ground-state electron configurations assigned to the neutral $\text{Cp}''_3\text{Th}$ and the anionic $(\text{Cp}''_3\text{Th})^{1-}$ of the disilyl-substituted cyclopentadienyl analogues.²⁹ To further verify the ground-state configuration of $(\text{Cp}^{\text{TIPS}}_3\text{Th})^{1-}$, geometry optimization was run on the same anion constrained to a triplet state. The total energy was >0.4 eV higher than the singlet ground state. The $6d_z^2$ character of the HOMO for $(\text{Cp}^{\text{TIPS}}_3\text{Th})^{1-}$ can be seen in Figure 3.9.

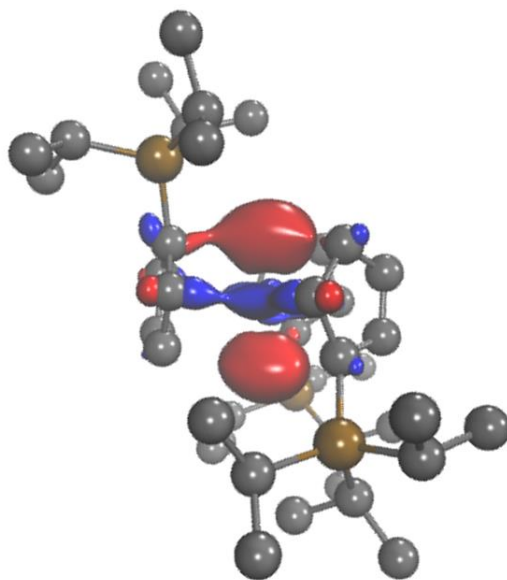


Figure 3.9. Calculated HOMO ($\epsilon = -1.235$) of $(\text{Cp}^{\text{TIPS}}_3\text{Th}^{\text{II}})^{1-}$ plotted with a contour value of 0.05.

Time-dependent DFT calculations were then conducted on the geometry-optimized structures and the resulting simulated UV–visible absorption spectra qualitatively reproduce the experimental spectra observed, Figure 3.10. For $\text{Cp}^{\text{TIPS}}_3\text{Th}$, the strongest absorptions >550 nm primarily correspond to $6d \rightarrow 5f$ transitions. For $(\text{Cp}^{\text{TIPS}}_3\text{Th})^{1-}$, the three absorptions between 450

and 650 nm with the greatest oscillator strengths correspond to $d \rightarrow f$ and/or $d \rightarrow p$ transitions. While further improvement of the agreement between experimental and computational spectra for **3.2** might be possible, the observed deviations are within the expected range for this type of calculation and measurement.

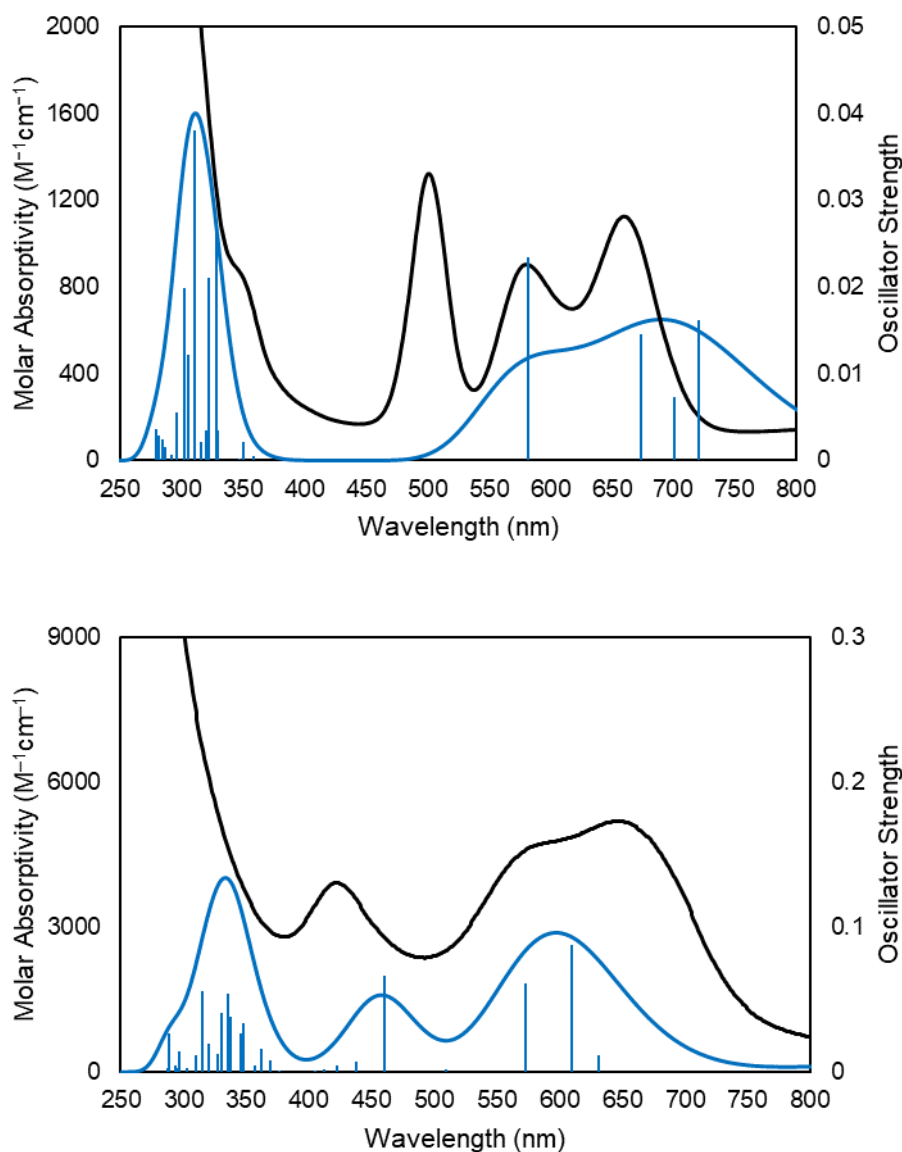


Figure 3.10. Simulated (blue) and experimental (black) UV–visible spectra for $Cp^{TIPS_3}Th$, **3.2** (top), and $[K(crypt)][Cp^{TIPS_3}Th]$, **3.3** (bottom). The computed TDDFT oscillator strengths are

shown as blue vertical lines. Each calculated spectrum was empirically blue-shifted by 0.30 eV and a Gaussian line broadening of 0.15 eV was applied.

The importance of steric saturation of the metal center in Th(III) and Th(II) complexes was evaluated using the Guzei Solid Angle method that provides G , an estimation of the percentage of the coordination sphere of the metal that is protected by the ligands.³⁴ Guzei G values were calculated for complexes **3.2** and **3.3** in addition to all of the crystallographically characterized Th(III) and Th(II) complexes, which have published crystal structures that include hydrogen atoms, Table 3.1. Although it is generally best to compare G values only for a structurally similar series of complexes, all of the isolable Th(III) complexes regardless of ligand have G values between 82 and 91%, except $(C_5Me_5)_3Th$.¹⁴ This defines a range of G values that can provide stable structures. The low value of 79% observed for $(C_5Me_5)_3Th$ can be rationalized by the fact that the Th–C_{nt} distances reported for this complex are substantially longer than those observed for other complexes as is characteristic of $(C_5Me_5)_3M$ complexes.⁵⁹ This causes the $(C_5Me_5)^{1-}$ ligands to be located further from the metal center, which leads to a lower G value.

The new Th(III) complex, **3.2**, has a G value of 89%, whereas the new Th(II) complex, **3.3**, has G values of 87 and 88%, falling within the range of those calculated for the other Th(III) and Th(II) complexes in the literature. The small decrease in the G value upon reduction from Th(III) in **3.2** to Th(II) in **3.3** is consistent with small changes in metal–ligand distances upon the addition of a 6d electron. Similarly, the G values for Cp''_3Th and $(Cp''_3Th)^{1-}$ are 91 and 90%, respectively.

Although complexes **3.2** and **3.3** have G values in the range typical of stable complexes, G values alone cannot always predict stability even within a class of structurally similar complexes. This is exemplified by theoretical calculations conducted on the monotrimethylsilyl-substituted cyclopentadienyl Th(III) complex, Cp'_3Th . A G value of 87% was calculated for this complex

using a DFT-calculated structure, which suggests that it should be isolable. However, no crystallographic data confirming its formation has been observed to date.²¹ It is noted here that a *G* value for Cp^{TIPS}₃Th was calculated to be 93% from a DFT -calculated structure prior to the crystallization of **3.2**, which provided an experimental value of 88%. Hence, *G* calculations based on DFT structures may be slightly overestimated and the actual value for Cp'₃Th could be at the lower limit of the range cited above. In addition, slight differences in the way molecules pack in the solid state can also introduce variations in the *G* value. This is exemplified by the 87 and 88% *G* values for the two crystal structures of [K(crypt)][Cp^{TIPS}₃Th], **3.3**, grown under different conditions, as shown in Figure 3.6.

Since the other tris(ligand) Th(III) complexes with polyalkylated cyclopentadienyl ligands, (C₅Me₅)₃Th, (C₅Me₄H)₃Th, and (C₅Me₅)₂Th[^{*i*}PrNC(Me)N^{*i*}Pr], have *G* values of 79, 82, and 84%, respectively, it is conceivable that reductions of these Th(III) complexes would form isolable Th(II) complexes. Although reductions of these Th(III) complexes form transient dark green solutions similar to that of (Cp''₃Th)¹⁻, none of these reactions yielded isolable Th(II) products.⁶⁰ In the case of (C₅Me₄H)₃Th, only the Th(IV) C–H bond activation product, [K(crypt)][{[C₅Me₄H]₂ThH[$\eta^5:\eta^1$ -C₅Me₃H(CH₂)]}], and the Th(IV) hydride complex, (C₅Me₄H)₃ThH, were isolated and characterized.¹³ In these cases, it is possible that the electron-donating ability of the ligands is making them more reactive and this should be considered in addition to the steric bulk of the cyclopentadienyl ligand when seeking isolable Th(II) complexes.

CONCLUSION

In summary, replacing trimethylsilyl with triisopropylsilyl as the trialkylsilyl substituent on the cyclopentadienyl ligand has led to the isolation of the first crystalline monosilyl-cyclopentadienyl Th(III) complex and the second example of a Th(II) complex of any kind.

Specifically, $\text{Cp}^{\text{TIPS}}_3\text{Th}$, **3.2**, and $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{Th}]$, **3.3**, can be isolated and structurally characterized while the isolation of $\text{Cp}'_3\text{Th}$ and $(\text{Cp}'_3\text{Th})^{1-}$ has been elusive. The synthetic utility of the Si^iPr_3 functional group compared to SiMe_3 has been long ago documented in organic chemistry.⁶¹ However, this is surprising in this case since the alkyl groups on the silyl substituents are not close to the metal center and the 89% *G* value for $\text{Cp}^{\text{TIPS}}_3\text{Th}$ is close to the 87% value estimated for $\text{Cp}'_3\text{Th}$. The superiority of the triisopropylsilylcyclopentadienyl ligand for isolating Th(III) and Th(II) complexes emphasizes the importance of ligand variation in optimizing chemistry. In addition, the successful isolation of complex **3.3** exemplifies the fact that Th(II) complexes are not limited to bis(trialkylsilyl)cyclopentadienyl coordination environments if the monotrialkylsilyl substituent is large enough. Clearly, the interplay of electronic and steric factors that stabilize Th(III) and Th(II) complexes remains to be fully defined.

EXPERIMENTAL DETAILS

Caution! ^{232}Th is an α emitter with a half-life of approximately 1.41×10^{10} years. Samples should be prepared and handled only in laboratories appropriately equipped to handle radioactive materials.

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP (99.999%) argon, dried by passage through columns containing Q-5 and molecular sieves, and stored over activated sieves overnight prior to use. Deuterated NMR solvents were degassed and dried over activated 3 Å molecular sieves overnight prior to use. ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AVANCE600 MHz spectrometer at 298 K unless otherwise stated. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced internally to residual protio-solvent resonances, and $^{29}\text{Si}\{^1\text{H}\}$ NMR

spectra were referenced internally to SiMe₄. Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR spectrometer. UV–visible spectra were collected under an inert atmosphere of argon in THF at 298 K using a Varian Cary 50 Scan UV–visible spectrometer in a 1 mm Schlenk cuvette fitted with a Teflon stopper unless otherwise stated. X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with an ER041Xg microwave bridge and calibrated with DPPH ($g = 2.0036$). Elemental analyses were conducted on a Thermo Scientific FlashSmart CHNS/O elemental analyzer at UC Irvine Materials Research Institute’s TEMPR facility in Irvine, California. NaC₅H₅⁶² and KC₈⁶³ were synthesized according to the literature procedures. ThBr₄(DME)₂ (DME = 1,2-dimethoxyethane) was synthesized by treating ThBr₄(THF)₄⁶⁴ with neat DME followed by filtration and drying under reduced pressure. Triisopropylsilyl triflate was purchased from TCI Chemicals and used as received. 2.2.2-Cryptand (crypt) was purchased from Sigma-Aldrich and recrystallized in Et₂O prior to use.

Synthesis of KC₅H₄Si^{*i*}Pr₃ from NaC₅H₅. In separate Schlenk flasks, solutions of NaC₅H₅ (2.01 g, 22.8 mmol) in THF (ca. 50 mL) and ^{*i*}Pr₃SiOTf (7.06 g, 23.0 mmol) in hexane (ca. 20 mL) were cooled to –78 °C. The ^{*i*}Pr₃SiOTf solution was then added dropwise over 2 hr to the NaC₅H₅ solution via cannula and the resulting mixture was allowed to stir and warm to room temperature over 3 hours at which point it became a pale-yellow mixture with much colorless precipitate. Solvent was removed under reduced pressure to yield a pale-yellow residue. The flask was then brought into a glovebox and the residue was extracted into hexane (ca. 20 mL). The mixture was then centrifuged and filtered to remove insoluble solids, presumably NaOTf. Solvent was removed under reduced pressure to yield a yellow oil, presumably HC₅H₄Si^{*i*}Pr₃ (4.37 g, 86%), which was directly used for the next step.

HC₅H₄Si^{*i*}Pr₃ (1.22 g, 5.46 mmol) was dissolved in toluene (ca. 3 mL) to afford a pale-yellow solution. With stirring, a solution of KN(SiMe₃)₂ (1.04 g, 5.21 mmol) in toluene (ca. 15 mL) was added dropwise at room temperature over 10 min. Colorless precipitate slowly formed throughout the addition and the mixture was allowed to stir at room temperature overnight. The mixture was filtered through a medium porosity glass frit and the solids were washed with toluene (ca. 5 mL) followed by hexane (ca. 20 mL). The solids were collected and dried in vacuo to yield KC₅H₄Si^{*i*}Pr₃ as white powdery solids (1.03 g, 76%). ¹H NMR (THF-*d*₈, 600 MHz): δ 5.96–5.95 (m, 2H, C₅H₄Si^{*i*}Pr₃), 5.83–5.82 (m, 2H, C₅H₄Si^{*i*}Pr₃), 1.18–1.13 (sept, ³*J*_{HH} = 7.3 Hz, 3H, CH of ^{*i*}Pr), 1.07–1.06 (d, ³*J*_{HH} = 7.3 Hz, 18H, CH₃ of ^{*i*}Pr). ¹³C{¹H} NMR (THF-*d*₈, 151 MHz): δ 115.1 (C₅H₄Si^{*i*}Pr₃), 108.0 (C₅H₄Si^{*i*}Pr₃), 103.1 (C₅H₄Si^{*i*}Pr₃), 20.1 (CH₃ of ^{*i*}Pr), 13.4 (CH of ^{*i*}Pr). ²⁹Si{¹H} NMR (THF-*d*₈, 119 MHz): δ –3.1 (C₅H₄Si^{*i*}Pr₃). IR: 3054w, 2935s, 2886m, 2860s, 1459m, 1434m, 1378w, 1361w, 1345w, 1246w, 1174m, 1074w, 1035s, 1009m, 979w, 878s, 813w, 738vs, 734vs, 660vs, 656vs. Anal. Calcd. for C₁₄H₂₄KSi: C, 64.54; H, 9.67. Found: C, 65.31; H, 9.69; C, 65.10; H, 9.70; C, 65.03; H, 9.70. The C/H ratios in the analytical data give formulas of C₁₄H_{24.7}, C₁₄H_{24.7}, and C₁₄H_{24.8}, respectively, close to the calculated value of C₁₄H₂₅.

Synthesis of (C₅H₄Si^{*i*}Pr₃)₃ThBr, **3.1.** KC₅H₄Si^{*i*}Pr₃ (624 mg, 2.39 mmol) was added as a solid in portions over 1 min to a stirred white suspension of ThBr₄(DME)₂ (584 mg, 0.798 mmol) in Et₂O (ca. 9 mL) at room temperature. The resulting mixture was allowed to stir at room temperature for 16 h at which point it became a white suspension. White insoluble solids, presumably KBr, were removed by centrifugation followed by filtration to yield a clear pale-yellow solution. Solvent was removed under reduced pressure to yield white solids. The solids were extracted into hexane (ca. 5 mL) and filtered to remove insoluble solids. Solvent was removed from the clear pale-yellow filtrate to yield **3.1** as white solids (664 mg, 85%). Colorless

crystals suitable for X-ray diffraction were grown from dilute solutions of toluene (approximately 15 mg/4 mL) stored at $-35\text{ }^{\circ}\text{C}$. The appropriately dilute solution was obtained by repeatedly harvesting powders that initially formed from more concentrated solutions. ^1H NMR (C_6D_6 , 600 MHz): δ 6.64–6.63 (m, 6H, $\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 6.60–6.59 (m, 6H, $\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 1.53–1.45 (sept, $^3J_{\text{HH}} = 7.4\text{ Hz}$, 9H, CH of ^iPr), 1.21–1.20 (d, $^3J_{\text{HH}} = 7.4\text{ Hz}$, 54H, CH_3 of ^iPr). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 151 MHz): δ 128.9 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 128.6 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 122.4 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 19.8 (CH_3 of ^iPr), 12.6 (CH of ^iPr). $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 119 MHz): δ -0.9 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$). IR: 2941s, 2887m, 2862s, 1460m, 1382w, 1367w, 1305w, 1293w, 1242w, 1163m, 1067w, 1043s, 996m, 917w, 880s, 845w, 782vs, 778vs, 667vs, 659vs. Anal. Calcd. for $\text{C}_{42}\text{H}_{75}\text{Si}_3\text{BrTh}$: C, 51.67; H, 7.74. Found: C, 54.42; H, 8.20; C, 52.35; H, 7.96; C, 52.78; H, 7.97. The C/H ratios in the analytical data give formulas of $\text{C}_{42}\text{H}_{75.2}$, $\text{C}_{42}\text{H}_{75.9}$, and $\text{C}_{42}\text{H}_{75.4}$, respectively, close to the calculated value of $\text{C}_{42}\text{H}_{75}$.

Synthesis of $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{Th}$, **3.2.** Solid KC_8 (18 mg, 0.133 mmol) was added to a solution of $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{ThBr}$, **3.1**, (104 mg, 0.106 mmol) in THF (ca. 3 mL) at room temperature to immediately produce a dark blue solution. The vial was swirled at room temperature for 5 min before being filtered to remove insoluble solids. Solvent was removed from the filtrate under reduced pressure to yield dark blue oily solids, which were then extracted into hexane (ca. 5 mL) and filtered. Solvent was removed under reduced pressure to yield dark blue solids which were then triturated with SiMe_4 (ca. 1 mL) and dried to yield $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{Th}$, **3.2**, as blue solids (94 mg, 98%). Dark blue crystals suitable for X-ray diffraction were grown from a saturated pentane solution stored at $-35\text{ }^{\circ}\text{C}$. $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 119 MHz): δ -21.8 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$). IR: 2941m, 2889w, 2862s, 1462m, 1382w, 1365w, 1261w, 1247w, 1159w, 1094w, 1066w, 1041s, 1015m, 997m, 917w, 880s, 860m, 841m, 769vs, 661vs, 652vs. UV–vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$): 350 (840, shoulder), 504 (1300), 582 (900), 664 (1100). EPR: $g_{\text{iso}} = 1.90$, $g_{\parallel} = 1.97$,

$g_{\perp} = 1.88$. Anal. Calcd. for $C_{42}H_{75}Si_3Th$: C, 56.28; H, 8.43. Found: C, 56.16; H, 8.52; C, 56.36; H, 8.48; C, 55.06; H, 8.18. The C/H ratios in the analytical data give formulas of $C_{42}H_{75.8}$, $C_{42}H_{75.1}$, and $C_{42}H_{74.2}$, respectively, close to the calculated value of $C_{42}H_{75}$.

Synthesis of $[K(2.2.2\text{-cryptand})][(C_5H_4Si^iPr_3)Th]$, **3.3.** Solid KC_8 (4.3 mg, 0.032 mmol) was added to a solution of **3.2** (24.0 mg, 0.0268 mmol) and crypt (11.0 mg, 0.0292 mmol) in THF (ca. 4 mL) at room temperature to immediately produce an inky blue-green solution. The mixture was swirled for ca. 5 min at room temperature before being filtered to remove insoluble solids. Solvent was removed under reduced pressure to yield dark blue-black solids. The solids were then washed with hexane (ca. 2 mL) to remove unreacted **3.2** and dried under reduced pressure to yield **3.3** as dark blue-black solids (34 mg). X-ray quality crystals can be grown from a THF/hexane or diethyl ether solution stored at $-35\text{ }^{\circ}C$. Colorless X-ray quality crystals of $[K(crypt)][Cp^{TIPS}]$, identified by X-ray crystallography, were found to co-crystallize from solutions of **3.3** in Et_2O or THF/hexane. ^1H NMR (THF- d_8 , 600 MHz): δ 6.85–6.1 (br, 12H, $C_5H_4Si^iPr_3$), 3.55 (s, 12H, OCH_2CH_2O), 3.51 (s, 12H, NCH_2CH_2O), 2.53 (s, 12H, NCH_2CH_2O), 1.50–1.31 (br, 9H, CH of ^iPr), 1.30–0.98 (br, 54H, CH_3 of ^iPr). $^{13}C\{^1H\}$ NMR (THF- d_8 , 151 MHz): δ 114.7 ($C_5H_4Si^iPr_3$), 107.7 ($C_5H_4Si^iPr_3$), 102.3 ($C_5H_4Si^iPr_3$), 71.3 (OCH_2CH_2O), 68.5 (NCH_2CH_2O), 54.8 (NCH_2CH_2O), 20.3 (CH_3 of ^iPr), 13.4 (CH of ^iPr). $^{29}Si\{^1H\}$ NMR (THF- d_8 , 119 MHz): δ -5.54 ($C_5H_4Si^iPr_3$). IR: 3037w, 2912w, 2883m, 2853s, 2817m, 1477w, 1460m, 1443m, 1418w, 1355s, 1296m, 1260m, 1239w, 1130s, 1101vs, 1077vs, 1033vs, 1011m, 986w, 948s, 932s, 881m, 830w, 781w, 750w, 700w, 661s. UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$): 424 (3910), 585 (4700, shoulder), 650 (5200). Anal. Calcd. for $C_{60}H_{111}N_2O_6Si_3KTh$: C, 54.93; H: 8.53; N: 2.14. Found: C, 55.79; H, 9.95; N: 5.81. C, 55.64; H, 8.80; N, 5.971. C, 55.82, H, 8.62, N, 5.76. The C/H/N ratios in the analytical data give formulas of $C_{60}H_{127}N_{5.4}$,

C₆₀H₁₁₃N_{5.5}, and C₆₀H₁₁₁N_{5.3}. The high N values can be accounted for by the presence of excess crypt (Anal. Calcd. for C₁₈H₃₆N₂O₆: C, 57.42; H, 9.64; N, 7.44) in crystalline samples of **3.3**.

Independent Synthesis of Crystallographically Characterized [K(2.2.2-cryptand)][C₅H₄Si^{*i*}Pr₃]. KC₅H₄Si^{*i*}Pr₃ (16.0 mg, 0.0614 mmol) and 2.2.2-cryptand (23.0 mg, 0.0614 mmol) were both added to a J. Young NMR tube fitted with a Teflon stopper. THF-*d*₈ (ca. 1 mL) and one drop of SiMe₄ were then added to the J. Young tube and the tube was shaken until all the solids were dissolved to form a colorless solution. NMR spectroscopy confirmed the quantitative formation of [K(2.2.2-cryptand)][C₅H₄Si^{*i*}Pr₃]. ¹H NMR (THF-*d*₈, 600 MHz): δ 5.81 (m, 2H, C₅H₄Si^{*i*}Pr₃), 5.66 (m, 2H, C₅H₄Si^{*i*}Pr₃), 3.46 (s, 12H, NCH₂CH₂O), 3.44 (m, 12H, NCH₂CH₂O), 2.47 (m, 12H, NCH₂CH₂O), 1.17–1.11 (sept, ³J_{HH} = 7.8 Hz, 3H, CH of ^{*i*}Pr), 1.07 (d, ³J_{HH} = 6.9 Hz, 18H, CH₃ of ^{*i*}Pr). ¹³C{¹H} NMR (THF-*d*₈, 151 MHz): δ 113.8 (C₅H₄Si^{*i*}Pr₃), 106.7 (C₅H₄Si^{*i*}Pr₃), 99.0 (C₅H₄Si^{*i*}Pr₃), 71.3 (OCH₂CH₂O), 68.4 (NCH₂CH₂O), 54.9 (NCH₂CH₂O), 20.5 (CH₃ of ^{*i*}Pr), 13.7 (CH of ^{*i*}Pr). ²⁹Si{¹H} NMR (THF-*d*₈, 119 MHz): δ –3.5 (C₅H₄Si^{*i*}Pr₃).

X-ray Data Collection, Structure Solution and Refinement for (C₅H₄Si^{*i*}Pr₃)₃ThBr, **3.1.**

A colorless crystal of approximate dimensions 0.069 x 0.129 x 0.319 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁶⁵ program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time). The raw frame data was processed using SAINT⁶⁶ and SADABS⁶⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁶⁸ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁶⁹ for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model. There was a molecule of toluene present. Least-squares analysis yielded $wR2 = 0.0591$ and $Goof = 1.148$ for 506 variables refined against 14315 data ($0.71 \text{ \AA}$), $R1 = 0.0299$ for those 12928 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $(C_5H_4Si^iPr_3)_3Th$, 3.2.

A blue crystal of approximate dimensions $0.224 \times 0.306 \times 0.402 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁶⁵ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT⁶⁶ and SADABS⁶⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁶⁸ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0538$ and $Goof = 1.043$ for 433 variables refined against 12586 data ($0.70 \text{ \AA}$), $R1 = 0.0213$ for those 11952 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $[K(2.2.2\text{-cryptand})][C_5H_4Si^iPr_3]$. A colorless crystal of approximate dimensions $0.154 \times 0.300 \times 0.365 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁶⁵ program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time). The raw frame data was processed using SAINT⁶⁶ and SADABS⁶⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁶⁸ program package. The diffraction symmetry was $2/m$ and the systematic absences

were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were two molecules of the formula unit present. Least-squares analysis yielded $wR2 = 0.0981$ and $Goof = 1.008$ for 769 variables refined against 21992 data ($0.70 \text{ \AA}$), $R1 = 0.0395$ for those 16406 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for [K(2.2.2-cryptand)][C₅H₄SiⁱPr₃]. A colorless crystal of approximate dimensions $0.150 \times 0.150 \times 0.327$ mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁶⁵ program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time). The raw frame data was processed using SAINT⁶⁶ and SADABS⁶⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁶⁸ program package. The diffraction symmetry was mmm and the systematic absences were consistent with the orthorhombic space group $Pbca$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0836$ and $Goof = 1.020$ for 385 variables refined against 11142 data ($0.70 \text{ \AA}$), $R1 = 0.0320$ for those 8744 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for [K(2.2.2-cryptand)][(C₅H₄SiⁱPr₃)₃Th], 3.3. A black crystal of approximate dimensions $0.188 \times 0.191 \times 0.320$ mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁶⁵ program package was used to determine the unit-cell parameters and for

data collection (30 sec/frame scan time). The raw frame data was processed using SAINT⁶⁶ and SADABS⁶⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁶⁸ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0600$ and $Goof = 1.026$ for 676 variables refined against 19609 data ($0.70 \text{ \AA}$), $R1 = 0.0260$ for those 15721 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for [K(2.2.2-cryptand)][(C₅H₄SiⁱPr₃)₃Th], 3.3. A black crystal of approximate dimensions $0.190 \times 0.214 \times 0.292 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁶⁵ program package and the CELL_NOW⁷⁰ were used to determine the unit-cell parameters. Data was collected using a 45 sec/frame scan time. The raw frame data was processed using SAINT⁶⁶ and TWINABS⁷¹ to yield the reflection data file (HKLF 5 format).⁷¹ Subsequent calculations were carried out using the SHELXTL⁶⁸ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were high residuals present in the final difference-Fourier map. The SQUEEZE^{72a} routine in the PLATON^{72b} program package used to account for the electrons in the solvent accessible voids did not improve the model. One tetrahydrofuran molecule was present and refined

anisotropically. It was probable that additional tetrahydrofuran solvent was present. Another tetrahydrofuran molecule was included with 50% occupancy and refined isotropically. Disordered atoms were included using thermal (SIMU, ISOR, and EADP) and geometric (DFIX, DANG, and SADI) restraints. Least-squares analysis yielded $wR2 = 0.1227$ and $Goof = 1.150$ for 738 variables refined against 13253 data ($0.83 \text{ \AA}$), $R1 = 0.0506$ for those 11603 with $I > 2.0\sigma(I)$. The structure was refined as a non-merohedral two-component twin, $BASF^{68} = 0.46101$. The low bond precision may have been due to disorder and/or the lower completeness.

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Chapter 4:

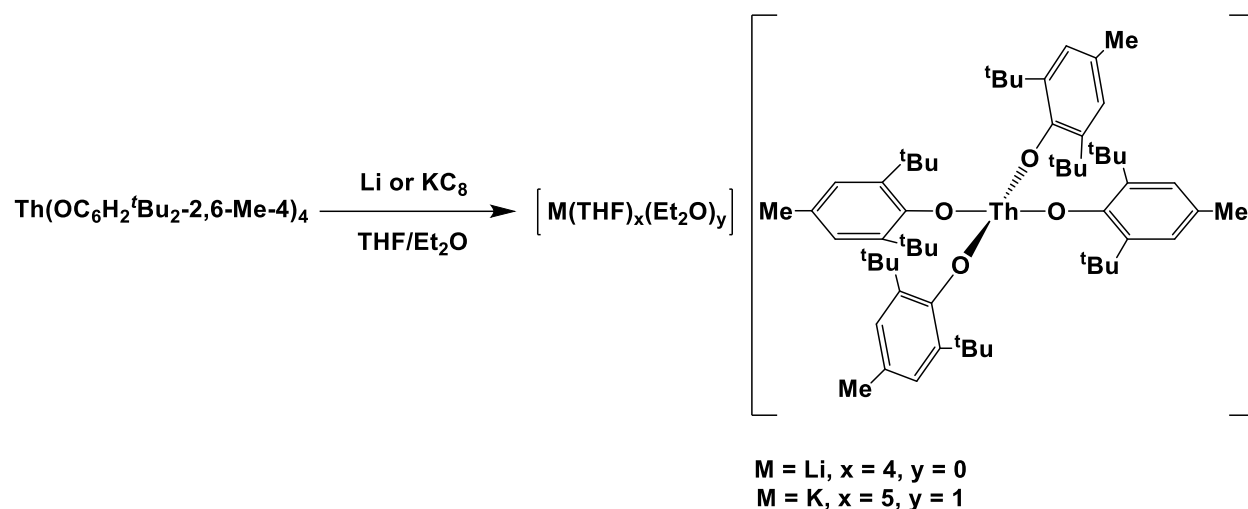
Investigating Steric and Electronic Effects in the Synthesis of Square Planar 6d¹ Th(III) Complexes

INTRODUCTION[†]

Progress in the field of thorium redox chemistry has lagged behind that of uranium even though thorium is over three times more abundant than uranium.¹ In fact, most of the literature on thorium chemistry involves its most stable +4 oxidation state.^{2–18} Although there are many studies showcasing the redox chemistry of thorium complexes, many of these require the use of redox-active ligands or reduced arenes.^{2–8} Up until 2024, only 12 structurally characterized Th(III) complexes have been reported.^{19–30} There are also only six published Th(II) crystal structures, five of which contain the $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{Th}^{\text{II}}\}^{1-}$ anion and one containing the $[(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{Th}^{\text{II}}]^{1-}$ anion as described in the previous Chapter.^{30–32} As a result, the development of synthetic routes to new examples of Th(III) and Th(II) complexes is an important research goal.

An unusual type of Th(III) complex is the $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-}$ anion that was synthesized by the reduction of the Th(IV) tetrakis(aryloxide) complex $\text{Th}(\text{OAr}^{\text{Me}})_4$ ($\text{OAr}^{\text{Me}} = \text{OC}_6\text{H}_2^i\text{Bu}_2\text{-2,6-Me-4}$), **4.1-Me**, Scheme 4.1.²⁰ The reduction product $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-}$ represented the first crystallographically characterized square planar complex in *f*-element chemistry. The geometry of this anionic complex was unexpected since steric effects, which are so important in actinide chemistry,³³ would predict a tetrahedral geometry over the less sterically favorable square planar geometry. Moreover, this complex was the first example of a square planar complex of any metal

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Scheme 4.1. Synthesis of the $[\text{Li}(\text{THF})_4]^{1+}$ and $[\text{K}(\text{THF})_5(\text{Et}_2\text{O})]^{1+}$ salts of the $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-}$ anion.²⁰

with a d^1 electron configuration. The square planar geometry is most typically seen for transition metal complexes with d^7 , d^8 , and d^9 electron configurations^{34–36} although examples of d^2 complexes such as $\text{W}(\text{OC}_6\text{H}_3^i\text{Pr}_{2,6})_4$ ³⁷ and $\text{W}(\text{OC}_6\text{H}_3\text{Me}_{2,6})_4$ ³⁷ and d^4 complexes such as $\text{Fe}(\text{NC}^t\text{Bu}_2)_4$ ³⁸ and $\text{OsO}_2(\text{P}^i\text{Pr}_3)_2$ ³⁹ have been reported.

Density functional theory (DFT) studies conducted on $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-}$ suggested that it has a low energy $6d_z^2$ orbital due to destabilization of the d_{xy} , $d_{x^2-y^2}$, d_{xz} , and d_{yz} orbitals resulting from π -donation of the oxygen donor atom lone pairs.²⁰ This effect has also been seen in the d^2 and d^4 complexes mentioned above.^{37–39} It was also possible that London dispersion forces between the *tert*-butyl groups on the aryloxy ligands contributed to the stability of this square planar complex.^{20,40}

The existence of this unusual square planar $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-}$ anion suggested that the reduction of other thorium aryloxy complexes should be examined. Previously, Gambarotta and coworkers reported that the potassium reduction of $\text{Th}(\text{OC}_6\text{H}_3\text{Ph}_{2,6})_4$ in toluene/DME (DME = 1,2-dimethoxyethane) formed the Th(IV) hydroxide $[\text{K}(18\text{-crown-6})(\text{THF})_2][\text{Th}(\text{OC}_6\text{H}_3\text{Ph}_{2,6})_4]^{1-}$.

2,6)₄(OH)(THF)].⁹ In contrast, when Th(OC₆H₃Ph₂-2,6)₄ was reacted with potassium naphthalenide in DME, the doubly *ortho*-metalated Th(IV) product [(μ-OC₆H₃Ph₂-2,6)K₂][(μ-2-Ph,6-C₆H₄)₂Th(OC₆H₃Ph₂-2,6)](μ-OC₆H₃Ph₂-2,6)[K(DME)₂] was isolated and crystallographically characterized.⁹ Other than these studies, little data on the reduction chemistry of other thorium aryloxides to new Th(III) and Th(II) complexes were in the literature.

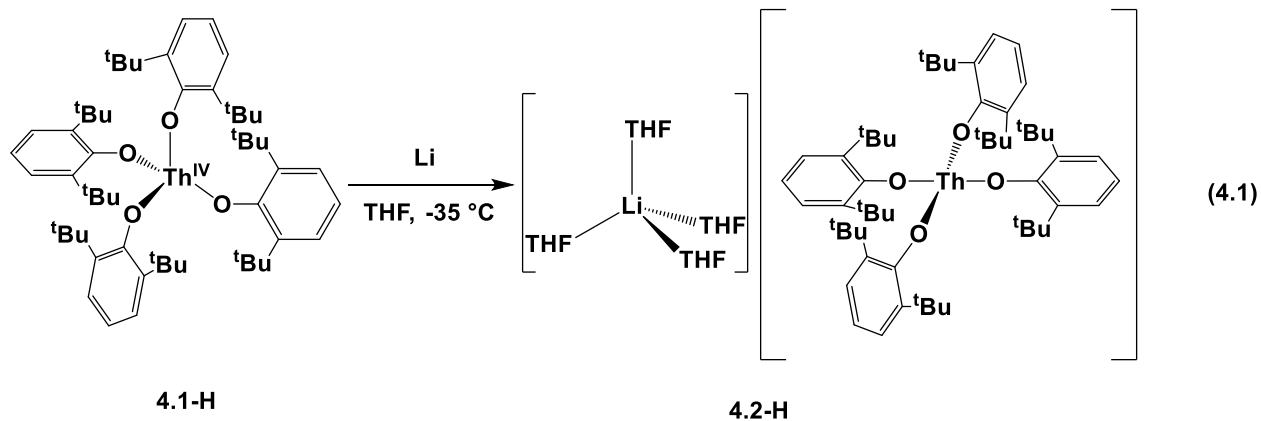
Another reason to study thorium aryloxide reduction chemistry was that it was desirable to have structural characterization of both the Th(IV) aryloxide precursor and its square planar Th(III) reduction product to determine if the reduction involved a structural change. Crystallographic data on the Th(OAr^{Me})₄ precursor to [Th(OAr^{Me})₄]¹⁻ were not reported. Variation in the counteranion component was also desirable. Although good crystallographic data on the [Th(OAr^{Me})₄]¹⁻ anion were obtained with the [Li(THF)₄]¹⁺ and [K(THF)₅(Et₂O)]¹⁺ salts, crystals of the [K(crypt)]¹⁺ (crypt = 2.2.2-cryptand) and [K(crown)]¹⁺ (crown = 18-crown-6) salts suitable for study by X-ray diffraction were not previously structurally characterized. To obtain more information on the unusual square planar Th(III) system, variations in the aryloxide ligand, reductant, and chelate were examined. In addition, the analogous reactions with uranium were examined for comparison.

RESULTS

Reduction of Th(OAr^H)₄, 4.1-H. Initially, the reduction of Th(OAr^H)₄ (OAr^H = OC₆H₃-2,6-*t*Bu₂), **4.1-H**, was examined because this Th(IV) precursor has been previously structurally characterized and was found to have a tetrahedral geometry around thorium.⁴¹ It was not expected that changing from a methyl to hydrogen substituent at the para position would affect the geometry. So, it was thought that the reduction of **4.1-H** would confirm a tetrahedral to square planar transformation upon reduction. The OAr^{Me} ligand was originally chosen to avoid possible radical

chemistry at the *para* position of the aryloxy ligand^{42,43} so attempting to reduce **4.1-H** would also test if this was a complication in making the Th(III) product.

Because the previously reported $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-}$ anion was isolated and crystallographically characterized with the unchelated cations of Li and K,²⁰ reductions with Li in the absence of chelating agents such as crypt and crown were attempted first to synthesize the analogous Th(III) complex. Lithium pellets were added to a colorless solution of **4.1-H** in THF at room temperature and stored in a $-35\text{ }^\circ\text{C}$ freezer. After 3 days, a dark purple solution similar to the color of $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-}$ had formed.²⁰ Crystallization from a mixture of THF and Et₂O generated dark purple crystals which were identified by single-crystal X-ray diffraction as $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{H}})_4]$, **4.2-H**, Figure 4.1, eq 4.1.



Complex **4.2-H** crystallizes in the $P2_1/c$ space group with one molecule in the asymmetric unit. The anion and cation in **4.2-H** are well separated, as is the case in the structures of the $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-}$ anion.²⁰ Although the X-ray diffraction data obtained on **4.2-H** were not of high enough quality to discuss detailed metrical parameters, the data show the square planar geometry of the ligands. The isolation and crystallographic characterization of **4.2-H** shows that this Th(IV) to Th(III) tetrakis(aryloxy) reduction involves a structural change since **4.1-H** is known to be tetrahedral.⁴¹ Moreover, the isolation of complex **4.2-H** also shows that the *para* position of the

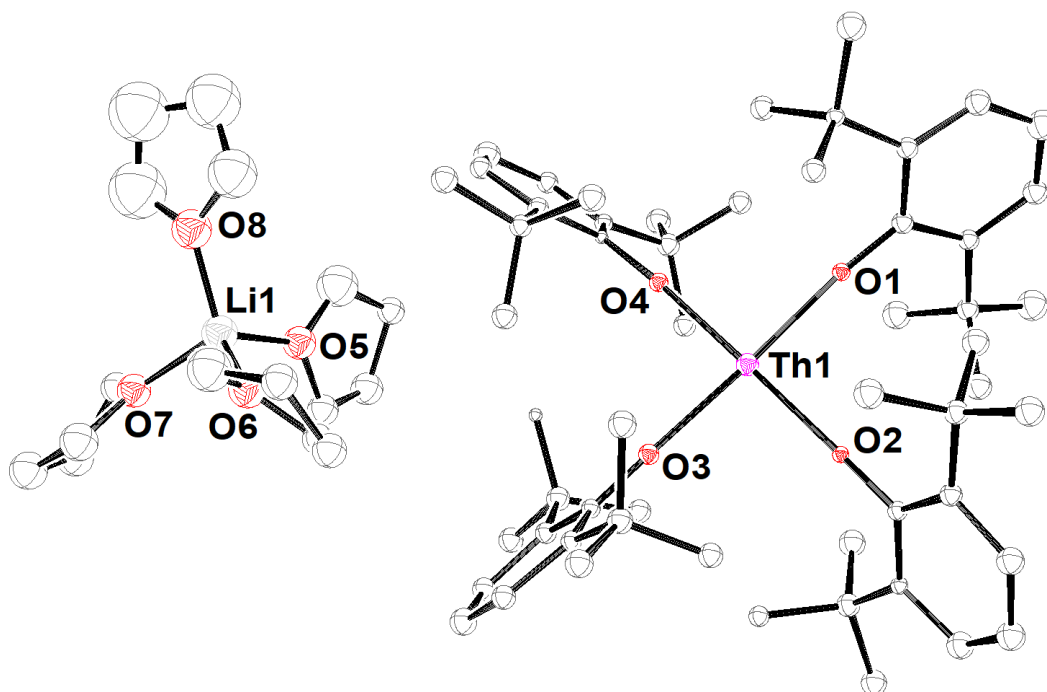
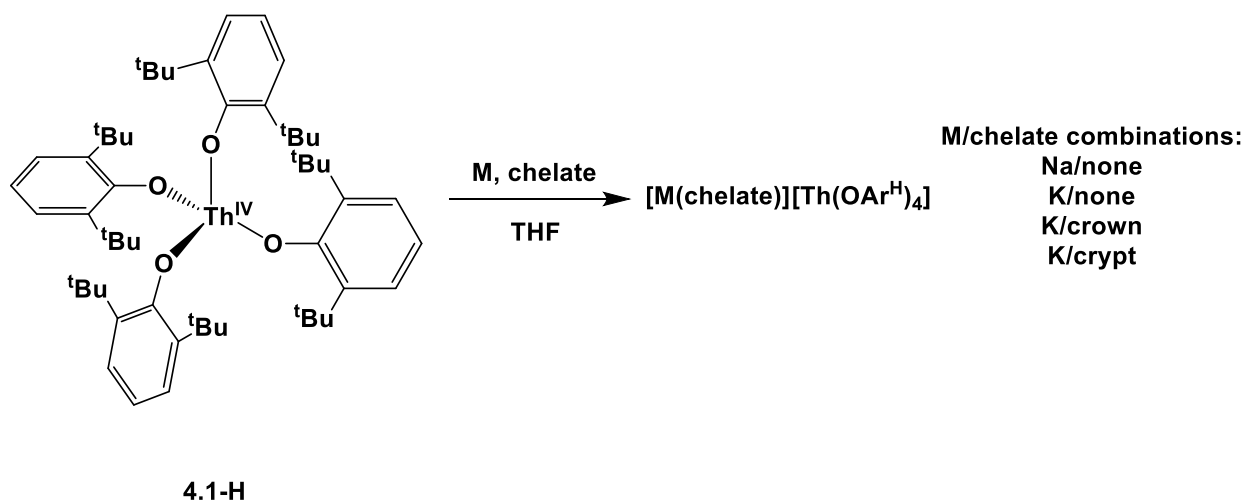


Figure 4.1. Connectivity plot of $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{H}})_4]$, **4.2-H**, with ellipsoids drawn at the 50% probability level and selective atom labelling. Hydrogen atoms are not shown for clarity.

aryloxy ligands is not susceptible to radical chemistry in these Th(III) complexes.^{42,43} The ^1H NMR spectrum of **4.2-H** in $\text{THF-}d_8$ at room temperature displays three broad resonances at 6.47, 5.86, and -8.23 ppm, which are tentatively assigned to the *para*-H, *meta*-H, and *tert*-butyl protons of the aryloxy ligands of the $[\text{Th}(\text{OAr}^{\text{H}})_4]^{1-}$ anion, respectively. Each of these resonances is shifted upfield compared to the analogous resonances in **4.1-H**.

The effects of the counteranion and chelate on the reduction of **4.1-H** were investigated next by varying the alkali metal and chelating agents in the reduction of **4.1-H**, Scheme 4.2. Reductions of **4.1-H** using KC_8 in the presence or absence of crypt or crown were examined to probe the effect of the chelate on the geometry and properties of the square planar $[\text{Th}(\text{OAr}^{\text{H}})_4]^{1-}$ anion. To investigate the effect of the identity of the alkali metal, the reduction of **4.1-H** using Na without chelate was also performed for comparison to the chelate free K and Li reductions.



Scheme 4.2. Synthesis of $[M(\text{chelate})][\text{Th}(\text{OAr}^{\text{H}})_4]$ Complexes from $\text{Th}(\text{OAr}^{\text{H}})_4$, **4.1-H**.

In all four of these cases, the reductions generated purple solutions that had UV–visible and EPR spectra that were similar to those of $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-20}$ and **4.2-H**, Figures 4.2 and 4.3.

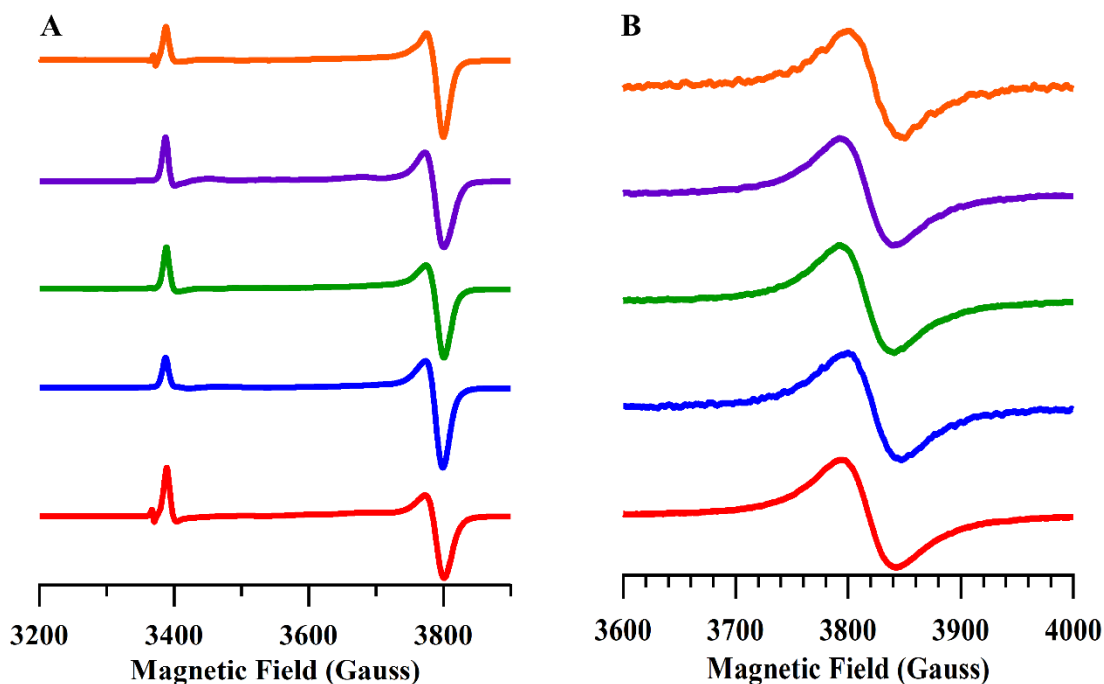


Figure 4.2. (A) 77 K EPR spectra of the products of the reactions between $\text{Th}(\text{OAr}^{\text{H}})_4$, **4.1-H**, and Na/no chelate (orange), Li/no chelate (purple), K/no chelate (green), K/crypt (blue), and K/crown

(red). The signals at $g = 2.00$ are attributed to the electride. (B) Room temperature EPR spectra of the products of the reactions between $\text{Th}(\text{OAr}^{\text{H}})_4$, **4.1-H**, and Na/no chelate (orange), Li/no chelate (purple), K/no chelate (green), K/crypt (blue), and K/crown (red).

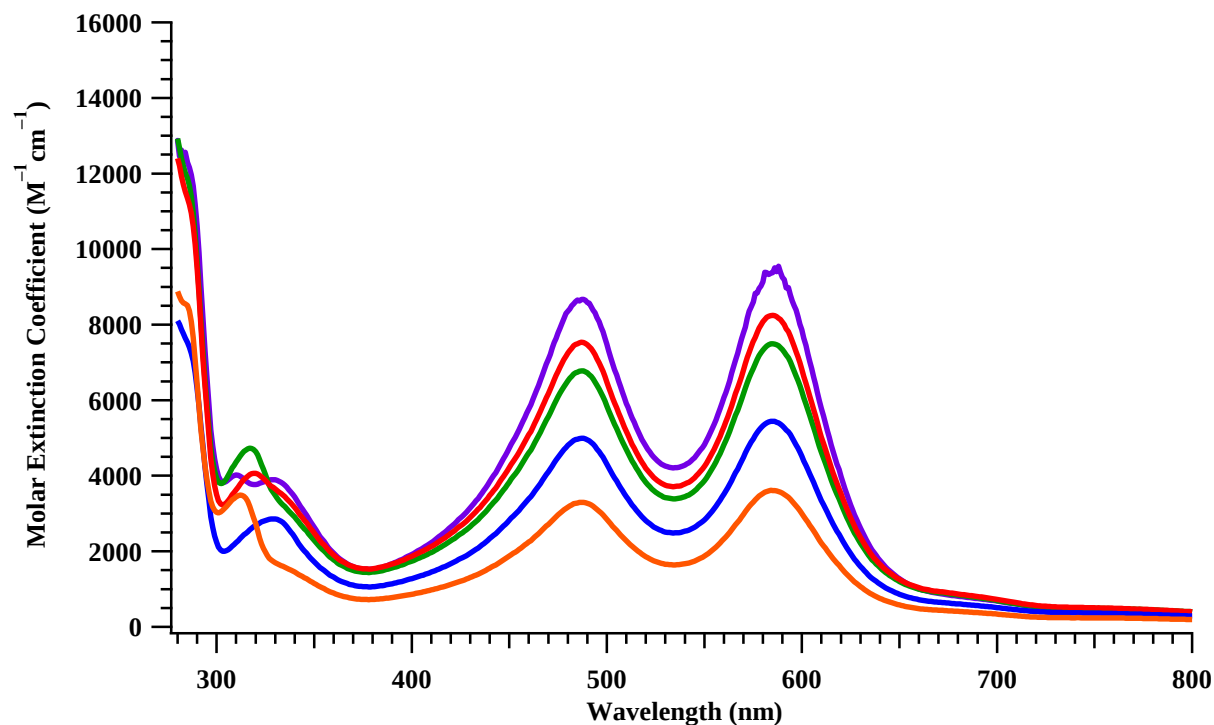


Figure 4.3. Room temperature UV–visible spectra of the products of the reactions between $\text{Th}(\text{OAr}^{\text{H}})_4$, **4.1-H**, and Li/no chelate (purple), K/crown (red), K/no chelate (green), K/crypt (blue), and Na/no chelate (red).

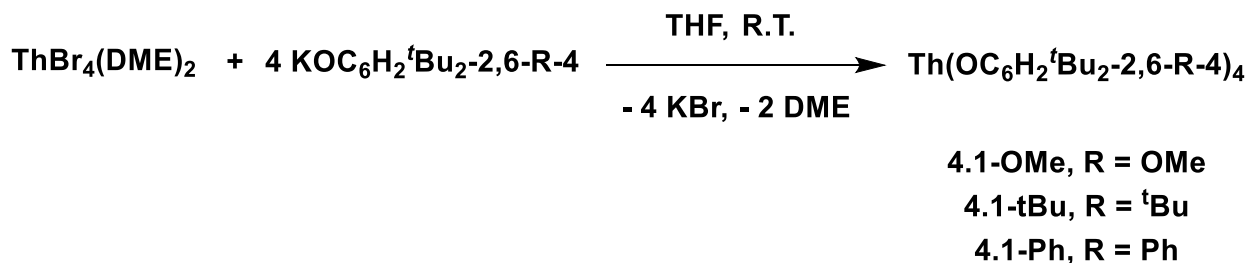
However, unlike the chelate-free Li reduction described above, crystals suitable for X-ray diffraction were not obtainable for any of these complexes despite multiple attempts to grow X-ray quality single crystals. In one instance, the reduction of **4.1-H** with KC_8 and crypt generated X-ray quality crystals, but the data could not be solved.

The EPR spectra of the products of these reduction combinations showed axial signals at 77 K with $g_{\parallel} = 1.99$ and $g_{\perp} = 1.78$. At 298 K, the EPR spectrum of each measured complex showed

an isotropic signal with $g_{\text{iso}} = 1.84$. These spectral properties are characteristic of $6d^1$ Th(III) complexes with square planar or trigonal planar geometries with respect to the ligands.^{19–24,30} The UV–visible spectra of all combinations also show two absorbance maxima at roughly 480 and 580 nm with molar absorptivity coefficients ranging from 3000–9500 $\text{M}^{-1} \text{cm}^{-1}$, assuming 100% conversion and no decomposition. These data suggest that there is no dependence of the alkali metal or chelate on the overall symmetry or electronic structure of the aryloxide reduction product. This is consistent with the X-ray crystal structures of $[\text{K}(\text{THF})_5(\text{Et}_2\text{O})][\text{Th}(\text{OAr}^{\text{Me}})_4]$,²⁰ $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{Me}})_4]$,²⁰ and **4.2-H**, where the different countercations are well separated from the same square planar anions.

Reduction of Th(OC₆H₂'Bu₂-2,6-OMe-4)₄, Th(OC₆H₂'Bu₃-2,4,6)₄, and Th(OC₆H₂'Bu₂-2,6-Ph-4)₄. Next, the electronic properties of the aryloxide ligands were varied to observe the effect on the reduction chemistry of the homoleptic Th(IV) precursors. Specifically, aryloxide ligands with *para*-substituents with different levels of electron-donating ability were examined. The homoleptic Th(IV) precursors, Th(OAr^{OMe})₄, **4.1-OMe**, Th(OAr^{tBu})₄, **4.1-tBu**, and Th(OAr^{Ph})₄, **4.1-Ph**, (OAr^{OMe} = OC₆H₂'Bu₂-2,6-OMe-4; OAr^{tBu} = OC₆H₂'Bu₃-2,4,6; OAr^{Ph} = OC₆H₂'Bu₂-2,6-Ph-4) were synthesized by the salt metathesis reaction between ThBr₄(DME)₂ and 4 equiv of the respective potassium aryloxide in THF. Each of these Th(IV) complexes was identified by ¹H NMR, ¹³C{¹H} NMR, and infrared spectroscopy, Scheme 4.3.

Reduction of all of these Th(IV) precursors with Li in the absence of an alkali metal chelate generated dark purple solutions with UV–visible and EPR spectra that are similar to those of **4.2-H**, Figures 4.4 and 4.5.



Scheme 4.3. Synthesis of Th(IV) aryloxy complexes via salt metathesis.

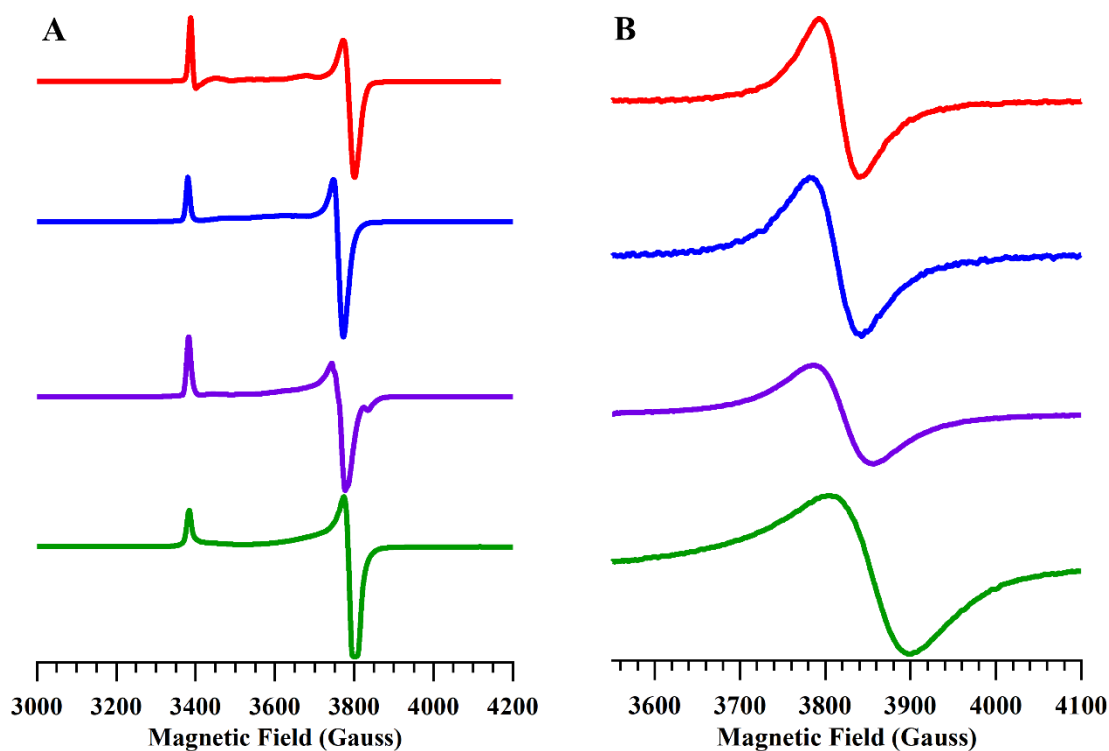


Figure 4.4. (A) 77 K EPR spectra of $[\text{Th}(\text{OAr}^{\text{H}})_4]^{1-}$ (red), $[\text{Th}(\text{OAr}^{\text{OMe}})_4]^{1-}$ (blue), $[\text{Th}(\text{OAr}^{\text{tBu}})_4]^{1-}$ (purple), and $[\text{Th}(\text{OAr}^{\text{Ph}})_4]^{1-}$ (green) obtained from reactions between **4.1-R** (R = H, OMe, ^tBu, Ph) and Li in THF. (B) Room temperature EPR of $[\text{Th}(\text{OAr}^{\text{H}})_4]^{1-}$ (red), $[\text{Th}(\text{OAr}^{\text{OMe}})_4]^{1-}$ (blue), $[\text{Th}(\text{OAr}^{\text{tBu}})_4]^{1-}$ (purple), and $[\text{Th}(\text{OAr}^{\text{Ph}})_4]^{1-}$ (green) obtained from reactions between **4.1-R** (R = H, OMe, ^tBu, Ph) and Li in THF.

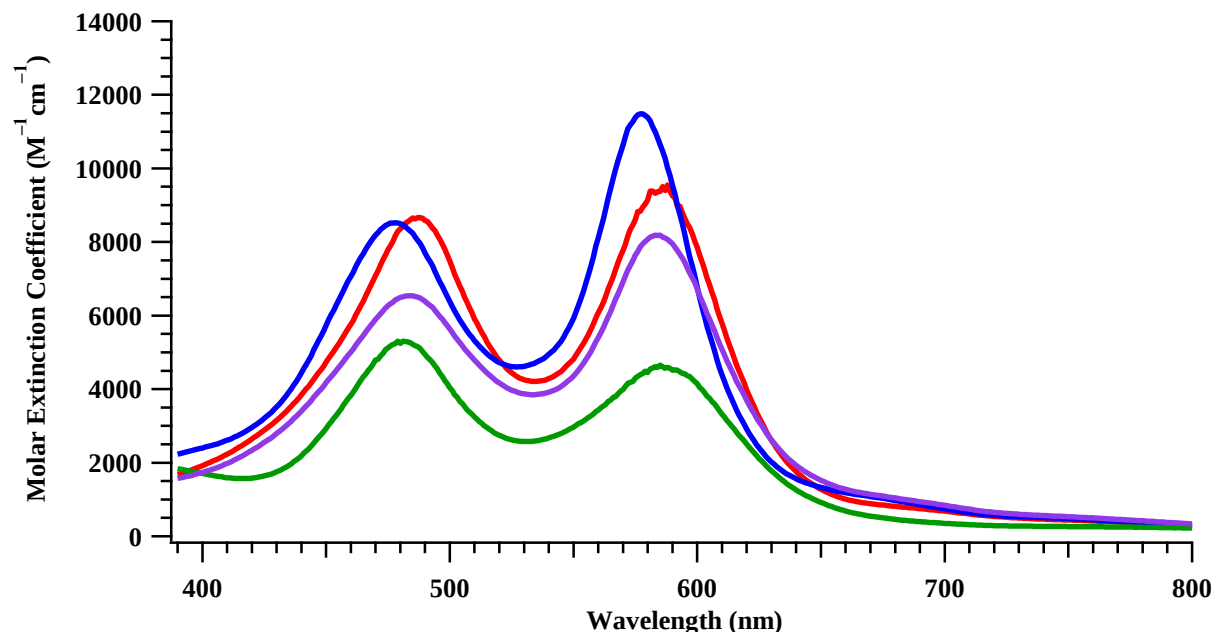


Figure 4.5. Room temperature UV–visible spectra of $[\text{Th}(\text{OAr}^{\text{OMe}})_4]^{1-}$ (blue), $[\text{Th}(\text{OAr}^{\text{H}})_4]^{1-}$ (red), $[\text{Th}(\text{OAr}^{\text{tBu}})_4]^{1-}$ (purple), and $[\text{Th}(\text{OAr}^{\text{Ph}})_4]^{1-}$ (green) obtained from reactions between **4.1-R** ($\text{R} = \text{H}, \text{OMe}, \text{tBu}, \text{Ph}$) and Li in THF.

The potassium reductions also generated products with UV–visible and EPR spectra similar to those of the other crystallographically characterized square planar Th(III) aryloxide complexes.²⁰ However, none of the potassium-generated reaction products formed single crystals suitable for X-ray crystallography either with or without alkali metal chelating agents such as crypt or crown.

Fortunately, the reductions of **4.1-OMe** and **4.1-tBu** using Li in the absence of an alkali metal chelate yielded X-ray quality crystals of $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{OMe}})_4]$, **4.2-OMe**, Figure 4.6, and $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{tBu}})_4]$, **4.2-tBu** from slow diffusion of hexane into THF solutions at -35°C , eq 4.2.

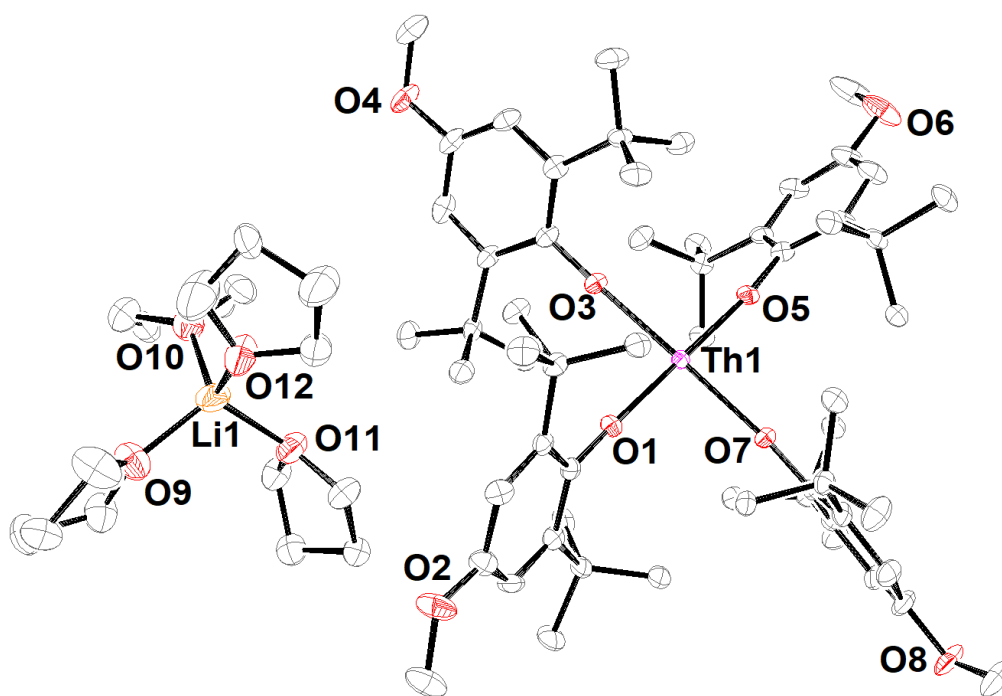
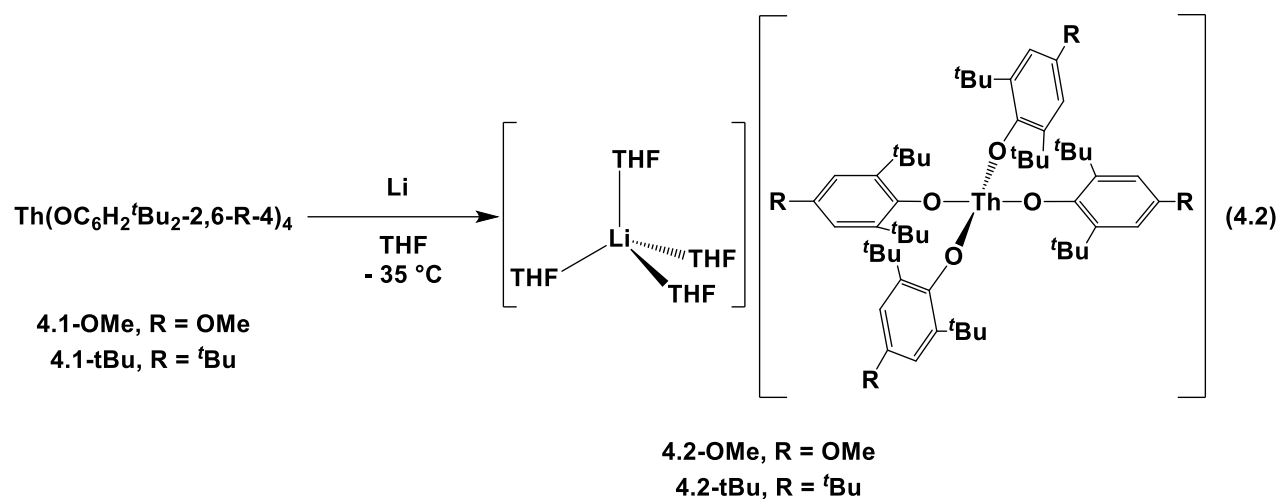


Figure 4.6. Molecular structure of $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{OMe}})_4]$, **4.2-OMe**, with thermal ellipsoids drawn at the 50% probability level and selective atom labelling. Hydrogen atoms and the molecules of cocrystallized THF are not shown for clarity.

Like **4.2-H**, the ^1H NMR spectra of **4.2-OMe** and **4.2-tBu** in THF- d_8 at room temperature both show three broad and paramagnetically shifted resonances corresponding to the protons of the aryloxide ligands of each Th(III) complex.

In the case of $\text{Th}(\text{OAr}^{\text{Ph}})_4$, **4.1-Ph**, reductions with KC_8 or Li also generated products with EPR and UV–visible spectra consistent with the presence of a Th(III) complex, but the products were unstable at room temperature. No X-ray quality crystals were obtained for salts of the $[\text{Th}(\text{OAr}^{\text{Ph}})_4]^{1-}$ anion. This thermal instability contrasts with that of **4.2-OMe**, which maintains its dark purple color in THF at room temperature for over 23 days before it decomposes to a clear, pale-yellow solution. Surprisingly, complex **4.2-OMe** is also more stable than **4.2-H** and **4.2-tBu**, which maintain their dark purple color in THF solution over 8 and 11 days, respectively, before transitioning to clear, pale-yellow solutions. Furthermore, it was found that the structural change upon reducing **4.1-OMe** to **4.2-OMe** was chemically reversible. **4.2-OMe** can be oxidized with AgBPh_4 in THF to regenerate the tetrahedral Th(IV) precursor, **4.1-OMe**, which can subsequently be reduced again to generate the square planar Th(III) complex, **4.2-OMe**.

Complex **4.2-OMe** crystallizes in the chiral $P2_12_12_1$ space group with one formula unit and four molecules of THF in the asymmetric unit. Like $[\text{K}(\text{THF})_5(\text{Et}_2\text{O})][\text{Th}(\text{OAr}^{\text{Me}})_4]$,²⁰ $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{Me}})_4]$,²⁰ and **4.2-H**, the cationic and anionic moieties in **4.2-OMe** crystallize as well separated species. The four Th–O distances of 2.250(3), 2.254(3), 2.246(3), and 2.254(3) Å observed in **4.2-OMe** are in good agreement with the 2.235(3)–2.260(3) and 2.238(2)–2.247(2) Å distances of $[\text{K}(\text{THF})_5(\text{Et}_2\text{O})][\text{Th}(\text{OAr}^{\text{Me}})_4]$ ²⁰ and $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{Me}})_4]$,²⁰ respectively. The Th–O–C_{ipso} angles of **4.2-OMe** range from 172.8(3) to 177.1(3)° with an average of 174.9°. In comparison, the analogous Th–O–C_{ipso} angles in $[\text{K}(\text{THF})_5(\text{Et}_2\text{O})][\text{Th}(\text{OAr}^{\text{Me}})_4]$ ²⁰ and $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{Me}})_4]$ ²⁰ are 174.2(3)–178.6(4)° and 173.9(2)–176.5(2)°, respectively. The four

O–Th–O angles of **4.2-OMe** lie within the range of 89.1(1)–90.9(1)° and sum up to 360°, i.e., the complex has a square planar geometry about the Th metal center.

Complex **4.2-tBu** was also identified by a preliminary X-ray crystallography study, but despite several attempts, no single crystals of sufficient quality to discuss detailed metrical parameters were isolated. The connectivity of **4.2-tBu** was established, however, and the [Th(OAr^{tBu})₄]^{1–} anion also has a square planar environment about the Th center as in [K(THF)₅(Et₂O)][Th(OAr^{Me})₄],²⁰ [Li(THF)₄][Th(OAr^{Me})₄],²⁰ **4.2-H**, and **4.2-OMe**.

Structural Evaluations of [Li(THF)₄][Th(OAr^{OMe})₄], 4.2-OMe. Because the structural data for complex **4.2-OMe** are of sufficient quality for the discussion of metrical parameters, the data were used to calculate a Guzei *G* value. This provides a measure of the steric shielding of the metal center by the ligands, where a *G* value of 100% suggests complete shielding of the metal center by its ligand environment.^{30,44–48} The calculated 90.8% *G* value for **4.2-OMe** is similar to the 91.2% *G* value for the previously reported [Li(THF)₄][Th(OAr^{Me})₄]¹⁷ as expected since the two complexes differ only in the nature of the *para*-substituent of the aryloxide ligands. These *G* values are among the largest calculated for crystallographically characterized Th(III) complexes of any kind, which have values that range from 79 to 91%.³⁰

The extent of the steric crowding around the Th metal center in **4.2-OMe** from the *tert*-butyl groups of the aryloxide ligands can be visualized using the space-filling models as depicted in Figure 4.7. Complex **4.2-OMe** is similar to [Li(THF)₄][Th(OAr^{Me})₄] in that some of the closest H(CMe₃)⋯H(CMe₃) distances range from 2.25 to 2.38 Å, which are less than twice the 1.2 Å van der Waals radius of hydrogen.⁴⁹ The short H(CMe₃)⋯H(CMe₃) distances in **2-OMe** and [Li(THF)₄][Th(OAr^{Me})₄] may be indicative of interligand dispersion force interactions, which has

been documented previously for several sterically crowded inorganic and organometallic molecules.^{40,50}

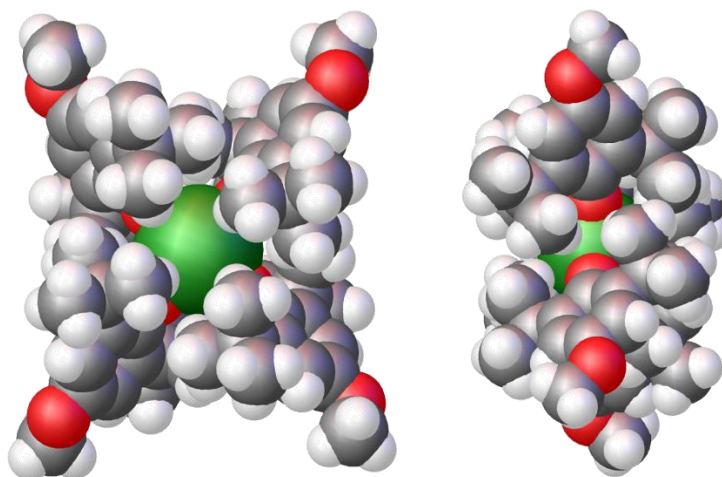


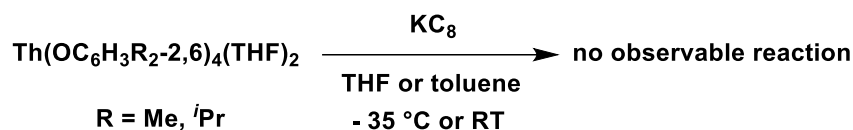
Figure 4.7. Space-filling model of $[\text{Th}(\text{OAr}^{\text{OMe}})_4]^{1-}$ (green = Th, red = O, gray = C, white = H). The left image is the top view of $[\text{Th}(\text{OAr}^{\text{OMe}})_4]^{1-}$ and the right image is the side view. The $[\text{Li}(\text{THF})_4]^{1+}$ cation and THF molecules present in the asymmetric unit are not shown for clarity.

Attempted Reduction of $\text{Th}(\text{OC}_6\text{H}_3^i\text{Pr}_2\text{-2,6})_4(\text{THF})_2$ and $\text{Th}(\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6})_4(\text{THF})_2$.

The role of the 2,6-substituents in the isolation of square planar Th(III) anions was also explored in this study by varying the *ortho*-positions of the aryloxide ligand. Th(IV) aryloxide complexes with less sterically encumbering aryloxide ligands, such as $\text{Th}(\text{Odipp})_4(\text{THF})_2$ (Odipp = $\text{OC}_6\text{H}_3^i\text{Pr}_2\text{-2,6}$) and $\text{Th}(\text{Odmp})_4(\text{THF})_2$ (Odmp = $\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6}$), differ from the precursors discussed above in that they exist as octahedral bis(THF) adducts,⁴¹ in contrast to the unsolvated tetrakis(aryloxide) thorium(IV) complexes in eqs 4.1 and 4.2.

Treating $\text{Th}(\text{Odipp})_4(\text{THF})_2$ and $\text{Th}(\text{Odmp})_4(\text{THF})_2$ with KC_8 either in THF or toluene at either room temperature or $-35\text{ }^\circ\text{C}$ yielded no color changes attributable to the formation of a d^1 Th(III) complex, Scheme 4.4. The characteristic color of a Th(III) complex was not generated and there was no discoloration of KC_8 that would indicate electron transfer had occurred. Evidently,

these octahedral precursors were not as prone to reduction as the $\text{Th}(\text{OC}_6\text{H}_3^t\text{Bu}_2\text{-2,6-R-4})_4$ complexes described above.



Scheme 4.4. Attempted potassium reductions of $\text{Th}(\text{Odipp})_4(\text{THF})_2$ and $\text{Th}(\text{Odmp})_4(\text{THF})_2$.



Complexes. It was desirable to synthesize analogous U(III) complexes for comparison to the square planar Th(III) complexes described above. Previously, $\{\text{K}[\text{U}(\text{OAr}^{\text{H}})_4]\}_n$ was synthesized from the reaction of $\text{U}(\text{OAr}^{\text{H}})_3$ with a potassium mirror under a dinitrogen atmosphere⁵¹ and identified by X-ray crystallography. $\{\text{K}[\text{U}(\text{OAr}^{\text{H}})_4]\}_n$ crystallizes as a polymer in which the arene rings of two of the aryloxide ligands of each $[\text{U}(\text{OAr}^{\text{H}})_4]^{1-}$ anion are linked through η^6 -arene interactions with the potassium cations. However, the $[\text{U}(\text{OAr}^{\text{H}})_4]^{1-}$ anions were found to have tetrahedral coordination geometries and not the square planar geometry of the Th(III) complexes described above. To determine if the addition of an alkali metal chelate had any effect on the geometry of the uranium metal center, the synthesis of the compounds, $[\text{K}(\text{crypt})][\text{U}(\text{OAr}^{\text{H}})_4]$, **4.3**, and $[\text{K}(\text{crown})(\text{THF})_2][\text{U}(\text{OAr}^{\text{H}})_4]$, **4.4**, was investigated.

Following an adaptation from the previous literature report,⁵² the reaction between UI_3 and KOAr^{H} in THF afforded $\text{U}(\text{OAr}^{\text{H}})_3(\text{THF})$ as a brown solid after workup in 95% yield. The identity of the product was verified by ^1H NMR spectroscopy.⁵² Addition of 1 equiv each of KOAr^{H} and crypt to $\text{U}(\text{OAr}^{\text{H}})_3(\text{THF})$ in THF at room temperature immediately generated a deep red solution from which dark red crystals of $[\text{K}(\text{crypt})][\text{U}(\text{OAr}^{\text{H}})_4]$, **4.3**, suitable for study by X-ray diffraction, were isolated in 58% yield, Figure 4.8, eq 4.3.

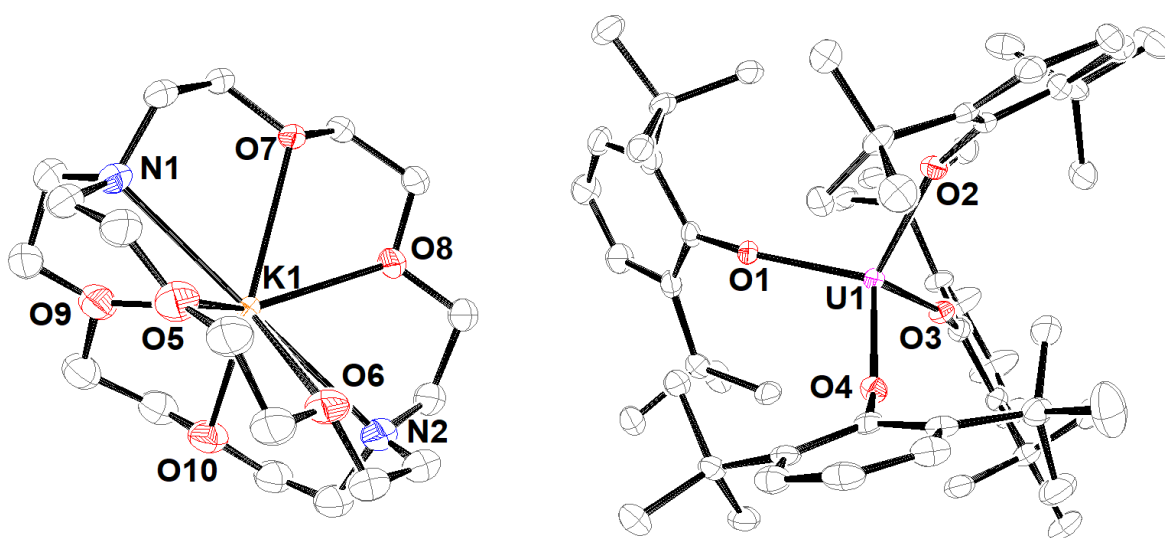
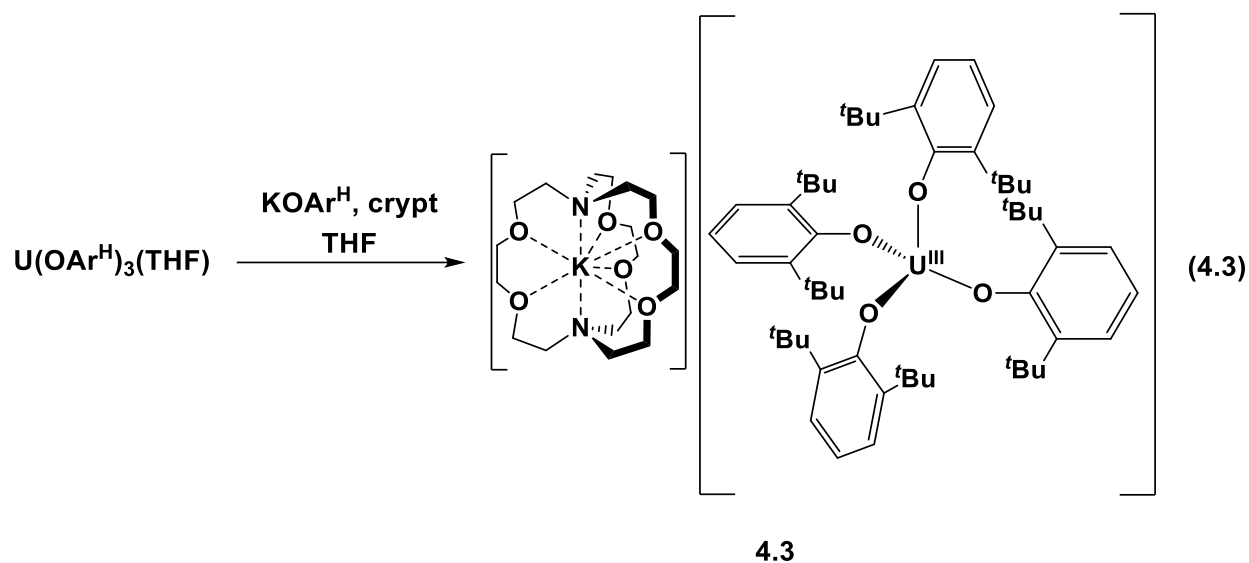


Figure 4.8. Molecular structure of $[\text{K}(\text{crypt})][\text{U}(\text{OAr}^{\text{H}})_4]$, **4.3**, with ellipsoids drawn at the 50% probability level and selective atom labelling. Hydrogen atoms, the cocrystallized THF molecule, and the disorder in the crypt moiety are omitted for clarity.

Similar results were observed when crown was used as a chelate in the one-pot reaction between UI_3 , 4 equiv of KOAr^{H} , and 1 equiv of crown in THF at room temperature. Dark red

crystals, which were identified by single-crystal X-ray diffraction as $[\text{K}(\text{crown})(\text{THF})_2][\text{U}(\text{OAr}^{\text{H}})_4]$, **4.4**, were isolated upon workup and crystallization from a solution in THF layered under hexane, Figure 4.9, eq 4.4.

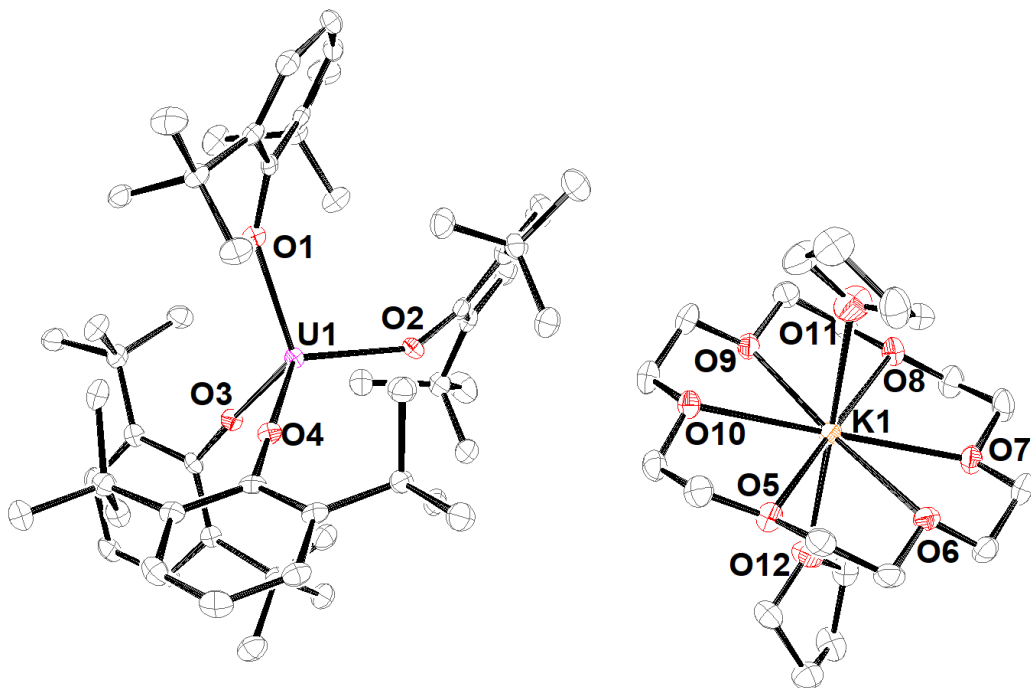
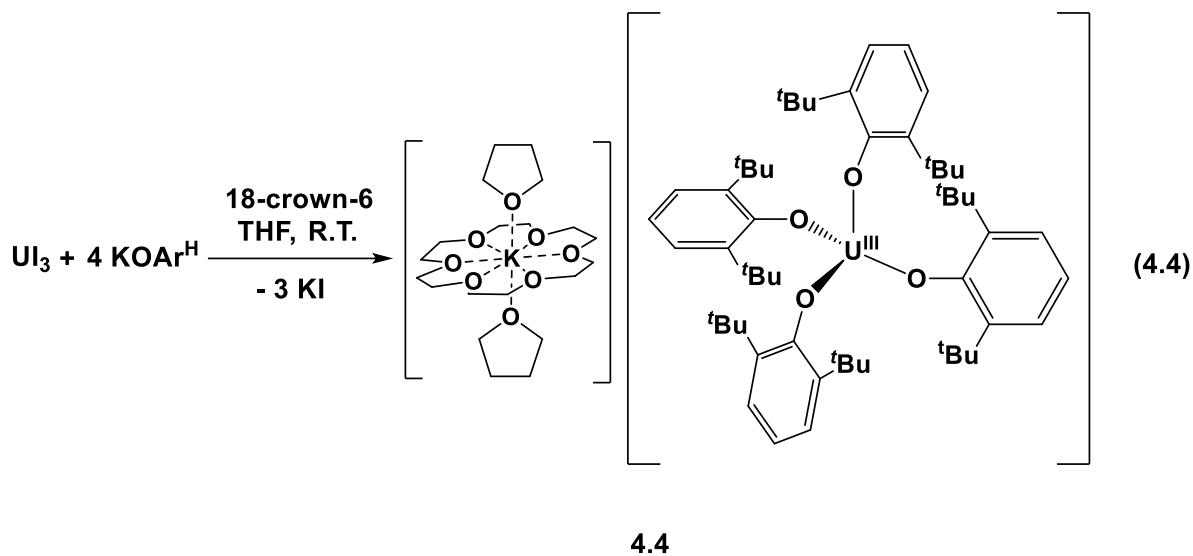


Figure 4.9. Molecular structure of $[\text{K}(\text{crown})(\text{THF})_2][\text{U}(\text{OAr}^{\text{H}})_4]$, **4.4**, with ellipsoids drawn at the 50% probability level and selective atom labelling. Hydrogen atoms are omitted for clarity.

$[\text{K}(\text{crypt})][\text{U}(\text{OAr}^{\text{H}})_4]$, **4.3**, crystallizes in the $P\bar{1}$ space group with one THF molecule present in the asymmetric unit, Figure 4.8. Similar to the square planar Th(III) complexes described above, the $[\text{K}(\text{crypt})]^{1+}$ cation is well separated from the uranium-containing anion. However, the structure of **4.3** differs from the thorium complexes described above in that the aryloxide ligands define a tetrahedral coordination geometry like that in polymeric $\{\text{K}[\text{U}(\text{OAr}^{\text{H}})_4]\}_n$.⁵¹ Complex **4.3** differs from the latter complex in that there are no η^6 -arene interactions with the potassium cation due to sequestration by the crypt chelate. The U–O distances range from 2.233(1)–2.296(1) Å and are in agreement with the U–O distances of other U(III) complexes containing aryloxide ligands, Table 4.1. The O–U–O angles range between 108.66(1) and 111.00(1)° with an average of 109.5°, i.e., tetrahedral. The four U–O–C_{ipso} angles are bent and range between 150.09(1) and 163.08(1)°, in contrast to the more linear Th–O–C_{ipso} 172.8(3)–177.1(3)° angles of $[\text{K}(\text{THF})_5(\text{Et}_2\text{O})][\text{Th}(\text{OAr}^{\text{Me}})_4]$,²⁰ $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{Me}})_4]$,²⁰ and **4.2-OMe**, Table 4.1.

Table 4.1. Comparison of M–O (Å) distances and M–O–C_{ipso} (°) angles between selected crystallographically characterized aryloxide containing An(III) (An = Th, U) complexes.

Complex	M–O (aryloxide) (Å)	M–O–C _{ipso} (aryloxide) (°)	Ref
$(\text{C}_5\text{Me}_5)_2\text{U}(\text{OAr}^{\text{Me}})^{\text{a}}$	2.201(6), 2.225(6)	160.0(5), 115.7(5)	53
$(\text{C}_5\text{Me}_4\text{H})_2\text{U}(\text{OAr}^{\text{Me}})$	2.270(4)	111.5(4)	53
$(\text{C}_5\text{Me}_4\text{H})_2\text{U}(\text{OAr}^{\text{Me}})(\text{THF})$	2.268(4)	159.5(4)	53
$\text{U}(\text{OAr}^{\text{H}})_3(\text{CN-2,6-Me}_2\text{C}_6\text{H}_3)^{\text{a}}$	2.172(6), 2.213(6), 2.170(6), 2.189(6), 2.169(5), 2.175(6)	169.1(6), 171.5(6), 175.4(6), 172.5(5), 175.6(5), 168.6(6)	54
$\text{U}(\text{OAr}^{\text{H}})_3^{\text{a}}$	2.151(3), 2.157(3), 2.164(3), 2.161(3), 2.165(3), 2.165(3)	159.7(3), 162.4(2), 158.3(3), 159.1(2), 157.8(2), 158.2(3)	51

U(OC ₆ H ₂ Ad ₂ -2,6-Me-4) ₃ ^b	2.151(3), 2.175(3), 2.177(3)	157.0(2), 157.4(4), 154.9(2)	55
[U(Odipp) ₃] ₂	2.214(7) (bridging), 2.132(8) (terminal)	156.8(7) (bridging), 164.5(8) (terminal), 166.8(9) (terminal)	52
[K(crypt)][U(OAr ^H) ₄], 4.3	2.295(4), 2.233(4), 2.252(4), 2.265(4)	150.1(4), 163.1(4), 157.6(4), 157.1(4)	c
[K(crown)(THF) ₂][U(OAr ^H) ₄], 4.4	2.222(2), 2.251(2), 2.280(2), 2.237(2)	147.5(2), 146.8(2), 170.5(2), 176.6(2)	c
[K(THF) ₅ (Et ₂ O)][Th(OAr ^{Me}) ₄]	2.235(3), 2.239(3), 2.257(3), 2.260(3)	174.2(3), 176.1(3), 178.5(3), 178.6(4)	20
[Li(THF) ₄][Th(OAr ^{Me}) ₄]	2.238(2), 2.244(2), 2.244(2), 2.247(2)	173.9(2), 174.7(2), 174.7(2), 176.5(2)	20
[Li(THF) ₄][Th(OAr ^{OMe}) ₄], 4.2-OMe	2.250(3), 2.254(3), 2.246(3), 2.254(3)	177.1(3), 175.7(3), 172.8(3), 174.3(3)	c

^a Two different molecules present in the asymmetric unit.

^b Ad = 1-adamantyl.

^c This work.

[K(crown)(THF)₂][U(OAr^H)₄], **4.4**, crystallizes in the *P*2₁/*c* space group, Figure 4.9, with one molecule in the asymmetric unit. Similar to the structure of [K(crypt)][U(OAr^H)₄], the cation is well separated from the anion and there are no η^6 -arene interactions with the potassium cation due to the presence of the 18-crown-6 chelate. The potassium cation is bound to all six crown ether oxygens and capped by two additional THF molecules. The metrical parameters of **4.4** are compared to those of **4.3** and other actinide aryloxide complexes in Table 4.1. In the structure of **4.4**, the aryloxide ligands adopt a tetrahedral geometry with O–U–O angles that range between 98.01(7) and 117.28(7)° with an average of 109.5°. The U–O distances are 2.222(2), 2.251(2), 2.280(2), and 2.297(2) Å. Two of the U–O–C_{ipso} angles are bent in **4.4**, with values of 146.84(18)

and 147.44(17)°, while the other two U–O–C_{ipso} angles approach linearity with values of 170.55(17) and 176.61(18)°.

DFT studies suggested that the hypothetical U(II) complex, [U^{II}(OAr^H)₄]²⁻, would adopt a square planar geometry⁵⁶ analogous to that of [Th^{III}(OAr^{Me})₄]¹⁻²⁰ and have a 5f³6d¹ electron configuration. Accordingly, the reaction of U(OAr^H)₃(THF), KC₈, and crypt in THF was attempted both at room temperature and –35 °C. Treating a brown solution of U(OAr^H)₃(THF) and crypt in THF with KC₈ generated a transient dark blue color, which is consistent with the formation of a U(II) species.^{57–60} However, the color quickly converted to dark red, and compound **4.3** was isolated. Moreover, no reaction was observed between the isolated samples of [K(chelate)][U(OAr^H)₄] (chelate = crypt, **4.3**, crown(THF)₂, **4.4**) with KC₈ or Li metal in THF at either room temperature or –35 °C with or without the addition of another equivalent of chelate. The solutions remained dark red, and no discoloration of KC₈ was observed after 3 days. Further reduction may be inhibited since [U(OAr^H)₄]¹⁻ is already an anionic species.

Electronic Structure Calculations on [Th(OAr^H)₄]¹⁻. To gain further insight into the electronic structure of the Th(III) compounds, [Th(OAr^H)₄]¹⁻ was studied at the density functional level of theory using the TPSSh functional⁶¹ with Grimme's D3 dispersion correction.^{62,63} Scalar-quasi-relativistic effective core potentials (ECPs)⁶⁴ with the def-TZVP⁶⁵ basis set were used for the thorium atom, and polarized split-valence basis sets with def2-SV(P)⁶⁶ were used for the other atoms. The implicit solvation model, COSMO,⁶⁷ was employed to model solvent effects with a dielectric constant $\epsilon = 7.52$ and refractive index $R_{\text{ind}} = 1.40$ for THF.⁶⁸ Structure optimizations began from the X-ray structure of [Th(OAr^{Me})₄]¹⁻²⁰. All computations were performed using the TURBOMOLE program suite V7.4.1.^{69,70}

The optimized geometry of $[\text{Th}(\text{OAr}^{\text{H}})_4]^{1-}$ was found to have D_4 symmetry. The resulting $^2\text{A}_1$ ground state was consistent with a 6d^1 configuration of Th, with the SOMO (singly occupied molecular orbital) localized entirely on the Th ion, exhibiting 6d_{z^2} and 7s character (51% 6d, 35% 7s from Mulliken population analysis), Figure 4.10. This is a result similar to what was previously observed for $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-}$.²⁰

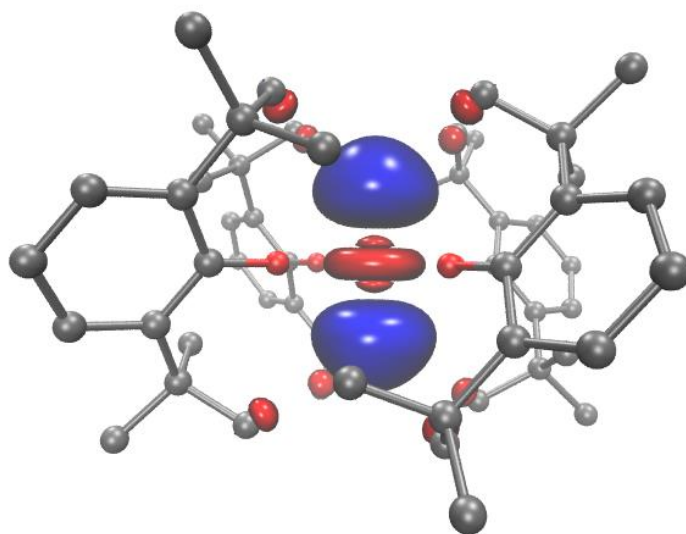


Figure 4.10. Calculated 6d_{z^2} -like HOMO of $[\text{Th}(\text{OAr}^{\text{H}})_4]^{1-}$ in D_4 symmetry (51% 6d, 35% 7s from Mulliken population analysis) plotted with a contour value of 0.05. $\varepsilon = -1.918$ eV.

$[\text{Th}(\text{OAr}^{\text{H}})_4]^{1-}$ was also studied at the DFT level of theory in a tetrahedral geometry, using the crystal structure of **4.3** as a starting point. The approximately tetrahedral geometry (C_1 symmetry) was found to be a local minimum that is 19.5 kcal/mol higher in energy than the square planar geometry above. The SOMO was predominantly Th-based but had significant ligand character (64% Th via Mulliken analysis). The SOMO had relatively equal 6d and 5f characters as judged by Mulliken analysis (58% 6d, 42% 5f). The calculated HOMO–LUMO gap, which can be related to the stability of the complex, was 1.932 eV in the square planar geometry, while it was only 0.814 eV in the tetrahedral geometry.

The G values calculated on the basis of the optimized structures in the DFT calculations are 97% for square planar Th(III) and 96% for tetrahedral Th(III). These can be compared, but it should be realized that the 97% G value in the DFT-optimized structure of $[\text{Th}(\text{OAr}^{\text{H}})_4]^{1-}$ is larger than the 91% value of **4.2-OMe** and 91% value of $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{Me}})_4]$,²⁰ calculated based on experimental data. Differences in G values based on DFT-calculated structures versus experimental structures have been observed before.³⁰

The UV–visible spectrum was simulated in the square planar geometry with identical basis sets as described above, Figure 4.11. The calculation was performed at the optimized geometry transformed into a C_1 -symmetric state. Three intense transitions were observed at roughly 680, 540, and 328 nm. The transitions at 680 and 540 nm are predominantly 6d to 5f in character, while the transition at 328 nm can be described as 6d to 7p and metal–ligand charge transfer in character. These results are very similar to the previous studies on $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-}$,²⁰ which further indicates that the substituents on the aryloxide ligand do not have a large impact on the electronic structure of the thorium atom.

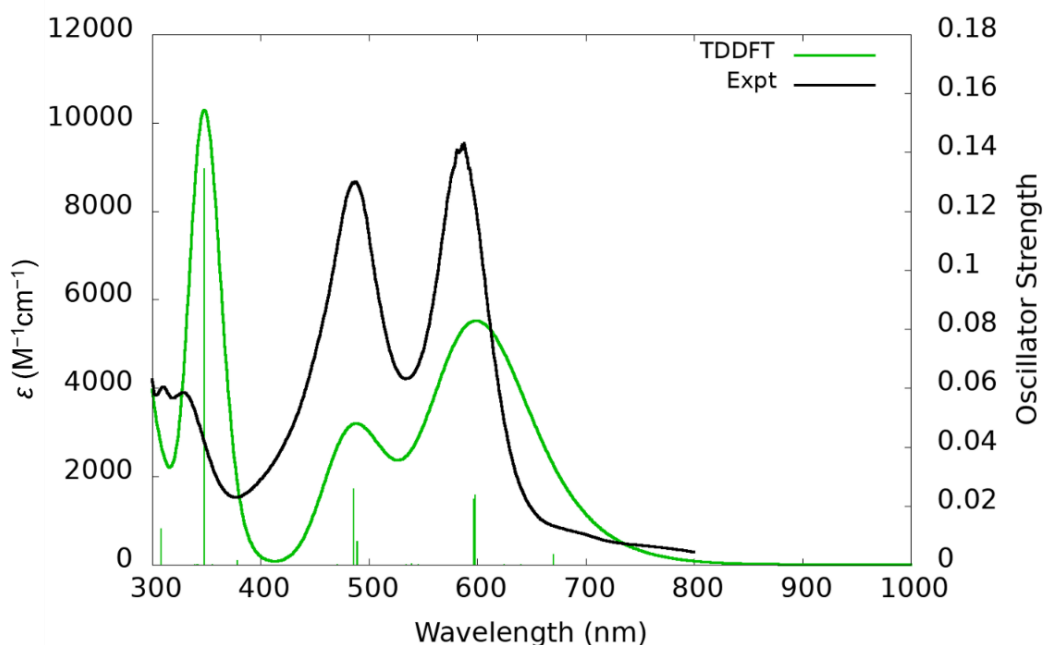


Figure 4.11. Experimental (black) and simulated (green) UV–visible spectra of $[\text{Th}(\text{OAr}^{\text{H}})_4]^{1-}$. A Gaussian line broadening of 0.15 eV was applied, and the computed spectrum was empirically blue-shifted by 0.25 eV.

Electronic Structure Calculations on $[\text{U}(\text{OAr}^{\text{H}})_4]^{1-}$. The U(III) complex $[\text{U}(\text{OAr}^{\text{H}})_4]^{1-}$ was studied at the DFT level of theory using the same methods described above (TPSSh, D3 dispersion correction, def-TZVP/def-ecp for U and def2-SV(P) for other atoms, COSMO solvent model with THF). Both tetrahedral and square planar geometries were studied, and it was found that the tetrahedral ligand arrangement was 15.6 kcal/mol more stable than the square planar geometry. Both had $5f^3$ electron configurations expected for a U(III) complex. The tetrahedral geometry had a larger HOMO–LUMO gap of 2.295 eV compared to the 1.201 eV gap of the square planar geometry.

Guzei G values were calculated to be 95% for tetrahedral U(III) and 97% for square planar U(III). The 95% G value for tetrahedral $[\text{U}(\text{OAr}^{\text{H}})_4]^{1-}$ is slightly larger than the value of 91% determined from the crystal structure of **4.3**. As in the thorium case above, both tetrahedral and square planar geometries had very large G values, suggesting that steric effects are not the explanation for the observed geometries.

DISCUSSION

The lithium reduction of the crystallographically characterized tetrahedral Th(IV) complex $\text{Th}(\text{OAr}^{\text{H}})_4$ to the square planar $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{H}})_4]$, **4.2-H**, shows that a structural change does occur in this Th(IV) to Th(III) tetrakis(aryloxide) reduction system. This was uncertain in the formation of $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{Me}})_4]$,²⁰ since the crystal structure of $\text{Th}(\text{OAr}^{\text{Me}})_4$ has not been reported. EPR and UV–visible spectra indicate that the reduction of $\text{Th}(\text{OAr}^{\text{H}})_4$ with KC_8 generates similar products regardless of the presence of crypt or crown. These spectra are similar

to the spectra reported for both the $[\text{Li}(\text{THF})_4][\text{Th}(\text{OAr}^{\text{Me}})_4]$ and $[\text{K}(\text{THF})_5(\text{Et}_2\text{O})][\text{Th}(\text{OAr}^{\text{Me}})_4]$ salts.²⁰ The similarity in spectra extends to the products of the KC_8 reduction of $\text{Th}(\text{OAr}^{\text{tBu}})_4$, $\text{Th}(\text{OAr}^{\text{OMe}})_4$, and $\text{Th}(\text{OAr}^{\text{Ph}})_4$. Hence, the *para*-substituent of the aryloxide ligand does not alter the Th(IV) to Th(III) reduction chemistry. The reductions of $\text{Th}(\text{OC}_6\text{H}_2'\text{Bu}_2\text{-2,6-R-4})_4$ (R = H, Me, *t*Bu, OMe, Ph) are also similar in that all of the reductions give crystalline products that are challenging to crystallographically analyze by X-ray diffraction. Although at least five variations of $[\text{ML}_x][\text{Th}(\text{OC}_6\text{H}_2'\text{Bu}_2\text{-2,6-R-4})_4]$ (M = alkali metal; L = crypt, crown, THF, Et_2O ; R = H, Me, *t*Bu, OMe, Ph) have yielded X-ray data sets, only three have given data sets with refinements suitable to discuss metrical parameters.

In contrast to the 2,6-di-*tert*-butyl-substituted $\text{Th}(\text{OC}_6\text{H}_2'\text{Bu}_2\text{-2,6-R-4})_4$ complexes which all can be reduced, the $\text{Th}(\text{Odipp})_4(\text{THF})_2$ and $\text{Th}(\text{Odmp})_4(\text{THF})_2$ complexes with isopropyl and methyl substituents at the *ortho*-positions show no evidence of reduction to Th(III) products. The reason for this is unknown. Since these Th(IV) tetrakis(aryloxide) complexes have smaller ligands, they form octahedral complexes with two additional THF molecules coordinated to the metal center.⁴¹ It is possible that this inhibits electron transfer, but clearly, a structural change is not an inhibition for the formation of the square planar 2,6-di-*tert*-butyl complexes. One might expect the products of reduction of $\text{Th}(\text{Odipp})_4(\text{THF})_2$ and $\text{Th}(\text{Odmp})_4(\text{THF})_2$ to be less stabilized by dispersion forces than those of $\text{Th}(\text{OC}_6\text{H}_2'\text{Bu}_2\text{-2,6-R-4})_4$, but some reduction chemistry could still occur. The reduction of $\text{Th}(\text{OAr}^{\text{Ph}})_4$, **4.1-Ph**, gives a Th(III) product less stable than those of the other $\text{Th}(\text{OC}_6\text{H}_2'\text{Bu}_2\text{-2,6-R-4})_4$ complexes, but EPR and UV–visible spectra consistent with Th(III) can still be obtained. It is interesting to note that the aryloxide ligand with the most electron withdrawing group in the *para* position, $(\text{OAr}^{\text{Ph}})^{1-}$, gives the least thermally stable product in the series and the $(\text{OAr}^{\text{OMe}})^{1-}$ derivative with the strongly donating substituent gives one of the most

stable products. This is reinforced by the fact that THF solutions of **4.2-H**, **4.2-tBu**, and **4.2-OMe** were observed to maintain their dark color at room temperature for 8, 11, and 23 days, respectively, before decomposing to clear, pale-yellow solutions. Moreover, THF solutions of the reduced product of **4.1-Ph** decompose within ca. 5 min at room temperature. This supports the idea that π -donation of the oxygen donor atom ligands is important in stabilization. However, that should be important for Odipp and Odmp ligands as well. For these smaller ligands, it is possible that solvated THF molecules are more readily maintained in solution, and this inhibits reduction.

The results with uranium provide analogous actinide examples with the expected tetrahedral geometry. Thus, whether the potassium cation is bound with a chelate as in $[\text{K}(\text{crypt})][\text{U}(\text{OAr}^{\text{H}})_4]$ and $[\text{K}(\text{crown})(\text{THF})_2][\text{U}(\text{OAr}^{\text{H}})_4]$ or incorporated into the structure through bridging arene rings as in $\{\text{K}[\text{U}(\text{OAr}^{\text{H}})_4]\}_n$,⁵¹ the U(III) complexes of $[\text{U}(\text{OAr}^{\text{H}})_4]^{1-}$ adopt the sterically optimal tetrahedral geometry around the metal. The structural difference from the Th(III) complexes is most likely a consequence of the difference in relative energies of the 6d and 5f orbitals, which favors 6d¹ Th(III) complexes and 5f³ U(III) compounds.^{71,72}

CONCLUSIONS

The square planar Th(III) coordination environment discovered in $[\text{Th}(\text{OAr}^{\text{Me}})_4]^{1-}$ can be extended to other $[\text{Th}(\text{OC}_6\text{H}_2'\text{Bu}_2\text{-2,6-R-4})_4]^{1-}$ complexes, where R = H, 'Bu, OMe, and Ph based on EPR and UV–visible spectroscopy. Reductions with Li, Na, and KC₈, both with and without crypt or crown, give similar results, but solvable X-ray diffraction data have only been obtained for $[\text{Li}(\text{THF})_4][\text{Th}(\text{OC}_6\text{H}_2'\text{Bu}_2\text{-2,6-R-4})_4]$ with R = H, 'Bu, and OMe due to difficulties in crystallization with this particular type of structure. In contrast, neither $\text{Th}(\text{Odipp})_4(\text{THF})_2$ nor $\text{Th}(\text{Odmp})_4(\text{THF})_2$ could be reduced to Th(III) products under the same conditions. Furthermore, the anions in the U(III) complexes, $[\text{K}(\text{crypt})][\text{U}(\text{OAr}^{\text{H}})_4]$ and $[\text{K}(\text{crown})(\text{THF})_2][\text{U}(\text{OAr}^{\text{H}})_4]$, are

tetrahedral, in contrast to those of the anionic square planar Th(III) complex, $[\text{Th}(\text{OAr}^{\text{H}})_4]^{1-}$. The $6d^1$ electron configuration of Th(III), the 2,6-di-*tert*-butyl substitution in aryloxide ligands that could result in attractive interligand dispersion effects, and the π -donation strength from the oxygen donor atoms of the aryloxide ligands appear to be crucial in forming the unusual square planar structure in these actinide compounds.

EXPERIMENTAL DETAILS

Caution! ^{232}Th and ^{238}U are α emitters with half-lives of approximately 1.41×10^{10} and 4.5×10^9 years, respectively. Samples should be prepared and handled only in laboratories appropriately equipped to handle radioactive materials.

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP (99.999%) argon and dried by passage through columns containing Q-5 and molecular sieves and stored over activated molecular sieves prior to use. Deuterated NMR solvents were degassed and dried over activated 3 Å molecular sieves overnight prior to use. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on Bruker GN500 or AVANCE600 MHz spectrometers at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. X-band EPR spectra were recorded in THF solutions at 298 K or frozen THF solutions at 77 K on a Bruker EMX spectrometer equipped with an ER041Xg microwave bridge and calibrated with DPPH ($g = 2.0036$). UV–visible spectra were collected in THF at 298 K using a Varian Cary 50 Scan UV–visible spectrometer in a 1 mm Schlenk cuvette fitted with a Teflon stopper unless otherwise stated. Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR. Elemental analyses were conducted on a Thermo Scientific FlashSmart CHNS/O Elemental Analyzer at UC Irvine Materials Research Institute's

TEMPR facility in Irvine, California. Combustion analysis data was collected for **4.1-OMe** and **4.2-OMe** as a representative set of structurally similar Th(IV) and Th(III) compounds. $\text{ThBr}_4(\text{DME})_2$ (DME = 1,2-dimethoxyethane),³⁰ $\text{Th}(\text{OC}_6\text{H}_3'\text{Bu}_2\text{-2,6})_4$ (**4.1-H**),⁴¹ UI_3 ,⁷³ KC_8 ,⁷⁴ and $\text{HOC}_6\text{H}_2'\text{Bu}_2\text{-2,6-Ph-4}$ ⁷⁵ were synthesized according to literature procedures. 2.2.2-Cryptand (crypt) was purchased from Sigma-Aldrich and recrystallized from Et_2O prior to use and 18-crown-6 (crown) was sublimed prior to use. All potassium aryloxide starting materials were synthesized by treating the respective phenol with $\text{KN}(\text{SiMe}_3)_2$ in toluene or KH in THF.

Synthesis of $[\text{Li}(\text{THF})_4][\text{Th}(\text{OC}_6\text{H}_3'\text{Bu}_2\text{-2,6})_4]$, **4.2-H.** Li pellets (5 mg, 0.7 mmol) were added to a solution of **4.1-H** (125 mg, 0.119 mmol) in THF (ca. 4 mL). The resulting mixture was stored at $-35\text{ }^\circ\text{C}$ for 2 days, at which point the solution became dark purple in color. The solution was filtered through a glass pipet packed with Kimwipe tissue to remove insoluble material, and the solvent was removed from the supernatant under reduced pressure to yield dark purple solids. The solids were then washed with hexane (ca. 4 mL) and dried under reduced pressure to yield **4.2-H** as dark purple solids (156 mg, 97%). Storage of a solution of **4.2-H** in THF (ca. 3 mL) layered under diethyl ether (ca. 10 mL) in a $-35\text{ }^\circ\text{C}$ freezer yielded dark purple crystals of **4.2-H**, identified by X-ray diffraction. ^1H NMR ($\text{THF-}d_8$, 500 MHz): δ 6.47 (br, 4H, *p*-Ar), 5.86 (br, 8H, *m*-Ar), 3.61 (m, 16H, OCH_2CH_2 on THF), 1.77 (m, 16H, OCH_2CH_2 on THF), -8.23 [br, 72H, $\text{C}(\text{CH}_3)_3$]. IR: 2946m, 2868m, 1582w, 1463w, 1396vs, 1381s, 1359m, 1221vs, 1195vs, 1133m, 1118m, 1105m, 1038s, 882m, 852vs, 814vs, 745vs cm^{-1} . UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$): 282 (12600), 310 (4000), 328 (3900), 488 (8700), 586 (9400). EPR $g_{\parallel} = 1.99$, $g_{\perp} = 1.78$, $g_{\text{iso}} = 1.84$ (100.9 MHz).

Reduction of $\text{Th}(\text{OC}_6\text{H}_3'\text{Bu}_2\text{-2,6})_4$, **4.1-H, with KC_8 and no chelate.** **4.1-H** (51 mg, 0.048 mmol) was dissolved in THF (ca. 4 mL) to yield a clear and colorless solution. The solution

was then transferred to a vial containing KC_8 (7.2 mg, 0.053 mmol) at room temperature to immediately produce a dark purple solution. The mixture was then vigorously swirled for 1 min before being filtered through a glass pipet packed with Kimwipe tissue to remove insoluble solids. The solvent was removed from the dark purple supernatant under reduced pressure to yield dark purple solids (52 mg, 70% assuming a chemical formula of $[\text{K}(\text{THF})_6][\text{Th}(\text{OC}_6\text{H}_3'\text{Bu}_2\text{-2,6})_4]$). Dark purple needle-like crystals could be grown from a solution in THF layered under diethyl ether stored at $-35\text{ }^\circ\text{C}$ for 2 days. Despite several attempts, no X-ray quality crystals were isolated. IR: 3060w, 2954m, 2864m, 1605w, 1580w, 1457w, 1396s, 1381s, 1359m, 1299w, 1223s, 1195s, 1116m, 1103m, 1047m, 880w, 852vs, 814s, 800w, 744vs cm^{-1} . UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$): 278 (13000, shoulder), 317 (4700), 487 (6800), 584 (7500). EPR $g_{\parallel} = 1.99$, $g_{\perp} = 1.78$, $g_{\text{iso}} = 1.84$ (100.9 MHz).

Reduction of $\text{Th}(\text{OC}_6\text{H}_3'\text{Bu}_2\text{-2,6})_4$, 4.1-H, with KC_8 and 2.2.2-Cryptand. 2.2.2-Cryptand (7.2 mg, 0.019 mmol) and 4.1-H (20 mg, 0.019 mmol) were dissolved in THF (ca. 3 mL) at room temperature. The solution was then added to a vial containing KC_8 (2.8 mg, 0.021 mmol) at room temperature. The solution immediately became dark purple and was vigorously swirled for 1 min. The solution was then filtered through a glass pipet packed with Kimwipe tissue to remove insoluble solids, and the solvent was removed from the dark purple supernatant to yield purple solids (27 mg, 97% assuming a chemical formula of $[\text{K}(2.2.2\text{-cryptand})][\text{Th}(\text{OC}_6\text{H}_3'\text{Bu}_2\text{-2,6})_4]$). Dark purple crystals could be grown from a solution in THF layered under diethyl ether stored at $-35\text{ }^\circ\text{C}$ for 2 days. Despite several attempts, no X-ray quality crystals were isolated. IR: 3051w, 2947m, 2864m, 2812w, 1580w, 1446w, 1396s, 1383s, 1353m, 1295w, 1256w, 1224vs, 1198s, 1131m, 1101vs, 1077s, 1060s, 1025w, 949m, 932w, 880w, 852vs, 814vs, 745vs cm^{-1} . UV–

vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 329 (2900), 487 (5000), 584 (5400). EPR $g_{\parallel} = 1.99$, $g_{\perp} = 1.78$, $g_{\text{iso}} = 1.84$ (100.9 MHz).

Reduction of Th(OC₆H₃'Bu₂-2,6)₄, 4.1-H, with KC₈ and 18-Crown-6. 18-Crown-6 (6.1 mg, 0.023 mmol) and **4.1-H** (25 mg, 0.023 mmol) were dissolved in THF (ca. 3 mL) at room temperature. The solution was then added to a vial containing KC₈ (3.5 mg, 0.026 mmol) at room temperature. The solution immediately became dark purple and was vigorously swirled for 1 min. The solution was then filtered through a glass pipet packed with Kimwipe tissue to remove insoluble solids and the solvent was removed from the dark purple supernatant to yield purple solids (30 mg, 84% assuming a chemical formula of [K(18-crown-6)(THF)₂][Th(OC₆H₃'Bu₂-2,6)₄]. Dark purple crystals could be grown from a solution in THF (ca. 2 mL) layered under diethyl ether (ca. 10 mL) stored at $-35\text{ }^{\circ}\text{C}$ for 2 days. Despite several attempts, no X-ray quality crystals were isolated. IR: 3062w, 2946m, 2896m, 2864m, 1580w, 1465w, 1424m, 1396s, 1381s, 1351m, 1249m, 1224vs, 1196m, 1131w, 1103vs, 1053w, 960m, 880w, 854vs, 814s, 744vs cm^{-1} . UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 278 (12500), 319 (4000), 487 (7500), 585 (8200). EPR $g_{\parallel} = 1.99$, $g_{\perp} = 1.78$, $g_{\text{iso}} = 1.84$ (100.9 MHz).

Reduction of Th(OC₆H₃'Bu₂-2,6)₄, 4.1-H, with Na and no chelate. **4.1-H** (50 mg, 0.047 mmol) was dissolved in THF (ca. 4 mL) to yield a clear and colorless solution. This was then added to a vial containing Na (7 mg, 0.3 mmol) and stored at $-35\text{ }^{\circ}\text{C}$ for 2 days, at which point the solution was dark purple. Spectroscopic data were collected on the *in situ* generated solution. UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 312 (3500), 487 (3300), 584 (3600). EPR $g_{\parallel} = 1.99$, $g_{\perp} = 1.78$, $g_{\text{iso}} = 1.84$ (100.9 MHz).

Synthesis of Th(OC₆H₂'Bu₂-2,6-OMe-4)₄, 4.1-OMe. ThBr₄(DME)₂ (363 mg, 0.469 mmol) was dissolved in THF (ca. 10 mL) to give a clear and colorless solution. Solid

KOC₆H₂'Bu₂-2,6-OMe-4 (515 mg, 1.88 mmol) was added portionwise as a solid at room temperature to immediately produce a mixture with much colorless precipitate. The resulting mixture was allowed to stir at room temperature for ca. 16 h. Insoluble solids were removed by centrifugation followed by filtration through a glass pipet packed with Kimwipe tissue to give a colorless solution. The removal of solvent under reduced pressure yielded colorless solids, which were then washed with hexane (ca. 3 mL) and dried under reduced pressure to give **4.1-OMe** as colorless solids (534 mg, 97%). ¹H NMR (C₆D₆, 500 MHz): δ 6.99 (s, 8H, *m*-Ar), 3.49 (s, 12H, OCH₃), 1.60 [s, 72H, C(CH₃)₃]. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 156.6 (aromatic C), 152.8 (aromatic C), 138.6 (aromatic C), 112.0 (aromatic C), 55.1 (OCH₃), 35.9 [C(CH₃)₃], 33.5 [C(CH₃)₃]. IR: 2952m, 2866w, 2829w, 1599m, 1444m, 1405vs, 1387s, 1291w, 1252m, 1193vs, 1108s, 1059vs, 818vs, 793vs, 762s cm⁻¹. Anal. Calcd for C₆₀H₉₂O₈Th: C, 61.42; H, 7.90. Found: C, 47.58; H, 6.07. C, 47.04; H, 6.05. C, 46.88; H, 6.15. Low C and H values were found across multiple runs and suggest incomplete combustion.^{76–81} The C:H ratios in the analytical data give formulas of C₆₀H₉₁, C₆₀H₉₂, and C₆₀H₉₃, respectively.

Synthesis of [Li(THF)₄][Th(OC₆H₂'Bu₂-2,6-OMe-4)₄], **4.2-OMe.** Li pellets (9 mg, 1 mmol) were crushed in a 20 mL scintillation vial, and to this vial was added solid **4.1-OMe** (273 mg, 0.233 mmol). THF (ca. 7 mL) was added to dissolve **4.1-OMe** to result in a colorless solution and this mixture was stored at –35 °C. After 3 days, the solution was inky dark purple, and the mixture was filtered through a glass pipet packed with Kimwipe tissue to remove insoluble solids. The solvent was removed under reduced pressure to yield dark purple solids. The solids were then washed with hexane (ca. 3 mL) and dried under reduced pressure to yield **4.2-OMe** as a dark purple powder (287 mg, 84%). Dark purple crystals suitable for study by X-ray diffraction can be grown from a THF (ca. 2 mL) solution of **4.2-OMe** layered under hexane (ca. 10 mL) stored at –35 °C.

^1H NMR (THF- d_8 , 600 MHz): δ 5.52 (br, 8H, *m*-Ar), 3.61 (m, 16H, OCH_2CH_2 on THF), 3.36 (br, 12H, OCH_3), 1.77 (m, 16H, OCH_2CH_2 on THF), -8.04 [br, 72H, $\text{C}(\text{CH}_3)_3$]. IR: 2950m, 2901w, 2866w, 1595w, 1440m, 1398s, 1382s, 1359m, 1232s, 1198s, 1176s, 1113w, 1042m, 1031s, 1016m, 870w, 865w, 818s, 792vs, 773s cm^{-1} . UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 298 (20 200), 332 (4300, shoulder), 481 (8500), 580 (11400). EPR $g_{\parallel} = 1.99$, $g_{\perp} = 1.78$, $g_{\text{iso}} = 1.84$ (100.9 MHz). Anal. Calcd for $\text{C}_{76}\text{H}_{124}\text{Li O}_{12}\text{Th}$: C, 62.15; H, 8.51. Found: C, 52.70; H, 6.90. C, 51.86; H, 6.84. C, 50.47; H, 6.59. Low C and H values were found across multiple runs and suggest incomplete combustion.^{76–81} The C:H ratios in the analytical data give formulas of $\text{C}_{76}\text{H}_{118}$, $\text{C}_{76}\text{H}_{119}$, and $\text{C}_{76}\text{H}_{118}$, respectively.

Synthesis of $\text{Th}(\text{OC}_6\text{H}_2'\text{Bu}_3\text{-2,4,6})_4$, **4.1-tBu.** $\text{ThBr}_4(\text{DME})_2$ (279 mg, 0.381 mmol) was dissolved in THF (ca. 10 mL) to give a clear and colorless solution. Solid $\text{KOC}_6\text{H}_2'\text{Bu}_2\text{-2,4,6}$ (458 mg, 1.52 mmol) was added portionwise as a solid at room temperature to immediately produce a mixture with much colorless precipitate. The resulting mixture was allowed to stir at room temperature for ca. 16 h. Insoluble solids were removed by centrifugation followed by filtration through a glass pipet packed with Kimwipe tissue to give a colorless solution. The removal of solvent under reduced pressure yielded colorless solids, which were then washed with hexane (3 mL) and dried under reduced pressure to give **4.1-tBu** as colorless solids (455 mg, 93%). ^1H NMR (C_6D_6 , 500 MHz): δ 7.40 (s, 8H, *m*-Ar), 1.61 [s, 72H, *o*- $\text{C}(\text{CH}_3)_3$], 1.38 [s, 36H, *p*- $\text{C}(\text{CH}_3)_3$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ 159.7 (aromatic C), 141.2 (aromatic C), 136.8 (aromatic C), 123.1 (aromatic C), 35.9 [$\text{C}(\text{CH}_3)_3$], 34.5 [$\text{C}(\text{CH}_3)_3$], 33.6 [$\text{C}(\text{CH}_3)_3$], 31.9 [$\text{C}(\text{CH}_3)_3$]. IR: 2950m, 2864w, 1457w, 1420s, 1360m, 1271w, 1221vs, 1195vs, 1113s, 885w, 877w, 827vs, 772s, 743vs cm^{-1} .

Synthesis of [Li(THF)₄][Th(OC₆H₂^tBu₃-2,4,6)]₄, 4.2-tBu. Li pellets (11 mg, 1.6 mmol) were crushed in a 20 mL scintillation vial, and to this vial was added solid **4.1-tBu** (311 mg, 0.244 mmol). THF (ca. 7 mL) was added to dissolve the **4.1-tBu** to result in a colorless solution, and this mixture was stored in a –35 °C freezer. After 3 days, the solution was inky dark purple, and the mixture was filtered through a glass pipet packed with Kimwipe tissue to remove insoluble solids. The solvent was removed under reduced pressure to yield dark purple solids. The solids were then washed with hexane (ca. 3 mL) and dried under reduced pressure to yield **4.2-tBu** as a dark purple powder (366 mg, 95%). **4.2-tBu** was identified by X-ray crystallography by growing dark purple crystals suitable for study by X-ray diffraction from a THF (ca. 2 mL) solution of **4.2-tBu** layered under hexane (ca. 10 mL) stored at –35 °C. ¹H NMR (THF-*d*₈, 500 MHz): δ 5.93 (br, 8H, *m*-Ar), 3.61 (m, 16H, OCH₂CH₂ on THF), 1.77 (m, 16H, OCH₂CH₂ on THF), 1.01 [br, 36H, *p*-C(CH₃)₃], –7.65 [br, 72H, *o*-C(CH₃)₃]. IR: 2946s, 2894m, 2868m, 1457w, 1416s, 1385m, 1357m, 1228vs, 1196vs, 1116s, 1038m, 893w, 835m, 829vs, 818vs, 747m, 742vs cm^{–1}. UV–vis (THF, room temperature) λ_{max}, nm (ε, M^{–1} cm^{–1}): 285 (12300), 317 (3700), 339 (3000), 485 (6500), 586 (8100). EPR *g*_{||} = 1.99, *g*_⊥ = 1.78, *g*_{iso} = 1.84 (100.9 MHz).

Synthesis of Th(OC₆H₂^tBu₂-2,6-Ph-4)₄, 4.1-Ph. ThBr₄(DME)₂ (225 mg, 0.308 mmol) was dissolved in THF (ca. 10 mL) to give a clear and colorless solution. Solid KOC₆H₂^tBu₂-2,6-Ph-4 (395 mg, 1.23 mmol) was added portionwise as a solid at room temperature to immediately produce a mixture with much colorless precipitate. The resulting mixture was allowed to stir at room temperature for ca. 16 h. Insoluble solids were removed by centrifugation followed by filtration through a glass pipet packed with Kimwipe tissue to give a colorless solution. The removal of solvent under reduced pressure yielded colorless solids, which were then washed with hexane (ca. 3 mL) and dried under reduced pressure to give **4.1-Ph** as colorless solids (410 mg,

98%). ^1H NMR (THF- d_8 , 600 MHz): δ 7.20–7.16 (m, 15H, aromatic H), 7.05–7.02 (m, 9H, aromatic H), 6.91–6.89 (m, 4H, aromatic H), 1.28 [s, 72H, $o\text{-C}(\text{CH}_3)_3$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 151 MHz): 161.9 (aromatic C), 142.8 (aromatic C), 138.4 (aromatic C), 133.0 (aromatic C), 129.1 (aromatic C), 127.2 (aromatic C), 126.8 (aromatic C), 125.5 (aromatic C), 36.1 [$\text{C}(\text{CH}_3)_3$], 30.5 [$\text{C}(\text{CH}_3)_3$]. IR: 2954w, 2915w, 2868w, 1599w, 1415vs, 1387m, 1359w, 1310w, 1258w, 1215vs, 1193vs, 1113s, 883s, 816vs, 775vs, 764vs, 695vs cm^{-1} .

Attempted Li Reduction of $\text{Th}(\text{OC}_6\text{H}_2'\text{Bu}_2\text{-2,6-Ph-4})_4$, **4.1-Ph.** Li pellets (5 mg, 0.7 mmol) were added to a colorless solution of $\text{Th}(\text{OC}_6\text{H}_2'\text{Bu}_2\text{-2,6-Ph-4})_4$, **4.1-Ph** (18 mg, 0.013 mmol), in THF (ca. 3 mL) at room temperature. The resulting mixture was stored at $-35\text{ }^\circ\text{C}$ for ca. 2 days at which point a dark purple color was present. Spectroscopic data was collected on the *in situ* generated solution. UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$): 479 (5300), 585 (4650). EPR $g_{\parallel} = 1.99$, $g_{\perp} = 1.78$, $g_{\text{iso}} = 1.82$ (100.9 MHz).

Synthesis of $\text{U}(\text{OC}_6\text{H}_3'\text{Bu}_2\text{-2,6})_3(\text{THF})$. This compound was synthesized via a different procedure than previously reported.⁵² $\text{KOC}_6\text{H}_3'\text{Bu}_2\text{-2,6}$ (65 mg, 0.266 mmol) was dissolved in THF (ca. 5 mL) to result in a colorless solution. UI_3 (55 mg, 0.089 mmol) was added as a solid at room temperature to immediately produce a red mixture. The resulting mixture was allowed to stir at room temperature for ca. 16 h before colorless, insoluble solids were removed via centrifugation to give a dark red supernatant. The solvent was removed under reduced pressure and the resulting residue was extracted into toluene (ca. 2 mL) and filtered through a glass pipet packed with Kimwipe tissue. The solvent was removed under reduced pressure to yield $\text{U}(\text{OC}_6\text{H}_3'\text{Bu}_2\text{-2,6})_3(\text{THF})$ as brown solids (58 mg, 71%). The spectroscopic data matched as previously reported.⁵²

Synthesis of [K(2.2.2-Cryptand)][U(OC₆H₃'Bu₂-2,6)₄], 4.3: Method A. U(OC₆H₃'Bu₂-2,6)₃(THF) (58 mg, 0.063 mmol) and 2.2.2-cryptand (24 mg, 0.064 mmol) were dissolved in THF (ca. 1 mL) to afford a brown solution. Solid KOC₆H₃'Bu₂-2,6 (15 mg, 0.061 mmol) was added and the solution immediately turned bright red. The solution was stirred for ca. 2 h and then dried under reduced pressure. The product was redissolved in minimal THF and layered under hexane at −35 °C. Dark red crystals of **4.3** suitable for study by X-ray diffraction formed overnight and were collected by decanting the mother liquor and drying the crystals under reduced pressure (54 mg, 58%). ¹H NMR (THF-*d*₈): δ 11.22 (m, 8H, *m*-Ar), 10.17 (t, 4H, *p*-Ar), 3.63 (m, 12H, crypt), 2.58 (m, 12H, crypt), 1.41 (m, 12H, crypt), −0.90 ppm (s, 72H, 'Bu). IR: 2951m, 2884m, 1579w, 1476w, 1399s, 1354m, 1234s, 1101s, 948m, 854s, 815m, 745s cm^{−1}. Anal. Calcd for C₇₄H₁₂₀N₂O₁₀KU: C, 60.26; H, 8.20; N, 1.90. Found: C, 58.17; H, 7.76; N, 1.99. Found: C, 56.36; H, 7.73; N, 1.91. Found: C, 56.97; H, 7.91; N, 1.99. Low C and H values were found across multiple runs and suggest incomplete combustion.^{76–81} The observed C:H:N ratios are C₇₄H₁₁₈N₂, C₇₄H₁₂₁N₂, and C₇₄H₁₂₂N₂, respectively.

Synthesis of [K(2.2.2-Cryptand)][U(OC₆H₃'Bu₂-2,6)₄], 4.3: Method B. U(OC₆H₃'Bu₂-2,6)₃(THF) (40 mg, 0.043 mmol) and 2.2.2-cryptand (15 mg, 0.040 mmol) were dissolved in THF (ca. 1 mL) to afford a brown solution. The solution was passed through a glass pipet packed with KC₈ (8 mg, 0.06 mmol) and Kimwipe tissue to generate a transient dark blue color which quickly turned red. The solution was dried under reduced pressure, washed with hexane (ca. 3 mL) and toluene (ca. 3 mL), and dried under vacuum. The resulting red solids were dissolved in minimal THF, layered under hexane, and stored at −35 °C. A few dark red crystals of **4.3**, identified by X-ray diffraction, formed overnight.

Synthesis of [K(crown)(THF)₂][U(OC₆H₃^tBu₂-2,6)₄], 4.4. UI₃ (50 mg, 0.081 mmol) and 18-crown-6 (21 mg, 0.080 mmol) were dissolved in THF (ca. 3 mL) to form a dark blue solution. KOC₆H₃^tBu₂-2,6 (79 mg, 0.32 mmol) was added to the solution as solids at room temperature to immediately produce a dark red mixture concomitant with precipitation. The mixture was allowed to stir at room temperature for ca. 1 h before insoluble solids were removed via centrifugation. The resulting dark red supernatant was dried under reduced pressure to yield oily red solids. Trituration with hexane followed by drying under reduced pressure yielded **4.4** as a bright red powder (110 mg, 91%). Red crystals of **4.4** suitable for study by X-ray diffraction were grown from a solution of **4.4** in THF layered under hexane stored at −35 °C. ¹H NMR (THF-*d*₈): δ 11.26 (br s, 8H, *m*-Ar), 10.21 (br s, 4H, *p*-Ar), 3.62 (m, 8H, OCH₂CH₂ on THF), 3.57 (s, 24H, OCH₂ on crown), 1.77 (m, 8H, OCH₂CH₂ on THF), −0.94 (br s, 72H, ^tBu). IR: 2946m, 2904m, 2863m, 1579w, 1454w, 1400s, 1351m, 1232vs, 1198m, 1103vs, 1055m, 960m, 854s, 837m, 816s, 794w, 744s cm^{−1}. Anal. Calcd for C₇₆H₁₂₄O₁₂KU: C, 60.58; H, 8.29. Found: C, 56.64; H, 7.81. Found: C, 57.85; H, 8.12. Found: C, 57.53; H, 8.08. Low C and H values were found across multiple runs and suggest incomplete combustion.^{76–81} The observed C:H ratios are C₇₆H₁₂₅, C₇₆H₁₂₇, and C₇₆H₁₂₇, respectively.

X-ray Data Collection, Structure Solution and Refinement for [Li(THF)₄][Th(OAr^H)₄], 4.2-H. A purple crystal of approximate dimensions 0.300 x 0.397 x 0.695 mm was mounted in a cryoloop fiber and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁸² program package was used to determine the unit-cell parameters. Data collection used a 90 sec/frame scan time. The raw frame data was processed using SAINT⁸³ and SADABS⁸⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁸⁵ program package. The diffraction symmetry was 2/*m* and the

systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁸⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The data were not high enough quality, so only connectivity could be established.

X-ray Data Collection, Structure Solution and Refinement for [Li(THF)₄][Th(OAr^{OMe})₄], 4.2-OMe. A purple crystal of approximate dimensions 0.265 x 0.290 x 0.355 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁸² program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time). The raw frame data was processed using SAINT⁸³ and SADABS⁸⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁸⁵ program package. The diffraction symmetry was mmm and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁸⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were four molecules of tetrahydrofuran present per formula unit. Several atoms were disordered and were included using multiple components, partial site-occupancy-factors, geometric (SADI), and displacement (SIMU) constraints. Least squares analysis yielded $wR2 = 0.0866$ and $Goof = 1.069$ for 1055 variables refined against 21552 data ($0.76 \text{ \AA}$), $R1 = 0.0358$ for those 20214 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.⁸⁷

X-ray Data Collection, Structure Solution and Refinement for [Li(THF)₄][Th(OAr^{tBu})₄], 4.2-tBu. A purple crystal of approximate dimensions 0.180 x 0.292 x

0.299 mm was mounted in a cryoloop fiber and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁸² program package was used to determine the unit-cell parameters. Data collection used a 45 sec/frame scan time. The raw frame data was processed using SAINT⁸³ and SADABS⁸⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁸⁵ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups $P2_1$ and $P2_1/m$. It was later determined that space group $P2_1$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁸⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The data were not high enough quality, so only connectivity could be established.

X-ray Data Collection, Structure Solution and Refinement for [K(crypt)][U(OAr^H)₄],
4.3. A red crystal of approximate dimensions 0.142 x 0.182 x 0.284 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁸² program package was used to determine the unit-cell parameters and for data collection (180 sec/frame scan time). The raw frame data was processed using SAINT⁸³ and SADABS⁸⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁸⁵ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁸⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Disordered atoms were included using multiple components, partial site-occupancy-factors, and geometric (SADI, DFIX, DANG, RIGU) and displacement (SIMU) constraints. There were two half tetrahydrofuran molecules present in

the asymmetric unit. One half molecule was located about an inversion center and included using negative parts. The other half molecule was located about a general position. Least-squares analysis yielded $wR2 = 0.1400$ and $Goof = 1.024$ for 1141 variables refined against 16239 data ($0.80 \text{ \AA}$), $R1 = 0.0601$ for those 11827 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for [K(crown)(THF)₂][U(OAr^H)₄], 4.4. A red crystal of approximate dimensions $0.148 \times 0.367 \times 0.449 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁸² program package was used to determine the unit-cell parameters. Data collection used a 40 sec/frame scan time. The raw frame data was processed using SAINT⁸³ and SADABS⁸⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁸⁵ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁸⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0761$ and $Goof = 0.984$ for 835 variables refined against 18872 data ($0.75 \text{ \AA}$), $R1 = 0.0357$ for those 14280 data with $I > 2.0\sigma(I)$.

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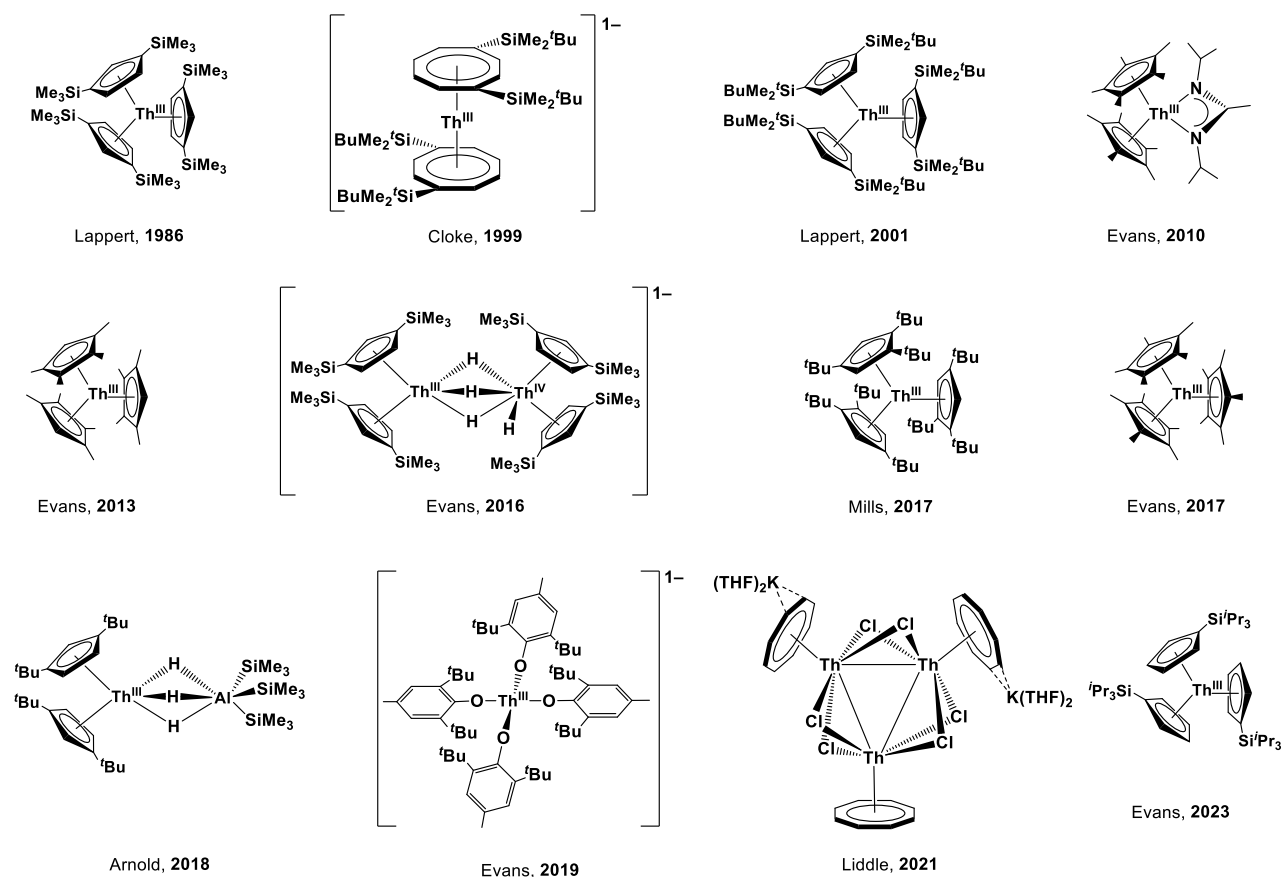
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Chapter 5:

Efforts Towards the Synthesis of a Th(II) Metallocene Amidinate Complex

INTRODUCTION

As stated in Chapter 3, the synthesis of new coordination complexes of thorium in low oxidation states, specifically the +2 oxidation state, can be explored by identifying suitable Th(III) complexes as candidates for further reductive chemistry.¹ Up until 2023, only a few examples of Th(III) complexes had been crystallographically characterized with most of them employing cyclopentadienyl ligands, Scheme 5.1.¹⁻¹² In addition, up until 2023, only two different ligand



Scheme 5.1. Crystallographically characterized Th(III) Complexes up until 2023.

environments have been identified to stabilize the relatively reducing Th(II) ion.^{1,13} Over the course of exploring different ligand environments that could stabilize a new Th(II) complex throughout the work of this Dissertation, the heteroleptic metallocene amidinate ligand environment was evaluated as a different and unique coordination environment that could potentially support a Th(II) ion. This research is described in this Chapter.

Walensky *et al.* previously demonstrated that the bis(pentamethylcyclopentadienyl) amidinate ligand environment can support a Th(III) ion in the Th(III) complex $(C_5Me_5)_2Th[{}^iPrNC(Me)N^iPr]$, **5.1**.² Complex **5.1** is a rare example of a heteroleptic Th(III) complex that contains two $(C_5Me_5)^{1-}$ ligands bonded to the thorium metal center in an η^5 fashion with a bent geometry. An anionic and bidentate amidinate ligand, specifically $[{}^iPrNC(Me)N^iPr]^{1-}$, coordinates to the thorium metal center in the wedge of the bent metallocene, Figure 5.1. Amidinate ligands are a suitable class of ligands to investigate substituent effects pertaining to the synthesis of low-valent *f*-element coordination complexes because like the cyclopentadienyl ligand, both the steric bulk and electronics of the ligand can be tuned through substituent variation. Amidinate ligands also appear to be stable to reducing conditions as they have been shown to support relatively reducing Tb(II), Dy(II), and Th(III) ions.^{2,14}

Electronic structure calculations on the dark purple complex **5.1** suggested that the thorium atom adopts a $6d^1$ electron configuration with a significant amount of electron density localized in the $6d_z^2$ orbital of the thorium atom,² similar to previously reported Th(III) complexes.^{1-8,15} Further density functional theory (DFT) calculations on complex **5.1** and its hypothetical reduction product performed by Dr. Justin Wedal in the Evans group suggested that upon reduction, the thorium atom in the anionic complex $\{(C_5Me_5)_2Th[{}^iPrNC(Me)N^iPr]\}^{1-}$ could adopt a $6d^2$ electron configuration

in its ground state¹⁵ similar to that of the previously reported $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{Th}\}^{1-}$ and $\{[\text{C}_5\text{H}_4(\text{Si}^i\text{Pr}_3)]_3\text{Th}\}^{1-}$.^{1,16}

Guided by these preliminary calculations, it seemed reasonable to explore thorium metallocene amidinate complexes as potential candidates for reduction to Th(II) complexes. In this Chapter, the synthesis and reductions of different thorium metallocene amidinate complexes are investigated as possible environments suitable for stabilizing a Th(II) ion.

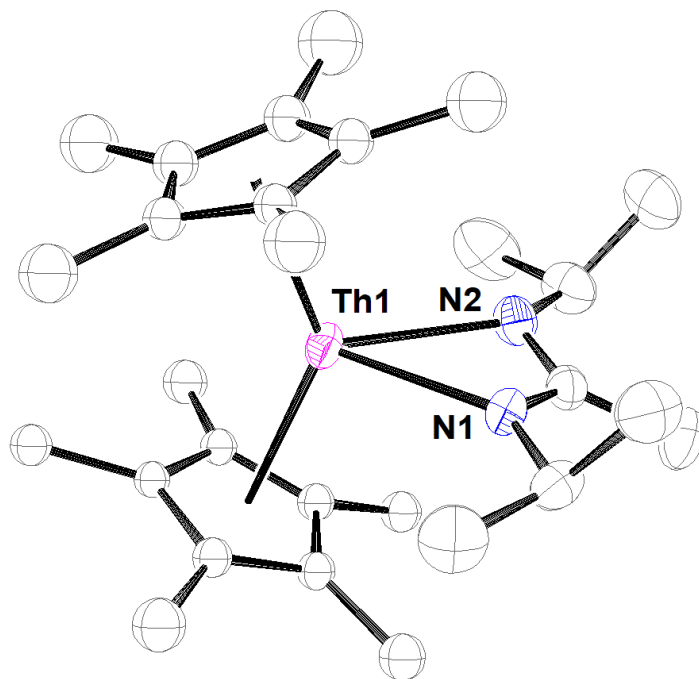
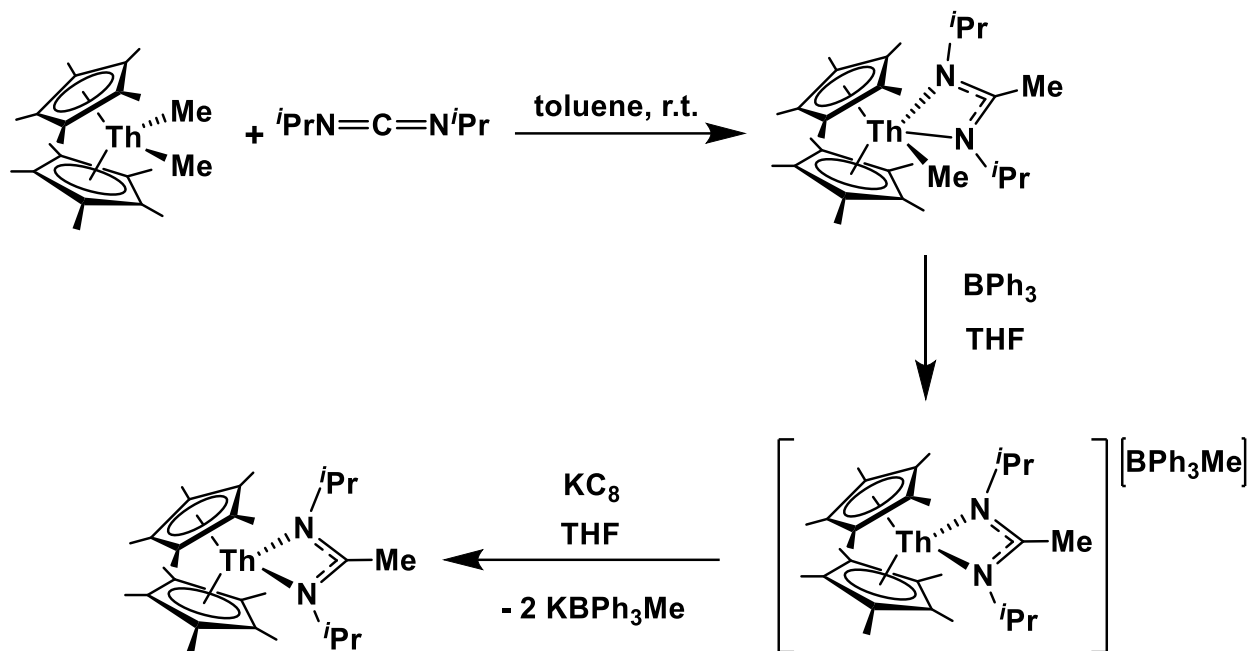


Figure 5.1. X-ray crystal structure of $(\text{C}_5\text{Me}_5)_2\text{Th}[\text{PrNC}(\text{Me})\text{NPr}]$, **5.1**, reported by Walensky *et al.* with ellipsoids drawn at 50% probability.² Hydrogen atoms are not shown for clarity.

RESULTS

Synthesis of Thorium Metallocene Amidinate Complexes. Exploration of the reduction chemistry of thorium metallocene amidinate complexes requires the development of routes for the synthesis of this class of compounds. Complex **5.1** was first synthesized by Walensky *et al.* by reacting the thorium metallocene dialkyl complex $(\text{C}_5\text{Me}_5)_2\text{ThMe}_2$ ¹⁷ with N,N'-

diisopropylcarbodiimide, $i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$, to generate the insertion product $(\text{C}_5\text{Me}_5)_2\text{ThMe}[i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$, Scheme 5.2.¹⁸ Treatment of $(\text{C}_5\text{Me}_5)_2\text{ThMe}[i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$ with BPh_3 presumably abstracts the methyl group from the Th(IV) complex to form the salt $\{(\text{C}_5\text{Me}_5)_2\text{Th}[i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]\}(\text{BPh}_3\text{Me})$ which subsequently forms the dark purple Th(III) complex $(\text{C}_5\text{Me}_5)_2\text{Th}[i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$, **5.1**, upon reduction with KC_8 , Scheme 5.2.² This specific route was explored for the synthesis of other thorium metallocene amidinate complexes.



Scheme 5.2. Synthetic route of $(\text{C}_5\text{Me}_5)_2\text{Th}[i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$, **5.1**, as reported by Walensky *et al.*^{2,18}

One possible variation of complex **5.1** was investigated by substituting the isopropyl groups of the amidinate ligand with cyclohexyl (Cy) groups which are electronically similar, but slightly different sterically. The reaction between $(\text{C}_5\text{Me}_5)_2\text{ThMe}_2$ ¹⁷ and 1 equiv of N,N'-dicyclohexylcarbodiimide, $\text{CyN}=\text{C}=\text{NCy}$, in toluene generated the mono-insertion product

$(C_5Me_5)_2ThMe[CyNC(Me)NCy]$, **5.2**, cleanly as determined by NMR spectroscopy, eq 5.1. X-ray quality crystals of **5.2** can be grown from saturated Et_2O solutions stored at $-35\text{ }^\circ\text{C}$, Figure 5.2.

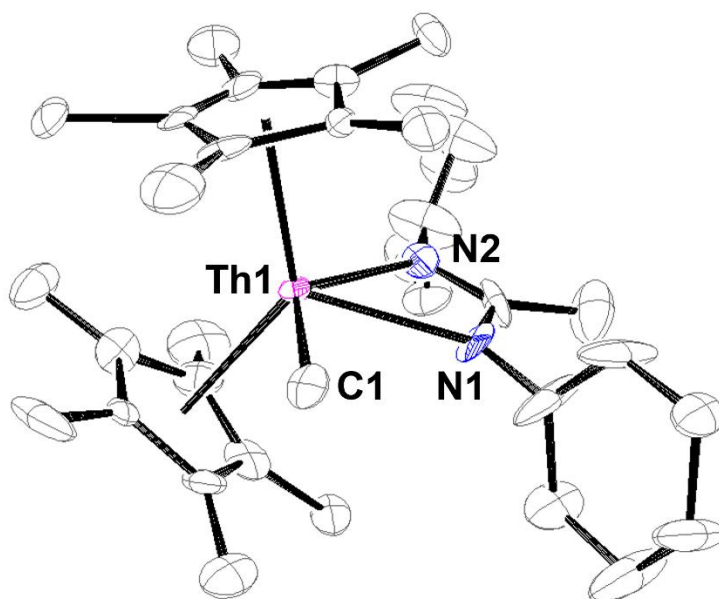
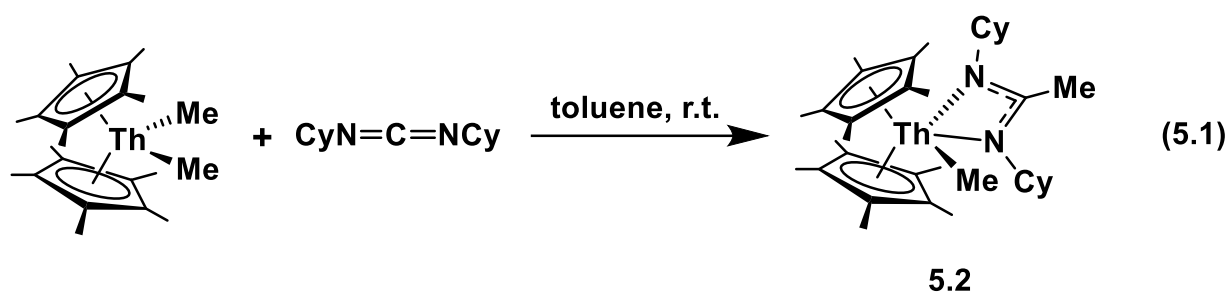


Figure 5.2. Connectivity structure of $(C_5Me_5)_2ThMe[CyNC(Me)NCy]$, **5.2**, with selective atom labelling. Ellipsoids are drawn at 30% probability and hydrogen atoms are not shown for clarity.

Complex **5.2** crystallizes in the chiral and orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit. The thorium metal center is coordinated to two $(C_5Me_5)^{1-}$ ligands in an η^5 fashion with a bent geometry, a monoanionic $[CyNC(Me)NCy]^{1-}$ ligand, and a methyl ligand. Although the data were not of sufficient quality to discuss metrical parameters, the connectivity structure confirmed the isolation of $(C_5Me_5)_2ThMe[CyNC(Me)NCy]$, **5.2**.

Addition of freshly sublimed BPh₃ to a pale-yellow THF solution of complex **5.2** at room temperature immediately generated a bright yellow solution similar to what was previously reported for the synthesis of $\{(C_5Me_5)_2Th[{}^iPrNC(Me)N^iPr]\}(BPh_3Me)$.² Subsequently, treatment with KC₈ immediately produced a dark purple solution that was characteristic of a Th(III) complex.^{2-7,11} Despite several attempts, no X-ray quality crystals of the presumably generated Th(III) complex “(C₅Me₅)₂ThMe[CyNC(Me)NCy],” **5.3**, could be isolated. However, spectroscopic data were collected to confirm the synthesis of a new Th(III) complex.

The EPR spectrum collected at 77 K for **5.3** displays an axial signal with $g_{\parallel} = 1.97$ and $g_{\perp} = 1.92$ as shown in Figure 5.3 (left) with no hyperfine coupling. Furthermore, the EPR spectrum of the same sample collected at room temperature displays an isotropic signal with $g_{iso} = 1.86$ in Figure 5.3 (right) with no hyperfine coupling either. These data are in agreement with previously characterized Th(III) compounds, Table 5.1 (²³²Th, $I = 0$, 100% abundance).

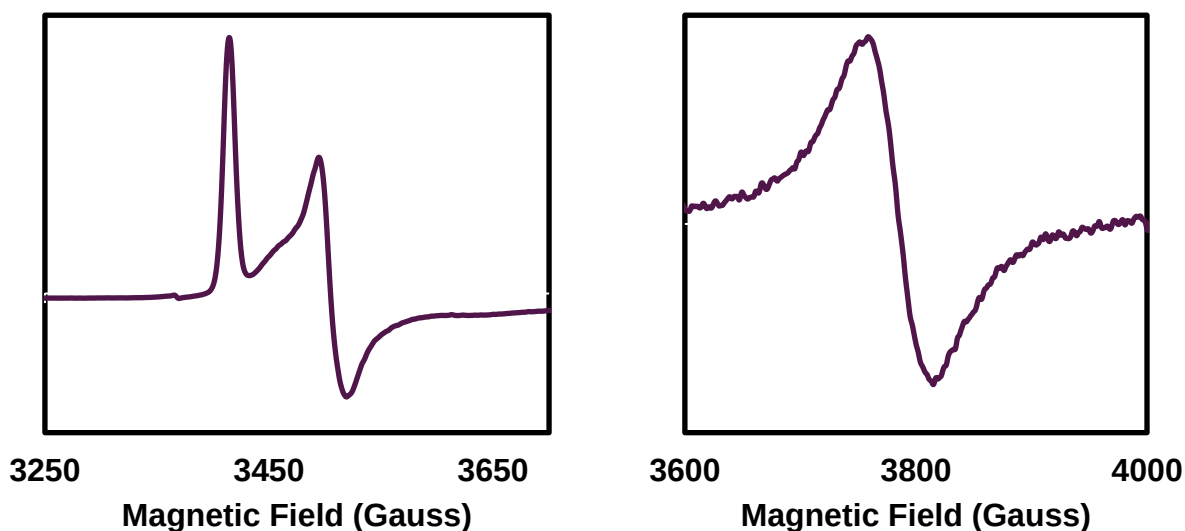


Figure 5.3. X-band EPR of “(C₅Me₅)₂Th[CyNC(Me)NCy],” **5.3**, in THF at 77 K (left; mode: perpendicular) and at room temperature (right; mode: perpendicular).

Table 5.1. EPR data for selected crystallographically characterized Th(III) complexes.

Th(III) Complex	g_{iso}	$g_{ }$	$g_{\perp}$
$(C_5Me_5)_3Th^{11}$	1.88	1.97	1.85
$(C_5Me_4H)_3Th^5$	1.92	-	-
$(C_5Me_5)_2Th[{}^iPrNC(Me)N^iPr]$, 5.1 ²	1.871	1.97	1.91
$[K(THF)_5(Et_2O)][Th(OC_6H_2-2,6-{}^tBu_2-4-Me)_4]^4$	1.84	1.99	1.79
$“(C_5H_4SiMe_3)_3Th”^{15}$	1.90	1.98	1.89
$(C_5H_3{}^tBu_2)_3Th^7$	-	1.974	1.880
$[K(DME)_2][C_8H_6(Si{}^tBuMe_2)_2]_2Th^{12}$	1.916	-	-
$(C_5H_4Si{}^iPr_3)_3Th^1$	1.90	1.97	1.88
$[C_5H_3(SiMe_3)_2]_3Th^{10}$	1.910	1.97	1.88
$“(C_5Me_5)_2Th[CyNC(Me)NCy],”$ 5.3 ^a	1.86	1.97	1.92

^a This Chapter.

The UV-visible spectrum for **5.3** was collected in THF at room temperature and is shown in Figure 5.4. Two major absorbance maxima are observed at 564 and 725 nm, both with molar extinction coefficients of $1300\text{ M}^{-1}\text{cm}^{-1}$. These data are in agreement with the absorbance maxima at 575 nm and 725 nm in the previously reported UV-visible spectrum of **5.1**.² The electronic transitions observed for complex **5.3** at 564 and 725 nm were assigned as Laporte allowed 6d to 5f transitions based on electronic structure calculations for the analogous Th(III) complex **5.1**.²

Inspired by the successful insertion of DCC into $(C_5Me_5)_2ThMe_2$,¹⁷ the insertion reactions of different carbodiimides into Th–C bonds were attempted. Reaction of $(C_5Me_5)_2ThMe_2$ ¹⁷ with 1 equiv of $DippN=C=NDipp$ ($Dipp = 2,6\text{-diisopropylphenyl}$) in toluene did not yield any observable reaction at room temperature or at elevated temperatures.

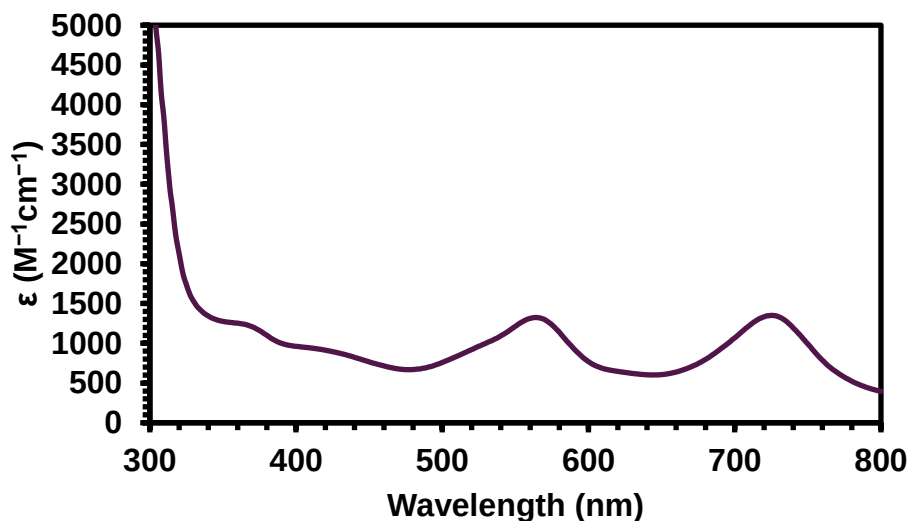
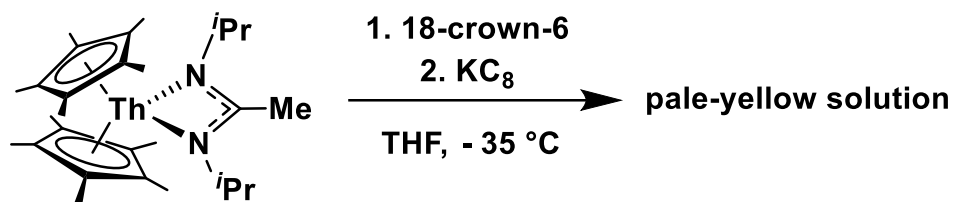


Figure 5.4. UV-visible spectrum of an 8 mM solution of “(C₅Me₅)₂Th[CyNC(Me)NCy],” **5.3**, in THF at room temperature.

In addition, attempts to insert *i*PrN=C=N*i*Pr into the Th–Ph bonds of (C₅Me₅)₂ThPh₂¹⁷ at room temperature resulted in no observable reaction. Elevated temperatures were not attempted due to the possible thermal decomposition of (C₅Me₅)₂ThPh₂ in toluene being a complication.¹⁷

Attempted Reductions of Thorium Metallocene Amidinate Complexes. Addition of a dark purple solution of (C₅Me₅)₂Th[*i*PrNC(Me)N*i*Pr],² **5.1**, and 18-crown-6 (crown) in THF to excess potassium graphite (KC₈) at room temperature immediately generated a thermally unstable dark green solution which quickly transitioned to a clear yellow solution within ca. 1-2 minutes at room temperature, Scheme 5.3, suggestive of decomposition to unidentified Th(IV) products. The color of the dark green solution was observed to be not as intense as those of the other characterized Th(II) complexes in THF. Performing the reduction at –35 °C produced a longer lived dark green solution, but decomposition occurred rapidly even when solutions were stored at –35 °C. No X-ray quality crystals of any Th(II) products or Th(IV) decomposition products were isolated from any of the attempted reductions. Attempts to collect UV-visible spectra of the green colored

product yielded flat line spectra with no outstanding absorbance features, indicative of decomposition.



Scheme 5.3. Attempted reduction of $(\text{C}_5\text{Me}_5)_2\text{Th}[\text{}^i\text{PrNC(Me)N}^i\text{Pr}]$, **5.1**.²

Preliminary density functional theory (DFT) studies predicted a diamagnetic $6d^2$ ground state configuration similar to the previously identified Th(II) complexes,^{1,16} suggesting that NMR spectroscopy could be used to characterize the Th(II) product. However, no definitive evidence of a Th(II) product was identified via ^1H NMR spectroscopy. The ^1H NMR spectrum of the decomposed product showed the presence of unreacted $(\text{C}_5\text{Me}_5)_2\text{ThMe}[\text{}^i\text{PrNC(Me)N}^i\text{Pr}]$ as well as several new species as evidenced by several new and different resonances that could be attributed to different $(\text{C}_5\text{Me}_5)^{1-}$ and $[\text{}^i\text{PrNC(Me)N}^i\text{Pr}]^{1-}$ environments. These could possibly pertain to several decomposition products.

Previously, the role of the countercation and alkali metal chelate was shown to have an influence on a compound's reactivity or thermal stability, so reductions in the presence of 2.2.2-cryptand (crypt) as the alkali metal chelate were attempted.^{19,20} However, similar results to the crown reactions were observed and the generated dark green solutions quickly decomposed to Th(IV) products and no isolable Th(II) compounds were isolated. Performing the control reaction without the addition of an alkali metal chelate yielded similar results.

Attempts to reduce a dark purple solution of **5.3** and crown in THF with the same conditions as described for **5.1** at $-35\text{ }^\circ\text{C}$ did not immediately produce a dark green solution, but

instead a delayed color change to a low intensity olive green was observed. The color faded to a yellow-orange color which was assumed to be a Th(IV) product that is the result of decomposition.

DISCUSSION

Insertion of carbodiimides into the Th–C bonds of thorium metallocene dialkyl complexes is a viable method for synthesizing new examples of thorium metallocene amidinate complexes as demonstrated by the synthesis of $(C_5Me_5)_2ThMe[{}^iPrNC(Me)N^iPr]$ ¹⁸ and $(C_5Me_5)_2ThMe[CyNC(Me)NCy]$, **5.2**, from the reaction between $(C_5Me_5)_2ThMe_2$ ¹⁷ and the carbodiimides, ${}^iPrN=C=N^iPr$ and $CyN=C=NCy$, respectively. However, the analogous reaction with $DippN=C=NDipp$ yielded no observable reaction. It is possible that $DippN=C=NDipp$ is too large and bulky of a substrate for $(C_5Me_5)_2ThMe_2$. Furthermore, switching from $(C_5Me_5)_2ThMe_2$ to $(C_5Me_5)_2ThPh_2$ in the reaction with ${}^iPrN=C=N^iPr$ produced no observable reaction. In this case, ${}^iPrN=C=N^iPr$ is likely too bulky of a substrate for $(C_5Me_5)_2ThPh_2$ whereas the reaction proceeds cleanly with $(C_5Me_5)_2ThMe_2$. These cases where no reactions were observed are presumably due to steric congestion around the thorium metal center which inhibits the insertion reaction. Salt metatheses routes starting from $(C_5Me_5)_2ThX_2$ ($X = Cl$,¹⁷ Br ,²¹ I ²²) and using alkali metal amidinate salts could be explored as alternative synthetic routes to explore this rare class of thorium metallocene complexes.²³

Attempts to reduce complexes **5.1** and **5.3** with KC_8 under several different conditions ultimately did not yield any isolable Th(II) complexes. The fact that the dark purple color of the Th(III) precursor transitioned to pale-yellow solutions after addition of KC_8 and that the KC_8 becomes discolored suggests that some reduction did occur. Presumably, a highly reactive and transient Th(II) complex was generated under these conditions and quickly oxidized to more stable Th(IV) products. Similar results were observed in the attempted reductions of $(C_5Me_5)_3Th$ and

$(C_5Me_4H)_3Th$.²⁴ This suggests that it may be possible to isolate a Th(II) metallocene amidinate complex if the ligands with suitable steric and electronic profiles are chosen.

In Chapter 3 and from previous electrochemical studies, Th(IV) complexes with polyalkylated cyclopentadienyl ligands tend to have more negative Th(III)/Th(IV) reduction potentials than Th(IV) complexes that have silyl-substituted cyclopentadienyl ligands.^{1,25} The difference in Th(III)/Th(IV) reduction potentials between these two types of thorium complexes may play a role in the isolation of new examples of Th(II) complexes as one would expect that the thorium complexes with less negative Th(III)/Th(IV) reduction potentials would generate more stable and less reactive low-valent thorium complexes. Therefore, it may be likely that the ligand environments in complexes **5.1** and **5.3** may be too electron-donating and this may lead to more reactive Th(II) complexes. Electrochemical studies can assess this hypothesis. Further studies to test this hypothesis will require designing thorium metallocene amidinate complexes that use less electron-donating cyclopentadienyl and amidinate ligands.

CONCLUSION

In summary, new examples of Th(III) metallocene amidinate complexes can be accessed through insertion of carbodiimides into Th–C bonds. The extent of steric congestion around the thorium metal center should be considered when determining the identity of the carbodiimide to insert into the Th–C bond. Reduction of $(C_5Me_5)_2ThMe[{}^iPrNC(Me)N^iPr]$,¹⁸ **5.1**, and $(C_5Me_5)_2Th[CyNC(Me)NCy]$, **5.3**, do not yield isolable Th(II) complexes although it appears some reduction to a highly reactive and transient Th(II) ion does occur before decomposition to more stable Th(IV) products.

EXPERIMENTAL DETAILS

Caution! ^{232}Th is an α emitter with half-lives of approximately 1.41×10^{10} years. Samples should be prepared and handled only in laboratories appropriately equipped to handle radioactive materials.

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP (99.999%) argon and dried by passage through columns containing Q-5 and molecular sieves prior to use and stored over activated molecular sieves prior to use. Deuterated NMR solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles before use. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker GN500 spectrometer at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR under an argon atmosphere. UV-visible spectra were collected under an inert atmosphere of argon in THF at 298 K using a Varian Cary 50 Scan UV-visible spectrometer in a 1 mm Schlenk cuvette fitted with a Teflon stopper unless otherwise stated. EPR spectra were recorded on a Bruker EMX spectrometer equipped with an ER041Xg microwave bridge and calibrated with DPPH ($g = 2.0036$). 2.2.2-cryptand (crypt) was purchased from Sigma-Aldrich and recrystallized in Et_2O prior to use. 18-crown-6 (crown) was sublimed under vacuum prior to use. Triphenylborane was sublimed under vacuum at 90 °C prior to use. $\text{N}_3\text{N}'$ -dicyclohexylcarbodiimide ($\text{CyN}=\text{C}=\text{NCy}$) was dried under vacuum overnight prior to use. $(\text{C}_5\text{Me}_5)_2\text{Th}[\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$,² $(\text{C}_5\text{Me}_5)_2\text{ThMe}_2$,¹⁷ and KC_8 ²⁶ were synthesized according to literature procedures.

Synthesis of $(\text{C}_5\text{Me}_5)_2\text{ThMe}[\text{CyNC}(\text{Me})\text{NCy}]$, 5.2. $\text{CyN}=\text{C}=\text{NCy}$ (50 mg, 0.241 mmol) was tapped into a stirring solution of $(\text{C}_5\text{Me}_5)_2\text{ThMe}_2$ (122 mg, 0.229 mmol) in toluene (ca. 7 mL)

at room temperature. The resulting solution was stirred at room temperature overnight before solvent was removed under reduced pressure to yield an oily white solid. Hexane (ca. 2 mL) was added, and the white suspension was stirred for 10 minutes. Solvent was removed under reduced pressure to yield $(C_5Me_5)_2ThMe[CyNC(Me)NCy]$, **5.2**, as a white solid (164 mg, 96%). X-ray quality crystals of $(C_5Me_5)_2ThMe[CyNC(Me)NCy]$, **5.2**, can be grown from saturated Et_2O solutions stored at $-35\text{ }^{\circ}C$. ^1H NMR (500 MHz, C_6D_6) δ 3.36-3.22 (m, 2H, cyclohexyl), 2.07 (s, 30H, C_5Me_5), 1.82-1.74 (m, 7H, cyclohexyl), 1.70 (s, 3H, amidinate *Me*), 1.58-1.56 (m, 4H, cyclohexyl), 1.36-1.20 (m, 9H, cyclohexyl), 0.36 (s, 3H, Th-*Me*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ 175.1 [NC(Me)N], 121.5 (C_5Me_5), 63.0 (Th-*Me*), 59.1 (NCH cyclohexyl), 57.1 (NCH cyclohexyl), 35.3 (CH_2 cyclohexyl), 35.1 (CH_2 cyclohexyl), 26.7 (CH_2 cyclohexyl), 26.2 (CH_2 cyclohexyl), 25.9 (CH_2 cyclohexyl), 11.9 (C_5Me_5). IR: 2918s, 2851s, 1487s, 1466m, 1447s, 1412s, 1370m, 1359s, 1343m, 1260w, 1167s, 1135w, 1095w, 1071m, 1020w, 893w, 813w, 800w, 770w, 725w cm^{-1} .

$(C_5Me_5)_2ThMe[CyNC(Me)NCy]$, **5.3**. Freshly sublimed BPh_3 (10 mg, 0.041 mmol) was tapped into a stirring solution of **5.2** (30 mg, 0.041 mmol) in THF (ca. 3 mL) at room temperature. The resulting solution turned bright yellow and was stirred for 30 minutes. The solution was then transferred to a vial containing KC_8 (6 mg, 0.042 mmol) and the solution immediately turned into a dark purple color. After letting the solution stand for 10 minutes, the suspension was filtered to remove any insoluble solids. Solvent was removed from the filtrate to result in a dark purple residue. This dark purple residue was then extracted into hexane (ca. 5 mL) and filtered to remove insoluble solids. Solvent was removed from the filtrate to yield presumably $(C_5Me_5)_2ThMe[CyNC(Me)NCy]$, **5.3**, as a purple solid (24 mg, 86%). Purple X-ray quality crystals of unreacted $(C_5Me_5)_2ThMe[CyNC(Me)NCy]$, **5.2**, were grown from saturated Et_2O

solutions stored at $-35\text{ }^{\circ}\text{C}$. IR: 2923s, 2846s, 1490s, 1441s, 1410s, 1357s, 1343s, 1253w, 1186w, 1165m, 1069m, 1013w, 890w, 826w, 802w, 698m, 664w cm^{-1} . EPR: $g_{\text{iso}} = 1.86$, $g_{\parallel} = 1.97$, $g_{\perp} = 1.92$. UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 376 (1200, shoulder), 430 (900, shoulder), 526 (1300), 725 (1300).

Attempted Reduction of $(\text{C}_5\text{Me}_5)_2\text{Th}[\text{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$, 5.1. A vial containing $(\text{C}_5\text{Me}_5)_2\text{Th}[\text{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]$ (17 mg, 0.026 mmol) and 18-crown-6 (7 mg, 0.026 mmol) dissolved in THF (ca. 2 mL) and a pipet packed with KC_8 (6 mg, 0.041 mmol) were chilled to $-35\text{ }^{\circ}\text{C}$. The solution was then quickly passed through the KC_8 column into an empty pre-chilled vial to yield a dark green solution. The solution quickly lost its color within minutes and became an orange-yellow color upon standing. ^1H NMR spectroscopy showed the presence of resonances pertaining to several different types of $(\text{C}_5\text{Me}_5)^{1-}$ and $[\text{}^i\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]^{1-}$ ligands, suggestive of multiple decomposition products which were not identified.

Attempted Reduction of $(\text{C}_5\text{Me}_5)_2\text{Th}[\text{CyNC}(\text{Me})\text{NCy}]$, 5.3. A vial containing **5.3** (15 mg, 0.021 mmol) and 18-crown-6 (6 mg, 0.021 mmol) dissolved in THF (ca. 2 mL) and a pipet packed with KC_8 (10 mg, 0.075 mmol) were chilled to $-35\text{ }^{\circ}\text{C}$. The solution was then passed through the KC_8 column while cold. Although no color change was immediately observed, the color quickly turned a low intensity olive green before immediately turning yellow-orange upon warming to room temperature, suggestive of decomposition to Th(IV) products.

X-ray Data Collection, Structure Solution and Refinement for $(\text{C}_5\text{Me}_5)_2\text{ThMe}[\text{CyNC}(\text{Me})\text{NCy}]$, 5.2. A purple crystal of approximate dimensions 0.152 x 0.220 x 0.435 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2²⁷ program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time). The raw frame data was processed

using SAINT²⁸ and SADABS²⁹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL³⁰ program package. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *P*2₁2₁2₁ that was later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors³¹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The poor quality of the data precluded a detailed discussion of metrical parameters and only confirmed connectivity.

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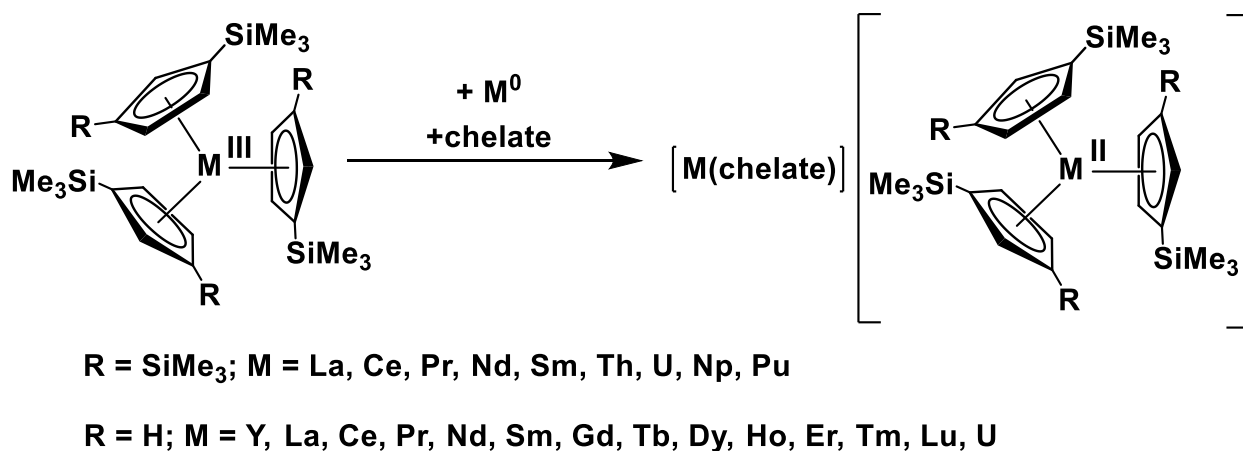
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Chapter 6:

The Triisopropylsilylcyclopentadienyl Ligand Also Stabilizes Uranium and Non-Traditional Rare-Earth Metal Ions in the +2 Oxidation State

INTRODUCTION

Having synthetic accessibility to a wide variety of oxidation states for any given element of the periodic table is essential for the development of that element's chemistry and reactivity. For example, the syntheses of molecular complexes of the +2 ions for the non-traditional rare-earth metals and actinides, specifically Sc,¹ Y,² La,³ Ce,³ Pr,⁴ Gd,⁴ Tb,⁴ Ho,⁵ Er,⁵ Lu,⁴ Th,⁶ U,⁷ Np,⁸ and Pu,⁹ have opened up pathways to unusual reactivity studies and complexes with interesting physical properties, Scheme 6.1.¹⁰⁻¹⁶ Being able to fine tune and measure the physical properties of these highly reducing species is highly dependent on determining what modifications to the molecule will still allow for the isolation of such species.



Scheme 6.1. General synthesis of tris(cyclopentadienyl) M(II) complexes.

The successful isolation of new coordination complexes of the rare-earth metals and actinides in low oxidation states requires the careful selection of ligands with suitable steric and

electronic properties that can stabilize a reduced metal center. While there are several examples of M(II) complexes in a variety of different ligand environments that include donor ligands such as amides,^{17,18} aryloxides,¹⁹⁻²¹ thiolates,²²⁻²⁵ or amidinates,^{16,26} most of the known compounds employ cyclopentadienyl ligands.^{2-10,27-32} However, despite the numerous examples that exist in the literature, not much is understood about the roles both steric and electronic effects play in the isolation and stability of the resulting reduced metal complexes.

Cyclopentadienyl ligands are favorable systems for studying steric and electronic effects in reduced *f*-element complexes due to the ease of varying cyclopentadienyl substituents with different steric and electronic properties. In Chapter 3, the triisopropylsilylcyclopentadienyl ligand, $(C_5H_4Si^iPr_3)^{1-}$, was shown to be very effective in stabilizing tris(mono-silylcyclopentadienyl) Th(III) and Th(II) complexes whereas for the related trimethylsilylcyclopentadienyl analogs, “[$C_5H_4(SiMe_3)$]₃Th” and “[$C_5H_4(SiMe_3)$]₃Th¹⁻,” isolation has remained elusive.^{27,33} It was hypothesized that a greater amount of steric saturation around the metal center facilitated the isolation of stable Th(III) and Th(II) complexes of the $(C_5H_4Si^iPr_3)^{1-}$ ligand compared to the $(C_5H_4SiMe_3)^{1-}$ ligand.²⁷ Studies on reduced tris(aryloxide) rare-earth metal complexes have demonstrated the importance of steric saturation in stabilizing highly reducing M(II) ions.^{20,21} Furthermore, electrochemical studies on a series of chemically related tris(cyclopentadienyl) *f*-element complexes suggest that silyl-substituted cyclopentadienyl ligands are less electron-donating than polyalkylated cyclopentadienyl ligands which may result in more stable M(II) complexes.^{34,35}

Among the first examples of molecular complexes containing non-traditional rare-earth metal ions in the +2 oxidation state, which exclude the traditional +2 ions, Nd(II), Eu(II), Sm(II), Dy(II), Tm(II), and Yb(II), were those consisting of the anionic species $[(C_5H_4SiMe_3)_3M]^{1-}$.^{2,4,5,7}

The mono-silylcyclopentadienyl ligand, $(\text{C}_5\text{H}_4\text{SiMe}_3)^{1-}$, provided M(II) complexes across the whole lanthanide series. In contrast, the di-silylcyclopentadienyl ligand, $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]^{1-}$, provided M(II) complexes for only the larger lanthanides and actinides.^{3,6-8} Although these $[(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{M}]^{1-}$ complexes are isolable as molecular species, they are reactive and must be synthesized, handled, and stored at low temperatures.^{2,4,5,7,36} This thermal instability can complicate reactivity studies as well as physical measurements. In this Chapter, the synthesis of new examples of tris(mono-silylcyclopentadienyl) rare-earth metal and uranium complexes is explored with the $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)^{1-}$ ligand for comparison with the $(\text{C}_5\text{H}_4\text{SiMe}_3)^{1-}$ ligand to examine the role steric and electronic effects play in the isolation and thermal stability of tris(mono-silylcyclopentadienyl) M(II) complexes.

RESULTS

Syntheses and Structure of $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{M}^{\text{III}}$ Precursors. The synthesis of $\text{Cp}^{\text{TIPS}}_3\text{La}$ ($\text{Cp}^{\text{TIPS}} = \text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), **6.1-La**, was first pursued via the salt metathesis reaction between LaCl_3 and 3 equiv of KCp^{TIPS} using a procedure analogous to the one previously reported for the synthesis of $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{Nd}$ from NdCl_3 and $\text{NaC}_5\text{H}_3(\text{SiMe}_3)_2$.³⁷ **6.1-La** was isolated as an oily pale-yellow residue upon workup and was characterized by NMR and infrared spectroscopies. The ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ spectra of **6.1-La** in C_6D_6 show signals in the diamagnetic region and display resonances for only one type of cyclopentadienyl ligand suggesting that all the cyclopentadienyl ligands are equivalent in solution. Crystals of **6.1-La** suitable for X-ray diffraction studies were grown from saturated pentane solutions of **6.1-La** stored at $-35\text{ }^\circ\text{C}$ and the connectivity of $\text{Cp}^{\text{TIPS}}_3\text{La}$ was confirmed crystallographically, Figure 6.1.

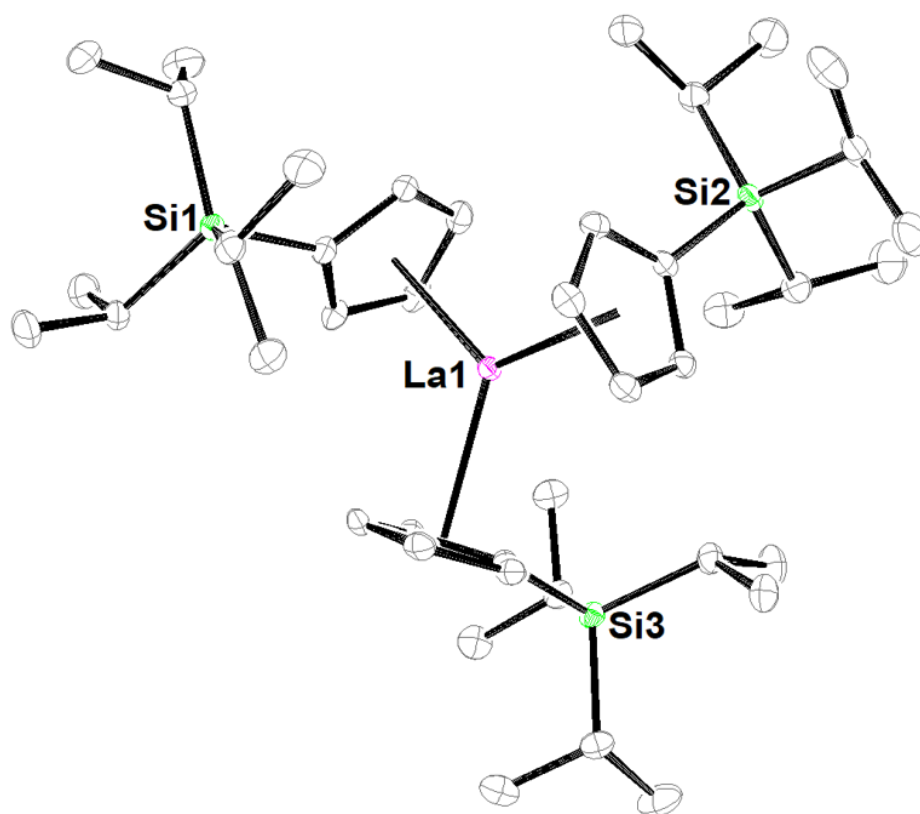
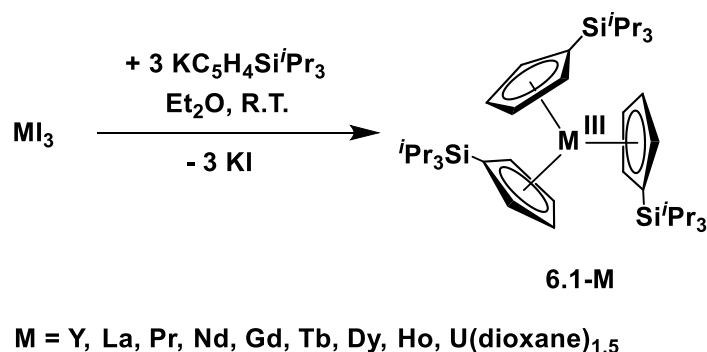


Figure 6.1. Molecular structure of $\text{Cp}^{\text{TIPS}}_3\text{La}$, **6.1-La**, with selective atom labelling. Ellipsoids are drawn at the 50% probability level and hydrogens are not shown for clarity.

The yttrium analog, $\text{Cp}^{\text{TIPS}}_3\text{Y}$, **6.1-Y**, can be synthesized by treating YCl_3 and 3 equiv of KCp^{TIPS} using the same procedure as described for **6.1-La** above and was identified via NMR and infrared spectroscopies also. The structure of **6.1-Y** was confirmed by X-ray crystallography by growing X-ray quality crystals from saturated hexane solutions stored at $-35\text{ }^\circ\text{C}$.

Efforts to synthesize $\text{Cp}^{\text{TIPS}}_3\text{Pr}$, **6.1-Pr**, and $\text{Cp}^{\text{TIPS}}_3\text{Nd}$, **6.1-Nd**, from PrCl_3 and NdCl_3 , respectively, using the same procedures as those employed for **6.1-La** and **6.1-Y** were unsuccessful in yielding any isolable tris(cyclopentadienyl) Pr or Nd complexes. Instead, salt metathesis reactions using MI_3 salts instead of MCl_3 were pursued since it was previously shown that the tris(cyclopentadienyl) U(III) complex $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{U}$ of the chemically similar 1,3-

bis(trimethylsilyl)cyclopentadienyl ligand, $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]^{1-}$, can be synthesized from UI_3 and 3 equiv of $\text{KC}_5\text{H}_3(\text{SiMe}_3)_2$ in Et_2O in high yields.³⁸ Following the same methodology, treatment of MI_3 ($\text{M} = \text{La, Pr, Nd, Gd, Tb, Dy, Ho, Y}$) with 3 equiv of KCp^{TIPS} in Et_2O overnight yielded the respective $\text{M(III) Cp}^{\text{TIPS}}_3\text{M}$ complexes in 69-85% crude yield as powders, Scheme 6.2. This procedure is superior to the reactions described above starting with LaCl_3 or YCl_3 since the iodide precursors allow the isolation of **6.1-La** and **6.1-Y** as powders in good yields rather than the oily residues. Additional purification steps including trituration with SiMe_4 and precipitation from cold SiMe_4 solutions were required to yield **6.1-U** as powders from syntheses using $\text{UI}_3(\text{dioxane})_{1.5}$ as a starting material.



Scheme 6.2. Synthesis of $\text{Cp}^{\text{TIPS}}_3\text{M}^{\text{III}}$ complexes from MI_3 salts described in this Chapter.

Informative and tractable ^1H NMR spectra can be collected for **6.1-Pr**, **6.1-Nd**, and **6.1-U** at room temperature in C_6D_6 and each of the spectra show paramagnetically shifted and broadened signals corresponding to only one type of cyclopentadienyl ligand environment.

Like **6.1-La** and **6.1-Y** described earlier, X-ray quality crystals of **6.1-Pr**, **6.1-Nd**, **6.1-Gd**, **6.1-Tb**, **6.1-Dy**, and **6.1-Ho** can be grown from saturated pentane or hexane solutions stored at $-35\text{ }^\circ\text{C}$ overnight. For **6.1-U**, X-ray quality crystals were grown from saturated SiMe_4 solutions stored at $-35\text{ }^\circ\text{C}$. All of the $\text{Cp}^{\text{TIPS}}_3\text{M}$, **6.1-M**, complexes crystallize in the $P\bar{1}$ space group and are isomorphous with each other as well as the previously characterized $\text{Cp}^{\text{TIPS}}_3\text{Th}$, **6.1-Th**.²⁷

Structurally, all **6.1-M** complexes are monometallic tris(cyclopentadienyl) complexes with the coordination geometry around each metal center being trigonal planar with respect to the (η^5 -cyclopentadienyl ligands, i.e. the sum of the three Cnt–M–Cnt (Cnt = cyclopentadienyl ring centroid) angles of each complex fall in the narrow range of 359.6° to 359.8°. Table 6.1 below lists the average M–Cnt distance for each **6.1-M** complex in order of decreasing M–Cnt of the trivalent **6.1-M** complexes. The decrease in the average M–Cnt distance for each metal is consistent with the differences in the ionic radii of the M(III) ions.³⁹

Table 6.1. Comparison of average M–Cnt distances for **6.1-M** and **6.2-M** ordered in decreasing M–Cnt distance for **6.1-M** complexes.

Metal (M)	M–Cnt (Å) 6.1-M	M–Cnt (Å) 6.2-M	Δ M–Cnt (Å) (6.2-M – 6.1-M)
La	2.566	2.600	+0.034
Th	2.520	2.521, ^a 2.516 ^b	+0.001, –0.004
Pr	2.520	2.548	+0.028
U	2.508	2.532	+0.024
Nd	2.503	2.533	+0.030
Gd	2.456	2.488	+0.032
Tb	2.437	2.470	+0.033
Dy	2.429	not isolated	not isolated
Y	2.421	unstable	unstable
Ho	2.413	unstable	unstable

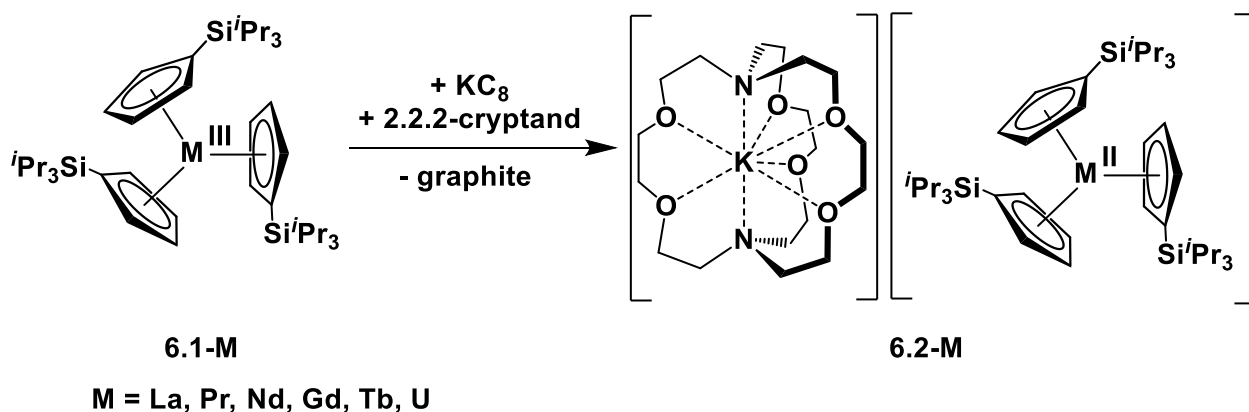
^aCrystallized in the $P2_1/c$ space group.

^bCrystallized in the $P2_1/n$ space group.

Synthesis and Structure of $[\text{K}(\text{2.2.2-cryptand})][(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{M}^{\text{II}}]$ Complexes.

Initially, reduction studies of the $\text{M}(\text{III}) \text{Cp}^{\text{TIPS}}_3\text{M}$, **6.1-M**, complexes involved the potassium graphite (KC_8) reduction of the tacky yellow residues of **6.1-La** synthesized from the route utilizing LaCl_3 described above. Addition of a THF solution of **6.1-La** and crypt (crypt = 2.2.2-cryptand) to a vial containing KC_8 at room temperature immediately generated an inky dark purple mixture consistent with the presence of a $\text{La}(\text{II})$ ion.³ Upon workup, a dark purple residue can be obtained. Despite several attempts, no X-ray quality crystals of the reduced product of **6.1-La** could be obtained and changing the potassium chelator to 18-crown-6 also did not yield crystals of suitable quality for X-ray diffraction studies either.

However, when the KC_8 reductions were attempted using the powders of **6.1-La** synthesized from the route utilizing LaI_3 instead, large, dark purple blocks of $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{La}]$, **6.2-La**, suitable for X-ray diffraction studies could be grown from saturated Et_2O solutions stored at $-35\text{ }^\circ\text{C}$ overnight, Figure 6.2, Scheme 6.3.



Scheme 6.3. Synthesis of crystallographically characterized $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{M}^{\text{II}}]$ complexes described in this Chapter.

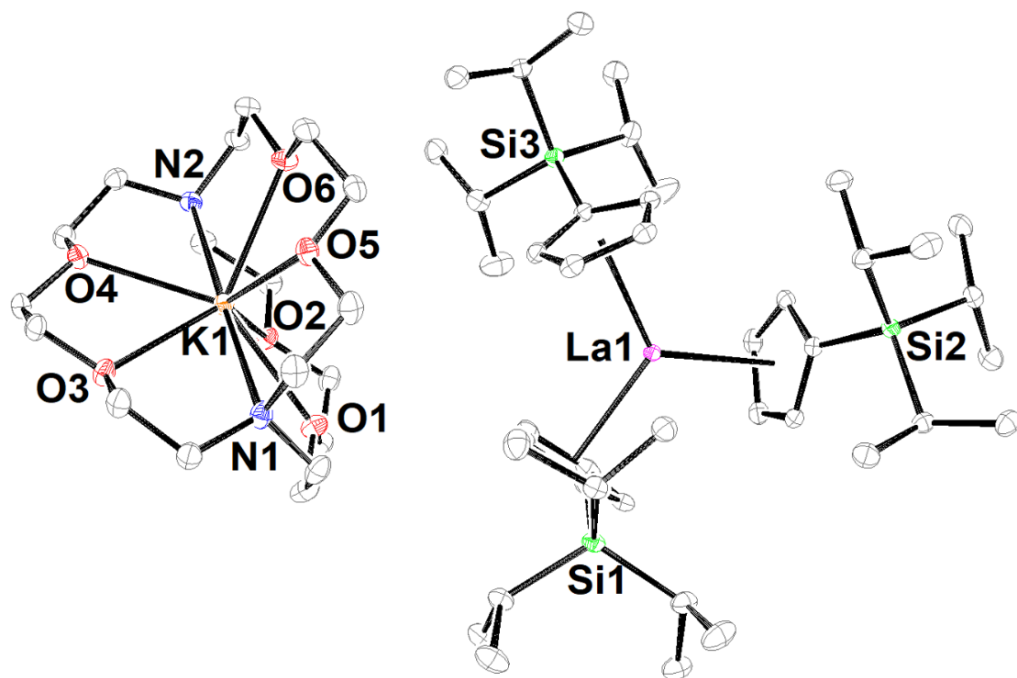


Figure 6.2. Molecular structure of $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{La}]$, **6.2-La**, with selective atom labelling. Ellipsoids are drawn at the 50% probability level and hydrogens are not shown for clarity.

Furthermore, **6.2-Pr**, **6.2-Nd**, **6.2-Gd**, **6.2-Tb**, and **6.2-U** can be synthesized and identified crystallographically using the same procedure as described for **6.2-La** above. Despite several attempts, no X-ray quality crystals from the reduction of **6.1-Dy** in the presence of crypt could be grown although the dark maroon color of the reduction product characteristic of a Dy(II) ion persisted for several weeks at $-35\text{ }^{\circ}\text{C}$.²⁹

Complexes **6.2-La**, **6.2-Pr**, **6.2-Nd**, **6.2-Gd**, **6.2-Tb**, **6.2-U**, and the reduction product of **6.1-Dy** can all be synthesized and handled at room temperature for at least ca. 2 hours without a significant amount of noticeable decomposition. Furthermore, crystalline material and THF solutions can be stored at $-35\text{ }^{\circ}\text{C}$ for several months. These compounds are more thermally stable than the previously isolated $[(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{M}]^{1-}$ complexes which were reported to require synthesizing and handling at colder temperatures.^{2,4,5,7,36}

In contrast, reduction of **6.1-Y** yielded a dark maroon solution that quickly transitioned to pale yellow solutions within ca. 1-2 minutes at room temperature, suggestive of decomposition to Y(III) products. Attempts to generate “**6.2-Y**” at $-35\text{ }^{\circ}\text{C}$ formed a longer-lived species but attempts to isolate X-ray quality crystals have been unsuccessful so far. The reduction product of **6.1-Y** is more thermally unstable than $[\text{K}(\text{crypt})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Y}]$, which has a $t_{1/2}$ of 71 ± 7 min at room temperature.³⁶ Attempts to isolate “**6.2-Ho**” were similarly unsuccessful. Interestingly, although more thermally stable **6.2-M** complexes can be isolated with the bulkier Cp^{TIPS} ligand for $\text{M} = \text{La}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy},$ and U compared to the $(\text{C}_5\text{H}_4\text{SiMe}_3)^{1-}$ analogs, the use of the bulkier Cp^{TIPS} ligand has generated less thermally stable M(II) complexes for Y and Ho such that crystallographic characterization has remained elusive.

All **6.2-M** ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}, \text{U}$) complexes crystallize in the $P2_1/n$ space group and are isomorphous to each other and the previously characterized Th(II) analog, $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{Th}]$, **6.2-Th**.²⁷ In all of the **6.2-M** structures, the cation and anion are well separated from each other. The anionic moiety, $(\text{Cp}^{\text{TIPS}}_3\text{M})^{1-}$, consists of three cyclopentadienyl rings oriented in a trigonal planar arrangement with the sum of the three Cnt–M–Cnt angles adding up to 359.9° for each Ln, indicating that no significant change to the coordination geometry about the metal center occurs upon reduction from M(III) to M(II). However, the average Cnt–M distances of **6.2-La** (2.600 Å), **6.2-Pr** (2.548 Å), **6.2-U** (2.532 Å), **6.2-Nd** (2.533 Å), **6.2-Gd** (2.488 Å), and **6.2-Tb** (2.470 Å) show a slight bond elongation between 0.02-0.03 Å when compared to their M(III) precursors, respectively. This is consistent with these complexes converting from $4f^n$ to $4f^{n+1}5d^1$ electron configurations upon reduction which generally show bond elongations between 0.02 to 0.05 Å as opposed to $4f^{n+1}$ electron configurations which typically show bond elongations on the order of 0.1 to 0.2 Å.^{10,21} In the case of **6.2-Nd** where the Nd(II) ion is a configurational

crossover ion, the crystallographic data suggest that in the tris(Cp^{TIPS}) ligand environment, the Nd(II) ion adopts a 4f³5d¹ electron configuration rather than a 4f⁴ configuration, similar to other Nd(II) complexes in tris(cyclopentadienyl) environments.¹⁰ The smaller bond elongation in the reduction of **6.1-Th** to **6.2-Th** ($\Delta M-Cnt = +0.001, -0.004$) is an interesting outlier in Table 6.1 above.²⁷ However, the only difference electronically is that the thorium atom transitions from a 6d¹ electron configuration to a 6d² electron configuration upon reduction rather than a 5f³6d⁰ to 5f³6d¹ electron configuration for the analogous uranium complexes.²⁷

EPR spectroscopy. Room temperature and 77 K EPR spectra were collected for **6.2-La**, **6.2-Gd**, and **6.2-Y** to further characterize the M(II) complexes. For the dark purple complex **6.2-La**, the room temperature EPR spectrum revealed an eight-lined pattern with isotropic signals centered around $g_{iso} = 1.97$ with an average hyperfine coupling constant of $A = 420$ MHz (152 G), Figure 6.3 (left), (¹³⁹La, $I = 7/2$, 99.9% abundance). For comparison, the hyperfine coupling constant of **6.2-La** is less than that of the previously characterized [(C₅Me₄H)₃La]¹⁻ ($A = 816$ MHz, 291 G)²⁹ and [(C₅H₄Me)₃La]¹⁻ ($A = 546$ MHz, 195 G),⁴⁰ but similar to that of [(C₅H₄SiMe₃)₃La]¹⁻ ($A = 432$ MHz, 154 G)⁴¹ and {[(C₅H₃(SiMe₃)₂)₃La]}¹⁻ ($A = 376$ MHz, 134 G).³ The trend in average hyperfine coupling constants is consistent with the difference in electron-donating ability between polyalkylated versus silyl-substituted cyclopentadienyl ligands.^{34,35}

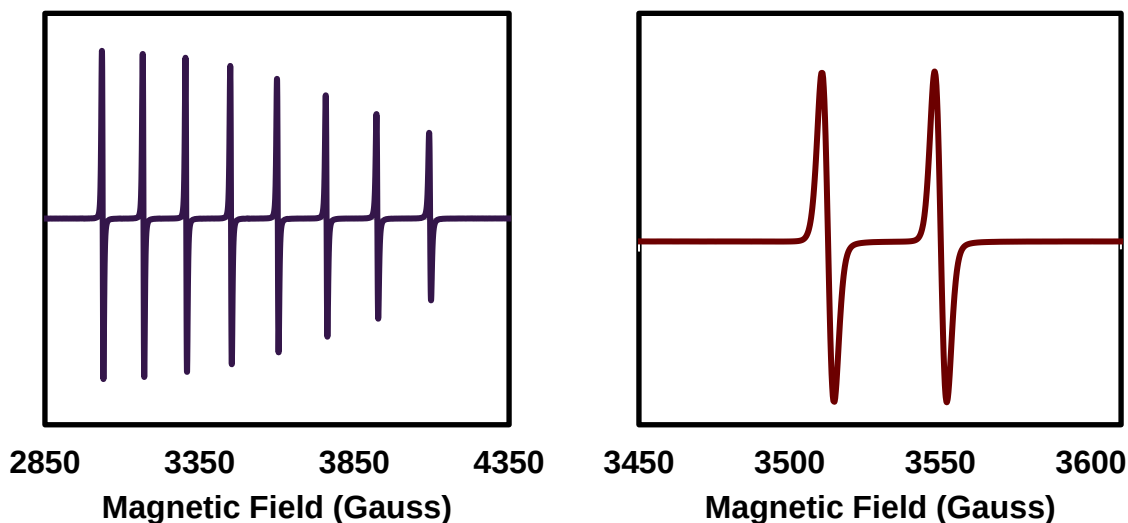


Figure 6.3. Room temperature EPR spectra of $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{La}]$, **6.2-La** (left), and the reduction product of $\text{Cp}^{\text{TIPS}}_3\text{Y}$, **6.1-Y** (right).

For the dark maroon **6.2-Gd**, both the 77 K and room temperature EPR show isotropic signals centered around $g = 1.98$ and 1.99 , respectively. For comparison, the EPR spectra of the reduction products of $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{Gd}$,⁴² $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Gd}(\text{C}_5\text{H}_5)$,⁴² and $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Gd}(\text{C}_5\text{H}_4\text{Me})$ ⁴² as well as the structurally characterized $[\text{K}(\text{crypt})][(\text{C}_5\text{Me}_4\text{H})_3\text{Gd}]$ ²⁹ and $[\text{K}(\text{crypt})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Gd}]$ ⁴ show similar isotropic signals centered around similar g values.

The dark maroon product obtained from reducing **6.1-Y** has a room temperature EPR spectrum that displays a two-lined isotropic signal centered at $g = 1.99$ with a hyperfine coupling constant of $A = 105$ MHz (37.5 G), Figure 6.3 (right), (^{89}Y , $I = 1/2$, 100% abundance). The crystallographically characterized $[(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Y}]^{1-}$ ($A = 103$ MHz, 36.6 G),² $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2(\text{C}_5\text{H}_5)\text{Y}\}^{1-}$ ($A = 97.0$ MHz, 34.6 G),⁴² and $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2(\text{C}_5\text{H}_4\text{Me})\text{Y}\}^{1-}$ ($A = 102$ MHz, 36.4 G)⁴² have similar EPR spectroscopic parameters. Although no X-ray quality

crystals were isolated to structurally authenticate “**6.2-Y**”, the data suggest that a Y(II) product was indeed formed.

UV-visible Spectroscopy. The UV-visible spectra of solutions of the darkly colored **6.2-M** (Ln = La, Pr, Nd, Gd, Dy, U) complexes were collected in THF at room temperature and a graph of the superimposed spectra is shown in Figure 6.4 below. The individual spectra of each **6.2-M** are displayed below the Experimental Section, Figures 6.6 to 6.13.

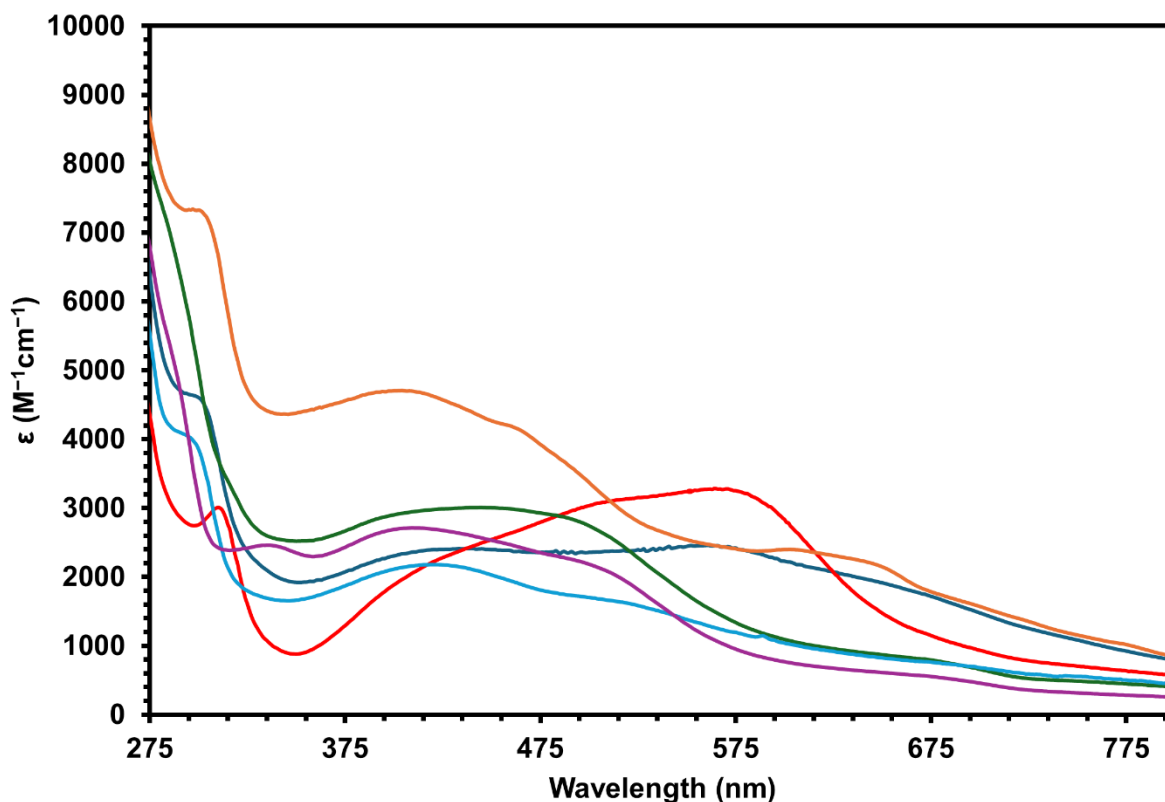


Figure 6.4. Room temperature UV-visible spectra of isolated $[K(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{M}]$, **6.2-M**, complexes described in this Chapter in THF. Red: **6.2-La**; Blue: **6.2-Pr**; Cyan: **6.2-Nd**; Orange: **6.2-U**; Purple: **6.2-Gd**; Green: **6.2-Dy**.

All M(II) complexes exhibit broad absorbances in the visible region typically between the range of 300 to 700 nm with extinction coefficients greater than $1500 \text{ M}^{-1}\text{cm}^{-1}$. Based on previous studies with chemically similar tris(cyclopentadienyl) M(II) complexes, these absorbances are

typical of M(II) ions that adopt $4d^1$ electron configurations for “**6.2-Y**,” $4f^m5d^1$ electron configurations for the lanthanide ions, and the $5f^36d^1$ electron configuration for **6.2-U**.¹⁰ For **6.2-Nd** and **6.2-Dy** which are known to be configurational crossover ions, the electronic spectra suggest that these ions adopt $4f^35d^1$ and $4f^95d^1$ electron configurations, respectively, corroborating the assignment from the crystallographic data.^{10,41}

Guzei *G*-Value Analysis. The importance of steric saturation around the metal center in stabilizing M(III) and M(II) complexes was investigated by calculating Guzei *G* values which provide an estimation of the percentage of the coordination sphere of the metal that is protected by the ligands.⁴³ Table 6.2 below summarizes the calculated *G* values for selected crystallographically characterized **6.1-M**, **6.2-M**, $(C_5H_4SiMe_3)_3M^{III}$, $[(C_5H_4SiMe_3)_3M^{II}]^{1-}$, $(C_5Me_4H)_3M^{III}$, and $[(C_5Me_4H)_3M^{III}]^{1-}$ complexes in order of increasing *G*-value of the M(III) precursor Cp^{TIPS}_3M , **6.1-M**. *G* values could not be determined for complexes that have not been isolated and crystallographically characterized.

Table 6.2. *G* values (%) of tris(cyclopentadienyl) M(II) and M(III) complexes of the $(Cp^{TIPS})^{1-}$, $(C_5H_4SiMe_3)^{1-}$, and $(C_5Me_4H)^{1-}$ ligands ordered in increasing *G* value (%) of **6.1-M**.

Metal (M)	<i>G</i> -value of 6.1-M	<i>G</i> -value of 6.2-M	<i>G</i> -value of $(C_5H_4SiMe_3)_3M$	<i>G</i> -value of $[(C_5H_4SiMe_3)_3M]^{1-}$	<i>G</i> -value of $(C_5Me_4H)_3M$	<i>G</i> -value of $[(C_5Me_4H)_3M]^{1-}$
La	88	84	81	81	-	79
Th	89	87, ^b 88 ^a	unstable	Not observed	82	Not observed
Pr	89	85	85	83	81	82
U	89	86	83	83	83	82
Nd	89	86	84	83	84	82
Gd	91	87	85	85	84	83

Tb	91	88	86	86	85	84
Dy	92	Not isolated	86	86	84	84
Y	92	unstable	86	86	85	unstable
Ho	92	unstable	87	87	85	unstable

Generally, the G values for stable M(III) complexes of the Cp^{TIPS} ligand range from $G = 88$ to 92 for $M = \text{Y, La to Ho}$. For the M(II) complexes, the range is lower and is between 84 - 88% . Upon reduction, the G value decreases around 3 - 4% which is consistent with the M–Cnt bond elongation placing the ligands further away from the metal center. As discussed in the structural description above, the average M–Cnt distance for $\text{Cp}^{\text{TIPS}}_3\text{Th}$, **6.1-Th**, does not change on the same order of magnitude as the other metals. This is supported by the fact that the G value of **6.2-Th** is only 1 - 2% lower than the G value of its Th(III) precursor, **6.1-Th**. It is interesting to note that for the M(III) complexes of the $\text{tris}(\text{Cp}^{\text{TIPS}})$ ligand system that achieve a G value greater than 91% , reduction does not seem to generate M(II) complexes stable enough to be crystallographically characterized.

Electrochemistry of $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{M}^{\text{III}}$ Complexes. To probe whether the identity of the cyclopentadienyl ligand influences the reduction potentials of the resulting M(II) species, the electrochemical behavior of **6.1-M** was investigated using cyclic voltammetry. Previously, it was shown that $[\text{nBu}_4\text{N}][\text{BPh}_4]$ is a suitable supporting electrolyte for measuring the M(III)/M(II) redox couple for a series of $\text{tris}(\text{cyclopentadienyl})$ rare-earth metal and actinide complexes in THF solutions.^{34,35} Thus, it was possible to collect electrochemical data for most of the **6.1-M** complexes described in this Chapter. The cyclic voltammograms for all measured **6.1-M**

complexes show redox events within the THF solvent window which were assigned to be the M(III)/M(II) redox couple. A representative example of **6.1-Pr** is shown in Figure 6.5 below. The rest of the individually collected voltammograms for **6.1-M** are displayed below the Experimental Section, Figures 6.14 to 6.20. The reduction potentials measured for most of the $\text{Cp}^{\text{TIPS}}_3\text{M}$, **6.1-M**, complexes described in this Chapter are summarized in Table 6.2 below and compared with previously reported electrochemical data on other chemically similar tris(cyclopentadienyl) rare-earth metal and actinide complexes.

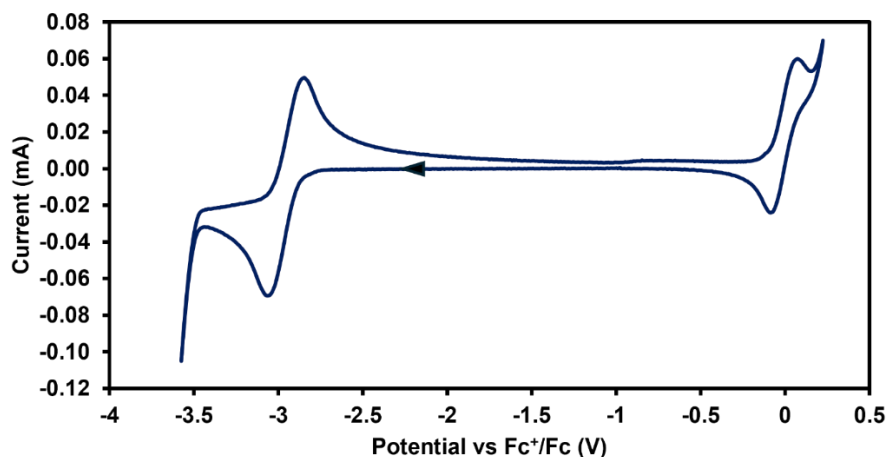


Figure 6.5. Cyclic voltammogram of $\text{Cp}^{\text{TIPS}}_3\text{Pr}$, **6.1-Pr**, in a 100 mM $[\text{nBu}_4\text{N}][\text{BPh}_4]$ solution of THF at room temperature with a scan rate of 100 mV/s. The event centered at 0 V is due to the internal standard $(\text{C}_5\text{H}_5)_2\text{Fe}$.

Table 6.3. M(III)/M(II) reduction potentials of various tris(cyclopentadienyl) rare-earth metal and actinide complexes measured in 100 mM $[\text{nBu}_4\text{N}][\text{BPh}_4]$ electrolyte concentrations in THF at room temperature referenced to the Fc^+/Fc redox couple.

M	$\text{Cp}^{\text{TIPS}}_3\text{M}^{\text{a}}$	$(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{M}^{34}$	$(\text{C}_5\text{Me}_4\text{H})_3\text{M}^{34}$
La	-3.03	-	-3.35

Pr	-2.94	-3.14	-3.27
U	-2.90	-2.26	-3.11
Nd	-2.92	-3.14	-3.19
Gd	-2.80	-2.98	-3.04
Tb	-	-2.95	-3.12
Dy	-2.92	-2.96	-3.20
Y	-3.04	-3.06	-
Ho	-	-3.02	-3.18

^a This work.

The M(III)/M(II) redox couples for each $\text{Cp}^{\text{TIPS}}_3\text{M}$, **6.1-M**, complex typically fall within the range of -2.81 to -3.07 V vs the ferrocenium/ferrocene (Fc^+/Fc) redox couple. Generally, these values are less negative when compared with the values previously reported for the $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{M}$ complexes of each respective metal, suggesting that $\text{Cp}^{\text{TIPS}}_3\text{M}$ complexes of the rare-earth metals generate less reducing complexes upon reduction. These contrast with the electrochemical data comparing the reduction potentials between $\text{Cp}^{\text{TIPS}}_3\text{ThBr}$ and $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{ThBr}$ which show that the reduction potential is similar between the two different cyclopentadienyl ligands.²⁷ Moreover, the M(III)/M(II) redox potential measured for $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}$ is significantly less negative than the M(III)/M(II) redox potential of $\text{Cp}^{\text{TIPS}}_3\text{U}$ which is an outlier to all the electrochemical data for $\text{Cp}^{\text{TIPS}}_3\text{M}$ complexes presented in this Chapter.³⁵ However, it should be noted that in general, the M(II)/M(III) reduction potentials of all $\text{Cp}^{\text{TIPS}}_3\text{M}$ complexes are less negative than that of their respective $(\text{C}_5\text{Me}_4\text{H})_3\text{M}$ complexes, which all fall within the range of -3.04 to -3.35 V vs the Fc^+/Fc redox couple.

DISCUSSION

Tris(cyclopentadienyl) complexes of the $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)^{1-}$ ligand can be isolated for the rare-earth metals and uranium from the reaction between the potassium cyclopentadienide reagent and metal triiodide or trichloride salts. The use of the metal triiodide salt proved to be a better starting material for the synthesis of $\text{Cp}^{\text{TIPS}}_3\text{M}$ complexes as evidenced by the isolation of cleaner products that allowed for crystallization of the subsequent divalent species upon reduction with KC_8 . It is possible that use of the metal trichloride salts may yield metal complexes that incorporate extra equivalents of “KCl” to form “ate” salts which is commonly seen in salt metathesis reactions with alkali metal cyclopentadienide reagents. Presumably, this may complicate purification and subsequently hinder crystallization of the products of further reactions. Switching the halide to iodide may allow for precipitation of KI as a byproduct which may be less likely to form “ate” salts.

Reduction of the M(III) $\text{Cp}^{\text{TIPS}}_3\text{M}$, **6.1-M**, complexes yield room temperature stable $[\text{K}(\text{crypt})][(\text{Cp}^{\text{TIPS}}_3\text{M})]$, **6.2-M**, complexes for La-Dy whereas for Ho and Y, the reduced species are thermally unstable. Spectroscopy and crystallographic data are supportive of the M(II) assignments.¹⁰ The change in thermal stability between using the Cp^{TIPS} ligand versus the $(\text{C}_5\text{H}_4\text{SiMe}_3)^{1-}$ ligand is supportive of the hypothesis that increasing the steric bulk of a substituent can kinetically stabilize a M(II) ion, extending the observation from the previously studied tris(aryloxide) ligand system^{20,21} to the tris(cyclopentadienyl) ligand system. However, it seems that the similarly sized Y and Ho do not follow this trend.

Structural analyses on the extent of steric saturation around the metal center using the Guzei Solid *G* method⁴³ suggest that based on this set of data, relatively stable $\text{Cp}^{\text{TIPS}}_3\text{M}^{\text{III}}$ complexes that have ionic radii that are within the range of La to Ho can fall in the range of 88-92%. Upon reduction, this range is lower by 3-4% and is in between 84-88% for La-Tb since no

X-ray crystallographic data were collected for the $(\text{Cp}^{\text{TIPS}}_3\text{M})^{1-}$ complexes of Dy, Ho, and Y. The isolable and crystallographically characterized $[\text{K}(\text{crypt})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Y}]^2$ and $[\text{K}(\text{crypt})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Ho}]$,⁵ have *G* values of 86% and 87%, respectively, both of which fall within this *G* value range of isolable M(II) complexes.

It should be noted that the *G* value ranges for isolable complexes of the Cp^{TIPS} ligand may not necessarily be generalizable to other ligand systems. For example, the related $(\text{C}_5\text{Me}_4\text{H})_3\text{Y}$ and $(\text{C}_5\text{Me}_4\text{H})_3\text{Ho}$, have calculated *G* values of 85% and 85%, respectively. However, they were previously reported to not yield thermally unstable Y(II) and Ho(II) species upon reduction and this precluded crystallographic characterization.²⁹ Contrastingly, $(\text{C}_5\text{Me}_4\text{H})_3\text{Gd}$ has a *G* value of 84% which is lower than the analogous Y(III) and Ho(III) complexes, but its reduced form, $[\text{K}(\text{crypt})][(\text{C}_5\text{Me}_4\text{H})_3\text{Gd}]$, is an isolable species.²⁹ Therefore, *G* values should not necessarily be used as a measure of the thermal stability, isolability, and reactivity of a M(II) complex and may be best used to compare a series of structurally related complexes. As another example, $(\text{C}_5\text{Me}_5)_3\text{La}$,⁴⁴ which readily undergoes sterically induced reduction chemistry, has a *G* value of 79.7% and this value is much lower than the range of stable isolable M(III) complexes of the Cp^{TIPS} ligand. It is evident that the extent of steric saturation around a metal center does not appear to be the sole explanation for what determines an isolable tris(cyclopentadienyl) M(II) complex and its thermal stability.

The electrochemical data suggests that tris(cyclopentadienyl) M(III) complexes of the silyl-substituted cyclopentadienyl ligands tend to have less negative reduction potentials compared to those of the polyalkylated cyclopentadienyl ligands, consistent with the more electron-donating nature of the polyalkylated cyclopentadienyl ligands.⁴⁵ Several complexes of the $(\text{Cp}^{\text{TIPS}})^{1-}$ ligand also appear to have less negative reduction potentials than those of the $(\text{C}_5\text{H}_4\text{SiMe}_3)^{1-}$ ligand,

which could correlate with more stable M(II) complexes. However, this observation is not supported by the fact that the Y(II)/Y(III) reduction potentials between $\text{Cp}^{\text{TIPS}}_3\text{Y}$, **6.1-Y**, and $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Y}^{34}$ are similar despite their corresponding reduced species having significantly different thermal stabilities with the $[(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Y}]^{1-}$ anion being more thermally stable. Furthermore, the Dy(II)/Dy(III) reduction potentials between $\text{Cp}^{\text{TIPS}}_3\text{Dy}$, **6.1-Dy**, and $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Dy}^{34}$ are also similar, but their corresponding reduced species follow a different trend in thermal stabilities from the analogous yttrium complexes described above. Therefore, the isolability and thermal stabilities of reduced tris(cyclopentadienyl) M(II) complexes cannot be solely explained by electronic factors as probed by electrochemistry.

Taken altogether, it appears that the thermal stability and isolability of reduced M(II) ions in the tris(cyclopentadienyl) ligand environment does however depend on a complicated interplay of steric and electronic effects and that they may need to be considered in tandem. The exact roles that they play in low-valent rare-earth metal chemistry has yet to be determined.

CONCLUSION

In summary, tris(cyclopentadienyl) rare-earth metal and uranium complexes of the $(\text{Cp}^{\text{TIPS}})^{1-}$ ligand can be readily synthesized from the potassium cyclopentadienide and metal triiodide salts. The use of the metal triiodides is advantageous over the metal trichlorides in yielding sufficiently pure products for use in further reactions. Reduction in the presence of crypt generates M(II) complexes more thermally stable than those of the $(\text{C}_5\text{H}_4\text{SiMe}_3)^{1-}$ ligand for $\text{M} = \text{La-Dy}$. However, for $\text{M} = \text{Y, Ho}$, the reduced complexes are less thermally stable than those of the $(\text{C}_5\text{H}_4\text{SiMe}_3)^{1-}$ ligand. Steric and electrochemical analyses suggest that the isolation of reduced M(II) ions in tris(cyclopentadienyl) environments is influenced by a complex combination of both steric and electronic effects.

EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP (99.999%) argon and dried by passage through columns containing Q-5 and molecular sieves prior to use and stored over activated molecular sieves prior to use. Deuterated NMR solvents were degassed and dried over molecular sieves overnight before use. ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, and $^{29}\text{Si}\{^1\text{H}\}$ spectra were recorded on a Bruker AVANCE600 spectrometer at 298 K unless otherwise stated. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR were referenced internally to residual protio-solvent resonances. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were referenced externally to SiMe_4 . Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR under an argon atmosphere. UV-visible spectra were collected under an inert atmosphere of argon in THF at 298 K using a Varian Cary 50 Scan UV-visible spectrometer in a 1 mm Schlenk cuvette fitted with a Teflon stopper unless otherwise stated. EPR spectra were recorded on a Bruker EMX spectrometer equipped with an ER041Xg microwave bridge and calibrated with DPPH ($g = 2.0036$). Elemental analyses were conducted on a Thermo Scientific FlashSmart CHNS/O elemental analyzer at UC Irvine Materials Research Institute's TEMPR facility in Irvine, California. Tetramethylsilane (SiMe_4) was degassed and dried over molecular sieves overnight prior to use. 2.2.2-cryptand (crypt) was purchased from Sigma-Aldrich and recrystallized in Et_2O prior to use. $\text{UI}_3(\text{dioxane})_{1.5}$,⁴⁶ $\text{KC}_5\text{H}_4\text{Si}^i\text{Pr}_3$,²⁷ and KC_8 ⁴⁷ were synthesized according to literature procedures. LaI_3 , YI_3 , PrI_3 , NdI_3 , GdI_3 , TbI_3 , DyI_3 , and HoI_3 were all synthesized using a modification of Meyer's procedure for the preparation of LnCl_3 .⁴⁸

General procedure for the synthesis of $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{M}$, 6.1-M. In a 20 mL scintillation vial, solid $\text{KC}_5\text{H}_4\text{Si}^i\text{Pr}_3$ (2.99 equiv) was added to a stirred suspension of MI_3 (1.00 equiv) in diethyl

ether (ca. 10 mL) at room temperature. The resulting mixture was allowed to stir at room temperature over 16 hours, at which point the reaction mixture became a suspension. Insoluble solids, presumably KI, were removed by centrifugation followed by filtration through a pipet packed with Kimwipe tissue. Volatiles were removed under reduced pressure to yield a residue which was then extracted into hexane (ca. 10 mL) and filtered to remove insoluble solids. Volatiles were removed under reduced pressure to yield a residue. Trituration with SiMe₄ followed by drying under reduced pressure yielded **6.1-M** as powdered solids. Crystals suitable for study by X-ray diffraction were grown from saturated pentane or hexane solutions of **6.1-M** stored at -35 °C overnight.

General procedure for the synthesis of [K(2.2.2-cryptand)][(C₅H₄SiⁱPr₃)₃M], **6.2-M.**

In a 20 mL scintillation vial, **6.1-M** (1.00 equiv) and crypt (1.00 equiv) were dissolved in THF (ca. 2 mL) to produce a clear solution. The solution was then quickly added to another vial containing KC₈ (1.20 equiv) at room temperature and an inky dark colored mixture was immediately generated. The mixture was swirled for about 2 minutes before it was filtered through a glass pipet packed with Kimwipe tissue to remove insoluble solids, presumably graphite. Volatiles were removed under reduced pressure from the filtrate to yield a dark colored residue. The residue was then washed with hexane (ca. 2 mL) and dried under reduced pressure to yield **6.2-M** as an oily dark colored residue. Dark colored X-ray crystals of **6.2-M** suitable for study by X-ray diffraction were grown from saturated Et₂O solutions of **6.2-M** stored at -35 °C overnight.

Synthesis of (C₅H₄SiⁱPr₃)₃La, **6.1-La.** KC₅H₄SiⁱPr₃ (301 mg, 1.15 mmol) was reacted with LaI₃ (200 mg, 0.385 mmol) according to the general procedure described for the synthesis of **6.1-M**. **6.1-La** was isolated as colorless solids (241 mg, 0.300 mmol, 78%). Crystals suitable for study by X-ray diffraction were grown from saturated pentane solutions of **6.1-La** stored at -35

°C overnight. ^1H NMR (C_6D_6 , 600 MHz): δ 6.61 (m, 6H, $\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 6.46 (m, 6H, $\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 1.30 (sept, $^3J_{\text{HH}} = 7.4$ Hz, 9H, CH of ^iPr), 1.14 (d, $^3J_{\text{HH}} = 7.4$ Hz, 54H, CH_3 of ^iPr) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz): δ 124.8 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 121.3 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 118.2 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 19.8 (CH_3 of ^iPr), 12.9 (CH of ^iPr) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, C_6D_6): δ 0.2 (SiMe_3). IR: 3077w, 2939m, 2891m, 2862s, 2110w, 2070w, 1461m, 1437w, 1380w, 1362m, 1306w, 1292w, 1292w, 1247w, 1192w, 1173m, 1159w, 1060w, 1040vs, 1009m, 992m, 918w, 881vs, 861m, 832m, 781s, 762vs, 669vs cm^{-1} .

Alternative Synthesis of $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{La}$, 6.1-La. This compound was synthesized via a procedure adapted from that of $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{Nd}$.³⁷ In a 100 mL Schlenk flask fitted with a Teflon stopper, THF (ca. 15 mL) was added to solid LaCl_3 (107 mg, 0.436 mmol) and $\text{KC}_5\text{H}_4\text{Si}^i\text{Pr}_3$ (341 mg, 1.31 mmol). The resulting mixture was allowed to stir at room temperature over 16 hours before volatiles were removed under reduced pressure to yield a colorless residue. Toluene (ca. 20 mL) was added and the resulting mixture was allowed to stir at ca. 110 °C for 48 h. Volatiles were removed under reduced pressure to yield a colorless residue which was then extracted into hexane (ca. 10 mL). Insoluble solids were removed via centrifugation followed by filtration through a pipet packed with Kimwipe tissue to yield a clear and pale-yellow solution. Volatiles were removed under reduced pressure to yield a yellow oily solid (205 mg, 59%). $\text{Cp}^{\text{TIPS}}_3\text{La}$, **6.1-La** was identified crystallographically and by ^1H NMR spectroscopy.

Synthesis of $[\text{K}(2.2.2\text{-cryptand})][(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{La}]$, 6.2-La. **6.1-La** (60 mg, 0.075 mmol) and crypt (28 mg, 0.075 mmol) were reacted with KC_8 (12 mg, 0.090 mmol) according to the general procedure described for the synthesis of **6.2-M**. **6.2-La** was isolated as an oily dark purple residue (90 mg). Dark purple-black X-ray crystals of **6.2-La** suitable for study by X-ray diffraction were grown from saturated Et_2O solutions of **6.2-La** stored at -35 °C overnight (61

mg, 67% crystalline yield). IR: 3070w, 2936w, 2914w, 2885m, 2856s, 2817w, 2101w, 1987w, 1460m, 1446w, 1431w, 1377w, 1355m, 1307w, 1295m, 1260w, 1238w, 1161m, 1135m, 1104vs, 1078s, 1038s, 1010m, 992m, 950s, 935m, 884s, 833w, 807m, 733s, 718m, 667s cm^{-1} . UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 312 (3000), 571 (3300, broad). Anal. Calcd. for $\text{C}_{60}\text{H}_{111}\text{N}_2\text{O}_6\text{Si}_3\text{KLa}$: C, 59.13; H, 9.18; N, 2.30. Found: C, 59.40; H, 9.44; N, 2.55.

Synthesis of $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{Pr}$, 6.1-Pr. $\text{KC}_5\text{H}_4\text{Si}^i\text{Pr}_3$ (300 mg, 1.15 mmol) was reacted with PrI_3 (200 mg, 0.383 mmol) according to the general procedure described for the synthesis of **6.1-M**. **6.1-Pr** was isolated as bright yellow solids (247 mg, 0.307 mmol, 80%). Yellow crystals of **1-Pr** suitable for study by X-ray diffraction were grown from saturated pentane solutions of **1-Pr** stored at -35°C overnight. ^1H NMR (C_6D_6 , 600 MHz): δ 51.10 (br s, 6H, $\Delta\nu_{1/2} = 125$ Hz, $\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 3.97 (s, 6H, $\Delta\nu_{1/2} = 66$ Hz, $\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), -10.01 (s, 9H, $\Delta\nu_{1/2} = 40$ Hz, CH of ^iPr), -12.40 (s, 54H, $\Delta\nu_{1/2} = 40$ Hz, CH_3 of ^iPr) ppm. IR: 3089w, 2940m, 2888m, 2862s, 2107w, 2061w, 1459m, 1440w, 1380w, 1362m, 1306w, 1297w, 1237w, 1189w, 1169m, 1065w, 1043s, 992m, 918w, 880vs, 850w, 832m, 781m, 762vs, 656vs cm^{-1} .

Synthesis of $[\text{K}(\text{2.2.2-cryptand})][(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{Pr}]$, 6.2-Pr. **6.1-Pr** (60 mg, 0.075 mmol) and crypt (28 mg, 0.075 mmol) were reacted with KC_8 (12 mg, 0.090 mmol) according to the general procedure described for the synthesis of **6.2-M**. **6.2-Pr** was isolated as an oily dark maroon residue (88 mg). Black X-ray crystals of **6.2-Pr** suitable for study by X-ray diffraction were grown from saturated Et_2O solutions of **6.2-Pr** spiked with a few drops of THF stored at -35°C overnight. IR: 3068w, 2911m, 2833s, 2853s, 2810m, 1457m, 1442m, 1429m, 1353s, 1293m, 1260w, 1236w, 1159s, 1131s, 1103vs, 1077vs, 1038vs, 1012m, 993m, 950vs, 932s, 882s, 807m, 734s, 714m cm^{-1} . UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 302 (4500, shoulder), 417 (2400, broad),

569 (2400). Anal. Calcd. for $C_{60}H_{111}N_2O_6Si_3KPr$: C, 59.03; H, 9.17; N, 2.29. Found: C, 59.20; H, 9.40; N, 2.54.

Synthesis of $(C_5H_4Si^iPr_3)_3Nd$, 6.1-Nd. $KC_5H_4Si^iPr_3$ (330 mg, 1.27 mmol) was reacted with NdI_3 (218 mg, 0.415 mmol) according to the general procedure described for the synthesis of **6.1-M**. **6.1-Nd** was isolated as pale-green solids (282 mg, 84%). Pale-green crystals of **6.1-Nd** suitable for study by X-ray diffraction were grown from saturated pentane solutions of **6.1-Nd** stored at $-35\text{ }^{\circ}C$ overnight. ^1H NMR (C_6D_6 , 600 MHz): δ 26.99 (br s, 6H, $\Delta\nu_{1/2} = 83\text{ Hz}$, $C_5H_4Si^iPr_3$), -2.24 (br s, 6H, $\Delta\nu_{1/2} = 66\text{ Hz}$, $C_5H_4Si^iPr_3$), -6.21 (br s, 9H, $\Delta\nu_{1/2} = 35\text{ Hz}$ CH of ^iPr), -7.42 (br s, 54H, $\Delta\nu_{1/2} = 35\text{ Hz}$, CH_3 of ^iPr) ppm. IR: 3071w, 2942m, 2888m, 2863s, 2106w, 2064w, 1461m, 1439w, 1380w, 1364m, 1308w, 1289w, 1243w, 1192w, 1172m, 1061w, 1043s, 1012m, 992m, 953w, 918w, 880vs, 853w, 839m, 790m, 762vs, 656vs cm^{-1} .

Synthesis of $[K(2.2.2\text{-cryptand})][(C_5H_4Si^iPr_3)_3Nd]$, 6.2-Nd. **6.1-Nd** (60 mg, 0.074 mmol) and crypt (28 mg, 0.074 mmol) were reacted with KC_8 (12 mg, 0.090 mmol) according to the general procedure described for **6.2-M**. **6.2-Nd** was isolated as an oily dark maroon residue (87 mg). Black X-ray crystals of **6.2-Nd** suitable for study by X-ray diffraction were grown from saturated Et_2O solutions of **6.2-Nd** stored at $-35\text{ }^{\circ}C$ overnight. IR: 3074w, 2936w, 2916w, 2885m, 2856s, 2811w, 2098w, 1988w, 1460m, 1443w, 1431w, 1377w, 1355m, 1295m, 1260w, 1238w, 1161m, 1134m, 1104vs, 1078s, 1040s, 1012m, 992m, 950s, 930m, 884s, 830w, 810m, 762w, 736s, 716m, 667s cm^{-1} . UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $M^{-1}\text{ cm}^{-1}$): 298 (4000, shoulder), 422 (2200), 529 (1600, shoulder). Anal. Calcd. for $C_{60}H_{111}N_2O_6Si_3KNd$: C, 58.87; H, 9.14; N, 2.29. Found: C, 58.88; H, 8.64; N, 2.82.

Synthesis of $(C_5H_4Si^iPr_3)_3Gd$, 6.1-Gd. $KC_5H_4Si^iPr_3$ (145 mg, 0.558 mmol) was reacted with GdI_3 (100 mg, 0.186 mmol) according to the general procedure described for **6.1-M**. **6.1-Gd**

was isolated as bright yellow solids (109 mg, 0.133 mmol, 71%). Yellow crystals of **6.1-Gd** suitable for study by X-ray diffraction were grown from saturated pentane solutions of **6.1-Gd** stored at $-35\text{ }^{\circ}\text{C}$ overnight. IR: 3074w, 2942m, 2891m, 2863s, 2115w, 2070w, 1462m, 1440w, 1380w, 1363m, 1305w, 1289w, 1243w, 1192w, 1172m, 1061w, 1041s, 1012m, 992m, 955w, 918w, 881vs, 861w, 844m, 793m, 762vs, 658vs cm^{-1} .

Synthesis of $[\text{K}(\text{2.2.2-cryptand})][(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{Gd}]$, **6.2-Gd.** **6.1-Gd** (60 mg, 0.074 mmol) and crypt (28 mg, 0.074 mmol) were reacted with KC_8 (12 mg, 0.090 mmol) according to the general procedure described for **6.2-M**. **6.2-Gd** was isolated as an oily dark maroon residue (78 mg). Black X-ray crystals of **6.2-Gd** suitable for study by X-ray diffraction were grown from saturated Et_2O solutions of **6.2-Gd** stored at $-35\text{ }^{\circ}\text{C}$ overnight (57 mg, xx% crystalline yield). IR: 3077w, 2936w, 2916w, 2885m, 2856s, 2813w, 2109w, 1460m, 1443w, 1431w, 1377w, 1355m, 1295m, 1260w, 1238w, 1163m, 1132m, 1101vs, 1078s, 1038s, 1010m, 992m, 950s, 930m, 884s, 824m, 810m, 767w, 742s, 719m, 668s cm^{-1} . UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 337 (2500), 412 (2700), 513 (2000, shoulder), 687 (500, shoulder). EPR: $g_{\text{iso}} = 1.99$ (100.9 mHz). Anal. Calcd. for $\text{C}_{60}\text{H}_{111}\text{N}_2\text{O}_6\text{Si}_3\text{KGd}$: C, 58.25; H, 9.04; N, 2.26. Found: C, 59.36; H, 9.09; N, 2.68.

Synthesis of $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{Dy}$, **6.1-Dy.** $\text{KC}_5\text{H}_4\text{Si}^i\text{Pr}_3$ (304 mg, 1.17 mmol) was reacted with DyI_3 (200 mg, 0.368 mmol) according to the general procedure described for **6.1-M**. **6.1-Dy** was isolated as yellow solids (210 mg, 0.254 mmol, 69%). Yellow crystals of **6.1-Dy** suitable for study by X-ray diffraction were grown from saturated pentane solutions of **6.1-Dy** stored at $-35\text{ }^{\circ}\text{C}$ overnight. IR: 3086w, 2942m, 2890m, 2864s, 2113w, 2067w, 1462m, 1440w, 1379w, 1364m, 1307w, 1292w, 1246w, 1192w, 1171m, 1061w, 1040s, 1012m, 995m, 954w, 920w, 880vs, 863w, 845m, 800m, 772vs, 658vs cm^{-1} .

Synthesis of [K(2.2.2-cryptand)][(C₅H₄Si^{*i*}Pr₃)₃Dy], 6.2-Dy. **6.1-Dy** (55 mg, 0.067 mmol) and crypt (25 mg, 0.067 mmol) were reacted with KC₈ (11 mg, 0.080 mmol) according to the general procedure described for the synthesis of **6.2-M**. **6.2-Dy** was isolated as an oily dark maroon residue (84 mg). Despite several attempts, no crystals of **6.2-Dy** suitable for study by X-ray diffraction could be grown. UV-vis (THF, room temperature) λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 450 (3000, broad), 680 (800, shoulder).

Synthesis of (C₅H₄Si^{*i*}Pr₃)₃Tb, 6.1-Tb. KC₅H₄Si^{*i*}Pr₃ (262 mg, 1.01 mmol) was reacted with TbI₃ (181 mg, 0.335 mmol) according to the general procedure as described for **6.1-M**. **6.1-Tb** was isolated as bright yellow solids (221 mg, 80%). Yellow crystals of **6.1-Tb** suitable for study by X-ray diffraction were grown from saturated pentane solutions of **6.1-Tb** stored at -35 °C overnight.

Synthesis of [K(2.2.2-cryptand)][(C₅H₄Si^{*i*}Pr₃)₃Tb], 6.2-Tb. **6.1-Tb** (50 mg, 0.061 mmol) and crypt (23 mg, 0.061 mmol) were reacted with KC₈ (10 mg, 0.073 mmol) according to the general procedure described for **6.2-M**. **6.2-Tb** was isolated as an oily dark maroon residue (74 mg, 98% crude yield). Black X-ray crystals of **6.2-Tb** suitable for study by X-ray diffraction were grown from saturated Et₂O solutions of **6.2-Tb** stored at -35 °C overnight.

Synthesis of (C₅H₄Si^{*i*}Pr₃)₃Y, 6.1-Y. KC₅H₄Si^{*i*}Pr₃ (330 mg, 1.27 mmol) was reacted with YI₃ (218 mg, 0.415 mmol) according to the general procedure described for the synthesis of **6.1-Y**. **6.1-Y** was isolated as colorless solids (282 mg, 84%). Crystals suitable for study by X-ray diffraction were grown from saturated hexane solutions of **6.1-Y** stored at -35 °C overnight. ¹H NMR (C₆D₆, 600 MHz): δ 6.68 (m, 6H, C₅H₄Si^{*i*}Pr₃), 6.46 (m, 6H, C₅H₄Si^{*i*}Pr₃), 1.30 (sept, ³*J*_{HH} = 7.3 Hz, 9H, CH of ^{*i*}Pr), 1.14 (d, ³*J*_{HH} = 7.4 Hz, 54H, CH₃ of ^{*i*}Pr) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 125.9 (C₅H₄Si^{*i*}Pr₃), 118.2 (C₅H₄Si^{*i*}Pr₃), 115.8 (C₅H₄Si^{*i*}Pr₃), 19.7 (CH₃ of ^{*i*}Pr), 12.9 (CH

of $i\text{Pr}$) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, C_6D_6): δ 0.5 (Si^iPr_3). IR: 3085w, 2942m, 2891m, 2865s, 2113w, 2058w, 1460m, 1440w, 1380w, 1366m, 1334w, 1306w, 1292w, 1215w, 1198w, 1172m, 1063w, 1041vs, 1012m, 998m, 955w, 920w, 881vs, 852w, 844w, 796s, 775vs, 656vs cm^{-1} .

Reduction of $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{Y}$, **6.1-Y.** In the cold well ($-78\text{ }^\circ\text{C}$: dry ice/isopropanol) of a glove box, a THF (ca. 4 mL) solution of **6.1-Y** (6.7 mg, 0.0089 mmol) and 2.2.2-cryptand (3.3 mg, 0.0088 mmol), two clean pipets, a pipet packed with Kimwipe tissue, and another vial containing KC_8 (2.0 mg, 0.015 mmol) were chilled to $-78\text{ }^\circ\text{C}$ over 30 minutes. The solution of **6.1-Y** and 2.2.2-cryptand were added to the vial and the solution immediately turned dark maroon. The mixture was filtered through a pipet packed with Kimwipe tissue to remove insoluble solids and yield a dark maroon solution. Spectroscopic data was collected on the *in situ* generated solution. UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$): 294 (7400, shoulder), 405 (6000, broad), 549 (6300, broad). The unusually high extinction coefficients could possibly be due to condensation forming on the cuvette during data collection which could lead to higher values.

Synthesis of $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{Ho}$, **6.1-Ho.** $\text{KC}_5\text{H}_4\text{Si}^i\text{Pr}_3$ (211 mg, 0.808 mmol) was reacted with HoI_3 (147 mg, 0.269 mmol) according to the general procedure for the synthesis of **6.1-M**. **6.1-Ho** was isolated as yellow-orange solids (190 mg, 85%). Yellow crystals suitable for study by X-ray diffraction were grown from saturated pentane solutions of **6.1-Ho** stored at $-35\text{ }^\circ\text{C}$ overnight.

Reduction of $(\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3)_3\text{Ho}$, **6.1-Ho.** **6.1-Ho** (50 mg, 0.061 mmol) and crypt (23 mg, 0.061 mmol) were reacted with KC_8 (10 mg, 0.073 mmol) according to the general procedure described for **6.2-M**. The generated dark maroon solution suggestive of the presence of Ho(II) decomposed to a yellow solution after ca. 1-2 min at room temperature, presumably to Ho(III) products.

Synthesis of $(C_5H_4Si^iPr_3)_3U$, **6.1-U.** $KC_5H_4Si^iPr_3$ (100 mg, 0.384 mmol) was reacted with $UI_3(dioxane)_{1.5}$ (96 mg, 0.13 mmol) according to the general procedure described for the synthesis of **6.1-M**. **6.1-U** was isolated as green-brown oily solids (96 mg, 83%). Green-brown crystals of **6.1-U** suitable for study by X-ray diffraction were grown from saturated $SiMe_4$ solutions of **6.1-U** stored at $-35\text{ }^\circ\text{C}$. ^1H NMR (C_6D_6 , 600 MHz): δ 11.02 (br s, 6H, $\Delta\nu_{1/2} = 29\text{ Hz}$, $C_5H_4Si^iPr_3$), -7.90 (br s, 9H, $\Delta\nu_{1/2} = 26\text{ Hz}$, CH of iPr), -8.78 (br s, 54H, $\Delta\nu_{1/2} = 16\text{ Hz}$, CH_3 of iPr), -23.05 (br s, 6H, $\Delta\nu_{1/2} = 51\text{ Hz}$, $C_5H_4Si^iPr_3$) ppm. $^{29}Si\{^1H\}$ NMR (119 MHz, C_6D_6): δ -107.6 (Si^iPr_3). UV-vis (hexane, room temperature) λ_{max} , nm (ϵ , $M^{-1}\text{ cm}^{-1}$): 441 (940, broad shoulder). Anal. Calcd. for $C_{42}H_{75}Si_3U$: C, 55.91; H, 8.38. Found: C, 54.62; H, 7.85. C, 54.32; H, 8.20. C, 54.54; H, 8.25.

Synthesis of $[K(2.2.2\text{-cryptand})][(C_5H_4Si^iPr_3)_3U]$, **6.2-U.** **6.1-U** (63 mg, 0.070 mmol) and crypt (26 mg, 0.070 mmol) were reacted with KC_8 (11 mg, 0.084 mmol) according to the general procedure described for the synthesis of **6.2-M**. **6.2-U** was isolated as an oily dark maroon residue (90 mg, 98%). Black crystals of **6.2-U** suitable for study by X-ray diffraction could be grown from saturated Et_2O solutions stored at $-35\text{ }^\circ\text{C}$. UV-vis (THF, room temperature) λ_{max} , nm (ϵ , $M^{-1}\text{ cm}^{-1}$): 304 (7200, shoulder), 407 (4700), 635 (2300). Anal. Calcd. for $C_{60}H_{111}N_2O_6Si_3KU$: C, 54.68; H, 8.49; N, 2.13. Found: C, 55.24; H, 8.45; N, 2.78. C, 55.49; H, 8.04; N, 2.87. C, 55.70; H, 7.92; N, 2.68.

General Electrochemistry Details. Electrochemical measurements were collected in an argon glovebox with freshly prepared 100 mM solutions of $[^nBu_4N][BPh_4]$ in THF at room temperature on a Princeton Applied Research PARSTAT 2273 Advanced Electrochemical System. A glassy carbon electrode, platinum wire counter electrode, and a silver wire pseudo-reference electrode were used for the electrochemical cell and all measurements were referenced against $(C_5H_5)_2Fe$ (Fc) as the internal standard. The internal resistance was measured for each solution

and the resistance was manually compensated by approximately 80-90% of the measured value prior to cyclic voltammetry experiments. All scans were conducted in the anodic direction.

General Electrochemistry Procedure. In an argon-containing glovebox, approximately 10-15 mg of **6.1-M** was dissolved in ca. 2 mL of the supporting electrolyte solution (100 mM [ⁿBu₄N][BPh₄] in THF) at room temperature in a 20 mL scintillation vial. The electrodes were placed into the vial and the vial was left open to the atmosphere during data collection. The internal resistance was measured, then cyclic voltammetry experiments were recorded. (C₅H₅)₂Fe (Fc) was added to the solution following all data collection. The internal resistance was measured again, and scans were collected to measure the internal standard redox event to reference the analyte redox event.

X-ray Data Collection, Structure Solution and Refinement for (C₅H₄SiⁱPr₃)₃La, **6.1-La.** A colorless crystal of approximate dimensions 0.264 x 0.281 x 0.326 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded wR₂ = 0.0744 and Goof = 1.055 for 433 variables refined against 12785 data (0.69 Å), R₁ = 0.0288 for those 11728 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for [K(2.2.2-cryptand)][(C₅H₄SiⁱPr₃)₃La], 6.2-La. A purple crystal of approximate dimensions 0.217 x 0.332 x 0.374 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0534$ and $Goof = 1.018$ for 676 variables refined against 18460 data (0.72 Å), $R1 = 0.0217$ for those 16297 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for (C₅H₄SiⁱPr₃)₃Pr, 6.1-Pr. A yellow crystal of approximate dimensions 0.178 x 0.193 x 0.326 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0458$ and $Goof = 1.042$ for 433 variables refined against 12932 data ($0.70 \text{ \AA}$), $R1 = 0.0190$ for those 12125 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for [K(2.2-cryptand)][(C₅H₄SiⁱPr₃)₃Pr], 6.2-Pr. A black crystal of approximate dimensions $0.166 \times 0.336 \times 0.378 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0617$ and $Goof = 1.022$ for 676 variables refined against 19066 data ($0.71 \text{ \AA}$), $R1 = 0.0249$ for those 15931 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for (C₅H₄SiⁱPr₃)₃Nd, 6.1-Nd. A blue crystal of approximate dimensions $0.249 \times 0.280 \times 0.381 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. There were no systematic absences nor any diffraction symmetry other than the Friedel

condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0406$ and $Goof = 1.066$ for 433 variables refined against 12947 data ($0.70 \text{ \AA}$), $R1 = 0.0158$ for those 12471 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for [K(2.2.2-cryptand)][(C₅H₄SiⁱPr₃)₃Nd], 6.2-Nd. A black crystal of approximate dimensions $0.217 \times 0.332 \times 0.374 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0661$ and $Goof = 1.020$ for 676 variables refined against 19686 data ($0.70 \text{ \AA}$), $R1 = 0.0264$ for those 16097 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for (C₅H₄SiⁱPr₃)₃Gd, 6.1-Gd. A yellow crystal of approximate dimensions $0.115 \times 0.133 \times 0.304 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (30

sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0598$ and $Goof = 1.036$ for 433 variables refined against 12519 data ($0.70 \text{ \AA}$), $R1 = 0.0272$ for those 11011 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for [K(2.2.2-cryptand)][(C₅H₄SiⁱPr₃)₃Gd], 6.2-Gd. A purple crystal of approximate dimensions $0.079 \times 0.137 \times 0.157 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0742$ and $Goof = 1.005$ for 676 variables refined against 19736 data ($0.70 \text{ \AA}$), $R1 = 0.0360$ for those 13279 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for (C₅H₄SiⁱPr₃)₃Tb, 6.1-Tb. A yellow crystal of approximate dimensions 0.120 x 0.148 x 0.259 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded wR2 = 0.0466 and Goof = 1.049 for 433 variables refined against 12830 data (0.70 Å), R1 = 0.0203 for those 11801 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for [K(2.2.2-cryptand)][(C₅H₄SiⁱPr₃)₃Tb], 6.2-Tb. A black crystal of approximate dimensions 0.199 x 0.362 x 0.466 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used

throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0480$ and $Goof = 1.027$ for 676 variables refined against 18202 data ($0.72 \text{ \AA}$), $R1 = 0.0196$ for those 16246 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $(C_5H_4SiPr_3)_3Dy$, 6.1-Dy. A yellow crystal of approximate dimensions $0.187 \times 0.211 \times 0.363 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX4⁵⁴ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT⁵⁵ and SADABS⁵⁶ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0343$ and $Goof = 1.073$ for 433 variables refined against 15193 data ($0.65 \text{ \AA}$), $R1 = 0.0137$ for those 14613 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $(C_5H_4SiPr_3)_3Ho$, 6.1-Ho. A yellow crystal of approximate dimensions $0.142 \times 0.256 \times 0.297 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. There were no systematic absences nor any diffraction symmetry other than the Friedel

condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0403$ and $Goof = 1.046$ for 433 variables refined against 12790 data (0.70 Å), $R1 = 0.0174$ for those 12036 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $(C_5H_4Si^iPr_3)_3Y$, 6.1-Y.

A colorless crystal of approximate dimensions 0.076 x 0.139 x 0.257 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0746$ and $Goof = 1.019$ for 433 variables refined against 12832 data (0.70 Å), $R1 = 0.0324$ for those 10601 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $(C_5H_4Si^iPr_3)_3U$, 6.1-U.

A brown crystal of approximate dimensions 0.135 x 0.182 x 0.247 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan

time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0449$ and $Goof = 1.038$ for 433 variables refined against 12920 data ($0.70 \text{ \AA}$), $R1 = 0.0192$ for those 11975 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for [K(2.2.2-cryptand)][(C₅H₄SiⁱPr₃)₃U], 6.2-U. A black crystal of approximate dimensions $0.170 \times 0.302 \times 0.321 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁴⁹ program package was used to determine the unit-cell parameters and for data collection (45 sec/frame scan time). The raw frame data was processed using SAINT⁵⁰ and SADABS⁵¹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵² program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵³ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0496$ and $Goof = 1.027$ for 676 variables refined against 16237 data ($0.75 \text{ \AA}$), $R1 = 0.0221$ for those 13461 data with $I > 2.0\sigma(I)$.

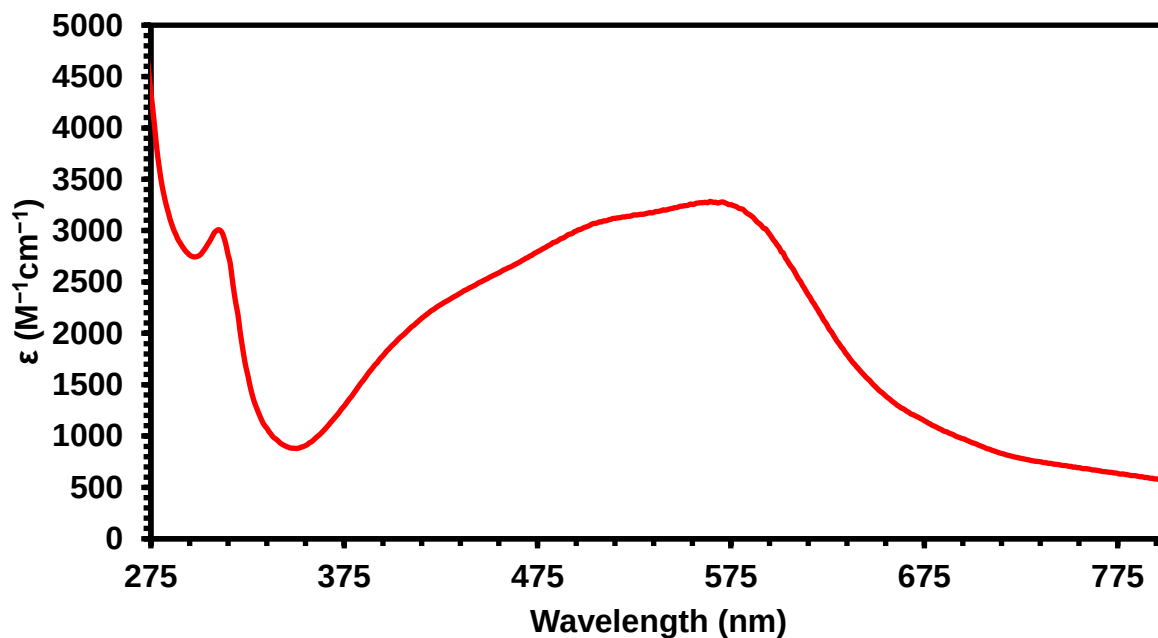


Figure 6.6. Room temperature UV-visible spectra of $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{La}]$, **6.2-La**, in THF.

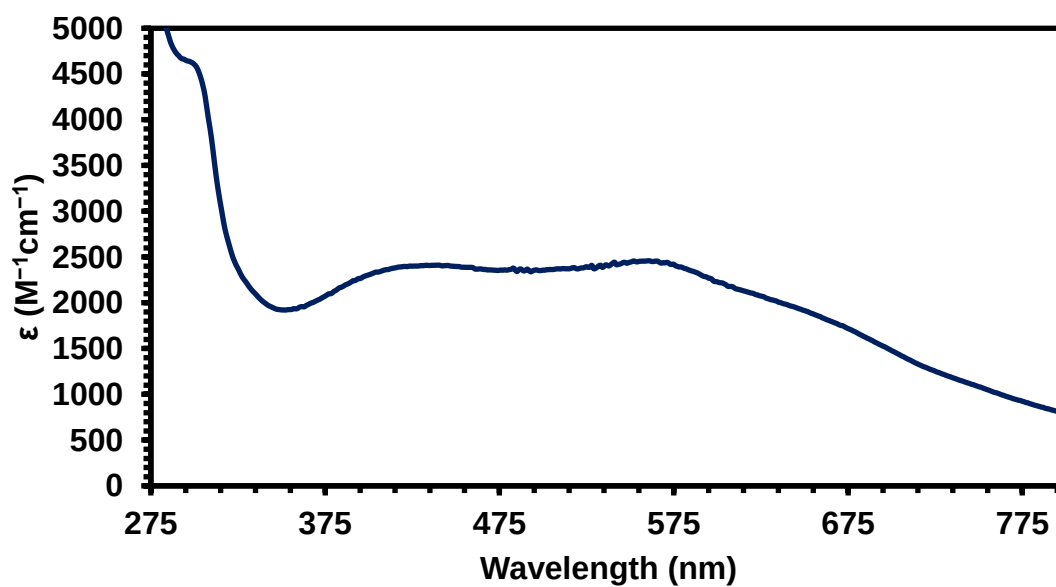


Figure 6.7. Room temperature UV-visible spectrum of $[\text{K}(\text{crypt})][\text{Cp}^{\text{TIPS}}_3\text{Pr}]$, **6.2-Pr**, in THF.

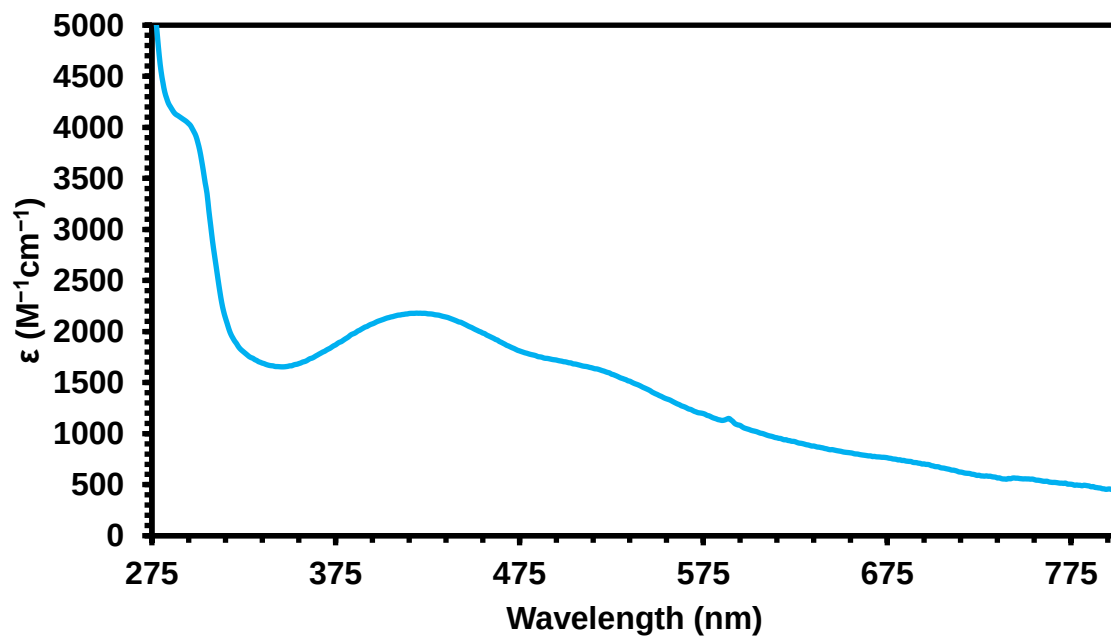


Figure 6.8. Room temperature UV-visible spectrum of [K(crypt)][Cp^{TIPS}₃Nd], **6.2-Nd**, in THF.

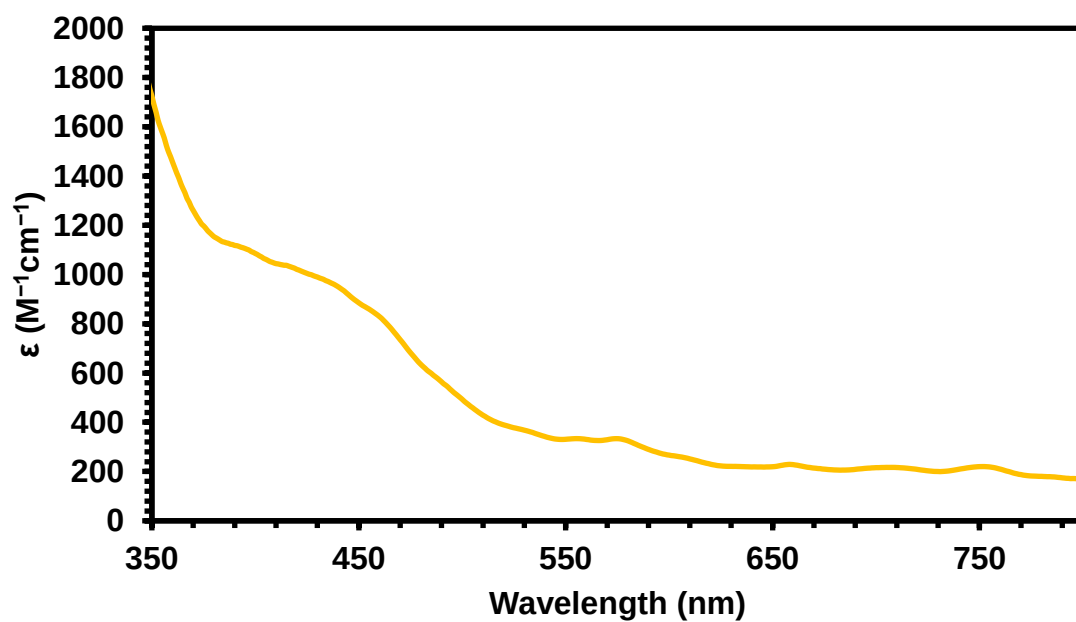


Figure 6.9. Room temperature UV-visible spectrum of Cp^{TIPS}₃U, **6.1-U**, in hexane.

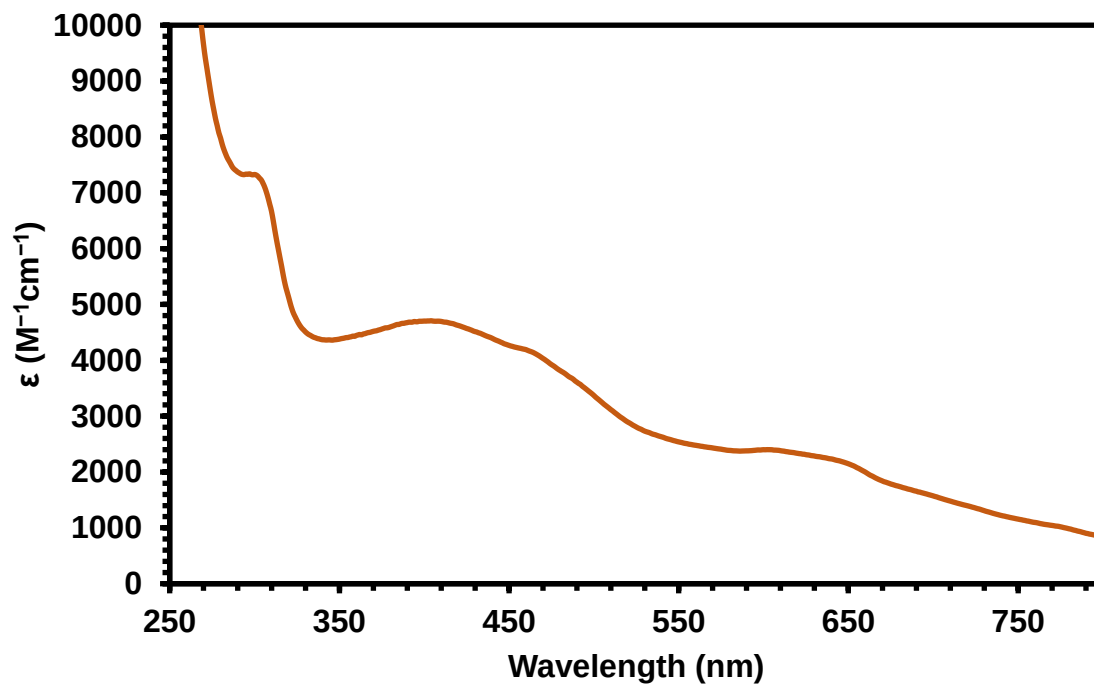


Figure 6.10. Room temperature UV-visible spectra of $[K(crypt)][Cp^{TIPS_3}U]$, **6.2-U**, in THF.

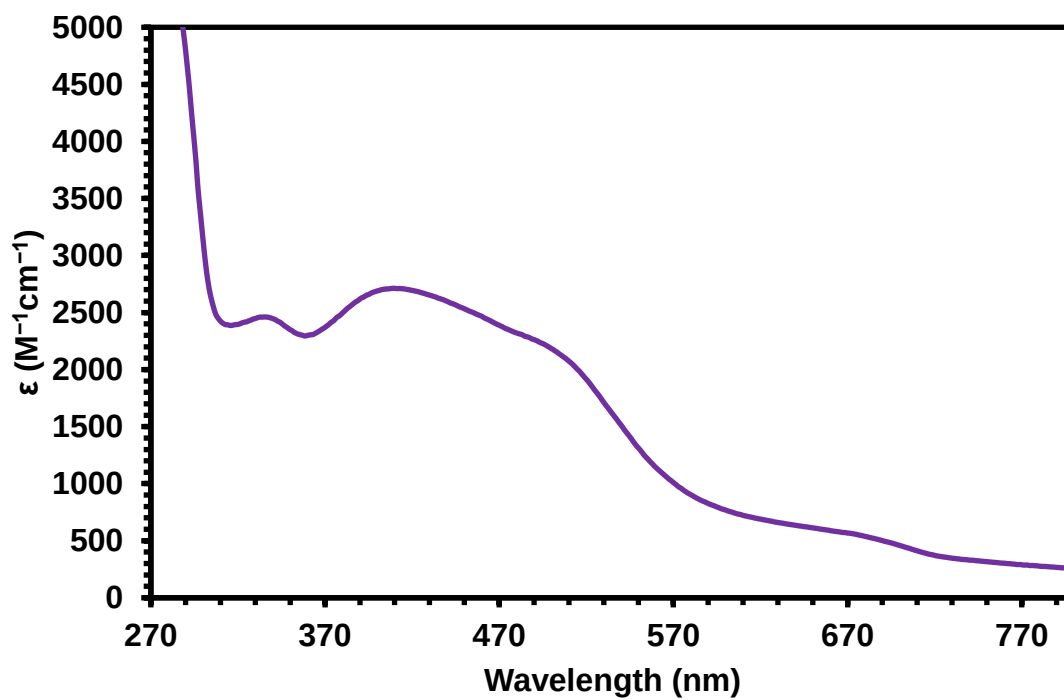


Figure 6.11. Room temperature UV-visible spectra of $[K(crypt)][Cp^{TIPS_3}Gd]$, **6.2-Gd**, in THF.

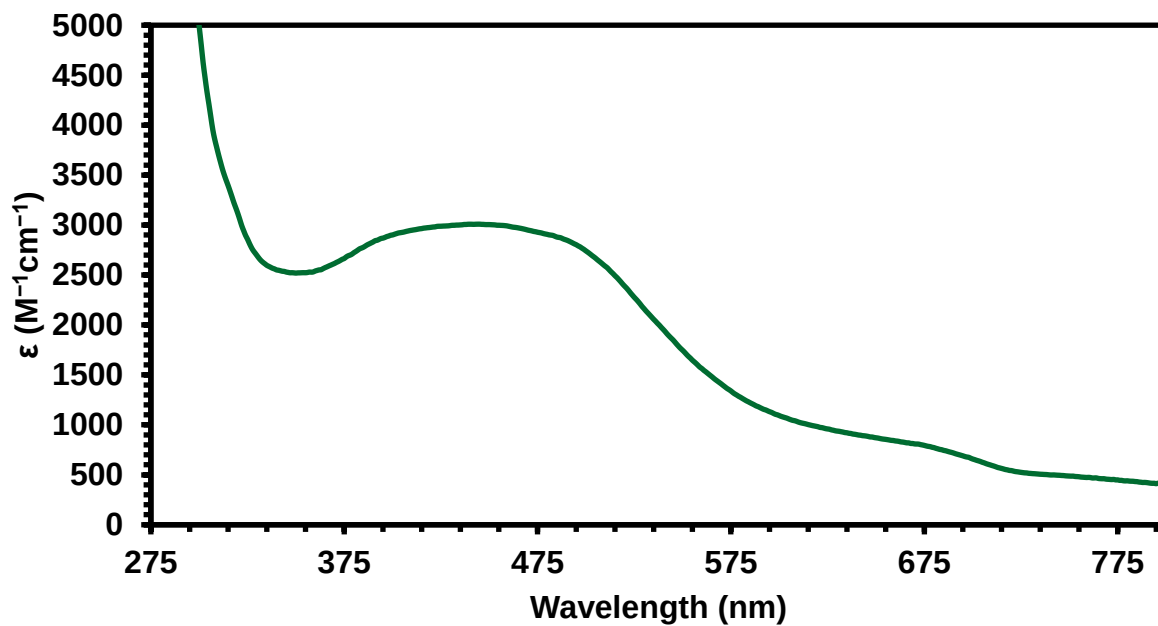


Figure 6.12. Room temperature UV-visible spectra of [K(crypt)][Cp^{TIPS}₃Dy], **6.2-Dy**, in THF.

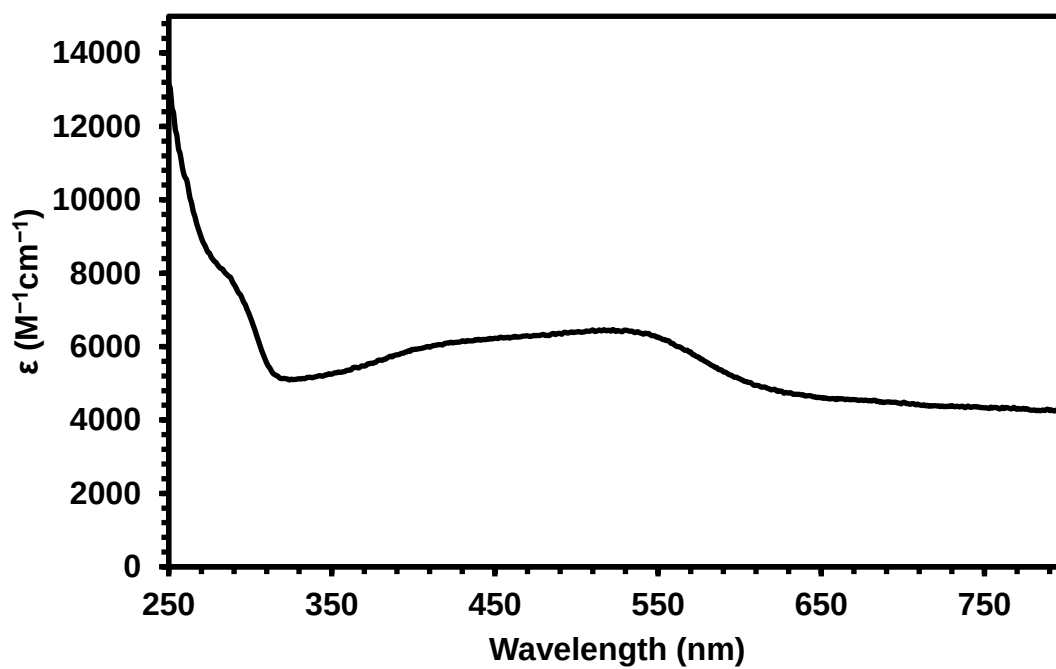


Figure 6.13. Room temperature UV-visible spectra of [K(crypt)][Cp^{TIPS}₃Y], **6.2-Y**, in THF.

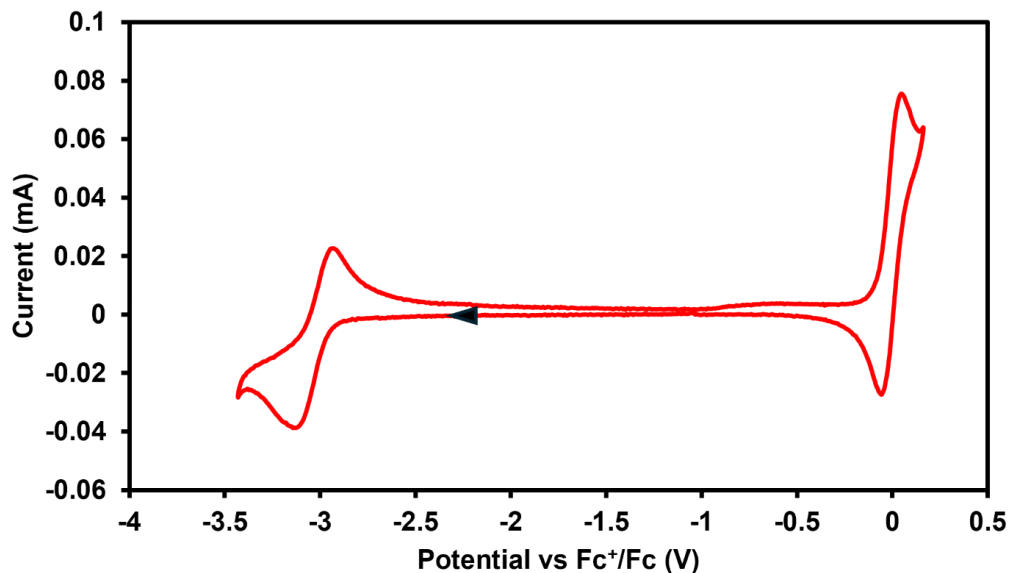


Figure 6.14. Cyclic voltammogram of Cp^{TIPS}₃La, **6.1-La**, in a 100 mM [ⁿBu₄N][BPh₄] solution of THF at room temperature with a scan rate of 100 mV/s. The event centered at 0 V is due to the internal standard (C₅H₅)₂Fe.

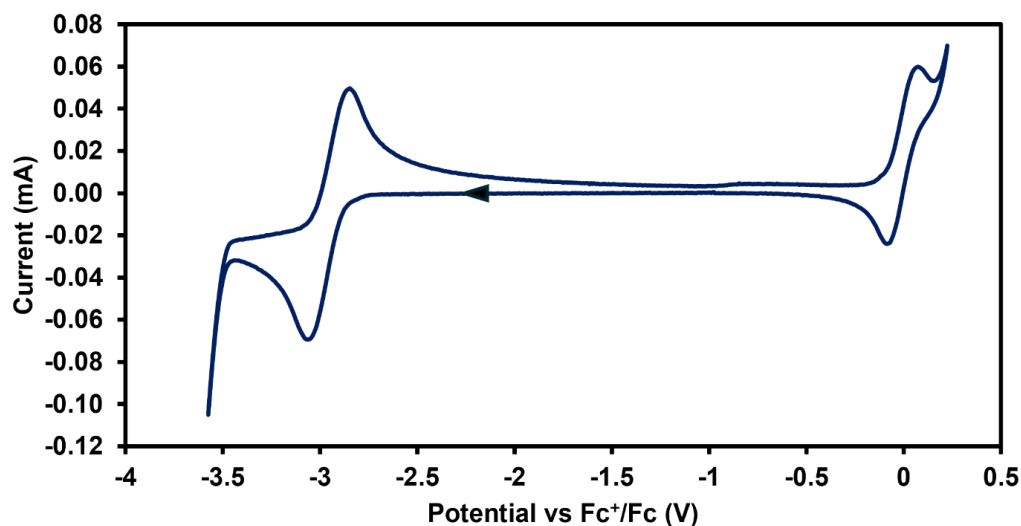


Figure 6.15. Cyclic voltammogram of Cp^{TIPS}₃Pr, **6.1-Pr**, in a 100 mM [ⁿBu₄N][BPh₄] solution of THF at room temperature with a scan rate of 100 mV/s. The event centered at 0 V is due to the internal standard (C₅H₅)₂Fe.

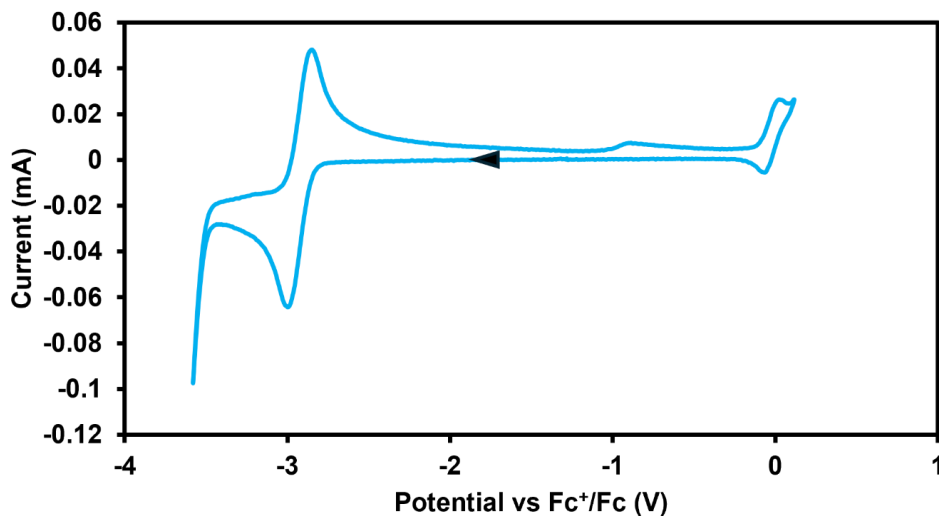


Figure 6.16. Cyclic voltammogram of $\text{Cp}^{\text{TIPS}}_3\text{Nd}$, **6.1-Nd**, in a 100 mM $[\text{nBu}_4\text{N}][\text{BPh}_4]$ solution of THF at room temperature with a scan rate of 100 mV/s. The event centered at 0 V is due to the internal standard $(\text{C}_5\text{H}_5)_2\text{Fe}$.

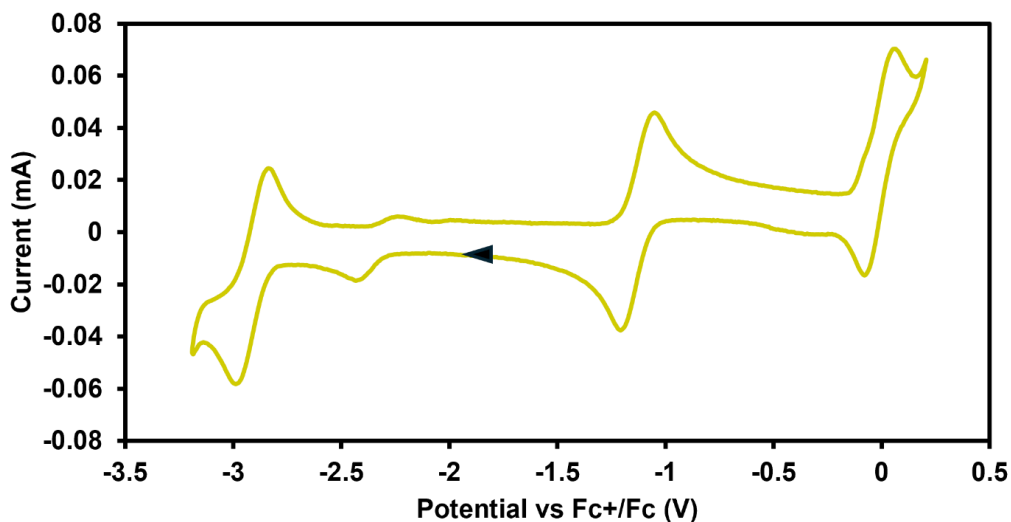


Figure 6.17. Cyclic voltammogram of $\text{Cp}^{\text{TIPS}}_3\text{U}$, **6.1-U**, in a 100 mM $[\text{nBu}_4\text{N}][\text{BPh}_4]$ solution of THF at room temperature with a scan rate of 100 mV/s. The event centered at 0 V is due to the internal standard $(\text{C}_5\text{H}_5)_2\text{Fe}$.

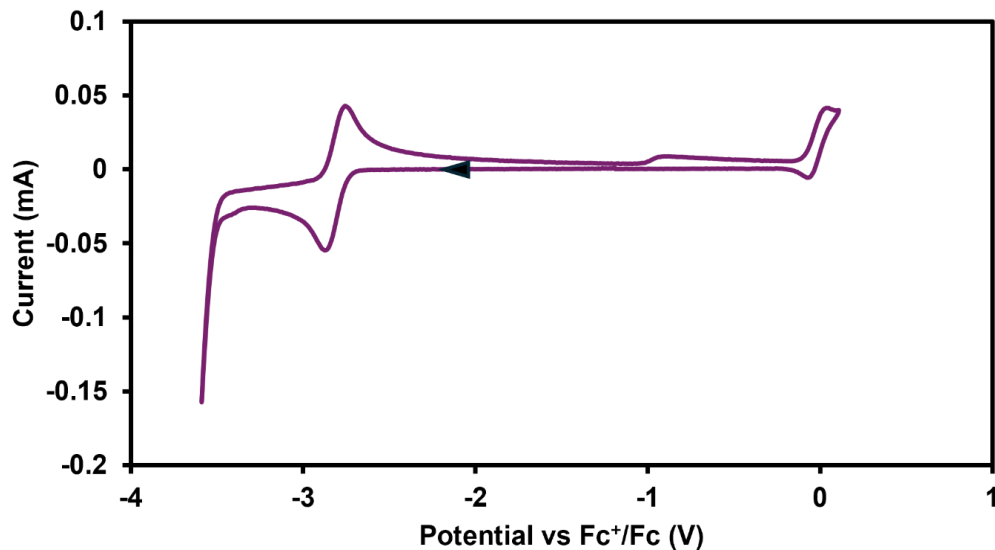


Figure 6.18. Cyclic voltammogram of $\text{Cp}^{\text{TIPS}}_3\text{Gd}$, **6.1-Gd**, in a 100 mM $[\text{nBu}_4\text{N}][\text{BPh}_4]$ solution of THF at room temperature with a scan rate of 100 mV/s. The event centered at 0 V is due to the internal standard $(\text{C}_5\text{H}_5)_2\text{Fe}$.

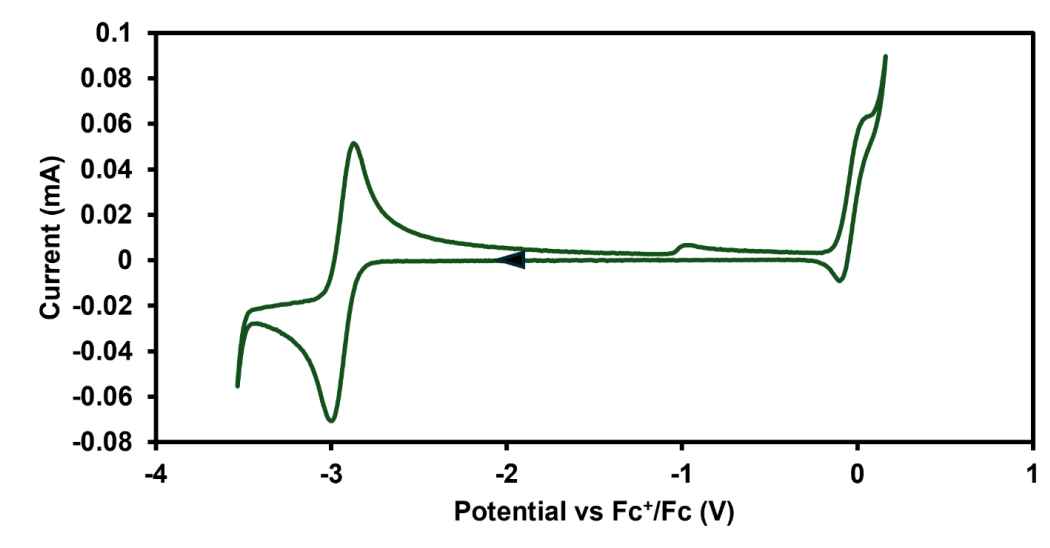


Figure 6.19. Cyclic voltammogram of $\text{Cp}^{\text{TIPS}}_3\text{Dy}$, **6.1-Dy**, in a 100 mM $[\text{nBu}_4\text{N}][\text{BPh}_4]$ solution of THF at room temperature with a scan rate of 100 mV/s. The event centered at 0 V is due to the internal standard $(\text{C}_5\text{H}_5)_2\text{Fe}$.

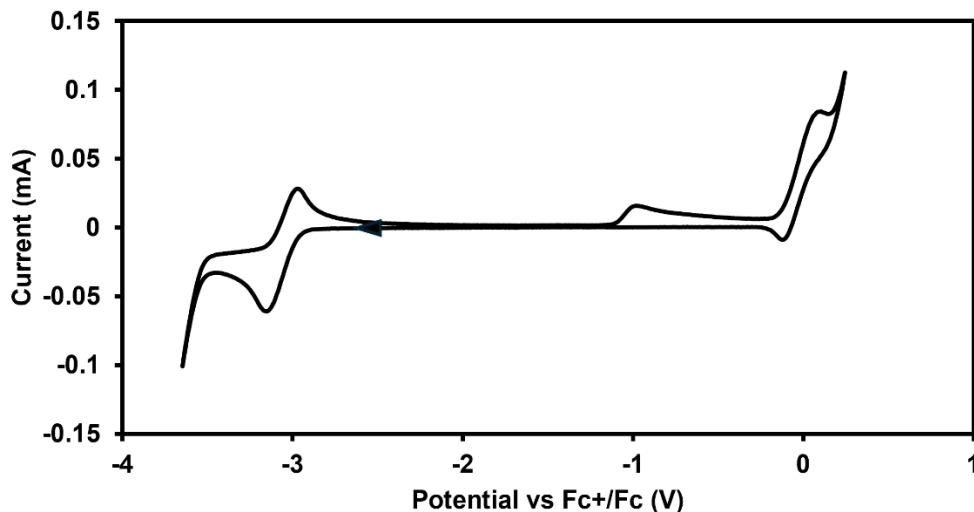


Figure 6.20. Cyclic voltammogram of $\text{Cp}^{\text{TIPS}}_3\text{Y}$, **6.1-Y**, in a 100 mM $[\text{nBu}_4\text{N}][\text{BPh}_4]$ solution of THF at room temperature with a scan rate of 100 mV/s. The event centered at 0 V is due to the internal standard $(\text{C}_5\text{H}_5)_2\text{Fe}$.

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Chapter 7:

Phenylsilyl-Substituted Tetramethylcyclopentadienide Uranium Chemistry:

Magnesocenes vs Grignard Reagents

INTRODUCTION[†]

The organometallic chemistry of the *f*-elements has benefited greatly from the use of cyclopentadienyl ligands which can be readily functionalized with substituents that provide different steric and electronic profiles.^{1–11} The *f*-element cyclopentadienyl complexes are typically synthesized from the metal halides and lithium, sodium, or potassium cyclopentadienyl salts.^{1–11} However, in the case of the commonly studied bis(cyclopentadienyl) uranium dihalide complex, $(C_5Me_5)_2UCl_2$,^{12–18} synthesis from UCl_4 and one equivalent of the Grignard reagent $[(C_5Me_5)MgCl(THF)]_2$ ^{12,19} in refluxing toluene is more common than reactions with reagents such as LiC_5Me_5 and KC_5Me_5 . This mode of synthesis was extended to the trimethylsilyltetramethyl-substituted analogue, $[C_5Me_4(SiMe_3)]_2UCl_2$, which was synthesized using $[C_5Me_4(SiMe_3)]MgCl(THF)$ rather than $KC_5Me_4(SiMe_3)$.²⁰ Hence, cyclopentadienyl Grignard reagents are fundamentally important to organometallic uranium chemistry.

The synthesis of $(C_5R_5)_2UCl_2$ complexes of the phenylsilyl-substituted tetramethylcyclopentadienides, $[C_5Me_4(SiMe_2Ph)]^{1-}$ and $[C_5Me_4(SiMePh_2)]^{1-}$, was of interest to determine if phenyl coordination of the substituent could occur as was found by Harder *et al.* in $[C_5Me_4(SiMe_2Ph)]_2Ba$, Figure 7.1.²¹ This complex adopts a bent metallocene geometry with a Cnt–Ba–Cnt (Cnt = ring centroid) angle of 130.7° and has two arene rings oriented toward the

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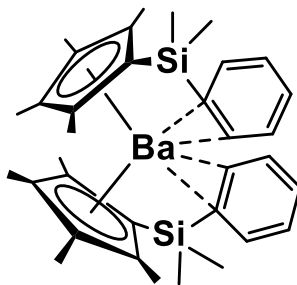
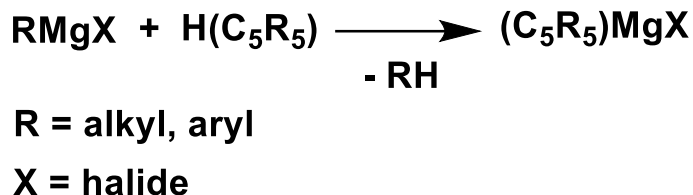


Figure 7.1. Representation of $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{Ba}$ showing the η^2 coordination of the aryl rings from the $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]^{1-}$ ligands to the Ba metal center.

barium metal center in an η^2 -fashion.²¹ Given that there is precedent for the stabilization of reduced uranium complexes through U–arene interactions,^{22–30} the use of phenylsilyl-substituted tetramethylcyclopentadienyl ligands could be an attractive method to synthesize new examples of low oxidation state uranium complexes.

Accordingly, syntheses of the necessary Grignard reagents, “[$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$] MgCl ” and “[$\text{C}_5\text{Me}_4(\text{SiMePh}_2)$] MgCl ”, were pursued for use in organouranium chemistry. Cyclopentadienyl Grignard reagents are typically synthesized by protonolysis of a cyclopentadiene with one equivalent of an alkyl or aryl Grignard reagent, RMgX (R = alkyl, aryl; X = halide), Scheme 7.1.^{12,20,31} Both $[(\text{C}_5\text{Me}_5)\text{MgCl}(\text{THF})]_2$ ^{12,19} and $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]\text{MgCl}(\text{THF})$ ²⁰ are made in this way by using a diethyl ether solution of $i\text{PrMgCl}$ and the corresponding cyclopentadiene.



Scheme 7.1. General synthesis of cyclopentadienyl Grignard reagents.

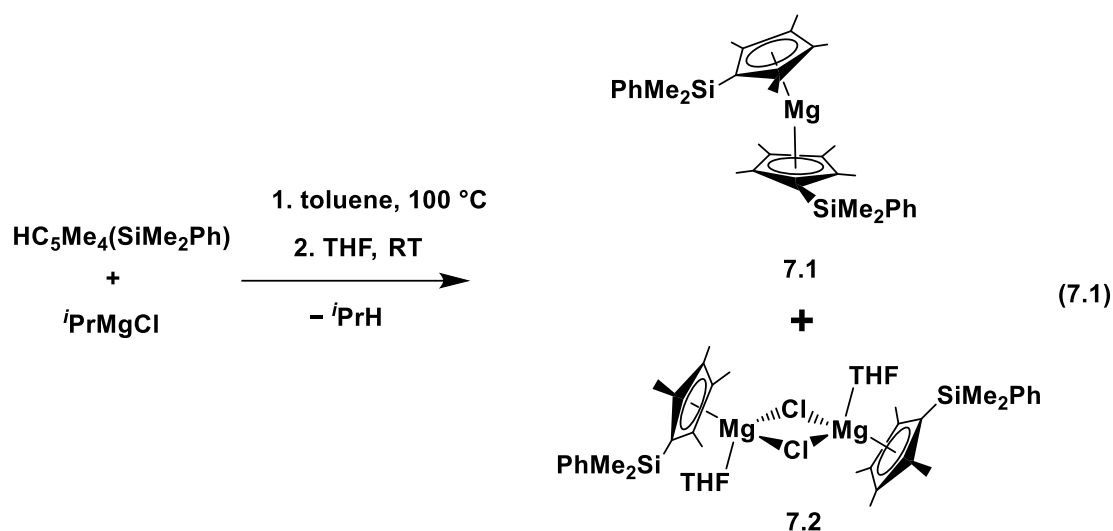
However, as reported in this Chapter, the targeted phenylsilylcyclopentadienide ligands prefer to form magnesocenes rather than the Grignard reagents. Precedent for this type of Schlenk

equilibrium dates back to the first report of $(C_5H_5)_2Mg$ by Cotton and Wilkinson; they reported that $(C_5H_5)_2Mg$ was formed from the Grignard reagent, $(C_5H_5)MgCl$.³² Although there is evidence for this reactivity, it is not a common complication in the synthesis of Grignard reagents such as $[(C_5Me_5)MgCl(THF)]_2$ ^{12,19} and $[C_5Me_4(SiMe_3)]MgCl(THF)$.²⁰ Herein, these surprising results, the conditions under which the targeted Grignard reagents can be isolated, and their ability to act as cyclopentadienyl transfer reagents in U(IV) chemistry are described.

RESULTS

Synthesis of $HC_5Me_4(SiMe_2Ph)$ and $HC_5Me_4(SiMePh_2)$. The synthesis of the two cyclopentadienes, $HC_5Me_4(SiMe_2Ph)$ and $HC_5Me_4(SiMePh_2)$, was accomplished following slightly modified literature procedures.^{21,33} Dropwise addition of neat $PhMe_2SiCl$ to a stirred suspension of KC_5Me_4H in either diethyl ether or toluene at room temperature yielded $HC_5Me_4(SiMe_2Ph)$ as an orange oil in 87% yield upon workup. Furthermore, the analogous reaction with $Ph_2MeSiCl$ yielded $HC_5Me_4(SiMePh_2)$ as a yellow, tacky solid in 86% yield upon workup. The NMR spectra of the isolated products were consistent with the formation of each cyclopentadiene.

Initial Attempts at Grignard Reagent Synthesis. The trimethylsilyltetramethylcyclopentadiene, $HC_5Me_4(SiMe_3)$, reacts readily with 0.9 equiv of $iPrMgCl$ in toluene at 100 °C for two hours to form after workup in THF the Grignard reagent, $[C_5Me_4(SiMe_3)]MgCl(THF)$, in 71% yield with respect to the isopropyl Grignard reagent $iPrMgCl$.²⁰ However, when one equivalent of $HC_5Me_4(SiMe_2Ph)$ is reacted with 0.95 equiv of $iPrMgCl$ under the same conditions, the magnesocene $[C_5Me_4(SiMe_2Ph)]_2Mg$, **7.1**, is isolated as a colorless solid after extraction of the reaction mixture with hexane in 47% yield with respect to the isopropyl Grignard reagent as the primary product, reaction 7.1.



Single crystals of **7.1** suitable for study by X-ray crystallography were grown from a concentrated solution in toluene stored at $-35\text{ }^\circ\text{C}$ and provided the structure shown in Figure 7.2. The ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **7.1** in C_6D_6 are typical for a diamagnetic compound, and the cyclopentadienyl peaks are shifted slightly downfield compared to the free ligand.

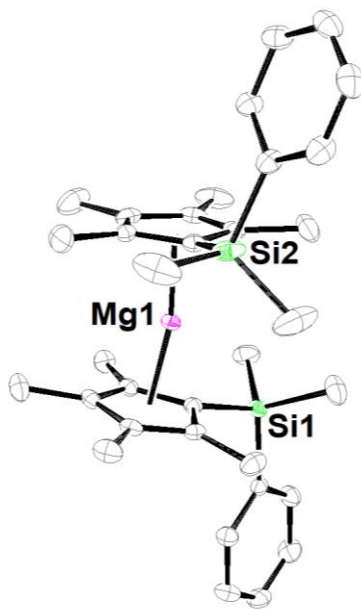


Figure 7.2. Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{Mg}$, **7.1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the half-molecule of cocrystallized toluene present are not shown for clarity.

A second product, $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]\text{Mg}(\mu\text{-Cl})(\text{THF})\}_2$, **7.2**, was isolated from reaction 7.1 by further extraction of the hexane insoluble residue with THF as a colorless solid in 34% crystalline yield with respect to the isopropyl Grignard reagent. Colorless crystals of **7.2** suitable for study by X-ray crystallography were grown by slowly diffusing hexane into a saturated THF solution at $-35\text{ }^\circ\text{C}$ and provided the structure shown in Figure 7.3.

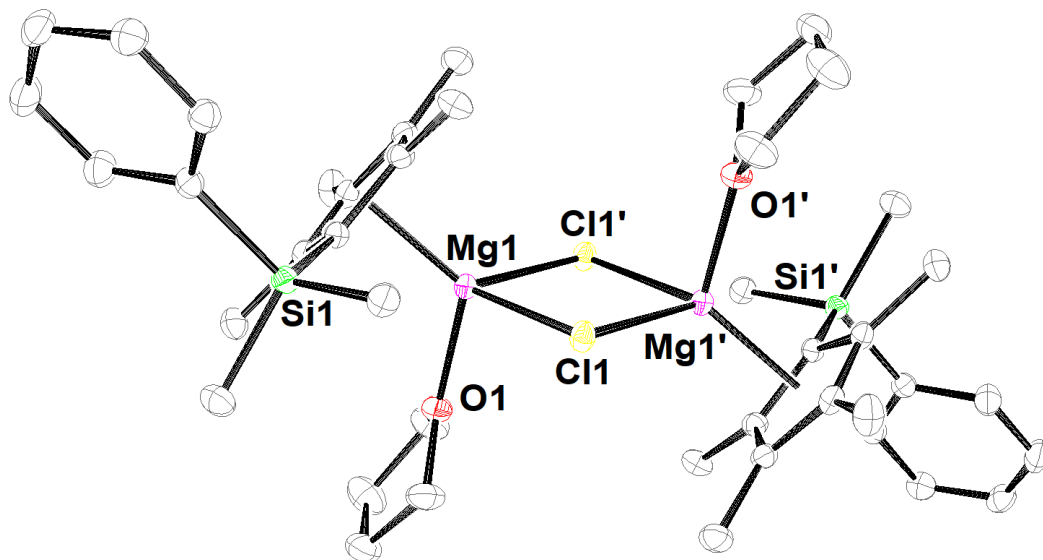


Figure 7.3. Molecular structure of $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]\text{Mg}(\mu\text{-Cl})(\text{THF})\}_2$, **7.2**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are not shown for clarity.

The ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **7.2** in C_6D_6 are distinct from that of complex **7.1** and the resonances of the bound THF molecules in the ^1H NMR spectrum of **7.2** are shifted slightly compared to those of free THF suggesting that THF is bound in solution. The IR spectra of **7.1** and **7.2** differ in that the infrared spectrum of **7.2** exhibits absorptions at 1034 and 883 cm^{-1} which are diagnostic of coordination of an O-donor ligand such as THF on a metal center.^{34,35}

In the solid state, complex **7.1** crystallizes in the $P\bar{1}$ space group as a base-free bent magnesocene where each of the cyclopentadienyl ligands is crystallographically independent. The average Mg–Cnt distance of **7.1** is $1.982\text{ \AA}$ which is in good agreement with the Mg–Cnt distance

of several other crystallographically characterized magnesocenes, Table 7.1. However, the 167.8° Cnt–Mg–Cnt angle of **7.1** is not linear as found in many, but not all of the compounds in Table 7.1.

Table 7.1. Comparison of Cnt–Mg–Cnt (°) and Mg–Cnt (Å) of Crystallographically Characterized Magnesocenes Ordered in Decreasing Cnt–Mg–Cnt.

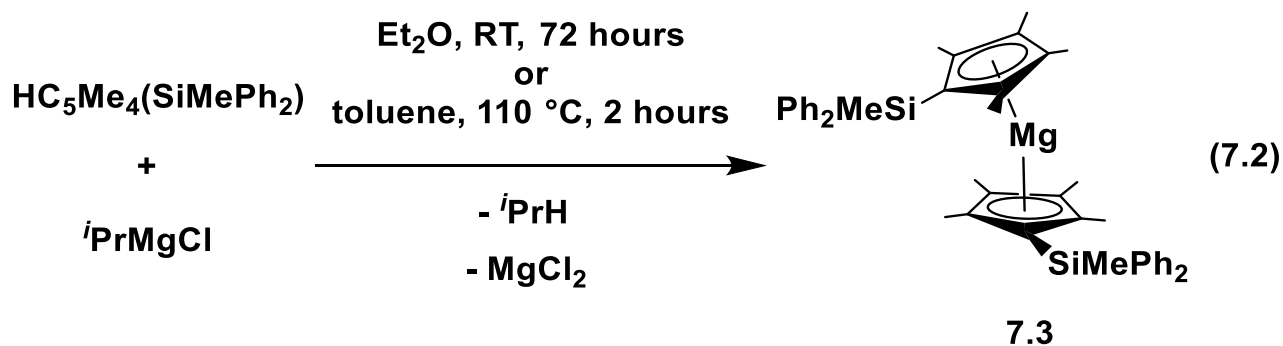
Compound	Mg–Cnt (Å)	Cnt–Mg–Cnt (°)
(C ₅ Ph ₄ H) ₂ Mg ³⁶	2.016	180.00
(C ₅ ⁱ Pr ₃ H ₂) ₂ Mg ³⁷	1.9852(1)	180.00(2)
(C ₅ H ₅) ₂ Mg ³⁸	1.985	180.00
(C ₅ Me ₄ H) ₂ Mg ³⁹	1.9702	180.00
(C ₅ Me ₅) ₂ Mg ⁴⁰	1.962, 1.971, 1.968	180.00, 176.43
[C ₅ H ₂ (SiMe ₃) ₃] ₂ Mg ⁴¹	2.019, 2.021, 2.024, 2.042	171.842, 170.438
(C ₅ Me ₄ ^t Bu) ₂ Mg ³⁹	1.9942(13), 1.9922(12)	168.96(6)
[C ₅ Me ₄ (SiMe ₂ Ph)] ₂ Mg, 7.1 ^a	1.977, 1.987	167.8
[C ₅ Me ₄ (SiMePh ₂)] ₂ Mg, 7.3 ^a	1.997, 1.998	166.0
[C ₅ Me ₄ (P ⁱ Pr ₂)] ₂ Mg ⁴²	2.0136(2)	159.790(5)

^a This work.

The Cnt–Mg–Cnt angle of **7.1** is significantly different from the 130.7° Cnt–Ba–Cnt angle seen in [C₅Me₄(SiMe₂Ph)]₂Ba, Figure 7.1, which has the additional η^2 -arene coordination. Furthermore, the structure of **7.1** differs from that of [C₅Me₄(SiMe₂Ph)]₂Ba in that both of the phenyl rings of the silyl substituents in complex **7.1** point away from the metal; there are no metal–arene interactions. It is possible that the much smaller size of the Mg(II) ion in comparison to the Ba(II) ion makes arene coordination less likely.

Complex **7.2** crystallizes in the $P\bar{1}$ space group as a centrosymmetric dimer where each of the Mg atoms are η^5 -bonded to one cyclopentadienyl ligand, bridged by two chloride anions, and coordinated to one molecule of THF. As in the structure of **7.1**, the phenyl groups of the silyl substituents point away from the metal and do not show metal–arene interactions. The 2.071 Å Mg–C_{nt} distance of complex **7.2** is longer than the 1.982 Å analogous distance in **7.1**, but the 2.430(1) and 2.433(1) Å Mg–Cl bond lengths are typical of bridging chloride ligands in magnesium complexes. For comparison, the complexes, $[(C_5H_5)Mg(OEt_2)(\mu-Cl)]_2$ and $[(C_5Me_5)Mg(OEt_2)(\mu-Cl)]_2$, have Mg–Cl distances of 2.419(2)–2.432(2) Å and 2.436(2)–2.449(2) Å, respectively.⁴³ Also, the Mg–O distance of 2.035(1) Å observed in **7.2** is in line with other Mg–O distances observed in complexes such as $[(C_5H_5)Mg(OEt_2)(\mu-Cl)]_2$ and $[(C_5Me_5)Mg(OEt_2)(\mu-Cl)]_2$ which have Mg–O distances of 2.048(3) and 2.067(2), respectively.⁴³

Attempts to synthesize the Grignard reagent of $HC_5Me_4(SiMePh_2)$ under similar conditions as for $HC_5Me_4(SiMe_2Ph)$ did not provide two isolable products as in reaction 7.1. Treating one equivalent of $HC_5Me_4(SiMePh_2)$ with one equivalent of $iPrMgCl$ in toluene at 110 °C for two hours generated the magnesocene $[C_5Me_4(SiMePh_2)]_2Mg$, **7.3**, as the only isolable product in 82% yield with respect to $iPrMgCl$, reaction 7.2.



After crystallization from a toluene/hexane mixture stored at –35 °C, complex **7.3** was identified by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy in C_6D_6 and X-ray crystallography, Figure 7.4.

Similarly, when the reaction was attempted in diethyl ether with stirring at room temperature for 3 days, only **7.3** was formed in 90% yield with respect to $i\text{PrMgCl}$, reaction 7.2. No Grignard reagent analogous to **7.2** was observed in either of these reactions.

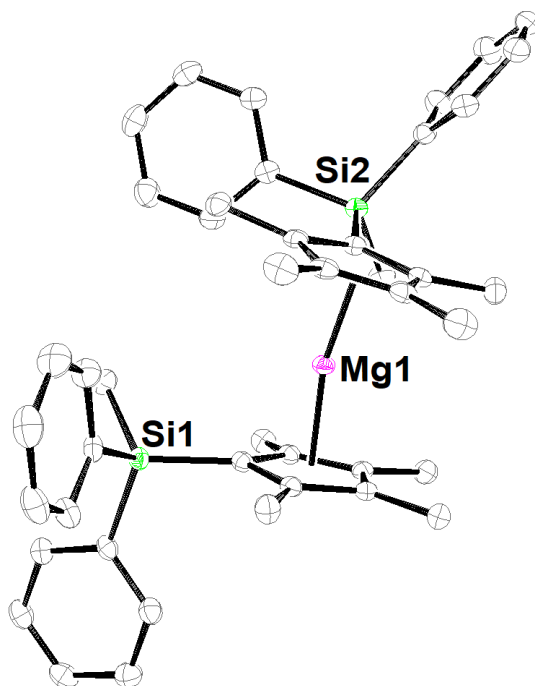


Figure 7.4. Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMePh}_2)]_2\text{Mg}$, **7.3**. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

Complex **7.3** crystallizes in the $P\bar{1}$ space group with one molecule in the asymmetric unit in which each of the cyclopentadienyl ligands is a crystallographically independent moiety. The metrical parameters of **7.3** are compared to those of **7.1** and other crystallographically characterized magnesocenes in Table 7.1. Complex **7.3** is a bent magnesocene that has a Cnt–Mg–Cnt angle of 166.1° and an average Cnt–Mg distance of $1.997 \text{ \AA}$. These numbers are close to the 167.8° angle and $1.982 \text{ \AA}$ in **7.1** despite the presence of a bulkier silyl substituent. Like **7.1** and **7.2**, complex **7.3** does not exhibit any metal–arene interactions as the phenyl rings point away from the metal.

Alternative Procedure for Grignard Reagent Synthesis. In light of the above results, alternative synthetic procedures were examined to try to precipitate the Grignard reagent, if formed initially, before it could further react to form the magnesocene. The reaction between one equivalent of $\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$ and one equivalent of a diethyl ether solution of $i\text{PrMgCl}$ in methylcyclohexane at room temperature generated $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})\}_2$, **7.4**, after 5 days in 36% yield with respect to the isopropyl Grignard reagent, reaction 7.3. Complex **7.4** was isolated by extraction of the dried reaction mixture with hexane and identified by X-ray crystallography by crystallization from a diethyl ether/hexane solution at $-35\text{ }^\circ\text{C}$, Figure 7.5.

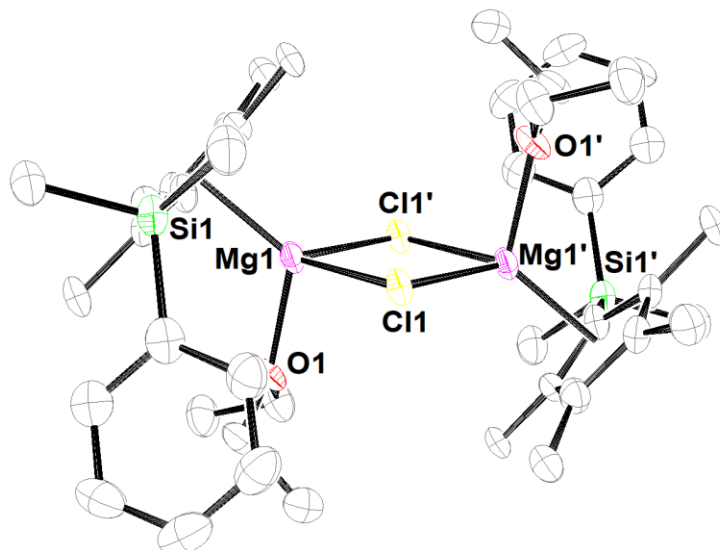
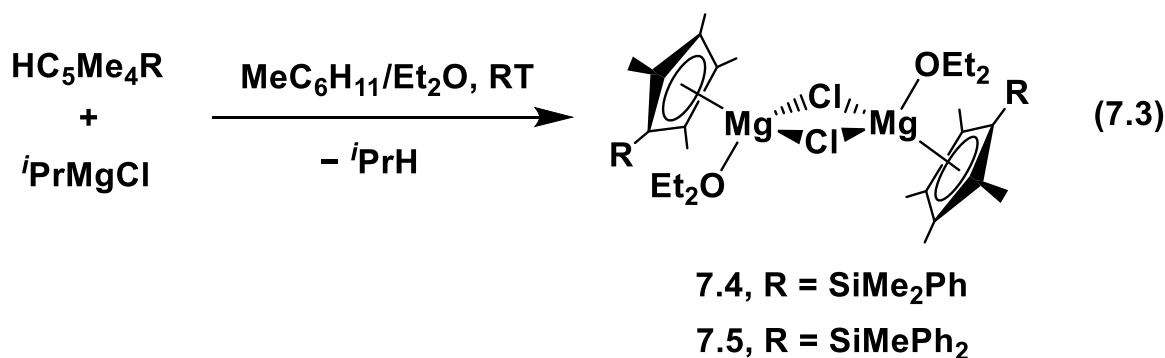


Figure 7.5. Molecular structure of $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})\}_2$, **7.4**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are not shown for clarity.

Complex **7.4** crystallizes in the $P2_1/c$ space group as a dimer in the solid state. Each magnesium atom is bound to one cyclopentadienyl ligand, bridged by two chloride ligands, and coordinated to one molecule of diethyl ether similar to what is observed in complex **7.2**. Although the connectivity of the molecule could be determined from the X-ray diffraction data, the data were not of high enough quality to discuss detailed metrical parameters. In contrast to the structures of **7.1**, **7.2**, and **7.3**, the phenyl rings in **7.4** are oriented toward the metal. However, the shortest $\text{Mg}\cdots\text{C}(\text{phenyl})$ distances are approximately 4.18 and 4.46 Å. These distances are relatively long when compared to the 3.239(4) and 3.286(4) Å $\text{Ba}\cdots\text{C}(\text{phenyl})$ distances in $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{Ba}$, Figure 7.1,²¹ especially considering that the ionic radius of Ba(II) is about 0.63 Å larger than that of Mg(II). Hence, in **7.4**, the phenyl rings are too far away from the Mg metal center for any significant interaction.

In a reaction parallel to reaction 7.3, the diphenylsilyl Grignard reagent, $\{[\text{C}_5\text{Me}_4(\text{SiMePh}_2)]\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})\}_2$, **7.5**, analogous to **7.4**, could also be isolated by treating one equivalent of $\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$ with one equivalent of $^i\text{PrMgCl}$ in methylcyclohexane at room temperature. In this case, the yield was 60% with respect to the isopropyl Grignard reagent. Complex **7.5** was isolated by an analogous procedure to **7.4** by extraction of the dried reaction mixture with hexane and identified by X-ray crystallography by crystallization from a diethyl ether/hexane solution at $-35\text{ }^\circ\text{C}$, Figure 7.6.

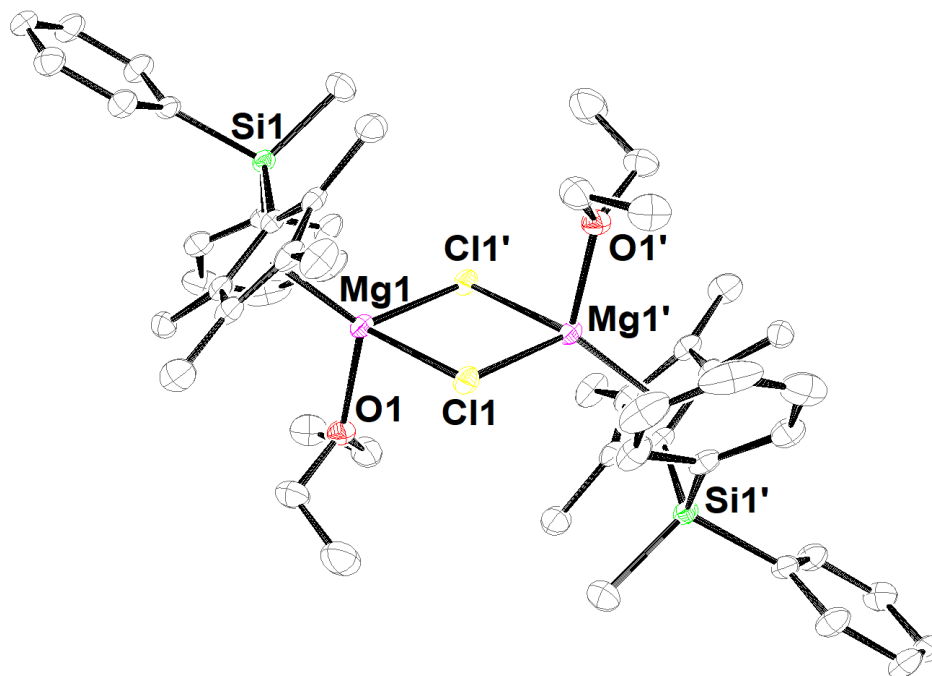


Figure 7.6. Molecular structure of $\{[\text{C}_5\text{Me}_4(\text{SiMePh}_2)]\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})\}_2$, **7.5**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are not drawn for clarity.

Although the connectivity of the structure for **7.5** is very similar to **7.4**, it crystallizes in a different space group, $P\bar{1}$, and the X-ray data were of suitable quality to discuss detailed metrical parameters. The 2.100 Å Mg–C_{nt}, 2.427(1) and 2.445(1) Å Mg–Cl, and 2.053(1) Å Mg–O distances in **7.5** are very similar to those in **7.2**, with distances of 2.071, 2.430(1), and 2.433(1), and 2.035(1) Å, respectively. The structure of complex **7.5** is similar to that of **7.4** in that there is one phenyl ring oriented toward each Mg atom. Again, however, the shortest Mg $\cdots$ C(phenyl) distances are very long at 4.392(1) and 4.654(1) Å, which indicates that no significant Mg–arene interactions occur.

The infrared spectra of **7.4** and **7.5** are similar to each other, but substantially different from the infrared spectrum of the Grignard reagent, **7.2**, since the strong absorptions at 1034 and 883 cm^{-1} attributed to THF coordination are absent. The ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of

complexes **7.2**, **7.4**, and **7.5** in C₆D₆ all show resonances that are distinct and slightly shifted from those of the protonated ligand.

Reactions of Grignard Reagents and Magnesocenes with UCl₄. Although the trimethylsilyltetramethylcyclopentadienyl Grignard reagent [C₅Me₄(SiMe₃)]MgCl(THF) reacts with 0.5 equiv of UCl₄ in toluene at 110 °C for 2 days to form the complex, [C₅Me₄(SiMe₃)₂UCl₂, in 92% yield,¹⁵ the analogous reaction with the THF-solvated phenyldimethylsilyl analogue, {[C₅Me₄(SiMe₂Ph)]MgCl(THF)}₂, **7.2**, generated a few X-ray quality crystals of a complex with just one cyclopentadienyl ring per uranium, {[C₅Me₄(SiMe₂Ph)]UCl₂(μ-Cl)₃Mg(THF)₂]₂, **7.6**, Figure 7.7, as the only isolable product, reaction 7.4.

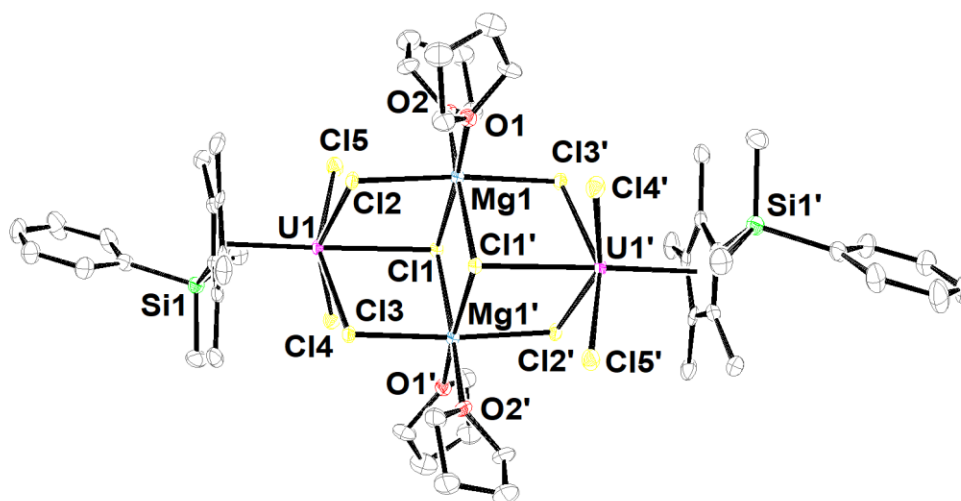
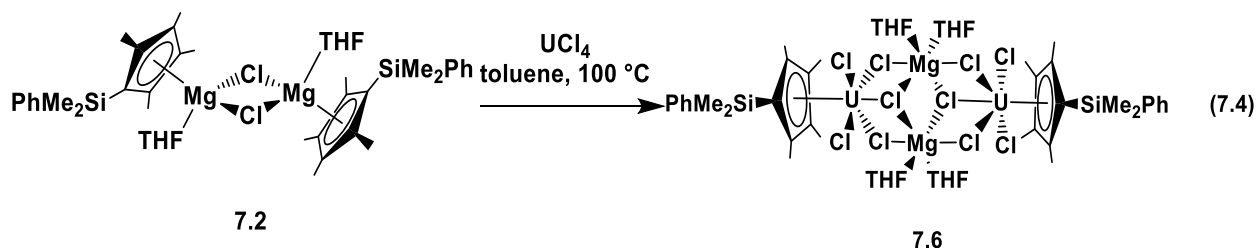
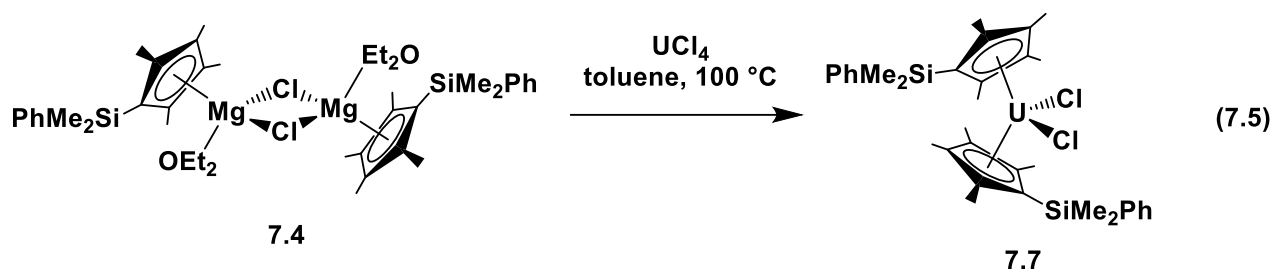


Figure 7.7. Molecular structure of {[C₅Me₄(SiMe₂Ph)]UCl₂(μ-Cl)₃Mg(THF)₂]₂, **7.6**. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are not shown for clarity.

Incorporation of Mg into actinide chloride organometallic complexes has been observed previously in structures such as $\{(C_5Me_5)U[\mu-(CH_2)PPh_2(CH_2)]\}_2Mg[CH_2PMePh_2]_2(\mu-Cl)_2(\mu-O)(\mu_3-O)$,⁴⁴ $\{[(C_8H_8)U]_2[Mg(THF)_4][U(THF)]_2(\mu-NPh)_6(\mu-Cl)_2\}_n$,⁴⁵ and $[\eta^4-C_4(SiMe_3)_4]AnCl(\mu-Cl)_3Mg(THF)_3$ (An = U, Th).⁴⁶ In addition, a thorium analogue of **7.6** with the $(C_5H_2^tBu_3)^{1-}$ cyclopentadienyl ligand was previously reported.⁴⁷

Complex **7.6** crystallizes in the $P\bar{1}$ space group as a centrosymmetric dimer with three molecules of toluene in the unit cell. In the solid state, compound **7.6** is a tetrametallic cluster comprised of two uranium atoms and two magnesium atoms bridged by six of the ten chloride atoms. The coordination geometry around each magnesium atom is pseudo-octahedral with two $\mu-Cl$ ligands, two μ_3-Cl ligands, and two THF molecules. Each uranium atom is coordinated by one cyclopentadienyl ligand, two terminal chloride ligands, two $\mu-Cl$ ligands, and one μ_3-Cl ligand for a formal coordination number of eight. The U–Cl distance is 2.432 Å, and there are no U–arene interactions as evidenced by the phenyl group pointing away from the metal center. The 2.589(1) and 2.591(1) Å U–Cl(terminal) distances are shorter than the 2.754(1), 2.761(1), and 2.864(1) Å U–Cl(bridging) distances as is typical for terminal and bridging chloride ligands. The 2.042(4) and 2.044(4) Å Mg–O distances are similar to the Mg–O distances in **7.2** and **7.5**.

In contrast to the reaction using the THF-solvated Grignard reagent, when 1 equiv of the Et₂O-solvated Grignard reagent, $\{[C_5Me_4(SiMe_2Ph)]Mg(\mu-Cl)(Et_2O)\}_2$, **7.4**, is combined with 0.95 equiv of UCl₄ in toluene at 110 °C for 24 h, $[C_5Me_4(SiMe_2Ph)]_2UCl_2$, **7.7**, can be isolated in 27% crude yield after extraction into toluene and drying under reduced pressure, reaction 7.5.



X-ray quality crystals of complex **7.7** could be grown by slowly diffusing hexane into a saturated THF solution at $-35\text{ }^\circ\text{C}$, Figure 7.8. The low yield is presumably due to the formation of magnesocene, **7.1**, as a byproduct from this reaction which was identified crystallographically from several attempts at this reaction.

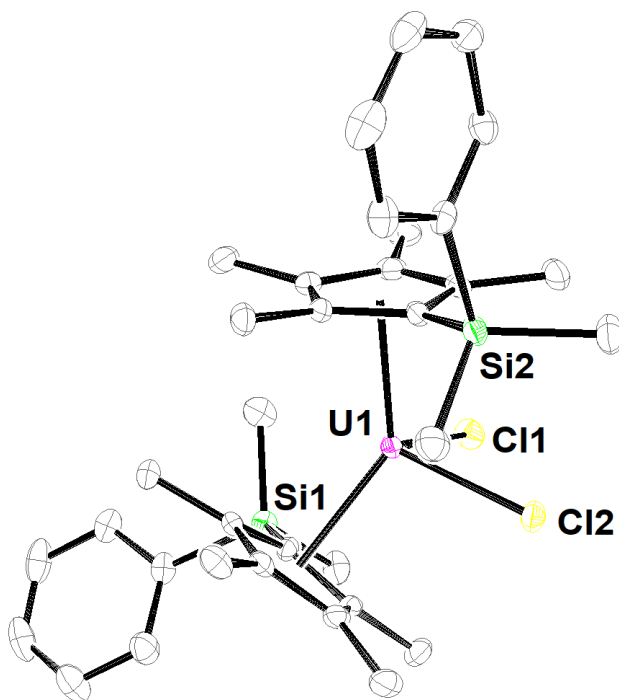


Figure 7.8. Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{UCl}_2$, **7.7**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms, the two THF molecules, and the second molecule of **7.7** in the asymmetric unit are not shown for clarity.

Complex **7.7** crystallizes in the $P\bar{1}$ space group with two molecules in the asymmetric unit and two molecules of cocrystallized THF. Each molecule adopts a typical bent metallocene

dichloride structure, again with no phenyl groups oriented toward the metal. The 136.0 and 137.9° Cnt–U–Cnt angles, the 2.435–2.445 Å Cnt–U distances, and the 2.582(1)–2.595(1) Å U–Cl distances are comparable to other bent metallocene U(IV) complexes with terminal chloride ligands.

Attempts to metalate UCl₄ with the cyclopentadienyl Grignard reagent, **7.5**, only gave the magnesocene **7.3** as an isolable product and did not yield any isolable organometallic uranium complexes. Furthermore, investigation of the reactivity of the magnesocenes, **7.1** and **7.3**, with UCl₄ yielded no observable formation of an organometallic U(IV) complex and led only to the recovery of the magnesocenes. Even when the reaction is attempted at 120 °C for 7 days in toluene, only some hydrolysis is observed.

DISCUSSION

The tendency of the phenylsilyl-substituted cyclopentadienes of this study, HC₅Me₄(SiMe₂Ph) and HC₅Me₄(SiMePh₂), to form the magnesocenes, [C₅Me₄(SiMe₂Ph)]₂Mg, **7.1**, and [C₅Me₄(SiMePh₂)]₂Mg, **7.3**, preferentially compared to the Grignard reagents was unexpected based on the chemistry of [(C₅Me₅)MgCl(THF)]₂^{12,19} and [C₅Me₄(SiMe₃)]MgCl(THF)²⁰ which do not exhibit this same behavior. Although Schlenk equilibria are well-known^{31,48} and (C₅H₅)₂Mg was first made from the Grignard reagent (C₅H₅)MgCl,³² the isolation of magnesocenes is not a common nuance in the preparation of Grignard reagents of peralkylated cyclopentadienides starting from alkylmagnesium chlorides. Also, it was unexpected to isolate the magnesocene, **7.3**, from the reaction between the Grignard reagent, **7.5**, and UCl₄. In fact, Walter and coworkers observed that the reaction between ThCl₄ and magnesocene (C₅H₂^tBu₃)₂Mg in toluene/pyridine (py) generated the Grignard reagent [(C₅H₂^tBu₃)Mg(μ -Cl)(py)]₂, i.e., the opposite of the reaction chemistry reported here.⁴⁷

Furthermore, it was surprising that the reaction between UCl_4 and either **7.1** or **7.3** yielded no observable reaction given that Andersen and co-workers reported that the reactions between $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Mg}$ and $[\text{C}_5\text{H}_3(\text{CMe}_3)_2]_2\text{Mg}$ with UCl_4 proceeded at room temperature in diethyl ether to give $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{UCl}_2$ and $[\text{C}_5\text{H}_3(\text{CMe}_3)_2]_2\text{UCl}_2$ in 50 and 80% crystalline yield, respectively.⁴⁹ However, Walter and coworkers have observed that the synthesis of bis-cyclopentadienyl Th(IV) complexes from $(\text{C}_5\text{H}_2'\text{Bu}_3)_2\text{Mg}$ and ThCl_4 in THF did not yield the targeted Th(IV) complexes.⁴⁷ From all of these studies, it is apparent that there are subtle nuances present in the synthesis of actinide metallocene complexes using bis(cyclopentadienyl) magnesium complexes and that the phenylsilyl-substituted magnesocenes do not act as good cyclopentadienide transfer reagents in organouranium chemistry.

Presumably, the replacement of alkyl groups with phenyl groups in the silyl substituent is the source of the results discussed above. The fact that switching the silyl substituent from trimethylsilyl to dimethylphenylsilyl affords a mixture of magnesocene, **7.1**, and the Grignard reagent, **7.2**, whereas switching to the diphenylmethylsilyl substituent gives only magnesocene, **7.3**, is consistent with this. The role of the phenyl groups in preferring the magnesocenes is not evident from any of the structural data reported here. The structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{Ba}$, Figure 7.1, shows that the phenyl groups can interact with alkaline earth metals, but for the $\text{Mg}(\text{II})$ ion which is much smaller than the $\text{Ba}(\text{II})$ ion, this interaction is less important and is not observed in the structural data.

Clearly, the solvent is important in isolating the Grignard reagents since both $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})\}_2$, **7.4**, and $\{[\text{C}_5\text{Me}_4(\text{SiMePh}_2)]\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})\}_2$, **7.5**, could be isolated from syntheses in methylcyclohexane rather than toluene. In the less polar solvent, the Grignard reagents precipitated out of solution and formation of the magnesocenes was not

observed. Solvent is also important in subsequent reactions with UCl_4 in that the THF-solvated Grignard reagent, **7.2**, forms $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]\text{UCl}_2(\mu\text{-Cl})_3\text{Mg}(\text{THF})_2\}_2$, **7.6**, whereas the Et_2O -solvated analog, **7.4**, generates the originally targeted complex, $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{UCl}_2$, **7.7**. Overall, the use of $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]^{1-}$ and $[\text{C}_5\text{Me}_4(\text{SiMePh}_2)]^{1-}$ ligands to coordinate uranium proved to be more challenging than expected based on the considerable success of the $(\text{C}_5\text{Me}_5)^{1-12}$ and $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]^{1-}$ ligands.²⁰

CONCLUSIONS

Reactions of the phenyl-substituted cyclopentadienes, $\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$ and $\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$, with $i\text{PrMgCl}$ in toluene at 100°C produce the magnesocenes $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{Mg}$, **7.1**, and $[\text{C}_5\text{Me}_4(\text{SiMePh}_2)]_2\text{Mg}$, **7.3**, as the primary products. In contrast, the analogous reactions with HC_5Me_5 and $\text{HC}_5\text{Me}_4\text{SiMe}_3$ form the THF-solvated Grignard reagents, $(\text{C}_5\text{Me}_5)\text{MgCl}(\text{THF})$ and $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]\text{MgCl}(\text{THF})$, in high yield. Only when the reaction medium is switched from toluene to methylcyclohexane are the phenylsilyl-substituted Grignard reagents, $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})\}_2$, **7.4**, and $\{[\text{C}_5\text{Me}_4(\text{SiMePh}_2)]\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})\}_2$, **7.5**, isolated as the primary products upon precipitation. It was unexpected that switching a methyl substituent in $\text{HC}_5\text{Me}_4(\text{SiMe}_3)$ for a phenyl group in $\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$ and $\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$ would change the nature of the Schlenk equilibrium. The propensity to form the magnesocenes is evidently strong since the reaction of **7.5** with UCl_4 gives the magnesocene, **7.3**, instead of an isolable uranium cyclopentadienyl product. It is apparent that there are subtle differences in the chemistry of the $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]^{1-}$ and $[\text{C}_5\text{Me}_4(\text{SiMePh}_2)]^{1-}$ ligands that differentiate it from that of the $(\text{C}_5\text{Me}_5)^{1-}$ and $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]^{1-}$ ligands.

EXPERIMENTAL DETAILS

Caution! ^{238}U is an α emitter with a half-life of approximately 4.5×10^9 years. Studies were conducted in a laboratory with appropriate radiological safety equipment.

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP (99.999%) argon, dried by passage through columns containing Q-5 and molecular sieves, and stored over activated sieves overnight prior to use. Deuterated NMR solvents were degassed and dried over activated 3 Å molecular sieves overnight prior to use. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR were recorded on a Bruker GN500 spectrometer at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR spectrometer. Elemental analyses were conducted on a Thermo Scientific FlashSmart CHNS/O Elemental Analyzer at UC Irvine Materials Research Institute's TEMPR facility in Irvine, California. UCl_4 ⁵⁰ and $\text{K}(\text{C}_5\text{Me}_4\text{H})$ ⁵¹ were synthesized according to literature procedures. Chlorodimethylphenylsilane and chloromethyldiphenylsilane were purchased from Sigma-Aldrich, degassed, and dried over activated 3 Å molecular sieves prior to use. Isopropylmagnesium chloride was purchased from Sigma-Aldrich as a 2.0 M solution in diethyl ether and was used without further purification.

Synthesis of $\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$. $\text{KC}_5\text{Me}_4\text{H}$ (5.00 g, 31.2 mmol) was suspended in diethyl ether (100 mL) to produce a white suspension. PhMe_2SiCl (5.34 g, 31.2 mmol) was then added slowly via syringe to the $\text{KC}_5\text{Me}_4\text{H}$ mixture at room temperature, and the resulting mixture was allowed to stir for 1 day, turning from light brown to yellow orange. The mixture was filtered to remove white, insoluble solids, presumably KCl. The solids were then washed once with hexane (10 mL) and twice with diethyl ether (2×10 mL). Solvent was removed under reduced pressure

from the combined supernatant and washes to give $\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$ as an orange oil (6.95 g, 87%). ^1H NMR (C_6D_6 , 500 MHz): δ 7.41–7.40 (m, 2H, SiMe_2Ph), 7.21–7.19 (m, 3H, SiMe_2Ph), 3.00 [s, 1H, $\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 1.77 [br s, 12H, $\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 0.17 (s, 6H, SiMe_2Ph) ppm. ^{13}C NMR (C_6D_6 , 125 MHz): δ 136.0 [$\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 134.0 [$\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 133.4 [$\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 132.9 [$\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 129.2 [$\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 127.9 [$\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 54.8 [$\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 14.7 [$\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 11.3 [$\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], –3.7 (SiMe_2Ph) ppm.

Synthesis of $\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$. $\text{KC}_5\text{Me}_4\text{H}$ (5.01 g, 31.3 mmol) was suspended in toluene (100 mL) to produce a white suspension. Ph_2MeSiCl (6.73 g, 28.9 mmol) was added slowly via syringe to the $\text{KC}_5\text{Me}_4\text{H}$ suspension at room temperature, and the resulting mixture was allowed to stir at room temperature for 2 days, turning from light brown to yellow. After the mixture was filtered to remove white insoluble solids, presumably KCl, the solids were washed once with hexane and twice with diethyl ether. Solvent was removed in vacuo from the combined supernatant and washes to give $\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$ as a yellow, tacky solid (7.88 g, 86%). ^1H NMR (C_6D_6 , 500 MHz): δ 7.50–7.48 (m, 4H, SiMePh_2), 7.16–7.15 (m, 6H, SiMePh_2), 3.38 [s, 1H, $\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], 1.74 [s, 6H, $\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], 1.65 [s, 6H, $\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], 0.35 (s, 3H, SiMePh_2) ppm. ^{13}C NMR (C_6D_6 , 125 MHz): δ 137.2 [$\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], 136.6 [$\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], 135.0 [$\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], 133.0 [$\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], 129.4 [$\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], 128.0 [$\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], 53.1 [$\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], 14.8 [$\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], 11.4 [$\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$], –6.5 (SiMePh_2) ppm. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{Si}$: C, 82.96; H, 8.23. Found: C, 82.27; H, 8.19.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{Mg}$, 7.1, and $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]\text{Mg}(\mu\text{-Cl})(\text{THF})\}_2$, 7.2. In a 100 mL Schlenk tube, a 2.0 M solution of $^i\text{PrMgCl}$ (9.50 mL, 19.0 mmol) in diethyl ether

was concentrated in vacuo to a viscous gray residue, and toluene was added (40 mL). $\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$ (5.00 g, 19.5 mmol) was added dropwise to the mixture at room temperature and subsequently was stirred at 100 °C for 2 h. Solvent was removed under reduced pressure, and the residue was extracted with hexane. The resulting solution was filtered, concentrated, and stored in a –35 °C freezer. X-ray quality crystals of **7.1** were grown overnight (2.47 g, 47% with respect to $^i\text{PrMgCl}$). X-ray quality crystals of **7.1** could also be obtained from toluene. ^1H NMR (C_6D_6 , 500 MHz): δ 7.39–7.37 (m, 4H, SiMe_2Ph), 7.15–7.14 (m, 6H, SiMe_2Ph), 2.05 [s, 12H, $\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 1.93 [s, 12H, $\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 0.65 (s, 12H, SiMe_2Ph) ppm. ^{13}C NMR (C_6D_6 , 125 MHz): δ 141.3 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 134.1 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 128.9 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 128.1 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 122.0 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 117.9 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 104.3 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 13.7 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 10.8 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 2.2 ppm (SiMe_2Ph). IR: 3701w, 3065w, 3042w, 2950m, 2909m, 2858m, 1426s, 1306s, 1247s, 1107s, 1020m, 982m, 834s, 809vs, 722vs, 695vs, 659vs cm^{-1} . Anal. Calcd for $\text{C}_{34}\text{H}_{46}\text{MgSi}_2$, **7.1**: C, 76.30; H, 8.66. Found: C, 74.34; H, 8.26. C, 75.57; H, 7.88. C, 76.22; H, 7.89. The C:H ratios in the analytical data give formulas of $\text{C}_{34}\text{H}_{45}$, $\text{C}_{34}\text{H}_{42}$, and $\text{C}_{34}\text{H}_{42}$, respectively.

After the hexane extraction described above, the remaining solid was extracted with THF. The THF extracts were filtered, and solvent was evaporated under reduced pressure to leave an off-white solid of $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]\text{Mg}(\mu\text{-Cl})(\text{THF})\}_2$, **7.2** (2.50 g, 34% with respect to $^i\text{PrMgCl}$). X-ray quality crystals of **7.2** were grown from slow diffusion of hexane into a THF solution at –35 °C. ^1H NMR (C_6D_6 , 500 MHz): δ 7.65–7.64 (m, 4H, SiMe_2Ph), 7.23–7.16 (m, 10H, SiMe_2Ph), 3.60 [br s, 8H, $\text{O}(\text{CH}_2\text{CH}_2)_2$], 2.14 [s, 12H, $\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 2.13 [s, 12H, $\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 1.28 [br s, 8H, $\text{O}(\text{CH}_2\text{CH}_2)_2$], 0.77 (s, 12H, SiMe_2Ph) ppm. ^{13}C NMR (C_6D_6 , 125 MHz): δ 143.0 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 134.6 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 128.5 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 128.3

[C₅Me₄(SiMe₂Ph)], 121.1 [C₅Me₄(SiMe₂Ph)], 116.0 [C₅Me₄(SiMe₂Ph)], 100.4 [C₅Me₄(SiMe₂Ph)], 69.9 [O(CH₂CH₂)₂], 25.2 [O(CH₂CH₂)₂], 14.5 [C₅Me₄(SiMe₂Ph)], 11.7 [C₅Me₄(SiMe₂Ph)], 2.3 (SiMe₂Ph) ppm. IR: 2976w, 2894w, 1458w, 1344w, 1296w, 1247w, 1179w, 1034vs, 917m, 883s, 676w cm⁻¹. Anal. Calcd for C₄₂H₆₂O₂Mg₂Si₂Cl₂, **7.2**: C, 65.12; H, 8.07. Found: C, 50.08; H, 7.80. C, 54.78; H, 7.39. C, 58.94; H, 7.54. The C:H ratios in the analytical data give formulas of C₄₂H₆₈, C₄₂H₆₆, and C₄₂H₆₄, respectively.

Synthesis of [C₅Me₄(SiMePh₂)]₂Mg, 7.3. In a 100 mL Schlenk tube, a 2 M solution of ⁱPrMgCl (3.92 mL, 7.84 mmol) in diethyl ether was concentrated in vacuo to a viscous gray residue, and toluene (60 mL) was added. HC₅Me₄(SiMePh₂) (2.50 g, 7.85 mmol) was added, and the resulting mixture was allowed to stir at 110 °C for two hours. The mixture was filtered, and solvent was removed under reduced pressure. The residue was then washed with hexane (5 mL) and dried under reduced pressure to yield colorless solids. Next, the solids were extracted with toluene and filtered. The resulting colorless filtrate was concentrated under reduced pressure, layered under hexane, and stored at -35 °C to yield colorless X-ray quality crystals of **7.3** (2.12 g, 82% with respect to ⁱPrMgCl). ¹H NMR (C₆D₆, 500 MHz): δ 7.69–7.68 (m, 8H, SiMePh₂), 7.20–7.17 (m, 12H, SiMePh₂), 2.15 [s, 12H, C₅Me₄(SiMePh₂)], 2.08 [s, 12H, C₅Me₄(SiMePh₂)], 1.12 (s, 6H, SiMePh₂) ppm. ¹³C NMR (C₆D₆, 125 MHz): δ 140.8 [C₅Me₄(SiMePh₂)], 136.1 [C₅Me₄(SiMePh₂)], 128.9 [C₅Me₄(SiMePh₂)], 128.3 [C₅Me₄(SiMePh₂)], 127.9 [C₅Me₄(SiMePh₂)], 122.1 [C₅Me₄(SiMePh₂)], 117.0 [C₅Me₄(SiMePh₂)], 14.9 [C₅Me₄(SiMePh₂)], 11.8 [C₅Me₄(SiMePh₂)], 1.46 (SiMePh₂) ppm. IR: 3065w, 3042w, 2953m, 2905m, 2857m, 1427s, 1386m, 1307s, 1249m, 1102s, 1042s, 1020w, 999w, 898w, 786vs, 740vs, 706vs cm⁻¹. Anal. Calcd for C₄₄H₅₀MgSi₂: C, 80.15; H, 7.64. Found: C, 74.63; H, 7.23. C, 76.14; H, 8.09. C, 75.67; H, 9.49. The C:H ratios in the analytical data give formulas of C₄₄H₅₀, C₄₄H₅₆, and C₄₄H₆₅, respectively.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})]_2$, 7.4. A 2.0 M solution of $i\text{PrMgCl}$ (1.95 mL, 3.90 mmol) in diethyl ether was concentrated in vacuo under reduced pressure to a viscous gray residue, and methylcyclohexane (12 mL) was added. $\text{HC}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$ (1.00 g, 3.90 mmol) was added, and the resulting mixture was allowed to stir at room temperature for 5 days, after which much white precipitate had formed. The white insoluble solids were filtered and washed with methylcyclohexane followed by diethyl ether. The solids were then extracted into toluene and filtered. Solvent was removed from the supernatant under reduced pressure to yield a colorless residue. Trituration of the residue with diethyl ether followed by drying under reduced pressure yielded $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})]_2$, 7.4, as a white powder (0.55 g, 36%). X-ray quality crystals of 7.4 can be grown from slow diffusion of hexane into a toluene solution at $-35\text{ }^\circ\text{C}$. ^1H NMR (C_6D_6 , 500 MHz): δ 7.60–7.59 (m, 4H, SiMe_2Ph), 7.21–7.16 (m, 6H, SiMe_2Ph), 3.42–3.38 (q, 8H, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$), 2.19 [s, 12H, $\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 2.11 [s, 12H, $\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 0.91–0.88 (t, 12H, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$), 0.75 (s, 12H, SiMe_2Ph) ppm. ^{13}C NMR (C_6D_6 , 125 MHz): δ 142.9 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 134.5 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 128.5 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 127.9 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 121.6 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 116.5 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 101.0 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 65.6 ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$), 14.8 ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$), 14.0 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 11.7 [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})$], 2.3 (SiMe_2Ph) ppm. IR: 3069w, 3048w, 2954m, 2901m, 2858m, 1427m, 1387m, 1306s, 1244s, 1102s, 1044s, 1019m, 1001m, 805vs, 757vs, 735vs, 701vs cm^{-1} . Anal. Calcd for $\text{C}_{42}\text{H}_{66}\text{Cl}_2\text{Mg}_2\text{O}_2\text{Si}_2$: C, 64.79; H, 8.54. Found: C, 62.85; H, 8.20. C, 55.80; H, 7.07. C, 60.62; H, 7.94. The C:H ratios in the analytical data give formulas of $\text{C}_{42}\text{H}_{66}$, $\text{C}_{42}\text{H}_{64}$, and $\text{C}_{42}\text{H}_{66}$, respectively.

Synthesis of $\{[\text{C}_5\text{Me}_4(\text{SiMePh}_2)]\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})\}_2$, 7.5. In a 100 mL Schlenk tube, a 2.0 M solution of $i\text{PrMgCl}$ (3.13 mL, 6.26 mmol) in diethyl ether was concentrated under reduced

pressure to a viscous gray residue, and methylcyclohexane (30 mL) was added. $\text{HC}_5\text{Me}_4(\text{SiMePh}_2)$ (2.00 g, 6.28 mmol) was added, and the resulting mixture was allowed to stir for 2 days at room temperature, at which point much white precipitate had formed. The white, insoluble solids were filtered and washed with hexane. The solids were then extracted into toluene and filtered to remove insoluble solids. Solvent was removed under reduced pressure from the toluene extract to yield a colorless residue. Trituration of the residue with hexane, followed by drying under reduced pressure yielded $\{[\text{C}_5\text{Me}_4(\text{SiMePh}_2)]\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})\}_2$, **7.5**, as a white solid (1.75 g, 62%). X-ray quality crystals of **7.5** were grown from slow diffusion of hexane into a toluene solution at -35°C . ^1H NMR (C_6D_6 , 500 MHz): δ 7.69–7.68 (m, 8H, SiMePh_2), 7.21–7.16 (m, 12H, SiMePh_2), 3.32–3.28 (q, 8H, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$), 2.15 [s, 12H, $\text{C}_5\text{Me}_4(\text{SiMePh}_2)$], 2.08 [s, 12H, $\text{C}_5\text{Me}_4(\text{SiMePh}_2)$], 1.12 (s, 6H, SiMePh_2), 0.82–0.79 (t, 12H, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) ppm. ^{13}C NMR (C_6D_6 , 125 MHz): δ 140.8 [$\text{C}_5\text{Me}_4(\text{SiMePh}_2)$], 136.0 [$\text{C}_5\text{Me}_4(\text{SiMePh}_2)$], 128.9 [$\text{C}_5\text{Me}_4(\text{SiMePh}_2)$], 127.9 [$\text{C}_5\text{Me}_4(\text{SiMePh}_2)$], 122.1 [$\text{C}_5\text{Me}_4(\text{SiMePh}_2)$], 117.0 [$\text{C}_5\text{Me}_4(\text{SiMePh}_2)$], 99.6 [$\text{C}_5\text{Me}_4(\text{SiMePh}_2)$], 65.4 ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$), 14.8 [$\text{C}_5\text{Me}_4(\text{SiMePh}_2)$], 13.8 ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$), 11.8 [$\text{C}_5\text{Me}_4(\text{SiMePh}_2)$], 1.4 (SiMePh_2) ppm. IR: 3064w, 3041w, 2952w, 2905w, 2856w, 1426m, 1386w, 1307m, 1249w, 1102m, 1042m, 999w, 786s, 739s, 707s cm^{-1} . Anal. Calcd for $\text{C}_{52}\text{H}_{70}\text{O}_2\text{Mg}_2\text{Si}_2\text{Cl}_2$: C, 69.18; H, 7.82. Found: C, 66.51; H, 6.91. C, 68.76; H, 8.25. C, 63.85; H, 6.73. The C:H ratios in the analytical data give formulas of $\text{C}_{52}\text{H}_{64}$, $\text{C}_{52}\text{H}_{74}$, and $\text{C}_{52}\text{H}_{66}$, respectively.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{UCl}_2$, 7.7. In a 100 mL Schlenk tube, $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]\text{Mg}(\mu\text{-Cl})(\text{Et}_2\text{O})\}_2$ (1.00 g, 1.28 mmol) and UCl_4 (0.450 g, 1.18 mmol) were suspended in toluene (20 mL). The mixture was stirred at 120°C for 1 day. Solvent was removed in vacuo, and the residue was washed with hexane before being extracted into toluene and filtered.

Solvent was removed under reduced pressure, yielding $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{UCl}_2$, **7.7**, as a dark red solid (0.260 g, 27%). X-ray quality crystals of **7.7** were grown from slow diffusion of hexane into a THF solution at $-35\text{ }^\circ\text{C}$. ^1H NMR (C_6D_6 , 500 MHz): δ 27.81 (br s, 4H), 20.71 (br s, 12H), 15.07–15.06 (d, 4H) 13.10 (s, 2H), -5.84 (br s, 12H), -7.83 (br s, 12H) ppm. The paramagnetism of the U(IV) ion precluded a definitive assignment of resonances in the ^1H NMR spectrum. IR: 3065w, 2953w, 2906w, 1484w, 1426w, 1381w, 1322w, 1248m, 1107m, 1018w, 810s, 770m, 734m, 700m, 653w cm^{-1} . Anal. Calcd for $\text{C}_{34}\text{H}_{46}\text{Si}_2\text{Cl}_2\text{U}$: C, 49.81; H, 5.66. Found: C, 39.26; H, 6.60. C, 49.09; H, 6.70. C, 51.37; H, 7.83. The C:H ratios in the analytical data give formulas of $\text{C}_{34}\text{H}_{68}$, $\text{C}_{34}\text{H}_{55}$, and $\text{C}_{34}\text{H}_{62}$, respectively.

X-ray Data Collection, Structure Solution and Refinement for $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{Mg}$, **7.1.** A colorless crystal of approximate dimensions 0.109 x 0.185 x 0.216 mm was mounted in a cryoloop and transferred to a Bruker X8 Prospector diffractometer system. The APEX3⁵² program package was used to determine the unit-cell parameters and for data collection (10-20 sec/frame scan time). The raw frame data was processed using SAINT⁵³ and SADABS⁵⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁵ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There was a half molecule of toluene present that was located about an inversion center that was included using negative parts, partial site-occupancy-factors, and displacement constraints (SIMU). Least-squares analysis yielded $wR2 =$

0.1067 and Goof = 1.049 for 410 variables refined against 6334 data (0.83 Å), R1 = 0.0396 for those 5606 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $\{[C_5Me_4(SiMe_2Ph)]Mg(\mu-Cl)(THF)\}_2$, 7.2. A colorless crystal of approximate dimensions 0.145 x 0.170 x 0.183 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁷ program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time). The raw frame data was processed using SAINT⁵⁸ and SADABS⁵⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁵ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about an inversion center. Least-squares analysis yielded $wR2 = 0.0974$ and Goof = 1.009 for 232 variables refined against 5329 data (0.74 Å), R1 = 0.0369 for those 4212 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $[C_5Me_4(SiMePh_2)]_2Mg$, 7.3. A colorless crystal of approximate dimensions 0.147 x 0.148 x 0.237 mm was mounted in a cryoloop and transferred to a Bruker X8 Prospector diffractometer system. The APEX3⁵² program package was used to determine the unit-cell parameters and for data collection (10-30 sec/frame scan time). The raw frame data was processed using SAINT⁵³ and SADABS⁵⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁵ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel

condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0906$ and $Goof = 1.043$ for 434 variables refined against 6751 data ($0.83 \text{ \AA}$), $R1 = 0.0338$ for those 6079 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $\{[C_5Me_4(SiMe_2Ph)]Mg(\mu-Cl)(Et_2O)\}_2$, 7.4. A colorless crystal of approximate dimensions $0.145 \times 0.179 \times 0.210 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker X8 Prospector diffractometer system. The APEX3⁵² program package was used to determine the unit-cell parameters and for data collection (10-30 sec/frame scan time). The raw frame data was processed using SAINT⁵³ and SADABS⁵⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁵ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about an inversion center. The data were not high enough quality, so only connectivity could be established.

X-ray Data Collection, Structure Solution and Refinement for $\{[C_5Me_4(SiMePh_2)]Mg(\mu-Cl)(Et_2O)\}_2$, 7.5. A colorless crystal of approximate dimensions $0.140 \times 0.186 \times 0.238 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker X8 Prospector diffractometer system. The APEX3⁵² program package was used to determine the unit-cell

parameters and for data collection (10-30 sec/frame scan time). The raw frame data was processed using SAINT⁵³ and SADABS⁵⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁵ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about an inversion center. Least-squares analysis yielded $wR_2 = 0.1066$ and $Goof = 1.058$ for 278 variables refined against 4540 data (0.83 Å), $R_1 = 0.0373$ for those 4293 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $\{[C_5Me_4(SiMe_2Ph)]UCl_2(\mu-Cl)_3Mg(THF)_2\}_2$, 7.6. An orange crystal of approximate dimensions 0.101 x 0.119 x 0.201 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁷ program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time). The raw frame data was processed using SAINT⁵⁸ and SADABS⁵⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁵ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about an inversion center. There was a molecule of toluene present that was disordered and included using multiple components, partial site-occupancy-

factors, geometric (DFIX, DANG, SADI, FLAT), and displacement (SIMU) constraints. There was also another molecule of toluene that was located about an inversion center and included using negative parts, partial site-occupancy-factors, geometric (DFIX, DANG, SADI, FLAT), and displacement (SIMU) constraints. Least-squares analysis yielded $wR2 = 0.0826$ and $Goof = 1.023$ for 514 variables refined against 7584 data ($0.82 \text{ \AA}$), $R1 = 0.0324$ for those 6557 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]_2\text{UCl}_2$, 7.7. A purple crystal of approximate dimensions $0.094 \times 0.229 \times 0.337$ mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁷ program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time). The raw frame data was processed using SAINT⁵⁸ and SADABS⁵⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁵ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were two molecules of the formula unit and two molecules of tetrahydrofuran (THF) present. One molecule of THF was included using displacement constraints (SIMU). The other molecule of THF was included using multiple parts, partial site-occupancy-factors, geometric (DFIX, DANG, SADI, RIGU), and displacement constraints (SIMU). Least-squares analysis yielded $wR2 = 0.0745$ and $Goof = 1.042$ for 835 variables refined against 22103 data ($0.70 \text{ \AA}$), $R1 = 0.0348$ for those 17847 data with $I > 2.0\sigma(I)$.

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Chapter 8:

Synthesis and Structure of Heteroleptic $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ Uranium(III) Complexes

INTRODUCTION[†]

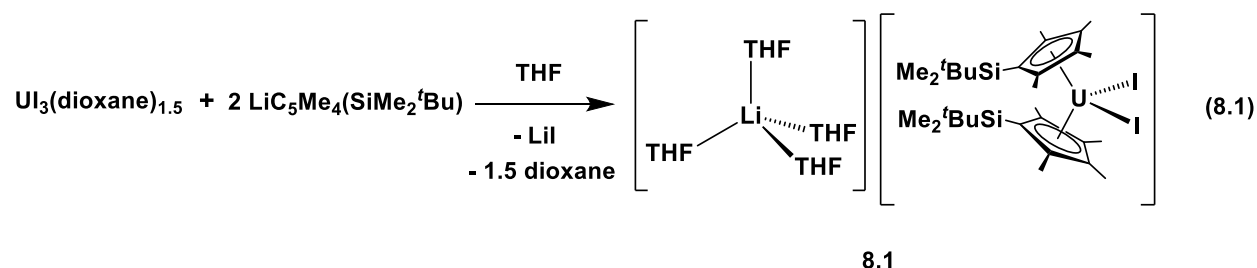
The metallocene chemistry of uranium has been dominated by the $(\text{C}_5\text{Me}_5)^{1-}$ ligand for decades.¹⁻¹⁰ Only a few variations of this peralkylated ligand have been investigated with uranium in the past, such as $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]^{1-}$,¹¹ $(\text{C}_5^i\text{Pr}_5)^{1-}$,^{12,13} $(\text{C}_5\text{Me}_4\text{Et})^{1-}$,¹⁴ $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}=\text{CH}_2)]^{1-}$,¹⁵ $[\text{C}_5(\text{CH}_2\text{Ph})_5]^{1-}$,¹⁶ and $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Ph})]^{1-}$.¹⁷ The $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]^{1-}$ ligand is interesting because it has been shown to have the capacity to form tethered analogs of $(\text{C}_5\text{Me}_5)^{1-}$ complexes.¹¹ For example, the U(IV) dialkyl complex, $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{UMe}_2$, can engage in C–H bond activation to form the tethered dialkyl complex, $[\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2)]_2\text{U}$, concomitant with the elimination of methane.¹¹

Given the interesting chemistry of the $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]^{1-}$ ligand^{11,18,19} and in hopes of generating more soluble uranium complexes, the syntheses of uranium complexes containing the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand²⁰⁻²³ which have not been previously investigated with the actinide elements were investigated. In this Chapter, the synthesis of U(III) complexes of the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand, including metallocene iodide, alkyl, and borohydride derivatives is reported. It was found that although this ligand provides greater solubility, its synthetic chemistry with U(III) is significantly more complicated than that of the $(\text{C}_5\text{Me}_5)^{1-}$ analogs.

[†] Portions of this Chapter have been published: Nguyen, J. Q.; Nachtigall, O.; Ryan, A. J.; Turpin, B. N.; Ziller, J. W.; Evans, W. J. Synthesis and Structure of Heteroleptic $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ Uranium(III) Complexes. *Organometallics* **2024**, *43*, 2767–2776. DOI: 10.1021/acs.organomet.4c00325

RESULTS

Synthesis of $[\text{Li}(\text{THF})_4][\{\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})\}_2\text{UI}_2\}$, **8.1.** The reaction between 2 equiv of the previously published lithium cyclopentadienyl reagent, $\text{LiC}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})$,²⁰ with $\text{UI}_3(\text{dioxane})_{1.5}$ ²⁴ yielded the ionic salt, $[\text{Li}(\text{THF})_4][\{\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})\}_2\text{UI}_2]$, **8.1**, in 44% crystalline yield, eq 8.1. Compound **8.1** can also be prepared using UI_3 ²⁵ and $\text{UI}_3(\text{THF})_4$.²⁶



Complex **8.1** is highly soluble in nonpolar organic solvents and tends to form oils upon removal of solvent. Despite this, green X-ray quality crystals of **8.1** were obtained from concentrated hexane solutions stored at $-35\text{ }^\circ\text{C}$ although they easily dissolve in the presence of residual amounts of solvents upon warming to room temperature.

Several X-ray diffraction studies of **8.1**, Figure 8.1, showed it forms several polymorphs. Three different unit cells and two different space groups were identified for compound **8.1**. Two of the unit cells identified for complex **8.1** yielded structural solutions in the triclinic space group, $P\bar{1}$, with two molecules in the asymmetric unit in both cases. Although both of the data sets confirmed the connectivity of **8.1**, only one of them yielded structural data of sufficient quality to discuss detailed metrical parameters. In contrast, the third unit cell identified for **8.1** yielded a solution in the monoclinic space group, $P2_1/n$, with one molecule in the asymmetric unit.

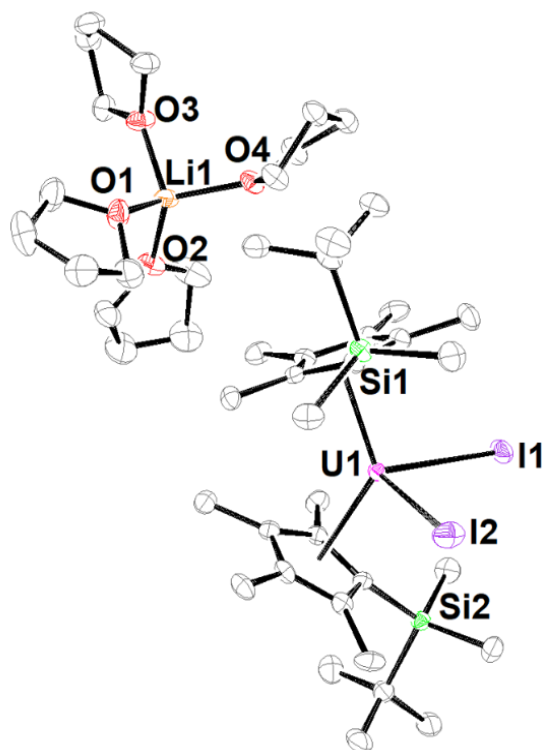


Figure 8.1. Molecular structure of $[\text{Li}(\text{THF})_4][\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2\text{UI}_2]$, **8.1**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are not shown for clarity.

Complex **8.1** is a classic monometallic U(III) bent metallocene with two terminal iodide ligands similar to the previously reported U(III) complexes of the $(\text{C}_5\text{Me}_5)^{1-}$ ligand, namely $[\text{Li}(\text{THF})_4][(\text{C}_5\text{Me}_5)_2\text{UI}_2]$ and $[\text{K}(2.2.2\text{-cryptand})][(\text{C}_5\text{Me}_5)_2\text{UI}_2]$.²⁷ The anion and cation are well separated in the crystal structure of **8.1** and the Li atom does not bridge to the iodide ligands as found for $[\text{Li}(\text{THF})_3][(\text{C}_5\text{Me}_5)_2\text{UI}(\mu\text{-I})]$.²⁷ Selected metrical data for **8.1** are summarized in Table 8.1 below along with the other complexes described in this Chapter.

Table 8.1. Selected Bond Distances (Å) and Angles (°) for $[\text{Li}(\text{THF})_4][\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2\text{UI}_2]$,

8.1,	$[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2\text{UI}(\text{THF})$,	8.2,	$[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})\text{UI}_2(\text{THF})_3$,	8.3,
	$[\text{Me}_4\text{C}_5(\text{SiMe}_2)\text{O}(\text{SiMe}_2)\text{C}_5\text{Me}_4]\text{UI}(\text{THF})$,	8.4,	$[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2\text{UI}_2$,	8.5,

$[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{U}[\text{CH}(\text{SiMe}_3)_2]$, **8.6**, $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{UI}_2\text{Li}(\text{THF})_2$, **8.7**,
 $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{U}(\text{BH}_4)(\text{THF})$, **8.8**. Cnt is defined as the cyclopentadienyl ring centroid.

Compound	U–Cnt	U–I	U–O	Cnt–U–Cnt
$[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]\text{UI}_2(\text{THF})_3$, 8.3	2.519	3.134(5), 3.156(6)	2.150(4), 2.556(4), 2.628(4)	-
$[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{UI}(\text{THF})$, 8.2	2.509, 2.510	3.086(3)	2.498(2)	132.6
$[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{U}(\text{BH}_4)(\text{THF})$, 8.8	2.530, 2.532	-	2.510(2)	130.7
$[\text{Me}_4\text{C}_5(\text{SiMe}_2)\text{O}(\text{SiMe}_2)\text{C}_5\text{Me}_4]\text{UI}(\text{THF})$, 8.4	2.490, 2.494	3.095(9)	2.483(4)	136.2
$[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{U}[\text{CH}(\text{SiMe}_3)_2]$, 8.6	2.522, 2.534	-	-	133.8
$[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{U}(\mu\text{-I})_2\text{Li}(\text{THF})_2$, 8.7	2.519, 2.519	3.119(6), 3.142(6)	-	134.6
$[\text{Li}(\text{THF})_4][\{\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})\}_2\text{UI}_2]$, 8.1	2.535, ^a	3.082(4), ^a	-	131.2, ^a
	2.536, ^a	3.111(3), ^a		131.7, ^b
	2.528, ^b	3.115(8), ^b		132.5 ^c
	2.531, ^b	3.123(8), ^b		
	2.536, ^c	3.104(8), ^c		
	2.537 ^c	3.118(7) ^c		
$[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{UI}_2$, 8.5	2.467, 2.467	2.970(1), 2.976(1)	-	137.1

Compound	I–U–I	O–U–O	Cnt–U–I	Cnt–U– O	O–U–I

[C₅Me₄(SiMe₂'Bu)]UI₂(THF)₃, 8.3	146.93(2)	74.0(2), 153.6(2), 79.6(1)	110.7	174.0, 104.1, 102.2	88.8(1), 83.7(1), 74.1(1), 86.5(1), 86.1(1), 73.1(1)
[C₅Me₄(SiMe₂'Bu)]₂UI(THF), 8.2	-	-	110.6, 108.3	102.3, 104.9	88.50(5)
[C₅Me₄(SiMe₂'Bu)]₂U(BH₄)(THF), 8.8	-	-	-	105.3	-
[Me₄C₅(SiMe₂)O(SiMe₂)C₅Me₄]UI(THF), 8.4	-	-	106.1, 106.8	103.9, 104.1	90.22(9)
[C₅Me₄(SiMe₂'Bu)]₂U[CH(SiMe₃)₂], 8.6	-	-	-	-	-
[C₅Me₄(SiMe₂'Bu)]₂U(μ-I)₂Li(THF)₂, 8.7	85.41(2)	-	113.3, 101.1, 106.1, 103.7	-	-
[Li(THF)₄][{C₅Me₄(SiMe₂'Bu)}₂UI₂], 8.1	92.60(1), ^a 91.23(2), ^b 89.94(2) ^c	-	102.1, ^a 108.8, ^a 110.5, ^a 105.0, ^a 108.3, ^b 104.6, ^b 109.3, ^b 102.6, ^b 108.3, ^c 106.7, ^c 108.7, ^c 103.6 ^c	-	-
[C₅Me₄(SiMe₂'Bu)]₂UI₂, 8.5	93.20(4)	-	102.0, 102.0, 106.8, 106.8	-	-

^a from the {[C₅Me₄(SiMe₂'Bu)]₂UI₂}¹⁻ unit of the crystal that crystallized in the *P*2₁/*n* space group.

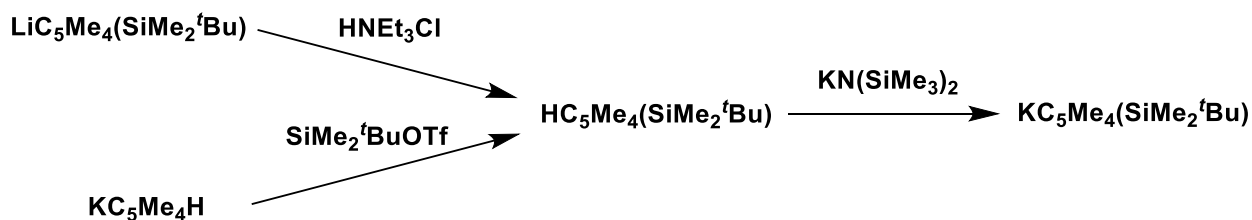
^b from one of the {[C₅Me₄(SiMe₂'Bu)]₂UI₂}¹⁻ units of the crystal that crystallized in the *P* $\bar{1}$ space group.

^c from the other {[C₅Me₄(SiMe₂'Bu)]₂UI₂}¹⁻ unit of the crystal that crystallized in the *P* $\bar{1}$ space group.

Complex **8.1** has U–Cnt distances (Cnt = cyclopentadienyl ring centroid) that range from 2.528 to 2.537 Å, which are similar to the 2.515 to 2.521 Å range of the (C₅Me₅)¹⁻ analogs,

$[\text{Li}(\text{THF})_4][(\text{C}_5\text{Me}_5)_2\text{UI}_2]$ and $[\text{K}(2.2.2\text{-cryptand})][(\text{C}_5\text{Me}_5)_2\text{UI}_2]$.²⁷ The Cnt–U–Cnt angles of **8.1** range from 131.2° to 132.5° whereas the analogous angles in $[\text{Li}(\text{THF})_4][(\text{C}_5\text{Me}_5)_2\text{UI}_2]$ and $[\text{K}(2.2.2\text{-cryptand})][(\text{C}_5\text{Me}_5)_2\text{UI}_2]$ are 133.7° and 133.4°, respectively.²⁷ The *tert*-butyl substituent attached to the silyl group in each cyclopentadienyl ring points away from the interior of the metallocene wedge presumably to minimize steric repulsion. This is observed in all the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ complexes in this Chapter.

Switching from $\text{LiC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ to $\text{KC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$. In order to obtain alkali-metal-free uranium complexes of the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand, use of the potassium salt of the ligand was examined. $\text{KC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ was obtained via the deprotonation of $\text{HC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ with $\text{KN}(\text{SiMe}_3)_2$ in diethyl ether and characterized by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ spectroscopy. Since the precursor for this reaction $\text{HC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ cannot be synthesized directly from $\text{KC}_5\text{Me}_4\text{H}$ and $\text{SiMe}_2'\text{BuCl}$, it was synthesized either by protonating $\text{LiC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ with HNEt_3Cl or by the reaction between *tert*-butyldimethylsilyl trifluoromethanesulfonate $\text{tBuMe}_2\text{SiOTf}$ and $\text{KC}_5\text{Me}_4\text{H}$, Scheme 8.1.



Scheme 8.1. Synthesis of $\text{KC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ via two different routes.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]\text{UI}_2(\text{THF})_3$, **8.2, and $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{UI}(\text{THF})$, **8.3**.**

Unlike the reaction described above between UI_3 , $\text{UI}_3(\text{dioxane})_{1.5}$, or $\text{UI}_3(\text{THF})_4$ and 2 equiv of $\text{LiC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$, the reaction between 2 equiv of $\text{KC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ and $\text{UI}_3(\text{dioxane})_{1.5}$ in THF generated the neutral metallocene halide, $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{UI}(\text{THF})$, **8.2**, in 51% crystalline yield, Figure 8.2, eq 8.2, as the major product.

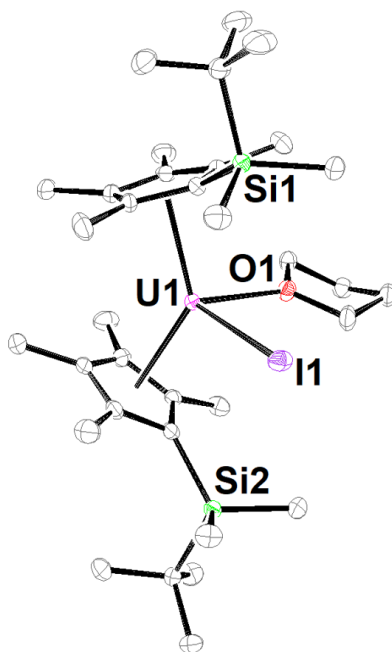
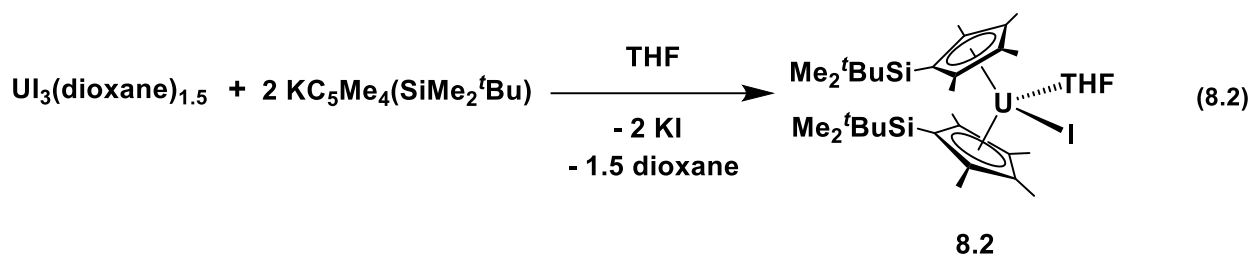


Figure 8.2. Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{UI}(\text{THF})$, **8.2**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are not shown for clarity.

X-ray quality crystals of complex **8.2** were grown from a concentrated toluene solution of **8.2** layered under hexane stored at $-35\text{ }^\circ\text{C}$. Complex **8.2** crystallizes in the $P2_1/n$ space group with one molecule in the asymmetric unit and is a bent U(III) metallocene iodide complex solvated by one molecule of THF. This type of structure has been observed previously in the analogous U(III) complexes, $(\text{C}_5\text{Me}_5)_2\text{UI}(\text{THF})$,²⁷ $(\text{C}_5\text{Me}_4\text{Et})_2\text{UI}(\text{THF})$,¹⁴ $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}=\text{CH}_2)]_2\text{UI}(\text{THF})$,¹⁵ and $[\text{C}_5(\text{CH}_2\text{Ph})]_2\text{UI}(\text{THF})$.¹⁶ In **8.2**, the 2.509 and 2.510 Å U–Cnt, 2.498(2) U–O, and 3.086(3) U–I distances as well as the 132.6° Cnt–U–Cnt angle

are all within a typical range for a U(III) bent metallocene iodide complex solvated by a THF molecule, Table 8.1.^{14–16,27}

When 1 rather than 2 equiv of $\text{KC}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})$ was used in the reaction with $\text{UI}_3(\text{dioxane})_{1.5}$, the neutral, monocyclopentadienyl complex, $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]\text{UI}_2(\text{THF})_3$, **8.3**, was isolated in 60% crystalline yield and identified by X-ray crystallography, Figure 8.3, eq 8.3.

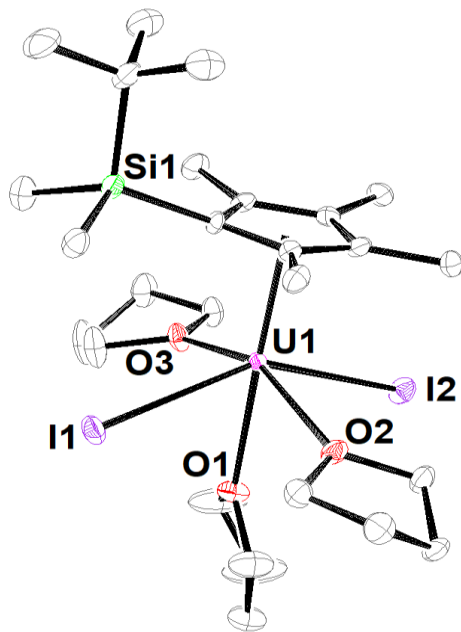
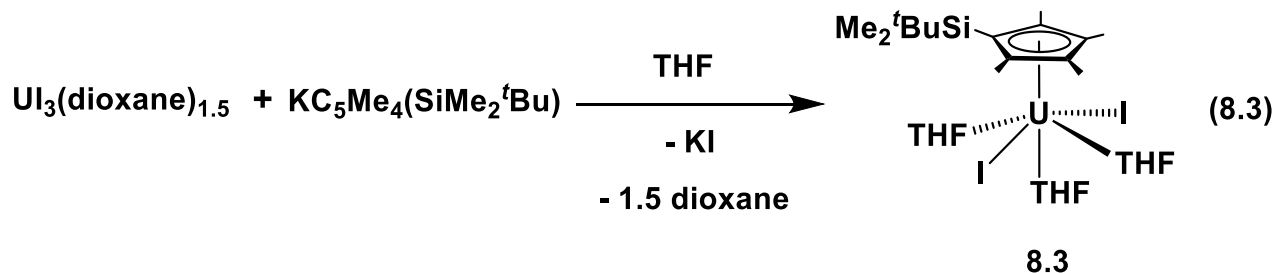


Figure 8.3. Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]\text{UI}_2(\text{THF})_3$, **8.3**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are not shown for clarity.

Complex **8.3** crystallizes in the $P\bar{1}$ space group with one molecule in the asymmetric unit. The uranium metal center in **8.3** is coordinated to one η^5 -bonded $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]^{1-}$ ligand, two iodide ligands, and three THF molecules for a formal coordination number of eight. The

cyclopentadienyl ring centroid and the other five ligands form a distorted octahedral structure with the iodide ligands trans to each other. Interestingly, the structure of **8.3** has the same arrangement of ligands and solvent molecules as the previously reported mono-(C₅Me₅)¹⁻ analogs, (C₅Me₅)UI₂(THF)₃ and (C₅Me₅)UI₂(py)₃ (py = pyridine).²⁸

Inadvertent Synthesis of [Me₄C₅(SiMe₂)O(SiMe₂)C₅Me₄]UI(THF), 8.4. In one reaction between 2 equiv of KC₅Me₄(SiMe₂'Bu) and UI₃(dioxane)_{1.5}, not only was the expected product, [C₅Me₄(SiMe₂'Bu)]₂UI(THF), **8.2**, isolated and crystallographically characterized, but an *ansa*-metallocene impurity, [Me₄C₅(SiMe₂)O(SiMe₂)C₅Me₄]UI(THF), **8.4**, Figure 8.4, was isolated in very low yield and also identified by X-ray crystallography. Complex **8.4** is included in this Chapter to document that such a species could form in these reactions and be isolated. Retrospectively, the origin of **8.4** was evidently from the synthesis of HC₅Me₄(SiMe₂Cl) from KC₅Me₄H and Me₂SiCl₂ that was performed in diethyl ether containing an approximate water content of 100 ppm as determined by subsequent Karl Fischer titration. Evidently, an oxygen-bridged *ansa*-type ligand precursor, HMe₄C₅(SiMe₂)O(SiMe₂)C₅Me₄H, was formed as a byproduct. Treatment of this mixture with 2 equiv of 'BuLi followed by HNEt₃Cl and KN(SiMe₃)₂ generated the desired KC₅Me₄(SiMe₂'Bu), but apparently, the dipotassium salt of the impurity, K₂Me₄C₅(SiMe₂)O(SiMe₂)C₅Me₄, was present since reaction with UI₃(dioxane)_{1.5} gave X-ray quality crystals of **8.4**.

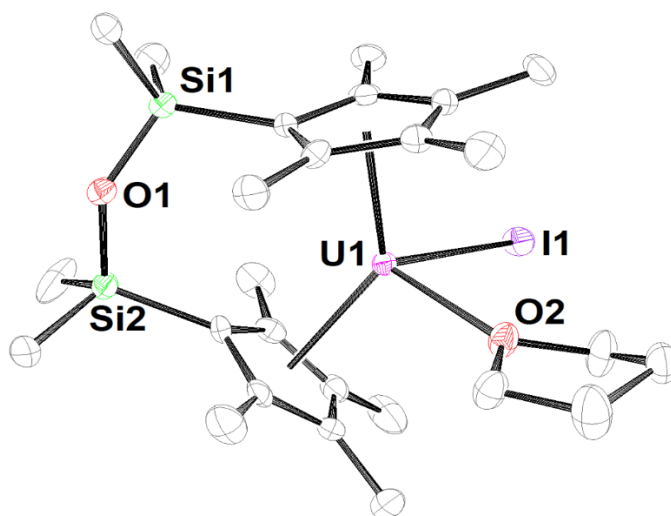


Figure 8.4. Molecular structure of $[\text{Me}_4\text{C}_5(\text{SiMe}_2)\text{O}(\text{SiMe}_2)\text{C}_5\text{Me}_4]\text{UI}(\text{THF})$, **8.4**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are not shown for clarity.

Complex **8.4** crystallizes in the monoclinic $P2_1/n$ space group with one molecule in the asymmetric unit. The uranium metal center is coordinated to both cyclopentadienyl rings of the oxygen-bridged *ansa*-dicyclopentadienyl ligand in an η^5 fashion, one iodide ligand, and one THF molecule, analogous to **8.2**. Although **8.4** is a U(III) bent metallocene very similar to **8.2** with comparable U–C_{nt}, U–O, and U–I distances and C_{nt}–U–C_{nt} angles, Table 8.1, the oxygen-bridged *ansa*-dicyclopentadienyl ligand has not been previously observed with the *f*-elements. However, three other complexes have been reported with this ligand, namely $[\text{Me}_4\text{C}_5(\text{SiMe}_2)\text{O}(\text{SiMe}_2)\text{C}_5\text{Me}_4]\text{Fe}$,²⁹ $[\text{Me}_4\text{C}_5(\text{SiMe}_2)\text{O}(\text{SiMe}_2)\text{C}_5\text{Me}_4]\text{TiCl}_2$,³⁰ and $[\text{Me}_4\text{C}_5(\text{SiMe}_2)\text{O}(\text{SiMe}_2)\text{C}_5\text{Me}_4]\text{Ti}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)$.³¹

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{tBu})]_2\text{UI}_2$, **8.5.** While complexes **8.1**, **8.3**, and **8.4** as well as the $(\text{C}_5\text{Me}_5)^{1-}$ complex, $(\text{C}_5\text{Me}_5)_2\text{UI}(\text{THF})$, can be covered with Paratone or Fomblin oil under an argon atmosphere and then handled at room temperature in air for several minutes, complex **8.2** quickly oxidized under the same conditions. As soon as the oil-protected compound was exposed to air, the green crystals turned into a red-purple liquid inside the oil. From this liquid inside the

oil, $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{UI}_2$, **8.5**, crystallized as purple plates within a few minutes! These plates were identified by X-ray diffraction and crystallize in the monoclinic space group, $C2/c$, Figure 8.5 (left). The poor quality of the X-ray diffraction data obtained from the crystal grown this way precluded a detailed discussion of its metrical parameters, but better quality data were collected when **8.5** was synthesized rationally in 31% crystalline yield via salt metathesis from $\text{UI}_4(\text{dioxane})_2$ ²⁴ and 2 equiv of $\text{KC}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})$, eq 8.4. Interestingly, the product of this direct synthesis crystallizes from toluene in the orthorhombic space group, $Pnma$, with an orientation of ligands different from the $C2/c$ structure, Figure 8.5 (right).

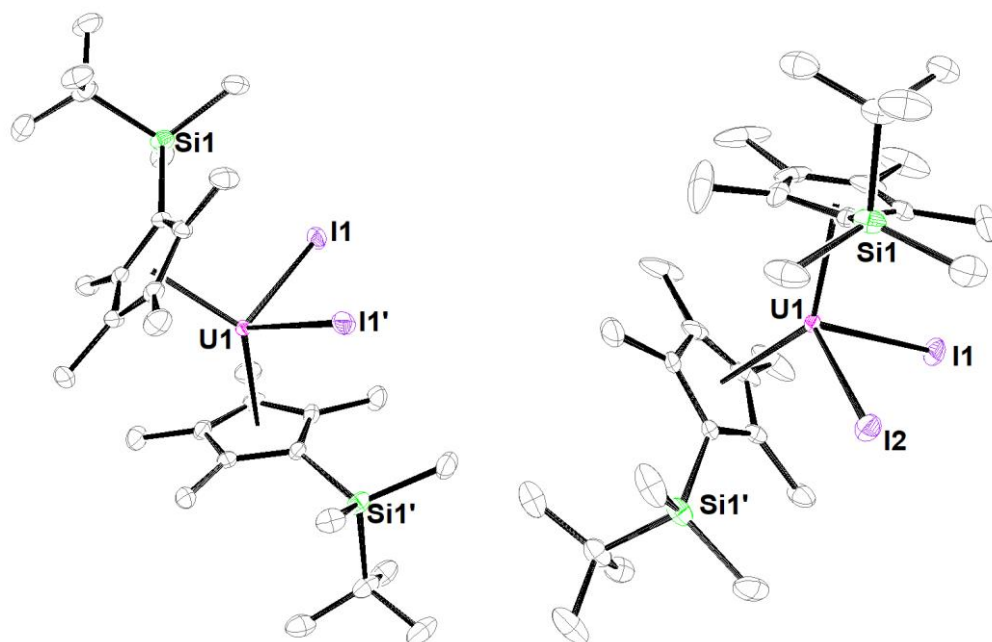
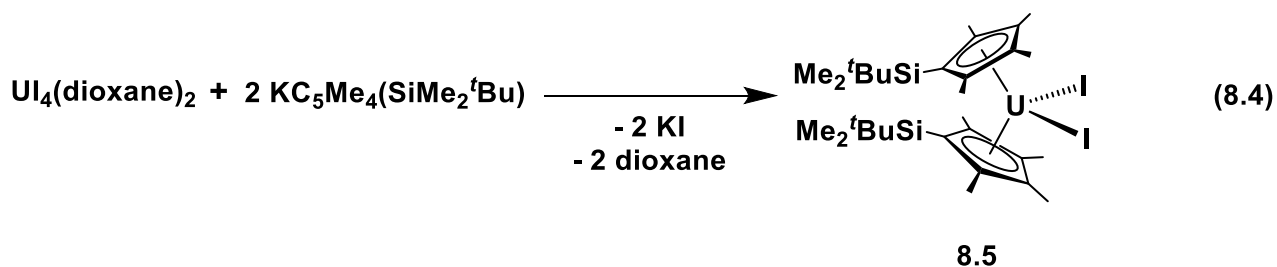


Figure 8.5. (Left) Connectivity plot of $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{UI}_2$, **8.5**, crystallized in $C2/c$. (Right) Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{UI}_2$, **8.5**, crystallized in $Pnma$. Thermal ellipsoids are

drawn at the 50% probability level and hydrogen atoms are not shown for clarity for both crystal structures.

Complex **8.5** has metrical parameters comparable to previously reported U(IV) bent metallocene diiodide complexes, Table 8.1.^{16,32–36} In comparison to the U(III) analog **8.1**, which has an average U–Cnt distance of 2.534 Å, the average U–Cnt of **8.5** is shorter at 2.467 Å, consistent with the smaller ionic radius of U(IV) versus U(III). The polymorphism of uranium complexes of the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand is further shown by the fact that **8.5** can crystallize in at least two different unit cells. In the *C2/c* structure, the molecule lies about a 2-fold rotation axis that coincides with the uranium metal center and bisects the I–U–I angle. In the *Pnma* structure, the molecule lies about a mirror plane that is coplanar with the uranium metal center and two iodide ligands.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{U}[\text{CH}(\text{SiMe}_3)_2]$, **8.6, and $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{U}(\mu\text{-I})_2\text{Li}(\text{THF})_2$, **8.7**.** The reactivity of **8.2** with the large organolithium reagent, $\text{LiCH}(\text{SiMe}_3)_2$, was studied to determine if the bulky silyl groups would lead to a more stable U(III) complex. Treatment of a green solution of **8.2** in diethyl ether with 0.5 equiv of $\text{LiCH}(\text{SiMe}_3)_2$ immediately produced a brown suspension upon mixing. After workup, both the alkyl product, $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{U}[\text{CH}(\text{SiMe}_3)_2]$, **8.6**, and the diiodide lithium “ate” salt, $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{U}(\mu\text{-I})_2\text{Li}(\text{THF})_2$, **8.7**, were isolated in very low yield from the reaction mixture and identified crystallographically, eq 8.5. Compound **8.6** crystallizes in the *P2₁/c* space group, is extremely soluble in many solvents, and could only be isolated as a few small crystals by extraction of the crude product with $(\text{Me}_3\text{Si})_2\text{O}$ followed by concentration and storage at $-35\text{ }^\circ\text{C}$, Figure 8.6.

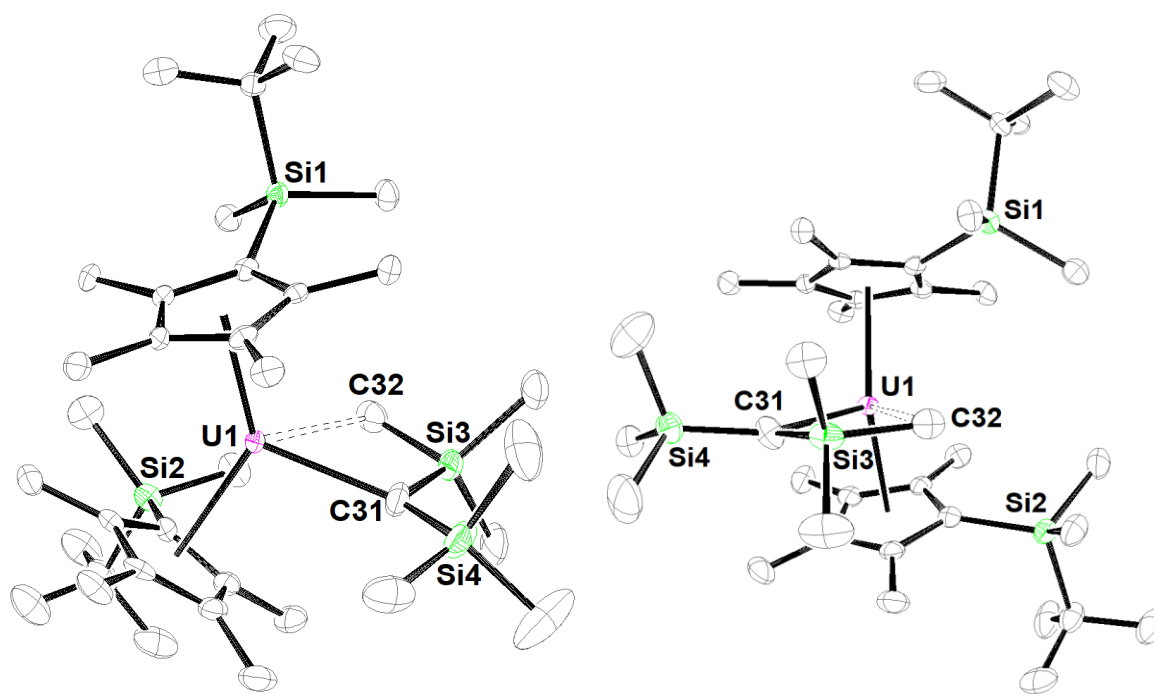
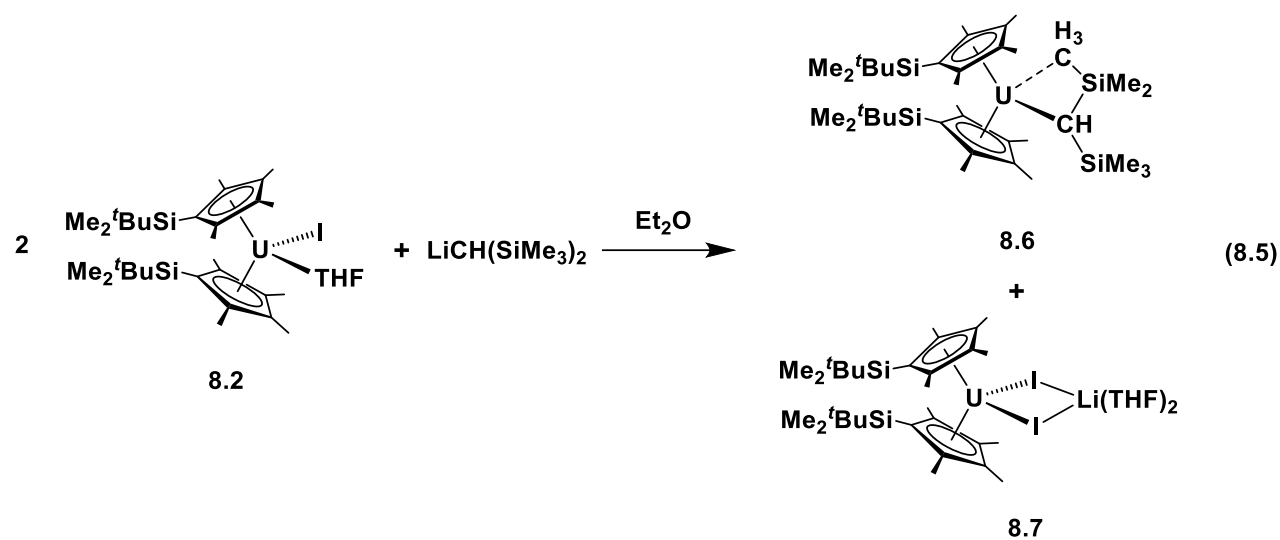


Figure 8.6. (Left) Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{U}[\text{CH}(\text{SiMe}_3)_2]$, **8.6**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are not shown for clarity. (Right) Equatorial view of the attractive interaction between U1 and C32 in **8.6**.

The bis(trimethylsilyl)methyl ligand is not coordinated symmetrically about the uranium metal center in **8.6**. An agostic interaction between one of the methyl groups of a trimethylsilyl group and the uranium metal center in **8.6** was suggested by a U–C(32) distance of 2.883(4) Å and

a close U–H(32A) distance of 2.544 Å. This is pictorially shown in Figure 8.6 where one of the trimethylsilyl groups is bent toward the uranium metal center such that C32 approaches an empty coordination site on the uranium atom. As a result, the U1–C31–Si3 angle is 99.0(2)° whereas the U1–C31–Si4 is 138.9(2)°. A similar interaction is found in the (C₅Me₅)^{1–} analog, (C₅Me₅)₂U[CH(SiMe₃)₂], which for comparison, has a close U–C distance of 2.844(9) Å and a close U–H distance of 2.504 Å.³⁷ This kind of interaction between an *f*-element and a silyl group has been well documented in organometallic and inorganic complexes.^{38–41}

After complex **8.6** was separated by an extraction with (Me₃Si)₂O, a few small crystals of **8.7** were obtained from crystallization in hexane at –35 °C, Figure 8.7. Complex **8.7** crystallizes in the *P*2₁/*n* space group and is a variation of [Li(THF)₄]{[C₅Me₄(SiMe₂'Bu)]₂UI₂}, **8.1**, with two less THF molecules per formula unit.

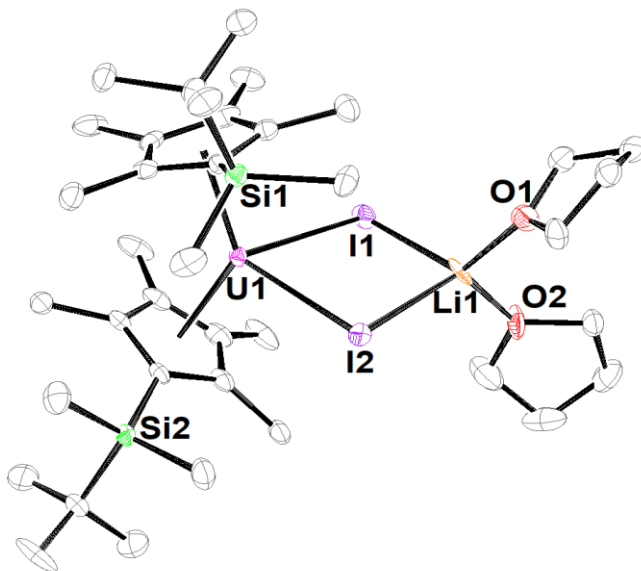


Figure 8.7. Molecular structure of [C₅Me₄(SiMe₂'Bu)]₂U(μ-I)₂Li(THF)₂, **8.7**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are not shown for clarity.

[C₅Me₄(SiMe₂'Bu)]₂U(BH₄)(THF), **8.8**. Previously, Arnold, Love, and coworkers investigated borohydride complexes as U(III) precursors due to synthetic difficulties with the

analogous uranium iodides.⁴² Since $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{UI}(\text{THF})$, **8.2**, is highly sensitive toward oxidation, the synthesis of a borohydride analog was also pursued to test if it would be more stable. $\text{U}(\text{BH}_4)_3(\text{THF})_2$ ^{42,43} reacts with 2 equiv of $\text{KC}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})$ in THF to form $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{U}(\text{BH}_4)(\text{THF})$, **8.8**, in 64% crystalline yield, Figure 8.8, eq 8.6.

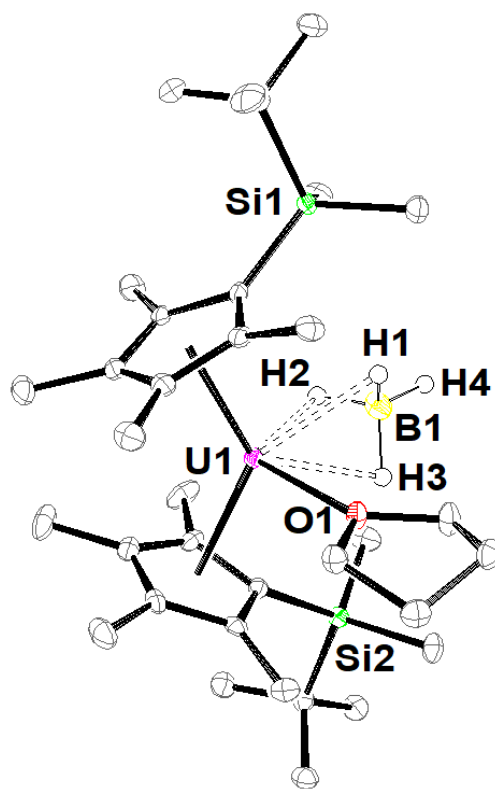
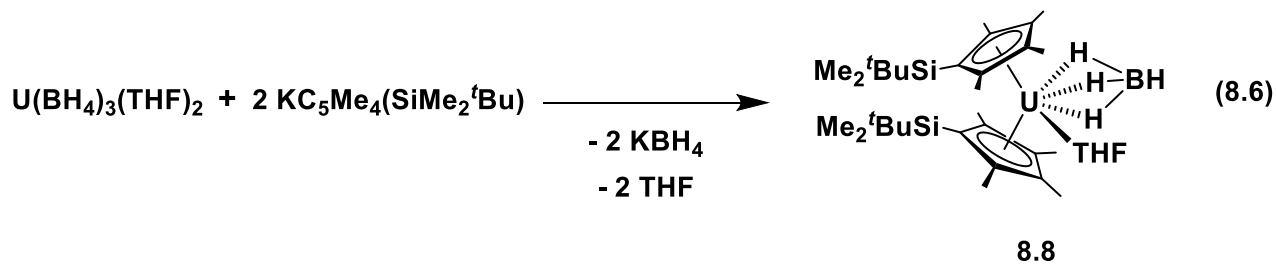


Figure 8.8. Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{U}(\text{BH}_4)(\text{THF})$, **8.8**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms H1, H2, H3, and H4 are shown to convey the tridentate coordination of the borohydride ligand; the rest of the hydrogen atoms are not shown for clarity.

In contrast to complex **8.2**, it was observed that X-ray quality crystals of **8.8** could be handled under Fomblin oil in air for several minutes, suggesting that **8.8** is more stable to oxidation than **8.3**. Complex **8.8** crystallizes in the $P2_1/n$ space group with one molecule in the asymmetric unit when X-ray quality crystals are grown from THF/hexane solutions stored at $-35\text{ }^{\circ}\text{C}$. Like the other complexes presented above, **8.8** is a bent metallocene U(III) complex that is the borohydride analog of **8.2**. In the solid-state, the uranium metal center is coordinated to the borohydride ligand in a tridentate fashion. This was identified by locating H1, H2, and H3 from a difference-Fourier map during the refinement of the crystal structure of **8.8**. The three bridging hydrogens have U–H distances of 2.370(3), 2.475(3), and 2.482(3) Å while the U–B distance is 2.644(3) Å, supporting the notion of tridentate borohydride coordination. Furthermore, the infrared spectrum of **8.8** exhibits a sharp signal at 2423 cm^{-1} and a broad signal at 2235 cm^{-1} , suggesting a tridentate coordination of the borohydride ligand to the uranium metal center in the bulk material.^{44,45}

NMR Analyses. The ^1H NMR spectra of complexes **8.1**, **8.2**, **8.3**, **8.5**, and **8.8** all display resonances corresponding to the ligand protons that are paramagnetically shifted and broadened, consistent with the presence of either a U(III) or U(IV) ion. For each compound, the cyclopentadienyl ligands are equivalent in solution as only one type of cyclopentadienyl environment was observed in each case. While reasonable integrations and assignments can be obtained for complexes **8.1**, **8.3**, and **8.5**, the proton assignments for complexes **8.2** and **8.8** could not be definitively determined. The ^1H NMR spectrum of **8.2** shows six broad resonances that could be attributed to one type of cyclopentadienyl ligand environment and one bound THF molecule. Furthermore, the ^1H NMR spectrum of **8.8** shows seven broad resonances corresponding to one type of cyclopentadienyl ligand environment, one THF molecule, and one borohydride ligand. Attempts to collect $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for complexes **8.1**, **8.2**, **8.3**, **8.5**,

and **8.8** all yielded spectra where no resonances definitively assignable to the paramagnetic uranium complexes were observed. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of complexes **8.1**, **8.2**, **8.3**, **8.5**, and **8.8**, however, all show one resonance, consistent with equivalent cyclopentadienyl ligands in solution. For complexes **8.1**, **8.2**, **8.3**, and **8.8**, which are U(III) complexes, the resonances are observed in the range of -150 to -170 ppm, consistent with previously characterized silyl-substituted cyclopentadienyl U(III) complexes.⁴⁶ The signal for **8.5** is observed at -39.9 ppm, which is in agreement with the similar $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{UCl}_2$, which has an analogous signal at -51 ppm.⁴⁶ The ^{11}B NMR spectrum for the borohydride complex **8.8** exhibits a broad resonance at 82.6 ppm, similar to the previously characterized U(IV) complex $[\text{C}_5\text{H}_4(\text{SiMe}_3)]_3\text{U}(\text{BH}_4)$, which has a resonance at 79.1 ppm.⁴⁷

DISCUSSION

The $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand is viable for the synthesis of uranium(III) metallocene complexes. As anticipated, the presence of the *tert*-butyl substituent on the silyl substituent in the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand significantly increases the solubility of its metal complexes compared to similar $(\text{C}_5\text{Me}_5)^{1-}$ and $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]^{1-}$ analogs. However, as a result, most of the compounds containing two $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligands are challenging to crystallize and purify. Only solvents with very low polarities, such as hexane or $(\text{Me}_3\text{Si})_2\text{O}$ can be used to obtain crystals of **8.1**, **8.3**, **8.5**, **8.6**, or **8.7** and low crystallization temperatures are required. The polymorphism of **8.1** and **8.5** and the fast disintegration of the crystalline structures in the presence of hydrocarbon solvents suggest low lattice energies for U(III) and U(IV) complexes of the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand. Effective packing in the solid state may be hindered by the bulky $\text{SiMe}_2'\text{Bu}$ group with its various possible conformers. This also makes recrystallization, which is essential for the purification of such compounds low yielding.

It is worth noting that attempts to produce good combustion analysis data for complexes **8.1**, **8.2**, **8.3**, and **8.8** typically yielded low carbon and hydrogen values. With C:H ratios that are consistent with each complex's respective empirical formula, the data suggest incomplete combustion. This problem is prevalent throughout organometallic *f*-element chemistry and has been well documented.^{48–53} It is also possible that the discrepancy between the calculated and measured carbon and hydrogen values are due to the bulk purity of complexes **8.1**, **8.2**, **8.3**, and **8.8**, which suggests that purifying U(III) complexes of the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand is relatively difficult.

To avoid the complexation of the alkali metal halide byproducts of salt metatheses with the $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand and uranium iodides, it was necessary to replace the previously used starting material, $\text{LiC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$, with the potassium salt, $\text{KC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$. Effective precipitation of KI in these salt metathesis reactions resulted in the formation of neutral uranium(III) complexes with $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligands rather than anionic complexes. Unexpectedly, a rare *ansa*-metallocene ligand was identified in these studies through the isolation of $[\text{Me}_4\text{C}_5(\text{SiMe}_2)\text{O}(\text{SiMe}_2)\text{C}_5\text{Me}_4]\text{UI}(\text{THF})$, **8.4**.

Although $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{UI}(\text{THF})$, **8.2**, is structurally similar to the $(\text{C}_5\text{Me}_5)^{1-}$ analog the U–Cnt distances are only 0.02 Å longer than in those in $(\text{C}_5\text{Me}_5)_2\text{UI}(\text{THF})$. Evidently, the larger size of the $\text{SiMe}_2'\text{Bu}$ substituent compared to Me, does not affect the U–Cnt parameter. The fact that the *tert*-butyl group always points away from the metallocene wedge minimizes its contribution to increased steric crowding. Although this orients the two methyl groups of the $\text{SiMe}_2'\text{Bu}$ substituent toward the wedge, they are attached to a silicon atom with a longer distance to the ring carbon than a methyl group. Despite these structural similarities, complex **8.2** oxidizes readily to complex **8.5**, whereas crystals of $(\text{C}_5\text{Me}_5)_2\text{UI}(\text{THF})$, can be handled for several minutes

in air when covered in Paratone oil without decomposition. Hence, subtle variations in the cyclopentadienyl ligand substitution can have a major impact on stability.

CONCLUSIONS

The bulkier cyclopentadienyl ligand, $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$, was investigated as a source of analogs for the commonly investigated $(\text{C}_5\text{Me}_5)^{1-}$ uranium complexes. Syntheses starting with the known $\text{LiC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ reagent repeatedly gave the salt, $[\text{Li}(\text{THF})_4]\{[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{UI}_2\}$, **8.1**, but the synthesis of $\text{KC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ provided a reagent that allowed for formation of the neutral $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{UI}(\text{THF})$, **8.2**. As expected, the $\text{SiMe}_2'\text{Bu}$ substituent increases the solubility of these metal complexes in organic solvents. However, it also apparently fosters polymorphism in several of its crystalline uranium complexes, making crystallization much more challenging.

EXPERIMENTAL DETAILS

Caution! ^{238}U is radioactive and an α emitter with a half-life of approximately 4.5×10^9 years. Studies were conducted in a laboratory with appropriate radiological safety equipment. All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere.

Solvents were sparged with UHP (99.999%) argon before drying and collection using an S2 Grubbs-type solvent purification system⁵⁴ (JC Meyer) and were stored over activated molecular sieves overnight prior to use. Deuterated NMR solvents were dried over molecular sieves and degassed by three freeze–pump–thaw cycles before use. NMR spectra were recorded on a Bruker AVANCE600 or GN500 MHz spectrometer at 298 K unless otherwise stated. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced internally to residual protio-solvent resonances and

$^{29}\text{Si}\{^1\text{H}\}$ and ^{11}B NMR spectra were referenced externally to SiMe_4 and $\text{BF}_3(\text{Et}_2\text{O})$, respectively. Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR under an argon atmosphere. Bis(trimethylsilyl)ether was degassed and dried by overnight storage over activated molecular sieves prior to use. Triethylammonium chloride was purchased from Sigma-Aldrich and was dried under reduced pressure overnight prior to use. *Tert*-butyldimethylsilyl triflate was purchased from TCI Chemicals and used as received. Potassium bis(trimethylsilyl)amide (95%) was purchased from Sigma-Aldrich and recrystallized from toluene prior to use. $\text{LiC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$,²⁰ $\text{UI}_3(\text{dioxane})_{1.5}$,²⁴ $\text{UI}_4(\text{dioxane})_2$,²⁴ UI_3 ,²⁵ $\text{UI}_3(\text{THF})_4$,²⁶ $\text{U}(\text{BH}_4)_3(\text{THF})_2$,^{42,43} and $\text{LiCH}(\text{SiMe}_3)_2$ ⁵⁵ were synthesized according to literature procedures.

Synthesis of $\text{HC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ from $\text{KC}_5\text{Me}_4\text{H}$ and ${}^t\text{BuMe}_2\text{SiOTf}$. In a 100 mL round-bottom flask, a solution of ${}^t\text{BuMe}_2\text{SiOTf}$ (1.13 g, 4.27 mmol) in Et_2O (ca. 10 mL) was added dropwise to a stirred suspension of $\text{KC}_5\text{Me}_4\text{H}$ (720 mg, 4.49 mmol) in Et_2O (ca. 30 mL) over a period of 5 min at room temperature. The resulting mixture was allowed to stir at room temperature overnight before solvent was removed under reduced pressure to yield a colorless residue. The product was extracted into hexane (ca. 15 mL) and was centrifuged then filtered through a pipet packed with Kimwipe tissue to yield a pale-yellow solution. Solvent was removed under reduced pressure to yield $\text{HC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ as a pale-yellow oil (0.923 g, 3.90 mmol, 91%). ^1H NMR (600 MHz, C_6D_6): δ 2.61 (s, 1H, $\text{HC}_5\text{Me}_4\text{SiR}_3$), 1.95 (s, 6H, $\text{HC}_5\text{Me}_4\text{SiR}_3$), 1.78 (s, 6H, $\text{HC}_5\text{Me}_4\text{SiR}_3$), 0.80 (s, 9H, $\text{SiMe}_2'\text{Bu}$), 0.15 (s, 6H, $\text{SiMe}_2'\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, C_6D_6): δ 135.5 (alkene C of $\text{C}_5\text{Me}_4\text{SiR}_3$), 134.2 (alkene C of $\text{C}_5\text{Me}_4\text{SiR}_3$), 54.8 (allylic C of $\text{C}_5\text{Me}_4\text{SiR}_3$), 27.4 (CMe_3), 19.4 (CMe_3), 15.2 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 11.5 ($\text{C}_5\text{Me}_4\text{SiR}_3$), -2.7 ($\text{SiMe}_2'\text{Bu}$). ^{29}Si NMR (119 MHz, C_6D_6): δ -6.9 ($\text{SiMe}_2'\text{Bu}$). IR: 2926m, 2855m, 1472w, 1461w, 1388w, 1359w, 1249m, 1217w, 1111w, 1049w, 986w, 824vs, 760s, 688w, 680m, 667m cm^{-1} .

Synthesis of $\text{HC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ from $\text{LiC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ and HNEt_3Cl . In a 100 mL round-bottom flask, solid triethylammonium chloride (1.42 g, 10.3 mmol) was slowly added to a solution of $\text{LiC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ (2.50 g, 10.3 mmol) in diethyl ether (ca. 50 mL) at room temperature. After stirring overnight, the mixture was filtered through a medium porosity frit to remove insoluble solids, which were further washed with diethyl ether (ca. 2×5 mL). The washes were then collected and combined with the filtrate. Removal of solvent from the combined solutions under reduced pressure yielded the product $\text{HC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ as a colorless oil (2.39 g, 10.1 mmol, 98%).

Synthesis of $\text{KC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$. In a 100 mL round-bottom flask, solid potassium bis(trimethylsilyl)amide (3.40 g, 17.0 mmol) was slowly added to a solution of $\text{HC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ (2.00 g, 8.46 mmol) in diethyl ether (ca. 50 mL) at room temperature. After stirring overnight, colorless precipitate was present, and the mixture was filtered through a medium porosity frit. The solids were then washed with diethyl ether (ca. 2×10 mL) and subsequently dried under reduced pressure to yield the product as a colorless powder (1.97 g, 7.18 mmol, 85%). ^1H NMR (500 MHz, $\text{THF}-d_8$): δ 2.08 (s, 6H, $\text{C}_5\text{Me}_4\text{SiR}_3$), 1.91 (s, 6H, $\text{C}_5\text{Me}_4\text{SiR}_3$), 0.83 (s, 9H, $\text{SiMe}_2'\text{Bu}$), 0.16 (s, 6H, $\text{SiMe}_2'\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{THF}-d_8$): δ 118.0 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 112.1 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 98.7 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 27.6 (CMe_3), 20.1 (CMe_3), 15.0 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 11.4 ($\text{C}_5\text{Me}_4\text{SiR}_3$), -0.6 ($\text{SiMe}_2'\text{Bu}$). ^{29}Si NMR (119 MHz, $\text{THF}-d_8$): δ -4.7 ($\text{SiMe}_2'\text{Bu}$). IR: 2950m, 2920m, 2887m, 2849s, 2727w, 1459w, 1383w, 1355w, 1312s, 1246s, 1130w, 1006m, 816vs, 803vs, 754s, 665s cm^{-1} . Anal. Calcd. for $\text{C}_{15}\text{H}_{27}\text{SiK}$: C, 65.62; H, 9.91. Found: C, 69.73; H, 10.73. C, 67.95; H, 10.50. C, 68.51; H, 10.61. The C/H ratios in the analytical data give formulas of $\text{C}_{15}\text{H}_{27}$, $\text{C}_{15}\text{H}_{27}$, and $\text{C}_{15}\text{H}_{28}$, respectively.

Synthesis of [Li(THF)₄][{C₅Me₄(SiMe₂'Bu)}₂UI₂], **8.1.** In a 20 mL scintillation vial, solid LiC₅Me₄(SiMe₂'Bu) (100 mg, 0.412 mmol) was slowly added to a suspension of UI₃(dioxane)_{1.5} (150 mg, 0.200 mmol) in THF (ca. 5 mL) at room temperature. After stirring overnight, volatiles were removed under reduced pressure and the residue was extracted into a mixture of toluene and hexane (ca. 11 mL, 10:1). Insoluble solids were removed via filtration and the resulting green filtrate was stored at −35 °C for 5 days. Under these conditions, the product accumulated at the bottom of the 20 mL scintillation vial as a viscous green oil. After 2 more days, the oil slowly crystallized as green plates of **8.1** suitable for study by X-ray diffraction (110 mg, 0.0874 mmol, 44%). ¹H NMR (500 MHz, THF-*d*₈): δ 14.76 (s, 18H, SiMe₂'Bu), 3.60 (m, 16H, α-carbon of THF), 1.77 (m, 16H, β-carbon of THF), −0.37 (br s, 12H, C₅Me₄SiR₃), −3.85 (s, 12H, SiMe₂'Bu), −13.15 (br s, 12H, C₅Me₄SiR₃). ¹³C{¹H} NMR (150 MHz, THF-*d*₈): δ No signals definitively assignable to **8.1** were observed in the range of +200 to −400 ppm. ²⁹Si NMR (119 MHz, THF-*d*₈): δ −163.9 (SiMe₂'Bu). IR: 2951m, 2923m, 2879s, 2849s, 1460m, 1384w, 1317m, 1242s, 1180w, 1125w, 1041vs, 886s, 817vs, 762s, 664s cm^{−1}. Anal. Calcd. for C₄₆H₈₆O₄Si₂ILiU: C, 43.91; H, 6.89. Found: C, 33.13; H, 5.33. C, 36.60; H, 5.87. C, 36.87; H, 5.84. The C/H ratios in the analytical data give formulas of C₄₆H₈₈, C₄₆H₈₈, and C₄₆H₈₇, respectively.

Synthesis of [C₅Me₄(SiMe₂'Bu)]₂UI(THF), **8.2.** In a 20 mL scintillation vial, solid KC₅Me₄(SiMe₂'Bu) (370 mg, 1.35 mmol) was slowly added to a suspension of UI₃(dioxane)_{1.5} (500 mg, 0.666 mmol) in THF (ca. 10 mL) at room temperature. After stirring overnight, volatiles were removed from the green mixture under reduced pressure and the resulting residue was washed with hexane (ca. 2 mL) and dried. The remaining residue was then extracted into toluene (ca. 15 mL) and filtered to remove insoluble solids. The resulting green filtrate was concentrated under reduced pressure to ca. 5 mL and layered under hexane (ca. 10 mL). Storage of the resulting

mixture at $-35\text{ }^{\circ}\text{C}$ over several days yielded **8.2** as green crystals suitable for study by X-ray diffraction (310 mg, 0.341 mmol, 51%). ^1H NMR (500 MHz, THF- d_8): δ 25.37 (br, $\Delta\nu_{1/2} = 979$ Hz), 16.80 (br, $\Delta\nu_{1/2} = 68$ Hz), -5.52 (br, $\Delta\nu_{1/2} = 896$ Hz), -10.05 (br, $\Delta\nu_{1/2} = 823$ Hz), -23.66 (br, $\Delta\nu_{1/2} = 856$ Hz), -25.95 (br, $\Delta\nu_{1/2} = 834$ Hz). The paramagnetism of the U(III) ion precluded a definitive assignment of the resonances (see Supporting Information). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, THF- d_8): δ No signals definitively assignable to **8.2** were observed in the range of $+300$ to -300 ppm. ^{29}Si NMR (119 MHz, THF- d_8): δ -154.5 (*SiMe₂'Bu*). IR: 2952w, 2923w, 2891w, 2850m, 1461w, 1383w, 1322m, 1242s, 1121w, 1007s, 814vs, 763s, 664m cm^{-1} . Anal. Calcd. for $\text{C}_{34}\text{H}_{62}\text{OSi}_2\text{IU}$: C, 44.98; H, 6.88. Found: C, 42.73; H, 6.53. C, 43.60; H, 6.64. C, 43.04; H, 6.58. The C/H ratios in the analytical data give formulas of $\text{C}_{34}\text{H}_{62}$, $\text{C}_{34}\text{H}_{62}$, and $\text{C}_{34}\text{H}_{62}$, respectively.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]\text{UI}_2(\text{THF})_3$, **8.3.** In a 20 mL scintillation vial, solid $\text{KC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ (180 mg, 0.656 mmol) was slowly added to a blue suspension of $\text{UI}_3(\text{dioxane})_{1.5}$ (500 mg, 0.666 mmol) in THF (ca. 10 mL) at room temperature. After stirring overnight, volatiles were removed from the green-blue mixture under reduced pressure and the resulting residue was washed with hexane (ca. 3 mL) and dried. The remaining residue was then extracted into toluene (ca. 15 mL) and filtered to remove insoluble solids. Volatiles were removed under reduced pressure from the green filtrate to yield green crude solids. Afterward, the crude solids were dissolved in THF (ca. 5 mL) and layered under hexane (ca. 10 mL). Storage of the resulting mixture at $-35\text{ }^{\circ}\text{C}$ yielded **8.3** as a blue-green crystalline solid (380 mg, 0.403 mmol, 60%). ^1H NMR (500 MHz, THF- d_8): δ 10.61 (s, 9H, *SiMe₂'Bu*), 3.64 (br s, 12H, α -carbon of THF), 1.80 (br s, 12H, β -carbon of THF), 0.99 (s, 6H, $\text{C}_5\text{Me}_4\text{SiR}_3$), -1.12 (s, 6H, $\text{C}_5\text{Me}_4\text{SiR}_3$), -7.30 (s, 6H, *SiMe₂'Bu*). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, THF- d_8): δ No signals definitively assignable to **8.3** were observed in the range of $+300$ to -300 ppm. ^{29}Si NMR (119 MHz, THF- d_8): δ -167.7

(SiMe₂'Bu). IR: 2950w, 2926w, 2853w, 1462w, 1249m, 870vs, 833vs, 777s, 675m cm⁻¹. Anal. Calcd. for C₂₇H₅₁O₃SiIU: C, 39.71; H, 6.29. Found: C, 32.53; H, 5.15. C, 31.37; H, 4.97. C, 32.00; H, 5.02. The C/H ratios in the analytical data give formulas of C₂₇H₅₁, C₂₇H₅₁, and C₂₇H₅₀, respectively.

Synthesis of [Me₄C₅(SiMe₂)O(SiMe₂)C₅Me₄]UI(THF), 8.4. In a 20 mL scintillation vial, solid KC₅Me₄(SiMe₂'Bu) (370 mg, 1.33 mmol) with a slight amount of the impurity K₂[Me₄C₅(SiMe₂)O(SiMe₂)C₅Me₄], was added to a stirred blue solution of UI₃(dioxane)_{1.5} (500 mg, 0.666 mmol) in THF (ca. 8 mL) at room temperature. The resulting green-brown mixture was allowed to stir at room temperature overnight. Insoluble solids were removed via centrifugation followed by filtration through a syringe fitted with a PTFE syringe filter to yield a green-brown solution. Volatiles were removed under reduced pressure to yield a brown residue. Hexane (ca. 5 mL) was added, and the resulting mixture was filtered through a pipet packed with Kimwipe tissue to yield a green-brown solution, which was concentrated to ca. 2 mL under reduced pressure. Storage of the resulting solution at -35 °C yielded a few green crystals of both [Me₄C₅(SiMe₂)O(SiMe₂)C₅Me₄]UI(THF), **8.4**, and **8.2**, which were both identified crystallographically from the same batch of crystals.

Synthesis of [C₅Me₄(SiMe₂'Bu)]₂UI₂, 8.5. In a 20 mL scintillation vial, solid KC₅Me₄(SiMe₂'Bu) (300 mg, 1.09 mmol) was slowly added to a suspension of UI₄(dioxane)₂ (500 mg, 0.542 mmol) in toluene (ca. 10 mL) at room temperature to produce a dark red mixture with colorless precipitate. After stirring overnight, insoluble solids were removed via filtration and the resulting dark red filtrate was concentrated under reduced pressure to ca. 5 mL. After, the dark red toluene solution was layered under hexane (ca. 10 mL). Storage of the resulting mixture at -35 °C yielded **8.5** as dark purple crystalline solids suitable for study by X-ray diffraction (160 mg,

0.166 mmol, 31%). ^1H NMR (600 MHz, C_6D_6): δ 25.55 (br s, 18H, SiMe_2^tBu), 23.55 (br s, 12H, $\text{C}_5\text{Me}_4\text{SiMe}_2^t\text{Bu}$), -4.51 (br s, 12H, SiMe_2^tBu), -5.39 (br s, 12H, $\text{C}_5\text{Me}_4\text{SiMe}_2^t\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, C_6D_6): no signals definitively assignable to **8.5** were observed in the range of $+300$ to -300 ppm. ^{29}Si NMR (119 MHz, C_6D_6): δ -39.9 (SiMe_2^tBu). IR: 2954m, 2927m, 2894m, 2854m, 1469m, 1446m, 1428m, 1385m, 1359w, 1341w, 1320m, 1248s, 1117w, 1012m, 936w, 806vs, 762s, 741m, 684w, 661m cm^{-1} . Anal. Calcd. for $\text{C}_{30}\text{H}_{54}\text{Si}_2\text{I}_2\text{U}$: C, 37.43; H, 5.65. Found: C, 37.42; H, 5.68.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{U}[\text{CH}(\text{SiMe}_3)_2]$, **8.6, and $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{U}(\mu\text{-D})_2\text{Li}(\text{THF})_2$, **8.7**.** In a 20 mL scintillation vial, $\text{LiCH}(\text{SiMe}_3)_2$ (10 mg, 0.060 mmol) was added as a solid to a solution of **8.2** (100 mg, 0.110 mmol) in diethyl ether (ca. 5 mL) at room temperature. After stirring overnight, volatiles were removed under reduced pressure and the resulting residue was extracted into bis(trimethylsilyl) ether (ca. 5 mL) and filtered through a syringe fitted with a PTFE filter to remove insoluble solids. Storage of this solution at -35 °C yielded a few light brown crystals of **8.6** overnight suitable for study by X-ray diffraction. The bis(trimethylsilyl) ether insoluble solids were then extracted into hexane (ca. 5 mL) and filtered through a syringe fitted with a PTFE filter to remove insoluble solids. Afterward, the resulting brown-green filtrate was concentrated to ca. 2 mL. Storage of this solution at -35 °C yielded only a few green crystals of **8.7** overnight suitable for study by X-ray diffraction.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{U}(\text{BH}_4)(\text{THF})$, **8.8.** In a 20 mL scintillation vial, $\text{KC}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})$ (130 mg, 0.473 mmol) was slowly added as a solid to a stirring solution of $\text{U}(\text{BH}_4)_3(\text{THF})_2$ (100 mg, 0.234 mmol) in THF (ca. 5 mL) at room temperature. After stirring overnight, volatiles were removed under reduced pressure and the resulting residue was washed with hexane ($2 \times$ ca. 3 mL). The residue was then extracted into toluene (ca. 10 mL) and filtered

through a PTFE syringe filter to remove insoluble solids, presumably KBH_4 . Afterward, solvent was removed from the resulting filtrate under reduced pressure to yield a green crude solid, which was then dissolved again in THF (ca. 5 mL). Storage of the resulting green THF solution layered under hexane (ca. 10 mL) at $-35\text{ }^\circ\text{C}$ yielded **8.8** as green crystalline solids suitable for study by X-ray diffraction (120 mg, 0.151 mmol, 64%). ^1H NMR (500 MHz, $\text{THF-}d_8$): δ 19.88 (br, $\Delta\nu_{1/2} = 653\text{ Hz}$), 10.99 (br, $\Delta\nu_{1/2} = 59\text{ Hz}$), 5.71 (br, $\Delta\nu_{1/2} = 657\text{ Hz}$), -4.34 (br, $\Delta\nu_{1/2} = 649\text{ Hz}$), -11.87 (br, $\Delta\nu_{1/2} = 676\text{ Hz}$), -15.91 (br, $\Delta\nu_{1/2} = 682\text{ Hz}$), -30.69 (br, $\Delta\nu_{1/2} = 675\text{ Hz}$). The paramagnetism of the U(III) ion precluded a definitive assignment of the resonances (see Supporting Information). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, $\text{THF-}d_8$): no signals definitively assignable to **8.8** were observed in the range of $+300$ to -300 ppm . ^{11}B NMR (193 MHz, $\text{THF-}d_8$): δ 82.6 (br, BH_4). $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, $\text{THF-}d_8$): δ -158.7 ($\text{SiMe}_2'\text{Bu}$). IR: 2953m, 2925m, 2852m, 2484w, 2424w, 2235w, 2098w, 1461m, 1357m, 1322s, 1242s, 1169s, 1011m, 810vs, 762s, 665s cm^{-1} . Anal. Calcd. for $\text{C}_{34}\text{H}_{66}\text{BOSi}_2\text{U}$: C, 51.31; H, 8.36. Found: C, 47.20; H, 7.70. C, 46.53; H, 7.60. C, 49.26; H, 7.98. The C/H ratios in the analytical data give formulas of $\text{C}_{34}\text{H}_{66}$, $\text{C}_{34}\text{H}_{66}$, and $\text{C}_{34}\text{H}_{65}$, respectively.

X-ray Data Collection, Structure Solution and Refinement for $[\text{Li}(\text{THF})_4][\{\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})\}_2\text{U}_2]$, **8.1.** A green crystal of approximate dimensions $0.306 \times 0.324 \times 0.663\text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods

and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There are two molecules of the formula-unit present. The data were not high enough quality, so only connectivity could be established.

X-ray Data Collection, Structure Solution and Refinement for [Li(THF)₄][{C₅Me₄(SiMe₂'Bu)}₂UI₂], 8.1. A green crystal of approximate dimensions 0.138 x 0.191 x 0.220 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were two molecules of the formula-unit present. Atoms O4, C73, C74, C75, and C76 were included using displacement constraints (SIMU). Least-squares analysis yielded $wR2 = 0.1101$ and $Goof = 1.006$ for 1045 variables refined against 18952 data (0.82 Å), $R1 = 0.0463$ for those 12347 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for [Li(THF)₄][{C₅Me₄(SiMe₂'Bu)}₂UI₂], 8.1. A green crystal of approximate dimensions 0.120 x 0.143 x 0.169 mm was mounted in a cryoloop and transferred to a Bruker X8 Prospector APEX II diffractometer system. The APEX3⁶¹ program package was used to determine the unit-cell

parameters and for data collection (10-20 sec/frame scan time). The raw frame data was processed using SAINT⁶² and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Disordered atoms were included using multiple components, partial site-occupancy-factors, and displacement (SIMU) constraints. Least-squares analysis yielded $wR2 = 0.0774$ and $Goof = 1.027$ for 541 variables refined against 9745 data ($0.83 \text{ \AA}$), $R1 = 0.0317$ for those 8639 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Bu})_2\text{UI}(\text{THF})]$, **8.2.** A blue crystal of approximate dimensions $0.085 \times 0.085 \times 0.825 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0622$ and $Goof = 1.092$ for 370 variables refined against 9122 data ($0.75 \text{ \AA}$), $R1 = 0.0295$ for those 7900 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for [C₅Me₄(SiMe₂Bu)]UI₂(THF)₃, 8.3. A green crystal of approximate dimensions 0.184 x 0.204 x 0.449 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The TWINROTMAT routine in the PLATON⁶³ program package was used to determine a twin law and to yield another reflection data file (HKL F5 format) which was used for subsequent calculations. Least-squares analysis yielded wR₂ = 0.0891 and Goof = 1.063 for 317 variables refined against 7162 data (0.78 Å), R₁ = 0.0365 for those 6801 data with I > 2.0σ(I). The structure was refined as a two-component twin, BASF⁴ = 0.16330.

X-ray Data Collection, Structure Solution and Refinement for [Me₄C₅(SiMe₂)O(SiMe₂)C₅Me₄]UI(THF), 8.4. A green crystal of approximate dimensions 0.256 x 0.377 x 0.392 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was 2/m and the

systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0856$ and $Goof = 1.033$ for 301 variables refined against 6609 data ($0.78 \text{ \AA}$), $R1 = 0.0375$ for those 5388 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2\text{UI}_2$, 8.5. A green crystal of approximate dimensions $0.140 \times 0.267 \times 0.282$ mm was mounted in a cryoloop fiber and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters. Data collection used a 90 sec/frame scan time. The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that space group $C2/c$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on a two-fold rotation axis. The data were not high enough quality, so only connectivity could be established.

X-ray Data Collection, Structure Solution and Refinement for $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2\text{UI}_2$, 8.5. A purple crystal of approximate dimensions $0.071 \times 0.090 \times 0.254$ mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for

data collection (90 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups *Pnma* and *Pna2₁*. It was later determined that space group *Pnma* was correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about a mirror plane. Least-squares analysis yielded wR2 = 0.0679 and Goof = 1.056 for 172 variables refined against 3886 data (0.78 Å), R1 = 0.0318 for those 3363 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for [C₅Me₄(SiMe₂tBu)]₂U[CH(SiMe₃)₂]₂, 8.6. A brown crystal of approximate dimensions 0.115 x 0.166 x 0.303 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters. Data collection used a 60 sec/frame scan time. The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was *2/m* and the systematic absences were consistent with the monoclinic space group *P2₁/c* that was later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded wR2 = 0.0664 and Goof = 1.043 for 403 variables refined against 8065 data (0.82 Å), R1 = 0.0334 for those 6275 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for [C₅Me₄(SiMe₂'Bu)]₂U(μ -I)₂Li(THF)₂, 8.7. A green crystal of approximate dimensions 0.146 x 0.234 x 0.255 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for data collection (45 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded wR2 = 0.1290 and Goof = 1.043 for 433 variables refined against 9045 data (0.80 Å), R1 = 0.0523 for those 7157 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for [C₅Me₄(SiMe₂'Bu)]₂U(BH₄)(THF), 8.8. A green crystal of approximate dimensions 0.162 x 0.188 x 0.416 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used

throughout the analysis. Hydrogen atoms H1, H2, H3, and H4 were located from a difference-Fourier map and refined (x,y,z and U_{iso}). The rest of the hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0417$ and $Goof = 1.081$ for 386 variables refined against 8008 data ($0.78 \text{ \AA}$), $R1 = 0.0235$ for those 7101 data with $I > 2.0\sigma(I)$.

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Chapter 9:

Synthesis and Structure of Silyl-Substituted Bis(Cyclopentadienyl)

Scandium Halide Complexes

INTRODUCTION[†]

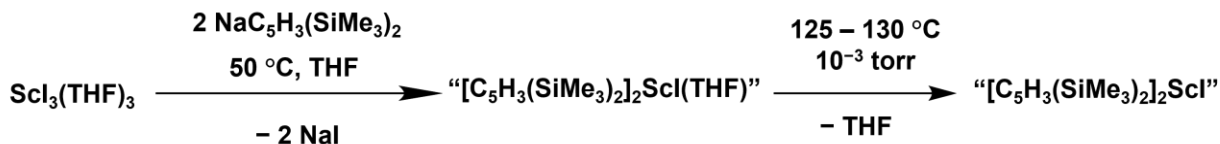
Bis(cyclopentadienyl) scandium(III) halide complexes represent an important class of starting materials for organoscandium chemistry due to the ease with which the halide ligand can be replaced.^{1–12} Atwood and Smith reported the first synthesis and crystallographic characterization of the dimeric Sc(III) complex $[(C_5H_5)_2Sc(\mu-Cl)]_2$ ¹ in 1973 while the trimeric fluoride analogue $[(C_5H_5)_2Sc(\mu-F)]_3$ ² was synthesized over a decade later by Bottomley *et al.* in 1985. In 1998, the mixed cyclopentadienyl complex, $(C_5Me_4H)(C_5H_4CH_2CH_2NMe_2)ScCl$,⁵ was characterized by Schumann and co-workers and Conley and coworkers obtained the X-ray crystal structures¹¹ of the unsolvated monometallic $(C_5Me_5)_2ScX$ complexes ($X = F, Cl, Br, \text{ and } I$)³ in 2018. The X-ray crystal structure of the unsolvated $(C_5H_2^tBu_3)_2ScI$ ¹³ was also reported in 2023. However, there are no further examples of unsolvated Sc(III) $[(C_5R_5)_2ScX]_n$ ($R = H, \text{ alkyl, silyl; } X = \text{halide}$) complexes in the literature prior to 2025. The THF-solvated complexes $(C_5Me_5)_2ScCl(THF)$ ¹⁴ and $(C_5Me_4H)_2ScCl(THF)$ ¹⁵ have been structurally characterized as well as the ansa-metallocene “ate” salt $\{Me_2Si[C_5H_2(CHMe_2)_2]_2\}Sc(\mu-Cl)_2Li(THF)_2$.⁶

The bis(1,2,4-tri-*tert*-butylcyclopentadienyl) scandium iodide complex $(C_5H_2^tBu_3)_2ScI$ proved to be a critical precursor in the potassium graphite (KC_8) reduction reaction that generated the first crystallographically characterized neutral Sc(II) metallocene, namely $(C_5H_2^tBu_3)_2Sc$.¹³

[†] Portions of this Chapter have been published: Nguyen, J. Q.; Anderson-Sanchez, L. M.; Ziller, J. W.; Evans, W. J. Synthesis and Structure of Silyl-Substituted Bis(cyclopentadienyl) Scandium(III) Halide Complexes. *Organometallics* **2025**, 44, 137–147. DOI: 10.1021/acs.organomet.4c00412

The steric bulk of the cyclopentadienyl ligand and its substitution pattern is evidently important in this system because KC_8 reductions of the analogous $(\text{C}_5\text{Me}_5)_2\text{ScI}$ and $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$ did not give isolable $(\text{C}_5\text{R}_5)_2\text{Sc}$ products, although the latter complex provided the anionic Sc(II) metallocene $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}\}^{1-}$.¹³ The identity of the halide also appears to be important because the KC_8 reduction of “[$\text{C}_5\text{H}_3(\text{SiMe}_3)_2$] $_2\text{ScCl}$ ” has not generated a crystallizable Sc(II) product. The study described in this Chapter was initiated to remedy the deficiency in the literature of unsolvated crystallographically characterized $[(\text{C}_5\text{R}_5)_2\text{ScX}]_n$ complexes with a variety of cyclopentadienyl ligands.

The bis(cyclopentadienyl) Sc(III) halide complex $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$ was originally reported by Lappert and co-workers in 2012 and was prepared from the reaction between $\text{ScI}_3(\text{THF})_3$ and 2 equiv of $\text{NaC}_5\text{H}_3(\text{SiMe}_3)_2$ followed by desolvation under reduced pressure at elevated temperatures, as shown in Scheme 9.1.⁹ Although it was reported that the THF-solvated



Scheme 9.1. Original preparation of “[$\text{C}_5\text{H}_3(\text{SiMe}_3)_2$] $_2\text{ScI}$ ” reported by Lappert and coworkers.⁹

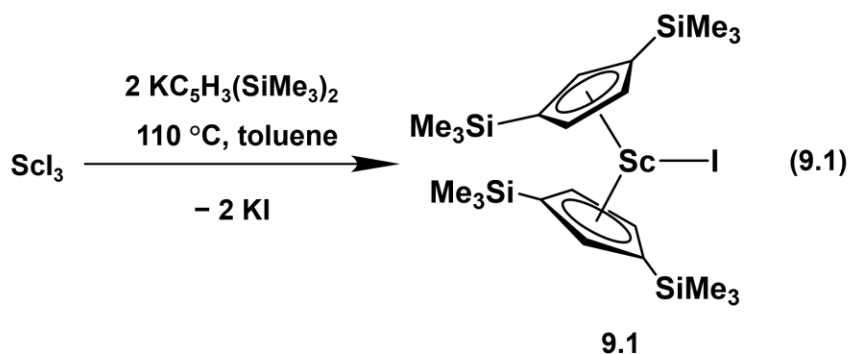
complex $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}(\text{THF})$ could be isolated as nearly colorless crystals and the solvent-free complex $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$ could be isolated as yellow crystals, X-ray crystal structures for neither complex were provided.

Initial attempts to characterize $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$ in the Evans group by X-ray diffraction surprisingly led to a crystal structure containing presumably a mixture of the oxide $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}\}_2(\mu\text{-O})$ and hydroxide $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-OH})\}_2$ which initiated this study. Since $[(\text{C}_5\text{R}_5)_2\text{ScX}]_n$ complexes are critical to developing Sc(II) chemistry, the synthesis of

$[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$ was revisited and the synthesis of the chloride variation $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-Cl})\}_2$, and four cyclopentadienyl variations of $[(\text{C}_5\text{R}_5)_2\text{ScI}]_n$ complexes was examined. In this Chapter, a general synthesis for these unsolvated bis(cyclopentadienyl) Sc(III) halide complexes and their corresponding crystal structures that should put this area of organoscandium precursors on a firm basis of structurally characterized compounds is described.

RESULTS

X-ray Crystal Structure of Monometallic $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$, **9.1.** Previously, it was found that the reaction between ScI_3 ¹⁶ and 2 equiv of $\text{KC}_5\text{H}_2/\text{Bu}_3$ in toluene at 110 °C gave unsolvated $(\text{C}_5\text{H}_2/\text{Bu}_3)_2\text{ScI}$ in good yields.¹³ In a preparation analogous to that procedure, ScI_3 was treated with 2 equiv of $\text{KC}_5\text{H}_3(\text{SiMe}_3)_2$ in a sealed vessel in toluene at 110 °C over 16 h. This generated light-yellow solids upon workup identified as $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$, **9.1**, by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy when compared to Lappert's initial report, eq 9.1.⁹



Crystallization from saturated toluene solutions stored at $-35\text{ }^\circ\text{C}$ yielded pale-yellow crystals of monometallic **9.1** in 50% crystalline yield suitable for study by X-ray diffraction, Figure 9.1.

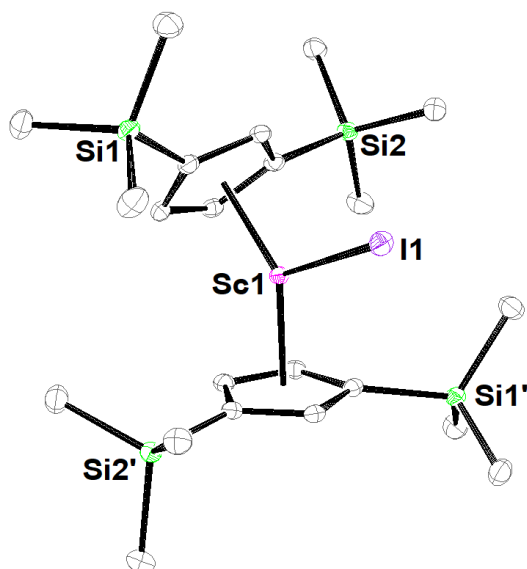


Figure 9.1. Molecular structure of $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$, **9.1**, with ellipsoids drawn at the 50% probability level and selective atom labelling. Hydrogen atoms are not shown for clarity.

Complex **9.1** crystallizes as a monomer in the $P2/c$ space group with half of a molecule in the asymmetric unit. The molecule is located on a 2-fold rotation axis that is coincident with the Sc–I bond such that the two cyclopentadienyl ligands are crystallographically equivalent. Complex **1** has a bent metallocene structure with a Sc–Cnt distance (Cnt = cyclopentadienyl ring centroid) of 2.146 Å and a Cnt–Sc–Cnt angle of 134.8°, Table 9.1. The average Sc–Cnt distance of **9.1** is similar to the 2.164 Å analogous distance of $(\text{C}_5\text{Me}_5)_2\text{ScI}^{11}$ and shorter than the 2.229 Å distance in $(\text{C}_5\text{H}_2'\text{Bu}_3)_2\text{ScI}^{13}$. However, the Cnt–Sc–Cnt angle of **9.1** is smaller than that of both $(\text{C}_5\text{Me}_5)_2\text{ScI}^{11}$ (140.5°) and $(\text{C}_5\text{H}_2'\text{Bu}_3)_2\text{ScI}^{13}$ (147.0°). The 2.800(4) Å Sc–I distance of **9.1** is in a range typical for Sc(III) complexes containing iodide ligands; e.g., $(\text{C}_5\text{Me}_5)_2\text{ScI}^{11}$ and $(\text{C}_5\text{H}_2'\text{Bu}_3)_2\text{ScI}^{13}$ have analogous distances of 2.8194(3) Å and 2.8569(3) Å, respectively.

Table 9.1. Selected interatomic distances (Å) and angles (°) of crystallographically characterized *monometallic* unsolvated bis(cyclopentadienyl) scandium halide complexes ordered in increasing Sc–Cnt distance.

Sc(III) complex	Sc–Cnt (av.)	Cnt–Sc–Cnt	Sc–X	Cnt–Sc–X (X = F, Cl, Br, I)
[C ₅ H ₃ (SiMe ₃) ₂] ₂ ScI, 9.1	2.146	134.8	2.800(4)	112.6
(C ₅ Me ₅) ₂ ScBr ¹¹	2.157	141.7	2.584(4)	108.9, 109.4
(C ₅ Me ₅) ₂ ScCl ^{11, a}	2.158	142.0	2.417(2)	109.0
(C ₅ Me ₅) ₂ ScI ¹¹	2.164	140.4	2.819(3)	108.9, 109.6
(C ₅ Me ₅) ₂ ScF ¹¹	2.164	143.4	1.927(1)	108.3
[C ₅ Me ₄ (SiMe ₃)] ₂ ScI, 9.2	2.165	139.1	2.860(5)	110.4
[C ₅ Me ₄ (SiMe ₂ ^t Bu)] ₂ ScI, 9.3	2.181	143.5	2.802(6)	108.3
(C ₅ H ₂ ^t Bu ₃) ₂ ScI ¹³	2.229	147.0	2.857(3)	105.9, 107.1

^a Values were averaged between each crystallographically unique scandium complex in the asymmetric unit.

Monometallic [C₅Me₄(SiMe₃)]₂ScI, 9.2 and [C₅Me₄(SiMe₂^tBu)]₂ScI, 9.3. Trialkylsilyl variants of the common (C₅Me₅)¹⁻ ligand were also examined for comparison with the known monometallic (C₅Me₅)₂ScI¹¹ and (C₅H₂^tBu₃)₂ScI¹³ complexes. Thus, the reaction between ScI₃ and 2 equiv of KC₅Me₄(SiMe₃) produced bright yellow solids that crystallized from saturated hexane solutions stored at –35 °C as the monometallic bis(cyclopentadienyl) Sc(III) iodide complex [C₅Me₄(SiMe₃)]₂ScI, **9.2**, in 53% crystalline yield, Figure 9.2, eq 9.2.

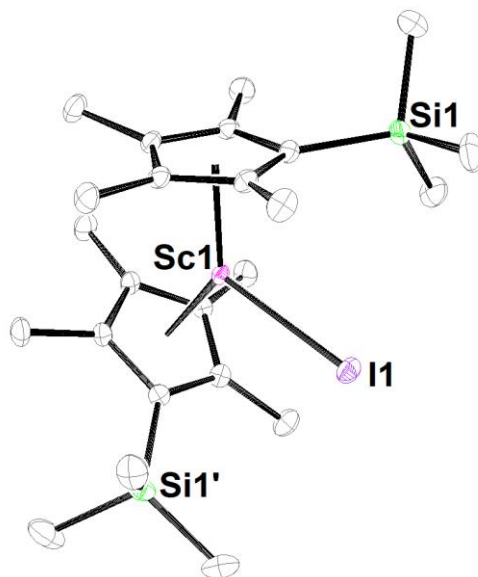
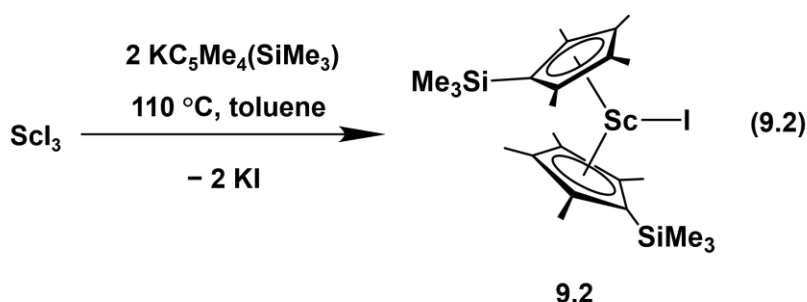


Figure 9.2. Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ScI}$, **9.2**, with ellipsoids drawn at 50% probability level and selective atom labelling. Hydrogen atoms are not shown for clarity.

The $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligand was also explored because previous studies of uranium metallocenes as described in Chapter 8 with this ligand revealed that its complexes had significantly different chemistry compared to analogous complexes of $(\text{C}_5\text{Me}_5)^{1-}$.¹⁷ To examine $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ chemistry with the much smaller rare-earth metal scandium, ScI_3 was treated with 2 equiv of $\text{KC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ using the same procedure that was used to prepare **9.2** as described in eq 9.2. This reaction afforded $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{ScI}$, **9.3**, which was crystallized as bright yellow blocks from saturated hexane solutions stored at -35°C in 54% crystalline yield, Figure 9.3, eq 9.3.

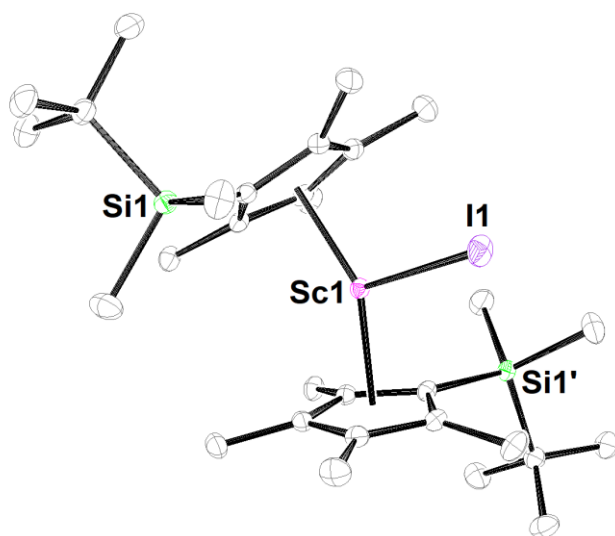
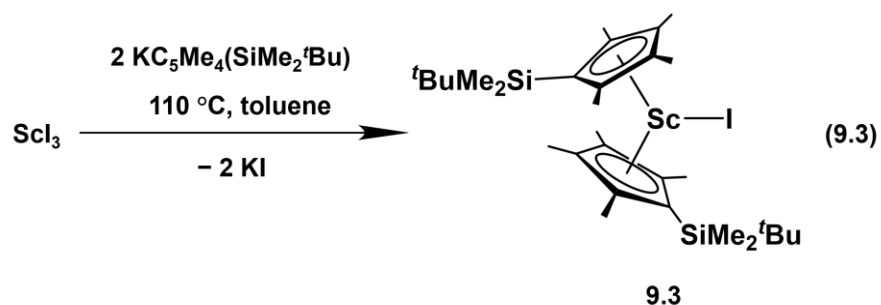


Figure 9.3. Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{ScI}$, **9.3**, with ellipsoids drawn at 50% probability level and selective atom labelling. Hydrogen atoms are not shown for clarity.

Complexes **9.2** and **9.3** both crystallize as monomers in the *Pbcn* and *C2/c* space groups, respectively, with half of a molecule in the asymmetric unit. As with the structure of complex **9.1**, complexes **9.2** and **9.3** are each located on a 2-fold rotation axis that is collinear with the Sc–I bond. Complex **9.2** has an average Sc–Cnt distance of 2.165 Å and a Cnt–Sc–Cnt angle of 139.1° while complex **9.3** has a similar analogous distance of 2.181 Å and a wider angle of 143.5°. Table 9.1 shows that the average Sc–Cnt distances of **9.2** and **9.3** are longer than those of **9.1** but similar to those of $(\text{C}_5\text{Me}_5)_2\text{ScI}^{11}$ and shorter than those of $(\text{C}_5\text{H}_2^t\text{Bu}_3)_2\text{ScI}^{13}$. This is consistent with the difference in steric bulk between the cyclopentadienyl ligands and the fact that $(\text{C}_5\text{H}_2^t\text{Bu}_3)_2\text{ScI}$ has

the widest Cnt–Sc–Cnt angle of all of the bis(cyclopentadienyl) scandium halide complexes discussed in this Chapter.

Bimetallic $\{[C_5H_4(SiMe_3)]_2Sc(\mu-I)\}_2$, **9.4**, and $\{[C_5H_4(Si^iPr_3)]_2Sc(\mu-I)\}_2$, **9.5**. To compare the scandium chemistry of the *bis*(trimethylsilyl)cyclopentadienyl ligand to that of the smaller *mono*(trimethylsilyl)cyclopentadienyl ligand, the synthesis of “[C₅H₄(SiMe₃)]₂ScI” was pursued. The reaction between ScI₃ and 2 equiv of KC₅H₄(SiMe₃) using the same procedure as described for the synthesis of **9.1** gave colorless solids upon workup rather than the light-yellow solids described for complex **9.1**. Crystallization from saturated toluene solutions stored at –35 °C yielded colorless X-ray quality crystals of the dimeric species $\{[C_5H_4(SiMe_3)]_2Sc(\mu-I)\}_2$, **9.4**, Figure 9.4, eq 9.4.

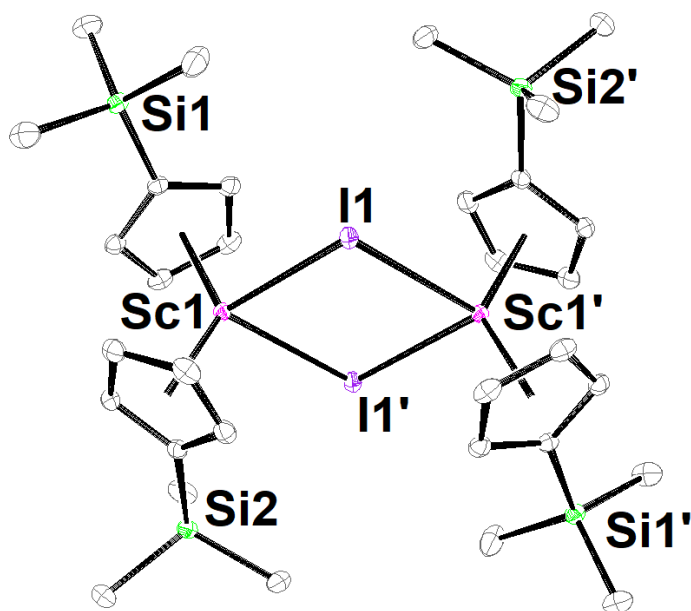
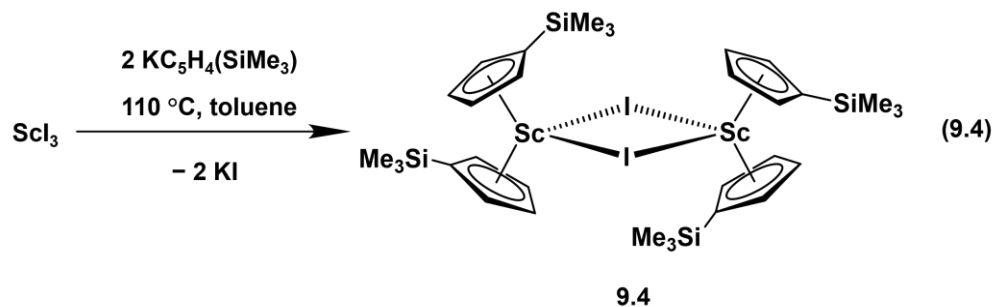


Figure 9.4. Molecular structure of $\{[\text{C}_5\text{H}_4(\text{SiMe}_3)]_2\text{Sc}(\mu\text{-I})\}_2$, **9.4**, with ellipsoids drawn at the 50% probability level and selective atom labelling. Hydrogen atoms are not shown for clarity.

Complex **9.4** crystallizes as a centrosymmetric dimer in the $P\bar{1}$ space group. The molecule lies on an inversion center that is located in the center of the plane formed by the iodine and scandium atoms. Each scandium atom binds two cyclopentadienyl ligands in an η^5 fashion and two bridging iodide ligands in a distorted tetrahedral geometry with respect to the cyclopentadienyl ring centroids and iodide ligands. The average Cnt–Sc–I angle of 107.9° is close to the 109.5° angle of a tetrahedral compound, however the Cnt–Sc–Cnt angle is 131.5° and the I–Sc–I angle is $82.9(1)^\circ$, Table 9.2. This leads to a τ_4 value of 0.85 with respect to the scandium atoms, where $\tau_4 = 1.00$ for a perfect tetrahedral geometry.¹⁸ The 2.182 Å average Sc–Cnt distance in **9.4** is similar to that in **9.1**, but the 2.955(2) and 3.002(4) Å Sc–I distances are longer, which is typical of bridging versus terminal ligands.

Table 9.2. Selected bond distances (Å) and angles ($^\circ$) of crystallographically characterized *bimetallic* bis(cyclopentadienyl) scandium halide and oxide complexes in order of increasing Sc–Cnt distance.

Sc(III) complex	Sc–Cnt (av.)	Cnt–Sc–Cnt	Sc–X (X = O, Cl, I)	Cnt–Sc–X (X = O, Cl, I)	Sc···Sc
$[(\text{C}_5\text{H}_5)_2\text{Sc}(\mu\text{-Cl})]_2^1$	2.170	129.5, 131.5, 130.5	2.583(5), 2.584(4), 2.581(5), 2.559(5), 2.57(2), 2.565(2)	109.5, 108.3, 108.8, 108.7, 106.7, 107.1, 109.2, 109.2,	3.92(1), 3.89(1)

				109.1, 107.6, 108.6, 108.6	
$\{[C_5H_4(Si^iPr_3)]_2Sc(\mu-I)\}_2$, 9.5	2.181	133.8	2.969(3), 2.976(3)	108.5, 105.9, 105.1, 108.4	4.424(3)
$\{[C_5H_4(SiMe_3)]_2Sc(\mu-I)\}_2$, 9.4	2.182	131.5	2.955(2), 3.002(4)	109.0, 107.4, 106.2, 109.1	4.466(7)
$\{[C_5H_3(SiMe_3)_2]_2Sc(\mu-Cl)\}_2$, 9.6	2.202	131.2	2.545(7), 2.548(7)	109.7, 109.6, 106.8, 106.5	3.845(8)
$[(C_5Me_4H)_2Sc]_2(\mu-O)^{15}$	2.205	132.5, 132.8	1.910(5), 1.925(5)	113.9, 113.6, 113.3, 113.7	3.830(2)
$\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu-O)$, 9.7	2.224	130.8	1.868(4)	111.5 117.8	3.736(6)

Given the surprising differences in the Th(III) chemistry of the $[C_5H_4(SiMe_3)]^{1-}$ ligand versus its triisopropyl analogue $[C_5H_4(Si^iPr_3)]^{1-}$,¹⁹ the synthesis and structure of a bis(cyclopentadienyl) scandium iodide complex of the latter ligand were also pursued. Like the synthesis of complex **9.4**, the reaction between ScI_3 and 2 equiv of $KC_5H_4(Si^iPr_3)$ in toluene at 110 °C provided colorless solids upon workup. Crystallization from saturated toluene solutions stored at –35 °C yielded colorless X-ray quality crystals of the dimeric species $\{[C_5H_4(Si^iPr_3)]_2Sc(\mu-I)\}_2$, **9.5**, Figure 9.5, eq 9.5.

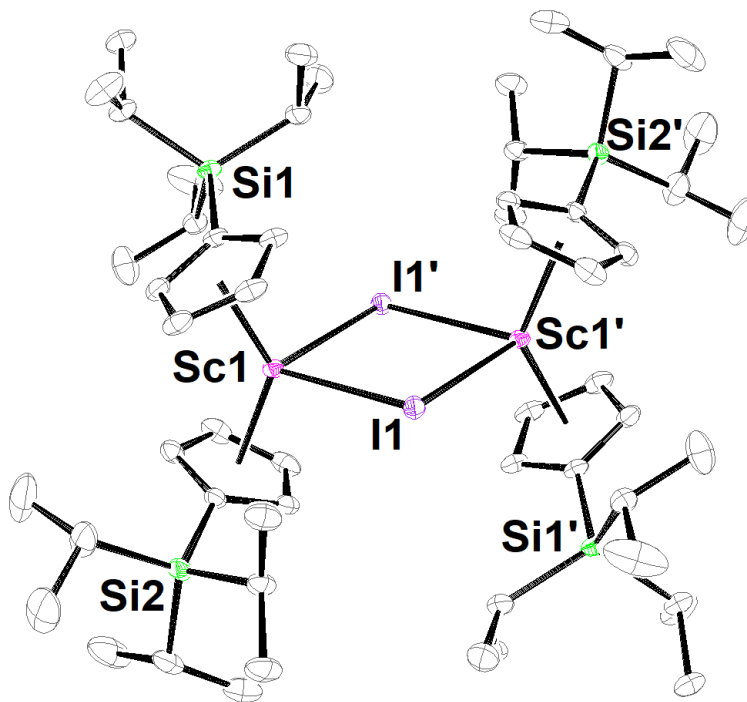
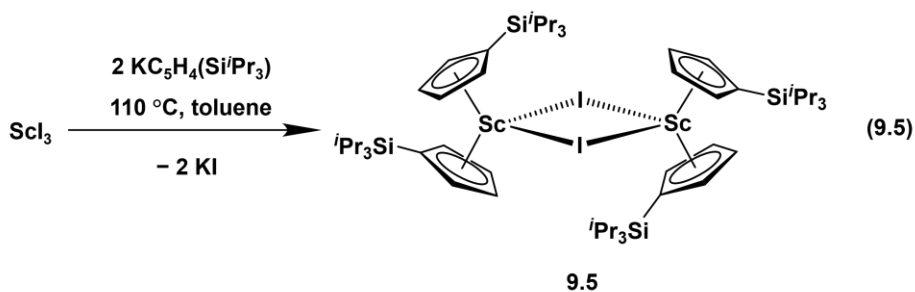


Figure 9.5. Molecular structure of $\{[\text{C}_5\text{H}_4(\text{Si}^i\text{Pr}_3)]_2\text{Sc}(\mu\text{-I})\}_2$, **9.5**, with ellipsoids drawn at the 50% probability level and selective atom labelling. Hydrogen atoms are not shown for clarity.

Complex **9.5** crystallizes as a centrosymmetric dimer in the $P\bar{1}$ space group as was found for **9.4** with the molecule on an inversion center located in the center of the plane formed by the iodine and scandium atoms. Complex **9.5** has a similar molecular structure and metrical data compared to **9.4** with a similar τ_4 value of 0.83, Table 9.2, despite the difference in steric bulk of the cyclopentadienyl ligands.¹⁹

Bimetallic $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu-Cl)\}_2$, **9.6**. In pursuit of another crystalline bis(cyclopentadienyl) scandium halide with the $[C_5H_3(SiMe_3)_2]^{1-}$ ligand, the synthesis of the analogous scandium chloride complex “[$C_5H_3(SiMe_3)_2$] $_2ScCl$ ” was explored. The reaction between $ScCl_3$ and 2 equiv of $KC_5H_3(SiMe_3)__2$ in toluene at 110 °C yielded off-white solids upon workup. Saturated toluene solutions of this material stored at –18 °C yielded X-ray quality crystals that were identified as the dimeric complex $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu-Cl)\}_2$, **9.6**, in 88% crystalline yield, Figure 9.6, eq 9.6.

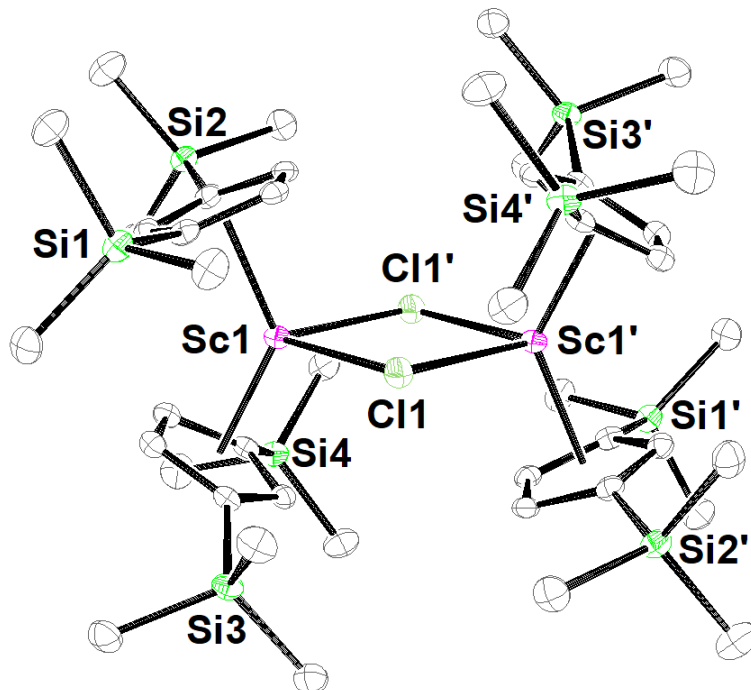
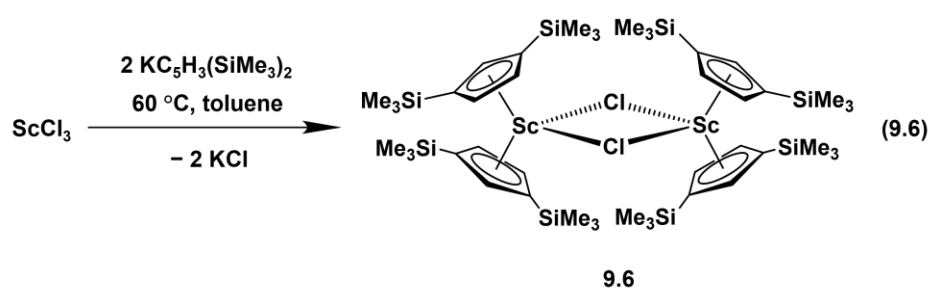


Figure 9.6. Molecular structure of $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-Cl})\}_2$, **9.6**, with ellipsoids drawn at the 50% probability level and selective atom labelling. Hydrogen atoms are not shown for clarity.

The bimetallic $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-Cl})\}_2$, **9.6**, crystallizes in the $P2_1/n$ space group, again with half of the molecule in the asymmetric unit. An inversion center is located in the middle of the chlorine and scandium atoms in the asymmetric unit. In contrast to complex **9.1**, complex **9.6** crystallizes as a dimeric species in the solid state when the halide is switched from an iodide to a chloride ligand. The 2.202 Å average Sc–Cnt distance of the formally eight-coordinate dimeric chloride complex **9.6** is larger than the 2.146 Å analogous distance in the seven-coordinate iodide complex of the same ligand $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$, **9.1**, which is consistent with the larger coordination number. The 131.2° Cnt–Sc–Cnt angle is slightly more bent than the 134.8° angle of **9.1**. Compared to complexes **9.4** and **9.5**, the 3.845(8) Å Sc⋯Sc distance in the chloride-bridged **9.6** is shorter than the Sc⋯Sc distances in the iodide-bridged complexes **9.4** (4.466(7) Å) and **9.5** (4.424(3) Å), which is consistent with the difference in the ionic radii of the halide atoms.²⁰ Furthermore, complex **9.6** has a τ_4 value of 0.84, which is very similar to those of **9.4** and **9.5**.

Bimetallic Oxide $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}\}_2(\mu\text{-O})$, **9.7, and Hydroxide $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-OH})\}_2$, **9.8**.** Initial attempts to synthesize and obtain crystals of $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$, **9.1**, following the procedure described above resulted in the isolation of X-ray quality crystals of a bridging oxo complex $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}\}_2(\mu\text{-O})$, **9.7**, Figure 9.7, which cocrystallized presumably with the bridging hydroxide complex $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-OH})\}_2$, **9.8**. The crystallographic data were modeled as a 75:25 mixture of **9.7**:**9.8**. Further attempts to synthesize and grow X-ray quality crystals of **9.1** with the same batch of ScI_3 made from Sc metal and NH_4I ¹⁶ yielded similar results. Since it was known that the ScI_3 preparation required stringent methods to obtain pure material,¹⁶ a new batch of ScI_3 was generated and used to form complex

9.1 free of oxide **9.7** and hydroxide **9.8**. Consequently, it was suspected that the earlier sample of ScI_3 was contaminated with an oxygen-containing impurity that can be eliminated with the proper procedure.¹⁶ Evidently, the bimetallic oxide **9.7** and the hydroxide **9.8** were the least soluble and most readily crystallizable materials in a mixture of **9.1**, **9.7**, and **9.8**. Complexes **9.7** and **9.8** are included in this Chapter to show how sensitive these organometallic scandium complexes are to oxygen-containing impurities.

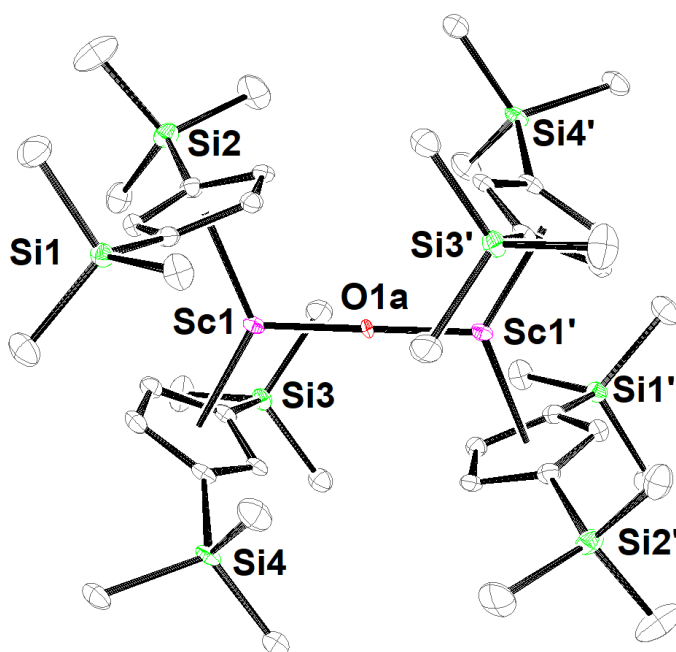


Figure 9.7. Molecular structure of $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}\}_2(\mu\text{-O})$, **9.7**, drawn at the 50% probability level with selective atom labelling. Hydrogen atoms are not shown for clarity. The bridging hydroxide $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-OH})\}_2$, **9.8**, is not shown here.

Complex **9.7** is an example of an oxo-bridged bis(cyclopentadienyl) bimetallic complex that is commonly encountered in the organometallic chemistry of the oxophilic rare-earth metals.^{21–25} For example, most reactions of $(\text{C}_5\text{Me}_5)_2\text{Sm}$ can use the NMR peak of the $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu\text{-O})$ ²¹ oxide impurity at 0.06 ppm in C_6D_6 to calibrate the spectrum of the main

product since the oxide is almost always formed as a byproduct. Similarly, the synthesis of the sterically crowded $(C_5Me_5)_3La$ was previously reported to be commonly complicated by the generation of $[(C_5Me_5)_2La]_2(\mu-O)$.²⁶ Hydroxide complexes like **9.8** have previously been observed as hydrolysis products in rare-earth organometallic chemistry, however relatively few X-ray crystal structures have been reported.^{27–31}

The cocrystallization of a bimetallic oxide or hydroxide with another bimetallic complex of similar structure is also a common problem with oxygen-containing contaminants. For example, the oxide complexes of Nd³² and Gd,³³ $[K_2(18\text{-crown-}6)_3][\{(R_2N)_3Ln\}_2(\mu-O)]$, cocrystallize with the $(N=N)^{2-}$ complexes, $[K_2(18\text{-crown-}6)_3][\{(R_2N)_3Ln\}_2(\mu-\eta^x:\eta^x-N_2)]$ ($Ln = Nd, Gd$; $R = SiMe_3$). In another example, cocrystallization of $\{[C_5H_4(SiMe_3)]_2Nd(\mu-OH)\}_2$ with $[C_5H_4(SiMe_3)]_3NdGa(C_5Me_5)$ was observed.³⁴ Also, a pair of closely related scandium oxide and hydroxide complexes of a pentadentate pyridine-based pyrazolylborate ligand system has been reported by Piers and co-workers.³⁵

Complexes **9.7** and **9.8** cocrystallize in the $P2_1/n$ space group with half of the dimeric molecule in the asymmetric unit. An inversion center is located on the bridging oxygen atom of **9.7** which is also between the scandium atoms and the two μ -hydroxide ligands (see Supporting Information). Complex **9.7** comprises about 75% of the crystal structure and has a 180° Sc–O–Sc angle and a Sc–O distance of 1.868(4) Å, whereas for the minor component, **9.8**, which has a $111.4(3)^\circ$ Sc–O–Sc angle, the analogous average Sc–O distance is longer at 2.261(6) Å. For comparison, the only other previously reported bimetallic bis(cyclopentadienyl) scandium oxo complex is $[(C_5Me_4H)_2Sc]_2(\mu-O)$ ¹⁵ which has a similar average Sc–O distance of 1.917(5) Å and a close to linear O–Sc–O angle of $174.1(3)^\circ$. Both the 2.224 Å average Sc–C_{nt} distance and the

130.8 °C—Sc—C angle of **9.7** are similar to the values in $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-Cl})\}_2$, **9.6**, Table 9.2. However, the 3.736(6) Å Sc···Sc distance of **9.7** is shorter than the 3.845(4) Å distance of **9.6**.

NMR Analyses. Complexes **9.1–9.4** exhibit diamagnetic ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra containing resonances for just one type of cyclopentadienyl environment. This indicates that the cyclopentadienyl ligands are all equivalent in solution for these Sc(III) complexes and no monomer–dimer equilibria are observed at room temperature.

Solution-phase ^{45}Sc NMR data were also obtained for complexes **9.1–9.6** and the chemical shifts and associated line width at half-height values are summarized in Table 9.3 along with data on other previously reported bis(cyclopentadienyl) Sc(III) complexes. In addition, data are reported on samples of **9.1–9.6** in deuterobenzene (C_6D_6) to which a few drops of THF were added. These samples are labeled **9.1+THF** to **9.6+THF**, and the expected compositions based on the ^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{29}Si NMR spectra are noted.

Table 9.3. ^{45}Sc NMR chemical shifts (ppm) and line widths at half-height values (Hz) for selected bis(cyclopentadienyl) Sc(III) Complexes ordered in decreasing chemical shift.

Complex	Chemical Shift (ppm)	$\Delta\nu_{1/2}$ (Hz)
$[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ScI}$, 9.2	264.2	3200
$[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{ScI}$, 9.3	263.8	3300
$(\text{C}_5\text{Me}_5)_2\text{ScI}^{11}$	256.9	-
$[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$, 9.1	208.3	4300
$(\text{C}_5\text{Me}_5)_2\text{ScBr}^{11}$	203.3	-

$[(C_5Me_4H)_2Sc][(\mu-Ph)BPh_3]^{15}$	190	7800
$[C_5Me_4(SiMe_3)]_2ScI(THF)$, 9.2+THF	176.3	340
$\{[C_5H_4(Si^iPr_3)]_2Sc(\mu-I)\}_2$, 9.5	172.8 ^a	7000 ^a
$[C_5Me_4(SiMe_2^tBu)]_2ScI(THF)$, 9.3+THF	167.5	850
$(C_5Me_4H)_2Sc(\eta^3-C_3H_5)^{15}$	153	350
$\{[C_5H_3(SiMe_3)_2]_2Sc(\mu-Cl)\}_2$, 9.6	138.3 ^a	2700 ^a
$[C_5H_3(SiMe_3)_2]_2ScI(THF)$, 9.1+THF	81.9	370
$\{[C_5H_4(SiMe_3)]_2Sc(\mu-I)\}_2$, 9.4	71.2 ^b	1900
$[C_5H_4(Si^iPr_3)]_2ScI(THF)$, 9.5+THF	68.9	540
$(C_5H_5)_2Sc(BH_4)^{36}$	67.5	250
$(C_5Me_5)_2ScF^{11}$	65.7	-
$[C_5H_4(SiMe_3)]_2ScI(THF)$, 9.4+THF	59.7	160
$(C_5Me_4H)_2ScCl(THF)^{15}$	55	400
$\{[C_5H_3(SiMe_3)_2]_2Sc(\mu-Cl)\}_2$, 9.6	43.3 ^b	1900 ^b
$\{[C_5H_4(Si^iPr_3)]_2Sc(\mu-I)\}_2$, 9.5	34.5 ^b	2600 ^b
$[C_5H_3(SiMe_3)_2]_2ScCl(THF)$, 9.6+THF	29.9	940
$\{(C_5H_5)_2Sc(\mu-Cl)\}_2^{37}$	-9.5	85

^a Resonance assigned to the monomeric species in neat C₆D₆.

^b Resonance assigned to the dimeric species in neat C₆D₆.

In general, the ^{45}Sc NMR spectra for monomeric complexes **9.1–9.3** show one broad resonance in neat C_6D_6 at room temperature in the range of 200–270 ppm with line widths of approximately 3200–4300 Hz. These data are similar to those of the unsolvated bis(cyclopentadienyl) Sc(III) halides that have been studied previously by Conley and co-workers.¹¹ For bimetallic complex **9.4**, the ^{45}Sc NMR signal has a much lower chemical shift at 71.2 ppm and a line width value of about 1900 Hz that is narrower than those of the monometallic complexes. The sharper line width and lower chemical shift are consistent with a Sc(III) metal center that has a higher symmetry local environment and higher coordination number than that of complexes **9.1–9.3**.^{38,39} For example, Gauvin *et al.* reported that coordination of the neutral Lewis base triphenylphosphine oxide to $\text{Sc}[\text{N}(\text{SiMe}_3)_2]_3$ shifted the ^{45}Sc NMR resonance from 396 to 350 ppm.³⁸ Their studies on Sc(III) amide complexes grafted onto silica also showed peak sharpening in the ^{45}Sc NMR spectra upon coordination of triphenylphosphine oxide.³⁸

The ^1H NMR spectra for complexes **9.5** and **9.6** display two different resonances with different line widths. These spectra presumably arise due to the presence of both monomeric and dimeric species in equilibrium in neat C_6D_6 at room temperature. The higher chemical shift resonance with a broader line width is assigned to the monomeric form, and the lower chemical shift resonance with the sharper line width is assigned to the dimeric form on the basis that higher coordinate scandium complexes are observed to have relatively lower chemical shifts and sharper line widths, Table 9.3.^{38,39} The dynamic nature of bridging cyclopentadienyl Sc(III) complexes in solution has been previously observed and studied using ^{45}Sc NMR by McGlinchey and co-workers.³⁷ The single resonance observed for **9.4** suggests that it remains predominantly dimeric in solution in C_6D_6 at room temperature.

Addition of a few drops of THF to C₆D₆ solutions of either **9.5** or **9.6** produced ⁴⁵Sc NMR spectra that do not contain the original two broad signals but show the presence of one new Sc(III) compound with a different chemical shift and a sharper line width in each spectrum. In addition, the ¹H, ¹³C{¹H}, and ²⁹Si{¹H} NMR spectra of complexes **9.5** and **9.6** after being treated with THF show clean conversion to new Sc(III) complexes that have only one unique type of cyclopentadienyl environment. This is presumably due to the quantitative formation of the higher coordinate monomeric THF adducts, [C₅H₄(Si^{*i*}Pr₃)₂ScI(THF), **9.5+THF**, and [C₅H₃(SiMe₃)₂]₂ScCl(THF), **9.6+THF**. Indeed, addition of a few drops of THF to C₆D₆ solutions of monomeric **9.1**, **9.2**, **9.3** and dimeric **9.4** produced ⁴⁵Sc NMR spectra that show the presence of new Sc(III) complexes consistent with the formation of THF-solvated complexes, Table 9.3. In the case of complexes **9.2** and **9.3**, there appears to be a mixture of both the unsolvated and THF-solvated complexes, as evidenced by the presence of two distinct resonances with the signal for the THF-solvated complex appearing with a lower chemical shift and with a sharper line width relative to that of the unsolvated complex.

The ¹H NMR spectrum of the sample of **9.1** in toluene-d₈ that also had crystals containing a mixture of the oxide {[C₅H₃(SiMe₃)₂]₂Sc}₂(μ-O), **9.7**, and the hydroxide {[C₅H₃(SiMe₃)₂]₂Sc(μ-OH)}₂, **9.8**, contains resonances corresponding to one major product with resonances at +7.77, +7.07, and +0.21 ppm assignable to the cyclopentadienyl and trimethylsilyl substituent protons, respectively. Also, there is at least one other identifiable [C₅H₃(SiMe₃)₂]¹⁻ containing minor product with resonances at +7.46, +7.13, and +0.40 ppm analogous to complex **9.1**, which may be assignable to complex **9.7** or **9.8**. Presumably, the major product is complex **9.1** as it was found that this oxide-containing impure sample of [C₅H₃(SiMe₃)₂]₂ScI gave the Sc(II) metallocene complex {[C₅H₃(SiMe₃)₂]₂ScI}¹⁻ in good yields when treated with KC₈.¹³ Therefore, it may be

likely that **9.7** and **9.8** are only minor byproducts of reactions forming **9.1** using samples of ScI₃-containing oxide impurities, yet are readily crystallizable.

Guzei Analysis. The extent of steric saturation for the scandium atom in its primary coordination sphere for each metal complex described in this Chapter was evaluated using the Guzei solid angle method that provides G , an estimation of the percentage of the coordination sphere of the metal that is protected by ligands.⁴⁰ All Guzei G values in Table 9.4 were calculated on X-ray crystal structures that include hydrogen atoms. For the bimetallic molecules, only the coordination sphere of one metal was used for the calculations, i.e., [(C₅R₅)₂ScX₂]¹⁻ for the halides (R = H, alkyl, trialkylsilyl; X = Cl, I) and [(C₅R₅)₂Sc(μ -O)]¹⁻ for the oxides.

Table 9.4. Solid G values (%) for selected bis(cyclopentadienyl) scandium halide complexes in increasing $G(\text{complex})$ value (%).

Sc(III) Complex	$G(\text{Cp})$ (av.)	$G(\text{X} = \text{F, O, Cl, Br, I})$	$G(\text{complex})$
[(C ₅ H ₅) ₂ Sc(μ -Cl)] ₂ ^{1,a}	28	11	78
[(C ₅ Me ₄ H) ₂ Sc] ₂ (μ -O) ^{15,a}	33	18	81
(C ₅ Me ₅) ₂ ScI ¹¹	34	14	81
(C ₅ Me ₅) ₂ ScCl ¹¹	35	13	81
(C ₅ Me ₅) ₂ ScBr ¹¹	34	15	82
(C ₅ Me ₅) ₂ ScF ¹¹	35	16	83
[C ₅ Me ₄ (SiMe ₃) ₂ ScI, 9.2	38	13	88
[C ₅ Me ₄ (SiMe ₂ ^{<i>t</i>} Bu) ₂ ScI, 9.3	38	14	88
{[C ₅ H ₄ (SiMe ₃) ₂ Sc(μ -I)] ₂ , 9.4	33	12	89
{[C ₅ H ₃ (SiMe ₃) ₂ Sc] ₂ (μ -O), 9.7	35	19	89
[C ₅ H ₃ (SiMe ₃) ₂ ScI, 9.1	38	14	90

$\{[C_5H_3(SiMe_3)_2]_2Sc(\mu-Cl)\}_2$, 9.6	35	11	90
$\{[C_5H_4(Si^iPr_3)]_2Sc(\mu-I)\}_2$, 9.5	35	12	92
$(C_5H_2^tBu_3)_2ScI^{13}$	40	13	92

^a Values were averaged between each crystallographically unique scandium metal center in the asymmetric unit.

The analysis of this set of complexes shows the variation in the ligand *G* values as a function of the specific crystal structure. For example, iodide ligand *G* values are typically 13–14% for terminal iodides and 12% in the bridging complexes. The analogous terminal and bridging chloride *G* values of 13% and 11%, respectively, are numerically less as expected for a smaller ligand, but it only differs by 1% from the iodide, which may be within the accuracy of these calculations. Further examination of the series of $(C_5Me_5)_2ScX$ (*X* = F, Cl, Br, and I)¹¹ complexes shows that the *G* values for the fluoride (16%) and bromide (15%) ligands do not necessarily follow the same periodic trend as the ionic size of the halogens. The *G* values vary from 38% for the $[C_5H_3(SiMe_3)_2]^{1-}$ ligands in monomeric **9.1** to 28% for the $(C_5H_5)^{1-}$ ligands in the dimeric $[(C_5H_5)_2Sc(\mu-Cl)]_2$.¹ Overall, the *G* values for the complexes are in the high range, i.e., 88–92%, as is expected for stable sterically saturated compounds.^{19,41–43}

DISCUSSION

Bis(cyclopentadienyl)scandium iodide complexes can be readily synthesized and crystallographically characterized with a variety of ligands including $(C_5Me_5)^{1-}$,¹¹ $(C_5H_2^tBu_3)^{1-}$,¹³ and the $[C_5H_3(SiMe_3)_2]^{1-}$, $[C_5Me_4(SiMe_3)]^{1-}$, $[C_5Me_4(SiMe_2^tBu)]^{1-}$, $[C_5H_4(SiMe_3)]^{1-}$, and $[C_5H_4(Si^iPr_3)]^{1-}$ examples described here when the synthesis starts with pure samples of ScI_3 . As shown by the isolation of crystals of the oxide $\{[C_5H_3(SiMe_3)_2]_2Sc\}_2(\mu-O)$, **9.7**, and hydroxide $\{[C_5H_3(SiMe_3)_2]_2Sc(\mu-OH)\}_2$, **9.8**, from reactions designed to form $[C_5H_3(SiMe_3)_2]_2ScI$, **9.1**, oxide impurities in a metal halide starting material can give different products and compounds that are

more readily crystallized. This is a good cautionary tale of both starting materials and crystallographic characterization. One should always be aware that small impurities in starting reagents can lead to preferentially crystallized products and that an isolated X-ray crystal structure may not be representative of the bulk material.

The solution NMR data on complexes **9.1–9.6** suggest that the ^{45}Sc NMR chemical shift and line width are highly sensitive to the ligand environment and coordination number around the scandium metal center.^{38,39,44} Monomeric and dimeric species as well as unsolvated and solvated species appear to be discernible based on this set of data due to the variable range of chemical shifts and line width values in the ^{45}Sc NMR spectra. The ^{45}Sc NMR chemical shift also seems to vary depending on the electron-donating properties of the ligands. For the $(\text{C}_5\text{Me}_5)_2\text{ScX}$ ($\text{X} = \text{F}$, Cl , Br , and I) complexes, the ^{45}Sc NMR chemical shifts increase with the less electronegative halides. As an example, the peak for $(\text{C}_5\text{Me}_5)\text{ScF}$ has a chemical shift of 65.7 ppm, whereas for $(\text{C}_5\text{Me}_5)\text{ScI}$, it is 256.9 ppm, Table 9.3. Similarly, with more electron-donating cyclopentadienyl ligands,⁴⁵ the ^{45}Sc NMR shift increases. For example, the resonances for $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]\text{ScI}$, **9.1** and $(\text{C}_5\text{Me}_5)\text{ScI}$ are 208.3 and 256.9 ppm, respectively, Table 9.3. Moreover, the fact that complexes $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ScI}$, **9.2**, and $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{ScI}$, **9.3**, have very similar chemical shifts is consistent with this observation as one would not expect a significant difference in electron-donating ability between the $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]^{1-}$ and $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]^{1-}$ ligands. This type of method can be useful to study the dynamic speciation of different scandium complexes in solution or electronic effects when conventional methods such as ^1H NMR or $^{13}\text{C}\{^1\text{H}\}$ NMR do not produce easily resolvable signals due to minute differences in the proton and carbon environments.

The structural analysis of the complexes shows that both monomeric and dimeric complexes can form, depending on the size of the ligands. Complexes of the larger cyclopentadienyl and halide ligands, specifically $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$, **9.1**, $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ScI}$, **9.2**, $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{ScI}$, **9.3**, and $(\text{C}_5\text{H}_2^t\text{Bu}_3)_2\text{ScI}^{13}$ crystallize as monometallic species that achieve steric saturation of the metal center, as shown by high 88–92% *G* values, without coordination of another halide. The 81% *G* value for $(\text{C}_5\text{Me}_5)_2\text{ScI}^{11}$ is a curious outlier and is consistent with the fact that it forms a complex with THF. It is worth noting that although $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$, **9.1**, has a relatively high *G* value of 90%, it can still complex with THF, as shown previously by Lappert and co-workers.⁹ In addition, $[(\text{C}_5\text{H}_5)_2\text{Sc}(\mu\text{-Cl})]_2^1$ can be isolated and crystallized even though it has a low *G* value of 78% as expected due to the small size of the $(\text{C}_5\text{H}_5)^{1-}$ ligand. Therefore, these values should not be used as a definitive measure of the reactivity of a complex.⁴² The suitability of the monomer versus dimer for reductive formation of Sc(II) complexes remains to be determined, but the identity of these Sc(III) starting materials is well-established.

CONCLUSION

A series of bis(cyclopentadienyl) scandium halide complexes have been synthesized in good yields and high purity and structurally characterized to provide a firm basis for available starting materials for the elaboration of organometallic scandium chemistry. Syntheses must be started from precursors free of oxide impurities that could readily form oxide complexes such as $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}\}_2(\mu\text{-O})$, **9.7**, or hydroxide complexes such as $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-OH})\}_2$, **9.8**.

EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP (99.999%) argon before drying and collection using an S2 Grubbs-type⁴⁶ solvent purification system (JC Meyer) and stored over activated molecular sieves overnight prior to use. Deuterated NMR solvents were degassed and dried over activated molecular sieves before use. NMR spectra were recorded on a Bruker GN500 or AVANCE600 spectrometer at 298 K unless otherwise stated, and ¹H NMR and ¹³C{¹H} NMR spectra were referenced internally to residual protio-solvent resonances. ²⁹Si{¹H} NMR spectra were referenced externally to SiMe₄. ⁴⁵Sc NMR spectra were referenced externally to ScCl₃ dissolved in D₂O. Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR instrument under an argon atmosphere. Elemental analyses were conducted on a Thermo Scientific FlashSmart CHNS/O elemental analyzer at UC Irvine Materials Research Institute's TEMPR facility in Irvine, California. ScI₃,¹⁶ KC₅Me₄(SiMe₂^{*i*}Bu),¹⁷ KC₅H₄(Si^{*i*}Pr₃),¹⁹ KC₅H₄(SiMe₃),⁴⁷ and KC₅H₃(SiMe₃)₂⁴⁸ were synthesized according to literature procedures. ScCl₃ was synthesized via a modification of a literature procedure.⁴⁹ KC₅Me₄(SiMe₃) was synthesized by treating HC₅Me₄(SiMe₃)⁵⁰ with KN(SiMe₃)₂ in toluene.

Synthesis of [C₅H₃(SiMe₃)₂]₂ScI, 9.1. In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with ScI₃ (116 mg, 0.272 mmol), solid KC₅H₃(SiMe₃)₂ (135 mg, 0.543 mmol), and toluene (ca. 15 mL). The flask was sealed, brought out of the glovebox, and was allowed to stir at ca. 110 °C for 16 h to produce a yellow mixture containing a colorless precipitate. The mixture was then cooled to room temperature and brought back into an argon-containing glovebox. Insoluble solids, presumably KI, were removed via centrifugation, followed by filtration through a Kimwipe-packed pipet to produce a clear yellow

supernatant. The solution was concentrated to ca. 2 mL and stored at $-35\text{ }^{\circ}\text{C}$. Pale-yellow crystals of $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$, **9.1**, suitable for study by X-ray diffraction were grown overnight (80 mg, 50% crystalline yield). ^1H NMR (500 MHz, C_6D_6): δ 7.84 (s, 2H, cyclopentadienyl H), 7.10 (s, 4H, cyclopentadienyl H), 0.23 (s, 36H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6): δ 138.9 (cyclopentadienyl C), 135.1 (cyclopentadienyl C), 125.7 (cyclopentadienyl C), 0.14 (SiMe_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, C_6D_6): δ -9.0 (SiMe_3). ^{45}Sc NMR (145 MHz, C_6D_6): δ 208.3 (br, $\Delta\nu_{1/2} = 4300\text{ Hz}$). IR: 3068w, 2950m, 2894w, 1441w, 1403w, 1318w, 1256m, 1241vs, 1206w, 1087s, 1064m, 921s, 874m, 824vs, 801vs, 749vs, 688s cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_4\text{Si}_4\text{ScI}$: C, 44.73; H, 7.17. Found: C, 44.50; H, 7.04. Addition of excess THF to C_6D_6 solutions of **9.1** quantitatively shows the conversion of $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}$, **9.1**, to $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{ScI}(\text{THF})$, **9.1+THF**, by NMR spectroscopy. ^1H NMR (600 MHz, C_6D_6): δ 7.04 (s, 2H, cyclopentadienyl H), 6.67 (s, 4H, cyclopentadienyl H), 3.57 (m, 4H, α -carbon of THF), 1.43 (m, 4H, β -carbon of THF), 0.36 (s, 36H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ 137.2 (cyclopentadienyl C), 126.1 (cyclopentadienyl C), 122.7 (cyclopentadienyl C), 68.0 (α -carbon of THF), 25.8 (β -carbon of THF), 1.0 (SiMe_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, C_6D_6): δ -8.6 (SiMe_3). ^{45}Sc NMR (145 MHz, C_6D_6): δ 81.6 (br, $\Delta\nu_{1/2} = 370\text{ Hz}$).

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ScI}$, **9.2.** In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with ScI_3 (100 mg, 0.235 mmol), $\text{KC}_5\text{Me}_4(\text{SiMe}_3)$ (109 mg, 0.470 mmol), and toluene (ca. 15 mL). The flask was sealed, brought out of the glovebox, and allowed to stir at ca. $110\text{ }^{\circ}\text{C}$ for 16 h to produce a golden yellow mixture containing a colorless precipitate. The mixture was then cooled to room temperature and brought back into an argon-containing glovebox. Insoluble solids, presumably KI, were removed via centrifugation, followed by filtration through a Kimwipe-packed pipet to produce a golden yellow

supernatant. Volatiles were removed under reduced pressure to yield waxy yellow solids. The yellow solids were extracted into hexane (ca. 10 mL) and filtered through a Kimwipe-packed pipet. Volatiles were removed from the supernatant under reduced pressure to yield a yellow crude solid, which was then washed with cold SiMe₄ (ca. 1 mL) and dried under reduced pressure to yield [C₅Me₄(SiMe₃)₂ScI, **9.2**, as a yellow powder (118 mg, 90% crude yield). Yellow crystals of [C₅Me₄(SiMe₃)₂ScI, **9.2**, suitable for study by X-ray diffraction were grown from saturated hexane solutions stored at −35 °C overnight (70 mg, 53% crystalline yield). ¹H NMR (600 MHz, C₆D₆): δ 2.44 (s, 12H, C₅Me₄SiMe₃), 1.76 (s, 12H, C₅Me₄SiMe₃), 0.27 (s, 18H, SiMe₃). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 135.4 (C₅Me₄SiMe₃), 127.7 (C₅Me₄SiMe₃), 124.9 (C₅Me₄SiMe₃), 17.9 (C₅Me₄SiMe₃), 12.0 (C₅Me₄SiMe₃), 1.9 (SiMe₃). ²⁹Si{¹H} NMR (119 MHz, C₆D₆): δ −9.7 (SiMe₃). ⁴⁵Sc NMR (145 MHz, C₆D₆): δ 264.2 (br, Δν_{1/2} = 3200 Hz). IR: 2948w, 2894w, 1461w, 1429w, 1405w, 1380w, 1325m, 1241s, 1129w, 1019m, 831vs, 755s, 686s cm^{−1}. Anal. Calcd for C₂₄H₄₂Si₂ScI: C, 51.60; H, 7.58. Found: C, 51.81; H, 7.66. Addition of excess THF to C₆D₆ solutions of **9.2** partially converted [C₅Me₄(SiMe₃)₂ScI, **9.2**, to [C₅Me₄(SiMe₃)₂ScI, **9.2**+THF, as determined by ⁴⁵Sc NMR spectroscopy. ¹H NMR (600 MHz, C₆D₆): δ 3.57 (m, 4H, α-carbon of THF), 2.42 (s, 12H, C₅Me₄SiMe₃), 1.77 (s, 12H, C₅Me₄SiMe₃), 1.43 (m, 4H, β-carbon of THF), 0.25 (s, 18H, SiMe₃). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 135.4 (C₅Me₄SiMe₃), 127.7 (C₅Me₄SiMe₃), 124.9 (C₅Me₄SiMe₃), 67.8 (α-carbon of THF), 25.8 (β-carbon of THF), 17.8 (C₅Me₄SiMe₃), 12.0 (C₅Me₄SiMe₃), 1.8 (SiMe₃). ²⁹Si{¹H} NMR (119 MHz, C₆D₆): δ −9.7 (SiMe₃). ⁴⁵Sc NMR (145 MHz, C₆D₆): δ 176.3 (br, Δν_{1/2} = 340 Hz).

Synthesis of [C₅Me₄(SiMe₂tBu)]₂ScI, **9.3.** In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with ScI₃ (132 mg, 0.310 mmol), KC₅Me₄(SiMe₂tBu) (170 mg, 0.620 mmol), and toluene (ca. 15 mL). The flask was sealed, brought

out of the glovebox, and allowed to stir at ca. 110 °C for 16 h to produce a golden yellow containing a colorless precipitate. The mixture was then cooled to room temperature and dried under reduced pressure to yield yellow and colorless solids before it was sealed and brought back into an argon-containing glovebox. The product was extracted into hexane (ca. 10 mL) and centrifuged, then filtered through a Kimwipe-packed pipet to remove insoluble solids, presumably KI. Volatiles were removed under reduced pressure from the golden yellow supernatant to yield waxy yellow solids. The solids were then washed with cold SiMe₄ (ca. 1 mL) and dried under reduced pressure to yield [C₅Me₄(SiMe₂^{*t*}Bu)]₂ScI, **9.3**, as a bright yellow powder (150 mg, 75% crude yield). Yellow crystals of [C₅Me₄(SiMe₂^{*t*}Bu)]₂ScI, **9.3**, suitable for study by X-ray diffraction were grown from saturated hexane solutions stored at –35 °C overnight (108 mg, 54% crystalline yield). ¹H NMR (600 MHz, C₆D₆): δ 2.58 (s, 12H, C₅Me₄SiR₃), 1.76 (s, 12H, C₅Me₄SiR₃), 0.80 (s, 18H, SiMe₂^{*t*}Bu), 0.40 (s, 12H, SiMe₂^{*t*}Bu). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 136.5 (C₅Me₄SiR₃), 128.0 (C₅Me₄SiR₃), 124.2 (C₅Me₄SiR₃), 27.8 (CMe₃), 20.6 (CMe₃), 18.9 (C₅Me₄SiR₃), 12.2 (C₅Me₄SiR₃), –1.0 (SiMe₂^{*t*}Bu). ²⁹Si{¹H} NMR (119 MHz, C₆D₆): δ –2.4 (SiMe₂^{*t*}Bu). ⁴⁵Sc NMR (145 MHz, C₆D₆): δ 263.9 (br, Δν_{1/2} = 3300 Hz). IR: 2928m, 2853m, 1463m, 1379w, 1314m, 1247s, 1124w, 1012m, 956w, 805vs, 762vs, 742s, 677vs cm^{–1}. Anal. Calcd for C₃₀H₅₄Si₂ScI: C, 56.06; H, 8.47. Found: C, 55.86; H, 8.51. Addition of excess THF to C₆D₆ solutions of **9.3** partially converted [C₅Me₄(SiMe₂^{*t*}Bu)]₂ScI, **9.3**, to [C₅Me₄(SiMe₂^{*t*}Bu)]₂ScI(THF), **9.3+THF**, as determined by ⁴⁵Sc NMR spectroscopy. ¹H NMR (600 MHz, C₆D₆): δ 3.57 (m, 4H, α-carbon of THF), 2.57 (s, 12H, C₅Me₄SiR₃), 1.76 (s, 12H, C₅Me₄SiR₃), 1.43 (m, 4H, β-carbon of THF), 0.79 (s, 18H, SiMe₂^{*t*}Bu), 0.39 (s, 12H, SiMe₂^{*t*}Bu). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 136.5 (C₅Me₄SiR₃), 128.0 (C₅Me₄SiR₃), 124.2 (C₅Me₄SiR₃), 67.9 (α-carbon of THF), 27.8 (CMe₃), 25.8 (β-carbon of THF), 20.6 (CMe₃), 18.9 (C₅Me₄SiR₃), 12.1 (C₅Me₄SiR₃), –1.0 (SiMe₂^{*t*}Bu). ²⁹Si{¹H}

NMR (119 MHz, C₆D₆): δ -2.4 (*SiMe₂tBu*). ⁴⁵Sc NMR (145 MHz, C₆D₆): δ 167.5 (br, $\Delta\nu_{1/2}$ = 850 Hz).

Synthesis of {[C₅H₄(SiMe₃)]₂Sc(μ -I)}₂, **9.4.** In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with ScI₃ (202 mg, 0.475 mmol), KC₅H₄(SiMe₃) (167 mg, 0.947 mmol), and toluene (ca. 15 mL). The flask was sealed, brought out of the glovebox, and allowed to stir at ca. 110 °C for 16 h to produce a yellow-orange mixture containing colorless precipitate. The flask was then sealed, cooled to room temperature, and brought back into an argon-containing glovebox. The mixture was then centrifuged and filtered through a Kimwipe-packed pipet to remove insoluble solids, presumably KI. Volatiles were removed under reduced pressure to yield brown and white solids. The solids were then washed with cold hexane (ca. 2 mL) and dried under reduced pressure to yield {[C₅H₄(SiMe₃)]₂Sc(μ -I)}₂, **9.4**, as colorless solids (133 mg, 63%). Colorless X-ray quality crystals of **9.4** can be grown from saturated toluene solutions of **9.4** stored at -35 °C overnight. ¹H NMR (600 MHz, C₆D₆): δ 7.05 (m, 8H, C₅H₄SiMe₃), 6.58 (m, 8H, C₅H₄SiMe₃), 0.31 (s, 36H, SiMe₃). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 124.3 (C₅H₄SiMe₃), 123.3 (C₅H₄SiMe₃), 118.7 (C₅H₄SiMe₃), 0.5 (SiMe₃). ²⁹Si{¹H} NMR (119 MHz, C₆D₆): δ -8.6 (SiMe₃). ⁴⁵Sc NMR (145 MHz, C₆D₆): δ 71.2 (br, $\Delta\nu_{1/2}$ = 1900 Hz). IR: 2948w, 2889w, 1444w, 1403w, 1366m, 1316w, 1243s, 1174s, 1044s, 904s, 859w, 829vs, 792vs, 751vs, 688s cm⁻¹. Anal. Calcd for C₃₂H₅₂Si₄Sc₂I₂: C, 43.05; H, 5.87. Found: C, 43.27; H, 6.07. Addition of excess THF to C₆D₆ solutions of **9.4** quantitatively shows the conversion of {[C₅H₄(SiMe₃)]₂Sc(μ -I)}₂, **9.4**, to [C₅H₄(SiMe₃)]₂ScI(THF), **9.4+THF**, by NMR spectroscopy. ¹H NMR (600 MHz, C₆D₆): δ 6.66 (br s, 4H, C₅H₄SiMe₃), 6.19 (s, 4H, C₅H₄SiMe₃), 3.55 (m, 4H, α -carbon of THF), 1.44 (m, 4H, β -carbon of THF), 0.36 (s, 18H, SiMe₃). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 123.8 (C₅H₄SiMe₃), 121.7 (C₅H₄SiMe₃), 115.6 (br, C₅H₄SiMe₃), 67.9 (α -carbon of THF),

25.8 (β -carbon of THF), 0.63 (SiMe_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, C_6D_6): δ -8.6 (SiMe_3). ^{45}Sc NMR (145 MHz, C_6D_6): δ 59.7 (br, $\Delta\nu_{1/2} = 160$ Hz).

Synthesis of $\{[\text{C}_5\text{H}_4(\text{Si}^i\text{Pr}_3)]_2\text{Sc}(\mu\text{-I})\}_2$, **9.5.** In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with ScI_3 (100 mg, 0.235 mmol), $\text{KC}_5\text{H}_4(\text{Si}^i\text{Pr}_3)$ (122 mg, 0.470 mmol), and toluene (ca. 15 mL). The flask was sealed, brought out of the glovebox, and allowed to stir at ca. 110 °C for 16 h to produce a pale-yellow mixture containing a colorless precipitate. The flask was then cooled to room temperature and brought back into an argon-containing glovebox. The mixture was centrifuged and filtered through a Kimwipe-packed pipet to remove insoluble solids, presumably KI. Volatiles were removed under reduced pressure to yield waxy, off-white solids. The solids were then washed with cold hexane (ca. 2 mL) and dried under reduced pressure to yield $\{[\text{C}_5\text{H}_4(\text{Si}^i\text{Pr}_3)]_2\text{Sc}(\mu\text{-I})\}_2$, **9.5**, as colorless solids (98 mg, 94%). Colorless X-ray quality crystals can be grown from saturated toluene solutions of **9.5** stored at -35 °C overnight. ^1H NMR (600 MHz, C_6D_6): δ 7.38 (m, 8H, $\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 6.53 (m, 8H, $\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 1.28 (m, 12H, CH of Si^iPr_3), 1.09 (m, 72H, CH_3 of Si^iPr_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ 126.1 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 124.3 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 119.0 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 19.6 (CH_3 of Si^iPr_3), 12.5 (CH of Si^iPr_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, C_6D_6): δ 0.8 (Si^iPr_3). ^{45}Sc NMR (145 MHz, C_6D_6): δ 172.8 (br, $\Delta\nu_{1/2} = 7000$ Hz), 34.5 (br, $\Delta\nu_{1/2} = 2600$ Hz). IR: 2939m, 2861s, 1459m, 1366w, 1362w, 1239w, 1167m, 1046s, 1001m, 880s, 790vs, 652vs cm^{-1} . Anal. Calcd for $\text{C}_{56}\text{H}_{100}\text{Si}_4\text{Sc}_2\text{I}_2$: C, 54.71; H, 8.20. Found: C, 54.55; H, 8.26. Addition of excess THF to C_6D_6 solutions of **9.5** quantitatively shows the conversion of $\{[\text{C}_5\text{H}_4(\text{Si}^i\text{Pr}_3)]_2\text{Sc}(\mu\text{-I})\}_2$, **9.5**, to $[\text{C}_5\text{H}_4(\text{Si}^i\text{Pr}_3)]_2\text{ScI}(\text{THF})$, **9.5+THF**, by NMR spectroscopy. ^1H NMR (600 MHz, C_6D_6): δ 6.75 (m, 4H, $\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 6.31 (m, 4H, $\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 3.56 (m, 4H, α -carbon of THF), 1.56 (sept, 6H, CH of Si^iPr_3 , $^3J_{\text{HH}} = 7.2$ Hz), 1.45 (m, 4H, β -carbon of THF), 1.18 (d, 36H, CH_3 of Si^iPr_3 , $^3J_{\text{HH}} = 7.2$

Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ 125.0 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 120.5 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 115.7 ($\text{C}_5\text{H}_4\text{Si}^i\text{Pr}_3$), 67.9 (α -carbon of THF), 25.8 (β -carbon of THF), 19.7 (CH_3 of Si^iPr_3), 12.8 (CH of Si^iPr_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, C_6D_6): δ -0.6 (Si^iPr_3). ^{45}Sc NMR (145 MHz, C_6D_6): δ 68.9 (br, $\Delta\nu_{1/2} = 540$ Hz).

Synthesis of $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-Cl})\}_2$, **9.6.** In an argon-containing glovebox, a 100 mL Schlenk flask fitted with a Teflon stopper was charged with ScCl_3 (116 mg, 0.767 mmol), $\text{KC}_5\text{H}_3(\text{SiMe}_3)_2$ (381 mg, 1.33 mmol), and toluene (ca. 15 mL). The flask was sealed, brought out of the glovebox, and allowed to stir at ca. 110 °C for 16 h to yield a cloudy brown-yellow mixture containing colorless precipitate. Removal of the solvent under reduced pressure yielded off-white solids. The Schlenk flask was then brought back into an argon-containing glovebox, and toluene (ca. 15 mL) was added. The resulting cloudy brown-yellow mixture was centrifuged and filtered through a pipet packed with Kimwipe tissue to yield a clear brown solution. Removal of the solvent under reduced pressure yielded light brown solids. The solids were then washed with cold hexane (ca. 2 mL) and subsequently dried under reduced pressure to yield $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-Cl})\}_2$, **9.6**, as colorless solids (128 mg, 33%). Yellow X-ray quality crystals of **9.6** can be grown from saturated toluene solutions of **9.6** stored at -18 °C overnight. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **9.6** in neat C_6D_6 at room temperature presumably contain an equilibrium mixture of isomers and monomeric and dimeric species, so assignments could not be definitively determined. $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, C_6D_6): δ -9.0 (br, SiMe_3). ^{45}Sc NMR (145 MHz, C_6D_6): δ 138.3 (br, $\Delta\nu_{1/2} = 2700$ Hz), 43.3 (br, $\Delta\nu_{1/2} = 1900$ Hz). IR: 2948w, 2893w, 1437w, 1398w, 1321w, 1242s, 1217w, 1209w, 1077s, 917s, 865m, 821s, 799s, 746s, 686m cm^{-1} . EA: Anal. Calcd for $\text{C}_{44}\text{H}_{84}\text{Si}_8\text{Sc}_2\text{Cl}_2$: C, 52.92; H, 8.48. Found: C, 43.78; H, 6.98. C, 42.34; H, 6.74. C, 37.53; H, 6.18. Low C and H values were observed across multiple runs and suggest incomplete

combustion.^{43,51–55} The C/H ratios in the analytical data give formulas of C₄₄H_{83.4}, C₄₄H_{83.3}, and C₄₄H₈₆, respectively, close to the calculated ratio of C₄₄H₈₄. Addition of excess THF to C₆D₆ solutions of **9.6** quantitatively show the conversion of {[C₅H₃(SiMe₃)₂]₂Sc(μ -Cl)}₂, **9.6**, to [C₅H₃(SiMe₃)₂]₂ScCl(THF), **9.6+THF**, by NMR spectroscopy. ¹H NMR (600 MHz, C₆D₆): δ 6.73 (m, 2H, cyclopentadienyl H), 6.64 (m, 4H, cyclopentadienyl H), 3.57 (m, 4H, α -carbon of THF), 1.44 (m, 4H, β -carbon of THF), 0.35 (s, 36H, CH₃ of SiMe₃). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 134.6 (cyclopentadienyl C), 125.7 (cyclopentadienyl C), 121.9 (cyclopentadienyl C), 68.1 (α -carbon of THF), 25.8 (β -carbon of THF), 0.8 (CH₃ of SiMe₃). ²⁹Si{¹H} NMR (119 MHz, C₆D₆): δ -9.0 (SiMe₃). ⁴⁵Sc NMR (145 MHz, C₆D₆): δ 29.9 (br, $\Delta\nu_{1/2}$ = 940 Hz).

Synthesis of [C₅H₃(SiMe₃)₂]₂ScI, **9.1 Containing {[C₅H₃(SiMe₃)₂]₂Sc}₂(μ -O), **9.7** and {[C₅H₃(SiMe₃)₂]₂Sc(μ -OH)}₂, **9.8**.** In an argon-containing glovebox, ScI₃ (500 mg, 1.17 mmol), presumably containing an oxide impurity, and KC₅H₃(SiMe₃)₂ (490 mg, 2.35 mmol) were combined in toluene (ca. 40 mL) in a 100 mL Schlenk flask containing a Teflon-coated stir bar and fitted with a Teflon stopcock. The reaction mixture was heated to ca. 60 °C in an oil bath and was allowed to stir for 24 h. Solvent was removed under reduced pressure to yield a yellow/green oil that was then brought back into the glovebox for continued workup. The residue was then extracted into hexane (ca. 15 mL) and centrifuged to yield a white precipitate, presumably KI, and a golden yellow supernatant. The supernatant was collected and dried under reduced pressure to yield flaky golden solids (598 mg). Colorless crystals of a mixture of {[C₅H₃(SiMe₃)₂]₂Sc}₂(μ -O), **9.7**, and {[C₅H₃(SiMe₃)₂]₂Sc(μ -OH)}₂, **9.8**, were grown from saturated toluene solutions stored at -18 °C overnight. NMR data for **9.1**: ¹H NMR (600 MHz, C₇D₈): δ 7.77 (m, 2H, cyclopentadienyl H), 7.07 (m, 4H, cyclopentadienyl H), 0.21 (s, 36H, SiMe₃). NMR data for **7**: ¹H NMR (600 MHz, C₇D₈): δ 7.46 (m, 4H, cyclopentadienyl H), 7.13 (m, 8H, cyclopentadienyl H), 0.40 (s, 72H,

SiMe₃). IR: 2950w, 2890w, 1441w, 1399w, 1319w, 1242s, 1204w sh, 1078s, 917m, 824s, 796m, 747s, 692s cm⁻¹.

X-ray Data Collection, Structure Solution and Refinement for [C₅H₃(SiMe₃)₂]₂ScI,

9.1. A yellow crystal of approximate dimensions 0.171 x 0.177 x 0.211 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for data collection (45 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was *2/m* and the systematic absences were consistent with the monoclinic space groups *Pc* and *P2/c*. It was later determined that space group *P2/c* was correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. The molecule was located on a two-fold rotation axis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded wR₂ = 0.0448 and Goof = 1.050 for 134 variables refined against 4434 data (0.70 Å), R₁ = 0.0181 for those 4048 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for [C₅Me₄(SiMe₃)]₂ScI,

9.2. A yellow crystal of approximate dimensions 0.128 x 0.315 x 0.389 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX4⁶¹ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time). The raw frame data was processed using SAINT⁶² and SADABS⁶³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *Pbcn* that was later determined to be correct. The structure was

solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. The molecule was located on a two-fold rotation axis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0573$ and $Goof = 1.129$ for 135 variables refined against 4231 data ($0.69 \text{ \AA}$), $R1 = 0.0256$ for those 3464 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2\text{ScI}$, 9.3. A yellow crystal of approximate dimensions $0.166 \times 0.176 \times 0.221 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that space group $C2/c$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. The molecule was located about a two-fold rotation axis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0539$ and $Goof = 1.045$ for 164 variables refined against 4984 data ($0.70 \text{ \AA}$), $R1 = 0.0225$ for those 4406 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $\{[\text{C}_5\text{H}_4(\text{SiMe}_3)]_2\text{Sc}(\mu\text{-I})\}_2$, 9.4. A colorless crystal of approximate dimensions $0.193 \times 0.200 \times 0.295 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX4⁶¹ program package was used to determine the unit-cell parameters and for data collection (5

sec/frame scan time). The raw frame data was processed using SAINT⁶² and SADABS⁶³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule is located on an inversion center. Least-squares analysis yielded $wR2 = 0.0523$ and $Goof = 1.060$ for 187 variables refined against 0.0523 data (0.69 Å), $R1 = 0.0199$ for those 5465 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $\{[C_5H_4(Si^iPr_3)]_2Sc(\mu-D)\}_2$, 9.5. A colorless crystal of approximate dimensions 0.100 x 0.149 x 0.504 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. The molecule was located about an inversion center. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0649$ and $Goof = 1.080$ for 301 variables refined against 9087 data (0.70 Å), $R1 = 0.0251$ for those 8415 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-Cl})\}_2$, 9.6. A colorless crystal of approximate dimensions 0.088 x 0.163 x 0.248 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁵⁶ program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time). The raw frame data was processed using SAINT⁵⁷ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule is located on an inversion center. Least-squares analysis yielded $wR2 = 0.1103$ and $\text{Goof} = 1.013$ for 265 variables refined against 8321 data (0.70 Å), $R1 = 0.0465$ for those 5473 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}\}_2(\mu\text{-O})$, 9.7, and $\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Sc}(\mu\text{-OH})\}_2$, 9.8. A colorless crystal of approximate dimensions 0.162 x 0.183 x 0.265 mm was mounted in a cryoloop and transferred to a Bruker X8 Prospector diffractometer system. The APEX3⁶⁴ program package was used to determine the unit-cell parameters and for data collection (5-10 sec/frame scan time). The raw frame data was processed using SAINT⁶⁵ and SADABS⁵⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁵⁹ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁰ for neutral

atoms were used throughout the analysis. H2 was located from a difference-Fourier map and refined (x,y,z and U_{iso}) using constraints/restraints (DFIX, SIMU). The rest of the hydrogen atoms were included using a riding model. The molecule was located on an inversion center. The crystal structure possibly contained a mixture of a bridging oxo complex and bridging hydroxide complex that was modeled as 75:25 oxo:di-hydroxide. Least-squares analysis yielded $wR2 = 0.980$ and $Goof = 1.047$ for 275 variables refined against 5131 data ($0.83 \text{ \AA}$), $R1 = 0.0391$ for those 4787 data with $I > 2.0\sigma(I)$.

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Chapter 10:

A Linear Metallocene of Sc(II) Supported by $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Bu})]^{1-}$ Ligands

INTRODUCTION[†]

The discovery of ferrocene, $(\text{C}_5\text{H}_5)_2\text{Fe}$,¹ in the 1950's is often cited as the beginning of modern organometallic chemistry.²⁻⁸ This compound ignited interest in the study of organometallic complexes since it was the first example of a previously unknown structural motif wherein a metal ion is “sandwiched” between two parallel cyclopentadienyl rings with a Cnt–M–Cnt angle of 180° (Cnt = cyclopentadienyl ring centroid). Since then, the bis(cyclopentadienyl) ligand environment has been extended to other elements throughout the periodic table and many examples throughout the *d*-block have the same parallel ring structure as ferrocene.⁴⁻¹² However, bis(cyclopentadienyl) complexes of the early transition metals as well as the heavier *s*- and *f*-block elements appear to preferentially adopt bent metallocene structures.¹³⁻²⁰ Numerous hypotheses have been proposed to explain the origin of bending in a bent metallocene such as interligand attractive van der Waals forces, contributions from the metal valence orbitals, dipole–dipole interactions due to polarization of the metal ion, and intermolecular agostic interactions.^{13,20-25} Sterically bulky cyclopentadienyl ligands that overcome these interactions through interligand steric repulsion can be employed to enforce linearity.²⁶⁻³¹

The metallocene chemistry of the first element in the transition metal series, scandium, has lagged behind other metals due partly to the experimental difficulties associated with the electropositive Sc(III) ion and the fact that crystallographically characterizable Sc(II) complexes were not reported until 2017.³² In 2024, the first crystallographically characterized neutral

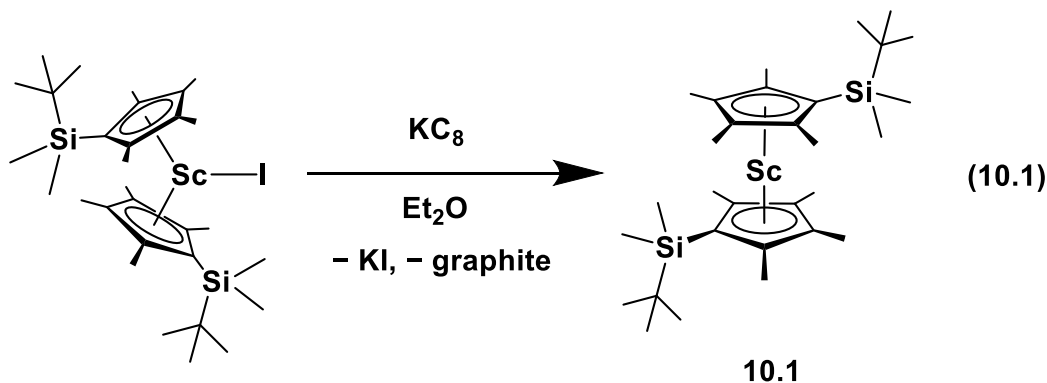
[†]This work was in collaboration with Ahmadreza Rajabi and Professor Filipp Furché at the University of California, Irvine, who performed the electronic structure calculations.

bis(cyclopentadienyl) Sc(II) complex was isolated, namely $(C_5H_2^tBu_3)_2Sc$.³³ It has a bent metallocene structure with a Cnt–Sc–Cnt angle of 170.6° that was explained by a first-order Jahn-Teller effect. It does not have the sterically optimal linear metallocene structure of ferrocene despite the large size of the ligand and the small size of the metal.³³

By using the $[C_5Me_4(SiMe_2^tBu)]^{1-}$ ligand,^{28,34-37} a Sc(II) metallocene with the same parallel ring structure of ferrocene can be isolated. The synthesis, structure, spectroscopy, and reactivity of this complex, $[C_5Me_4(SiMe_2^tBu)]_2Sc$, are detailed in this Chapter. The synthesis and structure of the Ca(II) analog are presented for comparison, as well as computational studies investigating the electronic structures of $[C_5Me_4(SiMe_2^tBu)]_2Sc$ and $[C_5Me_4(SiMe_2^tBu)]_2Ca$.

RESULTS AND DISCUSSION

The reduction of $C_5Me_4(SiMe_2^tBu)_2ScI$ ³⁸ with 1.2 equiv of potassium graphite (KC_8) in Et_2O at room temperature generated red solids of $[C_5Me_4(SiMe_2^tBu)]_2Sc$, **10.1**, in 84% crude yield after work up, eq 10.1. The reaction can also be performed in hexane or toluene at room



temperature, but the reaction rate is slower. For instance, when the reaction is done in toluene, it does not reach full conversion even after 10 days. Complex **10.1** is soluble in hydrocarbons, arenes, Et_2O , and $SiMe_4$. It crystallizes from saturated hexane solutions stored at $-30^\circ C$ as dark

red cubes suitable for study by X-ray diffraction, Figure 10.1. In the presence of THF or 1,2-dimethoxyethane, dark red solutions of **10.1** quickly transition to clear yellow solutions which suggests decomposition to unidentified Sc(III) products. Complex **10.1** melts without decomposition between 137–143 °C. For comparison, $(C_5H_2/Bu_3)_2Sc$ melts between 268–271 °C.³³ Moreover, **10.1** is paramagnetic and has a room temperature EPR spectrum in hexane that displays an isotropic eight-line pattern centered at $g_{iso} = 1.99$ with an average hyperfine coupling

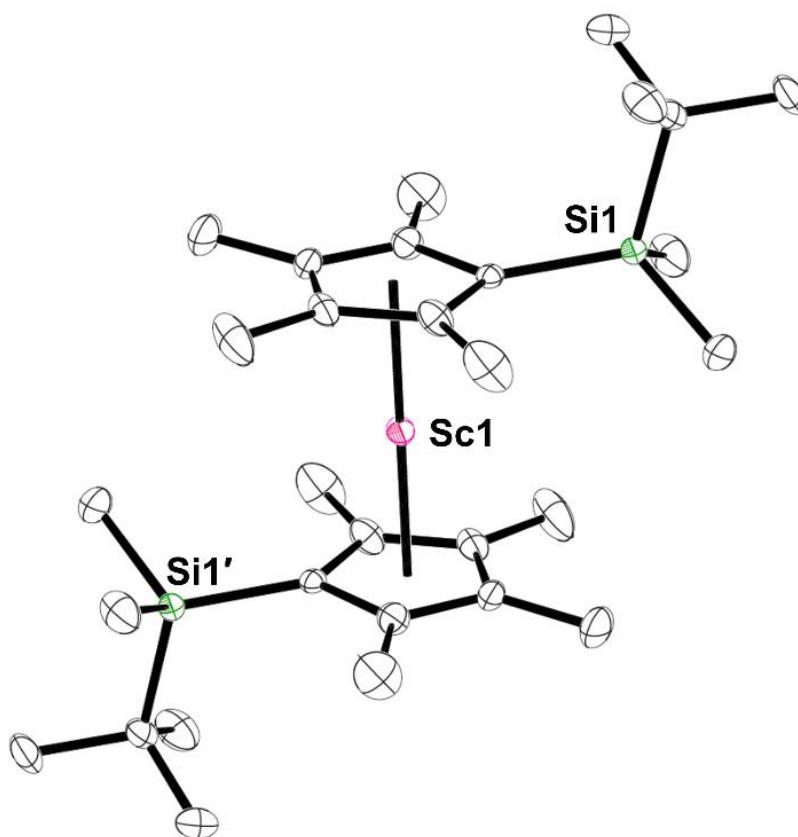


Figure 10.1. Molecular structure of $[C_5Me_4(SiMe_2'Bu)]_2Sc$, **10.1**, with ellipsoids drawn at 50% probability. Hydrogen atoms are not shown for clarity.

constant of $A_{iso} = 88$ MHz, consistent with a Sc(II) ion (^{45}Sc , $I = 7/2$, 100% abundance), Figure 10.2 (left).^{32,33,39-41} A room temperature magnetic moment^{42,43} of $1.3 \mu_B$ was measured for **10.1** which is consistent with a $3d^1$ electron configuration. The room temperature UV-visible spectrum

of a red solution of **10.1** in hexane shows an absorbance maximum at approximately 410 nm and shoulders at 330 and 510 nm with molar extinction coefficients of 1500, 3700, and 520 M⁻¹cm⁻¹, respectively, Figure 10.2 (right).

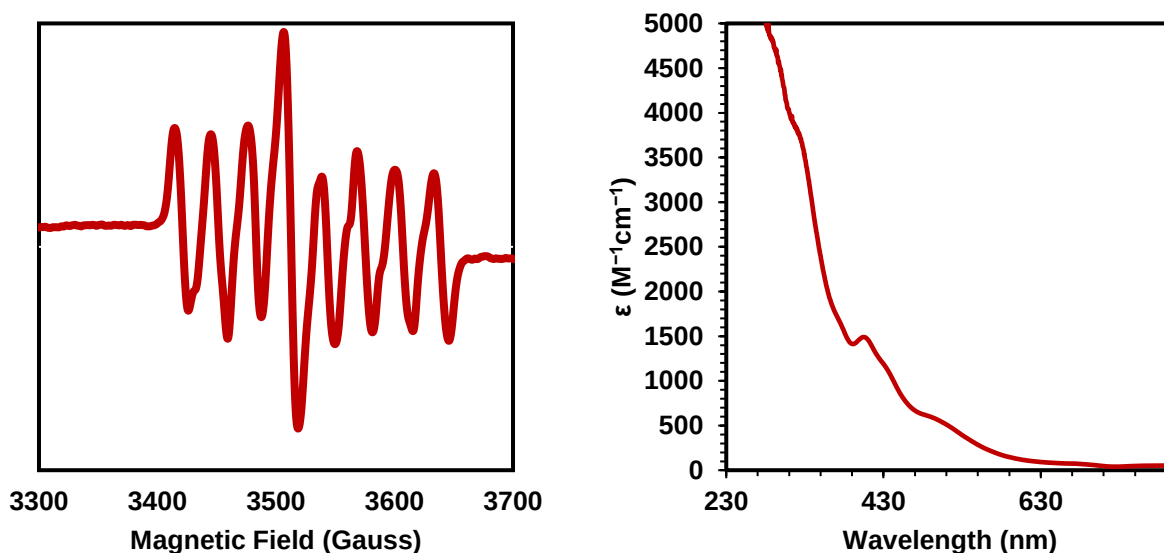


Figure 10.2. (Left) EPR spectrum and (Right) UV-visible spectrum of **10.1** in hexane at room temperature.

[C₅Me₄(SiMe₂tBu)]₂Sc, **10.1**, crystallizes in the *P*2₁/*n* space group with the scandium atom lying on an inversion center. The structure of **10.1** is that of a linear metallocene with a Sc–Cnt distance of 2.102 Å and a Cnt–Sc–Cnt angle of 180° as required by crystallographic symmetry. Its structure is isomorphous to that of the previously characterized transition metal [C₅Me₄(SiMe₂tBu)]₂M complexes where M = Ti²⁸, Fe³⁴ and the main group elements, Ge,³⁵ Sn,³⁵ and Pb.³⁵ In contrast, [C₅Me₄(SiMe₂tBu)]₂Zn crystallizes with one η⁵- and one η¹-cyclopentadienyl ligand.³⁶

In the solid-state, the silyl substituents on the cyclopentadienyl rings of **10.1** are oriented such that the *tert*-butyl groups point away from the scandium metal center, Figure 10.1. The

cyclopentadienyl rings are in a staggered conformation which contrasts with the bent $(C_5H_2^tBu_3)_2Sc^{33}$ where the cyclopentadienyl rings are eclipsed as shown in the top-down views in Figure 10.3 below. In both cases, it is likely that steric repulsion between the substituents begets the orientation in which the cyclopentadienyl rings adopt with respect to each other. For $(C_5H_2^tBu_3)_2Sc^{33}$ to minimize steric clash between *tert*-butyl groups, the cyclopentadienyl ligands align in a way so that two *tert*-butyl groups of each ligand are eclipsed over the hydrogen

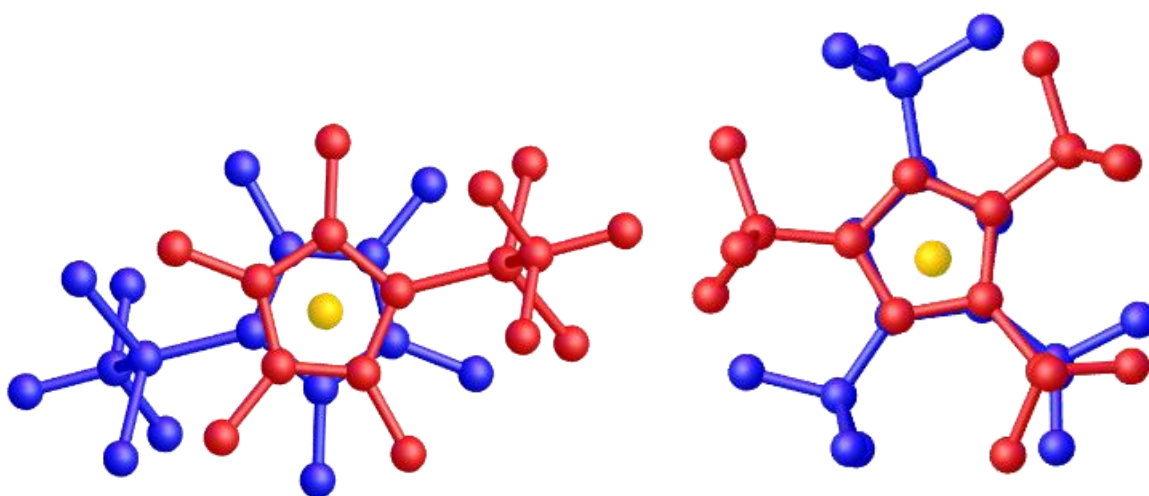
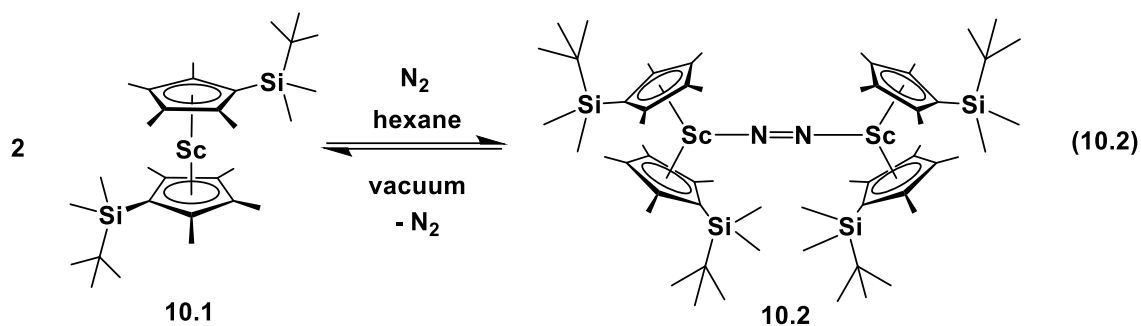


Figure 10.3. Top-down view of the solid-state structures of $[C_5Me_4(SiMe_2^tBu)]_2Sc$, **10.1**, (left) and $(C_5H_2^tBu_3)_2Sc^{33}$ (right). Sc atoms are yellow and cyclopentadienyl ligands are red or blue.

substituents of the opposite ligand. The remaining *tert*-butyl group on one of the rings is eclipsed with one on the other ring and these are located at the open part of the bent metallocene wedge to minimize repulsive effects. In **10.1**, bending is presumably not favorable due to steric repulsion from the four methyl groups and the bulky silyl group on each $[C_5Me_4(SiMe_2^tBu)]^{1-}$ ligand. Full substitution of the cyclopentadienyl ring appears to be important to favor a linear geometry over a bent geometry.²⁶⁻³¹

The extent of steric saturation around the metal center of **10.1** was calculated using the Guzei Solid-Angle method which provides a G value as an estimation of the percentage of the coordination sphere around the metal that is protected by its ligand environment.⁴⁴ Surprisingly, the 81% G value of **10.1** is less than the $G = 87\%$ of $(C_5H_2^tBu_3)_2Sc$. Hence, the less sterically crowded **10.1** adopts the structure that keeps the ligands furthest apart rather than the bent structure of more crowded $(C_5H_2^tBu_3)_2Sc$. However, the G value of **10.1** is greater than the 75% value for the calculated structure of “ $(C_5Me_5)_2Sc$ ” which was reported to be thermally unstable.³³ It should be noted that the calculated G values are calculated on static crystal structures and may not be representative of the extent of steric shielding that coordination complexes experience in solution. Thus, while the G value for complex **10.1** is calculated on a structure that orients the silyl substituent such that the *tert*-butyl group is pointed away from the metal, free rotation of the silyl substituent in solution likely allows for the scandium metal center in complex **10.1** to experience a greater extent of steric shielding than is portrayed by the crystal structure.

The reactivity of **10.1** with N_2 was explored because $(C_5H_2^tBu_3)_2Sc$ was not observed to react with N_2 ,⁴⁵ yet the thermally unstable reduction product of $(C_5Me_5)_2ScI$ does.^{33,46} Upon exposure to a dinitrogen atmosphere, dark red solutions of **10.1** in either hexane or C_6D_6 immediately transitioned to dark blue-purple solutions similar to the previously reported end-on coordinated reduced dinitrogen scandium complex $[(C_5Me_5)_2Sc]_2(\mu-\eta^1:\eta^1-N_2)$.⁴⁶ Indeed, dark blue-purple crystals identified as $\{[C_5Me_4(SiMe_2^tBu)]_2Sc\}_2(\mu-\eta^1:\eta^1-N_2)$, **10.2**, were grown from saturated hexane solutions stored at $-35\text{ }^\circ\text{C}$, eq 10.2, Figure 10.4.



Complex **10.2** crystallizes from hexane in the $C2/c$ space group on a two-fold rotation axis. The average 2.203 Å Sc–Cnt and 2.133(4) Å Sc–N distances of **10.1** are longer than the analogous 2.17 Å Sc–Cnt and 2.049(3) Å Sc–N distances in $[(C_5Me_5)_2Sc]_2(\mu-\eta^1:\eta^1-N_2)$.⁴⁶ Furthermore, the 141.5° average Cnt–Sc–Cnt angle of **10.2** is smaller than the 146.7° of $[(C_5Me_5)_2Sc]_2(\mu-\eta^1:\eta^1-N_2)$.⁴⁶ The nitrogen atoms of the $(N=N)^{2-}$ moiety are crystallographically unique and have an N–N distance of 1.180(6) Å, longer than the analogous distance in free dinitrogen (1.0975 Å)⁴⁷ and consistent with a lower bond order. Compared to previously reported $(N=N)^{2-}$ scandium complexes, the N–N distance of **10.2** is most similar to that of $[(C_5Me_5)_2Sc]_2(\mu-\eta^1:\eta^1-N_2)$,⁴⁶ 1.174(5) Å, and is shorter than the complexes with side-on coordinated $(N_2)^{2-}$ moieties which range from 1.232(2)–1.250(2) Å.^{46,48,49}

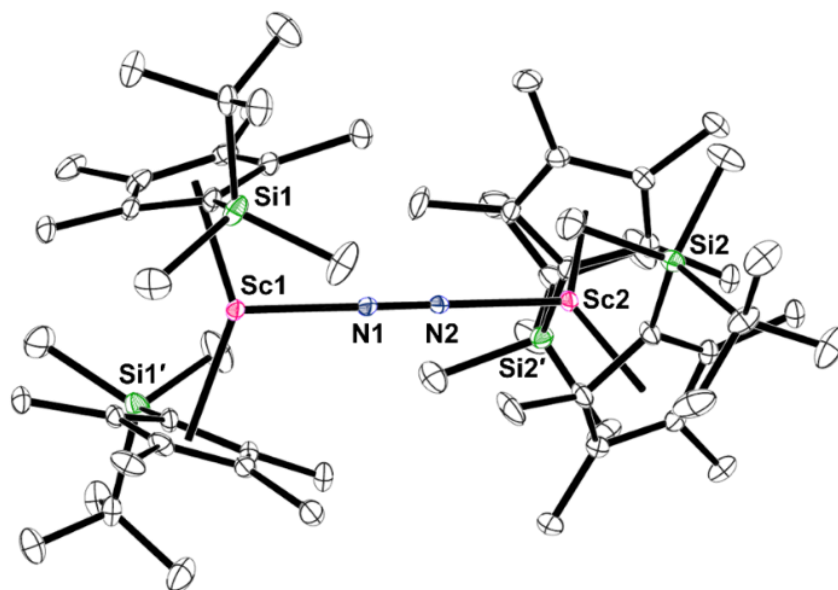


Figure 10.4. Molecular structure of $\{[C_5Me_4(SiMe_2'Bu)]_2Sc\}_2(\mu-\eta^1:\eta^1-N_2)$, **10.2**, with ellipsoids drawn at 30% probability. Hydrogen atoms and the cocrystallized solvent molecule are not shown for clarity.

In solution, the conversion of complex **10.1** to **10.2** is reversible, eq 10.2. Removal of solvent from dark blue-purple solutions of **10.2** under vacuum regenerates red solids of **10.1**. However, no noticeable interconversion between **10.1** and **10.2** was observed upon introducing a dinitrogen atmosphere to dry solids of **10.1** or placing solid **10.2** under vacuum. Reversible dinitrogen chemistry was previously observed for the Sm(II) metallocene $(C_5Me_5)_2Sm$ which exists under dinitrogen in a temperature-dependent equilibrium with $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-N_2)$.⁵⁰ The Sc(II) tris(amide) complex $\{Sc[N(SiMe_3)_2]_3\}^{1-}$ also reversibly binds dinitrogen.⁵¹

Over the course of isolating **10.1**, the hydrolysis product $[C_5Me_4(SiMe_2'Bu)]_2Sc(OH)$, **10.3**, was isolated and structurally characterized, Figure 10.5. Complex **10.3** is a rare example of a crystallographically characterized Sc(III) compound with a terminal hydroxide ligand. It has a

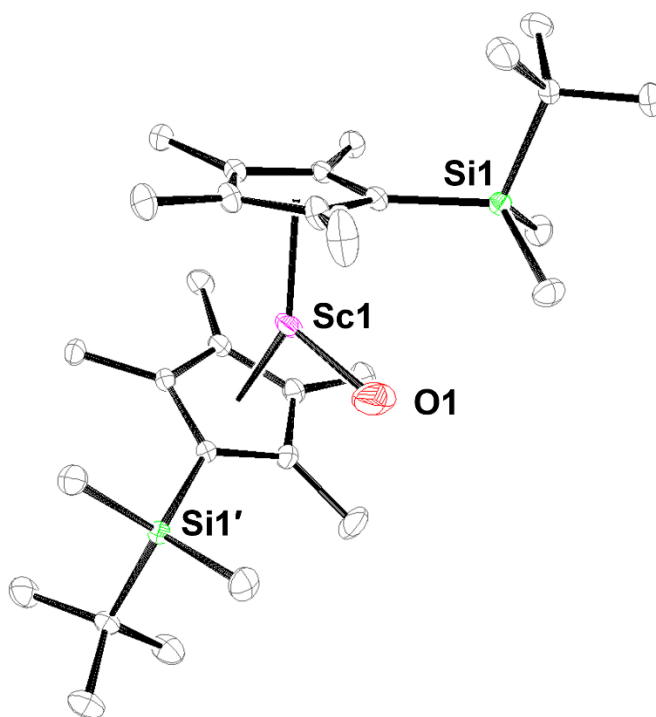
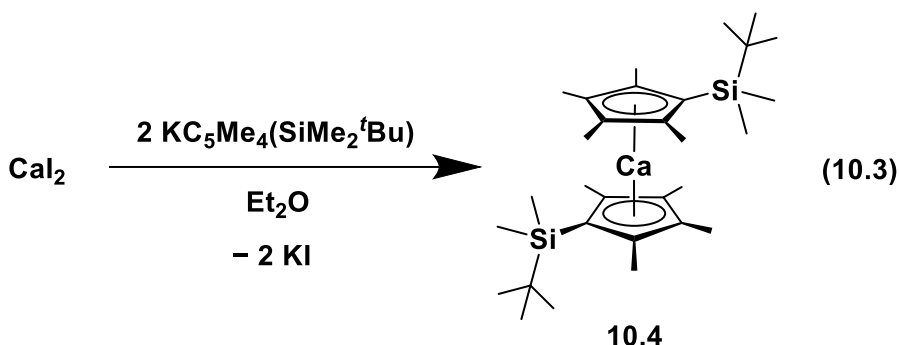


Figure 10.5. Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_2^t\text{Bu})]_2\text{Sc}(\text{OH})$, **10.3**, with ellipsoids drawn at 50% probability. Hydrogen atoms and the second part of the disordered O1 atom are not shown for clarity.

Cnt–Sc–Cnt angle of 142.5° and Sc–Cnt and Sc–O distances of 2.172 and 1.973(5) Å, respectively. The ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of **10.3** in C_6D_6 show that both cyclopentadienyl ligands are equivalent in solution at room temperature and only one species is discernable. However, the ^{45}Sc NMR suggests a monomer-dimer equilibrium at room temperature as evidenced by the presence of two broad resonances observed at 87.2 ($\Delta\nu_{1/2} = 3200$ Hz) and 36.6 ppm ($\Delta\nu_{1/2} = 1800$ Hz).³⁸ The infrared spectrum of **10.2** contains a sharp absorbance at approximately 3698 cm^{-1} , consistent with an O–H stretching vibration.⁵²

To evaluate the importance of the electron configuration of the M(II) ion in stabilizing the linear geometry of **10.1**, the synthesis of the Ca(II) analog was pursued. The reaction between

CaI₂ and 2 equiv of KC₅Me₄(SiMe₂^tBu) in Et₂O yielded colorless solids of [C₅Me₄(SiMe₂^tBu)]₂Ca, **10.4**, in 87% yield, eq 10.3. Colorless X-ray quality crystals of **10.4** can be grown from saturated hexane solutions stored at −35 °C. Complex **10.4** is also a linear metallocene with a Cnt–Ca–Cnt angle of 180° and is isomorphous to **10.1** and other previously reported [C₅Me₄(SiMe₂^tBu)]₂M complexes.^{28,34,35} Complex **10.4** is a rare example of a linear calcocene; the only other example isolated previously involved the perphenylated cyclopentadienyl ligand [C₅(C₆H₄-4-ⁿBu)₅]^{1−}.⁵³ Sitzmann and coworkers previously isolated (C₅^tPr₅)₂Ca which is presumably a linear calcocene too, but no X-ray data has been provided.²⁸



The 2.304 Å Ca–Cnt distance in **10.4** is significantly longer than the 2.102 Å Sc–Cnt distance of **10.1**. This increase matches the difference between the 1.00 Å Shannon ionic radius of six-coordinate Ca(II) and the 0.795 Å extrapolated value for Sc(II) assuming it is 0.05 Å larger than six-coordinate Sc(III), 0.745 Å.^{33,54–56} The observation that the d⁰ Ca(II) metallocene **10.4** also adopts a linear geometry with the [C₅Me₄(SiMe₂^tBu)]^{1−} ligand suggests that the linear geometry of complexes **10.1**, **10.4** and the Ti, Fe, Ge, Sn, and Pb analogs is primarily driven by interligand steric repulsion rather than electronic effects.^{28,34,35}

Electronic structure calculations using density functional theory (DFT) were carried out to investigate the electronic structures of [C₅Me₄(SiMe₂^tBu)]₂Sc, **10.1**, and its calcium analog, **10.4**. A structure with the observed C_{2h} symmetry was confirmed to be a local minimum for **10.4** through

vibrational analysis. The computed structure had a 2.30 Ca–Cnt distance and 180° Cnt–Ca–Cnt angle that matched the experimental values. The calculated HOMO of **10.4**, Figure 10.6 (left), shows little orbital overlap and is consistent with the Mulliken population analysis that indicated the bonding is primarily ionic.

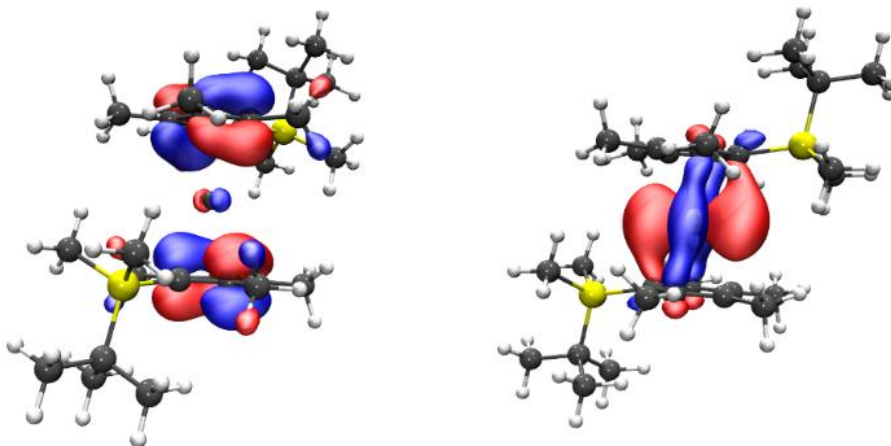


Figure 10.6. (Left) HOMO of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Ca}$, **10.4**, and (Right) HOMO of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Sc}$, **10.1**, with a contour value of 0.04.

In contrast, geometry optimization on **10.1** in C_{2h} does not yield a local minimum. However, geometry optimization with C_1 symmetry results in a fully linear structure with a 2.12 Å Sc–Cnt distance close to the experimental 2.10 Å value. The 95 MHz computed hyperfine coupling constant for the optimized linear structure also closely matches the measured value of 88 MHz. The Mulliken population analysis of the singly occupied HOMO, Figure 10.6 (right), of **10.1** shows covalent interactions arising from the overlap of a d_{z^2} orbital (oriented parallel to the cyclopentadienyl ligand plane) with the π orbitals of the ligands. The indicated $3d^1$ electron configuration is consistent with the transitions observed in the UV-visible spectrum as simulated by TDDFT methods. In contrast to Sc(II) metallocenes with C_{5v} , D_{5h} , and S_{10} symmetries that undergo first-order Jahn-Teller distortions due to their $3d^1$ configuration and degenerate frontier

orbitals,^{33,57} structures with C_{2h} and C_1 symmetries are not subject to such distortions as they lack degenerate frontier orbitals. The coordination geometries of **10.1** and **10.4**, despite their different electronic structures, highlight the effectiveness of the sterically bulky $[C_5Me_4(SiMe_2^tBu)]^{1-}$ ligand in enforcing linear structures.

CONCLUSION

In summary, over 70 years after the discovery of ferrocene, the first example of a linear Sc(II) analog, $[C_5Me_4(SiMe_2^tBu)]_2Sc$, **10.1**, has been isolated using the $[C_5Me_4(SiMe_2^tBu)]^{1-}$ ligand. The result is surprising given that the more sterically crowded $(C_5H_2^tBu)_2Sc$ ³³ adopts a bent geometry. Evidently, the substitution pattern and steric profile of the $[C_5Me_4(SiMe_2^tBu)]^{1-}$ ligand play an important role. In contrast to the unreactive bent $(C_5H_2^tBu)_2Sc$,³³ the linear **10.1** reversibly reacts with N_2 to form an end-on $(N=N)^{2-}$ complex and has provided the first example of a terminal hydroxide complex of scandium.

EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or nitrogen atmosphere. Solvents were sparged with UHP (99.999%) argon before drying and collection using an S2 Grubbs-type⁵⁸ solvent purification system (JC Meyer) and stored over activated molecular sieves overnight prior to use. Deuterated NMR solvents were degassed and dried over activated molecular sieves before use. ^1H , $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, and ^{45}Sc NMR spectra were recorded on a Bruker AVANCE600 spectrometer at 298 K unless otherwise stated. ^1H and $^{13}C\{^1H\}$ were referenced internally to residual protio-solvent resonances. $^{29}Si\{^1H\}$ and ^{45}Sc NMR spectra were referenced externally to $SiMe_4$ and $ScCl_3$ in D_2O , respectively. Infrared spectra were

recorded as compressed solids on an Agilent Cary 630 ATR-FTIR under an argon atmosphere. UV-visible spectra were collected in hexane at 298 K using a Varian Cary 50 Scan UV-visible spectrometer in a 1 mm Schlenk cuvette fitted with a Teflon stopper unless otherwise stated. X-band EPR spectra were recorded in hexane solutions at 298 K or frozen hexane solutions at 77 K on a Bruker EMX spectrometer equipped with an ER041Xg microwave bridge and calibrated with DPPH ($g = 2.0036$). Elemental analyses were conducted on a Thermo Scientific FlashSmart CHNS/O elemental analyzer at UC Irvine Materials Research Institute's TEMPR facility in Irvine, California. $\text{KC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$,³⁷ $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2]_2\text{ScI}$,³⁸ and KC_8 ⁵⁹ were synthesized according to literature procedures. CaI_2 (AnhydroBeads™, -10 mesh, 99.999% trace metals basis) was purchased from Sigma-Aldrich and ground into a fine powder with a pestle and mortar prior to use.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Sc}$, 10.1 in Diethyl Ether. In an argon containing glovebox, $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2]_2\text{ScI}$ (150 mg, 0.233 mmol) was dissolved in Et_2O (ca. 10 mL) at room temperature. Solid KC_8 (38 mg, 0.28 mmol) was added in one portion at room temperature to immediately yield a dark red mixture. The resulting mixture was allowed to stir at room temperature over 16 h at which point it became a darker shade of red. The resulting mixture was centrifuged and filtered through a pipet packed with Kimwipe tissue to remove insoluble solids, presumably graphite and KI. The solids were repeatedly washed with Et_2O (ca. 2 mL portions) until the filtrate became colorless. Volatiles were removed from the dark red filtrate under reduced pressure to yield a red residue. The residue was then extracted into hexane and filtered through a pipet packed with Kimwipe tissue. The solids were repeatedly extracted with hexane (ca. 2 mL portions) until the filtrate became colorless. Volatiles were removed from the dark red supernatant to yield dark red solids (127 mg). The crude red solids were then washed with cold SiMe_4 (ca. 0.5

mL) and dried under reduced pressure to yield $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2]\text{Sc}$, **10.1**, as a dark red powder (101 mg, 84%). Dark red cubes suitable for study by X-ray diffraction can be grown from saturated hexane solutions stored at $-30\text{ }^\circ\text{C}$. ^1H NMR (600 MHz, C_6D_6): δ 89.98 (br, 12H, $\text{C}_5\text{Me}_4\text{SiMe}_2'\text{Bu}$, $\Delta\nu_{1/2} = 4000\text{ Hz}$), 14.96 (br, 12H, $\text{C}_5\text{Me}_4\text{SiMe}_2'\text{Bu}$, $\Delta\nu_{1/2} = 400\text{ Hz}$), 4.40 (br, 12H, $\text{C}_5\text{Me}_4\text{SiMe}_2'\text{Bu}$, $\Delta\nu_{1/2} = 150\text{ Hz}$), 3.37 (br, 18H, $\text{C}_5\text{Me}_4\text{SiMe}_2'\text{Bu}$, $\Delta\nu_{1/2} = 100\text{ Hz}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): No resonances definitively assignable to $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2]\text{Sc}$, **10.1**, were observed in the range of +300 to -300 ppm . $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, C_6D_6): No resonances definitively assignable to $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2]\text{Sc}$, **10.1**, were observed in the range of +300 to -275 ppm . ^{45}Sc NMR (145 MHz, C_6D_6): No resonances definitively assignable to $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2]\text{Sc}$, **10.1**, were observed in the range of +600 to -200 ppm . Magnetic moment (Evans method, C_6D_6): $1.3\text{ }\mu\text{B}$. M.P. $137\text{--}144\text{ }^\circ\text{C}$. IR: 2922m, 2850s, 1461w, 1437w, 1383w, 1357w, 1299s, 1245vs, 1126w, 1005w, 805vs, 803vs, 759vs, 667vs cm^{-1} . UV-vis (hexane, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) 320 (3700, sh), 410 (1500, sh), 510 (520). Anal. Calcd. for $\text{C}_{30}\text{H}_{54}\text{Si}_2\text{Sc}$: C, 69.85; H, 10.55. Found: C, 69.37; H, 10.58. Note: $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2]\text{Sc}$, **10.1**, is unstable in THF and 1,2-dimethoxyethane and transitions to clear pale yellow solutions indicative of decomposition to Sc(III) products.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2]\text{Sc}$, **10.1, in Toluene.** In an argon containing glovebox, $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2]\text{ScI}$ (150 mg, 0.233 mmol) was dissolved in toluene (ca. 10 mL) at room temperature. Solid KC_8 (38 mg, 0.28 mmol) was added in one portion at room temperature. The resulting mixture was allowed to stir at room temperature over 10 days at which point it became a darker shade of red. Insoluble solids, presumably KI and graphite, were removed by filtration through a pipette packed with Kimwipe tissue to yield a dark red solution. Volatiles were removed under reduced pressure to yield $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2]\text{Sc}$, **10.1**, as dark red solids (117 mg, 98%).

The ^1H NMR spectrum showed the presence of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2]_2\text{ScI}$, suggesting the reaction did not reach full conversion.

Synthesis of $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Sc}\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)$, **10.2.** In a nitrogen containing glovebox, dry red solids of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Sc}$, **10.1** (122 mg, 0.236 mmol) were dissolved in hexane (ca. 8 mL) to immediately generate a dark blue-purple solution. The solution was then filtered through a pipette packed with Kimwipe tissue and concentrated under reduced pressure to ca. 2 mL before being stored at $-35\text{ }^\circ\text{C}$. Dark blue crystals of $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Sc}\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)$, **10.2**, suitable for study by X-ray diffraction grew overnight in two crops (75 mg, 0.14 mmol, 60% crystalline yield). IR: 2922m, 2883m, 2850m, 1463w, 1459w, 1383w, 1357w, 1314m, 1301m, 1245s, 1128w, 1005m, 936w, 805vs, 803vs, 760vs, 669s cm^{-1} . UV-vis (hexane, room temperature) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) 260 (23000), 290 (20000, sh), 330 (15000 sh), 410 (7500), 440 (5600), 560 (8600). Anal. Calcd. for $\text{C}_{60}\text{H}_{108}\text{N}_2\text{Si}_4\text{Sc}_2$: C, 68.00; H, 10.27; N, 2.64. Found: C, 69.27; H, 10.74; N, 2.07. Found: C, 69.05; H, 10.38; N, 1.97. Found: C, 69.33; H, 10.23; N, 2.01. Note: $\{[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Sc}\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)$, **10.2**, is unstable in THF and transitions to clear pale yellow solutions indicative of decomposition to Sc(III) products.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Sc}(\text{OH})$, **10.3.** In an argon containing glovebox, $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{ScI}$ (50 mg, 0.0777 mmol) was dissolved in a 1:1 mixture of Et_2O /toluene (ca. 10 mL) at room temperature. KC_8 (13 mg, 0.093 mmol) was added in one portion at room temperature and the resulting mixture was allowed to stir at room temperature for 72 h, at which point the reaction mixture became a dark red-orange color. Insoluble solids, presumably KI and graphite, were removed by filtration through a pipette packed with Kimwipe tissue to yield a dark red-orange solution. Solvent was removed under reduced pressure to yield a dark red-orange residue. The residue was then extracted into hexane (ca. 5 mL), filtered through a pipet packed

with Kimwipe tissue, and concentrated to ca. 1 mL. Storage of the solution at $-35\text{ }^{\circ}\text{C}$ yielded a few orange plates of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Sc}(\text{OH})$, **10.3**, suitable for study by X-ray diffraction (9 mg, 22% crystalline yield). ^1H NMR (600 MHz, C_6D_6): δ 5.47 (s, 1H, *OH*), 2.29 (s, 12H, $\text{C}_5\text{Me}_4\text{SiR}_3$), 1.86 (s, 12H, $\text{C}_5\text{Me}_4\text{SiR}_3$), 0.90 (s, 18H, $\text{SiMe}_2'\text{Bu}$), 0.40 (s, 12H, $\text{SiMe}_2'\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ 131.0 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 123.4 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 118.5 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 27.4 (CMe_3), 20.1 (CMe_3), 15.3 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 11.5 ($\text{C}_5\text{Me}_4\text{SiR}_3$), -1.4 ($\text{SiMe}_2'\text{Bu}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, C_6D_6): δ -2.5 ($\text{SiMe}_2'\text{Bu}$). ^{45}Sc NMR (145 MHz, C_6D_6): δ 87.2 (br, monomer, $\Delta\nu_{1/2} = 3200\text{ Hz}$), 36.6 (br, dimer, $\Delta\nu_{1/2} = 1800\text{ Hz}$). IR: 3698w, 2926m, 2853m, 1470w, 1461w, 1383w, 1359w, 1318m, 1247s, 1128w, 1006w, 986w, 820vs, 762vs, 669vs cm^{-1} .

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Ca}$, **10.4.** In an argon containing glovebox, CaI_2 (105 mg, 0.357 mmol) and $\text{KC}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})$ (196 mg, 0.714 mmol) were added to a 20 mL scintillation vial. Et_2O (ca. 6 mL) was added, and the resulting white mixture was allowed to stir at room temperature over 5 days. Insoluble solids were removed via centrifugation and filtration through a Kimwipe packed pipette to yield a pale-yellow solution. Solvent was removed under reduced pressure to yield an oily residue. The product was then extracted into hexane (ca. 10 mL) and filtered to remove insoluble solids. Volatiles were removed under reduced pressure to yield $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Ca}$, **10.4**, as white solids (160 mg, 87%). Colorless crystals suitable for study by X-ray diffraction can be grown from saturated hexane solutions stored at $-35\text{ }^{\circ}\text{C}$. ^1H NMR (600 MHz, C_6D_6): δ 2.12 (s, 12H, $\text{C}_5\text{Me}_4\text{SiR}_3$), 2.00 (s, 12H, $\text{C}_5\text{Me}_4\text{SiR}_3$), 0.89 (s, 18H, $\text{SiMe}_2'\text{Bu}$), 0.30 (s, 12H, $\text{SiMe}_2'\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ 125.3 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 120.5 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 109.6 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 27.9 (CMe_3), 19.5 (CMe_3), 14.4 ($\text{C}_5\text{Me}_4\text{SiR}_3$), 11.1 ($\text{C}_5\text{Me}_4\text{SiR}_3$), -1.0 ($\text{SiMe}_2'\text{Bu}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, C_6D_6): δ -3.4 ($\text{SiMe}_2'\text{Bu}$). IR: 2922m, 2883m, 2850s,

1461w, 1437w, 1385w, 1357w, 1305s, 1249vs, 1129w, 1005w, 936w, 818vs, 803vs, 757vs, 669vs cm⁻¹. Anal. Calcd. for C₃₀H₅₄Si₂Ca: C, 70.51; H, 10.65. Found: C, 70.73; H, 10.81.

X-ray Data Collection, Structure Solution and Refinement for [C₅Me₄(SiMe₂Bu)]₂Sc,

10.1. A red crystal of approximate dimensions 0.187 x 0.306 x 0.330 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX4⁶⁰ program package and the CELL_NOW⁶¹ program were used to determine the unit-cell parameters. Data was collected using a 10 sec/frame scan time. The raw frame data was processed using SAINT⁶² and TWINABS⁶³ to yield the reflection data file (HKL 5 format).⁶³ Subsequent calculations were carried out using the SHELXTL⁶⁴ program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group *P*2₁/*n* that was later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors⁶⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on an inversion center. Least-squares analysis yielded wR₂ = 0.1281 and Goof = 1.117 for 161 variables refined against 4738 data (0.70 Å), R₁ = 0.0451 for those 4375 with I > 2.0σ(I). The structure was refined as a two-component twin, BASF⁶⁴ = 0.46.

X-ray Data Collection, Structure Solution and Refinement for {[C₅Me₄(SiMe₂Bu)]₂Sc}₂(μ-η¹:η¹-N₂), 10.2. A green crystal of approximate dimensions 0.258 x 0.270 x 0.346 mm was mounted in a cryoloop and transferred to a Bruker D8 Venture Photon III diffractometer system. The APEX5⁶⁶ program package was used to determine the unit-cell parameters and for data collection (1-4 sec/frame scan time). Data were collected at 100 K using Cu Kα radiation (λ = 1.54178 Å). The raw frame data was processed using SAINT⁶⁷ and SADABS⁶⁸ to yield the reflection data file. Subsequent calculations were carried out using the

SHELXTL⁶⁴ program package within the OLEX2 GUI.⁶⁹ The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups Cc , and $C2/c$. It was later determined that space group $C2/c$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on a two-fold rotation axis. Least-squares analysis yielded $wR2 = 0.1957$ and $Goof = 1.108$ for 327 variables refined against 7038 data ($0.78 \text{ \AA}$), $R1 = 0.0722$ for those 6231 data with $I > 2.0\sigma(I)$. There were several high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals although it was probable that half of a molecule of hexane solvent was present in the asymmetric unit. The MASK tool in the OLEX2 GUI was used to account for the electrons in the solvent accessible voids.⁶⁹

X-ray Data Collection, Structure Solution and Refinement for $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})_2\text{Sc}(\text{OH})]$, 10.3. A red-orange crystal of approximate dimensions $0.196 \times 0.234 \times 0.441 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2⁷⁰ program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time). The raw frame data was processed using SAINT⁷¹ and SADABS⁷² to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁶⁴ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that space group $C2/c$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁵ for neutral atoms were used throughout the analysis. The molecule was located on a two-fold rotation axis. Oxygen atom O1 was disordered and was included using multiple components, partial-site-

occupancy factors, and geometric (SADI) and displacement (ISOR, SIMU) constraints. Due to the disorder of oxygen atom O1, the hydrogen atom of the terminal hydroxyl group could not be refined. The rest of the hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0888$ and $Goof = 1.043$ for 173 variables refined against 4721 data ($0.70 \text{ \AA}$), $R1 = 0.0324$ for those 4175 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $[\text{C}_5\text{Me}_4(\text{SiMe}_2'\text{Bu})]_2\text{Ca}$,

10.4. A colorless crystal of approximate dimensions $0.062 \times 0.084 \times 0.165 \text{ mm}$ was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX4⁶⁰ program package was used to determine the unit-cell parameters and for data collection (60-180 sec/frame scan time). The raw frame data was processed using SAINT⁶² and SADABS⁶⁸ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁶⁴ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁶⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on an inversion center. Least-squares analysis yielded $wR2 = 0.1062$ and $Goof = 1.075$ for 160 variables refined against 3131 data ($0.80 \text{ \AA}$), $R1 = 0.0401$ for those 2636 data with $I > 2.0\sigma(I)$.

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Appendix A:

Yttrium-Mediated Acetylide C–C Coupling Yields a Bridging Butatrienylidene Dianion

INTRODUCTION[†]

Detailed studies of rare-earth metal reductive chemistry have provided new oxidation states of simple diatomic molecules such as N₂ and NO. For example, the first example of the (N₂)^{3−} radical trianion was observed in the complex, [(R₂N)₂(THF)Y]₂(μ₃-η²:η²:η²-N₂)}K (R = SiMe₃), Figure A.1 (left), which was generated by reduction of the side-on bridged (N=N)^{2−} bimetallic complex, [(R₂N)₂(THF)Y]₂(μ-η²:η²-N₂).^{1–3} This unexpected development subsequently led to a new class of single molecule magnets^{4,5} as well as the isolation of the first example of an (NO)^{2−} complex, namely [(R₂N)₂Y(THF)]₂(μ-η²:η²-NO), Figure A.1 (right).⁶

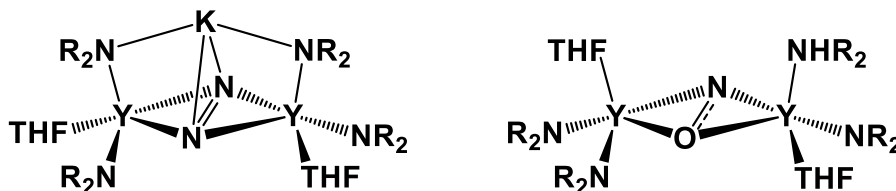
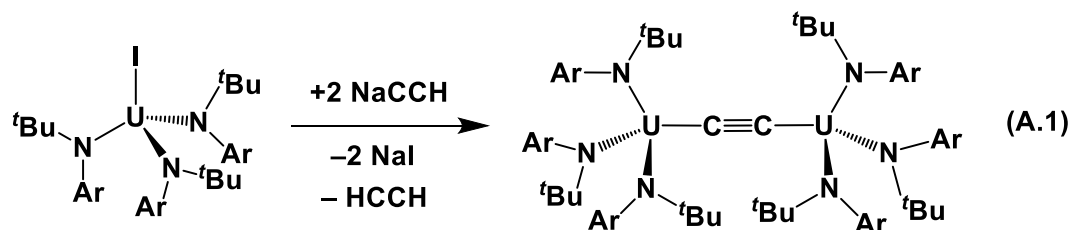


Figure A.1. Crystallographically characterized (N₂)^{3−} and (NO)^{2−} species.

These results suggest that the rare-earth metals could provide synthetic pathways to other unusual diatomic anions such as (CN)^{2–7} and (CC)^{3−}. Since rare-earth metal complexes with end-on (μ-η¹:η¹-CC)^{2−} acetylide ligands such as (C₅Me₅)₂Ln(μ-η¹:η¹-C₂)Ln(C₅Me₅)₂ (Ln = Sc, Sm)^{8,9} are known, the possibility of effecting (CC)^{2−} to (CC)^{3−} transformations exists.

[†]This work is in collaboration with Dr. William N. G. Moore and Professor Filipp Furche at the University of California, Irvine, who performed the electronic structure calculations. Dr. William N. G. Moore is also credited with the initial discovery of complex **A.1** described herein.

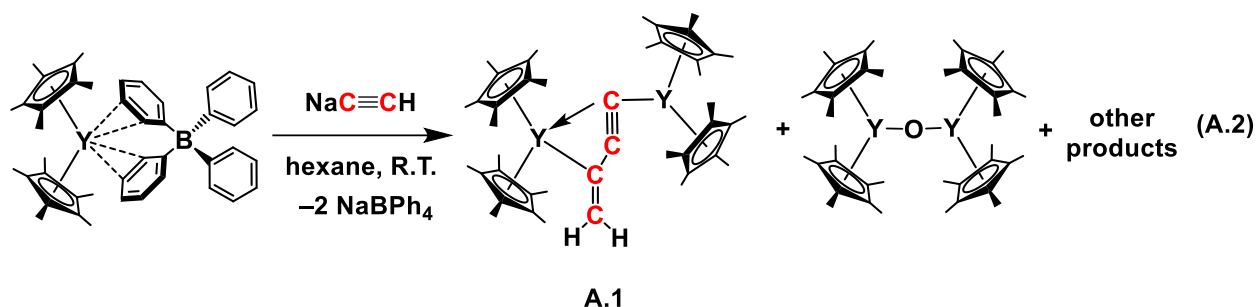
To explore the chemistry of $[\text{Ln}(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}_2)\text{Ln}]^{4+}$ units and their possible reduction to $(\text{C}_2)^{3-}$ species, the reaction between $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Ph})_2\text{BPh}_2$ ¹⁰ and $\text{NaC}\equiv\text{CH}$ was explored. Cummins and coworkers previously demonstrated that the reaction between $\text{U}[\text{N}^t\text{Bu}(\text{Ar})]_3\text{I}$ ($\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2\text{-3,5}$) and $\text{NaC}\equiv\text{CH}$ forms the end-on acetylides $\{\text{U}[\text{N}^t\text{Bu}(\text{Ar})]_3\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}_2)$, eq A.1.¹¹



Similarly, Hayton and coworkers reported the synthesis of the actinide acetylides, $\text{An}[\text{N}(\text{SiMe}_3)_2]_3(\text{C}\equiv\text{CH})$ ($\text{An} = \text{Th}, \text{U}$), by reaction of $\text{An}[\text{N}(\text{SiMe}_3)_2]_3\text{Cl}$ with $\text{NaC}\equiv\text{CH}$ which were subsequently used as synthons for the bridging acetylide complexes, $\{\text{An}[\text{N}(\text{SiMe}_3)_2]_3\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}_2)$.¹² Similar chemistry seemed conceivable for Y(III) since $(\text{C}_5\text{Me}_5)_2\text{Ln}(\mu\text{-Ph})_2\text{BPh}_2$ ($\text{Ln} = \text{rare-earth metal}$) readily reacts with alkali metal organometallic reagents to displace the loosely coordinated $(\text{BPh}_4)^{1-}$ anion and form Ln-C bonds.¹³⁻¹⁵

RESULTS AND DISCUSSION

Treatment of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Ph})_2\text{BPh}_2$ ¹⁰ with 1 equiv of solid $\text{NaC}\equiv\text{CH}$ in a 1:1 toluene:benzene mixture yielded a suspension that became increasingly orange when stirred overnight at room temperature from which yellow-orange solids were obtained upon workup. Crystallization from saturated pentane solutions at ambient temperature initially yielded a set of X-ray quality crystals of the bridging oxide, $[(\text{C}_5\text{Me}_5)_2\text{Y}]_2(\mu\text{-O})$, eq A.2.¹⁶ Complexes of the formula $[(\text{C}_5\text{Me}_5)_2\text{Ln}]_2(\mu\text{-O})$ ($\text{Ln} = \text{rare-earth metal}$) are common byproducts of reactions of rare-earth metal metallocenes involving $[(\text{C}_5\text{Me}_5)_2\text{Ln}]^{1+}$ units.¹⁶⁻¹⁹ However, this reaction has another



identifiable product. A few pale-yellow X-ray quality crystals, which were identified crystallographically and by NMR spectroscopy (discussed below) as $(C_5Me_5)_2Y(\mu-\eta^3:\eta^1-CCCCCH_2)Y(C_5Me_5)_2$, **A.1**, eq A.2, Figure A.2, were grown from the same mother liquor at ambient temperature after the separation of $[(C_5Me_5)_2Y]_2(\mu-O)$.¹⁶ Interestingly, performing the reaction in neat benzene did not generate any complex **A.1** as observed by NMR spectroscopy and the only identifiable product was $[(C_5Me_5)_2Y]_2(\mu-O)$. When the reaction was performed in neat hexane, complex **A.1** could be repeatedly reproduced and was isolated in 48% crude yield as the major product after separation from $[(C_5Me_5)_2Y]_2(\mu-O)$.¹⁶

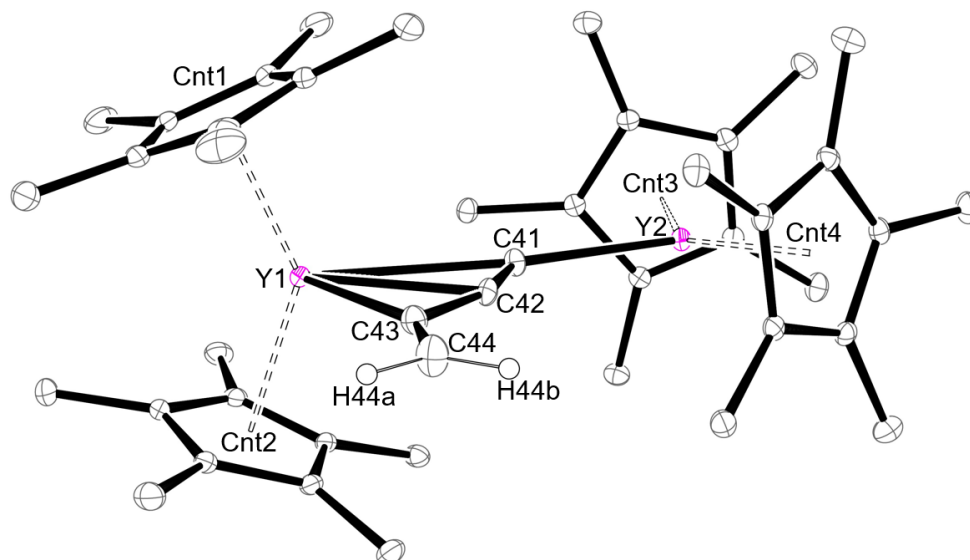


Figure A.2. Molecular structure of $(C_5Me_5)_2Y(\mu-\eta^3:\eta^1-CCCCCH_2)Y(C_5Me_5)_2$, **A.1**, with ellipsoids drawn at 50% probability. All hydrogen atoms except for H44a and H44b are omitted for clarity.

Complex **A.1** crystallizes in the $P2_1/c$ space group and is an asymmetric bimetallic Y(III)/Y(III) complex consisting of two $[(C_5Me_5)_2Y]^{1+}$ moieties bridged by a rare example of a planar and dianionic butatrienyldiene ligand. Hydrogen atoms H44a and H44b were located from the difference-Fourier map confirming the presence of a terminal methyldiene group. The butatrienyldiene dianion is presumably formed from the generation of intermediates like “ $(C_5Me_5)_2Y(C\equiv CH)$ ” that react with each other in a C–C coupling reaction involving two $(C\equiv CH)^{1-}$ units. The reaction also involves the migration of the hydrogen atom originating from a $(C\equiv CH)^{1-}$ ligand to another to form a terminal methyldiene ($=CH_2$) group. Several organolanthanide based systems including $(C_5Me_5)_2Sm(THF)_2$,²⁰ $(C_5Me_5)_2Sm$,²¹ $[(C_5Me_5)_2Sm(\mu-H)]_2$,²¹ and $(C_5Me_5)_2Y(\eta^3-CH_3CHCH_3)$ ²² have been previously observed to react with 2 equiv of $PhC\equiv CH$ to form the bridging trienediyl ligand, $(\mu-\eta^2:\eta^2-PhC_4Ph)^{2-}$. C–C coupling reactivity of acetylide ligands have also been observed with $(C_5Me_5)_2Ln(C\equiv CPh)(THF)$ ($Ln = Ce, Nd, Sm$) complexes, but these reactions typically require heating.²¹ The C–C coupling reaction as described in eq A.2 is distinct from previous examples of organolanthanide-based acetylide coupling reactions by the fact that this specific acetylide coupling also involves the formation of a terminal methyldiene ($=CH_2$) group formed from a hydrogen atom migration.

Structurally characterized metal complexes with butatrienyldiene ligands have only been reported for the ruthenium clusters, $Ru_5(\mu_5-CCCCH_2)(\mu_3-SMe)(\mu-SMe)(\mu-PPh_2)_2(CO)_{10}$ and $Ru_5(\mu_5-CCCCH_2)(\mu-SMe)_2(\mu-PPh_2)_2(CO)_{11}$.^{23,24} In these cases, the first three carbon atoms of the $(\mu_5-CCCCH_2)$ unit twist around the ruthenium clusters to give the six atoms root mean squared deviations (RMSD) of $\omega = 0.38$ Å and 0.43 Å, respectively.^{23,24} In contrast, the six atoms in the bridging $(CCCCH_2)^{2-}$ ligand of complex **A.1** are coplanar with an $\omega = 0.01$ Å. In addition, the six atoms of the $(CCCCH_2)^{2-}$ moiety and the two yttrium atoms are coplanar with an $\omega = 0.03$ Å.

Selected metrical data for complex **A.1** are summarized in Table A.1 below. The Y–Cnt distances (Cnt = cyclopentadienyl centroid) of 2.366 Å and 2.363 Å and Cnt–Y–Cnt angles of 137.6° and 138.6° are typical of Y(III) metallocene complexes.^{16,25–27} One yttrium atom binds to the (C₄H₂)^{2–} moiety in a pseudo η^3 -fashion with Y(1)–C(41,42,43) distances of 2.779(2), 2.532(2) Å, and 2.430(2), respectively. For comparison, (C₅Me₅)₂Y(η^3 -C₃H₅) has Y–C(η^3 -C₃H₅) distances of 2.582(2), 2.582(2), and 2.601(2) Å, so the bonding in complex **A.1** differs from simple allyl coordination.²⁵ The other yttrium atom is bound in an η^1 fashion with a Y(2)–C(41) distance of 2.420(2) Å, equivalent to the 2.419(3) Å Y–C(CH₂) distance in the ethyl yttrium metallocene, (C₅Me₅)₂Y(CH₂CH₃).²⁶

Table A.1. Selected bond distances and angles in (C₅Me₅)₂Y(μ - η^3 : η^1 -CCCCH₂)Y(C₅Me₅)₂, **A.1**.

Bond	Distance (Å)	Atoms	Angle (°)
Cnt1–Y1	2.366	Cnt1–Y1–Cnt2	137.6
Cnt2–Y1	2.363	Cnt3–Y2–Cnt3	138.6
Cnt3–Y2	2.328	C42–C41–Y2	131.04(14)
Cnt4–Y2	2.342	Y1–C41–Y2	163.30(8)
C41–C42	1.240(3)	C41–C42–C43	157.50(19)
C42–C43	1.404(3)	C42–C43–C44	130.11(19)
C43–C44	1.331(3)	C43–C44–H44a	119.3(14)
C44–H44a	0.97(2)	C43–C44–H44b	123.7(14)
C44–H44b	0.97(2)	H44a–C44–H44b	116.9(19)
Y1–C41	2.779(2)		
Y1–C42	2.532(2)		
Y1–C43	2.430(2)		
Y1–C44	3.660(2)		
Y2–C41	2.420(2)		
Y2–C42	3.367(2)		
Y2–C43	4.754(2)		
Y2–C44	5.588(2)		

In complex **A.1**, the C43–C44 distance of 1.331(3) Å is essentially identical to the prototypical C=C bond distance of 1.339 Å as measured in free ethylene.²⁸ Conversely, the C41–C42 distance in **A.1** of 1.240(3) Å is slightly longer than the C≡C triple bond distance of 1.20 Å found for acetylene.²⁸ This lengthening has also been seen in the formation of complexes

containing a formally $(\text{C}\equiv\text{C})^{2-}$ bridge. For instance, in $[\text{U}(\text{N}^t\text{BuAr})_3]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}_2)^{11}$ and $\{[\text{U}[\text{N}(\text{SiMe}_3)_2]_3\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}_2)^{12}$ the $\text{C}\equiv\text{C}$ distances are 1.227(10) and 1.225(10) Å, respectively. The central C–C bond in the butatrienyldiene ligand, C42–C43, has a bond distance of 1.404(3), which is intermediate between a typical C–C single bond and C=C double bond.

Complex **A.1** is diamagnetic and was characterized by a combination of ^1H , $^{13}\text{C}\{^1\text{H}\}$, and 2D NMR spectroscopies. The following NMR analysis suggests that in solution, complex **A.1** maintains the structure determined in the solid state. The ^1H NMR spectrum of complex **A.1** in C_6D_6 at room temperature displays two resonances at δ 1.95 and 2.14 ppm integrating to 30 hydrogens each which were assigned to the two different $(\text{C}_5\text{Me}_5)^{1-}$ environments in **A.1**. Two resonances assignable to H44a and H44b were observed at δ 5.54 and 6.58 ppm with geminal coupling to each other ($J_{\text{H,H}} = 4.6$ Hz), comparing well with the coupling constant for geminal hydrogens on sp^2 carbon atoms of ligands bound to yttrium ($J_{\text{H,H}} \approx 4$ Hz).²⁵ This is further supported by the ^1H – ^1H COSY NMR spectrum which shows correlations between H44a and H44b. For comparison, the hydrogen atoms of the butatrienyldiene ligand of $\text{Ru}_5(\mu_5\text{-CCCCCH}_2)(\mu_3\text{-SMe})(\mu\text{-SMe})(\mu\text{-PPh}_2)_2(\text{CO})_{10}$ are non-equivalent and are observed at δ 5.48 and 5.72 ppm.²⁴ Similarly, for $\text{Ru}_5(\mu_5\text{-CCCCCH}_2)(\mu\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{11}$, the analogous signals are observed at δ 4.67 and 5.18 ppm.²⁴

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **A.1** exhibits two resonances at δ 11.5 and 11.8 ppm, in the range expected for the methyl groups of the $(\text{C}_5\text{Me}_5)^{1-}$ ligands bound to yttrium.^{16,25-27} Additionally, two distinct resonances are visible centered around 116.9, in the typical range for the ring carbons of the $(\text{C}_5\text{Me}_5)^{1-}$ ligands.^{16,25-27} Four resonances corresponding to the $(\text{CCCCCH}_2)^{2-}$ moiety are centered at δ 119.7 ppm as a singlet, δ 145.4 and 175.6 as broad signals, and at δ 195.0 as a doublet. The resonance at 119.7 ppm was assigned to the methyldiene ($=\text{CH}_2$) carbon, C44,

of the butatrienyldiene ligand based on the HMQC spectra, showing correlations with the ^1H signals at δ 5.54 and 6.58 ppm, as well as the DEPT 135 spectrum. Additionally, the doublet in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at δ 195.0 ppm which has a $J_{\text{Y,C}} = 33.7$ Hz and has strong correlations with both H44a and H44b can be assigned to C43. The HMBC spectrum optimized for 10 Hz couplings shows a correlation between the $^{13}\text{C}\{^1\text{H}\}$ NMR signal at δ 145.4 ppm and ^1H NMR signal at δ 6.58 ppm, but for the 2 Hz optimized spectrum, that correlation is suppressed and replaced with another correlation with the ^1H NMR signal at δ 5.54 ppm. These suggest that the $^{13}\text{C}\{^1\text{H}\}$ NMR signal at 145.4 ppm can be assigned to C42. For the HMBC spectrum optimized for 2 Hz couplings, a weaker correlation is observed between the $^{13}\text{C}\{^1\text{H}\}$ NMR signal at δ 175.6 ppm and the ^1H NMR at δ 5.54 ppm, which can be assigned to C41 that is 4 bonds away from H44a and H44b.

Complex **A.1** is stable in hydrocarbon and arene solvents. However, addition of a few drops of THF to a C_6D_6 solution of **A.1** generates a new product with different resonances in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. In the ^1H NMR spectrum, the analogous resonances belonging to the hydrogens of the $(\text{CCCCH}_2)^{2-}$ ligand of **A.1** are shifted from δ 5.54 and 6.58 ppm to δ 4.45 ppm and 6.50 ppm. Furthermore, the $^{13}\text{C}\{^1\text{H}\}$ NMR resonances shift from δ 119.7, 145.4, 175.6, and 195.0 to δ 120.1, 160.6, 171.5, and 187.4 ppm, respectively. These observations suggest that complex **A.1** may coordinate THF and leave the butatrienyldiene ligand intact.

However, from that same C_6D_6 solution spiked with THF, a few colorless X-ray quality crystals were isolated that were identified to be the yttrium oxide hydroxide cluster $[\text{Na}(\text{THF})_6][(\text{C}_5\text{Me}_5)_6\text{Y}_6\text{O}_5(\text{OH})_3]$, **A.2**, Figure A.3. Complex **A.2** consists of a hexametallic

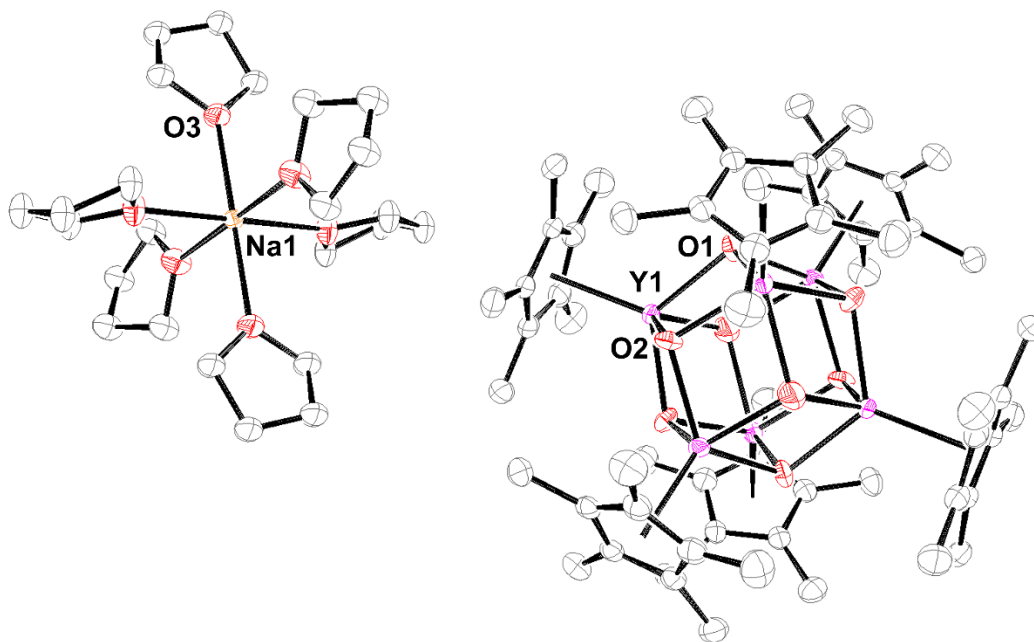


Figure A.3. Molecular structure of $[\text{Na}(\text{THF})_6][(\text{C}_5\text{Me}_5)_6\text{Y}_6\text{O}_5(\text{OH})_3]$, **A.2**, with ellipsoids drawn at 50% probability.

yttrium oxide hydroxide cluster capped by $(\text{C}_5\text{Me}_5)^{1-}$ ligands at each vertex occupied by a Y(III) atom and a $[\text{Na}(\text{THF})_6]^{1+}$ counteranion. The hydrogen atoms of the bridging hydroxide ligands could not be located from the difference-Fourier map and the formula was proposed based on charge balance. The similar rare-earth metal oxide hydroxide cluster, $[(\text{C}_5\text{Me}_5)\text{Sm}]_6\text{O}_9\text{H}_6$, was isolated previously from the reaction of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ with stoichiometric amounts of water.²⁹ Complex **A.2** is presumably another byproduct of the reaction depicted in eq A.2 above as evidenced by the presence of an absorption at 3691 cm^{-1} corresponding to an O–H stretch in crude samples of complex **A.1**. The addition of THF was evidently important in facilitating the crystallization of complex **A.2** from the solution.

Theoretical calculations were conducted on complex **A.1** to elucidate the electronic structure of the butatrienylidene ligand of **A.1**. Electronic structure calculations of complex **A.1** were performed at the density functional level of theory using the TPSSh hybrid meta-generalized

gradient density functional³⁰ with the D3 dispersion correction³¹ and the resolution of the identity (RI-J) approximation.³² Scalar relativistic effective core potentials with the def2-TZVP basis set³³ were used for yttrium and the polarized split-valence basis set def2-SV(P) was used for other atoms.³⁴ All calculations were performed with the TURBOMOLE package V7.6.^{35,36} Geometry optimization of the structure yielded a theoretical model with bond distances and angles that closely represent the structure derived from X-ray diffraction studies.

Wiberg bond indices (WBI)³⁷ calculated from the geometry-optimized structure for the $[\text{Y}(\mu\text{-}\eta^3\text{:}\eta^1\text{-CCCCCH}_2\text{)Y}]^{4+}$ unit are included in Table A.2 below. Notably, the sum of the Y–(C41, C42, C43) indices is 2.05, which is consistent with a total of two electron pairs shared with the two yttrium centers, but this sum is not distributed equally. The WBI for Y2–C41 is 0.72 while the index sum of Y1 with the C₄ bridge is 1.33. Additionally, the sum of the WBI for the carbon-carbon bonds in the bridge is 4.96, compared to the 6 predicted from a qualitative assessment of the primary resonance structure as depicted in eq A.2.

Table A.2. Wiberg bond index values for the Y–C and C–C bonds present in the $[\text{Y}(\text{C}_4\text{H}_2)\text{Y}]^{4+}$ moiety of **A.1**.

Bond	Wiberg Bond Index
Y1–C41	0.42
Y2–C41	0.72
Y1–C42	0.32
Y1–C43	0.59
C41–C42	1.95
C42–C43	1.12

C43–C42	1.89

CONCLUSIONS

In summary, the reaction between $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Ph})_2\text{BPh}_2$ and $\text{NaC}\equiv\text{CH}$ leads to the isolation of a bimetallic Y(III)/Y(III) complex that contains a rare example of a planar butatrienylidene ligand. The product is formally composed of two “ $(\text{C}_5\text{Me}_5)_2\text{Y}(\text{C}\equiv\text{CH})$ ” formula units that presumably undergo a C–C coupling reaction and a hydrogen atom migration to form the dianionic butatrienylidene ligand. Evidently, multiple side products are generated which include yttrium oxide and hydroxide complexes. This result adds a new and unique type of C–C coupling reactivity available to rare-earth element metallocene complexes.

EXPERIMENTAL SECTION

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP (99.999%) argon and dried by passage through columns containing Q-5 and molecular sieves prior to use and stored over activated molecular sieves prior to use. Deuterated NMR solvents were degassed and dried over molecular sieves overnight before use. ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, and 2D NMR spectra were recorded on a Bruker AVANCE600 spectrometer at 298 K unless otherwise stated. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR were referenced internally to residual protio-solvent resonances. Elemental analyses were conducted on a Thermo Scientific FlashSmart CHNS/O elemental analyzer at UC Irvine Materials Research Institute’s TEMPR facility in Irvine, California. Tetramethylsilane (SiMe_4) was degassed and dried over molecular sieves overnight prior to use. $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Ph})_2\text{BPh}_2^{10}$ was synthesized according to literature procedures. Sodium acetylide ($\text{NaC}\equiv\text{CH}$) was purchased from Sigma-

Aldrich as an 18 wt.% slurry in xylene:light mineral oil (95%), filtered through a medium porosity frit to collect insoluble solids, washed with hexane, and dried under reduced pressure prior to use.

(C₅Me₅)₂Y(μ - η^3 : η^1 -CCCCCH₂)Y(C₅Me₅)₂, A.1. Under an argon atmosphere free of coordinating solvents, a stirred suspension of (C₅Me₅)₂Y(μ -Ph)₂BPh₂ (246 mg, 0.363 mmol) in hexane (ca. 6 mL) was treated with solid sodium acetylide (0.018 g, 0.37 mmol) at room temperature. The initially colorless suspension first converts to a pale-yellow color, then to a pink/orange color over the next ca. 1 hour. After stirring overnight, the resulting orange suspension was filtered through a pipet packed with Kimwipe tissue and washed with hexane (ca. 2 mL) to remove insoluble solids, presumably NaBPh₄. Volatiles were removed from the clear orange filtrate under reduced pressure to yield an orange residue. The product was extracted into SiMe₄ (ca. 3 mL) and filtered through a glass pipet packed with Kimwipe tissue to remove insoluble off-white solids, determined to be [(C₅Me₅)₂Y]₂(μ -O) via ¹H NMR spectroscopy. Volatiles were removed under reduced pressure to yield (C₅Me₅)₂Y(μ - η^3 : η^1 -CCCCCH₂)Y(C₅Me₅)₂, **A.1**, as an orange solid (67 mg, 48%). Pale-yellow crystals of (C₅Me₅)₂Y(μ - η^3 : η^1 -CCCCCH₂)Y(C₅Me₅)₂, **A.1**, suitable for study by X-ray diffraction can be grown from pentane solutions stored at room temperature. ¹H NMR (600 MHz, C₆D₆): δ 6.58 (d, 1H, $J_{\text{H,H}} = 4.7$ Hz, $J_{\text{Y,H}} = 1.7$ Hz, CCCCCH₂), 5.54 (dd, 1H, $J_{\text{H,H}} = 4.7$ Hz, CCCCCH₂), 2.14 (s, 30H, C₅Me₅), 1.95 (s, 30H, C₅Me₅) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 194.4 (d, $J_{\text{Y,C}} = 33.7$ Hz, CCCCCH₂), δ 175.6 (br d, CCCCCH₂), 145.4 (br, CCCCCH₂), 119.7 (s, CCCCCH₂), 116.89 (C₅Me₅), δ 116.88 (C₅Me₅), 11.8 (C₅Me₅), 11.5 (C₅Me₅) ppm. IR: 2951m, 2900s, 2878s, 2722w, 1870w, 1587w, 1569w, 1435s, 1376m, 1360m, 1298w, 1260w, 1132w, 1105m, 1018m, 950w, 871m, 830w, 802w, 747w, 698m cm⁻¹. Anal. Calcd. For C₄₄H₆₂Y: C, 68.74; H, 8.13. Found: C, 67.43; H, 8.51. C, 68.58; H, 8.66. C, 68.71; H, 8.74. The C:H ratios in the analytical data give formulas of C₄₄H₆₆, C₄₄H₆₆, and C₄₄H₆₆, respectively.

Reaction of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu-\eta^3:\eta^1\text{-CCCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1, with THF.** In a J. Young NMR tube containing a pale-yellow C_6D_6 (ca. 0.8 mL) solution of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu-\eta^3:\eta^1\text{-CCCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1**, ca. 3 drops of THF were added and the J. Young tube was shaken for ca. 1 min to mix. NMR spectra were collected on the sample. ^1H NMR (600 MHz, C_6D_6): δ 6.50 (d, 1H, C_4H_2), 4.55 (dd, 1H, C_4H_2), 2.14 (s, 30H, C_5Me_5), 2.07 (s, 30H, C_5Me_5) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ 187.5 (d, CCCCCH_2), δ 171.5 (dd, CCCCCH_2), δ 160.5 (CCCCCH_2), δ 120.1 (CCCCCH_2), δ 116.7 (C_5Me_5), δ 116.6 (C_5Me_5), δ 67.8 (OCH_2CH_2 of THF), δ 25.7 (OCH_2CH_2 of THF), δ 12.1 (C_5Me_5), δ 11.9 (C_5Me_5) ppm. A few colorless crystals identified crystallographically as $[\text{Na}(\text{THF})_6][(\text{C}_5\text{Me}_5)_6\text{Y}_6\text{O}_5(\text{OH})_3]$, **A.2**, were grown over ca. 1 week at room temperature.

X-ray Data Collection, Structure Solution and Refinement for $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu-\eta^3:\eta^1\text{-CCCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1.** A yellow crystal of approximate dimensions 0.140 x 0.159 x 0.180 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2³⁸ program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time). The raw frame data was processed using SAINT³⁹ and SADABS⁴⁰ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴¹ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁴² for neutral atoms were used throughout the analysis. Hydrogen atoms H44A and H44B were located from a difference-Fourier map and refined (x, y, z and U_{iso}). The rest of the hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0751$ and $\text{Goof} = 1.020$ for 443 variables refined against 12094 data (0.70 Å), $R1 = 0.0336$ for those 9443 data with $I > 2.0\sigma(I)$.

Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

Table A.3. Crystal data and structure refinement for $(C_5Me_5)_2Y(\mu-\eta^3:\eta^1-CCCCH_2)Y(C_5Me_5)_2$,

A.1.

Identification code	wgml3
Empirical formula	C ₄₄ H ₆₂ Y ₂
Formula weight	768.75
Temperature	93(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	a = 15.962(2) Å a = 90°.
	b = 14.744(2) Å b = 100.706(2)°.
	c = 17.178(3) Å g = 90°.
Volume	3972.4(10) Å ³
Z	4
Density (calculated)	1.285 Mg/m ³
Absorption coefficient	2.935 mm ⁻¹
F(000)	1616
Crystal color	yellow
Crystal size	0.180 x 0.159 x 0.140 mm ³
Theta range for data collection	2.114 to 30.550°
Index ranges	-22 ≤ <i>h</i> ≤ 22, -20 ≤ <i>k</i> ≤ 21, -24 ≤ <i>l</i> ≤ 24
Reflections collected	78880
Independent reflections	12094 [R(int) = 0.0668]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.6975
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	12094 / 0 / 443
Goodness-of-fit on F ²	1.020
Final R indices [I>2sigma(I) = 9443 data]	R1 = 0.0336, wR2 = 0.0691
R indices (all data, 0.70 Å)	R1 = 0.0546, wR2 = 0.0751
Largest diff. peak and hole	0.439 and -0.431 e.Å ⁻³

Table A.4. Bond lengths [Å] and angles [°] for (C₅Me₅)₂Y(μ - η^3 : η^1 -CCCCH₂)Y(C₅Me₅)₂, **A.1.**

Cnt1-Y(1)	2.366	C(11)-C(12)	1.423(2)
Cnt2-Y(1)	2.363	C(11)-C(16)	1.503(3)
Y(1)-C(41)	2.7790(18)	C(12)-C(13)	1.422(2)
Y(1)-C(43)	2.4299(19)	C(12)-C(17)	1.502(3)
Y(1)-C(42)	2.5323(18)	C(13)-C(14)	1.425(3)
Y(1)-C(44)	3.660(2)	C(13)-C(18)	1.507(3)
Y(1)-C(15)	2.6418(18)	C(14)-C(15)	1.422(3)
Y(1)-C(5)	2.6421(19)	C(14)-C(19)	1.502(3)
Y(1)-C(13)	2.6468(18)	C(15)-C(20)	1.507(3)
Y(1)-C(1)	2.6543(18)	C(16)-H(16A)	0.9800
Y(1)-C(4)	2.6565(19)	C(16)-H(16B)	0.9800
Y(1)-C(2)	2.6576(18)	C(16)-H(16C)	0.9800
Y(1)-C(14)	2.6585(18)	C(17)-H(17A)	0.9800
Y(1)-C(12)	2.6629(18)	C(17)-H(17B)	0.9800
Y(1)-C(11)	2.6644(18)	C(17)-H(17C)	0.9800
Y(1)-C(3)	2.6699(18)	C(18)-H(18A)	0.9800
C(1)-C(5)	1.414(3)	C(18)-H(18B)	0.9800
C(1)-C(2)	1.420(3)	C(18)-H(18C)	0.9800
C(1)-C(6)	1.507(3)	C(19)-H(19A)	0.9800
C(2)-C(3)	1.424(3)	C(19)-H(19B)	0.9800
C(2)-C(7)	1.502(3)	C(19)-H(19C)	0.9800
C(3)-C(4)	1.420(3)	C(20)-H(20A)	0.9800
C(3)-C(8)	1.503(3)	C(20)-H(20B)	0.9800
C(4)-C(5)	1.413(3)	C(20)-H(20C)	0.9800
C(4)-C(9)	1.506(3)	Cnt3-Y(2)	2.328
C(5)-C(10)	1.505(3)	Cnt4-Y(2)	2.342
C(6)-H(6A)	0.9800	Y(2)-C(41)	2.4199(19)
C(6)-H(6B)	0.9800	Y(2)-C(42)	3.367(2)
C(6)-H(6C)	0.9800	Y(2)-C(43)	4.754(2)
C(7)-H(7A)	0.9800	Y(2)-C(44)	5.588(2)
C(7)-H(7B)	0.9800	Y(2)-C(22)	2.5895(17)
C(7)-H(7C)	0.9800	Y(2)-C(32)	2.6233(17)
C(8)-H(8A)	0.9800	Y(2)-C(33)	2.6272(18)
C(8)-H(8B)	0.9800	Y(2)-C(21)	2.6296(17)
C(8)-H(8C)	0.9800	Y(2)-C(23)	2.6299(18)
C(9)-H(9A)	0.9800	Y(2)-C(31)	2.6327(17)
C(9)-H(9B)	0.9800	Y(2)-C(25)	2.6365(17)
C(9)-H(9C)	0.9800	Y(2)-C(24)	2.6373(18)
C(10)-H(10A)	0.9800	Y(2)-C(35)	2.6376(18)
C(10)-H(10B)	0.9800	Y(2)-C(34)	2.6598(18)
C(10)-H(10C)	0.9800	C(21)-C(25)	1.420(2)
C(11)-C(15)	1.421(3)	C(21)-C(22)	1.426(2)

C(21)-C(26)	1.504(2)
C(22)-C(23)	1.422(3)
C(22)-C(27)	1.508(2)
C(23)-C(24)	1.427(3)
C(23)-C(28)	1.500(3)
C(24)-C(25)	1.424(2)
C(24)-C(29)	1.505(3)
C(25)-C(30)	1.511(2)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-C(32)	1.416(3)
C(31)-C(35)	1.425(3)
C(31)-C(36)	1.510(2)
C(32)-C(33)	1.424(3)
C(32)-C(37)	1.504(3)
C(33)-C(34)	1.420(3)
C(33)-C(38)	1.509(3)
C(34)-C(35)	1.423(3)
C(34)-C(39)	1.501(3)
C(35)-C(40)	1.502(3)
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800

C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-C(42)	1.240(3)
C(42)-C(43)	1.404(3)
C(43)-C(44)	1.331(3)
C(44)-H(44A)	0.97(2)
C(44)-H(44B)	0.97(2)
Cnt1-Y(1)-Cnt2	137.6
Cnt3-Y(2)-Cnt4	138.6
C(43)-Y(1)-C(42)	32.79(6)
C(43)-Y(1)-C(15)	89.47(6)
C(42)-Y(1)-C(15)	108.29(6)
C(43)-Y(1)-C(5)	80.38(6)
C(42)-Y(1)-C(5)	97.54(6)
C(15)-Y(1)-C(5)	112.52(6)
C(43)-Y(1)-C(13)	128.89(6)
C(42)-Y(1)-C(13)	121.88(6)
C(15)-Y(1)-C(13)	51.65(6)
C(5)-Y(1)-C(13)	139.93(6)
C(43)-Y(1)-C(1)	84.49(6)
C(42)-Y(1)-C(1)	85.17(6)
C(15)-Y(1)-C(1)	143.47(6)
C(5)-Y(1)-C(1)	30.96(6)
C(13)-Y(1)-C(1)	146.62(6)
C(43)-Y(1)-C(4)	107.29(7)
C(42)-Y(1)-C(4)	128.45(6)
C(15)-Y(1)-C(4)	97.35(6)
C(5)-Y(1)-C(4)	30.93(6)
C(13)-Y(1)-C(4)	109.21(6)
C(1)-Y(1)-C(4)	51.17(6)
C(43)-Y(1)-C(2)	114.47(6)
C(42)-Y(1)-C(2)	106.02(6)
C(15)-Y(1)-C(2)	143.84(6)
C(5)-Y(1)-C(2)	51.12(6)
C(13)-Y(1)-C(2)	116.15(6)
C(1)-Y(1)-C(2)	31.00(6)
C(4)-Y(1)-C(2)	51.08(6)
C(43)-Y(1)-C(14)	120.59(6)
C(42)-Y(1)-C(14)	135.03(6)
C(15)-Y(1)-C(14)	31.12(6)
C(5)-Y(1)-C(14)	114.23(6)
C(13)-Y(1)-C(14)	31.16(6)
C(1)-Y(1)-C(14)	137.53(6)

C(4)-Y(1)-C(14)	87.16(6)
C(2)-Y(1)-C(14)	118.57(6)
C(43)-Y(1)-C(12)	100.48(6)
C(42)-Y(1)-C(12)	91.36(6)
C(15)-Y(1)-C(12)	51.39(6)
C(5)-Y(1)-C(12)	163.67(6)
C(13)-Y(1)-C(12)	31.07(5)
C(1)-Y(1)-C(12)	164.90(6)
C(4)-Y(1)-C(12)	137.92(6)
C(2)-Y(1)-C(12)	138.74(6)
C(14)-Y(1)-C(12)	51.22(5)
C(43)-Y(1)-C(11)	77.95(6)
C(42)-Y(1)-C(11)	83.82(6)
C(15)-Y(1)-C(11)	31.06(5)
C(5)-Y(1)-C(11)	136.48(6)
C(13)-Y(1)-C(11)	51.41(6)
C(1)-Y(1)-C(11)	161.10(6)
C(4)-Y(1)-C(11)	128.23(6)
C(2)-Y(1)-C(11)	167.54(6)
C(14)-Y(1)-C(11)	51.21(5)
C(12)-Y(1)-C(11)	30.98(5)
C(43)-Y(1)-C(3)	131.09(6)
C(42)-Y(1)-C(3)	135.43(6)
C(15)-Y(1)-C(3)	112.87(6)
C(5)-Y(1)-C(3)	51.19(6)
C(13)-Y(1)-C(3)	97.30(6)
C(1)-Y(1)-C(3)	51.30(6)
C(4)-Y(1)-C(3)	30.92(6)
C(2)-Y(1)-C(3)	31.00(6)
C(14)-Y(1)-C(3)	89.47(6)
C(12)-Y(1)-C(3)	127.77(6)
C(11)-Y(1)-C(3)	140.61(6)
C(5)-C(1)-C(2)	107.62(17)
C(5)-C(1)-C(6)	126.1(2)
C(2)-C(1)-C(6)	126.15(19)
C(5)-C(1)-Y(1)	74.05(10)
C(2)-C(1)-Y(1)	74.63(10)
C(6)-C(1)-Y(1)	120.76(13)
C(1)-C(2)-C(3)	108.31(17)
C(1)-C(2)-C(7)	126.62(18)
C(3)-C(2)-C(7)	124.78(19)
C(1)-C(2)-Y(1)	74.37(10)
C(3)-C(2)-Y(1)	74.98(10)
C(7)-C(2)-Y(1)	121.64(12)
C(4)-C(3)-C(2)	107.38(17)

C(4)-C(3)-C(8)	127.51(19)
C(2)-C(3)-C(8)	124.6(2)
C(4)-C(3)-Y(1)	74.02(11)
C(2)-C(3)-Y(1)	74.02(10)
C(8)-C(3)-Y(1)	124.33(13)
C(5)-C(4)-C(3)	108.21(17)
C(5)-C(4)-C(9)	124.2(2)
C(3)-C(4)-C(9)	126.7(2)
C(5)-C(4)-Y(1)	73.97(11)
C(3)-C(4)-Y(1)	75.06(11)
C(9)-C(4)-Y(1)	125.76(13)
C(4)-C(5)-C(1)	108.48(18)
C(4)-C(5)-C(10)	123.8(2)
C(1)-C(5)-C(10)	127.4(2)
C(4)-C(5)-Y(1)	75.10(11)
C(1)-C(5)-Y(1)	75.00(11)
C(10)-C(5)-Y(1)	120.86(13)
C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(4)-C(9)-H(9A)	109.5
C(4)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(4)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5

H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(15)-C(11)-C(12)	107.96(16)
C(15)-C(11)-C(16)	126.78(17)
C(12)-C(11)-C(16)	124.96(16)
C(15)-C(11)-Y(1)	73.59(10)
C(12)-C(11)-Y(1)	74.45(10)
C(16)-C(11)-Y(1)	122.76(12)
C(13)-C(12)-C(11)	108.14(15)
C(13)-C(12)-C(17)	126.64(17)
C(11)-C(12)-C(17)	124.96(16)
C(13)-C(12)-Y(1)	73.84(10)
C(11)-C(12)-Y(1)	74.57(10)
C(17)-C(12)-Y(1)	122.14(12)
C(12)-C(13)-C(14)	107.78(16)
C(12)-C(13)-C(18)	126.11(17)
C(14)-C(13)-C(18)	125.92(17)
C(12)-C(13)-Y(1)	75.09(10)
C(14)-C(13)-Y(1)	74.87(10)
C(18)-C(13)-Y(1)	119.90(12)
C(15)-C(14)-C(13)	108.04(16)
C(15)-C(14)-C(19)	125.63(18)
C(13)-C(14)-C(19)	125.23(18)
C(15)-C(14)-Y(1)	73.79(10)
C(13)-C(14)-Y(1)	73.97(10)
C(19)-C(14)-Y(1)	127.56(12)
C(11)-C(15)-C(14)	108.03(16)
C(11)-C(15)-C(20)	125.48(17)
C(14)-C(15)-C(20)	126.44(17)
C(11)-C(15)-Y(1)	75.35(10)
C(14)-C(15)-Y(1)	75.09(10)
C(20)-C(15)-Y(1)	117.60(12)
C(11)-C(16)-H(16A)	109.5
C(11)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(11)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(12)-C(17)-H(17A)	109.5
C(12)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(12)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(13)-C(18)-H(18A)	109.5

C(13)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(13)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(14)-C(19)-H(19A)	109.5
C(14)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(14)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(15)-C(20)-H(20A)	109.5
C(15)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(15)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(41)-Y(2)-C(22)	98.82(6)
C(41)-Y(2)-C(32)	86.18(6)
C(22)-Y(2)-C(32)	134.31(6)
C(41)-Y(2)-C(33)	113.81(6)
C(22)-Y(2)-C(33)	111.96(6)
C(32)-Y(2)-C(33)	31.47(6)
C(41)-Y(2)-C(21)	83.51(6)
C(22)-Y(2)-C(21)	31.69(5)
C(32)-Y(2)-C(21)	159.38(6)
C(33)-Y(2)-C(21)	143.61(6)
C(41)-Y(2)-C(23)	130.31(6)
C(22)-Y(2)-C(23)	31.60(6)
C(32)-Y(2)-C(23)	127.00(6)
C(33)-Y(2)-C(23)	96.10(6)
C(21)-Y(2)-C(23)	52.10(6)
C(41)-Y(2)-C(31)	88.69(6)
C(22)-Y(2)-C(31)	163.71(6)
C(32)-Y(2)-C(31)	31.26(6)
C(33)-Y(2)-C(31)	51.79(5)
C(21)-Y(2)-C(31)	164.59(6)
C(23)-Y(2)-C(31)	139.61(6)
C(41)-Y(2)-C(25)	102.32(6)
C(22)-Y(2)-C(25)	52.14(5)
C(32)-Y(2)-C(25)	168.86(6)
C(33)-Y(2)-C(25)	143.00(6)
C(21)-Y(2)-C(25)	31.29(5)
C(23)-Y(2)-C(25)	51.93(6)
C(31)-Y(2)-C(25)	140.31(6)

C(41)-Y(2)-C(24)	132.95(6)
C(22)-Y(2)-C(24)	52.20(6)
C(32)-Y(2)-C(24)	140.88(6)
C(33)-Y(2)-C(24)	111.67(6)
C(21)-Y(2)-C(24)	51.92(6)
C(23)-Y(2)-C(24)	31.45(5)
C(31)-Y(2)-C(24)	130.09(6)
C(25)-Y(2)-C(24)	31.33(5)
C(41)-Y(2)-C(35)	118.15(6)
C(22)-Y(2)-C(35)	142.89(6)
C(32)-Y(2)-C(35)	51.83(6)
C(33)-Y(2)-C(35)	51.74(6)
C(21)-Y(2)-C(35)	148.23(6)
C(23)-Y(2)-C(35)	111.54(6)
C(31)-Y(2)-C(35)	31.37(6)
C(25)-Y(2)-C(35)	117.16(6)
C(24)-Y(2)-C(35)	99.08(6)
C(41)-Y(2)-C(34)	137.02(6)
C(22)-Y(2)-C(34)	116.01(6)
C(32)-Y(2)-C(34)	51.68(6)
C(33)-Y(2)-C(34)	31.14(6)
C(21)-Y(2)-C(34)	138.99(6)
C(23)-Y(2)-C(34)	88.09(6)
C(31)-Y(2)-C(34)	51.60(5)
C(25)-Y(2)-C(34)	118.55(6)
C(24)-Y(2)-C(34)	89.59(6)
C(35)-Y(2)-C(34)	31.17(5)
C(25)-C(21)-C(22)	107.63(15)
C(25)-C(21)-C(26)	127.25(16)
C(22)-C(21)-C(26)	124.76(16)
C(25)-C(21)-Y(2)	74.62(10)
C(22)-C(21)-Y(2)	72.61(10)
C(26)-C(21)-Y(2)	123.80(11)
C(23)-C(22)-C(21)	108.42(15)
C(23)-C(22)-C(27)	125.73(17)
C(21)-C(22)-C(27)	125.85(17)
C(23)-C(22)-Y(2)	75.76(10)
C(21)-C(22)-Y(2)	75.70(10)
C(27)-C(22)-Y(2)	114.88(12)
C(22)-C(23)-C(24)	107.65(16)
C(22)-C(23)-C(28)	125.10(17)
C(24)-C(23)-C(28)	126.51(17)
C(22)-C(23)-Y(2)	72.63(10)
C(24)-C(23)-Y(2)	74.56(10)
C(28)-C(23)-Y(2)	126.17(12)

C(25)-C(24)-C(23)	107.93(16)
C(25)-C(24)-C(29)	123.99(17)
C(23)-C(24)-C(29)	127.21(17)
C(25)-C(24)-Y(2)	74.30(10)
C(23)-C(24)-Y(2)	73.99(10)
C(29)-C(24)-Y(2)	125.97(12)
C(21)-C(25)-C(24)	108.31(15)
C(21)-C(25)-C(30)	127.27(16)
C(24)-C(25)-C(30)	124.06(16)
C(21)-C(25)-Y(2)	74.08(10)
C(24)-C(25)-Y(2)	74.36(10)
C(30)-C(25)-Y(2)	123.00(11)
C(21)-C(26)-H(26A)	109.5
C(21)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(21)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(22)-C(27)-H(27A)	109.5
C(22)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(22)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(23)-C(28)-H(28A)	109.5
C(23)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(23)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(24)-C(29)-H(29A)	109.5
C(24)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(24)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(25)-C(30)-H(30A)	109.5
C(25)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(25)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(32)-C(31)-C(35)	108.07(16)
C(32)-C(31)-C(36)	125.45(17)
C(35)-C(31)-C(36)	126.29(17)

C(32)-C(31)-Y(2)	74.00(10)
C(35)-C(31)-Y(2)	74.51(10)
C(36)-C(31)-Y(2)	121.36(12)
C(31)-C(32)-C(33)	107.96(16)
C(31)-C(32)-C(37)	126.00(17)
C(33)-C(32)-C(37)	125.79(17)
C(31)-C(32)-Y(2)	74.73(10)
C(33)-C(32)-Y(2)	74.42(10)
C(37)-C(32)-Y(2)	121.39(12)
C(34)-C(33)-C(32)	108.19(15)
C(34)-C(33)-C(38)	125.68(17)
C(32)-C(33)-C(38)	125.75(17)
C(34)-C(33)-Y(2)	75.69(10)
C(32)-C(33)-Y(2)	74.11(10)
C(38)-C(33)-Y(2)	121.87(12)
C(33)-C(34)-C(35)	107.80(16)
C(33)-C(34)-C(39)	126.41(17)
C(35)-C(34)-C(39)	124.53(17)
C(33)-C(34)-Y(2)	73.16(10)
C(35)-C(34)-Y(2)	73.55(10)
C(39)-C(34)-Y(2)	129.09(12)
C(34)-C(35)-C(31)	107.96(16)
C(34)-C(35)-C(40)	124.76(17)
C(31)-C(35)-C(40)	126.80(17)
C(34)-C(35)-Y(2)	75.28(10)
C(31)-C(35)-Y(2)	74.13(10)
C(40)-C(35)-Y(2)	122.84(12)
C(31)-C(36)-H(36A)	109.5
C(31)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(31)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(32)-C(37)-H(37A)	109.5
C(32)-C(37)-H(37B)	109.5

H(37A)-C(37)-H(37B)	109.5
C(32)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(33)-C(38)-H(38A)	109.5
C(33)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(33)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(34)-C(39)-H(39A)	109.5
C(34)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(34)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(35)-C(40)-H(40A)	109.5
C(35)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(35)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(42)-C(41)-Y(2)	131.04(14)
C(42)-C(41)-Y(1)	65.59(11)
Y(2)-C(41)-Y(1)	163.30(8)
C(41)-C(42)-C(43)	157.50(19)
C(41)-C(42)-Y(1)	87.93(12)
C(43)-C(42)-Y(1)	69.60(11)
C(44)-C(43)-C(42)	130.11(19)
C(44)-C(43)-Y(1)	152.24(16)
C(42)-C(43)-Y(1)	77.62(11)
C(43)-C(44)-H(44A)	119.3(14)
C(43)-C(44)-H(44B)	123.7(14)
H(44A)-C(44)-H(44B)	116.9(19)

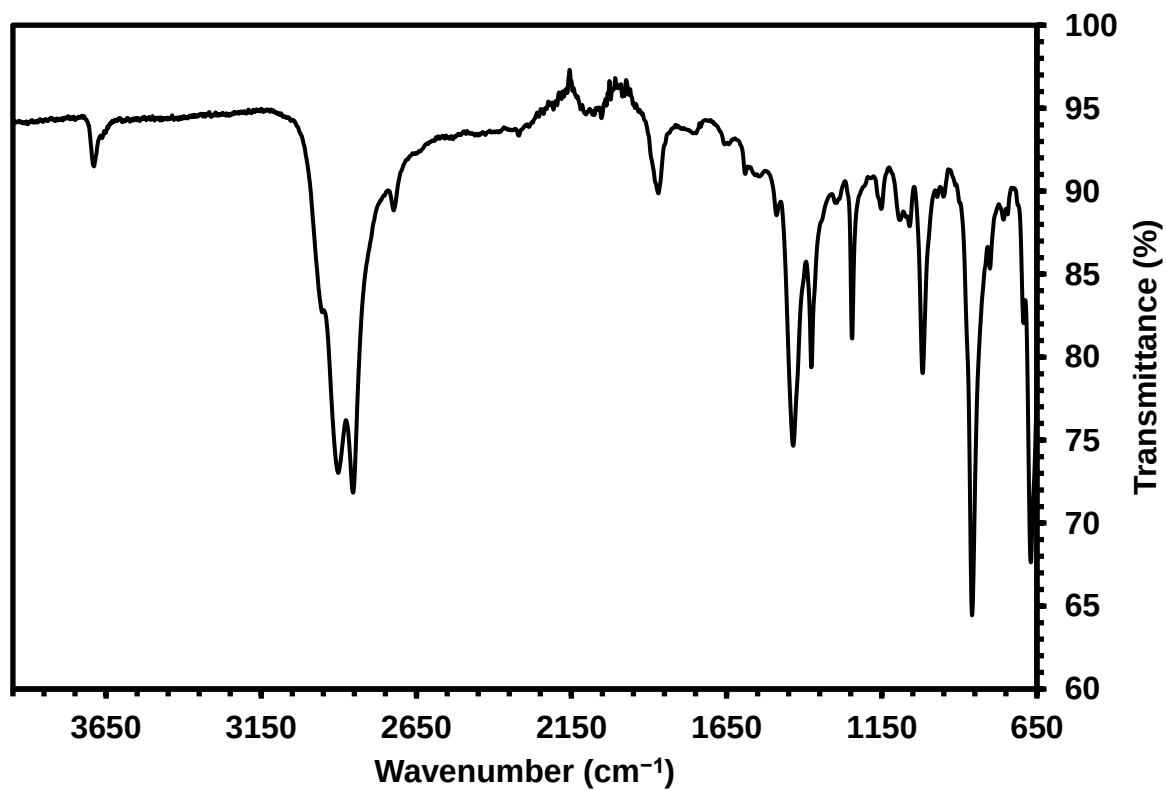


Figure A.4. Infrared spectrum of $(C_5Me_5)_2Y(\mu-\eta^3:\eta^1-CCCCH_2)Y(C_5Me_5)_2$, **A.1**.

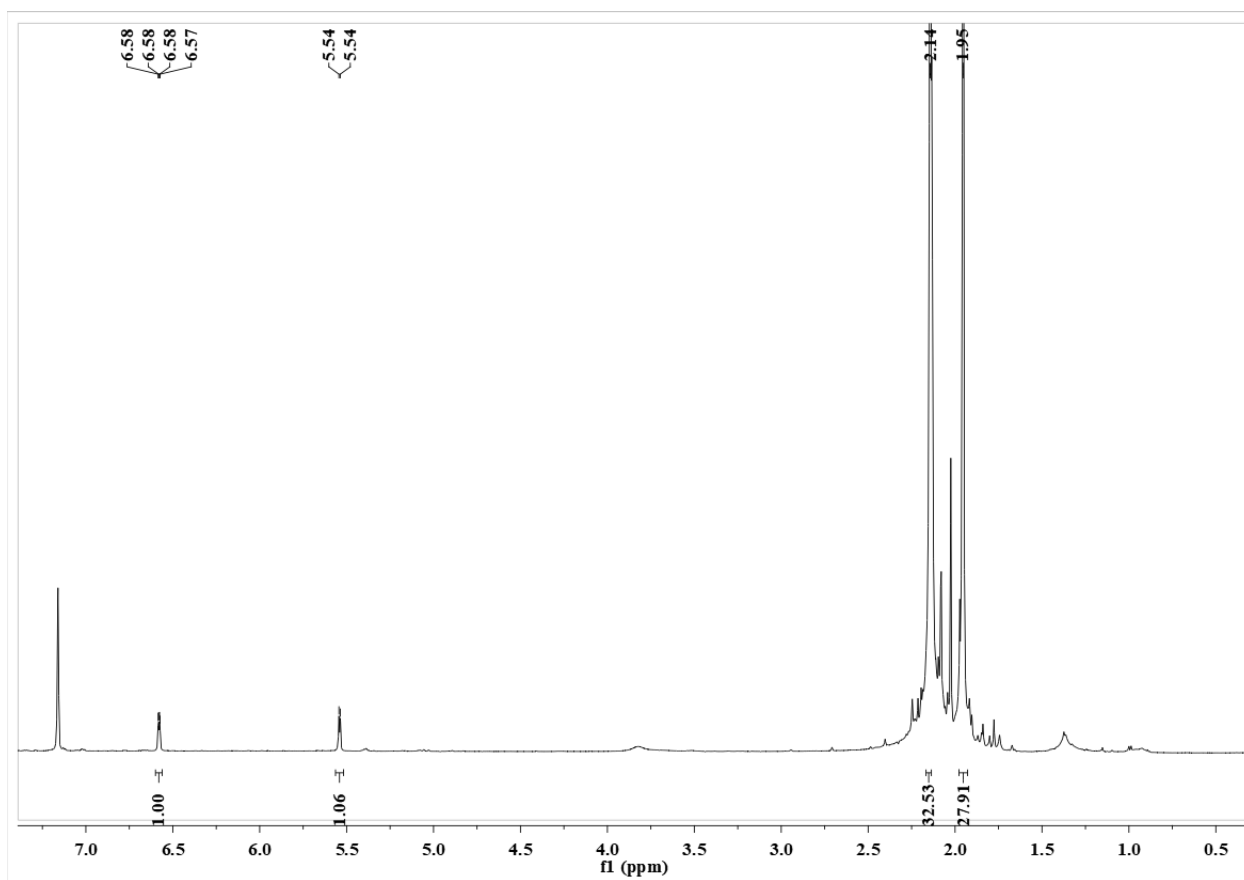


Figure A.5. ^1H NMR spectrum of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-}\eta^3\text{:}\eta^1\text{-CCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1**, in C_6D_6 .

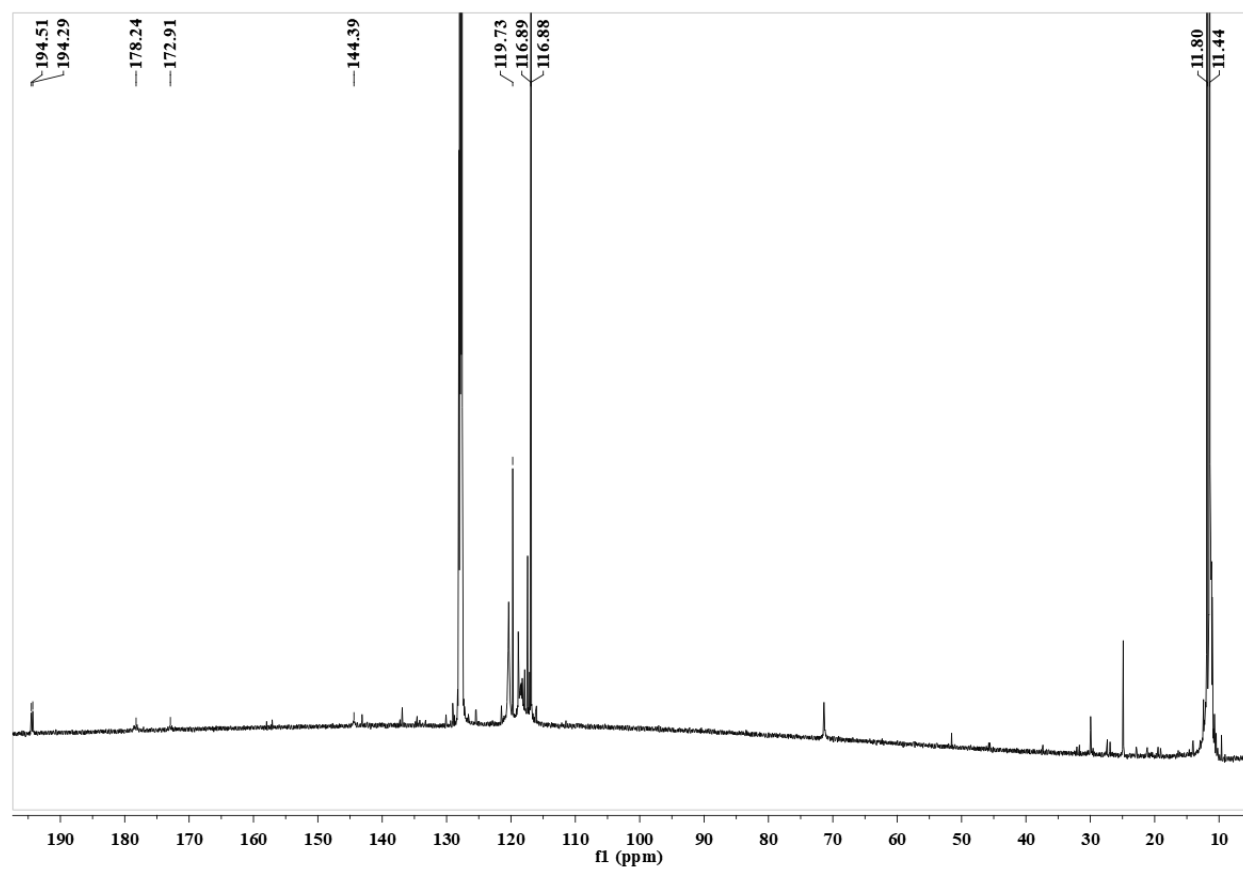


Figure A.6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-}\eta^3\text{:}\eta^1\text{-CCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1**, in C_6D_6 .

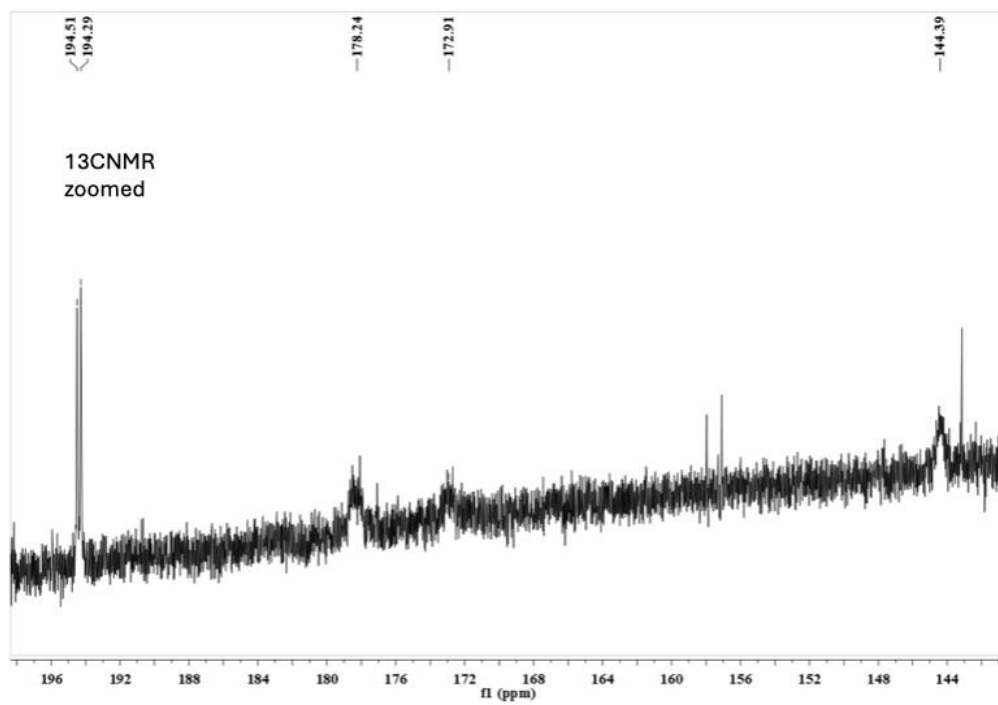


Figure A.7. Zoomed in portion of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-}\eta^3\text{:}\eta^1\text{-CCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1**, in C_6D_6 .

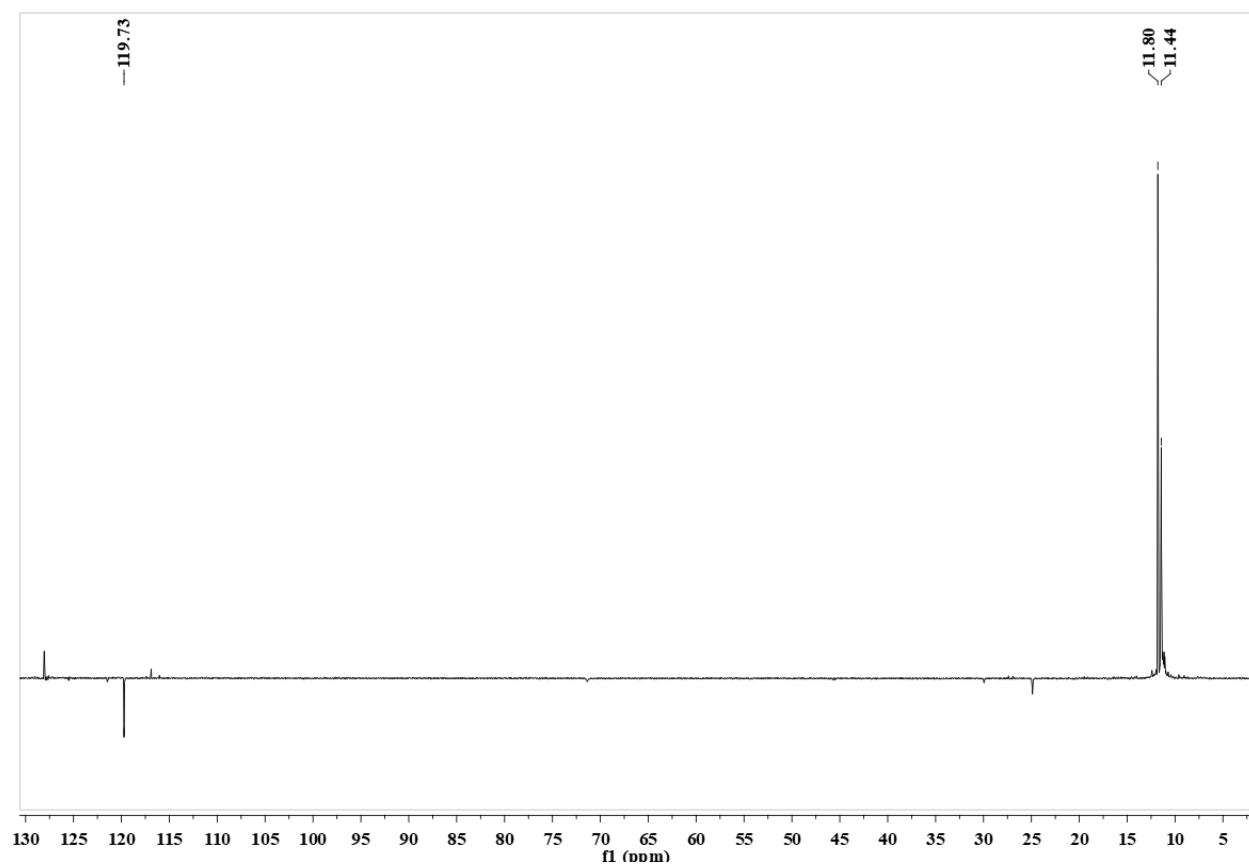


Figure A.8. DEPT135 NMR spectrum of $(C_5Me_5)_2Y(\mu-\eta^3:\eta^1-CCCCH_2)Y(C_5Me_5)_2$, **A.1**, in C_6D_6 .

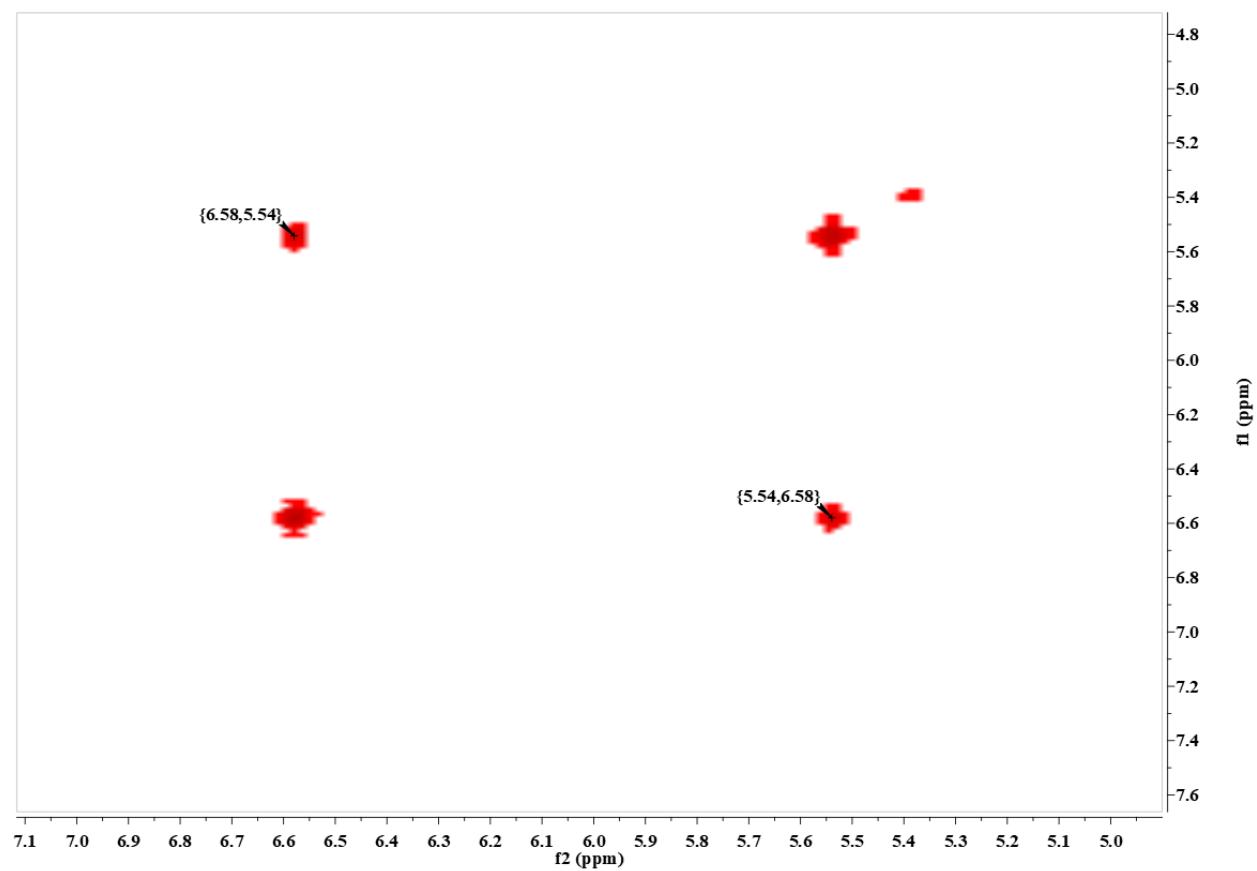


Figure A.9. Zoomed in ^1H - ^1H COSY NMR spectrum of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-}\eta^3\text{:}\eta^1\text{-CCCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1** showing correlations between the resonances at 6.58 and 5.54 ppm, in C_6D_6 .

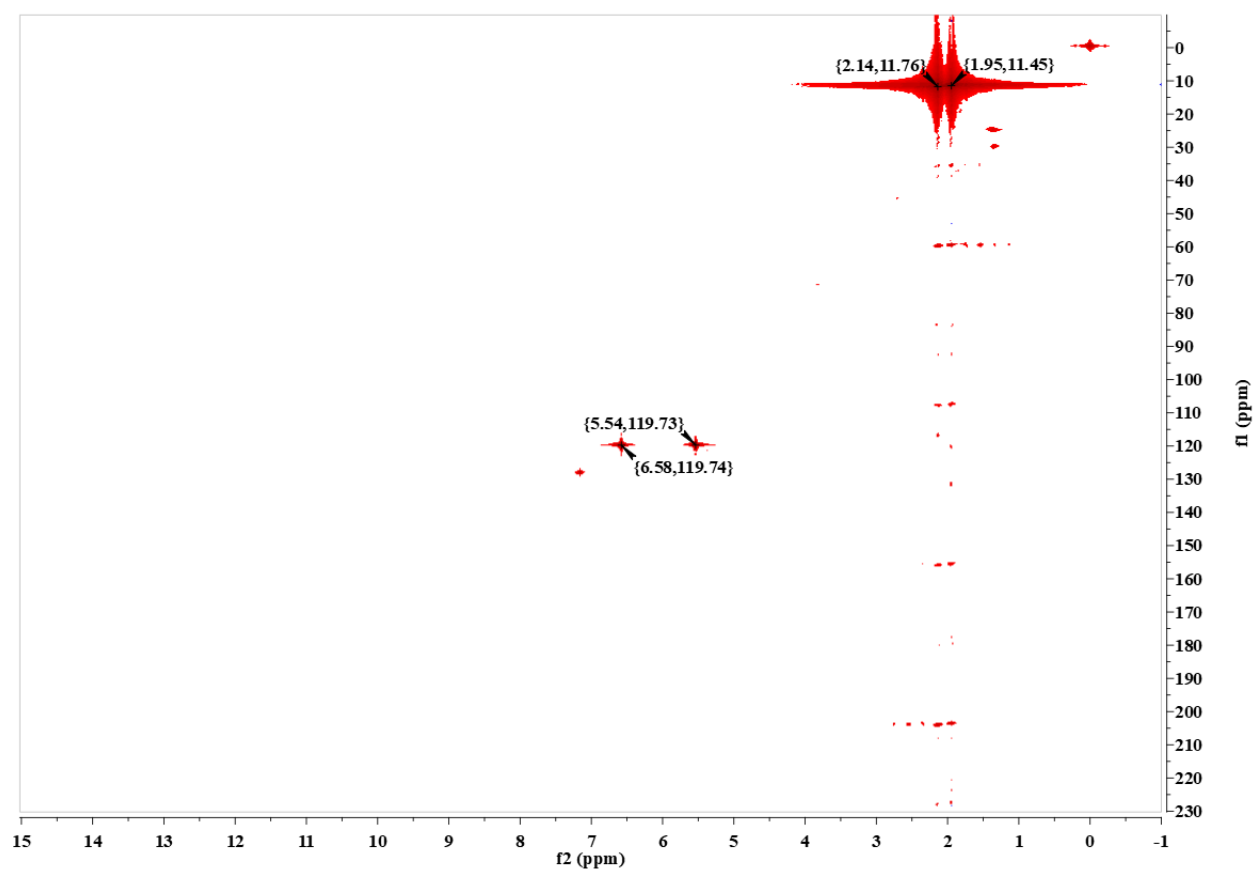


Figure A.10. Full ^{13}C - ^1H HMQC NMR spectrum of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-}\eta^3\text{:}\eta^1\text{-CCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1**, in C_6D_6 .

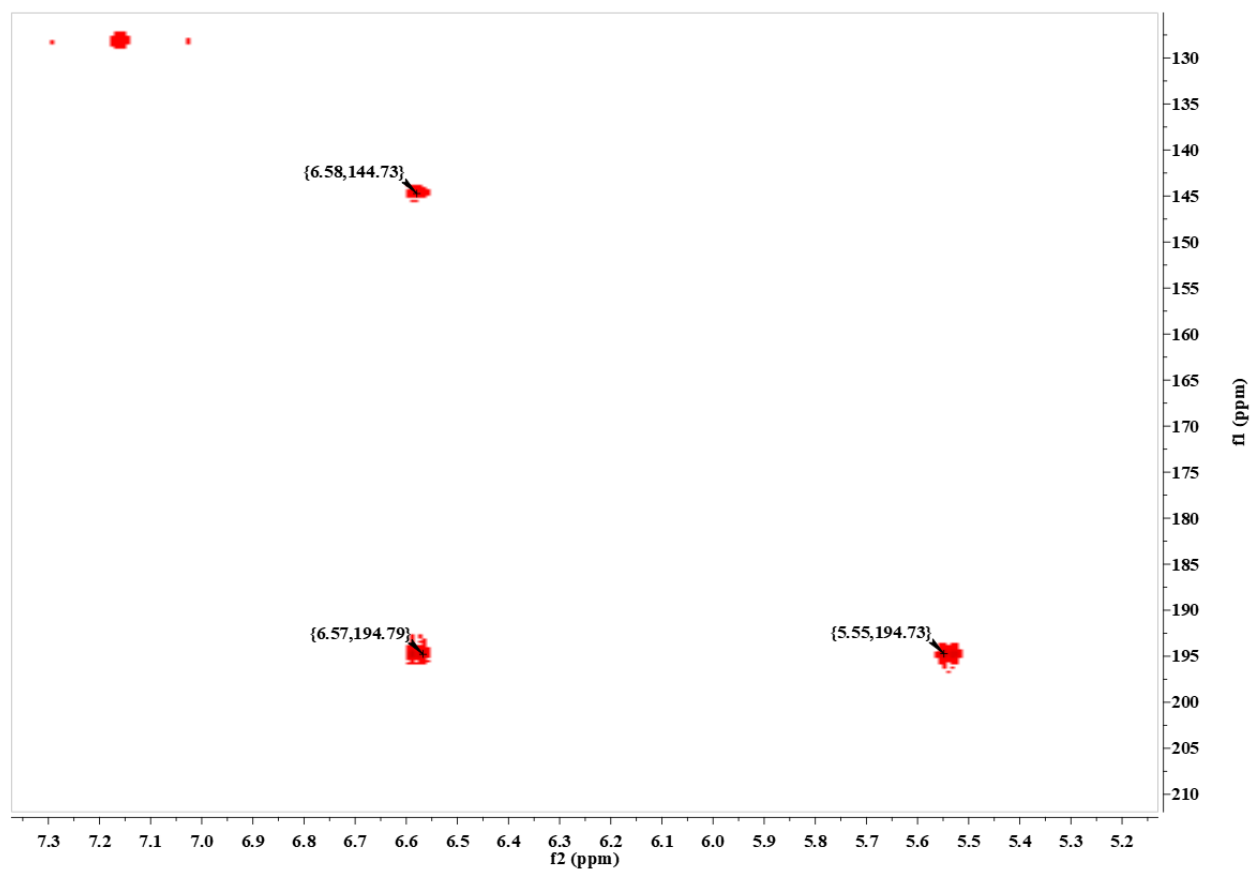


Figure A.11. Zoomed in ^{13}C - ^1H HMBC NMR spectrum optimized for 10 Hz couplings of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-}\eta^3\text{:}\eta^1\text{-CCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1**, in C_6D_6 .

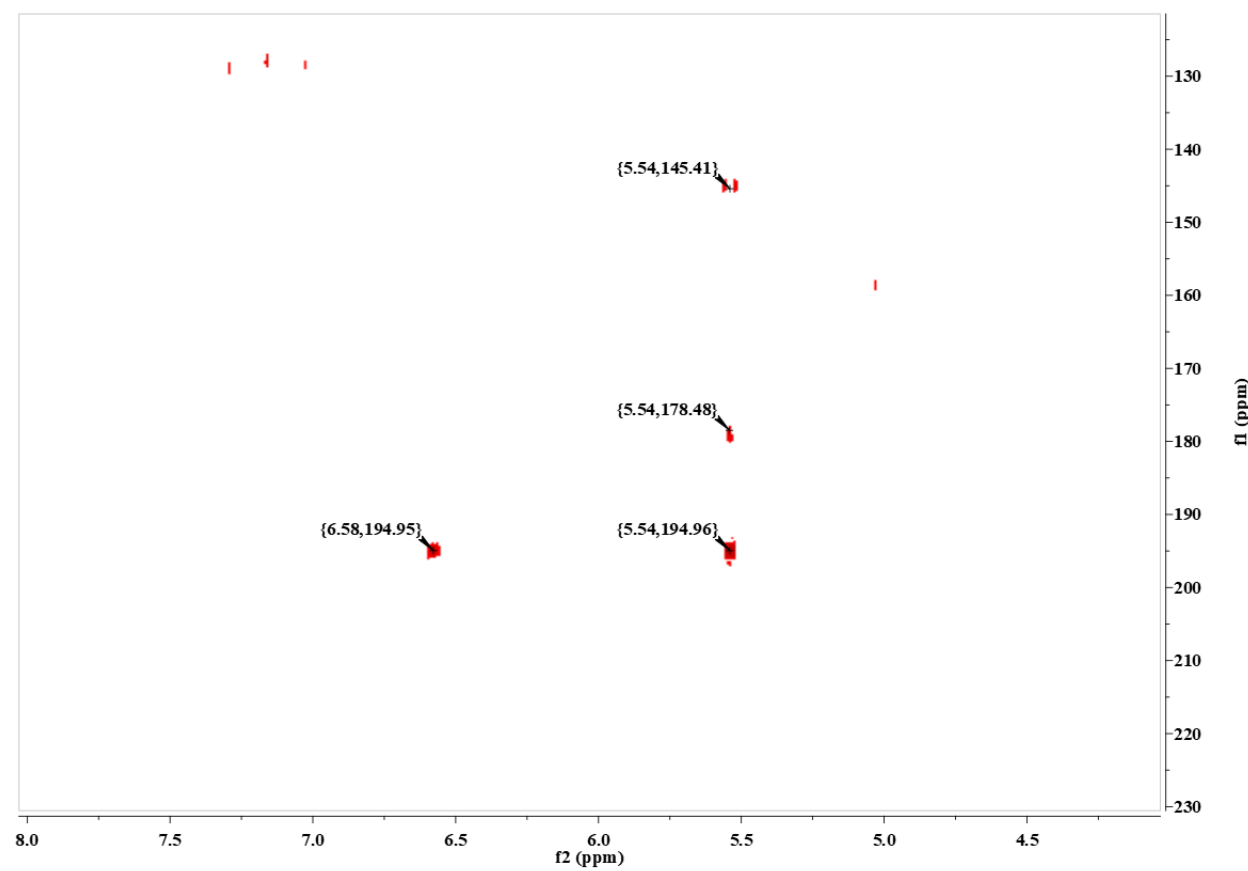


Figure A.12. Zoomed in ¹³C-¹H HMBC NMR spectrum optimized for 2 Hz couplings of (C₅Me₅)₂Y(μ-η³:η¹-CCCCH₂)Y(C₅Me₅)₂, **A.1**, in C₆D₆.

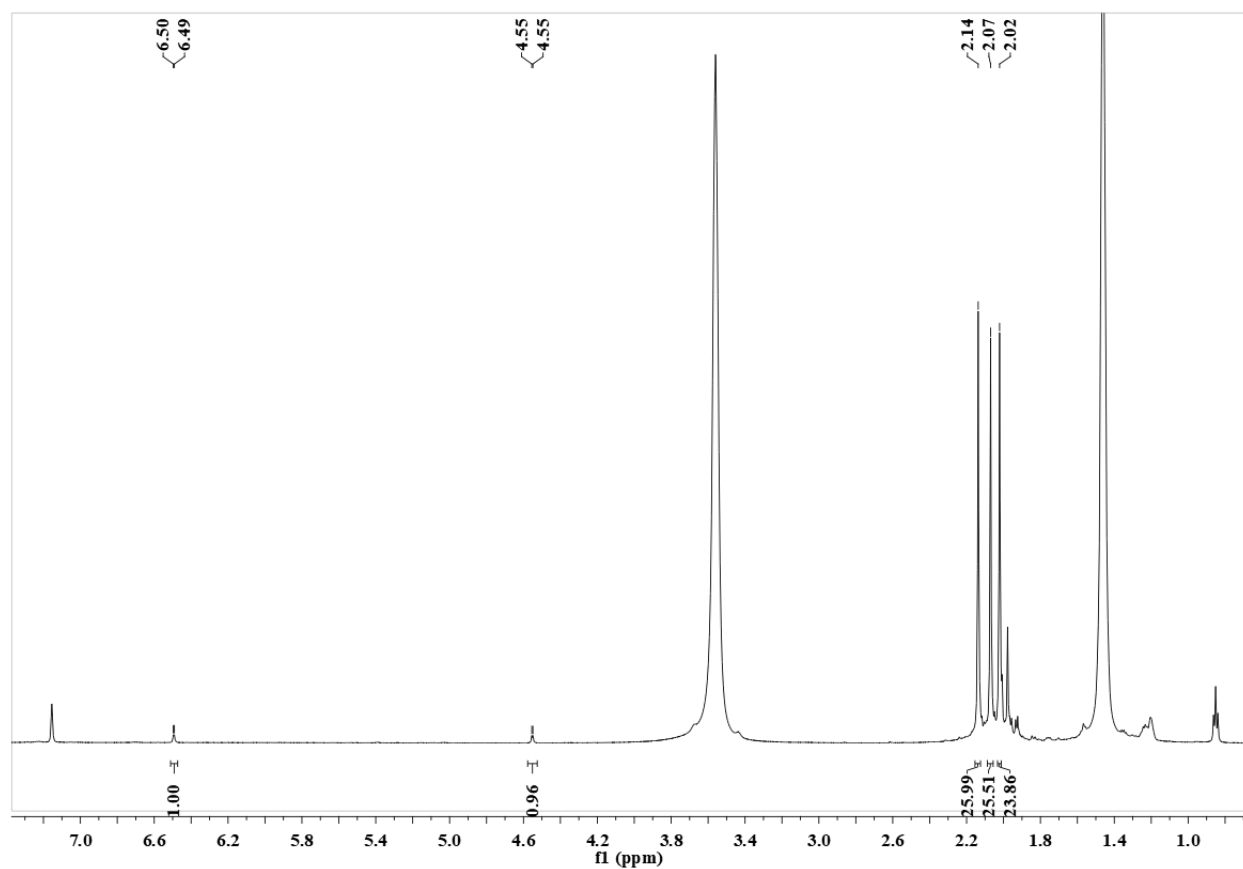


Figure A.13. ^1H NMR spectrum of a C_6D_6 solution of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-}\eta^3\text{:}\eta^1\text{-CCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1**, spiked with a few drops of THF.

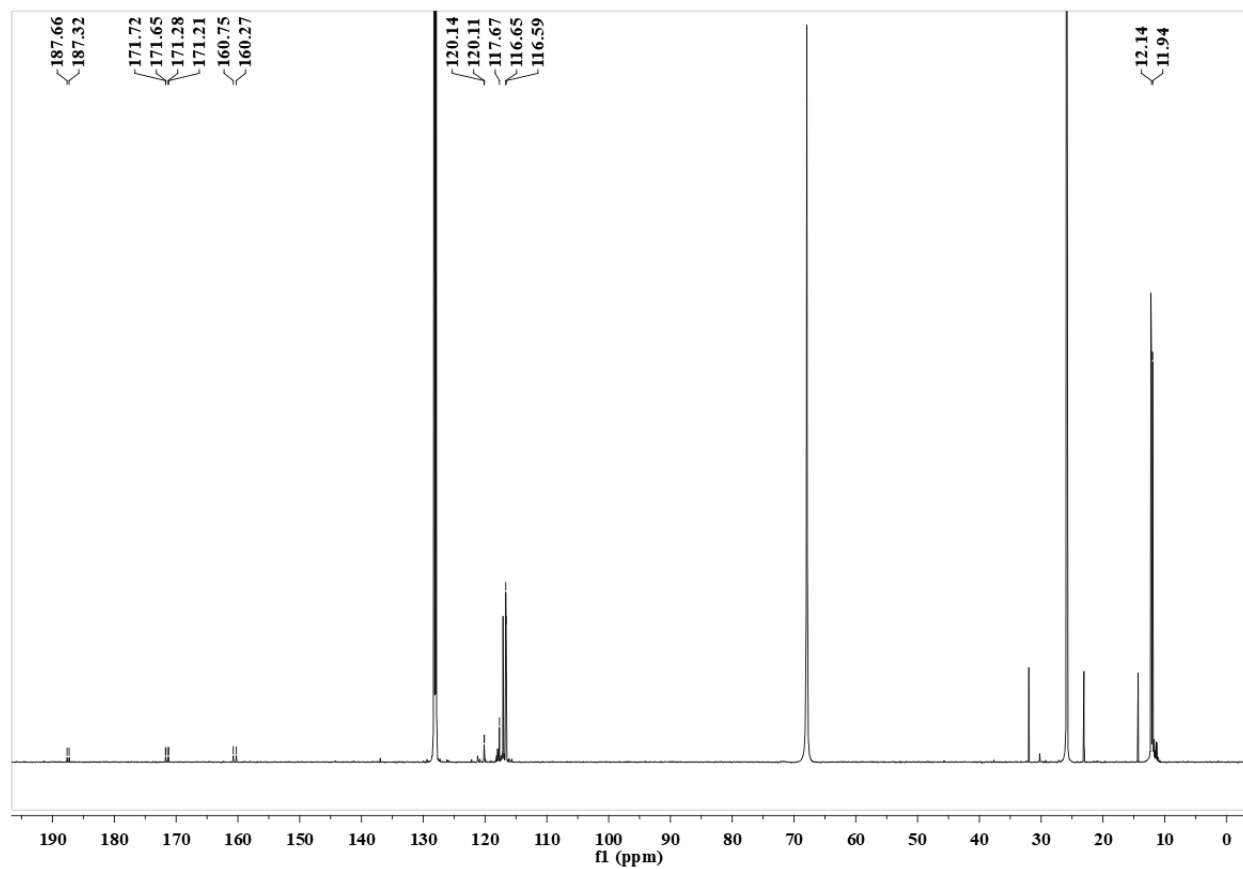


Figure A.14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a C_6D_6 solution of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-}\eta^3\text{:}\eta^1\text{-CCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1**, spiked with a few drops of THF.

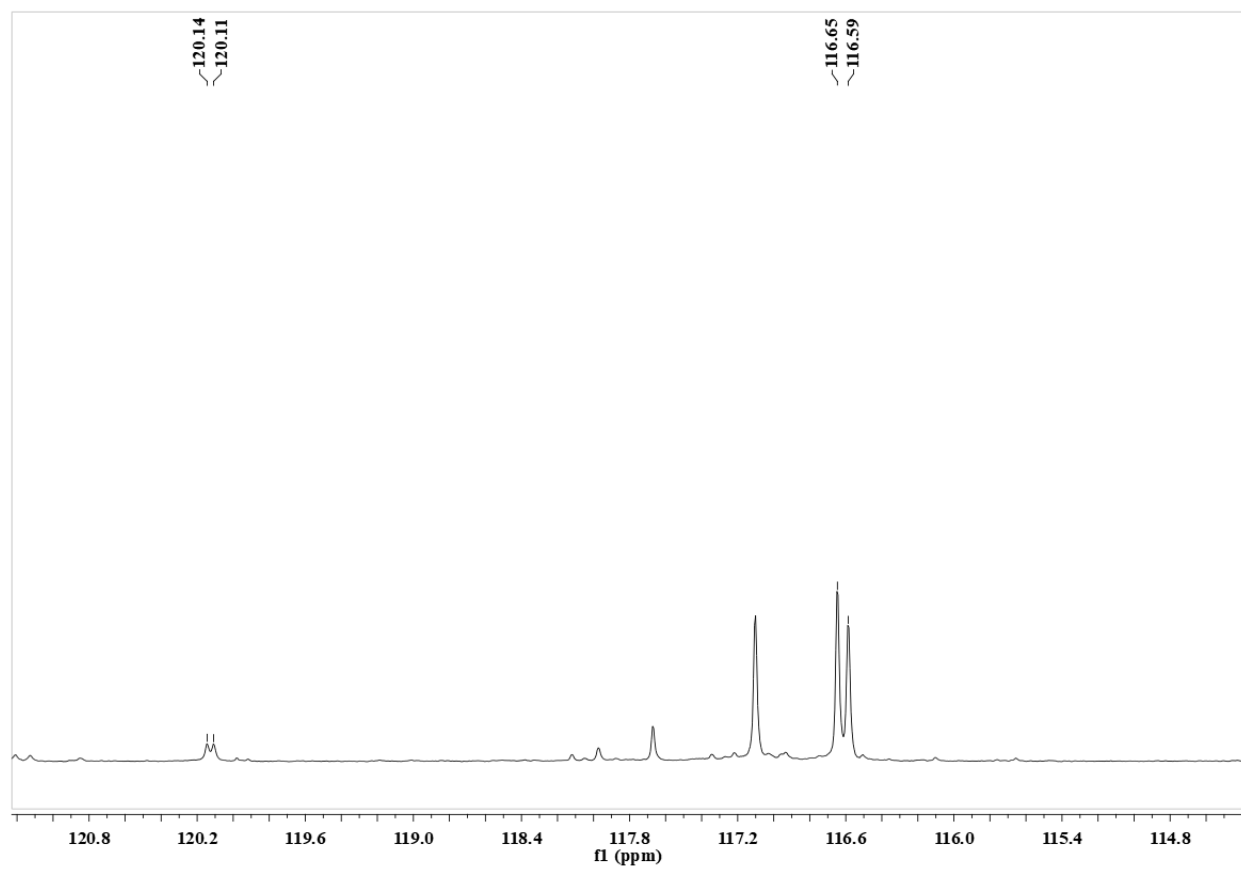


Figure A.15. Zoomed in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a C_6D_6 solution of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-}\eta^3\text{:}\eta^1\text{-CCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1**, spiked with a few drops of THF.

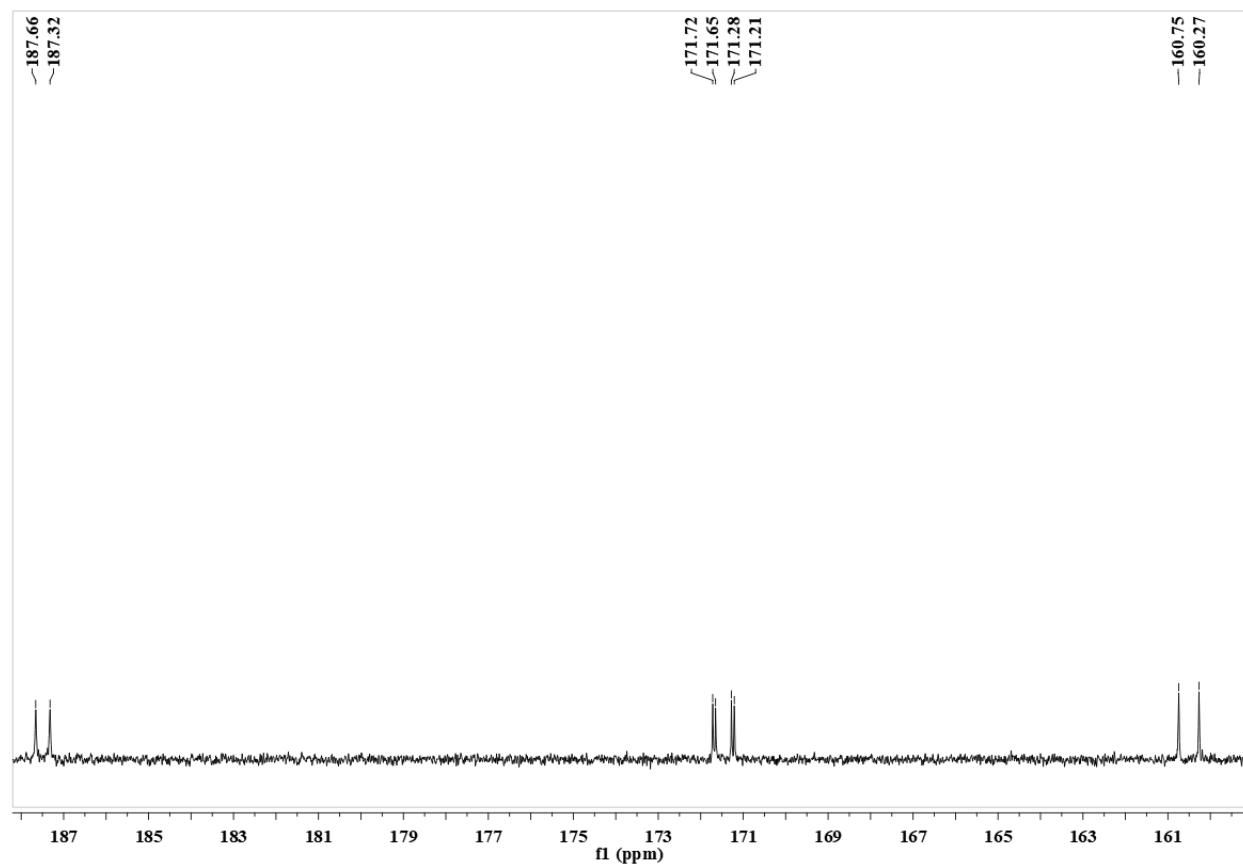


Figure A.16. Zoomed in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a C_6D_6 solution of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-}\eta^3\text{:}\eta^1\text{-CCCCH}_2)\text{Y}(\text{C}_5\text{Me}_5)_2$, **A.1**, spiked with a few drops of THF.

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Appendix B:

Synthesis and Structure of a Double Tuck-In Bis(Cyclopentadienyl) Complex of Thorium

INTRODUCTION

The metallocene chemistry of thorium is dominated by the use of the $(C_5Me_5)^{1-}$ ligand throughout the literature.¹⁻⁵ Relatively few variations of cyclopentadienyl ligands have been explored with the Th(IV) ion and even fewer have been explored with respect to Th(III) and Th(II) chemistry. To expand upon the study of the role steric and electronic effects play in the isolation of Th(III) and Th(II) complexes with cyclopentadienyl ligands, it is crucial that routes to new types of cyclopentadienyl thorium complexes are developed.

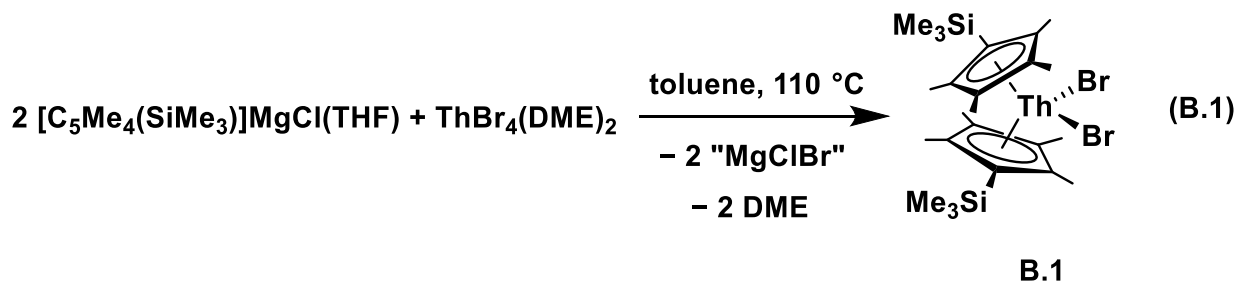
The organometallic chemistry of the Th(IV) ion with cyclopentadienyl ligands is comparable with that of the organometallic chemistry of the U(IV) ion as these two metals share similar chemistry.⁶ Therefore, uranium chemistry can be studied for possible extension to thorium chemistry as the organometallic chemistry of uranium is more developed than thorium. In fact, it is also common to study uranium and thorium chemistry for extension to the transuranium elements as the actinide elements are expected to display similar reaction chemistry. Previously, the U(IV) chemistry of the $[C_5Me_4(SiMe_3)]^{1-}$ ligand was explored.⁷ It was found that the U(IV) dialkyl complex $[C_5Me_4(SiMe_3)]_2UMe_2$ can engage in a C–H bond activation reaction with the trimethylsilyl groups of the $[C_5Me_4(SiMe_3)]^{1-}$ ligand to form the double tuck-in bis(cyclopentadienyl) U(IV) complex, $[\eta^5:\eta^1-C_5Me_4(SiMe_2CH_2)]_2U$, concomitant with release of methane.⁷ This type of molecule exhibits interesting insertion reactivity with unsaturated substrates such as CO, carbodiimides, organic azides, and isocyanides.^{8,9} Extension of this chemistry to thorium will not only allow for structural and reactivity comparisons between the

U(IV) and Th(IV) ions, but it will also provide another ligand system with which to explore thorium reactivity and low oxidation state chemistry.

In this Appendix, the coordination chemistry of the $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]^{1-}$ ligand with thorium was explored. The synthetic studies discussed herein have led to the isolation of a rare example of a double tuck-in bis(cyclopentadienyl) thorium metallocene.

RESULTS

The synthesis of bis(cyclopentadienyl) Th(IV) dihalide complexes is typically accomplished by using cyclopentadienyl Grignard reagents. Previously, Siladke *et al.* employed the Grignard reagent $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]\text{MgCl}(\text{THF})$ to synthesize $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{UCl}_2$.⁷ The reaction between 2 equiv of $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]\text{MgCl}(\text{THF})$ and $\text{ThBr}_4(\text{DME})_2$ (DME = 1,2-dimethoxyethane) in toluene at elevated temperatures cleanly yielded $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ThBr}_2$, **B.1**, as a pale-yellow solid in 95% crude yield following workup, eq B.1. Complex **B.1** is diamagnetic



and displays resonances in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum corresponding to one type of cyclopentadienyl environment suggesting both ligands are equivalent in solution. Storage of saturated toluene solutions of **B.1** at -35°C yielded large colorless blocks of complex **B.1** suitable for study by X-ray crystallography within ca. 30 minutes, Figure B.1. The metrical data for the bis(cyclopentadienyl) Th(IV) complexes crystallographically characterized in this Appendix are summarized in Table B.1 below.

Table B.1. Selected bond distances (Å) and angles (°) of crystallographically characterized bis(trimethylsilyltetramethylcyclopentadienyl) Th(IV) complexes described in this Appendix.

	$[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ThBr}_2$, B.1	$[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ThMe}_2$, B.2	$[\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2)]_2\text{Th}$, B.3^a
Th–Cnt	2.508	2.541	2.488
Th–X	2.782(2)	2.488(2)	2.462(19)
Cnt–Th–Cnt	135.2	138.8	142.6
Cnt–Th–X	102.3, 108.3	100.8, 107.5	94.8, 107.3

^a These data do not constitute the metrical data from a finalized refinement.

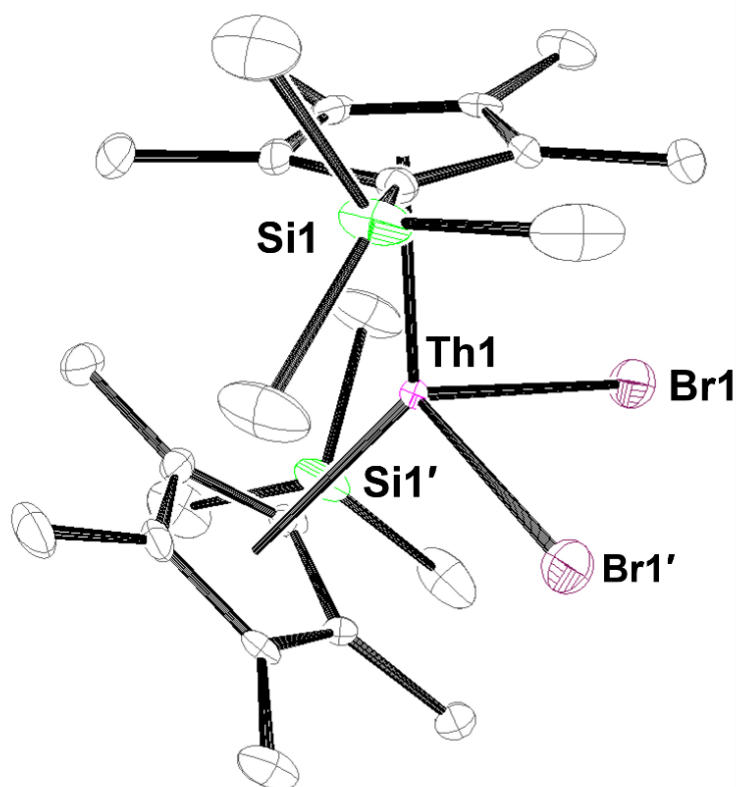
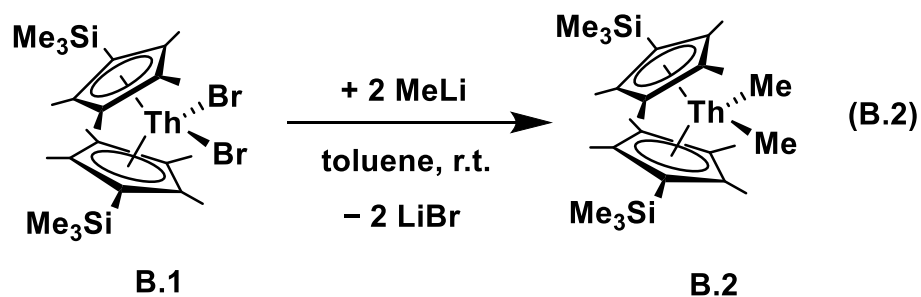


Figure B.1. Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ThBr}_2$, **B.1**, with selective atom labelling. Ellipsoids are drawn at 50% probability and hydrogen atoms are not shown for clarity.

Complex **B.1** crystallizes in the $C2/c$ space group with the thorium metal center located on a two-fold rotation axis. Both cyclopentadienyl ligands are crystallographically equivalent as well as the bromide ligands due to crystallographic symmetry. **B.1** is a Th(IV) bent metallocene dihalide complex with an average Th–Cnt (Cnt = cyclopentadienyl centroid) distance of 2.508 Å and a Cnt–Th–Cnt angle of 135.2°. For comparison, the Th–Cnt distances of the previously characterized and structurally similar $(C_5Me_5)_2ThCl_2$ [2.53(4) Å],¹⁰ $(C_5Me_5)_2ThBr_2$ (2.51 Å),¹¹ $(C_5H_2'Bu_3)_2ThBr_2$ [2.565(4) Å],¹² $(C_5H_2'Bu_3)_2ThCl_2$ [2.568(8) Å],¹³ $(C_5H_3'Bu_2)_2ThCl_2$ [2.511(5) Å],¹³ $(C_5H_3'Bu_2)_2ThBr_2$ [2.512(8) Å],¹⁴ and $(C_5H_3'Bu_2)_2ThI_2$ [2.514(8) Å]¹⁴ complexes are similar to that of complex **B.1**. In addition, the Cnt–Th–Cnt angles of the aforementioned complexes range from 127.1(5)° to 143.9(1)°, which includes the 135.2° Cnt–Th–Cnt angle observed for complex **B.1**. The average Th–Br distance of **B.1** is 2.782(5) Å, which is within a range typically seen for other bis(cyclopentadienyl) Th(IV) complexes with bromide ligands. For example, $(C_5Me_5)_2ThBr_2$,¹¹ $(C_5H_2'Bu_3)_2ThBr_2$,¹² and $(C_5H_3'Bu_2)_2ThBr_2$ ¹⁴ all have similar Th–Br distances of 2.800(2) Å, 2.785(1) Å, and 2.794(1) Å, respectively.

Addition of an excess of solid MeLi to complex **B.1** in toluene cleanly generated the bis(cyclopentadienyl) Th(IV) dialkyl complex $[C_5Me_4(SiMe_3)]_2ThMe_2$, **B.2**, in 90% crude yield, eq B.2, following workup. The complex was identified by ¹H NMR spectroscopy by the presence of a new singlet at δ –0.01 ppm assignable to the terminal methyl ligands of complex **B.2**.



The connectivity of complex **B.2** was confirmed crystallographically by growing large colorless crystals of **B.2** from saturated hexane solutions stored at $-35\text{ }^{\circ}\text{C}$, Figure B.2. Interestingly, like complex **B.1**, these crystals grew within ca. 30 min upon cooling to $-35\text{ }^{\circ}\text{C}$. It was also observed that X-ray quality crystals can be grown from small amounts of crude material, ca. 20-30 mg.

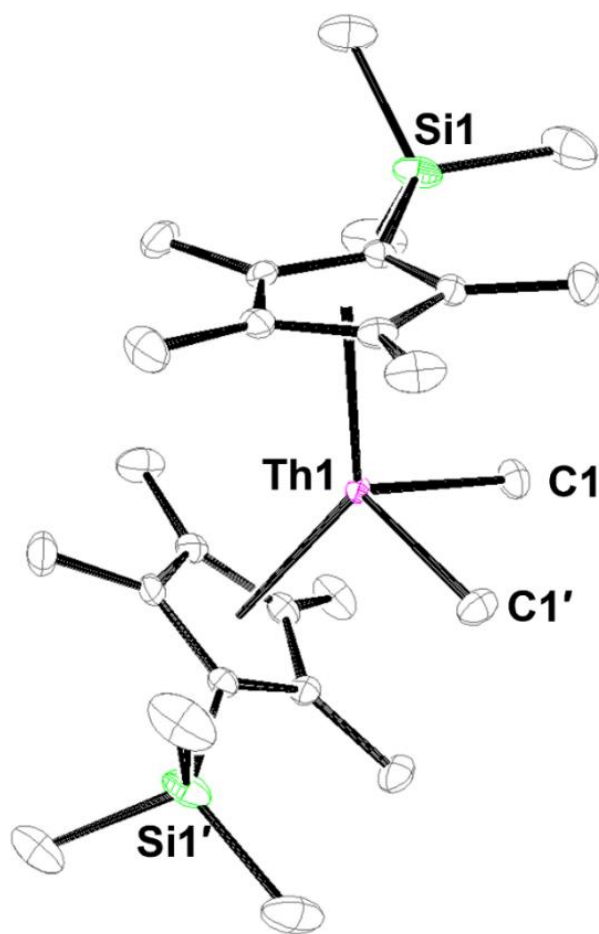


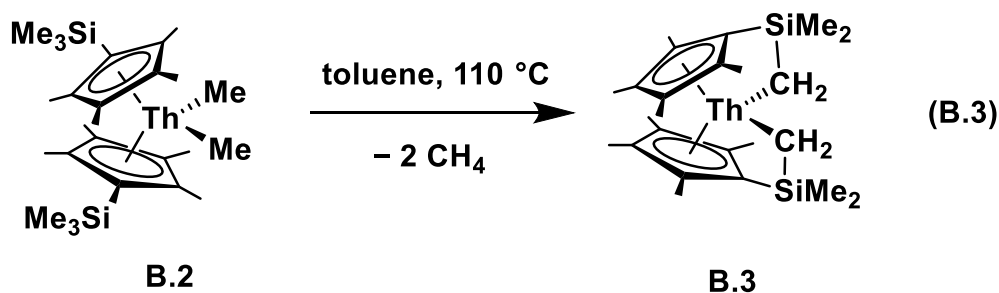
Figure B.2. Molecular structure of $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ThMe}_2$, **B.2**, with selective atom labelling. Ellipsoids are drawn at 50% probability and hydrogen atoms are not shown for clarity.

Like **B.1**, complex **B.2** also crystallizes in the $C2/c$ space group with a thorium atom located on a two-fold rotation axis. Due to crystallographic symmetry, both cyclopentadienyl rings are equivalent as well as the two methyl ligands. The metrical parameters of complex **B.2** are not

very different from that of **B.1** despite the replacement of bromide ligands with methyl ligands. The average Th–Cnt distance of **B.2** is 2.541 Å which is similar to that of the dihalide precursor which has an average Th–Cnt distance of 2.508 Å. The 138.8° Cnt–Th–Cnt angle is slightly larger than that of complex **B.1** which has an analogous Cnt–Th–Cnt angle of 135.2°. The Th–C(Me) distance of 2.488(2) for **B.2** is consistent with the analogous average Th–C(Me) distances of (C₅Me₅)₂ThMe₂ and (C₅Me₄H)₂ThMe₂, which are 2.475(9) Å¹⁵ and 2.497(2) Å,¹⁶ respectively.

Previously, both the U(IV) and Th(IV) ions have been shown to have the capacity to react with various ligands containing trimethylsilyl substituents through intramolecular C–H activation reactions.^{7,17,18} The U(IV) dialkyl metallocene, [C₅Me₄(SiMe₃)]₂UMe₂ can undergo an intramolecular C–H activation reaction to generate the double tuck-in metallocene, [η^5 : η^1 -C₅Me₄(SiMe₂CH₂)]₂U, concomitant with the generation of 2 equiv of methane.⁷

Analogous to that, heating a pale-yellow toluene solution of [C₅Me₄(SiMe₃)]₂ThMe₂, **B.2**, to ca. 110 °C generated a brown solution from which a brown residue was obtained upon workup. Only a few colorless X-ray quality crystals identified as [η^5 : η^1 -C₅Me₄(SiMe₂CH₂)]₂Th, **B.3**, were isolated from this brown residue by crystallization from a saturated THF solution stored at –35 °C, eq B.3, Figure B.3. Like the crystal structures of complexes **B.1** and **B.2**, complex **B.3** also



crystallizes as a half molecule in the *C2/c* space group with the thorium metal center lying on an inversion center. Complex **B.3** is isomorphous with the previously isolated [η^5 : η^1 -

$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2)]_2\text{U}$,⁷ but is not isomorphous with the Zr analog, $[\eta^5:\eta^1-\text{C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2)]_2\text{Zr}$.^{19,20} **B.3** is the first example of a Th(IV) double tuck-in metallocene that is presumably formed from the intramolecular C–H activation of the SiMe_3 substituents of both of the cyclopentadienyl ligands with the two methyl ligands of **B.2**, similar to that of the uranium analog. The metrical parameters discussed below for complex **B.3** do not constitute the finalized metrical parameters, but the data are not expected to significantly change upon finalizing the refinement of the X-ray crystallographic data.

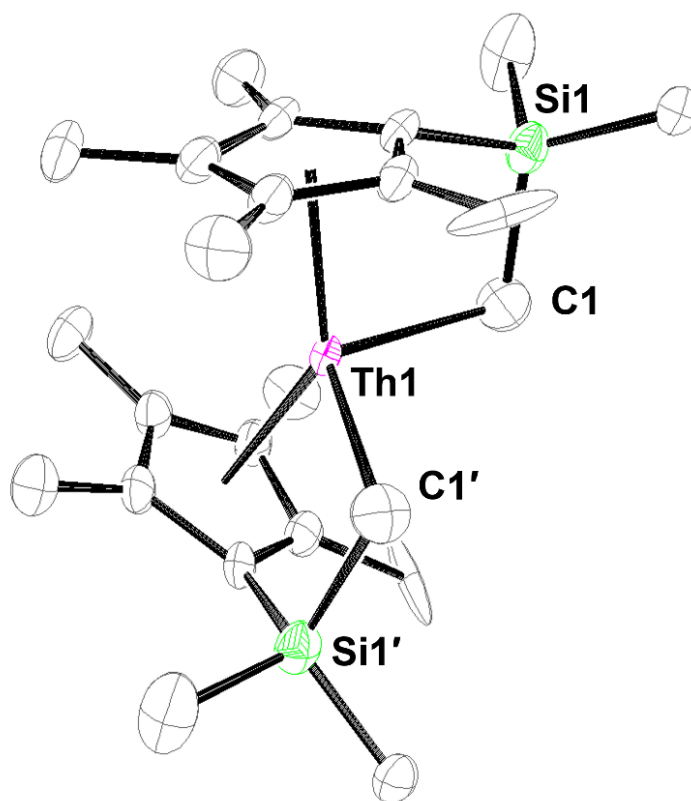


Figure B.3. Molecular structure of $[\eta^5:\eta^1-\text{C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2)]_2\text{Th}$, **B.3**, with selective atom labelling. Ellipsoids are drawn at 50% probability and hydrogen atoms are not shown for clarity.

Selected metrical data for complex **B.3** are summarized in Table B.1 above and are similar to that of complexes **B.1** and **B.2**. The Th–C_{nt} distance of **B.3** is 2.488 and is in a range typically

observed for Th(IV) bis(cyclopentadienyl) complexes.¹⁰⁻¹⁴ The Th–C(CH₂) distance is 2.462(19) Å, which is similar to that of the dimethyl precursor **B.2**. However, the Cnt–Th–Cnt angle of **B.3**, which is 142.6°, is larger than that of **B.2**, which is 138.8°. This is presumably influenced by the chelating nature of the C–H activated cyclopentadienyl ligand, which also displays the silyl group bending out of the plane of the cyclopentadienyl to bring it closer to the thorium metal center.

DISCUSSION

The metallocene chemistry of the Th(IV) ion can readily be extended to the [C₅Me₄(SiMe₃)]^{1–} ligand through the use of the cyclopentadienyl Grignard reagent [C₅Me₄(SiMe₃)]MgCl(THF).⁷ The coordination chemistry of the [C₅Me₄(SiMe₃)]^{1–} ligand with the Th(IV) ion exactly mirrors that of the U(IV) ion, supportive of the similar chemistry that these two elements share with each other. The dibromo and dimethyl Th(IV) metallocenes, [C₅Me₄(SiMe₃)]₂ThBr₂, **B.1**, and [C₅Me₄(SiMe₃)]₂ThMe₂, **B.2**, can be crystallized quickly (ca. 20-30 min) at –35 °C and from small amounts of crude material (ca. 20-30 mg)! All these characteristics make it a favorable ligand system to extend to the transuranium elements which typically require procedures to be optimized to be performed on small scales and under relatively facile conditions. Complex **B.3** is a rare example of a double tuck-in bis(cyclopentadienyl) Th(IV) complex and is analogous to the previously isolated Zr and U examples. This compound provides a new Th(IV) system to explore reactivity and reduction chemistry for comparisons with the Zr and U analogs.

CONCLUSION

In summary, bis(cyclopentadienyl) Th(IV) complexes of the (C₅Me₄(SiMe₃))^{1–} ligand can be made starting from the cyclopentadienyl Grignard reagent and Th(IV) tetrahalide salts. The

reaction proceeds cleanly and good quality crystals can be grown quickly with small amounts of crude material. The synthetic studies described has also yielded the first example of a double tuck-in Th(IV) metallocene, namely $[\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2)]_2\text{Th}$, **B.3**, presumably formed through the C–H activation of the trimethylsilyl groups of both of the $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]^{1-}$ ligands of the dialkyl metallocene precursor, $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ThMe}_2$, **B.2**. These studies should provide a good entryway into the exploration of the reduction chemistry and reactivity of thorium complexes with the $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]^{1-}$ ligand.

EXPERIMENTAL SECTION

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP (99.999%) argon and dried by passage through columns containing Q-5 and molecular sieves prior to use and stored over activated molecular sieves prior to use. Deuterated NMR solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles before use. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker GN500 spectrometer at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. $\text{ThBr}_4(\text{DME})_2$ was synthesized by treating $\text{ThBr}_4(\text{THF})_4^{21}$ with DME and collecting the precipitated white powder. $\text{C}_5\text{Me}_4\text{SiMe}_3\text{MgCl}(\text{THF})$ was synthesized according to literature procedures.⁷ MeLi was obtained as a 1.6 M solution in diethyl ether from Sigma-Aldrich and was dried under reduced pressure to yield a colorless powder prior to use.

Synthesis of $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ThBr}_2$, B.1. In a Schlenk flask equipped with a grease-free Teflon stopcock, $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]\text{MgCl}(\text{THF})$ (823 mg, 2.53 mmol, 2.05 equiv) and $\text{ThBr}_4(\text{DME})_2$ (903 mg, 1.23 mmol, 1.00 equiv) were suspended in toluene (ca. 25 mL). The resulting mixture

was stirred at ca. 110 °C for 48 h at which point the mixture became pale-yellow with much white precipitate. The reaction was cooled to room temperature and solvent was removed under vacuum. The flask was brought into an argon-filled glove box and the product was extracted into toluene (ca. 30 mL). The solution was then centrifuged and filtered to remove insoluble solids and the pale-yellow supernatant was dried under reduced pressure. The resulting pale-yellow solids were triturated with Et₂O (1 × ca. 2 mL) and dried under reduced pressure to yield **B.1** as a pale-yellow powder (913 mg, 95%). Colorless X-ray quality crystals of **B.1** can be grown from concentrated toluene solutions stored at −35 °C. ¹H NMR (C₆D₆, 500 MHz): δ 2.34 (s, 12H, C₅Me₄SiMe₃), 1.95 (s, 12H, C₅Me₄SiMe₃), 0.46 (s, 12H, C₅Me₄SiMe₃) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 138.2 (C₅Me₄SiMe₃), 132.9 (C₅Me₄SiMe₃), 15.3 (C₅Me₄SiMe₃), 12.1 (C₅Me₄SiMe₃), 2.4 (C₅Me₄SiMe₃) ppm. The third expected resonance for the cyclopentadienyl ring carbon could not be definitively located in the range of +200 to −200 ppm in C₆D₆.

Synthesis of [C₅Me₄(SiMe₃)]₂ThMe₂, B.2. Solid MeLi (45 mg, 2.05 mmol, 3.50 equiv) was added to a stirring pale-yellow solution of [C₅Me₄(SiMe₃)]₂ThBr₂, **B.1**, (459 mg, 0.586 mmol, 1.00 equiv) in toluene (ca. 8 mL) at room temperature and the resulting mixture was stirred at room temperature overnight. Insoluble white solids were isolated via centrifugation and the solution was filtered and dried under vacuum to yield pale-yellow solids. Addition of pentane (3 mL) followed by removal of solvent to help remove residual toluene yielded **B.2** as a pale-yellow powder (344 mg, 90%). Colorless X-ray quality crystals of **B.2** can be grown from concentrated hexane solutions stored at −35 °C. ¹H NMR (C₆D₆, 500 MHz): δ 2.19 (s, 12H, C₅Me₄SiMe₃), 1.86 (s, 12H, C₅Me₄SiMe₃), 0.37 (s, 12H, C₅Me₄SiMe₃), 0.01 (s, 6H, Th–Me) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 131.6 (C₅Me₄SiMe₃), 128.2 (C₅Me₄SiMe₃), 121.7 (C₅Me₄SiMe₃), 65.5 (Th–Me), 14.4 (C₅Me₄SiMe₃), 11.5 (C₅Me₄SiMe₃), 2.5 (C₅Me₄SiMe₃) ppm.

Synthesis of $[\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2)]_2\text{Th}$, **B.3.** In a Schlenk flask equipped with a grease-free Teflon stopcock, **B.2** (76 mg, 0.12 mmol) was dissolved in toluene (ca. 10 mL) and sealed. The flask was then heated to ca. 110 °C with stirring. Upon heating, the initially clear pale-yellow solution became a burnt orange-brown color after ca. 10 min. The mixture was allowed to stir at ca. 110 °C for 16 h at which point toluene was removed under reduced pressure to yield a brown colored residue. $[\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2)]_2\text{Th}$, **B.3**, was identified crystallographically by growing colorless crystals suitable for study by X-ray diffraction from concentrated THF solutions stored at –35 °C. Only a few colorless crystals were isolated.

X-ray Data Collection, Structure Solution and Refinement for $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ThBr}_2$, **B.1.** A colorless crystal of approximate dimensions 0.216 x 0.262 x 0.283 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2²² program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT²³ and SADABS²⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL²⁵ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that space group $C2/c$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors²⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on a two-fold rotation axis. Least-squares analysis yielded $wR2 = 0.0717$ and $\text{Goof} = 1.117$ for 139 variables refined against 3527 data (0.75 Å), $R1 = 0.0267$ for those 3336 data with $I > 2.0\sigma(I)$.

Table B.2. Crystal data and structure refinement for $[\text{C}_5\text{Me}_4(\text{SiMe}_3)]_2\text{ThBr}_2$, **B.1**.

Identification code	jqn13 (Joseph Nguyen)	
Empirical formula	C ₂₄ H ₄₂ Br ₂ Si ₂ Th	
Formula weight	778.61	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 19.565(2) Å	α = 90°.
	b = 8.3160(9) Å	β = 94.223(2)°.
	c = 17.4321(19) Å	γ = 90°.
Volume	2828.6(5) Å ³	
Z	4	
Density (calculated)	1.828 Mg/m ³	
Absorption coefficient	8.191 mm ⁻¹	
F(000)	1496	
Crystal color	colorless	
Crystal size	0.283 x 0.262 x 0.216 mm ³	
Theta range for data collection	2.087 to 28.354°	
Index ranges	-26 ≤ h ≤ 26, -11 ≤ k ≤ 11, -22 ≤ l ≤ 23	
Reflections collected	20043	
Independent reflections	3527 [R(int) = 0.0292]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4311 and 0.3136	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3527 / 0 / 139	
Goodness-of-fit on F ²	1.117	
Final R indices [I > 2σ(I) = 3336 data]	R1 = 0.0267, wR2 = 0.0708	
R indices (all data, 0.75 Å)	R1 = 0.0288, wR2 = 0.0717	
Largest diff. peak and hole	1.153 and -2.548 e.Å ⁻³	

Table B.3. Bond lengths [Å] and angles [°] for [C₅Me₄(SiMe₃)₂ThBr₂, **B.1**.

Th(1)-Cnt1	2.508	Th(1)-Cnt1#1	2.508
Th(1)-C(1)#1	2.740(4)	Th(1)-C(1)	2.740(4)
Th(1)-C(5)	2.752(4)	Th(1)-C(5)#1	2.752(4)
Th(1)-C(2)	2.779(4)	Th(1)-C(2)#1	2.779(4)

Th(1)-Br(1)#1	2.7819(5)	Th(1)-Br(1)	2.7820(5)
Th(1)-C(4)	2.827(4)	Th(1)-C(4)#1	2.827(4)
Th(1)-C(3)	2.829(4)	Th(1)-C(3)#1	2.829(4)
Si(1)-C(10)	1.863(7)	Si(1)-C(12)	1.871(6)
Si(1)-C(11)	1.876(6)	Si(1)-C(1)	1.883(5)
C(1)-C(5)	1.438(6)	C(1)-C(2)	1.438(6)
C(2)-C(3)	1.417(7)	C(2)-C(6)	1.503(6)
C(3)-C(4)	1.419(6)	C(3)-C(7)	1.498(6)
C(4)-C(5)	1.413(6)	C(4)-C(8)	1.497(6)
C(5)-C(9)	1.510(6)		
Cnt1-Th(1)-Cnt1#1	135.2	Cnt1-Th(1)-Br(1)	102.3
Cnt1#1-Th(1)-Br(1)	108.3	Cnt1-Th(1)-Br(1)#1	108.3
Cnt1#1-Th(1)-Br(1)#1	102.3	C(1)#1-Th(1)-C(1)	147.20(19)
C(1)#1-Th(1)-C(5)	153.48(13)	C(1)-Th(1)-C(5)	30.35(12)
C(1)#1-Th(1)-C(5)#1	30.35(12)	C(1)-Th(1)-C(5)#1	153.48(13)
C(5)-Th(1)-C(5)#1	173.54(18)	C(1)#1-Th(1)-C(2)	117.78(14)
C(1)-Th(1)-C(2)	30.20(13)	C(5)-Th(1)-C(2)	49.11(13)
C(5)#1-Th(1)-C(2)	137.23(13)	C(1)#1-Th(1)-C(2)#1	30.20(13)
C(1)-Th(1)-C(2)#1	117.78(14)	C(5)-Th(1)-C(2)#1	137.23(13)
C(5)#1-Th(1)-C(2)#1	49.11(12)	C(2)-Th(1)-C(2)#1	90.34(18)
C(1)#1-Th(1)-Br(1)#1	117.94(9)	C(1)-Th(1)-Br(1)#1	85.55(10)
C(5)-Th(1)-Br(1)#1	87.90(9)	C(5)#1-Th(1)-Br(1)#1	87.63(9)
C(2)-Th(1)-Br(1)#1	112.92(10)	C(2)#1-Th(1)-Br(1)#1	125.93(10)
C(1)#1-Th(1)-Br(1)	85.55(10)	C(1)-Th(1)-Br(1)	117.94(9)
C(5)-Th(1)-Br(1)	87.63(9)	C(5)#1-Th(1)-Br(1)	87.90(9)
C(2)-Th(1)-Br(1)	125.93(10)	C(2)#1-Th(1)-Br(1)	112.92(10)
Br(1)#1-Th(1)-Br(1)	92.37(2)	C(1)#1-Th(1)-C(4)	124.26(13)
C(1)-Th(1)-C(4)	49.22(13)	C(5)-Th(1)-C(4)	29.31(12)
C(5)#1-Th(1)-C(4)	152.88(12)	C(2)-Th(1)-C(4)	48.33(13)
C(2)#1-Th(1)-C(4)	116.07(13)	Br(1)#1-Th(1)-C(4)	115.59(9)
Br(1)-Th(1)-C(4)	77.84(9)	C(1)#1-Th(1)-C(4)#1	49.22(13)
C(1)-Th(1)-C(4)#1	124.26(13)	C(5)-Th(1)-C(4)#1	152.88(12)
C(5)#1-Th(1)-C(4)#1	29.30(12)	C(2)-Th(1)-C(4)#1	116.07(13)
C(2)#1-Th(1)-C(4)#1	48.33(13)	Br(1)#1-Th(1)-C(4)#1	77.84(9)
Br(1)-Th(1)-C(4)#1	115.59(9)	C(4)-Th(1)-C(4)#1	161.61(19)
C(1)#1-Th(1)-C(3)	107.67(13)	C(1)-Th(1)-C(3)	49.23(13)
C(5)-Th(1)-C(3)	48.49(12)	C(5)#1-Th(1)-C(3)	137.10(13)
C(2)-Th(1)-C(3)	29.26(14)	C(2)#1-Th(1)-C(3)	89.98(13)
Br(1)#1-Th(1)-C(3)	133.55(9)	Br(1)-Th(1)-C(3)	99.68(10)
C(4)-Th(1)-C(3)	29.05(13)	C(4)#1-Th(1)-C(3)	132.56(14)
C(1)#1-Th(1)-C(3)#1	49.23(13)	C(1)-Th(1)-C(3)#1	107.67(13)
C(5)-Th(1)-C(3)#1	137.09(13)	C(5)#1-Th(1)-C(3)#1	48.49(13)
C(2)-Th(1)-C(3)#1	89.98(13)	C(2)#1-Th(1)-C(3)#1	29.26(14)
Br(1)#1-Th(1)-C(3)#1	99.67(10)	Br(1)-Th(1)-C(3)#1	133.55(9)
C(4)-Th(1)-C(3)#1	132.56(14)	C(4)#1-Th(1)-C(3)#1	29.05(13)

C(3)-Th(1)-C(3)#1	103.52(19)	C(10)-Si(1)-C(12)	108.1(3)
C(10)-Si(1)-C(11)	108.4(3)	C(12)-Si(1)-C(11)	107.8(3)
C(10)-Si(1)-C(1)	111.8(3)	C(12)-Si(1)-C(1)	112.8(2)
C(11)-Si(1)-C(1)	107.9(2)	C(5)-C(1)-C(2)	106.1(4)
C(5)-C(1)-Si(1)	129.2(3)	C(2)-C(1)-Si(1)	123.3(3)
C(5)-C(1)-Th(1)	75.3(2)	C(2)-C(1)-Th(1)	76.4(2)
Si(1)-C(1)-Th(1)	124.1(2)	C(3)-C(2)-C(1)	108.7(4)
C(3)-C(2)-C(6)	124.3(4)	C(1)-C(2)-C(6)	126.3(4)
C(3)-C(2)-Th(1)	77.3(2)	C(1)-C(2)-Th(1)	73.4(2)
C(6)-C(2)-Th(1)	122.7(3)	C(2)-C(3)-C(4)	108.1(4)
C(2)-C(3)-C(7)	127.3(5)	C(4)-C(3)-C(7)	124.0(4)
C(2)-C(3)-Th(1)	73.4(2)	C(4)-C(3)-Th(1)	75.4(2)
C(7)-C(3)-Th(1)	124.4(3)	C(5)-C(4)-C(3)	108.2(4)
C(5)-C(4)-C(8)	127.7(4)	C(3)-C(4)-C(8)	123.9(4)
C(5)-C(4)-Th(1)	72.4(2)	C(3)-C(4)-Th(1)	75.6(2)
C(8)-C(4)-Th(1)	122.7(3)	C(4)-C(5)-C(1)	108.9(4)
C(4)-C(5)-C(9)	123.6(4)	C(1)-C(5)-C(9)	127.5(4)
C(4)-C(5)-Th(1)	78.3(2)	C(1)-C(5)-Th(1)	74.3(2)
C(9)-C(5)-Th(1)	114.8(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

X-ray Data Collection, Structure Solution and Refinement for [C₅Me₄(SiMe₃)₂ThMe₂, B.2. A colorless crystal of approximate dimensions 0.259 x 0.268 x 0.338 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2²² program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT²³ and SADABS²⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL²⁵ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that space group $C2/c$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors²⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined

(x,y,z and U_{iso}). The molecule was located on a two-fold rotation axis. Least-squares analysis yielded $wR2 = 0.0279$ and $Goof = 1.101$ for 228 variables refined against 3386 data ($0.76 \text{ \AA}$), $R1 = 0.0116$ for those 3328 data with $I > 2.0\sigma(I)$.

Table B.4. Crystal data and structure refinement for $[C_5Me_4(SiMe_3)]_2ThMe_2$, **B.2.**

Identification code	jqn16 (Joseph Nguyen)	
Empirical formula	$C_{26} H_{48} Si_2 Th$	
Formula weight	648.86	
Temperature	93(2) K	
Wavelength	$0.71073 \text{ \AA}$	
Crystal system	Monoclinic	
Space group	$C2/c$	
Unit cell dimensions	$a = 19.381(2) \text{ \AA}$	$\alpha = 90^\circ$.
	$b = 8.2987(8) \text{ \AA}$	$\beta = 94.371(2)^\circ$.
	$c = 17.6662(18) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$2833.1(5) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.521 Mg/m^3	
Absorption coefficient	5.358 mm^{-1}	
F(000)	1288	
Crystal color	colorless	
Crystal size	$0.338 \times 0.268 \times 0.259 \text{ mm}^3$	
Theta range for data collection	2.108 to 27.928°	
Index ranges	$-25 \leq h \leq 25$, $-10 \leq k \leq 10$, $-23 \leq l \leq 23$	
Reflections collected	19426	
Independent reflections	3386 [$R(\text{int}) = 0.0268$]	
Completeness to $\theta = 25.242^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4308 and 0.3662	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3386 / 0 / 228	
Goodness-of-fit on F^2	1.101	
Final R indices [$I > 2\sigma(I)$ = 3328 data]	$R1 = 0.0116$, $wR2 = 0.0278$	
R indices (all data, $0.76 \text{ \AA}$)	$R1 = 0.0120$, $wR2 = 0.0279$	
Largest diff. peak and hole	0.396 and $-0.754 \text{ e.\AA}^{-3}$	

Table B.5. Bond lengths [Å] and angles [°] for [C₅Me₄(SiMe₃)₂ThMe₂, **B.2**.

Th(1)-Cnt1	2.541	Th(1)-Cnt1#1	2.541
Th(1)-C(1)	2.4881(17)	Th(1)-C(1)#1	2.4882(17)
Th(1)-C(2)#1	2.7801(15)	Th(1)-C(2)	2.7802(15)
Th(1)-C(6)#1	2.7940(15)	Th(1)-C(6)	2.7940(15)
Th(1)-C(3)	2.8057(16)	Th(1)-C(3)#1	2.8058(16)
Th(1)-C(5)#1	2.8406(15)	Th(1)-C(5)	2.8406(15)
Th(1)-C(4)	2.8522(16)	Th(1)-C(4)#1	2.8523(16)
Si(1)-C(13)	1.863(2)	Si(1)-C(11)	1.871(2)
Si(1)-C(2)	1.8718(16)	Si(1)-C(12)	1.878(2)
C(2)-C(6)	1.438(2)	C(2)-C(3)	1.441(2)
C(3)-C(4)	1.415(2)	C(3)-C(7)	1.509(2)
C(4)-C(5)	1.421(2)	C(4)-C(8)	1.505(2)
C(5)-C(6)	1.408(2)	C(5)-C(9)	1.503(2)
C(6)-C(10)	1.510(2)		
Cnt1-Th(1)-Cnt1#1	138.8	Cnt1-Th(1)-C(1)	100.8
Cnt1#1-Th(1)-C(1)	107.5	Cnt1-Th(1)-C(1)#1	107.5
Cnt1#1-Th(1)-C(1)#1	100.8	C(1)-Th(1)-C(1)#1	92.15(9)
C(1)-Th(1)-C(2)#1	85.21(5)	C(1)#1-Th(1)-C(2)#1	116.19(5)
C(1)-Th(1)-C(2)	116.19(5)	C(1)#1-Th(1)-C(2)	85.21(5)
C(2)#1-Th(1)-C(2)	150.10(6)	C(1)-Th(1)-C(6)#1	112.44(6)
C(1)#1-Th(1)-C(6)#1	124.28(5)	C(2)#1-Th(1)-C(6)#1	29.89(4)
C(2)-Th(1)-C(6)#1	121.04(5)	C(1)-Th(1)-C(6)	124.28(5)
C(1)#1-Th(1)-C(6)	112.44(6)	C(2)#1-Th(1)-C(6)	121.04(5)
C(2)-Th(1)-C(6)	29.89(4)	C(6)#1-Th(1)-C(6)	94.14(6)
C(1)-Th(1)-C(3)	86.33(5)	C(1)#1-Th(1)-C(3)	87.38(5)
C(2)#1-Th(1)-C(3)	155.19(4)	C(2)-Th(1)-C(3)	29.90(4)
C(6)#1-Th(1)-C(3)	140.46(4)	C(6)-Th(1)-C(3)	48.43(4)
C(1)-Th(1)-C(3)#1	87.38(5)	C(1)#1-Th(1)-C(3)#1	86.33(5)
C(2)#1-Th(1)-C(3)#1	29.90(4)	C(2)-Th(1)-C(3)#1	155.19(4)
C(6)#1-Th(1)-C(3)#1	48.43(4)	C(6)-Th(1)-C(3)#1	140.46(4)
C(3)-Th(1)-C(3)#1	170.93(6)	C(1)-Th(1)-C(5)#1	132.64(5)
C(1)#1-Th(1)-C(5)#1	98.62(5)	C(2)#1-Th(1)-C(5)#1	48.73(4)
C(2)-Th(1)-C(5)#1	110.61(4)	C(6)#1-Th(1)-C(5)#1	28.93(5)

C(6)-Th(1)-C(5)#1	93.61(5)	C(3)-Th(1)-C(5)#1	139.81(5)
C(3)#1-Th(1)-C(5)#1	47.96(4)	C(1)-Th(1)-C(5)	98.62(5)
C(1)#1-Th(1)-C(5)	132.64(5)	C(2)#1-Th(1)-C(5)	110.61(4)
C(2)-Th(1)-C(5)	48.73(4)	C(6)#1-Th(1)-C(5)	93.61(5)
C(6)-Th(1)-C(5)	28.93(5)	C(3)-Th(1)-C(5)	47.96(4)
C(3)#1-Th(1)-C(5)	139.81(4)	C(5)#1-Th(1)-C(5)	106.80(7)
C(1)-Th(1)-C(4)	76.62(5)	C(1)#1-Th(1)-C(4)	114.65(5)
C(2)#1-Th(1)-C(4)	126.25(5)	C(2)-Th(1)-C(4)	48.67(4)
C(6)#1-Th(1)-C(4)	119.26(5)	C(6)-Th(1)-C(4)	47.84(5)
C(3)-Th(1)-C(4)	28.94(5)	C(3)#1-Th(1)-C(4)	153.67(5)
C(5)#1-Th(1)-C(4)	135.71(5)	C(5)-Th(1)-C(4)	28.91(5)
C(1)-Th(1)-C(4)#1	114.65(5)	C(1)#1-Th(1)-C(4)#1	76.62(5)
C(2)#1-Th(1)-C(4)#1	48.67(4)	C(2)-Th(1)-C(4)#1	126.25(5)
C(6)#1-Th(1)-C(4)#1	47.84(5)	C(6)-Th(1)-C(4)#1	119.26(5)
C(3)-Th(1)-C(4)#1	153.67(5)	C(3)#1-Th(1)-C(4)#1	28.94(5)
C(5)#1-Th(1)-C(4)#1	28.91(5)	C(5)-Th(1)-C(4)#1	135.71(5)
C(4)-Th(1)-C(4)#1	164.62(7)	C(13)-Si(1)-C(11)	107.58(12)
C(13)-Si(1)-C(2)	112.03(10)	C(11)-Si(1)-C(2)	113.29(9)
C(13)-Si(1)-C(12)	107.94(11)	C(11)-Si(1)-C(12)	107.38(11)
C(2)-Si(1)-C(12)	108.39(9)	C(6)-C(2)-C(3)	105.87(13)
C(6)-C(2)-Si(1)	123.51(11)	C(3)-C(2)-Si(1)	129.33(12)
C(6)-C(2)-Th(1)	75.59(8)	C(3)-C(2)-Th(1)	76.03(9)
Si(1)-C(2)-Th(1)	123.85(7)	C(4)-C(3)-C(2)	108.79(13)
C(4)-C(3)-C(7)	123.61(15)	C(2)-C(3)-C(7)	127.58(15)
C(4)-C(3)-Th(1)	77.35(9)	C(2)-C(3)-Th(1)	74.07(9)
C(7)-C(3)-Th(1)	116.45(11)	C(3)-C(4)-C(5)	108.06(14)
C(3)-C(4)-C(8)	127.32(16)	C(5)-C(4)-C(8)	124.22(16)
C(3)-C(4)-Th(1)	73.70(9)	C(5)-C(4)-Th(1)	75.09(9)
C(8)-C(4)-Th(1)	122.89(11)	C(6)-C(5)-C(4)	108.09(14)
C(6)-C(5)-C(9)	127.70(16)	C(4)-C(5)-C(9)	123.84(16)
C(6)-C(5)-Th(1)	73.70(9)	C(4)-C(5)-Th(1)	76.00(9)
C(9)-C(5)-Th(1)	121.87(11)	C(5)-C(6)-C(2)	109.18(13)
C(5)-C(6)-C(10)	124.42(16)	C(2)-C(6)-C(10)	126.03(15)
C(5)-C(6)-Th(1)	77.37(9)	C(2)-C(6)-Th(1)	74.53(8)
C(10)-C(6)-Th(1)	120.24(11)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

X-ray Data Collection, Structure Solution and Refinement for $[\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2)]_2\text{Th}$, B.3. A colorless crystal of approximate dimensions 0.268 x 0.334 x 0.371 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2²² program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time). The raw frame data was processed using SAINT²³ and SADABS²⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL²⁵ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that space group $C2/c$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors²⁶ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on a two-fold rotation axis. Atoms displaying relatively high thermal parameters were included using displacement constraints (SIMU). Least-squares analysis yielded $wR2 = 0.2301$ and $Goof = 1.073$ for 129 variables refined against 2605 data ($0.80 \text{ \AA}$), $R1 = 0.0881$ for those 2528 data with $I > 2.0\sigma(I)$. These statistics do not constitute a finalized refinement.

Table B.6. Crystal data and structure refinement for $[\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2)]_2\text{Th}$, B.3.

Identification code	jqn26 (Joseph Nguyen)	
Empirical formula	$\text{C}_{24} \text{H}_{40} \text{Si}_2 \text{Th}$	
Formula weight	616.78	
Temperature	133(2) K	
Wavelength	$0.71073 \text{ \AA}$	
Crystal system	Monoclinic	
Space group	$C2/c$	
Unit cell dimensions	$a = 19.342(6) \text{ \AA}$	$\alpha = 90^\circ$.
	$b = 8.542(3) \text{ \AA}$	$\beta = 121.747(4)^\circ$.

	$c = 17.932(8) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$2519.4(15) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.626 Mg/m^3	
Absorption coefficient	6.021 mm^{-1}	
F(000)	1208	
Crystal color	colorless	
Crystal size	$0.371 \times 0.334 \times 0.268 \text{ mm}^3$	
Theta range for data collection	2.477 to 26.493°	
Index ranges	$-24 \leq h \leq 24$, $-10 \leq k \leq 10$, $-22 \leq l \leq 22$	
Reflections collected	21017	
Independent reflections	2605 [R(int) = 0.0536]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4296 and 0.2883	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2605 / 12 / 129	
Goodness-of-fit on F^2	1.073	
Final R indices [$I > 2\sigma(I)$ = 2528 data]	$R1 = 0.0881$, $wR2 = 0.2286$	
R indices (all data, $0.80 \text{ \AA}$)	$R1 = 0.0896$, $wR2 = 0.2301$	
Largest diff. peak and hole	17.937 and $-2.109 \text{ e.\AA}^{-3}$	

Table B.7. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $[\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2)]_2\text{Th}$, **B.3**.

Cnt1-Th(1)	2.4884(6)	Th(1)-C(1)	2.462(19)
Th(1)-C(1)#1	2.462(19)	Th(1)-C(2)#1	2.701(16)
Th(1)-C(2)	2.701(16)	Th(1)-C(6)	2.726(14)
Th(1)-C(6)#1	2.726(14)	Th(1)-C(3)#1	2.750(18)
Th(1)-C(3)	2.750(18)	Th(1)-C(5)#1	2.808(17)
Th(1)-C(5)	2.808(16)	Th(1)-C(4)#1	2.820(17)
Th(1)-C(4)	2.820(17)	Si(1)-C(12)	1.88(2)
Si(1)-C(11)	1.880(17)	Si(1)-C(1)	1.896(19)
Si(1)-C(2)	1.948(18)	C(2)-C(3)	1.32(3)
C(2)-C(6)	1.46(2)	C(3)-C(4)	1.42(2)
C(3)-C(7)	1.51(2)	C(4)-C(5)	1.40(2)
C(4)-C(8)	1.52(2)	C(5)-C(6)	1.44(2)
C(5)-C(9)	1.50(2)	C(6)-C(10)	1.50(2)
		Cnt1-Th(1)-Cnt1#1	142.60(14)

Cnt1-Th(1)-C(1)	94.81(2)	Cnt1-Th(1)-C(1)#1	107.30(2)
C(1)-Th(1)-C(1)#1	107.1(10)	C(1)-Th(1)-C(2)#1	113.8(6)
C(1)#1-Th(1)-C(2)#1	68.8(6)	C(1)-Th(1)-C(2)	68.8(6)
C(1)#1-Th(1)-C(2)	113.8(6)	C(2)#1-Th(1)-C(2)	176.1(6)
C(1)-Th(1)-C(6)	87.3(6)	C(1)#1-Th(1)-C(6)	133.8(6)
C(2)#1-Th(1)-C(6)	144.8(5)	C(2)-Th(1)-C(6)	31.3(4)
C(1)-Th(1)-C(6)#1	133.8(6)	C(1)#1-Th(1)-C(6)#1	87.3(6)
C(2)#1-Th(1)-C(6)#1	31.3(4)	C(2)-Th(1)-C(6)#1	144.8(5)
C(6)-Th(1)-C(6)#1	114.2(7)	C(1)-Th(1)-C(3)#1	87.7(6)
C(1)#1-Th(1)-C(3)#1	85.4(6)	C(2)#1-Th(1)-C(3)#1	28.1(5)
C(2)-Th(1)-C(3)#1	152.8(5)	C(6)-Th(1)-C(3)#1	139.9(5)
C(6)#1-Th(1)-C(3)#1	49.1(5)	C(1)-Th(1)-C(3)	85.4(6)
C(1)#1-Th(1)-C(3)	87.7(6)	C(2)#1-Th(1)-C(3)	152.8(5)
C(2)-Th(1)-C(3)	28.1(5)	C(6)-Th(1)-C(3)	49.1(5)
C(6)#1-Th(1)-C(3)	139.9(5)	C(3)#1-Th(1)-C(3)	168.4(6)
C(1)-Th(1)-C(5)#1	111.5(6)	C(1)#1-Th(1)-C(5)#1	115.6(6)
C(2)#1-Th(1)-C(5)#1	49.2(5)	C(2)-Th(1)-C(5)#1	127.4(5)
C(6)-Th(1)-C(5)#1	97.7(5)	C(6)#1-Th(1)-C(5)#1	30.0(5)
C(3)#1-Th(1)-C(5)#1	48.2(5)	C(3)-Th(1)-C(5)#1	143.3(5)
C(1)-Th(1)-C(5)	115.6(6)	C(1)#1-Th(1)-C(5)	111.5(6)
C(2)#1-Th(1)-C(5)	127.4(5)	C(2)-Th(1)-C(5)	49.2(5)
C(6)-Th(1)-C(5)	30.0(5)	C(6)#1-Th(1)-C(5)	97.7(5)
C(3)#1-Th(1)-C(5)	143.3(5)	C(3)-Th(1)-C(5)	48.2(5)
C(5)#1-Th(1)-C(5)	95.4(7)	C(1)-Th(1)-C(4)#1	86.0(6)
C(1)#1-Th(1)-C(4)#1	114.1(5)	C(2)#1-Th(1)-C(4)#1	48.0(5)
C(2)-Th(1)-C(4)#1	130.5(5)	C(6)-Th(1)-C(4)#1	110.4(5)
C(6)#1-Th(1)-C(4)#1	48.9(5)	C(3)#1-Th(1)-C(4)#1	29.5(5)
C(3)-Th(1)-C(4)#1	158.1(5)	C(5)#1-Th(1)-C(4)#1	28.7(5)
C(5)-Th(1)-C(4)#1	119.6(5)	C(1)-Th(1)-C(4)	114.1(5)
C(1)#1-Th(1)-C(4)	86.0(6)	C(2)#1-Th(1)-C(4)	130.5(5)
C(2)-Th(1)-C(4)	48.0(5)	C(6)-Th(1)-C(4)	48.9(5)
C(6)#1-Th(1)-C(4)	110.4(5)	C(3)#1-Th(1)-C(4)	158.1(5)
C(3)-Th(1)-C(4)	29.5(5)	C(5)#1-Th(1)-C(4)	119.6(5)
C(5)-Th(1)-C(4)	28.7(5)	C(4)#1-Th(1)-C(4)	146.9(7)
C(12)-Si(1)-C(11)	107.0(10)	C(12)-Si(1)-C(1)	111.7(12)
C(11)-Si(1)-C(1)	115.9(8)	C(12)-Si(1)-C(2)	112.7(8)
C(11)-Si(1)-C(2)	110.6(8)	C(1)-Si(1)-C(2)	98.9(8)
C(12)-Si(1)-Th(1)	122.7(9)	C(11)-Si(1)-Th(1)	130.2(6)
C(1)-Si(1)-Th(1)	45.8(6)	C(2)-Si(1)-Th(1)	53.2(5)
Si(1)-C(1)-Th(1)	100.6(8)	C(3)-C(2)-C(6)	109.3(15)
C(3)-C(2)-Si(1)	125.4(11)	C(6)-C(2)-Si(1)	119.5(13)
C(3)-C(2)-Th(1)	78.0(10)	C(6)-C(2)-Th(1)	75.3(9)
Si(1)-C(2)-Th(1)	91.5(6)	C(2)-C(3)-C(4)	110.1(14)
C(2)-C(3)-C(7)	126.9(15)	C(4)-C(3)-C(7)	123.0(16)
C(2)-C(3)-Th(1)	73.9(10)	C(4)-C(3)-Th(1)	78.0(10)

C(7)-C(3)-Th(1)	115.5(10)	C(5)-C(4)-C(3)	107.5(15)
C(5)-C(4)-C(8)	125.1(16)	C(3)-C(4)-C(8)	127.2(16)
C(5)-C(4)-Th(1)	75.2(10)	C(3)-C(4)-Th(1)	72.5(10)
C(8)-C(4)-Th(1)	121.9(12)	C(4)-C(5)-C(6)	108.2(15)
C(4)-C(5)-C(9)	125.1(16)	C(6)-C(5)-C(9)	126.3(15)
C(4)-C(5)-Th(1)	76.1(10)	C(6)-C(5)-Th(1)	71.8(8)
C(9)-C(5)-Th(1)	123.6(12)	C(5)-C(6)-C(2)	104.8(14)
C(5)-C(6)-C(10)	124.9(15)	C(2)-C(6)-C(10)	130.3(15)
C(5)-C(6)-Th(1)	78.1(9)	C(2)-C(6)-Th(1)	73.4(8)
C(10)-C(6)-Th(1)	113.0(11)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

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Appendix C:

Synthesis and X-ray Crystal Structures of the THF, 2,2'-Bipyridine, and 2,2';6',2''-Terpyridine Adducts of the $(C_5Me_4SiMe_3)_2Ln$ Complexes of Sm, Yb, and Eu

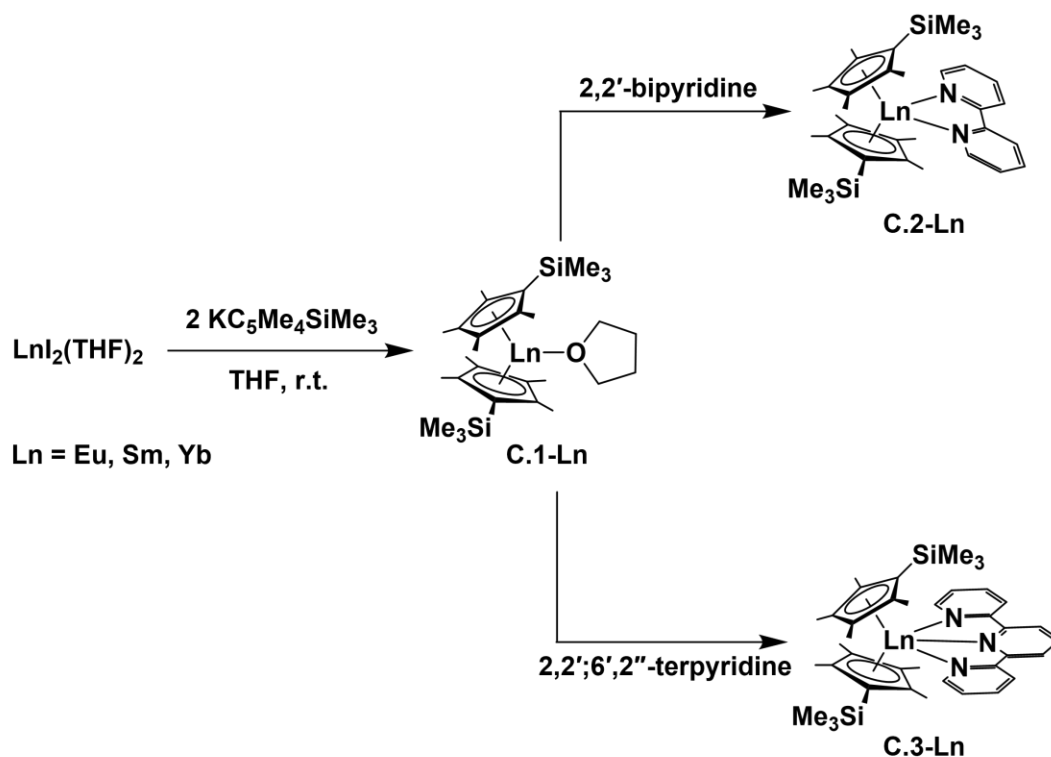
INTRODUCTION[†]

The use of redox-active ligands is a commonly employed strategy to enable redox chemistry in coordination complexes containing relatively redox inert metals.^{1,2} Previously, Walter and coworkers employed the 2,2'-bipyridine (bipy) ligand to produce reduced bis(cyclopentadienyl) actinide metal bipyridine complexes that mimic the reactivity of low oxidation state metal complexes by using the redox-active bipy ligand as an electron shuttle.³⁻⁵ In addition, Stennett *et al.* utilized a similar approach to model Ln(I)-like (Ln = lanthanide) reactivity with lanthanide metallocene bipyridine complexes.⁶ As part of a broader study in the Evans Group exploring substituent effects on the reductive chemistry of rare-earth metal and actinide cyclopentadienyl complexes, the syntheses of metallocenes containing $(C_5Me_4SiMe_3)^{1-}$ ligands and their adducts with THF, 2,2'-bipyridine (bipy), and 2,2';6',2''-terpyridine (terpy) were explored. Described in this Appendix are preliminary results summarizing the synthesis and structural data collected for the THF, bipy, and terpy adducts of the $(C_5Me_4SiMe_3)_2Ln$ complexes of Sm, Yb, and Eu. These syntheses described herein seek to provide a basis for exploring the role of the $(C_5Me_4SiMe_3)^{1-}$ ligand on the properties, reduction chemistry, and reactivity of the resulting rare-earth metal metallocenes bearing bipyridine and terpyridine ligands versus other cyclopentadienyl ligands such as $(C_5Me_5)^{1-}$.

[†]This work is in collaboration with Dr. Gabija Navickaite and Allison K. Bernardo who are credited with some of the experimental data described herein.

RESULTS AND DISCUSSION

The synthesis of the $(C_5Me_4SiMe_3)_2Ln(THF)$ complexes, **C.1-Ln**, was accomplished through a salt metathesis reaction between $KC_5Me_4SiMe_3$ (see Experimental Section) and the corresponding $LnI_2(THF)_2$ ($Ln = Eu, Sm, Yb$) salt in THF, Scheme C.1. This procedure was adapted from that of the solution synthesis of the analogous $(C_5Me_5)_2Sm(THF)_2$.⁷ X-ray quality crystals of **C.1-Ln** could be grown from saturated toluene solutions stored at $-35\text{ }^\circ\text{C}$ as mono-THF solvates. A representative figure of **C.1-Sm** is shown in Figure C.1 below. The **C.1-Ln** complexes described in this Appendix crystallize in similar unit cells in the monoclinic $P2_1/c$ space group.



Scheme C.1. General synthesis of **C.1-Ln**, **C.2-Ln**, and **C.3-Ln** described in this Appendix.

All **C.1-Ln** complexes are typical bent metallocenes that are commonly observed throughout the *f*-element literature.⁸ The coordinated molecule of THF is located in the open wedge of the bent

metallocene. A top-down view of **C.1-Ln** shows that the cyclopentadienyl rings are oriented staggered with respect to each other, Figure C.2. Furthermore, the SiMe₃ substituents on opposite cyclopentadienyl rings are anti with respect to each other.

Addition of 2,2'-bipyridine (bipy) to **C.1-Sm** and **C.1-Yb** in toluene immediately produced a color change from dark purple to dark blue-green for Sm and brown to dark brown-red for Yb, Scheme C.1. The analogous reaction for **C.1-Eu** was performed in THF due to precipitation of the product in toluene. Workup yielded (C₅Me₄SiMe₃)₂Ln(bipy), **C.2-Ln**, as darkly colored powders in high yields (see Experimental Section below). X-ray quality crystals of **C.2-Sm** and **C.2-Yb** could be grown from saturated Et₂O solutions stored at –35 °C. For **C.2-Eu**,

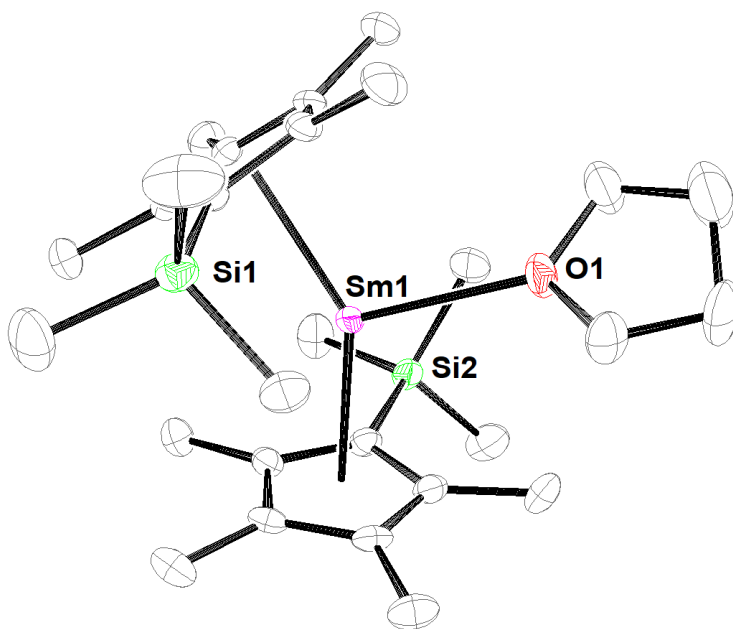


Figure C.1. Molecular structure of (C₅Me₄SiMe₃)₂Sm(THF), **C.1-Sm**, drawn at 50% probability with selective atom labelling. Hydrogen atoms are not shown for clarity.

crystals suitable for study by X-ray diffraction had to be grown from Et₂O solutions spiked with a few drops of THF. A representative figure of **C.2-Sm** is shown in Figure C.3 below.

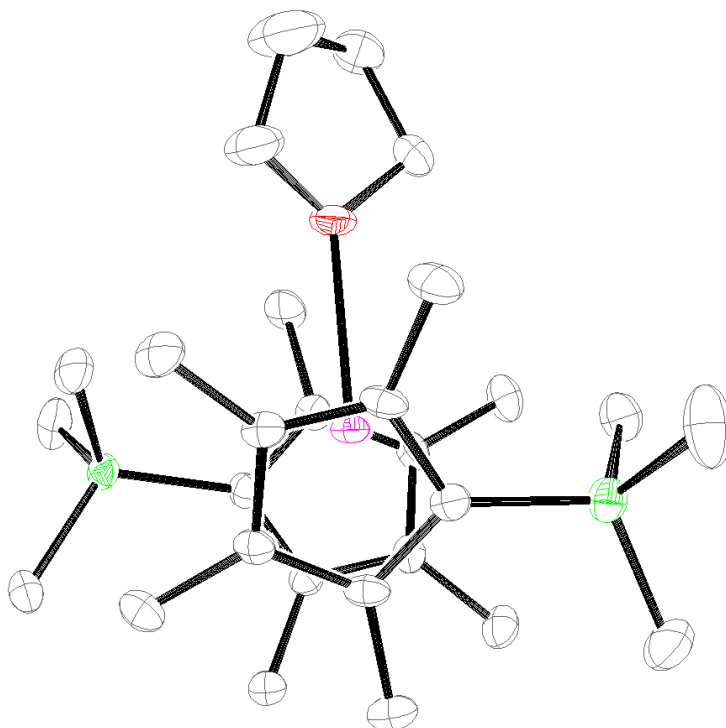


Figure C.2. Top-down view of the molecular structure of $(C_5Me_4SiMe_3)_2Sm(THF)$, **C.1-Sm**, drawn at 50% probability. Hydrogen atoms are not shown for clarity. The cyclopentadienyl rings are staggered with respect to each other and the trimethylsilyl substituents on opposite rings are anti with respect to each other.

Complexes **C.2-Yb** and **C.2-Eu** crystallize in the $C2/c$ space group with half of a molecule of diethyl ether solvent present in the asymmetric unit and are isomorphous with each other. However, **C.2-Sm** crystallizes in a different unit cell in the triclinic $P\bar{1}$ space group with no co-crystallized solvent molecules present in the crystal lattice. All **C.2-Ln** complexes are structurally similar bent metallocenes with the bipy ligand coordinating to the metal center in a bidentate fashion in the wedge of the bent metallocene. The cyclopentadienyl rings for each **C.2-Ln**

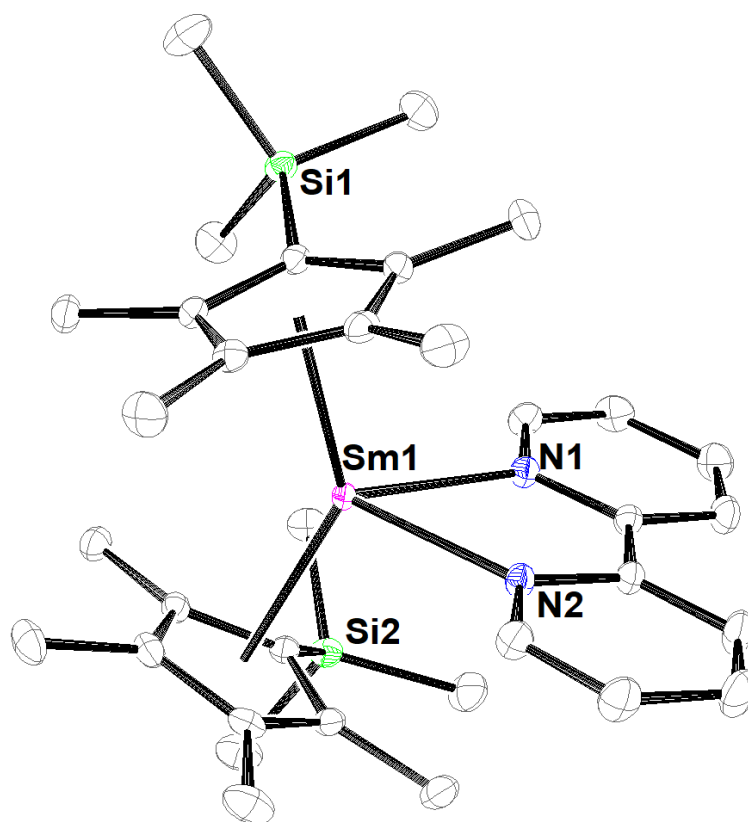


Figure C.3. Molecular structure of $(C_5Me_4SiMe_3)_2Sm(bipy)$, **C.2-Sm**, drawn at 50% probability with selective atom labelling. Hydrogen atoms are not shown for clarity.

complex adopt a staggered orientation with respect to each other in the solid-state, but most notably, the trimethylsilyl substituents on opposite cyclopentadienyl ligands adopt a gauche conformation with respect to each other as seen from a top-down view of the X-ray crystal structure, Figure C.4. This contrasts with the anti conformation observed in **C.1-Ln**.

Following the same methodology as described for the synthesis of **C.2-Ln**, treatment of **C.1-Ln** with 1 equiv of terpy in toluene generated **C.3-Ln** for Sm and Yb in good yields (see Experimental Section), Scheme C.1. Like that for **C.2-Eu**, complex **C.3-Eu** was synthesized in THF due to the precipitation of the product in toluene. Each **C.3-Ln** complex required different crystallization conditions despite the structural similarities between the complexes. For **C.3-Sm**,

X-ray quality crystals were grown from saturated toluene solutions stored at $-35\text{ }^{\circ}\text{C}$. Crystals of **C.3-Yb** were grown from saturated Et_2O solutions and the crystallization of **C.3-Eu** required a saturated THF solution spiked with a few drops of 1,2-dimethoxyethane (DME). Evidently, the addition of DME was important in the crystallization as there was one molecule of co-crystallized DME solvent present in the crystal structure of **C.3-Eu**. A representative figure of

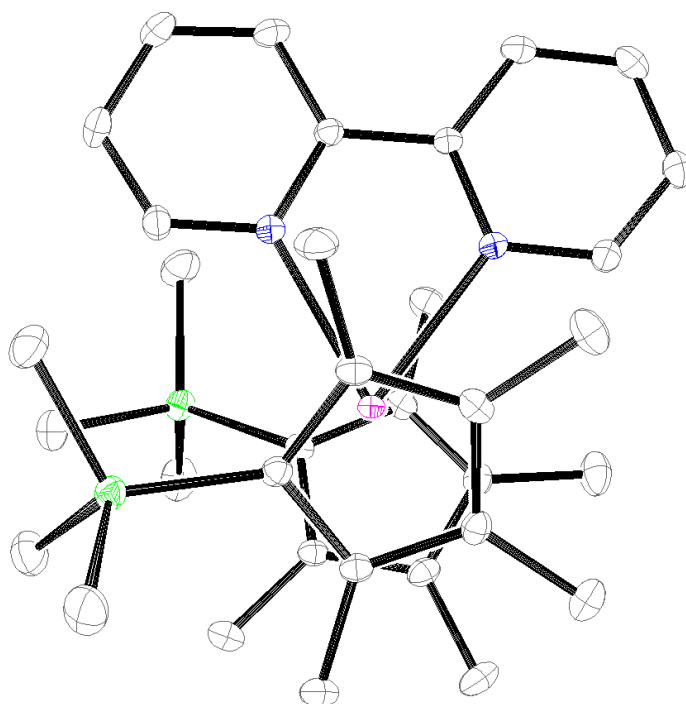


Figure C.4. Top-down view of the molecular structure of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Sm}(\text{bipy})$, **C.2-Sm**, drawn at 50% probability. Hydrogen atoms are not shown for clarity. The cyclopentadienyl rings are staggered with respect to each other and the trimethylsilyl substituents on opposite rings are gauche with respect to each other.

C.3-Sm is shown in Figure C.5 below. Complexes **C.3-Sm** and **C.3-Yb** crystallize in the orthorhombic $Pca2_1$ space group and are isomorphous to each other. On the other hand, **C.3-Eu** crystallizes in the $P2_12_12_1$ space group. **C.3-Ln** are bent metallocene complexes that coordinate

the tridentate terpy ligand in the wedge of the bent metallocene. Structurally, all **C.3-Ln** complexes are similar and the relative orientations of the cyclopentadienyl ligands with respect to each other are similar between the different structures.

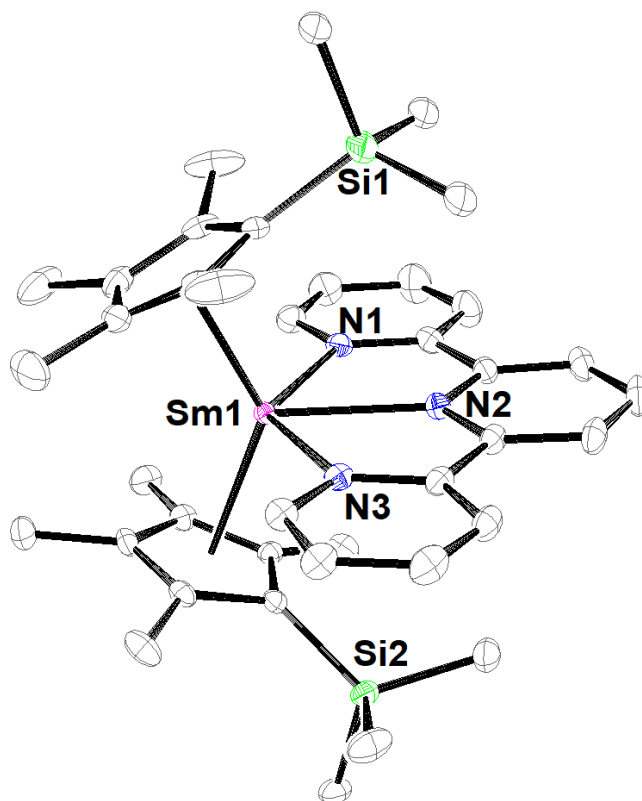


Figure C.5. Molecular structure of $(C_5Me_4SiMe_3)_2Sm(terpy)$, **C.3-Sm**, drawn at 50% probability with selective atom labelling. Hydrogen atoms are not shown for clarity.

Figure C.6 below shows a top-down view of the X-ray crystal structure of **C.3-Sm**. Like the structures of **C.1-Ln** and **C.2-Ln** discussed above, the opposite cyclopentadienyl rings are staggered with respect to each other. Interestingly, although the trimethylsilyl substituents are gauche with respect to each other like for **C.2-Ln**, for **C.3-Ln**, these silyl substituents are oriented over and below the plane of the coordinating tridentate terpy ligand, Figure C.6.

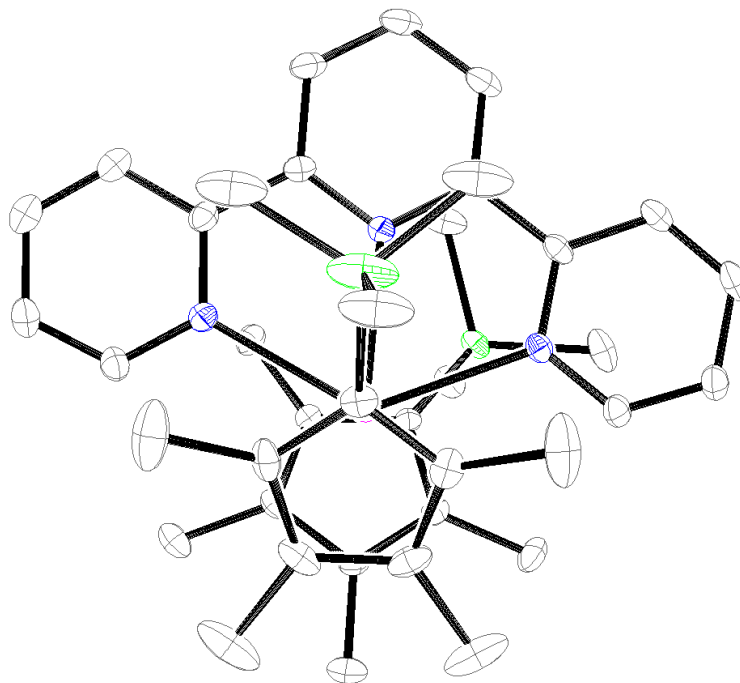


Figure C.6. Top-down view of the molecular structure of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Sm}(\text{terpy})$, **C.3-Sm**, drawn at 50% probability. Hydrogen atoms are not shown for clarity. The cyclopentadienyl rings are staggered with respect to each other and the trimethylsilyl substituents on opposite rings are gauche with respect to each other. Furthermore, the trimethylsilyl substituents are positioned above and below the plane of the terpy ligand.

It is unknown what factors influence the orientations of the silyl substituents on opposite cyclopentadienyl ligands between **C.1-Ln**, **C.2-Ln**, and **C.3-Ln** or the role of the bipy and terpy ligand on the way the molecules pack in the solid-state. However, it is noted that it is unusual that the silyl substituents adopt gauche conformations for **C.2-Ln** and **C.3-Ln**, which is expected to not be as energetically favorable as the anti conformations observed in **C.1-Ln**.

Tables C.1, C.2, and C.3 below summarize the selected metrical data for each complex crystallographically characterized in this Appendix. For **C.1-Ln**, the metrical data are similar

between the different metals employed. The Ln–Cnt and Ln–O distances trend with the decreasing size of the metal ion that is observed as a result of the lanthanide contraction.^{9,10}

For **C.2-Sm**, the average Ln–Cnt distance is 2.455 Å, which is shorter than that of **C.2-Eu** which has an analogous average Ln–Cnt distance of 2.573 Å. It is worth noting that the C_{bipy}–C'_{bipy} distances between **C.2-Sm** and **C.2-Eu** are different at 1.430(2) Å and 1.487(3) Å, respectively. Previously, it was shown that the C_{bipy}–C'_{bipy} distance of the bipy ligand can be a useful indicator of the oxidation state of the bipy ligand, where the C_{bipy}–C'_{bipy} distance was observed to shorten upon reduction of the bipy ligand.^{6,11,12} The crystallographic data suggest that for **C.2-Sm**, the complex is composed of a Sm(III) ion and a (bipy)^{1–} radical whereas for **C.2-Eu**, it is comprised of a Eu(II) ion and a (bipy)⁰ species. For **C.2-Yb** which has a C_{bipy}–C'_{bipy} distance of 1.485(4) Å similar to that of **C.2-Eu**, the crystallographic data suggest that **C.2-Yb** is composed of an Yb(II) ion and a (bipy)⁰ species.

The same treatment can be applied to **C.3-Ln** in determining the oxidation states of the metal ion and the terpy ligand. **C.3-Sm** and **C.3-Yb** have similar average C_{terpy}–C'_{terpy} distances of 1.450(6) Å and 1.454(6) Å, respectively, whereas for **C.3-Eu**, the analogous average C_{terpy}–C'_{terpy} is longer at 1.487(3) Å. These distances suggest that for **C.3-Sm** and **C.3-Yb**, the Ln ion is in the +3 oxidation state and the terpy ligands are monoanionic. For **C.3-Eu**, the complex is comprised of an Eu(II) ion and a (terpy)⁰ moiety.

Table C.1. Selected bond distances (Å) and angles (°) of the **C.1-Ln** complexes described in this Appendix.

Ln	Ln–Cnt	Ln–O	Cnt–Ln–Cnt	Cnt–Ln–O
Sm	2.524, 2.560	2.570(2)	141.9	106.3, 110.7

Yb	2.395, 2.421	2.428(1)	143.5	107.6, 108.4
Eu	2.516, 2.552	2.554(2)	142.0	106.5, 110.6

Table C.2. Selected bond distances (Å) and angles (°) of the **C.2-Ln** complexes described in this Appendix.

Ln	Ln–Cnt	Ln–N	Cnt–Ln–Cnt	Cnt–Ln–N	C ^{bipy} –C' ^{bipy}
Sm	2.450, 2.459	2.422(1), 2.434(1)	137.1	103.7, 104.7, 108.8, 111.7	1.430(2)
Yb	2.443, 2.443	2.455(2), 2.479(2)	140.7	103.1, 103.9, 105.8, 111.1	1.485(4)
Eu	2.575, 2.570	2.595(2), 2.640(2)	141.5	101.7, 102.4, 104.4, 113.4	1.487(3)

Table C.3. Selected bond distances (Å) and angles (°) of the **C.3-Ln** complexes described in this Appendix.

Ln	Ln–Cnt	Ln–N	Cnt–Ln–Cnt	Cnt–Ln–N	C ^{terpy} –C' ^{terpy}
Sm	2.523, 2.535	2.454(3), 2.496(3), 2.516(3)	132.2	98.5, 99.4, 100.1, 101.2, 112.3, 115.4	1.451(6), 1.448(6)
Yb	2.439, 2.462	2.352(3), 2.422(3), 2.440(3)	131.7	98.2, 98.6, 99.4, 100.6, 113.1, 115.1	1.450(6), 1.457(6)

Eu	2.642, 2.636	2.617(2), 2.624(2), 2.651(2)	137.7	97.5, 98.3, 101.4, 101.4, 108.1, 114.1	1.488(3), 1.486(3)

CONCLUSIONS

The coordination chemistry of the $(C_5Me_4SiMe_3)^{1-}$ ligand can be extended to Sm, Yb, and Eu through reaction of the corresponding $LnI_2(THF)_2$ salt with 2 equiv $KC_5Me_4SiMe_3$ in THF. These metallocenes readily crystallize from saturated toluene solutions as mono-THF adducts in the solid-state. Furthermore, the coordinated THF ligand can be easily displaced with bipy and terpy ligands to generate new examples of bis(cyclopentadienyl) lanthanide bipy and terpy complexes. The role of the substitution pattern of the cyclopentadienyl ligands on the properties, reduction chemistry, and reactivity of the rare-earth metal metallocenes have yet to be determined, but the syntheses described in this Appendix should place this class of compounds on a firm basis.

EXPERIMENTAL SECTION

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP (99.999%) argon and dried by passage through columns containing Q-5 and molecular sieves prior to use and stored over activated molecular sieves prior to use. $SmI_2(THF)_2$, $YbI_2(THF)_2$, and $EuI_2(THF)_2$ were synthesized according to literature procedures.¹³ $KC_5Me_4SiMe_3$ was synthesized by treating $HC_5Me_4SiMe_3$ ¹⁴ with $KN(SiMe_3)_2$ in toluene. 2,2'-bipyridine was sublimed under reduced pressure prior to use. 2,2';6',2''-terpyridine was purchased from Sigma-Aldrich and was dried under reduced pressure overnight prior to use.

General Synthesis of $(C_5Me_4SiMe_3)_2Ln(THF)$, C.1-Ln. In a 20 mL scintillation vial, THF (ca. 5 mL) was added to $LnI_2(THF)_2$ (1.00 equiv) and $KC_5Me_4SiMe_3$ (2.00 equiv) at room temperature. An immediate color change concomitant with the generation of an insoluble precipitate was observed. The resulting mixture was allowed to stir at room temperature over 16 h. Insoluble solids, presumably KI, were removed via centrifugation followed by filtration through a pipet packed with Kimwipe tissue. Volatiles were removed under reduced pressure to yield a colored oily residue. The product was then extracted into toluene and filtered through a pipet packed with Kimwipe tissue to remove insoluble solids. Volatiles were removed from the filtrate under reduced pressure to yield solids of $(C_5Me_4SiMe_3)_2Ln(THF)$, **C.1-Ln**.

General Synthesis of $(C_5Me_4SiMe_3)_2Ln(bipy)$, C.2-Ln. In a 20 mL scintillation vial, $(C_5Me_4SiMe_3)_2Ln(THF)$, **C.1-Ln**, (1.00 equiv) was dissolved in toluene (ca. 3 mL) at room temperature. 2,2'-bipyridine (bipy) (1.00 equiv) was added as a solid at room temperature and the resulting mixture was stirred at room temperature for 1 h. The resulting solution was filtered through a glass pipet packed with Kimwipe tissue to remove insoluble solids. Volatiles were removed under reduced pressure to yield solids of $(C_5Me_4SiMe_3)_2Ln(bipy)$, **C.2-Ln**.

General Synthesis of $(C_5Me_4SiMe_3)_2Ln(terpy)$, C.3-Ln. In a 20 mL scintillation vial, $(C_5Me_4SiMe_3)_2Ln(THF)$, **C.1-Ln**, (1.00 equiv) was dissolved in toluene (ca. 3 mL) at room temperature. 2,2';6',2''-Terpyridine (terpy) (1.00 equiv) was added as a solid at room temperature and the resulting mixture was stirred at room temperature for 1 h. The resulting solution was filtered through a glass pipet packed with Kimwipe tissue to remove insoluble solids. Volatiles were removed under reduced pressure to yield solids of $(C_5Me_4SiMe_3)_2Ln(terpy)$, **C.3-Ln**.

Synthesis of $(C_5Me_4SiMe_3)_2Sm(THF)$, C.1-Sm. $SmI_2(THF)_2$ (226 mg, 0.412 mmol) and $KC_5Me_4SiMe_3$ (192 mg, 0.824 mmol) were reacted according to the general procedure for the

synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ln}(\text{THF})$, **C.1-Ln**. $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Sm}(\text{THF})$, **C.1-Sm**, was isolated as a dark purple solid (225 mg, 90%).

Synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Yb}(\text{THF})$, C.1-Yb. $\text{YbI}_2(\text{THF})_2$ (196 mg, 0.343 mmol) and $\text{KC}_5\text{Me}_4\text{SiMe}_3$ (160 mg, 0.686 mmol) were reacted according to the general procedure for the synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ln}(\text{THF})$, **C.1-Ln**. $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Yb}(\text{THF})$, **C.1-Yb**, was isolated as a green solid (176 mg, 81%).

Synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Eu}(\text{THF})$, C.1-Eu. $\text{EuI}_2(\text{THF})_2$ (187 mg, 0.340 mmol) and $\text{KC}_5\text{Me}_4\text{SiMe}_3$ (158 mg, 0.680 mmol) were reacted according to the general procedure for the synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ln}(\text{THF})$, **C.1-Ln**. $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Eu}(\text{THF})$, **C.1-Eu**, was isolated as an orange solid (120 mg, 58%).

Synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Sm}(\text{bipy})$, C.2-Sm. $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Sm}(\text{THF})$, **C.1-Sm**, (150 mg, 0.246 mmol) and bipy (38 mg, 0.246 mmol) were reacted according to the general procedure for the synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ln}(\text{bipy})$, **C.2-Ln**. $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Sm}(\text{bipy})$, **C.2-Sm**, was isolated as a dark green solid (166 mg, 97%).

Synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Yb}(\text{bipy})$, C.2-Yb. $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Yb}(\text{THF})$, **C.1-Yb**, (150 mg, 0.237 mmol) and bipy (34 mg, 0.237 mmol) were reacted according to the general procedure for the synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ln}(\text{bipy})$, **C.2-Ln**. $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Yb}(\text{bipy})$, **C.2-Yb**, was isolated as a dark solid (161 mg, 95%).

Synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Eu}(\text{bipy})$, C.2-Eu. $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Eu}(\text{THF})$, **C.1-Eu**, (150 mg, 0.246 mmol) and bipy (38 mg, 0.246 mmol) were reacted according to the general procedure for the synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ln}(\text{bipy})$, **C.2-Ln** using THF (ca. 3 mL) as the solvent of reaction. $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Eu}(\text{bipy})$, **C.2-Eu**, was isolated as a dark solid (165 mg, 97%).

Synthesis of $(C_5Me_4SiMe_3)_2Sm(terpy)$, C.3-Sm. $(C_5Me_4SiMe_3)_2Sm(THF)$, C.1-Sm, (150 mg, 0.246 mmol) and terpy (58 mg, 0.246 mmol) were reacted according to the general procedure for the synthesis of $(C_5Me_4SiMe_3)_2Ln(terpy)$, C.3-Ln. $(C_5Me_4SiMe_3)_2Sm(terpy)$, C.3-Sm, was isolated as a dark blue-green solid (185 mg, 93%).

Synthesis of $(C_5Me_4SiMe_3)_2Yb(terpy)$, C.3-Yb. $(C_5Me_4SiMe_3)_2Yb(THF)$, C.1-Yb, (150 mg, 0.237 mmol) and terpy (53 mg, 0.237 mmol) were reacted according to the general procedure for the synthesis of $(C_5Me_4SiMe_3)_2Ln(terpy)$, C.3-Ln. $(C_5Me_4SiMe_3)_2Yb(terpy)$, C.3-Yb, was isolated as a dark solid (180 mg, 96%).

Synthesis of $(C_5Me_4SiMe_3)_2Eu(terpy)$, C.3-Eu. $(C_5Me_4SiMe_3)_2Eu(THF)$, C.1-Eu, (150 mg, 0.246 mmol) and terpy (58 mg, 0.246 mmol) were reacted according to the general procedure for the synthesis of $(C_5Me_4SiMe_3)_2Ln(terpy)$, C.3-Ln using THF (ca. 3 mL) as the solvent of reaction. $(C_5Me_4SiMe_3)_2Eu(terpy)$, C.3-Eu, was isolated as a dark brown-black solid (177 mg, 98%).

X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_4SiMe_3)_2Sm(THF)$, C.1-Sm. A red crystal of approximate dimensions 0.101 x 0.174 x 0.329 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2¹⁵ program package was used to determine the unit-cell parameters. Data collection used a 20 sec/frame scan time. The raw frame data was processed using SAINT¹⁶ and SADABS¹⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL¹⁸ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors¹⁹ for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0648$ and $Goof = 1.119$ for 303 variables refined against 7289 data ($0.76 \text{ \AA}$), $R1 = 0.0293$ for those 6323 data with $I > 2.0\sigma(I)$.

Table C.4. Crystal data and structure refinement for $(C_5Me_4SiMe_3)_2Sm(THF)$, **C.1-Sm**.

Identification code	jqn11 (Joseph Nguyen)	
Empirical formula	$C_{28} H_{50} O Si_2 Sm$	
Formula weight	609.21	
Temperature	133(2) K	
Wavelength	$0.71073 \text{ \AA}$	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 17.885(4) \text{ \AA}$	$\alpha = 90^\circ$.
	$b = 11.072(3) \text{ \AA}$	$\beta = 104.503(4)^\circ$.
	$c = 15.824(4) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$3033.7(13) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.334 Mg/m^3	
Absorption coefficient	2.031 mm^{-1}	
F(000)	1264	
Crystal color	red	
Crystal size	$0.329 \times 0.174 \times 0.101 \text{ mm}^3$	
Theta range for data collection	1.176 to 28.009°	
Index ranges	$-23 \leq h \leq 23$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$	
Reflections collected	63790	
Independent reflections	7289 [$R(\text{int}) = 0.0527$]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6369	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7289 / 0 / 303	
Goodness-of-fit on F^2	1.119	
Final R indices [$I > 2\sigma(I)$ = 6323 data]	$R1 = 0.0293$, $wR2 = 0.0620$	
R indices (all data, $0.76 \text{ \AA}$)	$R1 = 0.0374$, $wR2 = 0.0648$	

Largest diff. peak and hole	1.162 and -1.704 e.Å ⁻³	

Table C.5. Bond lengths [Å] and angles [°] for (C₅Me₄SiMe₃)₂Sm(THF), **C.1-Sm**.

Sm(1)-Cnt1	2.524	Sm(1)-Cnt2	2.560
Sm(1)-O(1)	2.570(2)	Sm(1)-C(1)	2.730(3)
Sm(1)-C(5)	2.776(3)	Sm(1)-C(13)	2.780(3)
Sm(1)-C(17)	2.784(3)	Sm(1)-C(2)	2.785(3)
Sm(1)-C(3)	2.843(3)	Sm(1)-C(14)	2.843(3)
Sm(1)-C(4)	2.852(3)	Sm(1)-C(16)	2.860(3)
Sm(1)-C(15)	2.886(3)	Si(1)-C(1)	1.856(3)
Si(1)-C(11)	1.864(4)	Si(1)-C(10)	1.866(4)
Si(1)-C(12)	1.884(3)	Si(2)-C(13)	1.851(3)
Si(2)-C(23)	1.872(3)	Si(2)-C(22)	1.876(3)
Si(2)-C(24)	1.882(3)	O(1)-C(25)	1.446(4)
O(1)-C(28)	1.448(4)	C(1)-C(5)	1.435(4)
C(1)-C(2)	1.435(4)	C(2)-C(3)	1.409(4)
C(2)-C(6)	1.514(4)	C(3)-C(4)	1.420(4)
C(3)-C(7)	1.500(4)	C(4)-C(5)	1.402(4)
C(4)-C(8)	1.504(4)	C(5)-C(9)	1.511(4)
C(13)-C(14)	1.430(4)	C(13)-C(17)	1.438(4)
C(14)-C(15)	1.406(4)	C(14)-C(18)	1.511(4)
C(15)-C(16)	1.423(4)	C(15)-C(19)	1.516(4)
C(16)-C(17)	1.405(4)	C(16)-C(20)	1.515(4)
C(17)-C(21)	1.510(4)	C(25)-C(26)	1.449(5)
C(26)-C(27)	1.517(6)	C(27)-C(28)	1.495(5)
		Cnt1-Sm(1)-Cnt2	141.9
Cnt1-Sm(1)-O(1)	106.3	Cnt2-Sm(1)-O(1)	110.7
O(1)-Sm(1)-C(1)	109.12(8)	O(1)-Sm(1)-C(5)	83.48(8)
C(1)-Sm(1)-C(5)	30.19(8)	O(1)-Sm(1)-C(13)	104.99(8)
C(1)-Sm(1)-C(13)	145.03(8)	C(5)-Sm(1)-C(13)	155.02(8)
O(1)-Sm(1)-C(17)	85.43(8)	C(1)-Sm(1)-C(17)	159.27(8)
C(5)-Sm(1)-C(17)	168.86(8)	C(13)-Sm(1)-C(17)	29.96(8)
O(1)-Sm(1)-C(2)	131.66(7)	C(1)-Sm(1)-C(2)	30.14(8)
C(5)-Sm(1)-C(2)	48.66(8)	C(13)-Sm(1)-C(2)	116.38(8)
C(17)-Sm(1)-C(2)	142.15(8)	O(1)-Sm(1)-C(3)	115.54(7)
C(1)-Sm(1)-C(3)	48.95(8)	C(5)-Sm(1)-C(3)	47.89(8)
C(13)-Sm(1)-C(3)	108.47(8)	C(17)-Sm(1)-C(3)	138.28(8)
C(2)-Sm(1)-C(3)	28.97(8)	O(1)-Sm(1)-C(14)	132.54(8)
C(1)-Sm(1)-C(14)	118.21(8)	C(5)-Sm(1)-C(14)	142.48(8)
C(13)-Sm(1)-C(14)	29.44(8)	C(17)-Sm(1)-C(14)	48.13(8)
C(2)-Sm(1)-C(14)	94.02(8)	C(3)-Sm(1)-C(14)	98.58(8)
O(1)-Sm(1)-C(4)	87.73(7)	C(1)-Sm(1)-C(4)	48.90(8)
C(5)-Sm(1)-C(4)	28.81(8)	C(13)-Sm(1)-C(4)	126.68(8)
C(17)-Sm(1)-C(4)	149.61(8)	C(2)-Sm(1)-C(4)	47.96(8)

C(3)-Sm(1)-C(4)	28.87(7)	C(14)-Sm(1)-C(4)	125.94(8)
O(1)-Sm(1)-C(16)	97.93(8)	C(1)-Sm(1)-C(16)	131.28(8)
C(5)-Sm(1)-C(16)	155.21(8)	C(13)-Sm(1)-C(16)	48.35(8)
C(17)-Sm(1)-C(16)	28.79(8)	C(2)-Sm(1)-C(16)	127.85(8)
C(3)-Sm(1)-C(16)	144.65(8)	C(14)-Sm(1)-C(16)	47.35(8)
C(4)-Sm(1)-C(16)	173.27(8)	O(1)-Sm(1)-C(15)	126.60(8)
C(1)-Sm(1)-C(15)	112.36(8)	C(5)-Sm(1)-C(15)	142.54(8)
C(13)-Sm(1)-C(15)	48.00(8)	C(17)-Sm(1)-C(15)	47.56(8)
C(2)-Sm(1)-C(15)	100.20(8)	C(3)-Sm(1)-C(15)	116.81(8)
C(14)-Sm(1)-C(15)	28.39(7)	C(4)-Sm(1)-C(15)	145.46(8)
C(16)-Sm(1)-C(15)	28.67(8)	C(1)-Si(1)-C(11)	113.51(15)
C(1)-Si(1)-C(10)	113.98(16)	C(11)-Si(1)-C(10)	107.0(2)
C(1)-Si(1)-C(12)	108.23(14)	C(11)-Si(1)-C(12)	107.30(17)
C(10)-Si(1)-C(12)	106.37(18)	C(13)-Si(2)-C(23)	114.63(14)
C(13)-Si(2)-C(22)	112.09(13)	C(23)-Si(2)-C(22)	106.36(16)
C(13)-Si(2)-C(24)	107.29(14)	C(23)-Si(2)-C(24)	107.28(15)
C(22)-Si(2)-C(24)	109.00(16)	C(25)-O(1)-C(28)	107.4(2)
C(25)-O(1)-Sm(1)	130.60(18)	C(28)-O(1)-Sm(1)	121.64(17)
C(5)-C(1)-C(2)	105.9(2)	C(5)-C(1)-Si(1)	124.5(2)
C(2)-C(1)-Si(1)	128.9(2)	C(5)-C(1)-Sm(1)	76.66(16)
C(2)-C(1)-Sm(1)	77.05(16)	Si(1)-C(1)-Sm(1)	105.13(12)
C(3)-C(2)-C(1)	108.7(2)	C(3)-C(2)-C(6)	124.1(3)
C(1)-C(2)-C(6)	127.1(3)	C(3)-C(2)-Sm(1)	77.77(15)
C(1)-C(2)-Sm(1)	72.81(15)	C(6)-C(2)-Sm(1)	119.14(18)
C(2)-C(3)-C(4)	108.2(2)	C(2)-C(3)-C(7)	127.1(2)
C(4)-C(3)-C(7)	124.4(3)	C(2)-C(3)-Sm(1)	73.26(15)
C(4)-C(3)-Sm(1)	75.94(14)	C(7)-C(3)-Sm(1)	121.14(18)
C(5)-C(4)-C(3)	107.9(2)	C(5)-C(4)-C(8)	127.2(3)
C(3)-C(4)-C(8)	124.4(3)	C(5)-C(4)-Sm(1)	72.57(15)
C(3)-C(4)-Sm(1)	75.18(14)	C(8)-C(4)-Sm(1)	124.57(19)
C(4)-C(5)-C(1)	109.3(2)	C(4)-C(5)-C(9)	125.2(3)
C(1)-C(5)-C(9)	125.5(3)	C(4)-C(5)-Sm(1)	78.62(16)
C(1)-C(5)-Sm(1)	73.15(15)	C(9)-C(5)-Sm(1)	116.42(19)
C(14)-C(13)-C(17)	106.3(2)	C(14)-C(13)-Si(2)	130.2(2)
C(17)-C(13)-Si(2)	123.5(2)	C(14)-C(13)-Sm(1)	77.72(16)
C(17)-C(13)-Sm(1)	75.17(15)	Si(2)-C(13)-Sm(1)	111.56(12)
C(15)-C(14)-C(13)	108.8(2)	C(15)-C(14)-C(18)	124.2(2)
C(13)-C(14)-C(18)	126.7(2)	C(15)-C(14)-Sm(1)	77.48(15)
C(13)-C(14)-Sm(1)	72.83(15)	C(18)-C(14)-Sm(1)	120.46(18)
C(14)-C(15)-C(16)	108.1(2)	C(14)-C(15)-C(19)	126.5(3)
C(16)-C(15)-C(19)	125.1(2)	C(14)-C(15)-Sm(1)	74.13(15)
C(16)-C(15)-Sm(1)	74.66(15)	C(19)-C(15)-Sm(1)	121.43(18)
C(17)-C(16)-C(15)	108.0(2)	C(17)-C(16)-C(20)	126.2(3)
C(15)-C(16)-C(20)	125.6(3)	C(17)-C(16)-Sm(1)	72.61(15)
C(15)-C(16)-Sm(1)	76.67(15)	C(20)-C(16)-Sm(1)	120.76(19)

C(16)-C(17)-C(13)	108.7(2)	C(16)-C(17)-C(21)	124.9(3)
C(13)-C(17)-C(21)	126.3(3)	C(16)-C(17)-Sm(1)	78.60(16)
C(13)-C(17)-Sm(1)	74.87(15)	C(21)-C(17)-Sm(1)	115.90(18)
O(1)-C(25)-C(26)	107.9(3)	C(25)-C(26)-C(27)	104.8(3)
C(28)-C(27)-C(26)	101.1(3)	O(1)-C(28)-C(27)	105.0(3)

X-ray Data Collection, Structure Solution and Refinement for (C₅Me₄SiMe₃)₂Yb(THF), C.1-Yb. A green crystal of approximate dimensions 0.112 x 0.367 x 0.466 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2¹⁵ program package was used to determine the unit-cell parameters. Data collection used a 45 sec/frame scan time. The raw frame data was processed using SAINT¹⁶ and SADABS¹⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL¹⁸ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors¹⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0507$ and $Goof = 1.036$ for 303 variables refined against 9032 data ($0.70 \text{ \AA}$), $R1 = 0.0224$ for those 7461 data with $I > 2.0\sigma(I)$.

Table C.6. Crystal data and structure refinement for (C₅Me₄SiMe₃)₂Yb(THF), C.1-Yb.

Identification code	jqn34 (Joseph Nguyen)	
Empirical formula	C ₂₈ H ₅₀ O Si ₂ Yb	
Formula weight	631.90	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 18.173(2) \text{ \AA}$	$\alpha = 90^\circ$.
	$b = 10.9125(12) \text{ \AA}$	$\beta = 106.103(2)^\circ$.
	$c = 15.7863(18) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$3007.8(6) \text{ \AA}^3$	
Z	4	

Density (calculated)	1.395 Mg/m ³	
Absorption coefficient	3.206 mm ⁻¹	
F(000)	1296	
Crystal color	green	
Crystal size	0.466 x 0.367 x 0.112 mm ³	
Theta range for data collection	1.166 to 30.621°	
Index ranges	-25 ≤ h ≤ 24, -15 ≤ k ≤ 15, -22 ≤ l ≤ 21	
Reflections collected	70816	
Independent reflections	9032 [R(int) = 0.0473]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.5875	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9032 / 0 / 303	
Goodness-of-fit on F ²	1.036	
Final R indices [I > 2sigma(I) = 7461 data]	R1 = 0.0224, wR2 = 0.0464	
R indices (all data, 0.70 Å)	R1 = 0.0346, wR2 = 0.0507	
Largest diff. peak and hole	0.866 and -0.616 e.Å ⁻³	

Table C.7. Bond lengths [Å] and angles [°] for (C₅Me₄SiMe₃)₂Yb(THF), **C.1-Yb**.

Cnt1-Yb(1)	2.395	Cnt2-Yb(1)	2.421
Yb(1)-O(1)	2.4276(14)	Yb(1)-C(1)	2.621(2)
Yb(1)-C(5)	2.658(2)	Yb(1)-C(13)	2.659(2)
Yb(1)-C(2)	2.6769(19)	Yb(1)-C(17)	2.678(2)
Yb(1)-C(14)	2.7095(19)	Yb(1)-C(3)	2.7277(19)
Yb(1)-C(4)	2.7330(19)	Yb(1)-C(16)	2.738(2)
Yb(1)-C(15)	2.7491(19)	Si(1)-C(1)	1.854(2)
Si(1)-C(12)	1.865(3)	Si(1)-C(11)	1.867(3)
Si(1)-C(10)	1.881(2)	Si(2)-C(13)	1.857(2)
Si(2)-C(24)	1.870(2)	Si(2)-C(23)	1.873(3)
Si(2)-C(22)	1.879(2)	O(1)-C(25)	1.446(3)
O(1)-C(28)	1.453(3)	C(1)-C(5)	1.436(3)
C(1)-C(2)	1.439(3)	C(2)-C(3)	1.411(3)

C(2)-C(6)	1.507(3)	C(3)-C(4)	1.425(3)
C(3)-C(7)	1.504(3)	C(4)-C(5)	1.406(3)
C(4)-C(8)	1.507(3)	C(5)-C(9)	1.508(3)
C(13)-C(17)	1.438(3)	C(13)-C(14)	1.439(3)
C(14)-C(15)	1.411(3)	C(14)-C(18)	1.508(3)
C(15)-C(16)	1.426(3)	C(15)-C(19)	1.509(3)
C(16)-C(17)	1.408(3)	C(16)-C(20)	1.509(3)
C(17)-C(21)	1.507(3)	C(25)-C(26)	1.506(3)
C(26)-C(27)	1.515(4)	C(27)-C(28)	1.506(3)
		Cnt1-Yb(1)-Cnt2	143.5
Cnt1-Yb(1)-O(1)	107.6	Cnt2-Yb(1)-O(1)	108.4
O(1)-Yb(1)-C(1)	108.73(6)	O(1)-Yb(1)-C(5)	82.95(6)
C(1)-Yb(1)-C(5)	31.57(6)	O(1)-Yb(1)-C(13)	104.23(6)
C(1)-Yb(1)-C(13)	146.68(6)	C(5)-Yb(1)-C(13)	155.88(6)
O(1)-Yb(1)-C(2)	133.83(6)	C(1)-Yb(1)-C(2)	31.50(6)
C(5)-Yb(1)-C(2)	51.03(6)	C(13)-Yb(1)-C(2)	116.69(6)
O(1)-Yb(1)-C(17)	82.28(6)	C(1)-Yb(1)-C(17)	159.79(6)
C(5)-Yb(1)-C(17)	165.19(6)	C(13)-Yb(1)-C(17)	31.26(6)
C(2)-Yb(1)-C(17)	143.60(6)	O(1)-Yb(1)-C(14)	132.46(6)
C(1)-Yb(1)-C(14)	118.11(6)	C(5)-Yb(1)-C(14)	143.84(6)
C(13)-Yb(1)-C(14)	31.09(6)	C(2)-Yb(1)-C(14)	92.98(6)
C(17)-Yb(1)-C(14)	50.62(6)	O(1)-Yb(1)-C(3)	118.51(5)
C(1)-Yb(1)-C(3)	51.25(6)	C(5)-Yb(1)-C(3)	50.31(6)
C(13)-Yb(1)-C(3)	107.68(6)	C(2)-Yb(1)-C(3)	30.24(6)
C(17)-Yb(1)-C(3)	138.66(6)	C(14)-Yb(1)-C(3)	97.70(6)
O(1)-Yb(1)-C(4)	89.08(5)	C(1)-Yb(1)-C(4)	51.19(6)
C(5)-Yb(1)-C(4)	30.20(6)	C(13)-Yb(1)-C(4)	125.85(6)
C(2)-Yb(1)-C(4)	50.20(6)	C(17)-Yb(1)-C(4)	148.20(6)
C(14)-Yb(1)-C(4)	126.31(6)	C(3)-Yb(1)-C(4)	30.24(6)
O(1)-Yb(1)-C(16)	93.65(6)	C(1)-Yb(1)-C(16)	130.03(6)
C(5)-Yb(1)-C(16)	152.98(6)	C(13)-Yb(1)-C(16)	50.76(6)
C(2)-Yb(1)-C(16)	128.32(6)	C(17)-Yb(1)-C(16)	30.11(6)
C(14)-Yb(1)-C(16)	49.90(6)	C(3)-Yb(1)-C(16)	146.44(6)
C(4)-Yb(1)-C(16)	176.14(6)	O(1)-Yb(1)-C(15)	123.74(6)
C(1)-Yb(1)-C(15)	111.11(6)	C(5)-Yb(1)-C(15)	142.58(6)
C(13)-Yb(1)-C(15)	50.62(6)	C(2)-Yb(1)-C(15)	99.36(6)
C(17)-Yb(1)-C(15)	49.97(6)	C(14)-Yb(1)-C(15)	29.95(6)
C(3)-Yb(1)-C(15)	117.23(6)	C(4)-Yb(1)-C(15)	147.17(6)
C(16)-Yb(1)-C(15)	30.12(6)	C(1)-Si(1)-C(12)	113.68(11)
C(1)-Si(1)-C(11)	113.12(11)	C(12)-Si(1)-C(11)	106.46(15)
C(1)-Si(1)-C(10)	108.52(10)	C(12)-Si(1)-C(10)	107.21(12)
C(11)-Si(1)-C(10)	107.52(14)	C(13)-Si(2)-C(24)	114.64(10)
C(13)-Si(2)-C(23)	111.89(10)	C(24)-Si(2)-C(23)	106.05(12)
C(13)-Si(2)-C(22)	108.72(10)	C(24)-Si(2)-C(22)	107.00(11)
C(23)-Si(2)-C(22)	108.26(12)	C(25)-O(1)-C(28)	108.55(16)

C(25)-O(1)-Yb(1)	127.79(12)	C(28)-O(1)-Yb(1)	123.52(12)
C(5)-C(1)-C(2)	106.12(17)	C(5)-C(1)-Si(1)	124.39(15)
C(2)-C(1)-Si(1)	129.38(15)	C(5)-C(1)-Yb(1)	75.65(12)
C(2)-C(1)-Yb(1)	76.40(11)	Si(1)-C(1)-Yb(1)	110.66(9)
C(3)-C(2)-C(1)	108.69(17)	C(3)-C(2)-C(6)	124.06(19)
C(1)-C(2)-C(6)	127.00(19)	C(3)-C(2)-Yb(1)	76.87(11)
C(1)-C(2)-Yb(1)	72.10(11)	C(6)-C(2)-Yb(1)	121.80(14)
C(2)-C(3)-C(4)	108.11(17)	C(2)-C(3)-C(7)	127.87(18)
C(4)-C(3)-C(7)	123.73(18)	C(2)-C(3)-Yb(1)	72.89(11)
C(4)-C(3)-Yb(1)	75.09(11)	C(7)-C(3)-Yb(1)	122.79(14)
C(5)-C(4)-C(3)	108.00(17)	C(5)-C(4)-C(8)	127.14(18)
C(3)-C(4)-C(8)	124.10(18)	C(5)-C(4)-Yb(1)	71.95(11)
C(3)-C(4)-Yb(1)	74.67(11)	C(8)-C(4)-Yb(1)	127.03(14)
C(4)-C(5)-C(1)	109.04(17)	C(4)-C(5)-C(9)	125.01(18)
C(1)-C(5)-C(9)	125.83(19)	C(4)-C(5)-Yb(1)	77.84(11)
C(1)-C(5)-Yb(1)	72.78(11)	C(9)-C(5)-Yb(1)	119.07(13)
C(17)-C(13)-C(14)	106.37(17)	C(17)-C(13)-Si(2)	123.66(15)
C(14)-C(13)-Si(2)	129.87(15)	C(17)-C(13)-Yb(1)	75.09(11)
C(14)-C(13)-Yb(1)	76.40(11)	Si(2)-C(13)-Yb(1)	116.95(9)
C(15)-C(14)-C(13)	108.52(17)	C(15)-C(14)-C(18)	124.73(18)
C(13)-C(14)-C(18)	126.41(18)	C(15)-C(14)-Yb(1)	76.58(11)
C(13)-C(14)-Yb(1)	72.52(11)	C(18)-C(14)-Yb(1)	122.37(13)
C(14)-C(15)-C(16)	108.23(18)	C(14)-C(15)-C(19)	126.90(19)
C(16)-C(15)-C(19)	124.61(18)	C(14)-C(15)-Yb(1)	73.47(11)
C(16)-C(15)-Yb(1)	74.50(11)	C(19)-C(15)-Yb(1)	122.71(13)
C(17)-C(16)-C(15)	108.06(17)	C(17)-C(16)-C(20)	126.6(2)
C(15)-C(16)-C(20)	124.82(19)	C(17)-C(16)-Yb(1)	72.58(11)
C(15)-C(16)-Yb(1)	75.38(11)	C(20)-C(16)-Yb(1)	124.32(14)
C(16)-C(17)-C(13)	108.82(18)	C(16)-C(17)-C(21)	124.94(18)
C(13)-C(17)-C(21)	126.07(18)	C(16)-C(17)-Yb(1)	77.31(12)
C(13)-C(17)-Yb(1)	73.65(11)	C(21)-C(17)-Yb(1)	119.21(13)
O(1)-C(25)-C(26)	105.85(19)	C(25)-C(26)-C(27)	101.60(19)
C(28)-C(27)-C(26)	101.45(19)	O(1)-C(28)-C(27)	105.40(18)

X-ray Data Collection, Structure Solution and Refinement for (C₅Me₄SiMe₃)₂Eu(THF), C.1-Eu. An orange crystal of approximate dimensions 0.116 x 0.276 x 0.413 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2¹⁵ program package was used to determine the unit-cell parameters. Data collection used a 20 sec/frame scan time. The raw frame data was processed using SAINT¹⁶ and SADABS¹⁷ to yield the reflection data file. Subsequent calculations were carried out using the

SHELXTL¹⁸ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors¹⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded $wR2 = 0.0652$ and $Goof = 1.163$ for 303 variables refined against 9255 data ($0.69 \text{ \AA}$), $R1 = 0.0314$ for those 7920 data with $I > 2.0\sigma(I)$.

Table C.8. Crystal data and structure refinement for $(C_5Me_4SiMe_3)_2Eu(THF)$, **C.1-Eu**.

Identification code	gn3 (Gabija Navickaite)	
Empirical formula	$C_{28} H_{50} Eu O Si_2$	
Formula weight	610.82	
Temperature	133(2) K	
Wavelength	$0.71073 \text{ \AA}$	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 17.872(3) \text{ \AA}$	$\alpha = 90^\circ$.
	$b = 11.0698(18) \text{ \AA}$	$\beta = 104.570(3)^\circ$.
	$c = 15.805(3) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$3026.4(9) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.341 Mg/m^3	
Absorption coefficient	2.168 mm^{-1}	
F(000)	1268	
Crystal color	orange	
Crystal size	$0.413 \times 0.276 \times 0.116 \text{ mm}^3$	
Theta range for data collection	1.177 to 31.131°	
Index ranges	$-25 \leq h \leq 25$, $-16 \leq k \leq 16$, $-22 \leq l \leq 22$	
Reflections collected	72722	
Independent reflections	9255 [$R(\text{int}) = 0.0460$]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7462 and 0.5889	

Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9255 / 0 / 303	
Goodness-of-fit on F ²	1.163	
Final R indices [I>2sigma(I) = 7920 data]	R1 = 0.0314, wR2 = 0.0625	
R indices (all data, 0.69 Å)	R1 = 0.0410, wR2 = 0.0652	
Largest diff. peak and hole	1.272 and -1.772 e.Å ⁻³	

Table C.9. Bond lengths [Å] and angles [°] for (C₅Me₄SiMe₃)₂Eu(THF), **C.1-Eu**.

Cnt1-Eu(1)	2.516	Cnt2-Eu(1)	2.552
Eu(1)-O(1)	2.5541(18)	Eu(1)-C(1)	2.727(3)
Eu(1)-C(13)	2.766(3)	Eu(1)-C(5)	2.768(3)
Eu(1)-C(2)	2.777(2)	Eu(1)-C(17)	2.778(3)
Eu(1)-C(3)	2.835(2)	Eu(1)-C(14)	2.837(2)
Eu(1)-C(4)	2.846(2)	Eu(1)-C(16)	2.855(2)
Eu(1)-C(15)	2.881(2)	Si(1)-C(1)	1.853(3)
Si(1)-C(11)	1.861(3)	Si(1)-C(12)	1.861(3)
Si(1)-C(10)	1.884(3)	Si(2)-C(13)	1.851(3)
Si(2)-C(24)	1.871(3)	Si(2)-C(23)	1.874(3)
Si(2)-C(22)	1.883(3)	O(1)-C(25)	1.443(4)
O(1)-C(28)	1.450(3)	C(1)-C(2)	1.435(3)
C(1)-C(5)	1.437(3)	C(2)-C(3)	1.405(4)
C(2)-C(6)	1.511(3)	C(3)-C(4)	1.423(3)
C(3)-C(7)	1.501(3)	C(4)-C(5)	1.403(4)
C(4)-C(8)	1.503(4)	C(5)-C(9)	1.512(3)
C(13)-C(14)	1.431(3)	C(13)-C(17)	1.437(3)
C(14)-C(15)	1.408(3)	C(14)-C(18)	1.507(3)
C(15)-C(16)	1.417(4)	C(15)-C(19)	1.515(4)
C(16)-C(17)	1.403(4)	C(16)-C(20)	1.514(3)
C(17)-C(21)	1.508(4)	C(25)-C(26)	1.452(5)
C(26)-C(27)	1.512(6)	C(27)-C(28)	1.489(4)
		Cnt1-Eu(1)-Cnt2	142.0
Cnt1-Eu(1)-O(1)	106.5	Cnt2-Eu(1)-O(1)	110.6
O(1)-Eu(1)-C(1)	109.19(7)	O(1)-Eu(1)-C(13)	104.91(7)
C(1)-Eu(1)-C(13)	145.05(7)	O(1)-Eu(1)-C(5)	83.52(7)
C(1)-Eu(1)-C(5)	30.30(7)	C(13)-Eu(1)-C(5)	154.90(7)
O(1)-Eu(1)-C(2)	131.84(7)	C(1)-Eu(1)-C(2)	30.20(7)
C(13)-Eu(1)-C(2)	116.32(7)	C(5)-Eu(1)-C(2)	48.77(7)
O(1)-Eu(1)-C(17)	85.27(7)	C(1)-Eu(1)-C(17)	159.30(8)

C(13)-Eu(1)-C(17)	30.04(7)	C(5)-Eu(1)-C(17)	168.73(7)
C(2)-Eu(1)-C(17)	142.14(7)	O(1)-Eu(1)-C(3)	115.81(7)
C(1)-Eu(1)-C(3)	49.06(8)	C(13)-Eu(1)-C(3)	108.27(7)
C(5)-Eu(1)-C(3)	48.03(7)	C(2)-Eu(1)-C(3)	28.98(7)
C(17)-Eu(1)-C(3)	138.16(7)	O(1)-Eu(1)-C(14)	132.51(7)
C(1)-Eu(1)-C(14)	118.16(7)	C(13)-Eu(1)-C(14)	29.56(7)
C(5)-Eu(1)-C(14)	142.50(7)	C(2)-Eu(1)-C(14)	93.93(7)
C(17)-Eu(1)-C(14)	48.21(7)	C(3)-Eu(1)-C(14)	98.42(7)
O(1)-Eu(1)-C(4)	87.84(7)	C(1)-Eu(1)-C(4)	49.08(8)
C(13)-Eu(1)-C(4)	126.44(7)	C(5)-Eu(1)-C(4)	28.90(7)
C(2)-Eu(1)-C(4)	48.10(7)	C(17)-Eu(1)-C(4)	149.42(8)
C(3)-Eu(1)-C(4)	29.01(7)	C(14)-Eu(1)-C(4)	125.88(7)
O(1)-Eu(1)-C(16)	97.67(7)	C(1)-Eu(1)-C(16)	131.29(8)
C(13)-Eu(1)-C(16)	48.51(7)	C(5)-Eu(1)-C(16)	155.24(8)
C(2)-Eu(1)-C(16)	127.91(7)	C(17)-Eu(1)-C(16)	28.81(7)
C(3)-Eu(1)-C(16)	144.64(7)	C(14)-Eu(1)-C(16)	47.47(7)
C(4)-Eu(1)-C(16)	173.35(7)	O(1)-Eu(1)-C(15)	126.27(7)
C(1)-Eu(1)-C(15)	112.43(7)	C(13)-Eu(1)-C(15)	48.14(7)
C(5)-Eu(1)-C(15)	142.72(8)	C(2)-Eu(1)-C(15)	100.31(7)
C(17)-Eu(1)-C(15)	47.51(8)	C(3)-Eu(1)-C(15)	116.88(7)
C(14)-Eu(1)-C(15)	28.51(7)	C(4)-Eu(1)-C(15)	145.68(7)
C(16)-Eu(1)-C(15)	28.60(7)	C(1)-Si(1)-C(11)	113.99(15)
C(1)-Si(1)-C(12)	113.39(14)	C(11)-Si(1)-C(12)	107.16(19)
C(1)-Si(1)-C(10)	108.25(12)	C(11)-Si(1)-C(10)	106.39(17)
C(12)-Si(1)-C(10)	107.25(16)	C(13)-Si(2)-C(24)	114.53(13)
C(13)-Si(2)-C(23)	112.31(13)	C(24)-Si(2)-C(23)	106.41(15)
C(13)-Si(2)-C(22)	107.10(13)	C(24)-Si(2)-C(22)	107.24(15)
C(23)-Si(2)-C(22)	109.05(15)	C(25)-O(1)-C(28)	107.3(2)
C(25)-O(1)-Eu(1)	130.51(16)	C(28)-O(1)-Eu(1)	121.85(16)
C(2)-C(1)-C(5)	105.8(2)	C(2)-C(1)-Si(1)	129.10(19)
C(5)-C(1)-Si(1)	124.40(19)	C(2)-C(1)-Eu(1)	76.83(15)
C(5)-C(1)-Eu(1)	76.46(15)	Si(1)-C(1)-Eu(1)	105.03(11)
C(3)-C(2)-C(1)	108.9(2)	C(3)-C(2)-C(6)	124.0(2)
C(1)-C(2)-C(6)	127.0(2)	C(3)-C(2)-Eu(1)	77.81(14)
C(1)-C(2)-Eu(1)	72.96(14)	C(6)-C(2)-Eu(1)	119.37(17)
C(2)-C(3)-C(4)	108.3(2)	C(2)-C(3)-C(7)	127.4(2)
C(4)-C(3)-C(7)	124.1(2)	C(2)-C(3)-Eu(1)	73.21(14)
C(4)-C(3)-Eu(1)	75.94(13)	C(7)-C(3)-Eu(1)	121.67(17)
C(5)-C(4)-C(3)	107.6(2)	C(5)-C(4)-C(8)	127.3(2)
C(3)-C(4)-C(8)	124.5(2)	C(5)-C(4)-Eu(1)	72.46(14)
C(3)-C(4)-Eu(1)	75.05(13)	C(8)-C(4)-Eu(1)	125.11(18)
C(4)-C(5)-C(1)	109.4(2)	C(4)-C(5)-C(9)	125.2(2)
C(1)-C(5)-C(9)	125.3(2)	C(4)-C(5)-Eu(1)	78.63(15)
C(1)-C(5)-Eu(1)	73.24(14)	C(9)-C(5)-Eu(1)	116.70(17)
C(14)-C(13)-C(17)	106.2(2)	C(14)-C(13)-Si(2)	130.21(19)

C(17)-C(13)-Si(2)	123.59(19)	C(14)-C(13)-Eu(1)	77.98(14)
C(17)-C(13)-Eu(1)	75.42(14)	Si(2)-C(13)-Eu(1)	112.03(11)
C(15)-C(14)-C(13)	108.6(2)	C(15)-C(14)-C(18)	124.5(2)
C(13)-C(14)-C(18)	126.7(2)	C(15)-C(14)-Eu(1)	77.47(14)
C(13)-C(14)-Eu(1)	72.46(14)	C(18)-C(14)-Eu(1)	120.46(17)
C(14)-C(15)-C(16)	108.4(2)	C(14)-C(15)-C(19)	126.2(2)
C(16)-C(15)-C(19)	125.2(2)	C(14)-C(15)-Eu(1)	74.03(13)
C(16)-C(15)-Eu(1)	74.67(14)	C(19)-C(15)-Eu(1)	121.64(17)
C(17)-C(16)-C(15)	108.0(2)	C(17)-C(16)-C(20)	126.4(2)
C(15)-C(16)-C(20)	125.4(2)	C(17)-C(16)-Eu(1)	72.54(14)
C(15)-C(16)-Eu(1)	76.73(14)	C(20)-C(16)-Eu(1)	121.27(17)
C(16)-C(17)-C(13)	108.9(2)	C(16)-C(17)-C(21)	124.9(2)
C(13)-C(17)-C(21)	126.1(2)	C(16)-C(17)-Eu(1)	78.65(15)
C(13)-C(17)-Eu(1)	74.54(14)	C(21)-C(17)-Eu(1)	116.06(17)
O(1)-C(25)-C(26)	108.1(3)	C(25)-C(26)-C(27)	104.6(3)
C(28)-C(27)-C(26)	101.7(3)	O(1)-C(28)-C(27)	105.1(2)

X-ray Data Collection, Structure Solution and Refinement for (C₅Me₄SiMe₃)₂Sm(bipy), C.2-Sm. A purple crystal of approximate dimensions 0.281 x 0.313 x 0.338 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2¹⁵ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time). The raw frame data was processed using SAINT¹⁶ and SADABS¹⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL¹⁸ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors¹⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded wR2 = 0.0582 and Goof = 1.072 for 366 variables refined against 9644 data (0.70 Å), R1 = 0.0223 for those 9188 data with I > 2.0σ(I).

Table C.10. Crystal data and structure refinement for (C₅Me₄SiMe₃)₂Sm(bipy), C.2-Sm.

Identification code	jqn24 (Joseph Nguyen)	
Empirical formula	C ₃₄ H ₅₀ N ₂ Si ₂ Sm	
Formula weight	693.29	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 10.2533(9) Å	α = 94.9500(10)°.
	b = 10.8973(9) Å	β = 91.2590(10)°.
	c = 14.9772(13) Å	γ = 99.9770(10)°.
Volume	1640.8(2) Å ³	
Z	2	
Density (calculated)	1.403 Mg/m ³	
Absorption coefficient	1.887 mm ⁻¹	
F(000)	716	
Crystal color	purple	
Crystal size	0.338 x 0.313 x 0.281 mm ³	
Theta range for data collection	1.366 to 30.523°	
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -21 ≤ l ≤ 20	
Reflections collected	40327	
Independent reflections	9644 [R(int) = 0.0568]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7437 and 0.6633	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9644 / 0 / 366	
Goodness-of-fit on F ²	1.072	
Final R indices [I > 2σ(I) = 9188 data]	R1 = 0.0223, wR2 = 0.0573	
R indices (all data, 0.70 Å)	R1 = 0.0237, wR2 = 0.0582	
Largest diff. peak and hole	0.603 and -0.407 e.Å ⁻³	

Table C.11. Bond lengths [Å] and angles [°] for (C₅Me₄SiMe₃)₂Sm(bipy), **C.2-Sm**.

Cnt1-Sm(1)	2.450	Cnt2-Sm(1)	2.459
Sm(1)-N(2)	2.4224(14)	Sm(1)-N(1)	2.4336(14)
Sm(1)-C(13)	2.6946(15)	Sm(1)-C(1)	2.7063(15)
Sm(1)-C(17)	2.7100(15)	Sm(1)-C(5)	2.7129(16)
Sm(1)-C(2)	2.7351(15)	Sm(1)-C(4)	2.7484(16)

Sm(1)-C(14)	2.7493(15)	Sm(1)-C(16)	2.7610(15)
Sm(1)-C(3)	2.7645(16)	Sm(1)-C(15)	2.7910(15)
Si(1)-C(12)	1.8636(18)	Si(1)-C(1)	1.8690(16)
Si(1)-C(11)	1.875(2)	Si(1)-C(10)	1.8825(19)
Si(2)-C(22)	1.869(2)	Si(2)-C(13)	1.8693(17)
Si(2)-C(23)	1.8748(18)	Si(2)-C(24)	1.8793(18)
N(1)-C(25)	1.355(2)	N(1)-C(29)	1.385(2)
N(2)-C(34)	1.356(2)	N(2)-C(30)	1.382(2)
C(1)-C(2)	1.441(2)	C(1)-C(5)	1.442(2)
C(2)-C(3)	1.407(2)	C(2)-C(6)	1.504(2)
C(3)-C(4)	1.420(2)	C(3)-C(7)	1.507(2)
C(4)-C(5)	1.415(2)	C(4)-C(8)	1.504(2)
C(5)-C(9)	1.508(2)	C(13)-C(14)	1.436(2)
C(13)-C(17)	1.438(2)	C(14)-C(15)	1.411(2)
C(14)-C(18)	1.508(2)	C(15)-C(16)	1.420(2)
C(15)-C(19)	1.506(2)	C(16)-C(17)	1.415(2)
C(16)-C(20)	1.507(2)	C(17)-C(21)	1.505(2)
C(25)-C(26)	1.370(2)	C(26)-C(27)	1.416(3)
C(27)-C(28)	1.366(3)	C(28)-C(29)	1.414(2)
C(29)-C(30)	1.430(2)	C(30)-C(31)	1.415(2)
C(31)-C(32)	1.368(3)	C(32)-C(33)	1.411(3)
C(33)-C(34)	1.366(2)		
Cnt1-Sm(1)-Cnt2	137.1	Cnt1-Sm(1)-N(1)	108.8
Cnt1-Sm(1)-N(2)	104.7	Cnt2-Sm(1)-N(1)	111.7
Cnt2-Sm(1)-N(2)	103.7	N(2)-Sm(1)-N(1)	66.73(5)
N(2)-Sm(1)-C(13)	106.76(5)	N(1)-Sm(1)-C(13)	87.94(5)
N(2)-Sm(1)-C(1)	120.82(5)	N(1)-Sm(1)-C(1)	94.33(5)
C(13)-Sm(1)-C(1)	129.01(5)	N(2)-Sm(1)-C(17)	80.13(5)
N(1)-Sm(1)-C(17)	91.49(5)	C(13)-Sm(1)-C(17)	30.85(5)
C(1)-Sm(1)-C(17)	158.83(5)	N(2)-Sm(1)-C(5)	128.52(5)
N(1)-Sm(1)-C(5)	125.20(5)	C(13)-Sm(1)-C(5)	122.32(5)
C(1)-Sm(1)-C(5)	30.87(4)	C(17)-Sm(1)-C(5)	138.68(5)
N(2)-Sm(1)-C(2)	90.16(5)	N(1)-Sm(1)-C(2)	83.14(5)
C(13)-Sm(1)-C(2)	155.94(5)	C(1)-Sm(1)-C(2)	30.70(5)
C(17)-Sm(1)-C(2)	170.16(5)	C(5)-Sm(1)-C(2)	49.95(5)
N(2)-Sm(1)-C(4)	101.09(5)	N(1)-Sm(1)-C(4)	131.90(5)
C(13)-Sm(1)-C(4)	138.42(5)	C(1)-Sm(1)-C(4)	50.43(5)
C(17)-Sm(1)-C(4)	133.84(5)	C(5)-Sm(1)-C(4)	30.02(5)
C(2)-Sm(1)-C(4)	49.47(5)	N(2)-Sm(1)-C(14)	129.44(5)
N(1)-Sm(1)-C(14)	114.81(5)	C(13)-Sm(1)-C(14)	30.57(5)
C(1)-Sm(1)-C(14)	109.62(5)	C(17)-Sm(1)-C(14)	49.84(5)
C(5)-Sm(1)-C(14)	93.42(5)	C(2)-Sm(1)-C(14)	139.99(5)
C(4)-Sm(1)-C(14)	108.35(5)	N(2)-Sm(1)-C(16)	84.70(5)
N(1)-Sm(1)-C(16)	119.92(5)	C(13)-Sm(1)-C(16)	50.20(5)
C(1)-Sm(1)-C(16)	144.31(5)	C(17)-Sm(1)-C(16)	29.95(5)

C(5)-Sm(1)-C(16)	114.14(5)	C(2)-Sm(1)-C(16)	151.31(5)
C(4)-Sm(1)-C(16)	103.89(5)	C(14)-Sm(1)-C(16)	49.15(5)
N(2)-Sm(1)-C(3)	79.52(5)	N(1)-Sm(1)-C(3)	103.96(5)
C(13)-Sm(1)-C(3)	168.05(5)	C(1)-Sm(1)-C(3)	50.10(5)
C(17)-Sm(1)-C(3)	146.91(5)	C(5)-Sm(1)-C(3)	49.45(5)
C(2)-Sm(1)-C(3)	29.65(5)	C(4)-Sm(1)-C(3)	29.85(5)
C(14)-Sm(1)-C(3)	138.15(5)	C(16)-Sm(1)-C(3)	121.96(5)
N(2)-Sm(1)-C(15)	113.45(5)	N(1)-Sm(1)-C(15)	137.16(5)
C(13)-Sm(1)-C(15)	49.89(5)	C(1)-Sm(1)-C(15)	116.76(5)
C(17)-Sm(1)-C(15)	49.32(5)	C(5)-Sm(1)-C(15)	89.54(5)
C(2)-Sm(1)-C(15)	138.16(5)	C(4)-Sm(1)-C(15)	90.87(5)
C(14)-Sm(1)-C(15)	29.51(5)	C(16)-Sm(1)-C(15)	29.62(5)
C(3)-Sm(1)-C(15)	118.45(5)	C(12)-Si(1)-C(1)	113.46(8)
C(12)-Si(1)-C(11)	106.22(9)	C(1)-Si(1)-C(11)	109.38(8)
C(12)-Si(1)-C(10)	106.78(9)	C(1)-Si(1)-C(10)	113.44(8)
C(11)-Si(1)-C(10)	107.14(10)	C(22)-Si(2)-C(13)	113.86(9)
C(22)-Si(2)-C(23)	108.25(9)	C(13)-Si(2)-C(23)	106.43(8)
C(22)-Si(2)-C(24)	106.17(9)	C(13)-Si(2)-C(24)	114.44(8)
C(23)-Si(2)-C(24)	107.41(9)	C(25)-N(1)-C(29)	117.63(14)
C(25)-N(1)-Sm(1)	122.63(11)	C(29)-N(1)-Sm(1)	119.67(10)
C(34)-N(2)-C(30)	117.98(14)	C(34)-N(2)-Sm(1)	121.91(11)
C(30)-N(2)-Sm(1)	120.05(10)	C(2)-C(1)-C(5)	105.87(13)
C(2)-C(1)-Si(1)	127.67(12)	C(5)-C(1)-Si(1)	124.02(12)
C(2)-C(1)-Sm(1)	75.76(9)	C(5)-C(1)-Sm(1)	74.82(9)
Si(1)-C(1)-Sm(1)	128.57(7)	C(3)-C(2)-C(1)	108.89(14)
C(3)-C(2)-C(6)	123.42(15)	C(1)-C(2)-C(6)	127.64(15)
C(3)-C(2)-Sm(1)	76.33(9)	C(1)-C(2)-Sm(1)	73.54(8)
C(6)-C(2)-Sm(1)	118.68(11)	C(2)-C(3)-C(4)	108.50(14)
C(2)-C(3)-C(7)	126.43(15)	C(4)-C(3)-C(7)	124.69(15)
C(2)-C(3)-Sm(1)	74.02(9)	C(4)-C(3)-Sm(1)	74.45(9)
C(7)-C(3)-Sm(1)	123.22(11)	C(5)-C(4)-C(3)	107.87(14)
C(5)-C(4)-C(8)	127.33(15)	C(3)-C(4)-C(8)	124.49(15)
C(5)-C(4)-Sm(1)	73.60(9)	C(3)-C(4)-Sm(1)	75.71(9)
C(8)-C(4)-Sm(1)	121.71(11)	C(4)-C(5)-C(1)	108.87(13)
C(4)-C(5)-C(9)	125.07(14)	C(1)-C(5)-C(9)	125.84(14)
C(4)-C(5)-Sm(1)	76.38(9)	C(1)-C(5)-Sm(1)	74.31(9)
C(9)-C(5)-Sm(1)	119.98(10)	C(14)-C(13)-C(17)	106.37(14)
C(14)-C(13)-Si(2)	123.46(12)	C(17)-C(13)-Si(2)	126.72(12)
C(14)-C(13)-Sm(1)	76.82(9)	C(17)-C(13)-Sm(1)	75.17(9)
Si(2)-C(13)-Sm(1)	130.24(7)	C(15)-C(14)-C(13)	108.78(14)
C(15)-C(14)-C(18)	125.04(15)	C(13)-C(14)-C(18)	125.77(15)
C(15)-C(14)-Sm(1)	76.88(9)	C(13)-C(14)-Sm(1)	72.61(8)
C(18)-C(14)-Sm(1)	122.62(10)	C(14)-C(15)-C(16)	108.10(14)
C(14)-C(15)-C(19)	127.50(16)	C(16)-C(15)-C(19)	123.64(15)
C(14)-C(15)-Sm(1)	73.61(9)	C(16)-C(15)-Sm(1)	74.02(9)

C(19)-C(15)-Sm(1)	126.09(11)	C(17)-C(16)-C(15)	108.24(14)
C(17)-C(16)-C(20)	127.55(16)	C(15)-C(16)-C(20)	123.71(16)
C(17)-C(16)-Sm(1)	73.03(8)	C(15)-C(16)-Sm(1)	76.36(9)
C(20)-C(16)-Sm(1)	123.10(11)	C(16)-C(17)-C(13)	108.50(14)
C(16)-C(17)-C(21)	124.56(15)	C(13)-C(17)-C(21)	126.89(15)
C(16)-C(17)-Sm(1)	77.02(9)	C(13)-C(17)-Sm(1)	73.98(8)
C(21)-C(17)-Sm(1)	117.56(11)	N(1)-C(25)-C(26)	124.63(16)
C(25)-C(26)-C(27)	117.83(16)	C(28)-C(27)-C(26)	119.11(16)
C(27)-C(28)-C(29)	120.73(16)	N(1)-C(29)-C(28)	120.02(15)
N(1)-C(29)-C(30)	116.46(14)	C(28)-C(29)-C(30)	123.53(15)
N(2)-C(30)-C(31)	119.72(15)	N(2)-C(30)-C(29)	116.82(14)
C(31)-C(30)-C(29)	123.45(15)	C(32)-C(31)-C(30)	120.73(16)
C(31)-C(32)-C(33)	119.06(16)	C(34)-C(33)-C(32)	118.11(16)
N(2)-C(34)-C(33)	124.38(16)		

X-ray Data Collection, Structure Solution and Refinement for (C₅Me₄SiMe₃)₂Yb(bipy), C.2-Yb. A black crystal of approximate dimensions 0.206 x 0.232 x 0.356 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2¹⁵ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time). The raw frame data was processed using SAINT¹⁶ and SADABS¹⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL¹⁸ program package. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that space group $C2/c$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors¹⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There was half a molecule of diethyl ether solvent present in the asymmetric unit. Least-squares analysis yielded $wR2 = 0.0683$ and $Goof = 1.057$ for 390 variables refined against 10681 data (0.70 Å), $R1 = 0.0286$ for those 9263 data with $I > 2.0\sigma(I)$.

Table C.12. Crystal data and structure refinement for (C₅Me₄SiMe₃)₂Yb(bipy), C.2-Yb.

Identification code	jqn39 (Joseph Nguyen)	

Empirical formula	C ₃₅ H _{52.50} N ₂ O _{0.50} Si ₂ Yb	
Formula weight	738.51	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.317(3) Å	α = 90°.
	b = 24.512(3) Å	β = 132.4130(10)°.
	c = 16.815(3) Å	γ = 90°.
Volume	7095.7(18) Å ³	
Z	8	
Density (calculated)	1.383 Mg/m ³	
Absorption coefficient	2.730 mm ⁻¹	
F(000)	3028	
Crystal color	black	
Crystal size	0.356 x 0.232 x 0.206 mm ³	
Theta range for data collection	1.445 to 30.560°	
Index ranges	-32 ≤ h ≤ 33, -34 ≤ k ≤ 34, -24 ≤ l ≤ 23	
Reflections collected	87266	
Independent reflections	10681 [R(int) = 0.0546]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6611	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10681 / 0 / 390	
Goodness-of-fit on F ²	1.057	
Final R indices [I > 2σ(I) = 9263 data]	R1 = 0.0286, wR2 = 0.0646	
R indices (all data, 0.70 Å)	R1 = 0.0363, wR2 = 0.0683	
Largest diff. peak and hole	2.502 and -2.101 e.Å ⁻³	

Table C.13. Bond lengths [Å] and angles [°] for (C₅Me₄SiMe₃)₂Yb(bipy), **C.2-Yb**.

Cnt1-Yb(1)	2.4425(3)	Cnt2-Yb(1)	2.4429(2)
Yb(1)-N(1)	2.455(2)	Yb(1)-N(2)	2.479(2)

Yb(1)-C(2)	2.699(3)	Yb(1)-C(13)	2.700(3)
Yb(1)-C(1)	2.700(3)	Yb(1)-C(14)	2.714(3)
Yb(1)-C(17)	2.724(3)	Yb(1)-C(5)	2.732(3)
Yb(1)-C(3)	2.732(3)	Yb(1)-C(16)	2.745(3)
Yb(1)-C(15)	2.749(3)	Yb(1)-C(4)	2.766(3)
Si(2)-C(13)	1.854(3)	Si(2)-C(23)	1.874(4)
Si(2)-C(24)	1.875(3)	Si(2)-C(22)	1.885(4)
Si(1)-C(1)	1.861(3)	Si(1)-C(12)	1.870(4)
Si(1)-C(10)	1.876(5)	Si(1)-C(11)	1.881(4)
N(2)-C(34)	1.341(3)	N(2)-C(30)	1.343(3)
N(1)-C(25)	1.337(3)	N(1)-C(29)	1.354(3)
C(14)-C(15)	1.408(4)	C(14)-C(13)	1.443(4)
C(14)-C(18)	1.507(4)	C(17)-C(16)	1.410(4)
C(17)-C(13)	1.436(4)	C(17)-C(21)	1.510(4)
C(15)-C(16)	1.420(4)	C(15)-C(19)	1.509(4)
C(29)-C(28)	1.393(4)	C(29)-C(30)	1.485(4)
C(34)-C(33)	1.387(4)	C(5)-C(4)	1.410(4)
C(5)-C(1)	1.436(4)	C(5)-C(9)	1.498(4)
C(1)-C(2)	1.435(4)	C(25)-C(26)	1.385(4)
C(30)-C(31)	1.402(4)	C(16)-C(20)	1.508(4)
C(32)-C(33)	1.382(5)	C(32)-C(31)	1.383(4)
C(4)-C(3)	1.421(4)	C(4)-C(8)	1.502(4)
C(2)-C(3)	1.413(4)	C(2)-C(6)	1.508(4)
C(3)-C(7)	1.508(4)	C(28)-C(27)	1.384(4)
C(27)-C(26)	1.378(5)	O(1)-C(35)#1	1.509(12)
O(1)-C(35)	1.509(12)	C(36)-C(35)	1.190(13)
		Cnt1-Yb(1)-Cnt2	140.67(6)
Cnt1-Yb(1)-N(1)	103.137(12)	Cnt1-Yb(1)-N(2)	105.784(18)
Cnt2-Yb(1)-N(1)	103.922(14)	Cnt2-Yb(1)-N(2)	111.139(7)
N(1)-Yb(1)-N(2)	65.74(7)	N(1)-Yb(1)-C(2)	128.90(8)
N(2)-Yb(1)-C(2)	119.19(8)	N(1)-Yb(1)-C(13)	104.75(8)
N(2)-Yb(1)-C(13)	86.59(8)	C(2)-Yb(1)-C(13)	125.80(8)
N(1)-Yb(1)-C(1)	115.20(8)	N(2)-Yb(1)-C(1)	88.59(8)
C(2)-Yb(1)-C(1)	30.83(9)	C(13)-Yb(1)-C(1)	133.33(8)
N(1)-Yb(1)-C(14)	79.47(8)	N(2)-Yb(1)-C(14)	92.13(8)
C(2)-Yb(1)-C(14)	143.31(8)	C(13)-Yb(1)-C(14)	30.90(8)
C(1)-Yb(1)-C(14)	163.97(8)	N(1)-Yb(1)-C(17)	129.38(8)
N(2)-Yb(1)-C(17)	112.64(8)	C(2)-Yb(1)-C(17)	97.32(8)
C(13)-Yb(1)-C(17)	30.69(8)	C(1)-Yb(1)-C(17)	115.31(8)
C(14)-Yb(1)-C(17)	49.99(8)	N(1)-Yb(1)-C(5)	85.21(8)
N(2)-Yb(1)-C(5)	81.14(8)	C(2)-Yb(1)-C(5)	50.07(8)
C(13)-Yb(1)-C(5)	159.42(8)	C(1)-Yb(1)-C(5)	30.64(8)
C(14)-Yb(1)-C(5)	164.68(8)	C(17)-Yb(1)-C(5)	145.33(8)
N(1)-Yb(1)-C(3)	104.24(8)	N(2)-Yb(1)-C(3)	130.71(8)
C(2)-Yb(1)-C(3)	30.16(8)	C(13)-Yb(1)-C(3)	140.00(8)

C(1)-Yb(1)-C(3)	50.39(8)	C(14)-Yb(1)-C(3)	135.19(8)
C(17)-Yb(1)-C(3)	109.75(8)	C(5)-Yb(1)-C(3)	49.57(8)
N(1)-Yb(1)-C(16)	115.80(8)	N(2)-Yb(1)-C(16)	136.77(8)
C(2)-Yb(1)-C(16)	93.84(8)	C(13)-Yb(1)-C(16)	50.39(8)
C(1)-Yb(1)-C(16)	122.25(8)	C(14)-Yb(1)-C(16)	49.69(8)
C(17)-Yb(1)-C(16)	29.89(8)	C(5)-Yb(1)-C(16)	140.89(8)
C(3)-Yb(1)-C(16)	92.00(8)	N(1)-Yb(1)-C(15)	86.33(8)
N(2)-Yb(1)-C(15)	121.00(8)	C(2)-Yb(1)-C(15)	118.76(9)
C(13)-Yb(1)-C(15)	50.30(8)	C(1)-Yb(1)-C(15)	149.48(8)
C(14)-Yb(1)-C(15)	29.87(8)	C(17)-Yb(1)-C(15)	49.42(8)
C(5)-Yb(1)-C(15)	149.87(8)	C(3)-Yb(1)-C(15)	105.33(8)
C(16)-Yb(1)-C(15)	29.96(8)	N(1)-Yb(1)-C(4)	79.31(8)
N(2)-Yb(1)-C(4)	104.90(8)	C(2)-Yb(1)-C(4)	49.67(8)
C(13)-Yb(1)-C(4)	168.42(8)	C(1)-Yb(1)-C(4)	50.08(8)
C(14)-Yb(1)-C(4)	144.16(8)	C(17)-Yb(1)-C(4)	139.62(8)
C(5)-Yb(1)-C(4)	29.72(8)	C(3)-Yb(1)-C(4)	29.95(8)
C(16)-Yb(1)-C(4)	118.04(8)	C(15)-Yb(1)-C(4)	120.17(8)
C(13)-Si(2)-C(23)	109.07(15)	C(13)-Si(2)-C(24)	113.74(14)
C(23)-Si(2)-C(24)	106.40(17)	C(13)-Si(2)-C(22)	114.29(15)
C(23)-Si(2)-C(22)	105.57(18)	C(24)-Si(2)-C(22)	107.18(17)
C(1)-Si(1)-C(12)	112.55(17)	C(1)-Si(1)-C(10)	114.50(18)
C(12)-Si(1)-C(10)	106.7(2)	C(1)-Si(1)-C(11)	109.20(16)
C(12)-Si(1)-C(11)	106.9(2)	C(10)-Si(1)-C(11)	106.5(2)
C(34)-N(2)-C(30)	118.0(2)	C(34)-N(2)-Yb(1)	121.47(18)
C(30)-N(2)-Yb(1)	120.47(17)	C(25)-N(1)-C(29)	117.9(2)
C(25)-N(1)-Yb(1)	120.84(18)	C(29)-N(1)-Yb(1)	121.24(17)
C(15)-C(14)-C(13)	108.7(2)	C(15)-C(14)-C(18)	124.9(2)
C(13)-C(14)-C(18)	126.3(2)	C(15)-C(14)-Yb(1)	76.44(15)
C(13)-C(14)-Yb(1)	74.03(15)	C(18)-C(14)-Yb(1)	118.77(18)
C(16)-C(17)-C(13)	109.1(2)	C(16)-C(17)-C(21)	124.3(3)
C(13)-C(17)-C(21)	126.3(3)	C(16)-C(17)-Yb(1)	75.88(15)
C(13)-C(17)-Yb(1)	73.75(15)	C(21)-C(17)-Yb(1)	121.37(19)
C(14)-C(15)-C(16)	108.4(2)	C(14)-C(15)-C(19)	126.8(3)
C(16)-C(15)-C(19)	124.4(3)	C(14)-C(15)-Yb(1)	73.70(15)
C(16)-C(15)-Yb(1)	74.86(15)	C(19)-C(15)-Yb(1)	123.03(19)
C(17)-C(13)-C(14)	105.9(2)	C(17)-C(13)-Si(2)	124.9(2)
C(14)-C(13)-Si(2)	126.5(2)	C(17)-C(13)-Yb(1)	75.56(15)
C(14)-C(13)-Yb(1)	75.07(15)	Si(2)-C(13)-Yb(1)	129.15(13)
N(1)-C(29)-C(28)	121.4(3)	N(1)-C(29)-C(30)	116.0(2)
C(28)-C(29)-C(30)	122.6(2)	N(2)-C(34)-C(33)	124.2(3)
C(4)-C(5)-C(1)	108.8(2)	C(4)-C(5)-C(9)	122.9(3)
C(1)-C(5)-C(9)	128.2(3)	C(4)-C(5)-Yb(1)	76.46(15)
C(1)-C(5)-Yb(1)	73.46(15)	C(9)-C(5)-Yb(1)	119.06(19)
C(2)-C(1)-C(5)	106.4(2)	C(2)-C(1)-Si(1)	123.1(2)
C(5)-C(1)-Si(1)	128.3(2)	C(2)-C(1)-Yb(1)	74.52(15)

C(5)-C(1)-Yb(1)	75.90(15)	Si(1)-C(1)-Yb(1)	128.00(13)
N(1)-C(25)-C(26)	123.6(3)	N(2)-C(30)-C(31)	121.4(3)
N(2)-C(30)-C(29)	116.4(2)	C(31)-C(30)-C(29)	122.2(2)
C(17)-C(16)-C(15)	107.9(2)	C(17)-C(16)-C(20)	125.9(3)
C(15)-C(16)-C(20)	125.4(3)	C(17)-C(16)-Yb(1)	74.24(15)
C(15)-C(16)-Yb(1)	75.18(15)	C(20)-C(16)-Yb(1)	124.68(19)
C(33)-C(32)-C(31)	119.6(3)	C(5)-C(4)-C(3)	108.0(2)
C(5)-C(4)-C(8)	126.0(3)	C(3)-C(4)-C(8)	125.4(3)
C(5)-C(4)-Yb(1)	73.82(15)	C(3)-C(4)-Yb(1)	73.72(15)
C(8)-C(4)-Yb(1)	125.26(18)	C(3)-C(2)-C(1)	108.6(2)
C(3)-C(2)-C(6)	124.7(3)	C(1)-C(2)-C(6)	126.4(3)
C(3)-C(2)-Yb(1)	76.23(15)	C(1)-C(2)-Yb(1)	74.64(15)
C(6)-C(2)-Yb(1)	120.86(19)	C(2)-C(3)-C(4)	108.2(2)
C(2)-C(3)-C(7)	127.5(3)	C(4)-C(3)-C(7)	124.0(3)
C(2)-C(3)-Yb(1)	73.61(15)	C(4)-C(3)-Yb(1)	76.33(15)
C(7)-C(3)-Yb(1)	121.51(19)	C(27)-C(28)-C(29)	119.8(3)
C(32)-C(31)-C(30)	119.3(3)	C(32)-C(33)-C(34)	117.5(3)
C(26)-C(27)-C(28)	118.7(3)	C(27)-C(26)-C(25)	118.6(3)
C(35)#1-O(1)-C(35)	122.6(9)	C(36)-C(35)-O(1)	114.7(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y,-z+3/2

X-ray Data Collection, Structure Solution and Refinement for (C₅Me₄SiMe₃)₂Eu(bipy), C.2-Eu. A black crystal of approximate dimensions 0.164 x 0.188 x 0.295 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2¹⁵ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time). The raw frame data was processed using SAINT¹⁶ and SADABS¹⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL¹⁸ program package. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C2/c*. It was later determined that space group *C2/c* was correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors¹⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There was a half

molecule of diethyl ether solvent present in the asymmetric unit. Least-squares analysis yielded $wR2 = 0.0640$ and $Goof = 1.059$ for 390 variables refined against 11074 data ($0.70 \text{ \AA}$), $R1 = 0.0241$ for those 9849 data with $I > 2.0\sigma(I)$.

Table C.14. Crystal data and structure refinement for $(C_5Me_4SiMe_3)_2Eu(bipy)$, **C.2-Eu**.

Identification code	jqn43 (Joseph Nguyen)	
Empirical formula	C ₃₅ H _{52.50} Eu N ₂ O _{0.50} Si ₂	
Formula weight	717.43	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.5172(16) Å	a = 90°.
	b = 24.8753(17) Å	b = 132.1440(10)°.
	c = 16.7403(12) Å	g = 90°.
Volume	7261.1(9) Å ³	
Z	8	
Density (calculated)	1.313 Mg/m ³	
Absorption coefficient	1.819 mm ⁻¹	
F(000)	2972	
Crystal color	black	
Crystal size	0.295 x 0.188 x 0.164 mm ³	
Theta range for data collection	2.318 to 30.549°	
Index ranges	-33 ≤ h ≤ 33, -35 ≤ k ≤ 35, -23 ≤ l ≤ 23	
Reflections collected	93157	
Independent reflections	11074 [R(int) = 0.0345]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6572	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11074 / 0 / 390	
Goodness-of-fit on F ²	1.059	
Final R indices [I > 2σ(I) = 9849 data]	R1 = 0.0241, wR2 = 0.0611	
R indices (all data, 0.70 Å)	R1 = 0.0293, wR2 = 0.0640	

Largest diff. peak and hole	2.087 and -0.762 e.Å ⁻³	

Table C.15. Bond lengths [Å] and angles [°] for (C₅Me₄SiMe₃)₂Eu(bipy), **C.2-Eu**.

Cnt1-Eu(1)	2.5753(11)	Cnt2-Eu(1)	2.5697(14)
Eu(1)-N(1)	2.5950(16)	Eu(1)-N(2)	2.6397(16)
Eu(1)-C(17)	2.8044(19)	Eu(1)-C(13)	2.8098(19)
Eu(1)-C(1)	2.8155(18)	Eu(1)-C(2)	2.8323(19)
Eu(1)-C(5)	2.8431(18)	Eu(1)-C(16)	2.8506(19)
Eu(1)-C(14)	2.8518(18)	Eu(1)-C(3)	2.8657(18)
Eu(1)-C(4)	2.8755(18)	Eu(1)-C(15)	2.8880(19)
Si(1)-C(1)	1.8570(19)	Si(1)-C(11)	1.879(2)
Si(1)-C(10)	1.880(2)	Si(1)-C(12)	1.880(2)
Si(2)-C(13)	1.855(2)	Si(2)-C(24)	1.873(3)
Si(2)-C(22)	1.877(3)	Si(2)-C(23)	1.879(3)
N(1)-C(25)	1.340(2)	N(1)-C(29)	1.348(2)
N(2)-C(34)	1.345(2)	N(2)-C(30)	1.349(2)
C(1)-C(5)	1.439(3)	C(1)-C(2)	1.440(3)
C(2)-C(3)	1.407(3)	C(2)-C(6)	1.515(3)
C(3)-C(4)	1.429(3)	C(3)-C(7)	1.512(3)
C(4)-C(5)	1.413(3)	C(4)-C(8)	1.503(3)
C(5)-C(9)	1.512(3)	C(13)-C(14)	1.438(3)
C(13)-C(17)	1.439(3)	C(14)-C(15)	1.412(3)
C(14)-C(19)	1.499(3)	C(15)-C(16)	1.425(3)
C(15)-C(20)	1.506(3)	C(16)-C(17)	1.409(3)
C(16)-C(21)	1.509(3)	C(17)-C(18)	1.511(3)
C(25)-C(26)	1.382(3)	C(26)-C(27)	1.383(3)
C(27)-C(28)	1.388(3)	C(28)-C(29)	1.395(3)
C(29)-C(30)	1.487(3)	C(30)-C(31)	1.396(3)
C(31)-C(32)	1.390(3)	C(32)-C(33)	1.384(3)
C(33)-C(34)	1.383(3)	O(1)-C(35)#1	1.585(9)
O(1)-C(35)	1.585(9)	C(35)-C(36)	1.240(9)
		Cnt1-Eu(1)-Cnt2	141.49(3)
Cnt1-Eu(1)-N(1)	102.42(6)	Cnt1-Eu(1)-N(2)	113.36(4)
Cnt2-Eu(1)-N(1)	101.65(5)	Cnt2-Eu(1)-N(2)	104.40(1)
N(1)-Eu(1)-N(2)	61.98(5)	N(1)-Eu(1)-C(17)	126.32(5)
N(2)-Eu(1)-C(17)	119.25(5)	N(1)-Eu(1)-C(13)	113.52(5)
N(2)-Eu(1)-C(13)	89.56(5)	C(17)-Eu(1)-C(13)	29.70(6)
N(1)-Eu(1)-C(1)	102.14(5)	N(2)-Eu(1)-C(1)	90.13(5)
C(17)-Eu(1)-C(1)	130.48(6)	C(13)-Eu(1)-C(1)	139.15(6)
N(1)-Eu(1)-C(2)	126.56(5)	N(2)-Eu(1)-C(2)	115.33(5)
C(17)-Eu(1)-C(2)	102.22(6)	C(13)-Eu(1)-C(2)	119.89(6)
C(1)-Eu(1)-C(2)	29.54(5)	N(1)-Eu(1)-C(5)	78.74(5)
N(2)-Eu(1)-C(5)	94.72(5)	C(17)-Eu(1)-C(5)	143.91(5)

C(13)-Eu(1)-C(5)	167.54(6)	C(1)-Eu(1)-C(5)	29.46(5)
C(2)-Eu(1)-C(5)	47.83(5)	N(1)-Eu(1)-C(16)	102.88(5)
N(2)-Eu(1)-C(16)	127.54(5)	C(17)-Eu(1)-C(16)	28.84(6)
C(13)-Eu(1)-C(16)	48.29(6)	C(1)-Eu(1)-C(16)	141.52(5)
C(2)-Eu(1)-C(16)	113.05(6)	C(5)-Eu(1)-C(16)	133.59(5)
N(1)-Eu(1)-C(14)	84.63(5)	N(2)-Eu(1)-C(14)	80.24(5)
C(17)-Eu(1)-C(14)	48.00(5)	C(13)-Eu(1)-C(14)	29.42(5)
C(1)-Eu(1)-C(14)	164.03(5)	C(2)-Eu(1)-C(14)	148.61(5)
C(5)-Eu(1)-C(14)	163.04(5)	C(16)-Eu(1)-C(14)	47.47(5)
N(1)-Eu(1)-C(3)	115.17(5)	N(2)-Eu(1)-C(3)	137.95(5)
C(17)-Eu(1)-C(3)	96.47(6)	C(13)-Eu(1)-C(3)	123.86(6)
C(1)-Eu(1)-C(3)	48.14(5)	C(2)-Eu(1)-C(3)	28.58(5)
C(5)-Eu(1)-C(3)	47.46(5)	C(16)-Eu(1)-C(3)	94.48(5)
C(14)-Eu(1)-C(3)	141.41(5)	N(1)-Eu(1)-C(4)	86.54(5)
N(2)-Eu(1)-C(4)	122.05(5)	C(17)-Eu(1)-C(4)	118.61(6)
C(13)-Eu(1)-C(4)	148.29(6)	C(1)-Eu(1)-C(4)	48.11(5)
C(2)-Eu(1)-C(4)	47.43(6)	C(5)-Eu(1)-C(4)	28.60(5)
C(16)-Eu(1)-C(4)	105.12(5)	C(14)-Eu(1)-C(4)	147.66(5)
C(3)-Eu(1)-C(4)	28.82(5)	N(1)-Eu(1)-C(15)	78.88(5)
N(2)-Eu(1)-C(15)	101.85(5)	C(17)-Eu(1)-C(15)	47.52(5)
C(13)-Eu(1)-C(15)	47.96(5)	C(1)-Eu(1)-C(15)	166.69(5)
C(2)-Eu(1)-C(15)	141.54(5)	C(5)-Eu(1)-C(15)	141.46(5)
C(16)-Eu(1)-C(15)	28.74(5)	C(14)-Eu(1)-C(15)	28.47(5)
C(3)-Eu(1)-C(15)	119.23(5)	C(4)-Eu(1)-C(15)	119.19(5)
C(1)-Si(1)-C(11)	109.61(10)	C(1)-Si(1)-C(10)	113.50(10)
C(11)-Si(1)-C(10)	107.19(11)	C(1)-Si(1)-C(12)	113.77(10)
C(11)-Si(1)-C(12)	105.80(12)	C(10)-Si(1)-C(12)	106.47(11)
C(13)-Si(2)-C(24)	114.41(11)	C(13)-Si(2)-C(22)	112.11(11)
C(24)-Si(2)-C(22)	106.32(14)	C(13)-Si(2)-C(23)	109.58(12)
C(24)-Si(2)-C(23)	106.73(15)	C(22)-Si(2)-C(23)	107.30(13)
C(25)-N(1)-C(29)	118.21(17)	C(25)-N(1)-Eu(1)	118.48(13)
C(29)-N(1)-Eu(1)	123.25(12)	C(34)-N(2)-C(30)	118.06(17)
C(34)-N(2)-Eu(1)	120.47(13)	C(30)-N(2)-Eu(1)	121.38(12)
C(5)-C(1)-C(2)	106.09(16)	C(5)-C(1)-Si(1)	127.63(14)
C(2)-C(1)-Si(1)	124.91(14)	C(5)-C(1)-Eu(1)	76.33(10)
C(2)-C(1)-Eu(1)	75.88(10)	Si(1)-C(1)-Eu(1)	123.78(9)
C(3)-C(2)-C(1)	109.00(17)	C(3)-C(2)-C(6)	124.08(18)
C(1)-C(2)-C(6)	126.80(18)	C(3)-C(2)-Eu(1)	77.03(11)
C(1)-C(2)-Eu(1)	74.59(10)	C(6)-C(2)-Eu(1)	118.07(13)
C(2)-C(3)-C(4)	108.14(16)	C(2)-C(3)-C(7)	126.36(19)
C(4)-C(3)-C(7)	125.18(18)	C(2)-C(3)-Eu(1)	74.39(10)
C(4)-C(3)-Eu(1)	75.97(10)	C(7)-C(3)-Eu(1)	120.85(13)
C(5)-C(4)-C(3)	107.87(16)	C(5)-C(4)-C(8)	127.25(18)
C(3)-C(4)-C(8)	124.54(18)	C(5)-C(4)-Eu(1)	74.42(10)
C(3)-C(4)-Eu(1)	75.21(10)	C(8)-C(4)-Eu(1)	121.59(13)

C(4)-C(5)-C(1)	108.89(16)	C(4)-C(5)-C(9)	124.66(17)
C(1)-C(5)-C(9)	126.39(17)	C(4)-C(5)-Eu(1)	76.97(11)
C(1)-C(5)-Eu(1)	74.21(10)	C(9)-C(5)-Eu(1)	117.52(12)
C(14)-C(13)-C(17)	106.22(16)	C(14)-C(13)-Si(2)	129.67(15)
C(17)-C(13)-Si(2)	123.06(14)	C(14)-C(13)-Eu(1)	76.91(10)
C(17)-C(13)-Eu(1)	74.94(10)	Si(2)-C(13)-Eu(1)	122.77(9)
C(15)-C(14)-C(13)	108.77(16)	C(15)-C(14)-C(19)	123.18(17)
C(13)-C(14)-C(19)	127.98(18)	C(15)-C(14)-Eu(1)	77.19(11)
C(13)-C(14)-Eu(1)	73.67(10)	C(19)-C(14)-Eu(1)	118.07(13)
C(14)-C(15)-C(16)	108.04(17)	C(14)-C(15)-C(20)	126.02(18)
C(16)-C(15)-C(20)	125.48(18)	C(14)-C(15)-Eu(1)	74.34(11)
C(16)-C(15)-Eu(1)	74.17(11)	C(20)-C(15)-Eu(1)	123.61(13)
C(17)-C(16)-C(15)	108.16(17)	C(17)-C(16)-C(21)	127.21(18)
C(15)-C(16)-C(21)	124.48(18)	C(17)-C(16)-Eu(1)	73.76(11)
C(15)-C(16)-Eu(1)	77.09(11)	C(21)-C(16)-Eu(1)	118.82(13)
C(16)-C(17)-C(13)	108.81(17)	C(16)-C(17)-C(18)	124.77(19)
C(13)-C(17)-C(18)	126.28(18)	C(16)-C(17)-Eu(1)	77.40(11)
C(13)-C(17)-Eu(1)	75.36(11)	C(18)-C(17)-Eu(1)	117.19(13)
N(1)-C(25)-C(26)	123.98(19)	C(25)-C(26)-C(27)	118.0(2)
C(26)-C(27)-C(28)	118.9(2)	C(27)-C(28)-C(29)	119.7(2)
N(1)-C(29)-C(28)	121.14(18)	N(1)-C(29)-C(30)	116.44(16)
C(28)-C(29)-C(30)	122.41(18)	N(2)-C(30)-C(31)	121.31(18)
N(2)-C(30)-C(29)	116.66(16)	C(31)-C(30)-C(29)	122.03(18)
C(32)-C(31)-C(30)	119.29(19)	C(33)-C(32)-C(31)	119.76(19)
C(34)-C(33)-C(32)	117.26(19)	N(2)-C(34)-C(33)	124.28(19)
C(35)#1-O(1)-C(35)	115.4(5)	C(36)-C(35)-O(1)	108.6(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

X-ray Data Collection, Structure Solution and Refinement for (C₅Me₄SiMe₃)₂Sm(terpy), C.3-Sm. A green crystal of approximate dimensions 0.193 x 0.220 x 0.278 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2¹⁵ program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time). The raw frame data was processed using SAINT¹⁶ and SADABS¹⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL¹⁸ program package. The diffraction symmetry was *mmm* and the

systematic absences were consistent with the orthorhombic space groups *Pbcm* and *Pca2₁*. It was later determined that space group *Pca2₁* was correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors¹⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Several atoms exhibited relatively high thermal motion and were included using displacement constraints (EADP). Least-squares analysis yielded wR2 = 0.0609 and Goof = 1.043 for 402 variables refined against 11133 data (0.70 Å), R1 = 0.0276 for those 10103 data with I > 2.0σ(I). The absolute structure was assigned by refinement of the Flack parameter.²⁰

Table C.16. Crystal data and structure refinement for (C₅Me₄SiMe₃)₂Sm(terpy), **C.3-Sm**.

Identification code	jqn25 (Joseph Nguyen)	
Empirical formula	C ₃₉ H ₅₃ N ₃ Si ₂ Sm	
Formula weight	770.37	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pca2₁</i>	
Unit cell dimensions	a = 17.1156(15) Å	α = 90°.
	b = 12.4999(11) Å	β = 90°.
	c = 17.3340(15) Å	γ = 90°.
Volume	3708.5(6) Å ³	
Z	4	
Density (calculated)	1.380 Mg/m ³	
Absorption coefficient	1.678 mm ⁻¹	
F(000)	1592	
Crystal color	green	
Crystal size	0.278 x 0.220 x 0.193 mm ³	
Theta range for data collection	1.629 to 30.538°	
Index ranges	-24 ≤ h ≤ 24, -17 ≤ k ≤ 17, -23 ≤ l ≤ 24	
Reflections collected	86660	
Independent reflections	11133 [R(int) = 0.0583]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from	

	equivalents	
Max. and min. transmission	0.7461 and 0.6281	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11133 / 1 / 402	
Goodness-of-fit on F ²	1.043	
Final R indices [I>2sigma(I) = 10103 data]	R1 = 0.0276, wR2 = 0.0582	
R indices (all data, 0.70 Å)	R1 = 0.0333, wR2 = 0.0609	
Absolute structure parameter	-0.024(4)	
Largest diff. peak and hole	1.099 and -1.739 e.Å ⁻³	

Table C.17. Bond lengths [Å] and angles [°] for (C₅Me₄SiMe₃)₂Sm(terpy), **C.3-Sm**.

Cnt1-Sm(1)	2.5231(16)	Cnt2-Sm(1)	2.5346(15)
Sm(1)-N(2)	2.454(3)	Sm(1)-N(3)	2.496(3)
Sm(1)-N(1)	2.516(3)	Sm(1)-C(13)	2.764(4)
Sm(1)-C(14)	2.772(4)	Sm(1)-C(3)	2.783(4)
Sm(1)-C(4)	2.785(5)	Sm(1)-C(1)	2.791(4)
Sm(1)-C(5)	2.804(3)	Sm(1)-C(17)	2.808(4)
Sm(1)-C(2)	2.812(4)	Sm(1)-C(15)	2.836(4)
Si(1)-C(12)	1.854(6)	Si(1)-C(1)	1.871(5)
Si(1)-C(11)	1.875(5)	Si(1)-C(10)	1.902(6)
Si(2)-C(13)	1.864(4)	Si(2)-C(22)	1.875(5)
Si(2)-C(24)	1.878(5)	Si(2)-C(23)	1.880(4)
N(1)-C(25)	1.347(6)	N(1)-C(29)	1.361(6)
N(2)-C(30)	1.379(5)	N(2)-C(34)	1.383(5)
N(3)-C(39)	1.343(5)	N(3)-C(35)	1.361(5)
C(1)-C(2)	1.416(6)	C(1)-C(5)	1.427(8)
C(2)-C(3)	1.399(7)	C(2)-C(6)	1.517(6)
C(3)-C(4)	1.409(7)	C(3)-C(7)	1.507(6)
C(4)-C(5)	1.417(8)	C(4)-C(8)	1.501(7)
C(5)-C(9)	1.509(6)	C(13)-C(14)	1.433(5)
C(13)-C(17)	1.439(5)	C(14)-C(15)	1.407(6)
C(14)-C(18)	1.507(5)	C(15)-C(16)	1.432(6)
C(15)-C(19)	1.503(6)	C(16)-C(17)	1.401(6)
C(16)-C(20)	1.502(6)	C(17)-C(21)	1.513(5)
C(25)-C(26)	1.364(6)	C(26)-C(27)	1.399(7)
C(27)-C(28)	1.367(6)	C(28)-C(29)	1.407(6)
C(29)-C(30)	1.451(6)	C(30)-C(31)	1.396(5)
C(31)-C(32)	1.388(6)	C(32)-C(33)	1.383(6)
C(33)-C(34)	1.394(6)	C(34)-C(35)	1.448(6)
C(35)-C(36)	1.407(6)	C(36)-C(37)	1.362(6)

C(37)-C(38)	1.400(6)	C(38)-C(39)	1.373(6)
		Cnt1-Sm(1)-Cnt2	132.33(3)
Cnt1-Sm(1)-N(1)	100.09(6)	Cnt1-Sm(1)-N(2)	115.39(3)
Cnt1-Sm(1)-N(3)	99.41(5)	Cnt2-Sm(1)-N(1)	98.53(3)
Cnt2-Sm(1)-N(2)	112.27(5)	Cnt2-Sm(1)-N(3)	101.17(6)
N(2)-Sm(1)-N(3)	65.00(11)	N(2)-Sm(1)-N(1)	65.20(13)
N(3)-Sm(1)-N(1)	130.17(14)	N(2)-Sm(1)-C(13)	89.76(11)
N(3)-Sm(1)-C(13)	79.30(11)	N(1)-Sm(1)-C(13)	101.92(11)
N(2)-Sm(1)-C(14)	91.79(11)	N(3)-Sm(1)-C(14)	107.27(11)
N(1)-Sm(1)-C(14)	75.68(12)	C(13)-Sm(1)-C(14)	30.01(11)
N(2)-Sm(1)-C(3)	133.49(12)	N(3)-Sm(1)-C(3)	91.73(13)
N(1)-Sm(1)-C(3)	122.22(12)	C(13)-Sm(1)-C(3)	126.63(12)
C(14)-Sm(1)-C(3)	134.49(12)	N(2)-Sm(1)-C(4)	135.71(13)
N(3)-Sm(1)-C(4)	119.99(13)	N(1)-Sm(1)-C(4)	94.95(14)
C(13)-Sm(1)-C(4)	134.17(13)	C(14)-Sm(1)-C(4)	122.64(12)
C(3)-Sm(1)-C(4)	29.32(14)	N(2)-Sm(1)-C(1)	89.60(12)
N(3)-Sm(1)-C(1)	89.87(13)	N(1)-Sm(1)-C(1)	88.37(12)
C(13)-Sm(1)-C(1)	168.33(13)	C(14)-Sm(1)-C(1)	161.66(13)
C(3)-Sm(1)-C(1)	48.63(12)	C(4)-Sm(1)-C(1)	48.80(12)
N(2)-Sm(1)-C(5)	106.80(15)	N(3)-Sm(1)-C(5)	118.75(14)
N(1)-Sm(1)-C(5)	74.95(10)	C(13)-Sm(1)-C(5)	159.22(16)
C(14)-Sm(1)-C(5)	133.98(14)	C(3)-Sm(1)-C(5)	48.27(12)
C(4)-Sm(1)-C(5)	29.37(16)	C(1)-Sm(1)-C(5)	29.56(16)
N(2)-Sm(1)-C(17)	116.73(11)	N(3)-Sm(1)-C(17)	81.13(12)
N(1)-Sm(1)-C(17)	123.60(12)	C(13)-Sm(1)-C(17)	29.92(11)
C(14)-Sm(1)-C(17)	48.51(11)	C(3)-Sm(1)-C(17)	96.86(12)
C(4)-Sm(1)-C(17)	107.28(14)	C(1)-Sm(1)-C(17)	144.27(12)
C(5)-Sm(1)-C(17)	136.46(15)	N(2)-Sm(1)-C(2)	104.60(12)
N(3)-Sm(1)-C(2)	74.38(12)	N(1)-Sm(1)-C(2)	117.40(12)
C(13)-Sm(1)-C(2)	140.64(12)	C(14)-Sm(1)-C(2)	162.16(13)
C(3)-Sm(1)-C(2)	28.95(15)	C(4)-Sm(1)-C(2)	47.91(14)
C(1)-Sm(1)-C(2)	29.27(12)	C(5)-Sm(1)-C(2)	47.86(13)
C(17)-Sm(1)-C(2)	115.85(12)	N(2)-Sm(1)-C(15)	118.80(12)
N(3)-Sm(1)-C(15)	126.40(12)	N(1)-Sm(1)-C(15)	80.26(14)
C(13)-Sm(1)-C(15)	48.82(12)	C(14)-Sm(1)-C(15)	29.03(11)
C(3)-Sm(1)-C(15)	107.50(13)	C(4)-Sm(1)-C(15)	93.91(13)
C(1)-Sm(1)-C(15)	140.04(13)	C(5)-Sm(1)-C(15)	110.85(16)
C(17)-Sm(1)-C(15)	47.90(12)	C(2)-Sm(1)-C(15)	136.43(13)
C(12)-Si(1)-C(1)	115.3(2)	C(12)-Si(1)-C(11)	107.1(3)
C(1)-Si(1)-C(11)	107.7(2)	C(12)-Si(1)-C(10)	106.6(3)
C(1)-Si(1)-C(10)	112.1(2)	C(11)-Si(1)-C(10)	107.6(3)
C(13)-Si(2)-C(22)	115.0(2)	C(13)-Si(2)-C(24)	114.1(2)
C(22)-Si(2)-C(24)	106.4(2)	C(13)-Si(2)-C(23)	106.3(2)
C(22)-Si(2)-C(23)	107.1(2)	C(24)-Si(2)-C(23)	107.5(2)
C(25)-N(1)-C(29)	117.8(3)	C(25)-N(1)-Sm(1)	122.1(3)

C(29)-N(1)-Sm(1)	120.0(3)	C(30)-N(2)-C(34)	116.7(3)
C(30)-N(2)-Sm(1)	121.6(2)	C(34)-N(2)-Sm(1)	121.7(3)
C(39)-N(3)-C(35)	118.0(3)	C(39)-N(3)-Sm(1)	121.1(3)
C(35)-N(3)-Sm(1)	120.8(3)	C(2)-C(1)-C(5)	106.5(4)
C(2)-C(1)-Si(1)	125.7(4)	C(5)-C(1)-Si(1)	125.9(3)
C(2)-C(1)-Sm(1)	76.2(2)	C(5)-C(1)-Sm(1)	75.7(2)
Si(1)-C(1)-Sm(1)	125.9(2)	C(3)-C(2)-C(1)	109.3(4)
C(3)-C(2)-C(6)	124.9(5)	C(1)-C(2)-C(6)	124.9(5)
C(3)-C(2)-Sm(1)	74.4(3)	C(1)-C(2)-Sm(1)	74.5(3)
C(6)-C(2)-Sm(1)	126.5(3)	C(2)-C(3)-C(4)	108.1(4)
C(2)-C(3)-C(7)	124.6(5)	C(4)-C(3)-C(7)	126.3(5)
C(2)-C(3)-Sm(1)	76.7(3)	C(4)-C(3)-Sm(1)	75.4(3)
C(7)-C(3)-Sm(1)	123.4(3)	C(3)-C(4)-C(5)	107.9(4)
C(3)-C(4)-C(8)	126.0(5)	C(5)-C(4)-C(8)	125.1(5)
C(3)-C(4)-Sm(1)	75.3(3)	C(5)-C(4)-Sm(1)	76.0(2)
C(8)-C(4)-Sm(1)	123.9(3)	C(4)-C(5)-C(1)	108.2(4)
C(4)-C(5)-C(9)	123.6(6)	C(1)-C(5)-C(9)	127.0(5)
C(4)-C(5)-Sm(1)	74.6(2)	C(1)-C(5)-Sm(1)	74.7(2)
C(9)-C(5)-Sm(1)	126.5(3)	C(14)-C(13)-C(17)	105.9(3)
C(14)-C(13)-Si(2)	123.1(3)	C(17)-C(13)-Si(2)	126.9(3)
C(14)-C(13)-Sm(1)	75.3(2)	C(17)-C(13)-Sm(1)	76.8(2)
Si(2)-C(13)-Sm(1)	131.44(18)	C(15)-C(14)-C(13)	109.2(3)
C(15)-C(14)-C(18)	125.3(4)	C(13)-C(14)-C(18)	125.4(3)
C(15)-C(14)-Sm(1)	78.0(2)	C(13)-C(14)-Sm(1)	74.7(2)
C(18)-C(14)-Sm(1)	117.3(2)	C(14)-C(15)-C(16)	107.8(4)
C(14)-C(15)-C(19)	128.1(4)	C(16)-C(15)-C(19)	123.0(4)
C(14)-C(15)-Sm(1)	73.0(2)	C(16)-C(15)-Sm(1)	76.5(2)
C(19)-C(15)-Sm(1)	126.1(3)	C(17)-C(16)-C(15)	108.0(3)
C(17)-C(16)-C(20)	126.9(4)	C(15)-C(16)-C(20)	123.8(4)
C(17)-C(16)-Sm(1)	73.6(2)	C(15)-C(16)-Sm(1)	74.4(2)
C(20)-C(16)-Sm(1)	128.2(3)	C(16)-C(17)-C(13)	109.2(3)
C(16)-C(17)-C(21)	123.4(4)	C(13)-C(17)-C(21)	126.6(4)
C(16)-C(17)-Sm(1)	77.8(2)	C(13)-C(17)-Sm(1)	73.3(2)
C(21)-C(17)-Sm(1)	123.4(3)	N(1)-C(25)-C(26)	124.7(4)
C(25)-C(26)-C(27)	117.9(4)	C(28)-C(27)-C(26)	118.8(4)
C(27)-C(28)-C(29)	120.7(4)	N(1)-C(29)-C(28)	120.1(4)
N(1)-C(29)-C(30)	116.7(4)	C(28)-C(29)-C(30)	123.2(4)
N(2)-C(30)-C(31)	122.2(4)	N(2)-C(30)-C(29)	116.5(3)
C(31)-C(30)-C(29)	121.2(4)	C(32)-C(31)-C(30)	120.0(4)
C(33)-C(32)-C(31)	118.7(4)	C(32)-C(33)-C(34)	120.0(4)
N(2)-C(34)-C(33)	122.3(4)	N(2)-C(34)-C(35)	116.0(4)
C(33)-C(34)-C(35)	121.6(4)	N(3)-C(35)-C(36)	120.2(4)
N(3)-C(35)-C(34)	116.3(4)	C(36)-C(35)-C(34)	123.4(4)
C(37)-C(36)-C(35)	120.4(4)	C(36)-C(37)-C(38)	119.4(4)
C(39)-C(38)-C(37)	117.4(4)	N(3)-C(39)-C(38)	124.5(4)

X-ray Data Collection, Structure Solution and Refinement for (C₅Me₄SiMe₃)₂Yb(terpy), C.3-Yb. A black crystal of approximate dimensions 0.144 x 0.223 x 0.330 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2¹⁵ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time). The raw frame data was processed using SAINT¹⁶ and SADABS¹⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL¹⁸ program package. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups *Pbcm* and *Pca*2₁. It was later determined that space group *Pca*2₁ was correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors¹⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Several atoms exhibited relatively high thermal motion and were included using displacement constraints (EADP). Least-squares analysis yielded wR2 = 0.0517 and Goof = 1.035 for 402 variables refined against 11030 data (0.70 Å), R1 = 0.0240 for those 9979 data with I > 2.0σ(I). The absolute structure was assigned by refinement of the Flack parameter.²⁰

Table C.18. Crystal data and structure refinement for (C₅Me₄SiMe₃)₂Yb(terpy), C.3-Yb.

Identification code	jqn42 (Joseph Nguyen)	
Empirical formula	C39 H53 N3 Si2 Yb	
Formula weight	793.06	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pca</i> 2 ₁	
Unit cell dimensions	a = 17.0913(15) Å	α = 90°.
	b = 12.4119(11) Å	β = 90°.
	c = 17.2441(15) Å	γ = 90°.
Volume	3658.1(6) Å ³	
Z	4	
Density (calculated)	1.440 Mg/m ³	
Absorption coefficient	2.653 mm ⁻¹	

F(000)	1624	
Crystal color	black	
Crystal size	0.330 x 0.223 x 0.144 mm ³	
Theta range for data collection	1.641 to 30.540°	
Index ranges	-24 ≤ h ≤ 23, -17 ≤ k ≤ 17, -24 ≤ l ≤ 24	
Reflections collected	87669	
Independent reflections	11030 [R(int) = 0.0504]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6383	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11030 / 1 / 402	
Goodness-of-fit on F ²	1.035	
Final R indices [I > 2sigma(I) = 9979 data]	R1 = 0.0240, wR2 = 0.0492	
R indices (all data, 0.70 Å)	R1 = 0.0297, wR2 = 0.0517	
Absolute structure parameter	-0.014(3)	
Largest diff. peak and hole	1.142 and -1.781 e.Å ⁻³	

Table C.19. Bond lengths [Å] and angles [°] for (C₅Me₄SiMe₃)₂Yb(terpy), **C.3-Yb**.

Cnt1-Yb(1)	2.4618(15)	Cnt2-Yb(1)	2.4393(16)
Yb(1)-N(2)	2.352(3)	Yb(1)-N(3)	2.422(3)
Yb(1)-N(1)	2.440(3)	Yb(1)-C(13)	2.677(4)
Yb(1)-C(14)	2.695(4)	Yb(1)-C(4)	2.702(5)
Yb(1)-C(3)	2.710(4)	Yb(1)-C(1)	2.714(4)
Yb(1)-C(5)	2.736(3)	Yb(1)-C(2)	2.737(4)
Yb(1)-C(17)	2.744(4)	Yb(1)-C(15)	2.787(4)
Si(1)-C(12)	1.853(6)	Si(1)-C(1)	1.868(5)
Si(1)-C(11)	1.877(5)	Si(1)-C(10)	1.895(6)
Si(2)-C(13)	1.861(4)	Si(2)-C(22)	1.872(5)
Si(2)-C(23)	1.873(4)	Si(2)-C(24)	1.876(5)
N(1)-C(25)	1.353(5)	N(1)-C(29)	1.354(5)
N(2)-C(34)	1.381(5)	N(2)-C(30)	1.383(5)
N(3)-C(39)	1.345(5)	N(3)-C(35)	1.360(5)
C(1)-C(5)	1.419(8)	C(1)-C(2)	1.421(6)
C(2)-C(3)	1.396(7)	C(2)-C(6)	1.519(6)
C(3)-C(4)	1.415(7)	C(3)-C(7)	1.508(6)
C(4)-C(5)	1.421(8)	C(4)-C(8)	1.506(7)

C(5)-C(9)	1.502(6)	C(13)-C(17)	1.435(5)
C(13)-C(14)	1.439(5)	C(14)-C(15)	1.409(6)
C(14)-C(18)	1.504(6)	C(15)-C(16)	1.431(6)
C(15)-C(19)	1.501(6)	C(16)-C(17)	1.393(6)
C(16)-C(20)	1.508(6)	C(17)-C(21)	1.515(6)
C(25)-C(26)	1.370(6)	C(26)-C(27)	1.394(7)
C(27)-C(28)	1.363(6)	C(28)-C(29)	1.405(6)
C(29)-C(30)	1.450(6)	C(30)-C(31)	1.391(6)
C(31)-C(32)	1.381(6)	C(32)-C(33)	1.381(6)
C(33)-C(34)	1.387(6)	C(34)-C(35)	1.457(6)
C(35)-C(36)	1.406(6)	C(36)-C(37)	1.364(6)
C(37)-C(38)	1.397(6)	C(38)-C(39)	1.379(6)
		Cnt1-Sm(1)-Cnt2	131.72(3)
Cnt1-Sm(1)-N(1)	98.22(3)	Cnt1-Sm(1)-N(2)	113.13(5)
Cnt1-Sm(1)-N(3)	100.59(6)	Cnt2-Sm(1)-N(1)	99.38(6)
Cnt2-Sm(1)-N(2)	115.14(3)	Cnt2-Sm(1)-N(3)	98.59(5)
N(2)-Yb(1)-N(3)	67.06(12)	N(2)-Yb(1)-N(1)	66.97(11)
N(3)-Yb(1)-N(1)	134.01(11)	N(2)-Yb(1)-C(13)	89.96(11)
N(3)-Yb(1)-C(13)	78.34(11)	N(1)-Yb(1)-C(13)	102.85(11)
N(2)-Yb(1)-C(14)	91.89(12)	N(3)-Yb(1)-C(14)	107.63(11)
N(1)-Yb(1)-C(14)	75.15(11)	C(13)-Yb(1)-C(14)	31.08(11)
N(2)-Yb(1)-C(4)	136.26(14)	N(3)-Yb(1)-C(4)	119.18(13)
N(1)-Yb(1)-C(4)	93.59(14)	C(13)-Yb(1)-C(4)	133.46(14)
C(14)-Yb(1)-C(4)	121.76(13)	N(2)-Yb(1)-C(3)	133.55(12)
N(3)-Yb(1)-C(3)	89.66(13)	N(1)-Yb(1)-C(3)	121.98(12)
C(13)-Yb(1)-C(3)	125.42(12)	C(14)-Yb(1)-C(3)	134.25(12)
C(4)-Yb(1)-C(3)	30.31(14)	N(2)-Yb(1)-C(1)	88.58(13)
N(3)-Yb(1)-C(1)	89.94(13)	N(1)-Yb(1)-C(1)	87.71(12)
C(13)-Yb(1)-C(1)	167.79(13)	C(14)-Yb(1)-C(1)	161.10(13)
C(4)-Yb(1)-C(1)	50.34(12)	C(3)-Yb(1)-C(1)	50.17(13)
N(2)-Yb(1)-C(5)	106.42(16)	N(3)-Yb(1)-C(5)	119.09(15)
N(1)-Yb(1)-C(5)	73.51(11)	C(13)-Yb(1)-C(5)	159.48(18)
C(14)-Yb(1)-C(5)	133.27(16)	C(4)-Yb(1)-C(5)	30.30(17)
C(3)-Yb(1)-C(5)	49.73(12)	C(1)-Yb(1)-C(5)	30.17(18)
N(2)-Yb(1)-C(2)	103.87(13)	N(3)-Yb(1)-C(2)	72.84(12)
N(1)-Yb(1)-C(2)	117.59(12)	C(13)-Yb(1)-C(2)	139.53(13)
C(14)-Yb(1)-C(2)	162.62(13)	C(4)-Yb(1)-C(2)	49.39(14)
C(3)-Yb(1)-C(2)	29.71(15)	C(1)-Yb(1)-C(2)	30.21(13)
C(5)-Yb(1)-C(2)	49.12(13)	N(2)-Yb(1)-C(17)	117.73(12)
N(3)-Yb(1)-C(17)	79.69(12)	N(1)-Yb(1)-C(17)	123.99(11)
C(13)-Yb(1)-C(17)	30.67(12)	C(14)-Yb(1)-C(17)	49.81(11)
C(4)-Yb(1)-C(17)	105.72(14)	C(3)-Yb(1)-C(17)	95.01(12)
C(1)-Yb(1)-C(17)	143.99(12)	C(5)-Yb(1)-C(17)	135.84(16)
C(2)-Yb(1)-C(17)	114.68(13)	N(2)-Yb(1)-C(15)	119.46(12)
N(3)-Yb(1)-C(15)	126.39(12)	N(1)-Yb(1)-C(15)	78.90(12)

C(13)-Yb(1)-C(15)	50.26(12)	C(14)-Yb(1)-C(15)	29.73(12)
C(4)-Yb(1)-C(15)	92.30(14)	C(3)-Yb(1)-C(15)	106.79(13)
C(1)-Yb(1)-C(15)	139.59(14)	C(5)-Yb(1)-C(15)	109.70(18)
C(2)-Yb(1)-C(15)	136.47(14)	C(17)-Yb(1)-C(15)	48.96(13)
C(12)-Si(1)-C(1)	115.5(2)	C(12)-Si(1)-C(11)	107.7(2)
C(1)-Si(1)-C(11)	107.1(2)	C(12)-Si(1)-C(10)	106.1(2)
C(1)-Si(1)-C(10)	112.5(2)	C(11)-Si(1)-C(10)	107.6(2)
C(13)-Si(2)-C(22)	115.27(19)	C(13)-Si(2)-C(23)	106.4(2)
C(22)-Si(2)-C(23)	106.8(2)	C(13)-Si(2)-C(24)	114.07(19)
C(22)-Si(2)-C(24)	106.4(2)	C(23)-Si(2)-C(24)	107.5(2)
C(25)-N(1)-C(29)	117.3(3)	C(25)-N(1)-Yb(1)	123.1(3)
C(29)-N(1)-Yb(1)	119.5(3)	C(34)-N(2)-C(30)	116.2(3)
C(34)-N(2)-Yb(1)	122.1(3)	C(30)-N(2)-Yb(1)	121.8(2)
C(39)-N(3)-C(35)	117.6(4)	C(39)-N(3)-Yb(1)	122.6(3)
C(35)-N(3)-Yb(1)	119.8(3)	C(5)-C(1)-C(2)	106.5(4)
C(5)-C(1)-Si(1)	125.9(4)	C(2)-C(1)-Si(1)	125.3(4)
C(5)-C(1)-Yb(1)	75.7(2)	C(2)-C(1)-Yb(1)	75.8(2)
Si(1)-C(1)-Yb(1)	127.9(2)	C(3)-C(2)-C(1)	109.4(4)
C(3)-C(2)-C(6)	125.0(4)	C(1)-C(2)-C(6)	124.4(5)
C(3)-C(2)-Yb(1)	74.1(2)	C(1)-C(2)-Yb(1)	74.0(3)
C(6)-C(2)-Yb(1)	128.1(3)	C(2)-C(3)-C(4)	107.9(4)
C(2)-C(3)-C(7)	125.3(4)	C(4)-C(3)-C(7)	125.6(4)
C(2)-C(3)-Yb(1)	76.2(2)	C(4)-C(3)-Yb(1)	74.6(3)
C(7)-C(3)-Yb(1)	125.5(3)	C(3)-C(4)-C(5)	107.7(4)
C(3)-C(4)-C(8)	125.9(5)	C(5)-C(4)-C(8)	124.8(5)
C(3)-C(4)-Yb(1)	75.1(3)	C(5)-C(4)-Yb(1)	76.1(2)
C(8)-C(4)-Yb(1)	126.3(3)	C(1)-C(5)-C(4)	108.4(4)
C(1)-C(5)-C(9)	126.5(5)	C(4)-C(5)-C(9)	123.7(6)
C(1)-C(5)-Yb(1)	74.1(2)	C(4)-C(5)-Yb(1)	73.6(2)
C(9)-C(5)-Yb(1)	128.7(3)	C(17)-C(13)-C(14)	105.7(3)
C(17)-C(13)-Si(2)	126.4(3)	C(14)-C(13)-Si(2)	122.9(3)
C(17)-C(13)-Yb(1)	77.2(2)	C(14)-C(13)-Yb(1)	75.1(2)
Si(2)-C(13)-Yb(1)	133.04(19)	C(15)-C(14)-C(13)	109.2(3)
C(15)-C(14)-C(18)	125.3(4)	C(13)-C(14)-C(18)	125.3(4)
C(15)-C(14)-Yb(1)	78.8(2)	C(13)-C(14)-Yb(1)	73.8(2)
C(18)-C(14)-Yb(1)	118.5(3)	C(14)-C(15)-C(16)	107.3(4)
C(14)-C(15)-C(19)	127.7(4)	C(16)-C(15)-C(19)	123.5(4)
C(14)-C(15)-Yb(1)	71.5(2)	C(16)-C(15)-Yb(1)	76.0(2)
C(19)-C(15)-Yb(1)	129.0(3)	C(17)-C(16)-C(15)	108.4(4)
C(17)-C(16)-C(20)	126.6(4)	C(15)-C(16)-C(20)	123.1(4)
C(17)-C(16)-Yb(1)	72.9(2)	C(15)-C(16)-Yb(1)	74.3(2)
C(20)-C(16)-Yb(1)	131.0(3)	C(16)-C(17)-C(13)	109.4(3)
C(16)-C(17)-C(21)	123.0(4)	C(13)-C(17)-C(21)	126.4(4)
C(16)-C(17)-Yb(1)	78.1(2)	C(13)-C(17)-Yb(1)	72.1(2)
C(21)-C(17)-Yb(1)	126.5(3)	N(1)-C(25)-C(26)	124.3(4)

C(25)-C(26)-C(27)	118.1(4)	C(28)-C(27)-C(26)	118.8(4)
C(27)-C(28)-C(29)	120.6(4)	N(1)-C(29)-C(28)	120.9(4)
N(1)-C(29)-C(30)	116.1(3)	C(28)-C(29)-C(30)	123.1(4)
N(2)-C(30)-C(31)	122.2(4)	N(2)-C(30)-C(29)	115.7(3)
C(31)-C(30)-C(29)	122.1(4)	C(32)-C(31)-C(30)	120.3(4)
C(33)-C(32)-C(31)	118.7(4)	C(32)-C(33)-C(34)	119.8(4)
N(2)-C(34)-C(33)	122.9(4)	N(2)-C(34)-C(35)	115.1(4)
C(33)-C(34)-C(35)	122.1(4)	N(3)-C(35)-C(36)	121.2(4)
N(3)-C(35)-C(34)	115.9(4)	C(36)-C(35)-C(34)	122.9(4)
C(37)-C(36)-C(35)	119.8(4)	C(36)-C(37)-C(38)	119.6(4)
C(39)-C(38)-C(37)	117.6(4)	N(3)-C(39)-C(38)	124.3(4)

X-ray Data Collection, Structure Solution and Refinement for (C₅Me₄SiMe₃)₂Eu(terpy), C.3-Eu. A black crystal of approximate dimensions 0.231 x 0.299 x 0.336 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2¹⁵ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time). The raw frame data was processed using SAINT¹⁶ and SADABS¹⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL¹⁸ program package. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *P*2₁2₁2₁ that was later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors¹⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There was one molecule of 1,2-dimethoxyethane solvent present. Least squares analysis yielded wR2 = 0.0415 and Goof = 1.043 for 476 variables refined against 13104 data (0.70 Å), R1 = 0.0195 for those 12441 data with I > 2.0σ(I). The absolute structure was assigned by refinement of the Flack parameter.²⁰

Table C.20. Crystal data and structure refinement for (C₅Me₄SiMe₃)₂Eu(terpy), C.3-Eu.

Identification code	gn6 (Gabija Navickaite)	
Empirical formula	C ₃₉ H ₅₃ Eu N ₃ Si ₂ · C ₄ H ₁₀ O ₂	
Formula weight	862.10	

Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	$a = 13.233(2)$ Å	$\alpha = 90^\circ$.
	$b = 17.094(3)$ Å	$\beta = 90^\circ$.
	$c = 19.232(3)$ Å	$\gamma = 90^\circ$.
Volume	$4350.1(11)$ Å ³	
Z	4	
Density (calculated)	1.316 Mg/m ³	
Absorption coefficient	1.534 mm ⁻¹	
F(000)	1796	
Crystal color	black	
Crystal size	0.336 x 0.299 x 0.231 mm ³	
Theta range for data collection	1.594 to 30.507°	
Index ranges	$-18 \leq h \leq 18, -24 \leq k \leq 24, -27 \leq l \leq 26$	
Reflections collected	107743	
Independent reflections	13104 [R(int) = 0.0440]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6573	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13104 / 0 / 476	
Goodness-of-fit on F ²	1.043	
Final R indices [I>2sigma(I) = 12441 data]	R1 = 0.0195, wR2 = 0.0403	
R indices (all data, 0.70 Å)	R1 = 0.0226, wR2 = 0.0415	
Absolute structure parameter	-0.015(2)	
Largest diff. peak and hole	0.587 and -0.344 e.Å ⁻³	

Table C.21. Bond lengths [Å] and angles [°] for (C₅Me₄SiMe₃)₂Eu(terpy), **C.3-Eu**.

Cnt1-Eu(1)	2.642	Cnt2-Eu(1)	2.636
Eu(1)-N(3)	2.6172(19)	Eu(1)-N(1)	2.6236(19)
Eu(1)-N(2)	2.6510(19)	Eu(1)-C(16)	2.856(2)
Eu(1)-C(15)	2.888(2)	Eu(1)-C(2)	2.889(2)
Eu(1)-C(3)	2.893(2)	Eu(1)-C(17)	2.893(2)
Eu(1)-C(1)	2.911(2)	Eu(1)-C(4)	2.914(2)
Eu(1)-C(5)	2.922(2)	Eu(1)-C(13)	2.926(2)

Si(1)-C(1)	1.856(3)	Si(1)-C(11)	1.873(3)
Si(1)-C(10)	1.877(3)	Si(1)-C(12)	1.878(3)
Si(2)-C(13)	1.855(2)	Si(2)-C(22)	1.866(3)
Si(2)-C(23)	1.874(3)	Si(2)-C(24)	1.880(3)
N(1)-C(25)	1.340(3)	N(1)-C(29)	1.346(3)
N(2)-C(34)	1.345(3)	N(2)-C(30)	1.346(3)
N(3)-C(39)	1.339(3)	N(3)-C(35)	1.348(3)
C(1)-C(2)	1.432(3)	C(1)-C(5)	1.434(3)
C(2)-C(3)	1.408(3)	C(2)-C(6)	1.510(3)
C(3)-C(4)	1.423(3)	C(3)-C(7)	1.503(3)
C(4)-C(5)	1.413(3)	C(4)-C(8)	1.504(3)
C(5)-C(9)	1.511(3)	C(13)-C(14)	1.432(3)
C(13)-C(17)	1.433(3)	C(14)-C(15)	1.404(4)
C(14)-C(18)	1.508(4)	C(15)-C(16)	1.423(3)
C(15)-C(19)	1.509(4)	C(16)-C(17)	1.405(3)
C(16)-C(20)	1.508(3)	C(17)-C(21)	1.512(3)
C(25)-C(26)	1.382(4)	C(26)-C(27)	1.375(4)
C(27)-C(28)	1.379(4)	C(28)-C(29)	1.396(3)
C(29)-C(30)	1.488(3)	C(30)-C(31)	1.396(3)
C(31)-C(32)	1.378(4)	C(32)-C(33)	1.380(4)
C(33)-C(34)	1.395(3)	C(34)-C(35)	1.486(3)
C(35)-C(36)	1.396(3)	C(36)-C(37)	1.386(4)
C(37)-C(38)	1.383(4)	C(38)-C(39)	1.391(3)
O(1)-C(41)	1.413(4)	O(1)-C(40)	1.418(4)
O(2)-C(43)	1.414(4)	O(2)-C(42)	1.418(4)
C(41)-C(42)	1.488(4)		
Cnt1-Eu(1)-Cnt2	137.7	Cnt1-Eu(1)-N(1)	97.5
Cnt1-Eu(1)-N(2)	108.1	Cnt1-Eu(1)-N(3)	101.4
Cnt2-Eu(1)-N(1)	101.4	Cnt2-Eu(1)-N(2)	114.1
Cnt2-Eu(1)-N(3)	98.3	N(3)-Eu(1)-N(1)	124.53(6)
N(3)-Eu(1)-N(2)	62.34(6)	N(1)-Eu(1)-N(2)	62.25(6)
N(3)-Eu(1)-C(16)	89.55(6)	N(1)-Eu(1)-C(16)	124.95(6)
N(2)-Eu(1)-C(16)	129.66(6)	N(3)-Eu(1)-C(15)	117.42(7)
N(1)-Eu(1)-C(15)	100.07(7)	N(2)-Eu(1)-C(15)	135.46(6)
C(16)-Eu(1)-C(15)	28.68(7)	N(3)-Eu(1)-C(2)	82.02(6)
N(1)-Eu(1)-C(2)	121.26(6)	N(2)-Eu(1)-C(2)	111.83(7)
C(16)-Eu(1)-C(2)	103.53(7)	C(15)-Eu(1)-C(2)	112.07(7)
N(3)-Eu(1)-C(3)	108.68(7)	N(1)-Eu(1)-C(3)	109.86(6)
N(2)-Eu(1)-C(3)	132.67(6)	C(16)-Eu(1)-C(3)	94.37(7)
C(15)-Eu(1)-C(3)	91.16(7)	C(2)-Eu(1)-C(3)	28.19(7)
N(3)-Eu(1)-C(17)	73.86(6)	N(1)-Eu(1)-C(17)	115.15(6)
N(2)-Eu(1)-C(17)	101.39(6)	C(16)-Eu(1)-C(17)	28.29(6)
C(15)-Eu(1)-C(17)	46.51(7)	C(2)-Eu(1)-C(17)	122.81(7)
C(3)-Eu(1)-C(17)	121.40(7)	N(3)-Eu(1)-C(1)	80.56(6)
N(1)-Eu(1)-C(1)	98.41(6)	N(2)-Eu(1)-C(1)	86.45(6)

C(16)-Eu(1)-C(1)	131.81(7)	C(15)-Eu(1)-C(1)	137.99(7)
C(2)-Eu(1)-C(1)	28.59(7)	C(3)-Eu(1)-C(1)	46.98(7)
C(17)-Eu(1)-C(1)	145.43(7)	N(3)-Eu(1)-C(4)	125.89(7)
N(1)-Eu(1)-C(4)	81.68(6)	N(2)-Eu(1)-C(4)	116.09(6)
C(16)-Eu(1)-C(4)	114.22(7)	C(15)-Eu(1)-C(4)	99.43(7)
C(2)-Eu(1)-C(4)	46.49(7)	C(3)-Eu(1)-C(4)	28.36(7)
C(17)-Eu(1)-C(4)	142.37(7)	C(1)-Eu(1)-C(4)	46.85(7)
N(3)-Eu(1)-C(5)	106.97(6)	N(1)-Eu(1)-C(5)	74.86(6)
N(2)-Eu(1)-C(5)	89.50(6)	C(16)-Eu(1)-C(5)	140.33(6)
C(15)-Eu(1)-C(5)	127.15(7)	C(2)-Eu(1)-C(5)	46.45(7)
C(3)-Eu(1)-C(5)	46.43(7)	C(17)-Eu(1)-C(5)	167.73(7)
C(1)-Eu(1)-C(5)	28.46(7)	C(4)-Eu(1)-C(5)	28.02(7)
N(3)-Eu(1)-C(13)	90.75(6)	N(1)-Eu(1)-C(13)	86.67(6)
N(2)-Eu(1)-C(13)	89.72(6)	C(16)-Eu(1)-C(13)	47.17(7)
C(15)-Eu(1)-C(13)	46.77(7)	C(2)-Eu(1)-C(13)	150.10(7)
C(3)-Eu(1)-C(13)	137.58(7)	C(17)-Eu(1)-C(13)	28.52(7)
C(1)-Eu(1)-C(13)	171.31(6)	C(4)-Eu(1)-C(13)	141.47(7)
C(5)-Eu(1)-C(13)	159.47(7)	C(1)-Si(1)-C(11)	108.05(12)
C(1)-Si(1)-C(10)	114.19(12)	C(11)-Si(1)-C(10)	106.80(13)
C(1)-Si(1)-C(12)	114.67(12)	C(11)-Si(1)-C(12)	105.52(13)
C(10)-Si(1)-C(12)	107.00(14)	C(13)-Si(2)-C(22)	114.66(14)
C(13)-Si(2)-C(23)	109.75(13)	C(22)-Si(2)-C(23)	106.23(17)
C(13)-Si(2)-C(24)	113.75(14)	C(22)-Si(2)-C(24)	105.6(2)
C(23)-Si(2)-C(24)	106.27(16)	C(25)-N(1)-C(29)	118.0(2)
C(25)-N(1)-Eu(1)	119.65(16)	C(29)-N(1)-Eu(1)	122.26(14)
C(34)-N(2)-C(30)	118.7(2)	C(34)-N(2)-Eu(1)	120.52(15)
C(30)-N(2)-Eu(1)	120.41(14)	C(39)-N(3)-C(35)	117.8(2)
C(39)-N(3)-Eu(1)	120.06(15)	C(35)-N(3)-Eu(1)	121.92(15)
C(2)-C(1)-C(5)	106.2(2)	C(2)-C(1)-Si(1)	125.99(18)
C(5)-C(1)-Si(1)	124.34(18)	C(2)-C(1)-Eu(1)	74.84(13)
C(5)-C(1)-Eu(1)	76.17(13)	Si(1)-C(1)-Eu(1)	131.16(11)
C(3)-C(2)-C(1)	109.1(2)	C(3)-C(2)-C(6)	124.4(2)
C(1)-C(2)-C(6)	126.3(2)	C(3)-C(2)-Eu(1)	76.04(13)
C(1)-C(2)-Eu(1)	76.57(13)	C(6)-C(2)-Eu(1)	117.96(15)
C(2)-C(3)-C(4)	108.0(2)	C(2)-C(3)-C(7)	126.2(2)
C(4)-C(3)-C(7)	125.2(2)	C(2)-C(3)-Eu(1)	75.77(13)
C(4)-C(3)-Eu(1)	76.66(13)	C(7)-C(3)-Eu(1)	120.71(16)
C(5)-C(4)-C(3)	107.9(2)	C(5)-C(4)-C(8)	127.5(2)
C(3)-C(4)-C(8)	124.1(2)	C(5)-C(4)-Eu(1)	76.29(13)
C(3)-C(4)-Eu(1)	74.98(13)	C(8)-C(4)-Eu(1)	121.08(16)
C(4)-C(5)-C(1)	108.9(2)	C(4)-C(5)-C(9)	125.5(2)
C(1)-C(5)-C(9)	125.5(2)	C(4)-C(5)-Eu(1)	75.68(13)
C(1)-C(5)-Eu(1)	75.37(13)	C(9)-C(5)-Eu(1)	117.54(16)
C(14)-C(13)-C(17)	106.0(2)	C(14)-C(13)-Si(2)	127.28(18)
C(17)-C(13)-Si(2)	125.44(18)	C(14)-C(13)-Eu(1)	76.17(13)

C(17)-C(13)-Eu(1)	74.44(13)	Si(2)-C(13)-Eu(1)	124.98(11)
C(15)-C(14)-C(13)	108.9(2)	C(15)-C(14)-C(18)	123.6(2)
C(13)-C(14)-C(18)	126.7(2)	C(15)-C(14)-Eu(1)	74.21(14)
C(13)-C(14)-Eu(1)	75.53(13)	C(18)-C(14)-Eu(1)	124.44(17)
C(14)-C(15)-C(16)	108.3(2)	C(14)-C(15)-C(19)	125.5(3)
C(16)-C(15)-C(19)	125.8(2)	C(14)-C(15)-Eu(1)	77.90(14)
C(16)-C(15)-Eu(1)	74.43(13)	C(19)-C(15)-Eu(1)	119.94(17)
C(17)-C(16)-C(15)	107.6(2)	C(17)-C(16)-C(20)	126.3(2)
C(15)-C(16)-C(20)	125.9(2)	C(17)-C(16)-Eu(1)	77.29(13)
C(15)-C(16)-Eu(1)	76.89(14)	C(20)-C(16)-Eu(1)	115.94(16)
C(16)-C(17)-C(13)	109.2(2)	C(16)-C(17)-C(21)	125.2(2)
C(13)-C(17)-C(21)	124.6(2)	C(16)-C(17)-Eu(1)	74.42(13)
C(13)-C(17)-Eu(1)	77.04(13)	C(21)-C(17)-Eu(1)	124.14(16)
N(1)-C(25)-C(26)	123.5(3)	C(27)-C(26)-C(25)	118.1(2)
C(26)-C(27)-C(28)	119.6(2)	C(27)-C(28)-C(29)	119.0(3)
N(1)-C(29)-C(28)	121.7(2)	N(1)-C(29)-C(30)	116.69(19)
C(28)-C(29)-C(30)	121.6(2)	N(2)-C(30)-C(31)	122.0(2)
N(2)-C(30)-C(29)	118.03(19)	C(31)-C(30)-C(29)	119.9(2)
C(32)-C(31)-C(30)	118.6(2)	C(31)-C(32)-C(33)	120.1(3)
C(32)-C(33)-C(34)	118.3(2)	N(2)-C(34)-C(33)	122.4(2)
N(2)-C(34)-C(35)	117.4(2)	C(33)-C(34)-C(35)	120.2(2)
N(3)-C(35)-C(36)	121.6(2)	N(3)-C(35)-C(34)	117.1(2)
C(36)-C(35)-C(34)	121.2(2)	C(37)-C(36)-C(35)	119.3(2)
C(38)-C(37)-C(36)	119.7(2)	C(37)-C(38)-C(39)	117.2(2)
N(3)-C(39)-C(38)	124.4(2)	C(41)-O(1)-C(40)	112.3(3)
C(43)-O(2)-C(42)	111.6(3)	O(1)-C(41)-C(42)	108.7(2)
O(2)-C(42)-C(41)	109.2(3)		

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Appendix D:

List of Crystal Structures

Listed below is a summary table of the single crystal X-ray crystallography data collected throughout the course of the work described in the dissertation. Cell lengths are expressed in units of Å, angles are expressed in units of deg (°), and cell volume is expressed in units of Å³.

Abbreviations used in the table below include:

crypt = 2.2.2-cryptand; DME = 1,2-dimethoxyethane; THF = tetrahydrofuran;

OAr^{Me} = OC₆H₂'Bu-2,6-Me-4, OAr^H = OC₆H₃'Bu-2,6; OAr^{OMe} = OC₆H₂'Bu-2,6-OMe-4; OAr^{tBu} = OC₆H₂'Bu-2,4,6; OAr^{Ph} = OC₆H₂'Bu-2,6-Ph-4

Cp* = C₅Me₅; Cp^N = C₅Me₄(SiMe₃); Cp^{TIPS} = C₅H₄(SiⁱPr₃); Cp' = C₅H₄(SiMe₃); Cp'' = C₅H₃(SiMe₃)₂; Cp^{iPr5} = C₅ⁱPr₅; Cp^S = C₅Me₄(SiMe₂'Bu); Cp^{tet} = C₅Me₄H;

N* = N(SiMe₃)₂, bipy = 2,2'-bipyridine, terpy = 2,2':6',2''-terpyridine, bipyrim = 2,2'-bipyrimidine, SA^{tBu} = SC₆H₂'Bu-2,4,6

Table D.1. Crystal structures collected throughout this Dissertation and unit-cell parameters.

JQN	Formula	a	b	c	α	β	γ	Volume
1	N/A; Not solved	-	-	-	-	-	-	-
2	[K(crypt)][OAr ^{Me}]	12.7	16.9	17.2	90	103	90	3578
3	[K(crypt)][Th(OAr ^H) ₄]	20.1	20.1	10.3	90	90	90	4162
4	Cp* ₂ PrN*	17.7	17.7	46.8	90	90	120	12773
5	[Cp* ₂ Sm(THF) ₂][Cp* ₂ SmN ₂ (C ₈ H ₈ B ₂ (CH ₃) ₂)]	11.3	33.0	15.8	90	98.9	90	5832
6	[Li(THF) ₄][Th(OAr ^H) ₄]	11.4	15.4	39.7	90	90.0	90	6947
7	[Cp*Sm] ₆ O ₉ H ₆	19.8	17.5	13.1	90	124.0	90	3766
8	N/A; Not solved	-	-	-	-	-	-	-
9	Cp* ₂ Th[CyNC(Me)NCy]Me	9.7	18.1	18.6	90	90	90	3243
10	ThBr ₄ (THF) ₄	17.5	17.5	9.7	90	90	90	2961
11	Cp ^N ₂ Sm(THF)	17.9	11.1	15.8	90	104.5	90	3034
12	Cp ^S ₂ Sm(THF)	29.9	35.8	21.2	90	102.2	90	22172

13	Cp ^N ₂ ThBr ₂	19.6	8.3	17.4	90	94.2	90	2829
14	[Li(THF) ₄][Th(OAr ^{OMe}) ₄]	19.3	19.5	24.1	90	90	90	9059
15	N/A; Not solved	-	-	-	-	-	-	-
16	Cp ^N ₂ ThMe ₂	19.4	8.3	17.7	90	94.4	90	2833
17	[Li(THF) ₄][Th(OAr ^{tBu}) ₄]	14.3	11.1	31.1	90	99.6	90	4868
18	N/A; Not solved	-	-	-	-	-	-	-
19	[Cp ^N Sm(μ -I)(THF) ₂] ₂	10.3	17.0	15.7	90	96.8	90	2742
20	Cp ^{tet} ₂ Sm(μ - η^3 : η^5 -Cp ^{tet})SmCp ^{tet} (THF) ₂	11.4	15.6	23.3	90	92.7	90	4159
21	[Cp ^N DyI(OEt)] ₄	10.3	14.6	23.3	83.5	84.8	89.1	3474
22	Cp ^N Th(C ₃ H ₅) ₃	10.1	14.3	15.3	90	104.8	90	2132
23	HOAr ^{Ph}	9.0	8.1	23.0	90	94.3	90	1658
24	Cp ^N ₂ Sm(bipy)	10.3	10.9	15.0	95.0	91.3	100.0	1641
25	Cp ^N ₂ Sm(terpy)	12.5	17.1	17.3	90	90	90	3709
26	(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ CH ₂) ₂ Th	19.3	8.5	18.2	90	123.0	90	2519
27	Dy(SAr ^{tBu}) ₃	10.1	37.6	14.3	90	100.0	90	5363
28	Gd(SAr ^{tBu}) ₃	10.1	37.6	14.3	90	100.0	90	5369
29	Cp* ₂ Gd(bipy)Cl	10.3	20.5	14.8	90	93.1	90	3117
30	Cp ^N ₂ Sm(bipyrim)SmCp ^N ₂	32.7	32.7	18.3	90	90	120	16949
31	Sm(SAr ^{tBu}) ₃	10.1	37.6	14.3	90	100.0	90	5376
32	Cp* ₂ Gd(bipy)	15.6	16.7	19.9	90	90	90	5191
33	[Cp*Yb(μ -I)(THF) ₂] ₂	14.9	13.1	21.0	90	98.6	90	4042
34	Cp ^N ₂ Yb(THF)	15.8	10.9	18.2	90	106.1	90	3008
35	Cp ^N ₂ Eu(THF)	15.8	11.1	17.8	90	104.6	90	3029
36	Cp ^N ₂ ThMe(AdN ₃ Me)	10.1	11.3	19.3	85.6	85.9	65.8	1987
37	Cp ^{tet} ₂ Sm(DME)	17.5	16.5	30.9	90	90.0	90	8891
38	[Mg(THF) ₆][BPh ₃ Me] ₂	12.1	12.1	23.5	90	90	120	2965
39	Cp ^N ₂ Yb(bipy)	23.3	24.5	17.2	90	134.0	90	7096
40	Sm(OAr ^{tBu}) ₃ (THF)	17.0	11.6	28.7	90	103.6	90	5512
41	Cp ^S ₂ Sm(THF)	36.9	15.1	20.6	90	100.0	90	11307
42	Cp ^N ₂ Yb(terpy)	17.1	12.4	17.2	90	90.0	90	3658
43	Cp ^N ₂ Eu(bipy)	23.5	24.9	16.7	90	132.1	90	7261
44	Cp ^{TIPS} ₂ Sm(DME)	14.9	8.4	28.4	90	103.0	90	3478
45	Sm(SAr ^{tBu}) ₂ (DME) ₂	21.6	21.6	22.1	90	90	90	10327
46	[K(crypt)][Cp ^{TIPS} ₃ Th]	23.5	13.1	25.2	90	100.4	90	7637
47	Cp* ₂ La(bipy)Cl(THF)	10.3	20.2	15.2	90	94.0	90	3178
48	Cp ^{tet} ₂ Sm(DME)	17.4	16.5	30.8	90	90	90	8845
49	[K(crypt)][Cp ^{TIPS} ₃ U(η^1 -Cp ^{TIPS})]	16.4	16.6	17.3	76.2	80.5	65.7	4147
50	Cp ^N ₂ ScCl	10.0	10.1	12.6	92.8	94.4	90.1	1271
51	Cp ^{TIPS} ₂ Eu(DME)	15.1	15.8	15.6	90	110.1	90	3493
52	Cp ^{TIPS} ₂ Yb(DME)	14.7	8.4	28.5	90	104.0	90	3418
53	Cp ^{TIPS} ₃ Th	12.0	14.2	14.9	65.7	87.6	67.8	2142
54	Cp ^{TIPS} ₃ U	11.9	14.3	15.0	65.2	85.6	67.6	2136
55	[K(crypt)][Cp ^{TIPS}]	21.9	17.4	19.9	90	105.2	90	7338
56	Cp ^{TIPS} ₃ ThBr	8.0	12.3	27.0	80.8	89.6	71.2	2485
57	[K(crypt)][Cp ^{TIPS}]	17.4	17.9	23.4	90	90	90	7294

58	[K(crypt)][Cp ^{TIPS} ₃ Th]	13.7	16.4	29.1	90	94.1	90	6530
59	[K(crypt)][Cp ^{TIPS} ₃ U]	13.7	16.4	29.2	90	94.6	90	6537
60	Cp ^{TIPS} ₃ Sm	11.9	14.3	15.0	65.1	86.0	67.8	2133
61	Tb(SAr ^{tBu}) ₃	10.1	37.6	14.3	90	100.0	90	5370
62	[Na(THF) ₆][C ₆₀ H ₉₀ Y ₆ O ₈]	26.2	26.2	26.2	90	90	90	17973
63	Cp ^{TIPS} ₃ Nd	12.0	14.3	15.0	65.2	86.0	67.7	2142
64	Cp ^{TIPS} ₃ Gd	11.9	14.3	15.0	65.1	86.1	67.8	2130
65	[K(crypt)][Cp ^{TIPS} ₃ Nd]	13.7	16.4	29.2	90	94.6	90	6535
66	[K(crypt)][Cp ^{TIPS} ₃ La]	13.7	16.4	29.3	90	94.9	90	6586
67	[K(crypt)][Cp ^{TIPS} ₃ Pr]	13.7	16.4	29.2	90	94.6	90	6548
68	Cp ^{TIPS} ₃ Dy	11.9	14.3	15.0	65.0	86.3	67.9	2132
69	Cp ^{TIPS} ₃ Pr	12.0	14.3	15.0	65.3	86.0	67.6	2144
70	[K(crypt)][Cp ^{TIPS} ₃ Gd]	13.7	16.3	29.1	90	94.6	90	6496
71	Ho(SAr ^{tBu}) ₃	10.1	37.6	14.3	90	100.0	90	5365
72	(DME)NaCp ^{iPr5}	10.5	16.6	14.2	90	95.4	90	2467
73	N/A; Not solved	-	-	-	-	-	-	-
74	[Cp ^{TIPS} ₂ Sc(μ-I)] ₂	8.2	14.2	14.2	106.9	101.5	100.6	1504
75	Cp ^N ₂ ScI	9.0	15.7	19.4	90	90	90	2750
76	Cp ^S ₂ ScI	10.2	15.1	21.4	90	95.8	90	3268
77	Cp ^{TIPS} ₃ Ho	11.9	14.3	15.0	65.0	86.3	68.0	2118
78	Cp ^{''} ₂ ScI	11.2	12.9	10.5	90	104.0	90	1457
79	Cp ^{TIPS} ₃ Tb	11.9	14.3	15.0	65.0	86.3	67.9	2123
80	[Cp ['] ₂ Sc(μ-I)] ₂	8.6	9.7	12.6	71.4	75.7	87.9	963
81	[K(crypt)][Cp ^{TIPS} ₃ Tb]	13.7	16.3	29.2	90	94.5	90	6493
82	Cp ^S ₂ Sc(OH)	21.7	8.9	16.9	90	108.4	90	3096
83	Cp ^S ₂ Sc	13.1	8.6	13.8	90	94.1	90	1558
84	Cp ^S ₂ Sc(μ-η ¹ :η ¹ -N ₂)ScCp ^S ₂	13.2	13.6	21.0	77.1	76.1	63.9	3272
85	Cp ^S ₂ Sc(μ-η ¹ :η ¹ -N ₂)ScCp ^S ₂	17.2	19.3	20.9	90	98.4	90	6851
86	Cp ^S ₂ Ca	13.0	8.9	13.7	90	94.4	90	1582
87	Cp ^N ₂ Sc(μ-η ¹ :η ¹ -N ₂)ScCp ^N ₂	19.4	19.4	27.5	90	90	90	10320