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S.D. Stults
(Ph.D. Thesis)

October 1988

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**Tris(cyclopentadienyl)cerium and -uranium:
Relative Basicity, Structure, and Reactions**

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October 1988

1

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Stephen Dale Stults

ABSTRACT

The trivalent cerium complexes $(RC_5H_4)_3Ce \cdot L$ have been prepared and structurally characterized in order to study the relative basicity of neutral donor ligands toward $(RC_5H_4)_3Ce$. The relative order of increasing basicity is found to be $PMe_3 > pyr > P(OCH_2)_3CEt > thf \approx quin > PEt_3 > P(OMe)_3 > > > NMe_3$. The steric properties of the metal environment and the steric and electronic properties of the donor ligand influence complex stability. The ligand displacement series is found to be qualitatively similar to that found in $(RC_5H_4)_3U$, when σ -only ligands are studied. Solution equilibria measurements and crystallographic analyses support the postulate that M-L π -bonding plays a role in $(RC_5H_4)_3U \cdot L$ compounds and not in $(RC_5H_4)_3Ce \cdot L$ compounds.

The base-free metallocenes, $(RC_5H_4)_3Ce$, react with a number of protic reagents to form stable $[(RC_5H_4)_2CeX]_2$ complexes via a ring protonation reaction. The reagent pKa values govern the thermodynamics of the reaction. The steric bulk of the protic substrate and the cyclopentadienyl ligands can be altered to achieve kinetically stable compounds. In contrast, the analogous uranium complexes, $(RC_5H_4)_3U$, react in an oxidative manner with protic reagents to form $(RC_5H_4)_3UX$ complexes. The complexes $[(Me_3CC_5H_4)_2CeEPr^i]_2$, where E is O and S, and $\{[(Me_3Si)_2C_5H_3]_2CeOH\}_2$ provide the first examples of structurally characterized neutral bis(cyclopentadienyl)-complexes of the early lanthanides.

The base-free cerium metallocenes also react with methyllithium to afford bis(cyclopentadienyl)cerium methyl complexes. Other alkyl complexes cannot be prepared in a similar manner. The structure of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ consists of two methyl groups symmetrically bridging two cerium atoms so that the carbon atom is five coordinate and the Ce-C-Ce angle is acute. The cerium methyl complexes readily polymerize ethylene, and they react with phenylacetylene, hydrogen, and ammonia to yield the bridging acetylide, hydride, and amide complexes, respectively.

The uranium metallocene, $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{thf}$, reacts with methyllithium at low temperature (-30°C) in the presence of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ (tmed) to form a complex that contains a methyl group that is linearly and symmetrically bridging between two $(\text{MeC}_5\text{H}_4)_3\text{U}$ groups, and a MeC_5H_4 group that is sandwiched between two $\text{Li}(\text{tmed})$ fragments.

Acknowledgements

This is by far the most enjoyable section of the thesis to write because it allows one to thank those who have made the graduate career successful and enjoyable, and to deliver one final blow to those who have effectively delivered so many over the last five years. I hope the latter "acknowledgements" are not taken seriously as they are not intended that way.

I am deeply indebted to my research director, Richard Andersen, for instilling a challenging research environment and giving me the opportunity to become a competent synthetic chemist. The beer sessions at the "Rock", green salsa at the "Rose", and Irish coffees at Brennan's probably took five years off my life, but they also demonstrated Dick's respect for molecules and his students.

Thanks to Norm Edelstein for financial support, thoughtful conversation, and constant nagging. Alan Zalkin and Fred Hollander deserve special gratitude for collecting all the data and solving all the crystal structures described within. The recognition deserved by Jerry Bucher, the person who single-handedly kept the lab running, would take up several pages; one look at his office proves he has been recognized by many. Thanks Jerry; see you on the slopes!

I could not have completed this work without the help of my colleagues; most importantly John Brennan, who taught me subtle techniques, gave me direction, and lost so often at darts. The Class of 83'; Dave, Carol, Nicki, and Joanne; gave me much appreciated support and needed friendship. My working environment was enjoyable because of the assistance, cooperation, and consideration of Sharon, Mike, Mark, Phil, and Wing. I wish you all the best of luck.

Some say that my greatest passion, outside chemistry of course, is softball, and some claim that I spent more time on the field than in the lab. Speaking of Norm and softball, I'm glad he only played one inning for the Stormin' Norman's; even though his at-bat was pretty amusing. Thanks to all of those who made playing softball really enjoyable, especially Oddibe, Motion, Spud, Tuna, Carolyn, Space, and Mark. Being a part of the Dux, What It Is, and Atom Smashers championship teams was a real honor.

The person I shared a lab, office, and home with deserves a special thank you. Rob, your freindship made life fun and pulled me through the rough times. I really appreciate it. You are truly a great friend; someone I will be able to count on for the rest of my life. Thanks also to my other roommate, Mary. You certainly are a great pillow target. Thank you C.P. (my dog) for being that constant source of companionship.

Finally, I could not have accomplished what I have in my lifetime if it were not for the love, moral support, and financial support given to me by my family. They provided me with a great living environment and gave me the opportunity to strive for every goal and dream that I ever had. I love you guys, this one's for you, THANKS!!

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To my mom and dad,
for their love and support.

Introduction

Over the last two decades organometallic chemistry of the lanthanides and actinides has been the focus of numerous investigations.¹ The interest stems from the belief that these elements possess several unique features, not found among alkaline earth and transition metals, that will produce reaction patterns and products not yet observed in the field of organometallic chemistry.

The lanthanides are the fourteen elements following lanthanum in the Periodic Table. On the basis of their location one would expect the lanthanides to display chemical and physical properties intermediate between the alkaline earths and transition elements. Because of their comparable sizes and tendency to form ionic bonds, the lanthanides are quite similar to the alkaline earths.

Within the lanthanide series the 4f orbitals are sequentially filled with electrons. These electrons do not shield each other efficiently from the nucleus, and the 4f orbital energies fall below the filled 5s² and 5p⁶ shells. Consequently, the 4f orbitals cannot overlap with ligand orbitals, and the bonding in organolanthanide complexes is mainly ionic in nature. Crystal field splitting energies observed for lanthanide ions are very small ($\leq 300 \text{ cm}^{-1}$), supporting the belief that the 4f valence electrons are not significantly perturbed by the ligand environment.² Since there are no orbital symmetry restrictions, these ions tend to form complexes which maximize coordination number; coordination numbers of eight to twelve are very common, while minimizing intramolecular ligand-ligand repulsions.

In aqueous solution, the most stable oxidation state of the lanthanides is the trivalent oxidation state, reflecting the stability

of the Xe electronic configuration. In general, the stability of the +3 oxidation state results in organolanthanide complexes which do not exhibit redox properties. Three lanthanide ions, samarium, ytterbium, and europium; possess a divalent oxidation state of sufficient stability to form organometallic complexes with redox properties.³ Only cerium has a stable tetravalent oxidation state, and Ce(IV) complexes have applications as oxidizing agents in organic synthesis.⁴

The actinides, or 5f metals, are the fourteen elements following actinium in the Periodic Table. Again, based on their location, one would expect the actinides to display chemical and physical properties intermediate between the alkaline earths and transition elements and very similar to the lanthanides. To a large extent this is true, but some properties of the actinides differ markedly from the lanthanides, resulting in chemistry that is available to the actinides and not to the lanthanides.

The 5f orbitals of the actinides are not nearly as shielded by filled 6s² and 6p⁶ orbitals as the 4f orbitals of the lanthanides are by the 5s² and 5p⁶ orbitals. This means that the 5f orbitals and electrons, especially for the early actinides, are more exposed to the ligand environment than the 4f orbitals of the lanthanides. The greater interaction of the 5f orbitals and electrons with ligands gives rise to larger crystal field splitting energies (ca. 1000-2000 cm⁻¹) and greater metal-ligand bond covalency.⁵ The overlap of actinide valence orbitals with ligand orbitals is still much less than in most transition metal complexes, however, and has been the focus of much debate.⁶ As the atomic number increases, the 5f orbitals become more contracted, and the properties of the later actinides more closely resemble those of the lanthanides.

The early actinides possess a greater range of oxidation states than do the lanthanides, because the 5f orbitals are more exposed to the chemical environment. Uranium, for example, has four accessible oxidation states, +3 through +6. Thus, organouranium complexes possessing redox behavior can be synthesized; and therefore, the chemical reactivity that is available to the early actinides is less limited than that available to the early lanthanides. The majority of trivalent organoactinide research has involved uranium because of the difficulties caused by the availability and radioactivity of the other actinide elements.

The aim of this research is three-fold: to study the relative basicity of neutral Lewis bases toward early organolanthanide environments; to develop the synthesis and study the reactivity of early bis(cyclopentadienyl)lanthanide(III) and early lanthanide alkyl complexes; and to compare the physical and chemical properties of these trivalent complexes with sterically similar, but electronically different actinide complexes.

When comparing the properties of similar lanthanide and actinide complexes, it is desirable to greatly reduce or eliminate the steric factors that influence metal-ligand bonding and overall complex stability. The Ce(III) ion was chosen as the focus of this work because it has an ionic radius, 1.21Å, that is very similar to U(III), 1.18Å.⁷ The steric demands that analogous cerium and uranium complexes display toward the ligand environment are similar, and any differences in the chemical properties of the complexes should reflect differences in only the electronic nature of the M-L interactions. Furthermore, most organolanthanide research has involved the heavier lanthanides, and the lighter lanthanides, such as cerium, have been left relatively unexplored. The larger size of these ions, relative

to the heavier congeners, might give rise to complexes with chemical properties different from those observed in previously studied organo-lanthanide complexes.

Chapter one addresses the question of the relative basicity of Lewis bases toward $(RC_5H_4)_3Ce$ complexes; an area of organo-f-metal chemistry that has not been rigorously studied. Comparisons with the analogous uranium complexes give insight into the nature of the metal-ligand bond. Chapter two focuses on the reaction of tris-(cyclopentadienyl) metallocenes with protic substrates. When cerium metallocenes are used, the neutral, base-free $[(RC_5H_4)_2CeX]_2$ complexes, whose synthesis have heretofore been difficult⁸, are isolated. The uranium metallocenes form an oxidation product, $(RC_5H_4)_3UX$, demonstrating the wider scope of reaction products and pathways available to uranium. Chapter three focuses on the preparation of stable cerium alkyl complexes, and investigates their reactivity toward unsaturated molecules, hydrogen, and ammonia.

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CHAPTER ONE: Coordination Chemistry of
Tris(cyclopentadienyl)cerium Complexes

Metal-ligand bond stability is an important concept to the synthetic chemist. A knowledge of which ligands form relatively strong or weak interactions with a metal ion is important in designing successful synthetic methods. Quite often labile, or weakly bound, ligands are required to open up metal coordination sites and promote chemical reactivity. In other cases kinetically inert, or strongly bound, ligands are necessary to stabilize an otherwise unstable molecule or to prevent undesirable reaction pathways from occurring.

Numerous studies have been made in an attempt to develop methods of predicting the relative stability of coordination complexes of transition metal ions. Other studies have been aimed at explaining observed trends in the relative coordinative affinity of Lewis bases toward these metal ions.¹ Although organometallic chemistry of the lanthanides and actinides has received great attention over the last twenty years, very little has been done in addressing the question of relative ligand basicity toward the f-metal environment; this is especially true for those ligands commonly used in organometallic synthesis.

In 1954, Wilkinson and Birmingham synthesized the first tris-cyclopentadienyl complexes of the lanthanides.² The compounds were shown to be tetrahydrofuran adducts, but modification of the initial synthetic procedure produced the solvent free complexes.³ These base-free complexes were isolated by sublimation and showed relatively low solubility in non-coordinating solvents. Since then, numerous derivatives of these complexes have been synthesized and structurally characterized in an effort to determine the modes of bonding in

organometallic lanthanide compounds.⁴ Few investigations, however, have involved the Ce(III) ion.

Generally, lanthanide and actinide ions are considered to be "hard" Lewis acids.⁵ That is, they preferentially bind to "hard" nitrogen and oxygen donor ligands over "soft" phosphorus and sulfur donor ligands, because the M-N and M-O bonding interactions are thermodynamically stronger than M-P and M-S interactions. These generalizations are based on the large number of reported nitrogen and oxygen donor ligand complexes of lanthanides and actinides and the difficulty encountered in attempts to make stable phosphine complexes. The large charge to size ratio, and therefore the nonpolarizable nature of the 4f and 5f metal ions, and the contraction of the valence f-orbitals is the usual rationalization for these beliefs.

Recently, however, several lanthanide and actinide phosphine complexes have been reported.⁶ Initial syntheses, however, usually involved the exclusion of any solvents that can behave as Lewis bases. This revealed nothing about the relative stability of the M-P bond, as isolation of a more weakly bound complex may be the result of the synthetic conditions employed.

Andersen and Edwards have shown that the bidentate phosphine ligand, DMPE, quantitatively displaces the analogous bidentate nitrogen ligand, TMEDA, from UCl_4 in hydrocarbon solvents,⁷ casting some doubt on the validity of previously held beliefs. Later, using UV-VIS spectroscopy, Ellis measured formation constants of Lewis bases with $(C_8H_8)_3Yb$ and surprisingly found the order of relative basicity toward the ytterbium environment to be pyrrolidine > triethylphosphine (PEt_3) > tetrahydrofuran (thf), tetrahydrothiophene (ttht).⁸ Brennan has recently found similar results by measuring equilibrium quotients

for competition reactions of Lewis bases toward $(C_5H_5)_3U$ and $(MeC_5H_4)_3U$.⁹

In view of the results of Ellis and Brennan, and the observation that trimethylphosphine quantitatively displaces thf from $(MeC_5H_4)_3Ce$,¹⁰ a number of $(MeC_5H_4)_3Ce \cdot L$ complexes, where L is a neutral Lewis base, have been synthesized. The relative basicity of the Lewis bases toward $(MeC_5H_4)_3Ce$ was examined in order to establish a relative basicity trend toward the larger lanthanide ions and to compare relative acidities of lanthanide and actinide environments.

Synthesis and Structure

The thf complex of tris-methylcyclopentadienyluranium, $(MeC_5H_4)_3U \cdot OC_4H_8$, proved to be a valuable starting material in the work of Brennan,¹¹ thus the analogous Ce complex seemed to be the most logical starting point. The complex, $(MeC_5H_4)_3Ce \cdot thf$, was prepared by the reaction of anhydrous $CeCl_3$ and $NaMeC_5H_4$ in thf, followed by crystallization from diethyl ether in 60% yield. Several other mono thf adducts of the lanthanides and actinides have been described;^{2,12,15} however, this represents the first completely characterized triscyclopentadienyl mono-thf adduct of cerium. The compound is sparingly soluble in hydrocarbon solvents, but exhibits good solubility in coordinating solvents, such as thf or diethyl ether, and aromatic solvents, such as benzene and toluene. The compound melts with decomposition at 142-146°C.

The ¹H NMR spectrum, like most of the other Lewis base adducts that will be described, shows an AA'BB'X₃ pattern for the ring protons plus the ligand resonances which are shifted upfield from the ring Me resonance (Table 1.1). Addition of excess thf to a solution of $(MeC_5H_4)_3Ce \cdot thf$ results in a spectrum containing only one set of

Table 1.1 ^1H NMR Data for $(\text{MeC}_5\text{H}_3)_3\text{Ce}\cdot\text{L}$ Complexes

<u>Ce-L</u>	<u>δ CH(A)</u>	<u>δ CH(B)</u>	<u>δ R(X)</u>	<u>δ ligand</u>
—	13.02 (43 Hz)	10.56 (58 Hz)	-4.52 (20 Hz)	—————
OC_4H_8	10.19 (20 Hz)	8.66 (20 Hz)	-1.41 (5 Hz)	-4.93 (4H, 8 Hz) -11.26 (4H, 20 Hz)
PMe_3	11.29 (26 Hz)	8.64 (26 Hz)	-2.64 (8 Hz)	-8.40 (9H, 8 Hz)
PEt_3	12.62 (30 Hz)	8.76 (28 Hz)	-3.04 (10 Hz)	-4.14 (9H, 16 Hz) -7.81 (6H, 22 Hz)
$\text{P}(\text{OCH}_2)_3\text{CEt}$	10.28 (40 Hz)	10.28 (40 Hz)	-1.64 (4 Hz)	-1.92 (3H, t, J=7 Hz) -2.28 (9H, 8 Hz) -2.51 (2H, q, J=7 Hz)
$\text{P}(\text{OMe})_3$	11.08 (38 Hz)	9.82 (34 Hz)	-2.26 (6 Hz)	-2.76 (9H, 16 Hz)
$\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$	12.16 (15 Hz)	6.90 (15 Hz)	-1.95 (5 Hz)	-3.48 (1H, 9 Hz) -4.32 (6H, 12 Hz) -11.14 (6H, 23 Hz)
NC_5H_5	9.28 (16 Hz)	8.98 (16 Hz)	-1.05 (5 Hz)	3.26 (1H, t, J=7) 1.56 (2H, d, J=7) -6.99 (2H, 20 Hz)
$\text{NC}_5\text{H}_4\text{NMe}_2$	8.86 (18 Hz)	8.32 (17 Hz)	-0.53 (8 Hz)	1.05 (2H, 6 Hz) -0.06 (6H, 3 Hz) -7.28 (2H, 15 Hz)
SC_4H_8	11.11 (30 Hz)	10.14 (36 Hz)	-2.48 (11 Hz)	-4.93 (4H, 11 Hz) -8.35 (4H, 15 Hz)
NCEt	11.04 (20 Hz)	7.86 (23 Hz)	-0.65 (7 Hz)	-3.81 (3H, t, J=6.8 Hz) -7.24 (2H, q, J=6.8 Hz)
CNEt	10.38 (25 Hz)	8.31 (28 Hz)	-0.73 (9 Hz)	-3.61 (3H) -5.86 (2H, q, J=6 Hz)
CNCMe_3	10.53 (24 Hz)	7.99 (28 Hz)	-0.57 (10 Hz)	-4.13 (9H, 5 Hz)

Although the spin system for the ring protons in $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ is $\text{AA}'\text{BB}'\text{X}_3$, the observed spectra show that $\text{A}=\text{A}'$ and $\text{B}=\text{B}'$. All spectra were recorded in C_6D_6 or C_7D_8 and referenced relative to tetramethylsilane, $\delta = 0$. Relative intensities and line widths at half peak height are given in parentheses.

ligand resonances due to the rapid exchange (on the NMR time-scale) of free and coordinated ligand. The barrier to ligand exchange could not be measured as resonances due to both free and coordinated ligand, or even coalescence of the ligand peaks, were not observed down to -70°C . Brennan has observed similar behavior in the analogous $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{thf}$ complex.

Crystals, suitable for X-ray diffraction studies, were obtained by cooling a saturated diethyl ether solution slowly to -20°C . The yellow needles were isolated, dried in vacuo, and sealed in quartz capillaries. The compound crystallizes in the orthorhombic space group, Pnma , and consists of a distorted tetrahedral arrangement of three $\eta^5\text{-MeC}_5\text{H}_4$ ligands and the oxygen-bound thf ligand. An ORTEP drawing is shown in Fig.1. Relevant bond distances and angles are given in Table 1.2. Several $\text{Cp}_3\text{M}\cdot\text{thf}$ complexes of the lanthanides and actinides have been structurally characterized, and all consist of this distorted tetrahedral geometry about the 10-coordinate metal ion.¹⁵ Table 1.3 lists some important bond distances and angles for comparison. Using the effective ionic radius for the Cp ligand, $1.64(4)\text{\AA}$, derived by Eigenbrot and Raymond¹⁶, all bond distances agree, within experimental error, with those predicted from a simple ionic model. All angles about the central metal atoms are identical.

Only one other thf adduct of Ce(III) has been structurally characterized. The compound $[(\text{C}_8\text{H}_8)\text{CeCl}\cdot 2\text{thf}]_2$ has Ce-O bond lengths of $2.577(3)\text{\AA}$ and $2.588(4)\text{\AA}$, with an average of $2.583(3)\text{\AA}$.¹⁷ One would expect the Ce-O distance in the 10-coordinate $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ complex to be about 0.05\AA larger than in the 9-coordinate COT complex. The drastically different chemical environments and structure types, and the low quality of the cyclopentadienyl structure, however, probably account for the shorter Ce-O distance in $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$.

Table 1.2

Bond Distances (Å) and Intramolecular Angles (°) for
 $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{OC}_4\text{H}_8$

Ce-C1	2.83(3)	Ce-C6	2.90(4)	Ce-O	2.52(3)
Ce-C2	2.80(3)	Ce-C7	2.83(2)	O-C11	1.47(3)
Ce-C3	2.74(2)	Ce-C7'	2.83(2)	C11-C12	1.55(5)
Ce-C4	2.82(3)	Ce-C8	2.81(1)	Ce-Cp1	2.55
Ce-C5	2.77(3)	Ce-C8'	2.81(1)	Ce-Cp2	2.59
Cp1-Ce-Cp1'		116.6	O-Ce-Cp2		98.7
Cp1-Ce-Cp2		117.4	Ce-O-C11		124.5
O-Ce-Cp1		100.5	C11-O-C11'		110.5

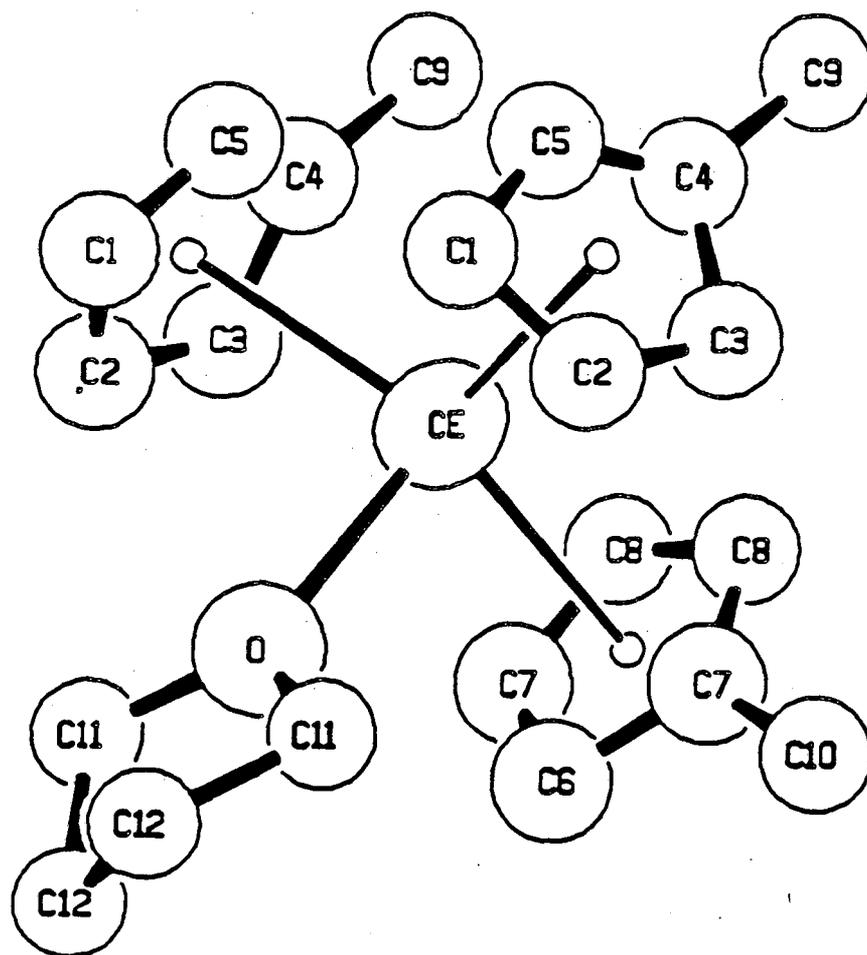
Cp1 and Cp2 are the centroids of the rings comprised of C1-C5 and C6-C8, C7', C8', respectively.

Table 1.3

Structurally Characterized $\text{Cp}_3\text{M}\cdot\text{thf}$ Complexes

Compound	M-O(Å)	M-C(Å)	M-Cp(Å)	Cp-M-O(°)	Cp-M-Cp(°)	Ref
$(\text{C}_5\text{H}_5)_3\text{Y}\cdot\text{thf}$	2.451(1)	2.71(3)	2.45	99.3	117.2	15a
$(\text{C}_5\text{H}_5)_3\text{La}\cdot\text{thf}$	2.57(1)	2.82(4)	2.57	99.7	117.7	15a
$(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$	2.52(3)	2.81(3)	2.56	99.9	117.1	Ch.1
$(\text{C}_5\text{H}_5)_3\text{Pr}\cdot\text{thf}$	2.56(1)	2.80(2)	2.53	—	—	15b
$(\text{C}_5\text{H}_5)_3\text{Nd}\cdot\text{thf}$	2.54(1)	2.78(2)	2.51	—	—	15b
$(\text{C}_5\text{H}_5)_3\text{U}\cdot\text{thf}$	2.55(1)	2.79(1)	2.52	98.9	117.6	15e
$(\text{C}_5\text{H}_5)_3\text{Gd}\cdot\text{thf}$	2.494(7)	2.74(3)	2.49	99.2	117.5	15c
$(\text{C}_5\text{H}_5)_3\text{Lu}\cdot\text{thf}$	2.39(2)	2.69(4)	2.42	99.0	117.6	15d

Fig. 1

ORTEP Drawing of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{OC}_4\text{H}_8$ 

It will become apparent, upon further reading, that the thf complex is not a suitable starting material for the synthesis of several $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ complexes. Tetrahydrofuran strongly competes with some Lewis bases for coordination to the cerium environment, preventing the isolation of pure $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ compounds. Often, addition of a large excess of a Lewis base, L, to a solution of the thf complex led to the isolation of starting material or mixtures of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ and $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$. It was therefore desirable to obtain the base-free $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ complex.

Addition of AlMe_3 to a toluene solution of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ or application of the "toluene reflux" method (see experimental section), followed by crystallization from toluene led to the isolation of yellow-orange crystals, m.p. 152-153°C. The ^1H NMR spectrum verifies that no neutral ligand is present in solution as only the $\text{AA}'\text{BB}'\text{X}_3$ pattern expected for the three equivalent Cp ligands is observed. The molecule is monomeric in the gas phase as shown by the mass spectrum which contains a parent ion at 377 amu.

Solution properties of $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ give some insight into the structure of the compound. The solution color in cold toluene (ca. -30°C and below) is yellow. Warming causes the solution color to change from yellow to green (ca. 20°C) and then to blue (ca. 50°C and higher). The yellow solution color is similar to that observed in the 10-coordinate $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ compounds, while the blue color resembles that observed in the 9-coordinate $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$ complex which is monomeric and blue in the solid state. Presumably, varying the temperature produces a change in the position of the monomer-oligomer solution equilibrium described by Equation 1.

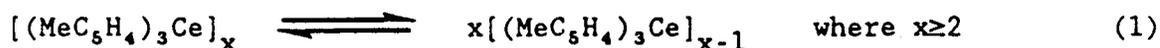
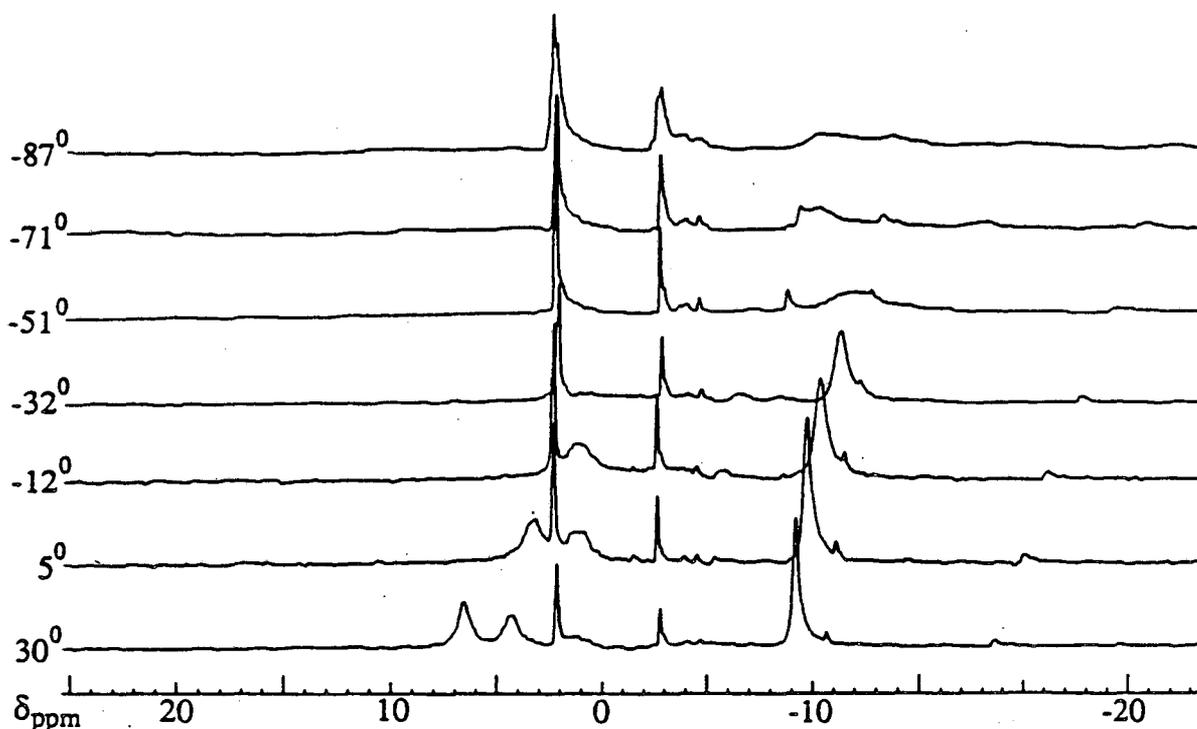


Fig. 2

VT ^1H NMR of $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ 

At higher temperature one observes the more, or completely, dissociated monomeric molecule, while at lower temperatures, equilibrium lies strongly toward the associated molecule. This association, or " $\text{Cp}_3\text{Ce}\cdot\text{L}$ -like" appearance, probably occurs through a bridging η^1 -interaction by one ring from an adjacent Ce atom.

Variable temperature ^1H NMR should reflect this observed color change since the "bridging" Cp ligand is chemically inequivalent from the other two. At 30°C , the spectrum shows only the $\text{AA}'\text{BB}'\text{X}_3$ pattern for the three equivalent Cp ligands (Fig 2). Cooling the solution produces a gradual broadening of the resonances and a change in chemical shift. At ca. -30°C , the A, A', B, and B' resonances broaden into the baseline, while the X_3 resonance nearly broadens in to the baseline at ca. -50°C . It appears that a new set of resonances begin to appear upon further cooling, indicating the presence of a

chemically different type of Cp ligand. Unfortunately, exact information about the structure of this low temperature species could not be elucidated because individual resonances were very broad (ca. 300 Hz. at half-height) and were poorly resolved. The use of a higher field magnet or the effect of solution concentration was not investigated.

Crystals, suitable for X-ray diffraction studies, were obtained by very slow cooling of a saturated toluene solution to -20°C . The molecule crystallizes in the monoclinic space group, $P2_1/a$, and is isostructural with the tetrameric $(\text{MeC}_5\text{H}_4)_3\text{Nd}$ complex.¹⁸ Each Ce atom is bound in an η^5 - fashion to three MeC_5H_4 ligands and in an η^1 - fashion to one ring of an adjacent $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ moiety. This sharing of a ring is repeated in a manner that produces tetrameric units. The geometry about the Ce atoms is again best described as a distorted tetrahedron. An ORTEP drawing is shown in Fig. 3. Some important bond distances and angles are given in Tables 1.4 and 1.5.

Several "base-free" triscyclopentadienyl complexes of the lanthanides and early transition metals have been structurally characterized (Table 1.6).^{18,21} Their structures show that coordination number and geometry about the central metal ion change markedly with metal ion radius and the cyclopentadienide steric bulk. In general, the coordination number increases with increasing metal ion radius and decreasing steric bulk of the cyclopentadienyl ligand. For example, R.D. Fischer and co-workers have structurally characterized $[(\text{C}_5\text{H}_5)_3\text{Pr}]_{\infty}$.¹⁹ Each Pr atom is η^5 -bound to three Cp ligands and η^2 -bound to one of the rings from an adjacent Pr atom. In this linear polymer, the coordination number of Pr is eleven. Apparently Pr is able to increase its coordination number by one over that in the Ce and Nd tetramers because of the sterically less

Fig. 3

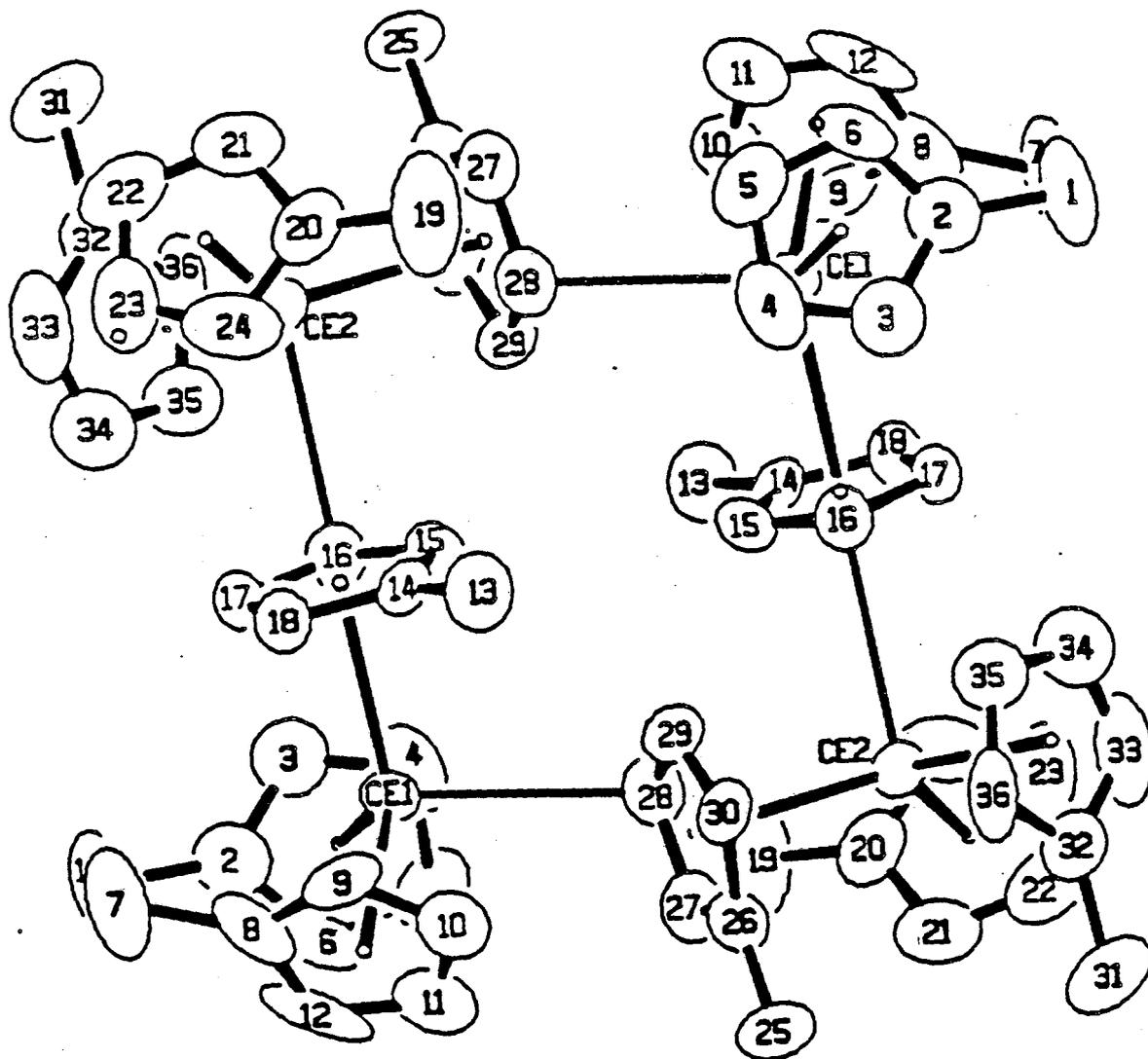
ORTEP Drawing of $[(\text{MeC}_5\text{H}_4)_3\text{Ce}]_4$ 

Table 1.4Bond Distances for $[(\text{MeC}_5\text{H}_4)_3\text{Ce}]_4$ (Å)

Ce1-C2	2.89(2)	Ce1-C8	2.79(2)	Ce1-C14	2.96(2)
Ce1-C3	2.84(2)	Ce1-C9	2.81(1)	Ce1-C15	2.91(1)
Ce1-C4	2.81(2)	Ce1-C10	2.79(2)	Ce1-C16	2.86(2)
Ce1-C5	2.81(1)	Ce1-C11	2.73(2)	Ce1-C17	2.82(1)
Ce1-C6	2.85(2)	Ce1-C12	2.79(2)	Ce1-C18	2.85(2)
Ce1-Cp1	2.58	Ce1-Cp2	2.52	Ce1-Cp3	2.62
		Ce1-C28	3.09(2)		
Ce2-C20	2.84(2)	Ce2-C26	2.92(2)	Ce2-C32	2.78(2)
Ce2-C21	2.80(2)	Ce2-C27	2.85(2)	Ce2-C33	2.81(2)
Ce2-C22	2.77(2)	Ce2-C28	2.83(2)	Ce2-C34	2.83(2)
Ce2-C23	2.74(2)	Ce2-C29	2.87(1)	Ce2-C35	2.79(2)
Ce2-C24	2.81(2)	Ce2-C30	2.92(1)	Ce2-C36	2.79(2)
Ce2-Cp4	2.53	Ce2-Cp5	2.62	Ce2-Cp6	2.53
		Ce2-C16	2.97(2)		

Table 1.5Intramolecular Angles for $[(\text{MeC}_5\text{H}_4)_3\text{Ce}]_4$ (°)

Cp1-Ce1-Cp2	119.1	Cp4-Ce2-Cp5	121.6
Cp1-Ce1-Cp3	114.5	Cp4-Ce2-Cp6	116.1
Cp2-Ce1-Cp3	115.8	Cp5-Ce2-Cp6	113.9
Cp1-Ce1-C28	94.6	Cp4-Ce2-C16	104.2
Cp2-Ce1-C28	104.0	Cp5-Ce2-C16	97.7
Cp3-Ce1-C28	104.2	Cp6-Ce2-C16	97.5

Cp1, Cp2, Cp3, Cp4, Cp5, and Cp6 are the centroids of the rings comprised of C2-C6, C8-C12, C14-C18, C20-C24, C26-C30, and C32-C36, respectively.

Table 1.6

Structurally Characterized Cp₃M Complexes

<u>Compound</u>	<u>Metal ion radius (Å)</u>	<u>C.N</u>	<u>M-C (Å)</u>	<u>Ref.</u>
[(C ₅ H ₅) ₃ Sc] ₂	0.87	8	2.49(2)	20
[(C ₅ H ₅) ₃ La] _x	1.22	10	2.85(8)	22
[(C ₅ H ₅) ₃ Pr] _∞	1.18	11	2.81	19
[(MeC ₅ H ₄) ₃ Ce] ₄	1.21	10	2.83(5)	this work
[(Me ₃ Si) ₂ C ₅ H ₃] ₃ Ce	1.20	9	2.83(5)	this work
(Me ₃ SiC ₅ H ₄) ₃ U	1.18	9	2.78(4)	26
[(MeC ₅ H ₅) ₃ Nd] ₄	1.17	10	2.79(5)	18
(C ₉ H ₇) ₃ Sm	1.13	9	2.75(5)	21
(C ₅ H ₅) ₃ Er	1.06	9	2.69, 2.67	24
(C ₅ H ₅) ₃ Tm	1.05	9	2.68, 2.66	24
(C ₅ H ₅) ₃ Yb	1.04	9	2.64	25
(C ₅ H ₅) ₃ Lu	1.03	8	2.60	23

demanding C₅H₅ ligand. The relatively small Sc(III) ion, in the dimeric Cp₃Sc structure, adopts an 8-coordinate geometry formed by two η⁵- rings, one η¹-ring, and a fourth bridging η¹-, η¹- ring.²⁰ Use of the more sterically demanding indenyl ligand results in the 9-coordinate, monomeric (C₉H₇)₃Sm structure with Sm bound in an η⁵-fashion to three rings.²¹

The relationship between structure, coordination number, and steric bulk about the central metal ion is also observed within the Cp₃Ce systems. Unlike (C₅H₅)₃Ce and (MeC₅H₄)₃Ce, which are polymeric and tetrameric, respectively, (Me₃SiC₅H₄)₃Ce and [(Me₃Si)₂C₅H₃]₃Ce adopt 9-coordinate, monomeric structures.

Addition of three equivalents of $K(\text{Me}_3\text{SiC}_5\text{H}_4)$ to CeCl_3 in thf, followed by crystallization from hexane, afforded the blue $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$ complex. This complex is extremely soluble in hydrocarbon solvents; approximately 3 grams dissolve in 5 mL of hexane. The melting point, 69-70°C, is much lower than other reported Cp_3M compounds, and its mass spectrum shows a parent ion at 551 amu. Brennan observed the similar properties in the analogous $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ complex, which has been structurally characterized by X-ray diffraction.²⁶ The structure of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ shows a monomeric, 9-coordinate, pseudo trigonal-planar geometry about uranium.

Due to its extreme solubility, crystals of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$, suitable for X-ray diffraction studies, could not be obtained. The X-ray powder pattern, however, was taken and corresponds to that observed for $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{M}$, where M is U and Pu (Table 1.7). This, along with the similar melting points and solubility properties, leads to the conclusion that $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$ is isostructural with the analogous uranium compound. Presumably, the more sterically demanding nature of $\text{Me}_3\text{SiC}_5\text{H}_4$, relative to MeC_5H_4 , prevents Ce from adopting the 10-coordinate, distorted tetrahedral geometry.

Use of an even more sterically demanding Cp ligand led to the isolation of single crystals suitable for X-ray diffraction studies. Addition of three equivalents of bis-trimethylsilylcyclopentadiene to an ether solution of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ce}$, followed by crystallization from hexane, affords the blue $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ complex. The compound crystallizes in the monoclinic space group, $I2/c$, and consists of a pseudo trigonal-planar arrangement of three η^5 -rings about the cerium ion which lies in the plane defined by the cyclopentadienyl centroids. The Cp-Ce-Cp angles are 120.7, 119.4, and 119.8°, and the Ce-Cp

distance averages to 2.57Å. An ORTEP drawing is shown in Fig. 4.

Bond distances and angles are given in Table 1.8

Table 1.7

Powder Pattern Data for $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{M}$, where M is Ce, U, and Pu

<u>Index</u>	<u>U</u> <u>$d_{hkl}(\text{calc})$</u>	<u>U</u> <u>$d_{hkl}(\text{meas})$</u> ⁵³	<u>Ce</u> <u>$d_{hkl}(\text{meas})$</u>	<u>Pu</u> <u>$d_{hkl}(\text{meas})$</u> ⁵³	<u>Int(Ce)</u>
2 0 0	11.315	11.518	11.226	11.297	s
2 1 0	10.550	---	10.495	---	w-
0 2 1	7.300	7.329	7.345	7.225	s
1 2 1	6.946	6.903	6.929	6.943	s
2 4 0	6.131	6.121	6,130	6.109	s
2 3 1	5.550	5.540	5.574	5.582	s-
3 2 1	5.245	5.216	5.246	5.254	m-
3 3 1	4.867	4.861	4.894	4.828	w
4 4 0	4.471	4.446	4.462	4.461	m
1 6 1	4.141	4.143	4.201	4.119	s-
6 1 0	3.741	3.712	3.719	---	s-
2 8 0	3.471	3.470	3.486	---	w-
4 7 0	3.358	3.354	3.357	---	w-
5 6 1	3.083	3.074	3.079	3.058	w+
1 10 1	2.737	2.736	2.747	2.732	m+
2 2 3	2.680	2.675	2.692	2.665	m
3 8 2	2.590	2.578	2.592	2.573	w+
0 6 3	2.433	2.478	2.483	2.473	w+
2 6 3	2.378	2.395	2.381	2.350	w
4 12 0	2.234	2.290	2.232	2.227	w
6 5 3	2.102	2.159	2.102	2.083	w+
1 4 4	2.016	2.056	2.026	2.011	w+
2 10 3	1.992	2.008	1.992	1.983	m+
3 14 1	1.944	1.954	1.946	---	m+

Fig. 4

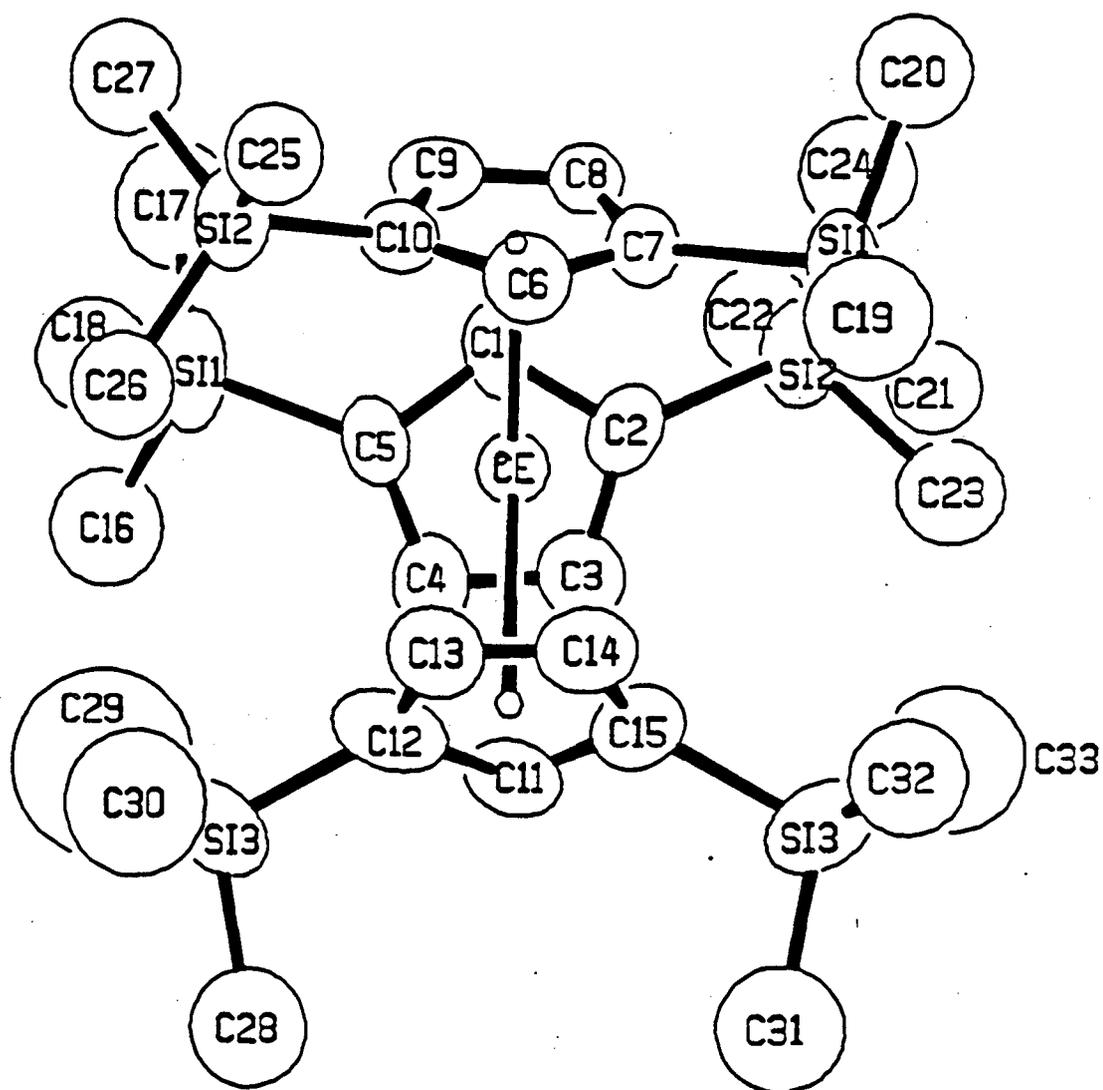
ORTEP Drawing of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ 

Table 1.8

Bond Distances (Å) and Intramolecular Angles (°) for
 $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$

Ce-C1	2.86(2)	Ce-C6	2.91(3)	Ce-C11	2.87(2)
Ce-C2	2.85(2)	Ce-C7	2.80(1)	Ce-C12	2.87(2)
Ce-C3	2.77(2)	Ce-C8	2.77(1)	Ce-C13	2.84(2)
Ce-C4	2.75(1)	Ce-C9	2.85(1)	Ce-C14	2.80(2)
Ce-C5	2.80(1)	Ce-C10	2.92(2)	Ce-C15	2.84(2)
Ce-Cp1	2.54	Ce-Cp2	2.59	Ce-Cp3	2.58
Cp1-Ce-Cp2	120.7	Cp1-Ce-Cp3	119.4	Cp2-Ce-Cp3	119.8

Cp1, Cp2, Cp3, Cp4, Cp5, and Cp6 are the centroids of the rings comprised of C2-C6, C8-C12, C14-C18, C20-C24, C26-C30, and C32-C36, respectively.

Since lanthanide ions are generally considered to be "hard" or "class A" acids, displacement of thf, an oxygen donor ligand, from the $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ environment by a phosphine ligand seemed unlikely. Surprisingly, addition of PMe_3 to a diethyl ether solution of the cerium thf complex, followed by crystallization from ether, afforded the $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{PMe}_3$ complex in 80% yield. The compound melts at 176-179°C with decomposition and evolution of PMe_3 .

The PEt_3 complex of $(\text{MeC}_5\text{H}_4)_3\text{Ce}$, however, was much more difficult to isolate. Addition of PEt_3 to an ether or toluene solution of the thf complex afforded only starting material. This result is in contrast to those of Brennan, as PEt_3 quantitatively displaces thf in the analogous uranium system. The displacement of thf by PMe_3 and the failure of PEt_3 to do so, suggests that steric effects are a major contributor in determining which Lewis base adducts are isolated from competition reactions. If gas phase proton affinity can be used as a measure of relative base strength toward Cp_3M environments, then one

would expect the more sterically demanding PEt_3 ligand to form the stronger interaction as it has a greater affinity ($231.7 \text{ kcal}\cdot\text{mol}^{-1}$) than does PMe_3 ($225.7 \text{ kcal}\cdot\text{mol}^{-1}$) toward the proton in the gas phase.²⁷

$(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{PEt}_3$ could be isolated from addition of PEt_3 to the base-free $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ in ether, followed by crystallization from ether. It appears that the Ce-P interaction is relatively weak, however, as integrated intensities of the ligand resonances in the ^1H NMR spectrum are a function of how long the complex is exposed to vacuum. As with the cerium-thf complex, addition of free ligand to both phosphine complexes produces a ^1H NMR spectrum ($+70^\circ\text{C}$ to -70°C) with only one set of ligand resonances whose chemical shift is a weighted average between the free and coordinated ligand chemical shifts.

Since lanthanide phosphine complexes are rare and none have been structurally characterized, single crystals suitable for X-ray diffraction studies were grown from a saturated ether solution slowly cooled to -20°C . The yellow $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{PMe}_3$ complex crystallizes in the monoclinic space group, Cc, and is crystallographically isomorphous to the related $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{PMe}_3$ complex.²⁸ An ORTEP drawing is shown in Fig. 5. Relevant bond distances and angles are given in Table 1.9. The Ce-Cp and U-Cp average distances, $2.56(3)\text{\AA}$ and $2.52(2)\text{\AA}$, respectively, reflect the ca. 0.03\AA larger size of the 10-coordinate Ce(III) ion. However, there are significant structural differences between the two molecules even though they are crystallographically isomorphous. The angles made by the four ligands about the metal atom are close to being tetrahedral in the uranium complex, while the geometry about the Ce atom is better described as a distorted trigonal pyramid, as in $(\text{C}_5\text{H}_5)_5\text{U}\cdot\text{thf}$ (Table 1.3). This

Fig. 5

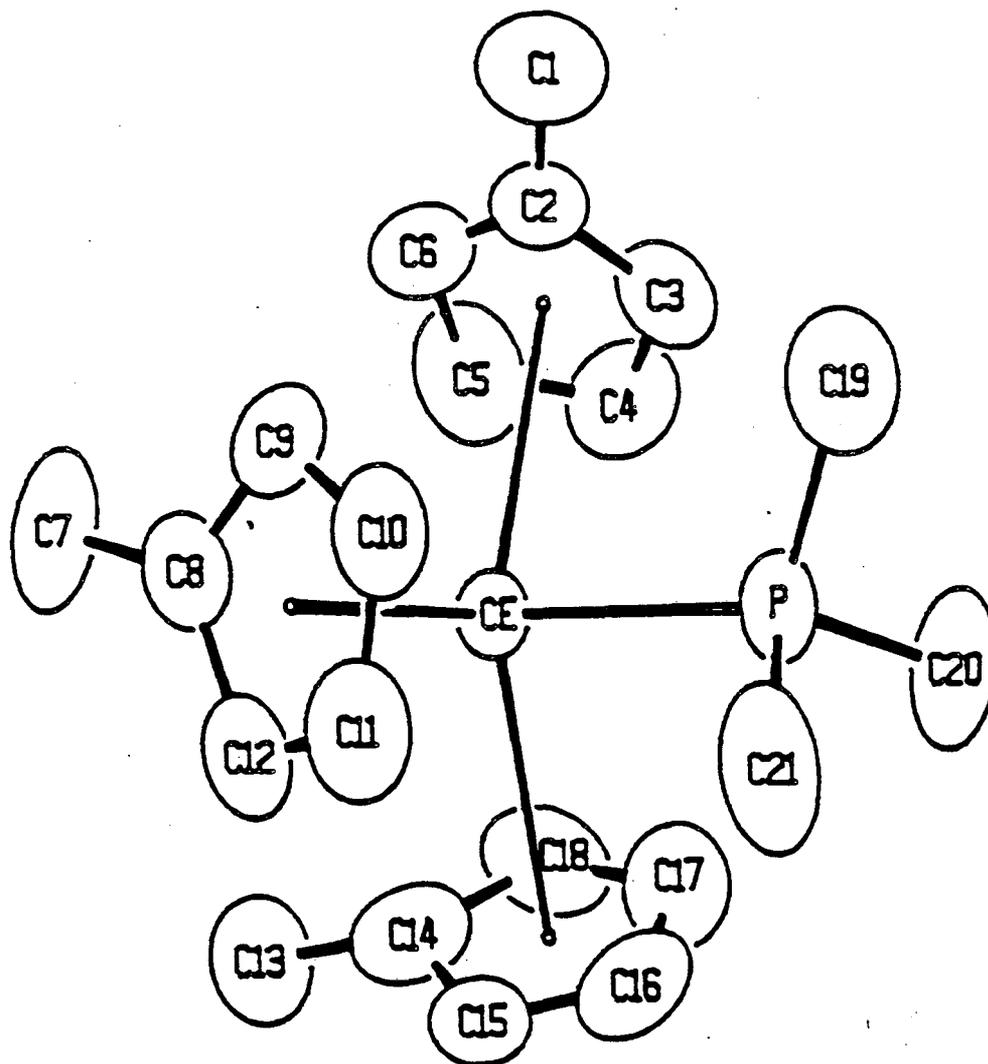
ORTEP Drawing of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{PMe}_3$ 

Table 1.9

Bond Distances (Å) and Intramolecular Angles (°) for
 $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{PMe}_3$

Ce-C2	2.88(1)	Ce-C8	2.90(2)	Ce-C14	2.76(2)
Ce-C3	2.84(1)	Ce-C9	2.83(1)	Ce-C15	2.83(1)
Ce-C4	2.78(2)	Ce-C10	2.86(1)	Ce-C16	2.84(1)
Ce-C5	2.75(1)	Ce-C11	2.82(2)	Ce-C17	2.84(1)
Ce-C6	2.78(2)	Ce-C12	2.82(1)	Ce-C18	2.81(1)
Ce-Cp1	2.55	Ce-Cp2	2.59	Ce-Cp3	2.54
			P-C19	1.88(2)	
			P-C20	1.84(1)	
			P-C21	1.857(1)	
	Ce-P	3.072(4)			
Cp1-Ce-Cp2	118.8	Cp2-Ce-P	98.9	Ce-P-C21	113.1(9)
Cp1-Ce-Cp3	118.2	Cp3-Ce-P	96.7	C19-P-C20	98.9(8)
Cp2-Ce-Cp3	117.8	Ce-P-C19	120(1)	C19-P-C21	98.2(8)
Cp1-Ce-P	97.3	Ce-P-C20	113(1)	C20-P-C21	106.2(8)

Cp1, Cp2, and Cp3 are the centroids of the rings comprised of C2-C6, C8-C12, and C14-C18, respectively.

difference in angles is a reflection of the longer Ce-P distance relative to the U-P distance. The Ce-P bond length, 3.072(4)Å, is a full 0.10Å longer than the U-P length, 2.972(6)Å. Based on a simple ionic model, a lengthening of only 0.03Å in Ce-P relative to U-P is predicted. The possible nature of this shorter U-P length will be discussed in a later section.

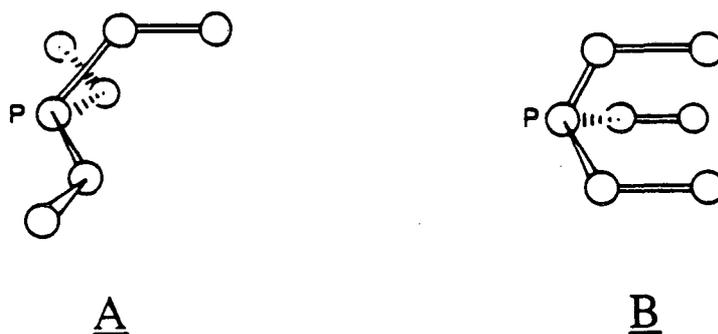
Phosphite complexes of the lanthanides are even rarer than phosphine complexes. They have been isolated by ligand displacement reactions from the thf complex or by addition of phosphite to the base-free compound. Verkade's phosphite, $\text{P}(\text{OCH}_2)_3\text{CEt}$, added to a toluene solution of the thf complex, followed by removal of solvent and crystallization from ether or toluene, afforded the $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{P}(\text{OCH}_2)_3\text{CEt}$ compound. Unlike the analogous uranium complex, this Ce complex has good solubility in Et_2O and toluene. It

is, however, less soluble than the phosphine and thf adducts, causing problems when studying the ^1H NMR spectra at temperatures lower than ca. -25°C . Trimethylphosphite, like PEt_3 , does not displace thf and the $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{P}(\text{OMe})_3$ complex must be synthesized from addition of the ligand to an ether solution of the base-free complex followed by crystallization. Once again, the Ce-P interaction appears to be relatively weak as the integrated intensity of the ligand resonance is a function of how long the complex is exposed to vacuum. Both phosphite complexes exchange rapidly with added ligand.

The difference in the steric bulk of the two phosphite ligands, similar to the previously described phosphines, might explain why one displaces thf and the other does not. Verkade's phosphite is sterically less demanding than $\text{P}(\text{OMe})_3$. The CEt group ties back the molecule, forcing it to adopt configuration B (Fig. 6). Several complexes containing $\text{P}(\text{OMe})_3$ have been structurally characterized, and, although the ligand has been found to adopt five different configurations, configuration B has never been observed.²⁹

Fig. 6:

Two Possible Configurations of Phosphites



Use of configuration A gives a revised Tolman cone angle of 128° for $P(OMe)_3$.³⁰ The reported cone angle for Verkade's phosphite is 101° .³¹

It should be noted that the synthetic conditions employed might also explain the same observation. Verkade's phosphite is a solid at room temperature and has a much lower vapor pressure than thf. Trimethylphosphite, on the other hand, has a higher vapor pressure than thf. If M-L bond strengths are similar, removal of solvent under reduced pressure during reaction mixture work-up might result in loss of the lower boiling ligand. However, since the lower boiling PMe_3 displaces thf, and since $P(OMe)_3$ displaces thf in the analogous uranium system, this concept does not appear to be consistent with all of the experimental observations.

Unfortunately, the configuration of the $P(OMe)_3$ ligand in $(MeC_5H_4)_3Ce \cdot P(OMe)_3$ could not be ascertained as crystals suitable for X-ray diffraction studies could not be isolated. However, $(MeC_5H_4)_3Ce \cdot P(OCH_2)_3Ct$ crystallized nicely and its X-ray structure was determined. The molecule crystallizes in the orthorhombic space group, $P2_12_12_1$, and again is isostructural with the analogous uranium complex.³² An ORTEP drawing is shown in Fig. 7. Selected distances and angles are given in Table 1.10.

The Ce-P distance in the $Ce \cdot P(OCH_2)_3Ct$ complex is slightly longer than the equivalent distance in the $Ce \cdot PMe_3$ complex. This increased M-P distance is also observed in the uranium system, and must be electronic in nature since the phosphite ligand is sterically less demanding than PMe_3 ; the calculated cone angles are $101(2)^\circ$ and $118(4)^\circ$, respectively.²⁷ Of greater interest, is the difference between the Ce-P and U-P bond lengths. Again, the average M-C distances, 2.82(3) and 2.80(5)Å, reflect the larger size of the Ce(III) ion. However, the Ce-P bond length, 3.086(3)Å, is ca. 0.10Å

Fig. 7

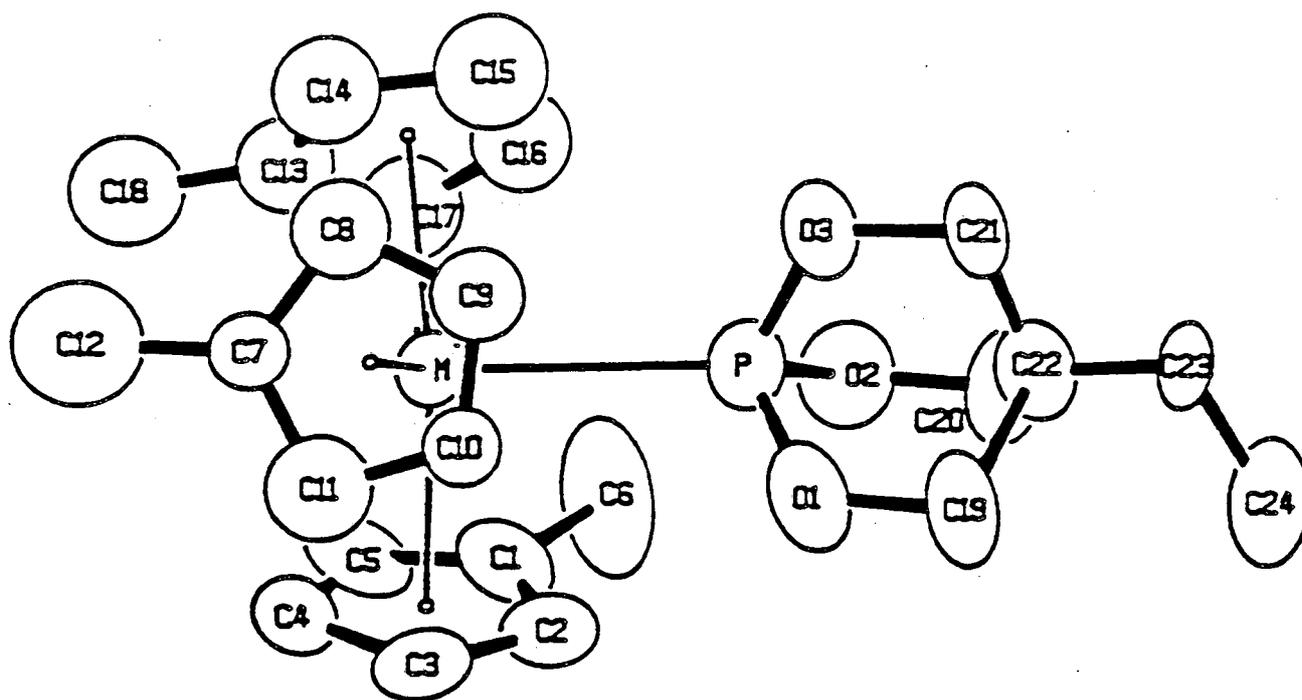
ORTEP Drawing of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{P}(\text{OCH}_2)_3\text{CET}$ 

Table 1.10

Bond Distances (Å) and Intramolecular Angles (°) for
 $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{P}(\text{OCH}_2)_3\text{CEt}$

Ce-C1	2.83(1)	Ce-C7	2.81(3)	Ce-C7'	2.82(3)	Ce-C13	2.81(1)
Ce-C2	2.83(1)	Ce-C8	2.90(3)	Ce-C8'	2.78(3)	Ce-C14	2.80(2)
Ce-C3	2.79(1)	Ce-C9	2.83(3)	Ce-C9'	2.86(2)	Ce-C15	2.81(2)
Ce-C4	2.82(1)	Ce-C10	2.79(3)	Ce-C10'	2.78(3)	Ce-C16	2.80(1)
Ce-C5	2.82(1)	Ce-C11	2.84(3)	Ce-C11'	2.81(3)	Ce-C17	2.87(1)
Ce-Cp1	2.55	Ce-Cp2	2.55	Ce-Cp2'	2.52	Ce-Cp3	2.54
Ce-P	3.086(3)	P-O1	1.597(7)	O1-C19	1.433(12)		
		P-O2	1.611(9)	O2-C20	1.440(13)		
		P-O3	1.591(9)	O3-C21	1.460(15)		
Cp1-Ce-Cp2	119.1	Cp1-Ce-P	94.7	Ce-P-O1	114.6(4)		
Cp1-Ce-Cp3	120.0	Cp2-Ce-P	94.1	Ce-P-O2	118.0(4)		
Cp2-Ce-Cp3	118.0	Cp2'-Ce-P	114.9	Ce-P-O3	118.5(4)		
Cp1-Ce-Cp2'	122.1	Cp3-Ce-P	98.3				
Cp3-Ce-Cp2'	114.9						
O1-P-O2	100.6(6)	O1-P-O3	101.5(6)	O2-P-O3	100.8(5)		
P-O1-C19	118.3(8)	P-O2-C20	117.8(8)	P-O3-C21	117.0(9)		

Cp1, Cp2, and Cp3 are the centroids of the rings comprised of C1-C5, C7-C11, and C13-C17, respectively.

longer than the observed U-P distance, 2.988(6)Å. Unlike the PMe_3 complexes, the lengthening of the Ce-P bond, relative to the U-P bond, is not reflected in different angles about the central metal atoms. In $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{P}(\text{OCH}_2)_3\text{CEt}$ and $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{P}(\text{OCH}_2)_3\text{CEt}$ the average Cp-M-P (95.4 and 95.3°, respectively) and Cp-M-Cp (119.0 and 118.7°, respectively) angles are identical within experimental error.

Initial attempts to make a tertiary amine complex failed. Adding NMe_3 gas to an ether solution of the thf complex or adding a NMe_3 saturated toluene solution to the thf complex resulted in isolation of starting material only. This observation agrees with those of Brennan in the analogous uranium system, and it is probably a reflection of

the ligand's higher vapor pressure and larger steric demand relative to thf and PMe_3 . Rosen has prepared the $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{NH}_3$ complex, in quantitative yield, from the addition of a NH_3 saturated toluene solution to $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{thf}$.³³ During the preparation of this thesis, Fabiano prepared the analogous Ce complex in a similar manner.⁵⁴ The smaller size of NH_3 , relative to NMe_3 , probably accounts for this behavior.

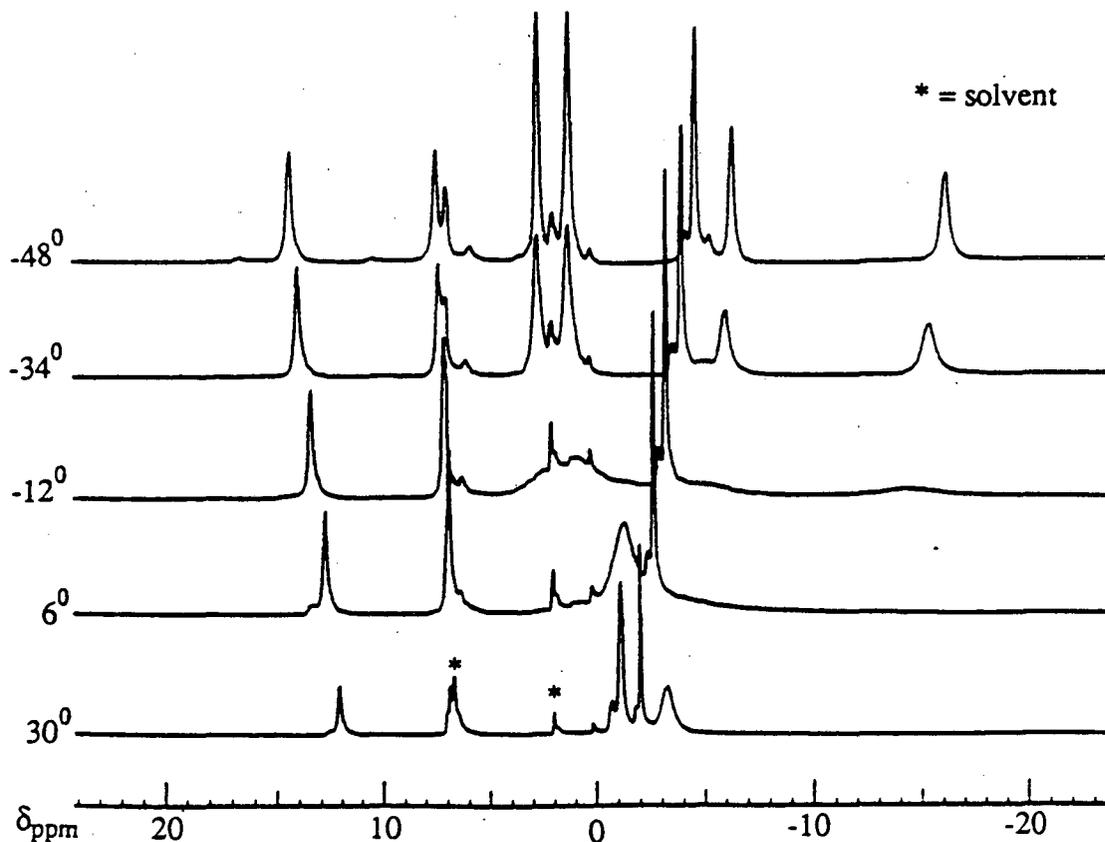
The use of a less volatile and sterically less demanding ligand led to the isolation of a stable $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ tertiary amine complex. Addition of a toluene solution of quinuclidine (quin), $\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$, to a toluene solution of the thf complex, followed by slow removal (ca. 45-60 min) of solvent and crystallization from ether or toluene, afforded the pale yellow $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$ complex. The Ce-N and Ce-O bond strengths in the thf and quinuclidine complexes appear to be quite similar, as mixtures of the two complexes are formed if the reaction is carried out in ether or the toluene is removed rapidly. Presumably the slow toluene removal drives the equilibrium of Equation 2 toward loss of the more volatile thf ligand leaving behind only quinuclidine to coordinate to $(\text{MeC}_5\text{H}_4)_3\text{Ce}$.



Furthermore, the tied-back nature of the quin ligand, similar to Verkade's phosphite, facilitates product formation over the more sterically demanding NMe_3 ligand.

Unlike all of the other $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ complexes, the coordinated quin does not exchange rapidly with added quinuclidine in solution at all temperatures. Instead, resonances due to both free and

Fig. 8

 ^1H NMR of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{quin} + \text{quin}$ 

coordinated ligand are observed at temperatures below -12°C in the ^1H NMR spectrum (Fig. 8).

This slow exchange phenomenon is consistent with an associative process for ligand exchange. The larger, more sterically demanding quinuclidine ligand, relative to any of the other studied Lewis bases, should cause an increase in the activation energy necessary to coordinate a second ligand in the transition state due to greater intramolecular repulsions. It would be premature to suggest a given

Table 1.11

Bond Distances (Å) and Intramolecular Angles (°) for
 $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$

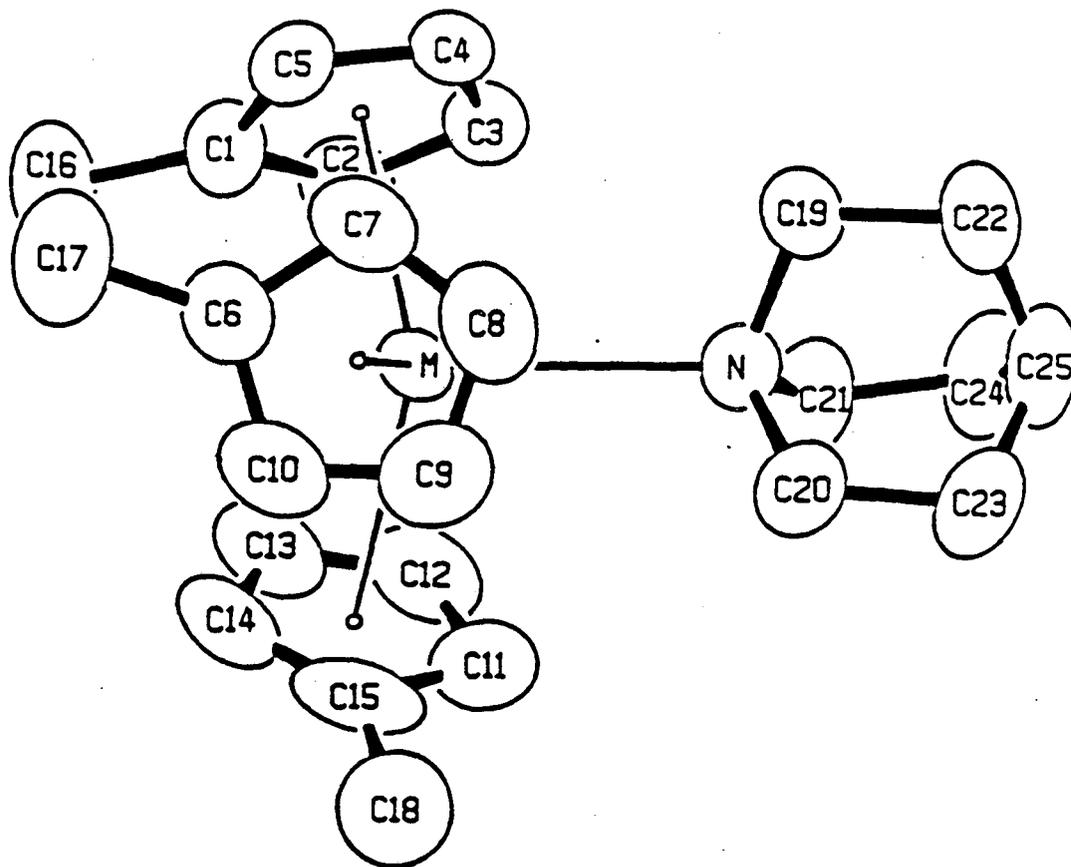
Ce-C1	2.868(3)	Ce-C6	2.866(3)	Ce-C11	2.882(4)
Ce-C2	2.871(3)	Ce-C7	2.859(4)	Ce-C12	2.815(4)
Ce-C3	2.834(3)	Ce-C8	2.838(4)	Ce-C13	2.804(4)
Ce-C4	2.816(3)	Ce-C9	2.815(4)	Ce-C14	2.841(4)
Ce-C5	2.832(3)	Ce-C10	2.835(3)	Ce-C15	2.911(4)
Ce-Cp1	2.58	Ce-Cp2	2.58	Ce-Cp3	2.59
		Ce-N	2.789(3)		
N-C19	1.488(5)	C19-C22	1.549(5)	C22-C25	1.520(8)
N-C20	1.490(4)	C20-C23	1.540(5)	C23-C25	1.508(7)
N-C21	1.498(4)	C21-C24	1.542(6)	C24-C25	1.513(8)
Cp1-Ce-Cp2	117.0	Cp1-Ce-N	100.9	Ce-N-C19	110.2(2)
Cp1-Ce-Cp3	115.8	Cp2-Ce-N	101.0	Ce-N-C20	110.3(2)
Cp2-Ce-Cp3	116.2	Cp3-Ce-N	101.6	Ce-N-C21	112.8(2)
C19-N-C20	108.9(3)	C19-N-C21	107.0(3)	C20-N-C21	107.4(3)

Cp1, Cp2, and Cp3 are the centroids of the rings comprised of C1-C5, C6-C10, and C11-C15, respectively.

mechanism, however, until relative rates, as a function of added ligand concentration, are measured.

Crystals of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$, suitable for X-ray diffraction, studies were grown by cooling a saturated toluene solution slowly to -20°C . The complex crystallizes in the triclinic space group, P1. Again the three η^5 -bound Cp ligands and the nitrogen-bound quin ligand adopt a distorted tetrahedral geometry about the Ce atom. An ORTEP drawing is shown in Fig. 9. Important distances and angle are given in Table 1.11. The average Cp-Ce-Cp angle, 116.3° , is smaller than any other structurally characterized $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ complex, reflecting the larger steric bulk that

Fig. 9

ORTEP Drawing of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$ 

quinuclidine displays toward the $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ environment. Consistent with this observation is the larger N-Ce-Cp average angle, 101.2° . For comparison, the average Cp-Ce-Cp and P-Ce-Cp angles in $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{PMe}_3$ are 118° and 98° , respectively. All angles about Ce and N are identical, within experimental error, to the isostructural $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{quin}$ complex.³² All bond distances, including Ce-N, about Ce are about 0.03\AA longer than those in the uranium complex. The elongation of the Ce-L bond relative to the U-L bond, observed in the PMe_3 and $\text{P}(\text{OCH}_2)_3\text{CEt}$ complexes, is not observed in the $\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$ environments. Instead, the Ce-N, $2.789(3)\text{\AA}$, and U-N, $2.764(4)\text{\AA}$, distances reflect only the difference in metal ion radii.

One other Ln·quin coordination complex has been structurally characterized.³⁴ In $(\text{DPM})_3\text{Eu}\cdot\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$, (DPM is 2,2,6,6-tetramethyl-heptan-3,5-dionate) the geometry about Eu is best described as a distorted octahedron with the nitrogen of quinuclidine located above the center of one of the octahedral faces formed by the three bidentate DPM ligands. The Eu-N bond length, $2.603(7)\text{\AA}$, is ca. 0.05\AA longer than expected relative to the U-N and Ce-N lengths in $(\text{MeC}_5\text{H}_4)_3\text{M}\cdot\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$. However, the steric demands of the ligand systems, the geometries about the central metal atoms, and the coordination numbers are very different between the complexes, and the lengthening of the Eu-N bond probably only reflects the sensitivity of bond lengths toward these factors.

Pyridine complexes of the lanthanide and actinide ions are more common than tertiary amine complexes, and their syntheses proved to be quite straightforward. The $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{NC}_5\text{H}_5$ and $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{NC}_5\text{H}_4\text{NMe}_2$ complexes were prepared from the thf complex. Both complexes crystallize from ether in good yield and melt with decomposition ($\text{Ce}\cdot\text{NC}_5\text{H}_5$ at $132\text{-}134^\circ\text{C}$, $\text{Ce}\cdot\text{NC}_5\text{H}_4\text{NMe}_2$ at $173\text{-}175^\circ\text{C}$). The

colors of the two complexes, in solution and solid states, are slightly different, possibly reflecting the stronger electron-donating ability of NMe_2 relative to H. UV-VIS spectroscopy would be a useful method for quantifying this energy difference, if the ligand to metal charge transfer gap could be identified. This experiment was not performed, however, nor was the attempted synthesis of the $\text{NC}_5\text{H}_4\text{CN}$ complex due to the gross insolubility found in the analogous $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{NC}_5\text{H}_4\text{CN}$ complex. Both pyridine complexes exchange rapidly, at all temperatures, with added ligand.

Crystals of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{NC}_5\text{H}_5$, suitable for X-ray studies, could not be isolated; however, suitable crystals of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{NC}_5\text{H}_4\text{NMe}_2$ were isolated by cooling a saturated diethyl ether solution slowly to -20°C . The molecule, best described as a distorted tetrahedron, crystallizes in the orthorhombic space group, $\text{P}2_12_12_1$, and is isostructural with the analogous uranium complex.³⁵ As with the other $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ complexes, the Ce atom is bound to three $\eta^5\text{-Cp}$ ligands and σ -bound through the N atom of $\text{NC}_5\text{H}_4\text{NMe}_2$. An ORTEP drawing is shown in Fig. 10. Relevant distances and angles are given in Table 1.12. Similar to the quinuclidine complex, all angles about Ce and N are identical to those found in the $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{NC}_5\text{H}_4\text{NMe}_2$ complex, while all bond distances about Ce, including Ce-N, are ca. 0.03\AA longer.

A few other lanthanide pyridine complexes have been structurally characterized.^{36,37} The geometry about the central metal ion is pseudo-tetrahedral in all of them, with the N atom of the pyridine ligand occupying one of the four tetrahedral sites. For comparison, selected distances and angles are given in Table 1.13. The only other structurally characterized Ce-pyridine coordination compound, $(\text{C}_9\text{H}_7)_3\text{Ce}\cdot\text{NC}_5\text{H}_5$, contains a Ce-N bond length, $2.684(4)\text{\AA}$, that is

Fig. 10

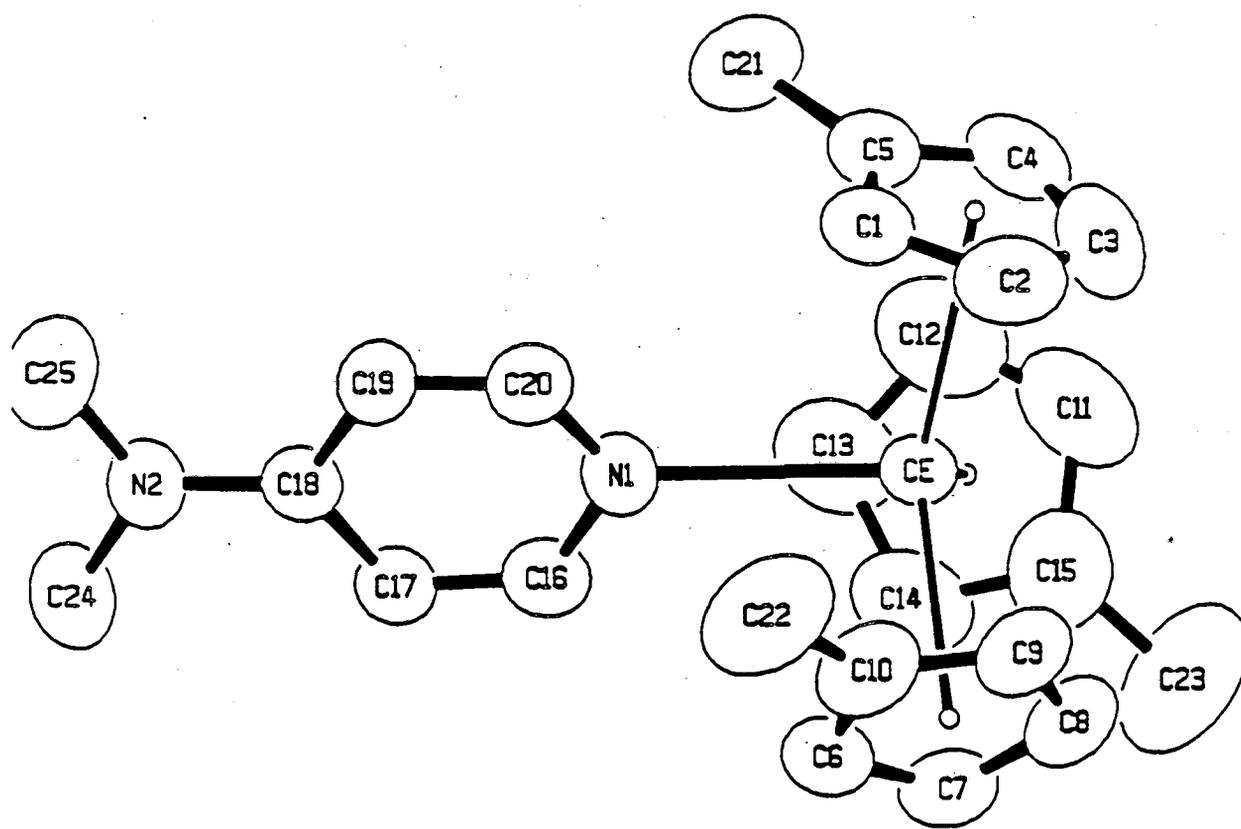
ORTEP Drawing of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{NC}_5\text{H}_4\text{NMe}_2$ 

Table 1.12

Bond Distances (Å) and Intramolecular Angles (°) for
 $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{NC}_5\text{H}_4\text{NMe}_2$

Ce-C1	2.869(8)	Ce-C6	2.848(9)	Ce-C11	2.805(11)
Ce-C2	2.832(9)	Ce-C7	2.821(8)	Ce-C12	2.854(13)
Ce-C3	2.826(13)	Ce-C8	2.791(9)	Ce-C13	2.836(9)
Ce-C4	2.892(11)	Ce-C9	2.858(9)	Ce-C14	2.830(10)
Ce-C5	2.903(8)	Ce-C10	2.866(9)	Ce-C15	2.835(11)
Ce-Cp1	2.608	Ce-Cp2	2.575	Ce-Cp3	2.562
Ce-N1	2.668(6)	C16-C17	1.352(11)	N2-C18	1.356(9)
N1-C16	1.356(11)	C17-C18	1.403(9)	N2-C24	1.447(12)
N1-C20	1.336(10)	C18-C19	1.415(10)	N2-C25	1.454(12)
		C19-C20	1.363(11)		
Cp1-Ce-Cp2	118.0	Cp2-Ce-N1	95.7	C16-N1-C20	114.3(6)
Cp1-Ce-Cp3	115.0	Cp3-Ce-N1	99.8	C18-N2-C24	120.4(6)
Cp2-Ce-Cp3	119.6	Ce-N1-C16	119.2(6)	C18-N2-C25	121.4(7)
Cp1-Ce-N1	102.0	Ce-N1-C20	126.5(5)	C24-N2-C25	118.2(7)

Cp1, Cp2, and Cp3 are the centroids of the rings comprised of C1-C5, C6-C10, and C11-C15, respectively.

Table 1.13

Pyridine Complexes of Lanthanides and Actinides

<u>Compound</u>	<u>M-N (Å)</u>	<u>M-C (Å)</u>	<u>Cp-M-Cp</u>	<u>Cp-M-N</u>
$(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{NC}_5\text{H}_4\text{NMe}_2$	2.668(6)	2.85(4)	118.9	99.2
$(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{NC}_5\text{H}_4\text{NMe}_2$	2.64(2)	2.82(4)	117.6	100.2
$(\text{C}_9\text{H}_7)_3\text{Ce}\cdot\text{NC}_5\text{H}_5$	2.684(4)	2.86(3)	116.2	101.2
$(\text{C}_5\text{H}_5)_3\text{Yb}\cdot\text{NC}_4\text{H}_4\text{N}\cdot\text{Yb}(\text{C}_5\text{H}_5)_3$	2.61(1)	2.68(1)	117.9	98.5

slightly longer than the 2.668(6)Å Ce-N distance in $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{NC}_5\text{H}_4\text{NMe}_2$. This is probably a reflection of the more sterically demanding nature of the indenyl ligand relative to the methylcyclopentadienyl ligand.

The "soft" nature of sulfur relative to oxygen, implies that $(\text{MeC}_5\text{H}_4)_3\text{Ce}$, considered a "hard" acid, should preferentially bind to oxygen donor ligands over sulfur donor ligands. That is to say, the Ce-O interaction should be stronger than the Ce-S interaction. To date, lanthanide complexes with neutral sulfur-donor ligands have not been reported, lending support to this belief.

Addition of tetrahydrothiophene (tth), SC_4H_8 , to an ether solution of the thf complex, followed by crystallization from ether, resulted in the isolation of both the cerium tth and thf complexes. As expected, tth does not quantitatively displace the thf, but it does effectively compete for coordination to the $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ environment, indicating that the Ce-O and Ce-S interactions are very similar in energy.

Pure $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{SC}_4\text{H}_8$ could be isolated by addition of tth to a toluene or ether solution of the base-free complex, followed by crystallization from ether. The Ce-tth interaction is stronger than the Ce-ether interaction presumably because tth is less sterically demanding than Et_2O . Unfortunately, suitable crystals for X-ray diffraction could not be isolated. Brennan and Zalkin have structurally characterized the analogous $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{SC}_4\text{H}_8$ complex.³⁸ Similar to other Lewis base coordination complexes, the cerium tth complex is expected to adopt the same geometry.

Lewis base adducts of nitriles and isocyanides are by far the most common and extensively studied coordination compounds of the triscyclopentadienyl lanthanides. The majority of these complexes

exist as 1:1 adducts similar to the coordination complexes described herein. However, due to the "rod-like", and therefore, relatively sterically undemanding, nature of nitriles and isocyanides, a number of $\text{Cp}_3\text{M}\cdot\text{L}_2$ complexes have been recently synthesized and structurally characterized.³⁹ These "skinny" ligands are of interest from a relative basicity viewpoint because of their relatively undemanding steric nature and because of their unique ability to form 2:1 complexes.

Addition of one equivalent or an excess of EtCN, EtNC, or Me_3CNC to an ether solution of the thf complex, followed by crystallization from hexane or ether, afforded the yellow 1:1 $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ complexes. Room temperature ^1H NMR spectroscopy verifies the 1:1 stoichiometry. The infrared CN stretching frequencies; 2260 [$\text{Ce}\cdot\text{NCEt}$], 2200 [$\text{Ce}\cdot\text{CNEt}$], and 2175 [$\text{Ce}\cdot\text{CNCMe}_3$] cm^{-1} ; are all shifted to higher energy relative to that found in the free ligands, consistent with a σ -only interaction⁴⁰ and with the ν_{CN} 's reported for the other Cp_3Ln nitrile and isocyanide complexes.⁴¹

Although no 2:1 isocyanide or nitrile adducts could be isolated in the solid state, evidence for their formation in solution is found in variable temperature ^1H NMR spectroscopic studies. Comparing the spectrum of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ with that of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L} + \text{L}$, one observes two phenomena. In one case, the chemical shifts of the Cp resonances follow Curie behavior and are identical in the two spectra at all temperatures, indicating that only one species, $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$, is present in solution (Fig. 11). In the other case, the chemical shifts of the Cp ligands in the $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L} + \text{L}$ spectrum do not follow Curie behavior and are different from those in the $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ spectrum, indicating that additional species, such as $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}_2$, are present in solution (Fig. 12). Coordination of a second base

Fig. 11

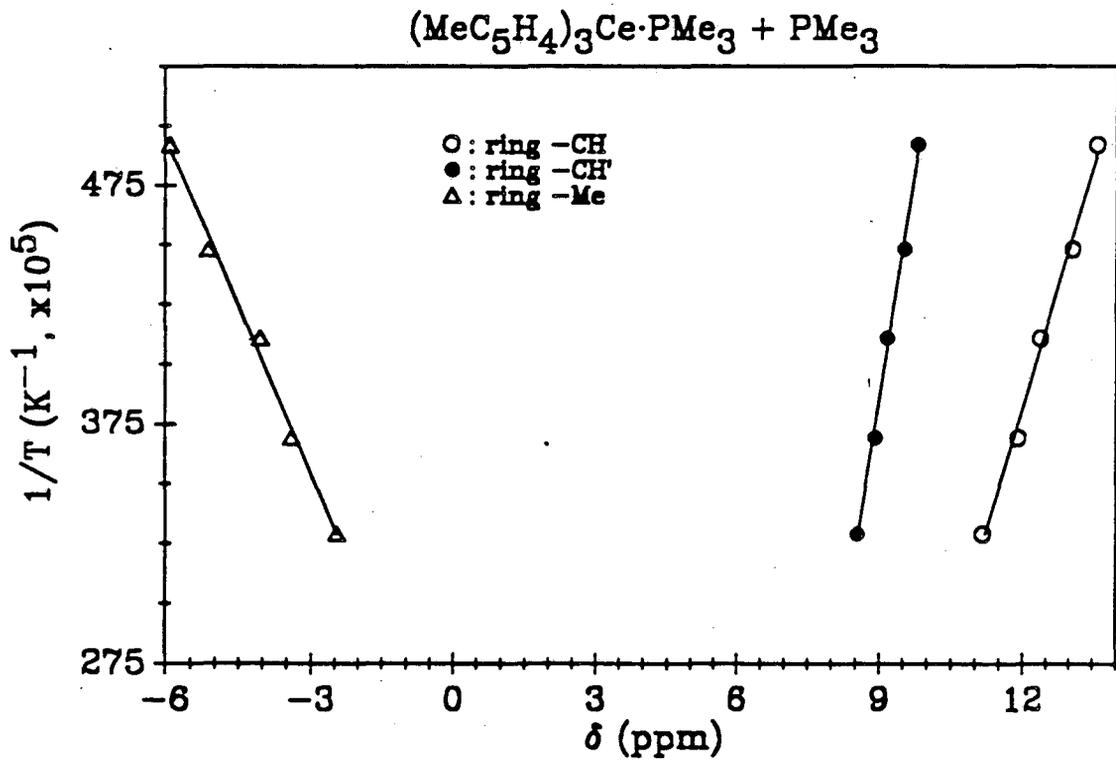
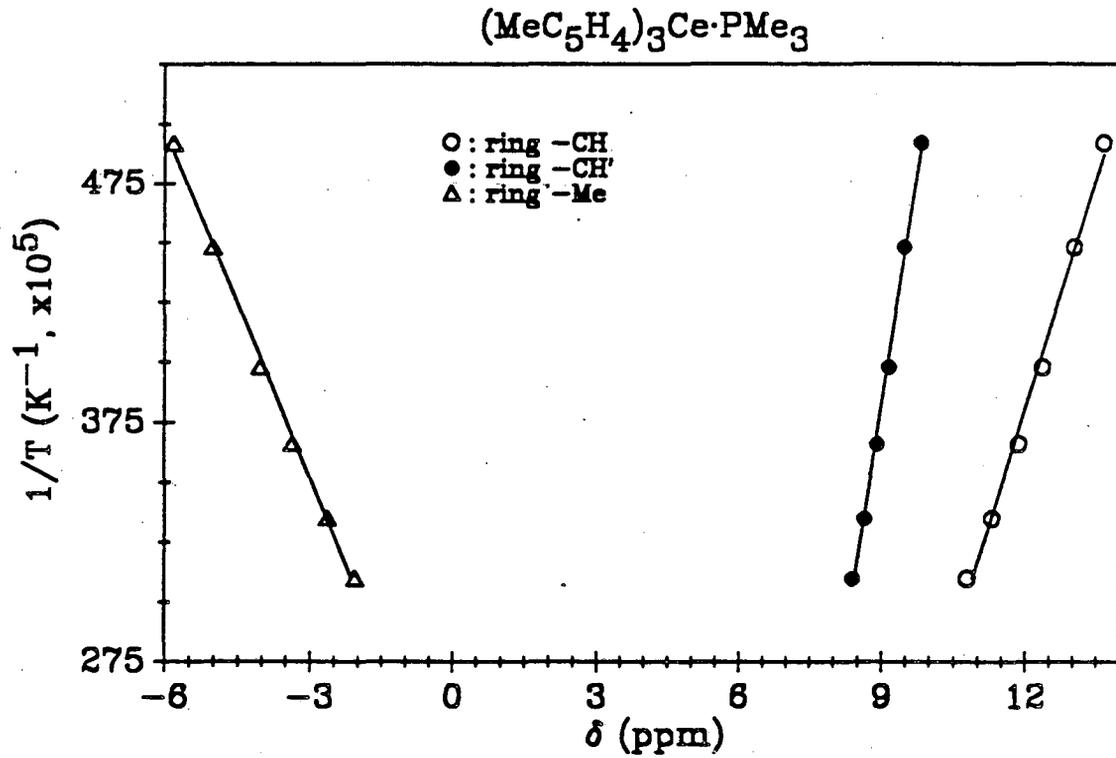
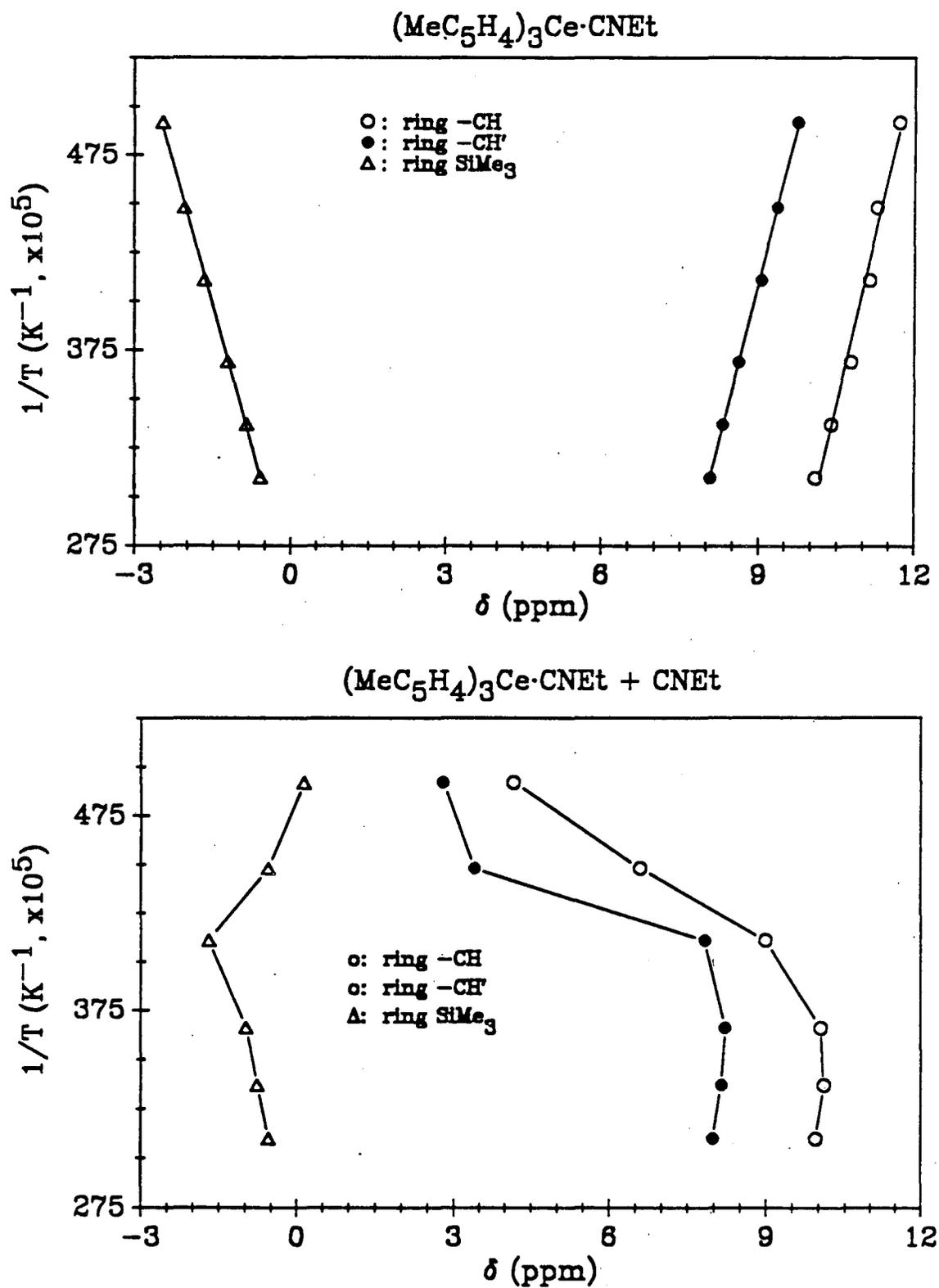
Plots of δ vs $1/T$ for $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{PMe}_3$ and $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{PMe}_3 + \text{PMe}_3$ 

Fig. 12

Plots of δ vs $1/T$ for $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNEt}$ and $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNEt} + \text{CNEt}$ 

should cause the Cp-Ce-Cp angles to approach 120° , those expected in a trigonal pyramid. This geometric perturbation has been shown to produce a noticeable effect on chemical shifts.⁴²

Crystals of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNCMe}_3$, suitable for X-ray diffraction, were isolated by cooling a saturated diethyl ether solution slowly to -20°C . The molecule crystallizes in the monoclinic space group, $P2_1/c$, and again exhibits a distorted tetrahedral geometry about the Ce atom. An ORTEP drawing is shown in Fig. 13. Some important bond distances and angles are given in Table 1.14. The average Cp-Ce-Cp angle, 118.7° , is identical to those found in $(\text{C}_5\text{H}_5)_3\text{Pr}\cdot\text{CNC}_6\text{H}_{11}$, 118.9° ,⁴³ and $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}\cdot\text{CNEt}$, 118.5° ,⁴⁴ and reflects the relatively undemanding steric nature of the isocyanide ligands. The Ce-C(CNR) distance, $2.69(2)\text{\AA}$, is identical to that predicted by ionic summation methods and the observed Pr-C(CNR) distance, $2.65(1)\text{\AA}$. Interestingly, however, these distances are about 0.1\AA longer than

Table 1.14

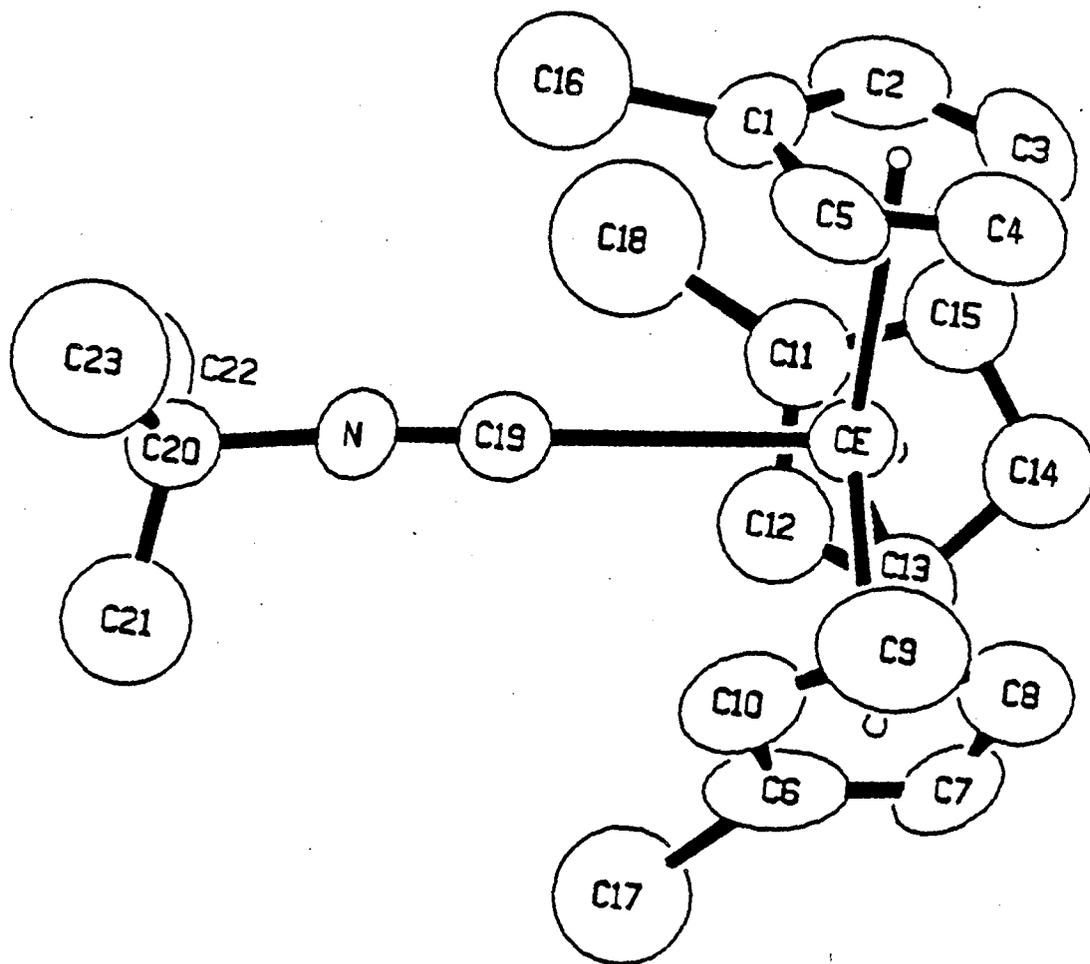
Bond Distances (\AA) and Intramolecular Angles ($^\circ$) for
 $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNCMe}_3$

Ce-C1	2.85(3)	Ce-C6	2.80(3)	Ce-C11	2.83(3)
Ce-C2	2.78(5)	Ce-C7	2.82(3)	Ce-C12	2.80(3)
Ce-C3	2.75(3)	Ce-C8	2.72(5)	Ce-C13	2.76(2)
Ce-C4	2.76(4)	Ce-C9	2.78(5)	Ce-C14	2.75(2)
Ce-C5	2.84(2)	Ce-C10	2.80(3)	Ce-C15	2.79(3)
Ce-Cp1	2.55	Ce-Cp2	2.54	Ce-Cp3	2.56
Ce-C19	2.71(2)	N-C20	1.39(2)	C20-C22	1.54(4)
C19-N	1.11(2)	C20-C21	1.53(3)	C20-C23	1.52(3)
Cp1-Ce-Cp2	118.5	Cp2-Ce-C19	95.7	N-C20-C21	110(2)
Cp1-Ce-Cp3	120.6	Cp3-Ce-C19	95.9	N-C20-C22	107(2)
Cp2-Ce-Cp3	116.9	Ce-C19-N	177(1)	N-C20-C23	113(2)
Cp1-Ce-C19	98.6	C19-N-C20	175(2)		

Cp1, Cp2, and Cp3 are the centroids of the rings comprised of C1-C5, C6-C10, and C11-C15, respectively.

Fig. 13

ORTEP Drawing of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNCMe}_3$

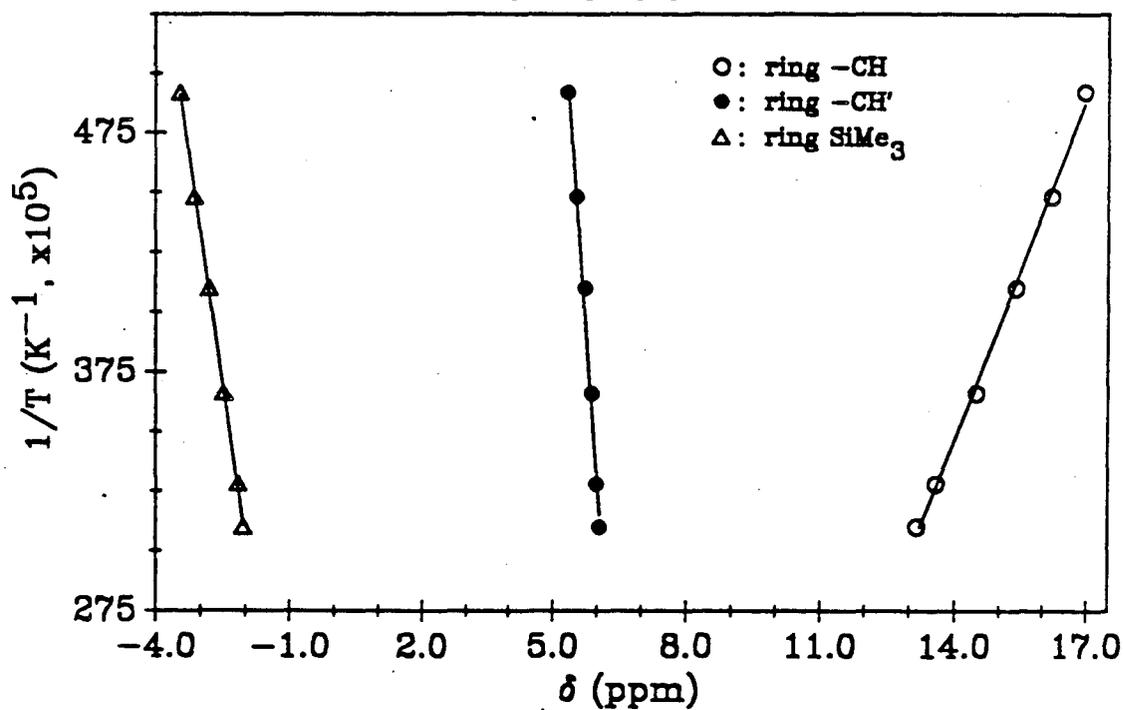
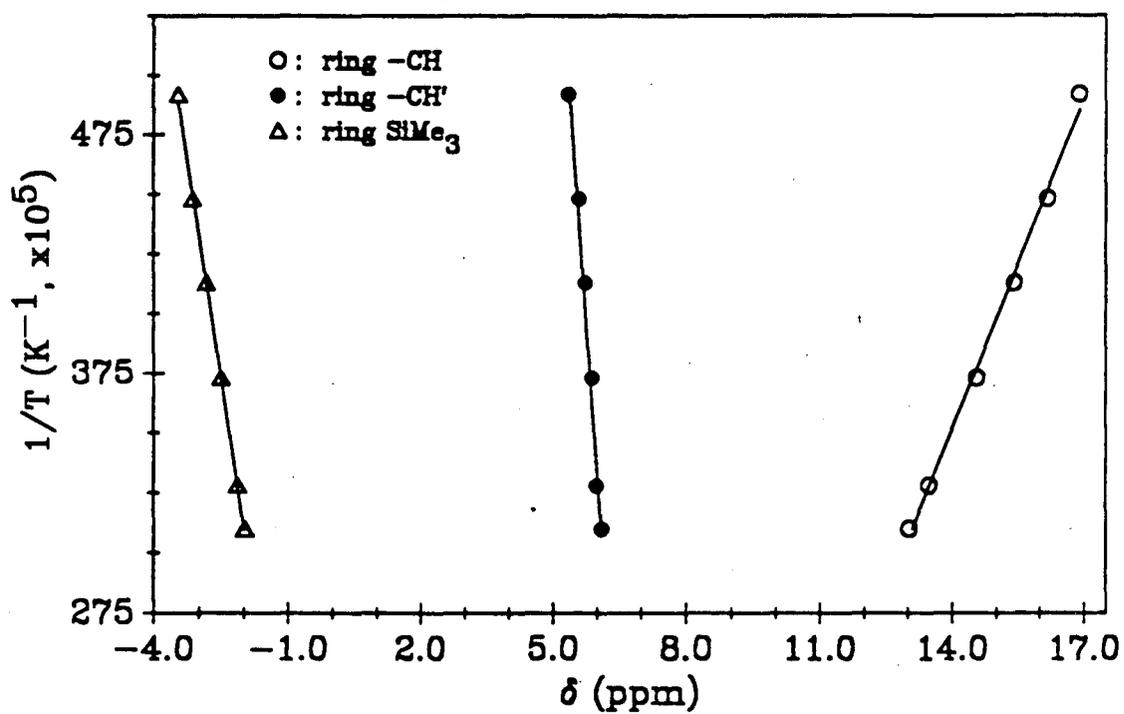


expected relative to the U-C(CNR) distance, 2.57(2)Å, in $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}\cdot\text{CNEt}$, again suggesting some extra bond stabilization available to uranium that is not available to the corresponding lanthanides.

The displacement of one monodentate ligand by another is by far the easiest to evaluate in a quantitative manner. The presence of additional species in solution, such as $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}_2$, greatly complicate the interpretation of the experimental data. It was, therefore, desirable to synthesize triscyclopentadienyl nitrile and isocyanide complexes that were not capable of coordinating a second ligand to any measurable extent. Since the only reported neutral $\text{Cp}_3\text{Ln}\cdot\text{L}_2$ compounds contain the unsubstituted C_5H_5 ligand and the small MeCN ligand, increasing the steric demands of the ligand environment about the Ce ion seemed to be a plausible approach toward eliminating the formation of 2:1 adducts. Use of a bulkier alkyl group on the nitrile or isocyanide ligand did not appear to be effective, as both $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNEt}$ and $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNCMe}_3$ show the same solution behavior at low temperature. This is not unexpected since the cone angles of these isocyanides are 52° and 68°, respectively.⁴⁵

Increasing the steric demand of the Cp ligand did prove successful. For this reason, $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}\cdot\text{NCEt}$, $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNEt}$, $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNCMe}_3$, and $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}\cdot\text{CNCMe}_3$ were prepared straightforwardly by the addition of ligand to the appropriate base-free Cp_3Ce complex, followed by crystallization from diethyl ether. Variable temperature ¹H NMR spectra of these four complexes show that no appreciable 2:1 adduct is present in solution as spectra of $\text{Cp}_3\text{Ce}\cdot\text{L}$ and $\text{Cp}_3\text{Ce}\cdot\text{L} + \text{L}$ follow Curie behavior in the temperature range studied, 70°C to -70°C, and show identical chemical shifts of the Cp ligand resonances (Fig. 14).

Fig. 14

Plots of δ vs $1/T$ for $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNEt}$ and $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNEt} + \text{CNEt}$ $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNEt}$  $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNEt} + \text{CNEt}$ 

In order to investigate how the increased steric bulk about the metal center affects the Ce-C(CNR) bond length, the X-ray crystal structure of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}\cdot\text{CNCMe}_3$ was determined. The compound crystallizes as yellow bricks from a toluene solution slowly cooled to -20°C in the monoclinic space group, $\text{P}2_1/\text{c}$. The geometry about the cerium atom is best described as trigonal-planar. An ORTEP drawing is shown in Fig. 15. Bond distances and angles are given in Table 1.15. The increased steric bulk of the $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$ ligand caused no lengthening of the Ce-C(CNR) distance relative to that observed in $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNCMe}_3$; the Ce-C(CNR) distances in the two complexes are $2.70(1)\text{\AA}$ and $2.71(2)\text{\AA}$, respectively. The average Cp-Ce-Cp angle, 119.5° , is identical, within experimental error, to that observed in $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$, 119.7° , and reflects the sterically demanding nature of the bis-substituted cyclopentadienyl ligand and the sterically undemanding nature of the isocyanide. All the other structurally characterized $\text{Cp}_3\text{Ce}\cdot\text{L}$ complexes show a distorted tetrahedral geometry about the central metal atom because the Cp ligands bend away from the incoming ligand (Table 1.16). In the $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}\cdot\text{CNCMe}_3$ complex, intramolecular repulsions prevent the bulky Cp ligands from bending away from the isocyanide which is small enough to coordinate to the sterically congested environment about the metal atom with little required reorganization energy.

Table 1.15

Bond Distances (Å) and Intramolecular Angles (°) for
 $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}\cdot\text{CNCMe}_3$

Ce-C1	2.93(1)	Ce-C6	2.90(2)	Ce-C11	2.87(2)
Ce-C2	2.90(2)	Ce-C7	2.92(2)	Ce-C12	2.84(2)
Ce-C3	2.85(2)	Ce-C8	2.85(1)	Ce-C13	2.84(2)
Ce-C4	2.83(2)	Ce-C9	2.84(1)	Ce-C14	2.83(2)
Ce-C5	2.91(2)	Ce-C10	2.87(1)	Ce-C15	2.91(2)
Ce-Cp1	2.62	Ce-Cp2	2.60	Ce-Cp3	2.59
Ce-C34	2.70(1)	N-C35	1.45(2)	C35-C37	1.47(4)
C34-N	1.15(1)	C35-C36	1.47(4)	C35-C38	1.47(3)
Cp1-Ce-Cp2	119.5	Cp2-Ce-C34	94.1	N-C35-C36	106.0
Cp1-Ce-Cp3	119.8	Cp3-Ce-C34	94.3	N-C35-C37	107.7
Cp2-Ce-Cp3	119.3	Ce-C34-N	175.8	N-C35-C38	107.8
Cp1-Ce-C34	93.3	C34-N-C35	176.9		

Cp1, Cp2, and Cp3 are the centroids of the rings comprised of C1-C5, C6-C10, and C11-C15, respectively.

Fig. 15

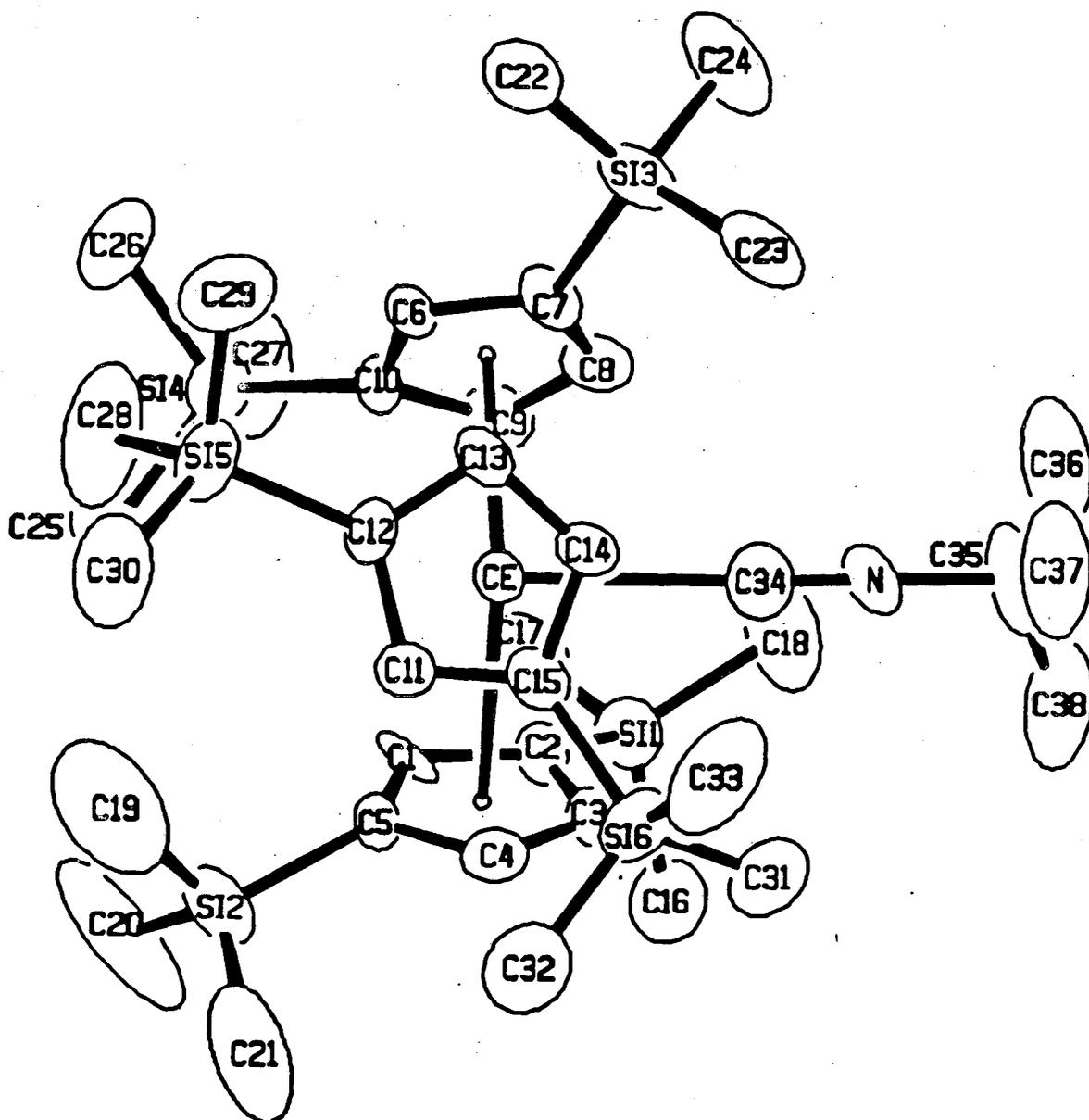
ORTEP Drawing of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}\cdot\text{CNCMe}_3$ 

Table 1.16

Significant Distances in $(RR'C_5H_3)_3Ce \cdot L$

<u>Ce·L</u>	<u>Ce-L (Å)</u>	<u>Ce-C ave. (Å)</u>	<u>Ce-C range</u>	<u>Figure</u>	
<u>R=H, R'=Me</u>	---	---	2.83(5)	2.73-2.92	3
thf	2.52(3)	2.81(4)	2.74-2.90	1	
PMe ₃	3.072(4)	2.82(4)	2.75-2.90	5	
P(OCH ₂) ₃ CEt	3.086(3)	2.82(3)	2.78-2.90	7	
N(CH ₂ CH ₂) ₃ CH	2.789(3)	2.85(3)	2.80-2.91	9	
NC ₅ H ₄ NMe ₂	2.668(6)	2.85(3)	2.79-2.90	10	
CNCMe ₃	2.71(2)	2.79(4)	2.72-2.85	13	
<u>R=R'=SiMe₃</u>	---	---	2.83(5)	2.75-2.92	4
CNCMe ₃	2.70(1)	2.87(4)	2.83-2.93	15	

Significant Angles in $(RR'C_5H_3)_3Ce \cdot L$

<u>Ce-L</u>	<u>X-Ce-Cp (°)</u>	<u>Ave.</u>	<u>Cp-Ce-Cp (°)</u>	<u>Ave.</u>
<u>R=H, R'=Me</u>	---	---	---	---
	94.5, 104.0, 104.2		114.5, 115.8, 119.1	
	97.5, 97.7, 104.2	100.4	113.9, 116.1, 121.6	116.8
OC ₄ H ₈	98.7, 100.5, 100.5	99.9	116.6, 117.4, 117.4	117.1
PMe ₃	96.7, 97.3, 98.9	97.6	117.8, 118.2, 118.8	118.3
P(OCH ₂) ₃ CEt	94.1, 94.7, 98.3	95.7	118.0, 119.1, 120.0	119.0
N(CH ₂ CH ₂) ₃ CH	100.9, 101.0, 101.6	101.2	115.8, 116.2, 117.0	116.3
NC ₅ H ₄ NMe ₂	95.7, 99.8, 102.0	99.2	115.0, 118.0, 119.6	117.5
CNCMe ₃	95.7, 95.9, 98.6	96.7	116.9, 118.5, 120.6	118.7
<u>R=R'=SiMe₃</u>	---	---	---	---
	---	---	119.4, 119.8, 120.7	120.0
CNCMe ₃	93.3, 94.1, 94.3	93.9	119.3, 119.5, 119.8	119.5

Relative Basicity

The observation that PMe_3 quantitatively displaces thf from $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ was initially surprising, even though it is consistent with the results of Ellis⁸ and Brennan⁹ who have shown that trialkylphosphines displace nitrogen and oxygen donor ligands from tris-cyclopentadienyl lanthanide and actinide environments. The observation that PEt_3 , a stronger base than PMe_3 toward the proton,²⁷ does not displace thf from $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ is in contrast to the results of Ellis and Brennan, but is consistent with the belief that lanthanide and actinide ions are hard acids and preferentially bind to hard bases. The discrepancy in these observations prompted us to address the question of relative Lewis basicity toward $(\text{MeC}_5\text{H}_4)_3\text{Ce}$.

The equilibrium quotient, K_{eq} , for the displacement of one monodentate Lewis base for another (Eq 3) was measured as a function of temperature using variable temperature ^1H NMR spectroscopy.



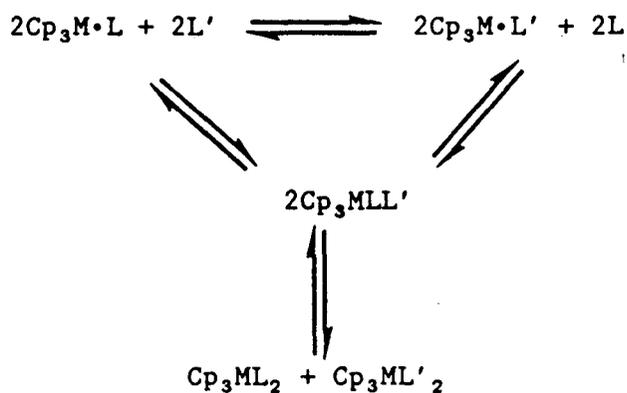
$$K_{\text{eq}} = \frac{[(\text{MeC}_5\text{H}_4)_3\text{M}\cdot\text{L}'] [\text{L}]}{[(\text{MeC}_5\text{H}_4)_3\text{M}\cdot\text{L}] [\text{L}']}$$

The $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ complexes are suitable for this study for several reasons. First of all, a large number of Lewis bases are capable of forming stable 1:1 coordination complexes with $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ (previous section). As a result of the ability to synthesize a number of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ complexes, one can examine how steric and/or electronic perturbations in the ligand environment effect Lewis basicity toward $(\text{MeC}_5\text{H}_4)_3\text{Ce}$. The examination of a large number of ligand displacement

reactions enables one to construct a relatively comprehensive ligand displacement series. The solubility of the $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ complexes in aromatic solvents allows one to study the Lewis base competition reactions over a large temperature range in a relatively noninteracting environment. Previously reported $(\text{C}_5\text{H}_5)_3\text{Ln}\cdot\text{L}$ complexes are, for the most part, soluble only in solvents that are capable of acting as Lewis bases. These coordinating solvents compete for coordination to the metal environment and complicate the evaluation of the desired ligand competition. Finally, modification of the cyclopentadienyl ligand is relatively easy, and it allows one to study how steric or electronic perturbations in the metal environment effect the relative Lewis acidity of $(\text{RC}_5\text{H}_4)_3\text{Ce}$ toward a given ligand.

Before measuring the ligand displacement equilibria it was necessary to establish that the $(\text{RC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ complexes were not capable of coordinating a second ligand to any appreciable extent. Several examples of trigonal-bipyramidal, $(\text{C}_5\text{H}_5)_3\text{Ln}\cdot\text{L}_2$, complexes have been reported.³⁹ Formation of such species in solution renders evaluation of the desired K_{eq} extremely difficult due to competing equilibria (Scheme 1).

Scheme 1:

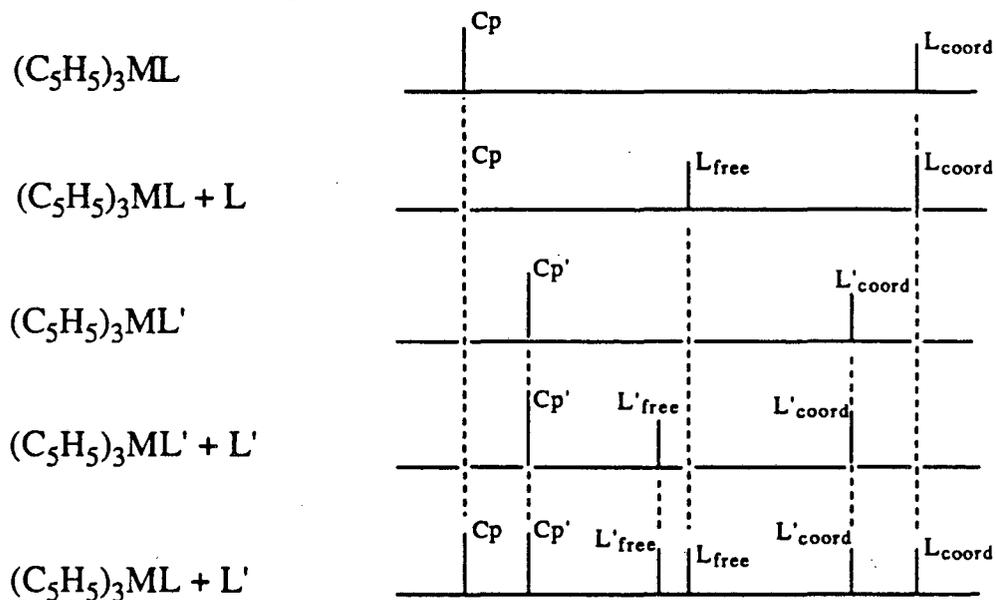


The presence of only one species, $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$, in solution was verified by first recording the ^1H NMR spectrum of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ at a set concentration as a function of temperature, and then recording the spectrum of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$, at the same concentration, with added ligand. If only one species is present in solution, the two spectra follow Curie behavior and have cyclopentadienyl ligand resonances with identical chemical shifts. If additional species, such as $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}_2$, are present in solution, the $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L} + \text{L}$ spectrum deviates from Curie behavior and has cyclopentadienyl ligand resonances whose chemical shifts differ from those in the $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ spectrum. Only the sterically undemanding isocyanide and nitrile ligands displayed this latter behavior. Fig 11 and Fig 12 show the plots of δ vs. $1/T$ from the ^1H NMR spectra of the PMe_3 and isocyanide complexes to illustrate the sensitivity of chemical shift toward the geometry about the metal atom.

The site exchange in the competition of two ligands for coordination to a metal environment can either be slow or fast relative to the NMR time scale. In the slow exchange case, resonances due to all species in solution are observed. All values needed to calculate K_{eq} can be obtained from the integrated intensities of these resonances (Fig. 16). Only the competition reactions involving quinuclidine display this slow exchange behavior at low temperature. All other ligands studied in this work undergo rapid site exchange. In the fast exchange case, only one set of resonances is observed (Fig. 17). The observed chemical shifts are a weighted average of the chemical shifts of the individual species in solution proportional to their relative concentration, and are given by

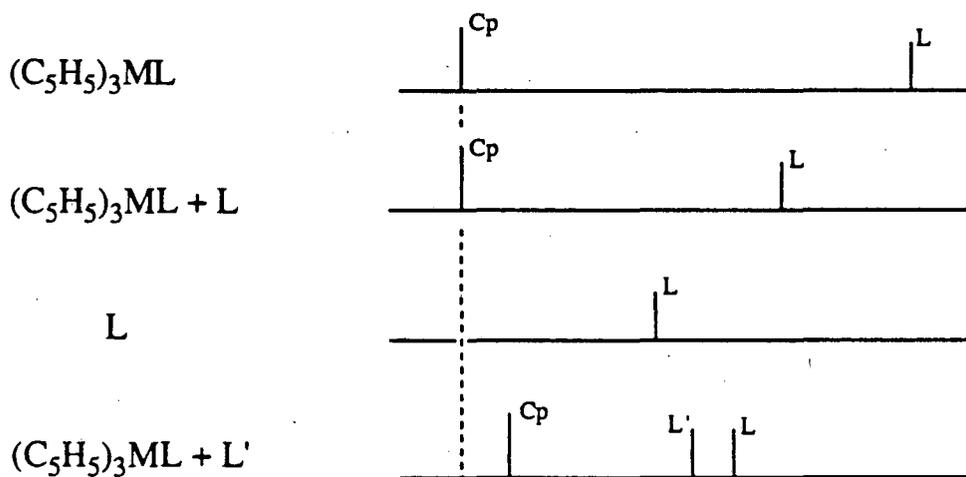
$$\delta_{\text{obs}} = x_a \delta_a + x_b \delta_b \quad (4)$$

Fig 16

Slow Exchange Case

Integration of ligand peaks gives all concentrations needed for K_{eq} .

Fig 17

Fast Exchange Case

Only one peak is observed for the ligand and Cp resonances; their observed chemical shifts are given by

$$\delta_{obs} = x \delta_a + (1-x) \delta_b$$

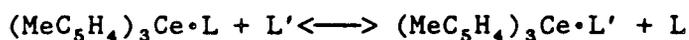
x = mole fraction of species a; δ_a and δ_b are the chemical shifts of species a and b, respectively.

where x_a and x_b are the mole fractions of species a and b, respectively, and δ_a and δ_b are the chemical shifts observed in the spectra of the pure species a and b, respectively. All concentrations needed to calculate K_{eq} are obtained from Eq 4 and the integrated intensities of the observed resonances. It should be noted that Eq 4 is valid only for systems undergoing rapid exchange and it is not valid for slow or intermediate exchange rates.

Having established the type of exchange rate and the absence of 2:1 adducts in solution, ligand displacement reactions were measured for several base pairs. A partial listing of equilibrium quotients for the reaction $(MeC_5H_4)_3Ce \cdot L + L' \rightleftharpoons (MeC_5H_4)_3Ce \cdot L' + L$ are given in Table 1.17

Table 1.17

K_{eq} Values for the Reaction



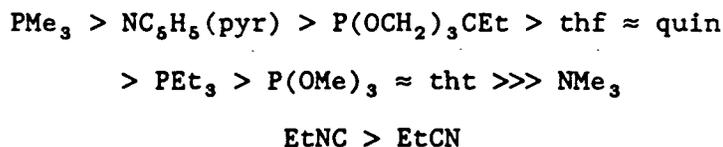
<u>L</u>	<u>L'</u>	<u>K_{eq} (ca. °C)</u>
pyr	PMe ₃	7 (-50°C)
P(OCH ₂) ₃ CEt	PMe ₃	300 (30°C)
tht	thf	19 (26°C)
P(OMe) ₃	PEt ₃	5 (29°C)
tht	PEt ₃	7 (30°C)
EtCN	EtNC	32 (-50°C)

In the course of measuring some of the competition reactions, it became apparent that using ¹H NMR spectroscopy to evaluate equilibrium constants had limitations. Accurate evaluation of K_{eq} depends upon the accurate measurement of integrated intensities and chemical shifts. This is especially true in cases where the two complexes,

$(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ and $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}'$, have resonances with similar chemical shifts. In these cases, small errors in the evaluation of the chemical shift produce large errors in χ_a and χ_b obtained from Eq 4. In many competitions this was not a problem because the paramagnetic nature of the Ce(III) ion produces resonances with large chemical shift differences. In other cases, however, resonances had similar chemical shifts and/or were broad, preventing accurate measurement. For this reason, full variable temperature analyses could not be quantitatively evaluated for some competition studies. A qualitative, but more comprehensive, list of the relative basicity toward $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ is given in Table 1.18.

Table 1.18

Qualitative Ligand Displacement Series Toward $(\text{Me}_5\text{C}_4\text{H}_3)\text{Ce}$



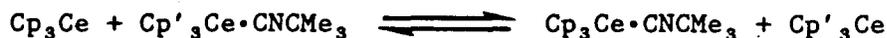
The data in tables 1.17 and 1.18 show that PMe_3 is thermodynamically favored over pyridine. These two ligands quantitatively displace $\text{P}(\text{OCH}_2)_3\text{CEt}$ which displaces thf. Tetrahydrofuran and quin show similar Lewis basicity toward $(\text{MeC}_5\text{H}_4)_3\text{Ce}$. The Lewis bases PEt_3 , $\text{P}(\text{OMe})_3$, and tht do not displace thf, and they form the least stable coordination complexes. Trimethylamine does not form an isolable complex with $(\text{MeC}_5\text{H}_4)_3\text{Ce}$. Ethylisocyanide is a better base than propionitrile.

Within a given class of ligands, *i.e.* phosphines or phosphites, the order of relative Lewis basicity toward $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ can be rationalized by steric arguments, reflecting the sensitivity of complex stability toward intramolecular ligand-ligand repulsions. From purely electrostatic arguments, the substitution of ethyl groups for methyl groups on a phosphine ligand should enhance the interaction between the positively charge Ce(III) ion and the phosphorus lone pair of electrons.⁴⁶ The $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ environment, however, shows greater coordinative affinity toward PMe_3 than toward the sterically more demanding PEt_3 ligand. Calculated cone angles for the two phosphines are 118° and 137° , respectively.³¹ The sterically less demanding $\text{P}(\text{OCH}_2)_3\text{CEt}$ ligand (cone angle; 101°) forms a more thermodynamically stable complex with $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ than $\text{P}(\text{OMe})_3$ (cone angle; 128°).³⁰ A similar ligand-size to complex stability relationship has been observed in the examination of phosphite Lewis basicity toward transition metal environments.³¹ The increasing steric bulk of the nitrogen donor ligands probably lies in the order $\text{NMe}_3 > \text{quin} > \text{pyr}$. Crystal structures of the $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{quin}$ and $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{NC}_5\text{H}_4\text{NMe}_2$ complexes have been determined and the average Cp-Ce-N angles, 101.2° and 99.2° , respectively, reflect the more sterically demanding nature of quin relative to the pyridine ligand. The tied-back nature of quin, however, makes it less sterically demanding than NMe_3 . In solution, pyridine quantitatively displaces quin which is not displaced to any measurable extent by NMe_3 .

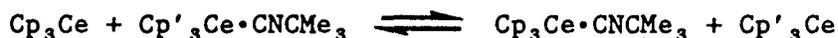
The relationship between complex stability and intramolecular donor ligand-cyclopentadienyl repulsions is also observed in the comparison of the coordinative affinity of two different $(\text{RC}_5\text{H}_4)_3\text{Ce}$ compounds toward a given ligand. Data from equilibrium quotient measurements for the reaction

Table 1.19

K_{eq} Values for the Reaction



<u>Cp</u>	<u>Cp'</u>	K_{eq}
MeC ₅ H ₄	Me ₃ SiC ₅ H ₄	20 (30°C)
Me ₃ SiC ₅ H ₄	(Me ₃ Si) ₂ C ₅ H ₃	54 (30°C)



is given in Table 1.19.

The equilibrium quotients show that the most thermodynamically stable coordination complex is the one involving the least sterically demanding cyclopentadienyl ligand. The absolute magnitude of K_{eq} in the competition involving MeC₅H₄ may not be accurate because linewidths are broad and (MeC₅H₄)₃Ce is capable of forming 2:1 adducts in solution with the sterically undemanding isocyanide and nitrile ligands. The ability to form 2:1 adducts is additional support for the claim that the steric contribution to M-L bond stability is dominant in these equilibria because (Me₃SiC₅H₄)₃Ce and [(Me₃Si)₂C₅H₃]₃Ce do not form 2:1 adducts in solution to any measurable extent.

It is not clear, however, whether or not the steric contribution to M-L bond stability is the only feature governing the solution equilibria. Substitution of the more electron donating SiMe₃ group for the methyl group in MeC₅H₄ or substitution of a SiMe₃ group for H in Me₃SiC₅H₄ could make the Ce(III) ion less electropositive through inductive effects. This in turn could weaken the electrostatic M-L bonding interaction and produce the same observed trend in K_{eq} . Green

and Brennan have measured the gas phase photoelectron spectra of several $(RC_5H_4)_3U$ complexes and have shown that substitution of $SiMe_3$ for Me slightly lowers the ionization energies of the cyclopentadienyl ligand and the first ionization energy of the metal valence electrons.⁴⁷ It is uncertain that the same effect would be observed in the analogous cerium compounds and whether or not this energy perturbation significantly alters the M-L interaction.

Although steric arguments can be used to rationalize the trend in relative Lewis basicity toward $(MeC_5H_4)_3Ce$ within a given class of ligands, the trend in relative basicity between different classes is difficult to explain. The separation of steric and electronic contributions to metal-ligand bond stability is a recurring problem in the evaluation of ligand basicity. Relative ligand basicity toward $(MeC_5H_4)_3Ce$ is no exception. Verkade's phosphite, $P(OCH_2)_3CEt$, is sterically less demanding than PMe_3 , yet $(MeC_5H_4)_3Ce$ shows greater coordinative affinity toward PMe_3 . This observation must stem from dominance of the electronic contribution to M-L bond stability, and is consistent with the observation that PMe_3 is a better base than Verkade's phosphite toward the $AlMe_3$ and the proton.²⁷ Coordination of PMe_3 is also favored over pyridine, and here the reasons are less clear. Is PMe_3 less sterically demanding than pyridine, or does the relative stability of the Ce-P bond reflect the fact that PMe_3 is a better base than pyridine toward $AlMe_3$ and the proton?²⁷

In order to gain more information about the nature of the Ce-P bond relative to the Ce-N bond, variable temperature analysis of the competition between PMe_3 and pyridine for coordination to $(MeC_5H_4)_3Ce$ was examined. Plotting $\ln K_{eq}$ versus $1/T$ produces a straight line with the slope of $-\Delta H^0/R$ and y-intercept of $\Delta S^0/R$ (Fig. 19). The ΔH^0 and ΔS^0 values (Table 1.20) show that entropy is lost upon

Fig. 19

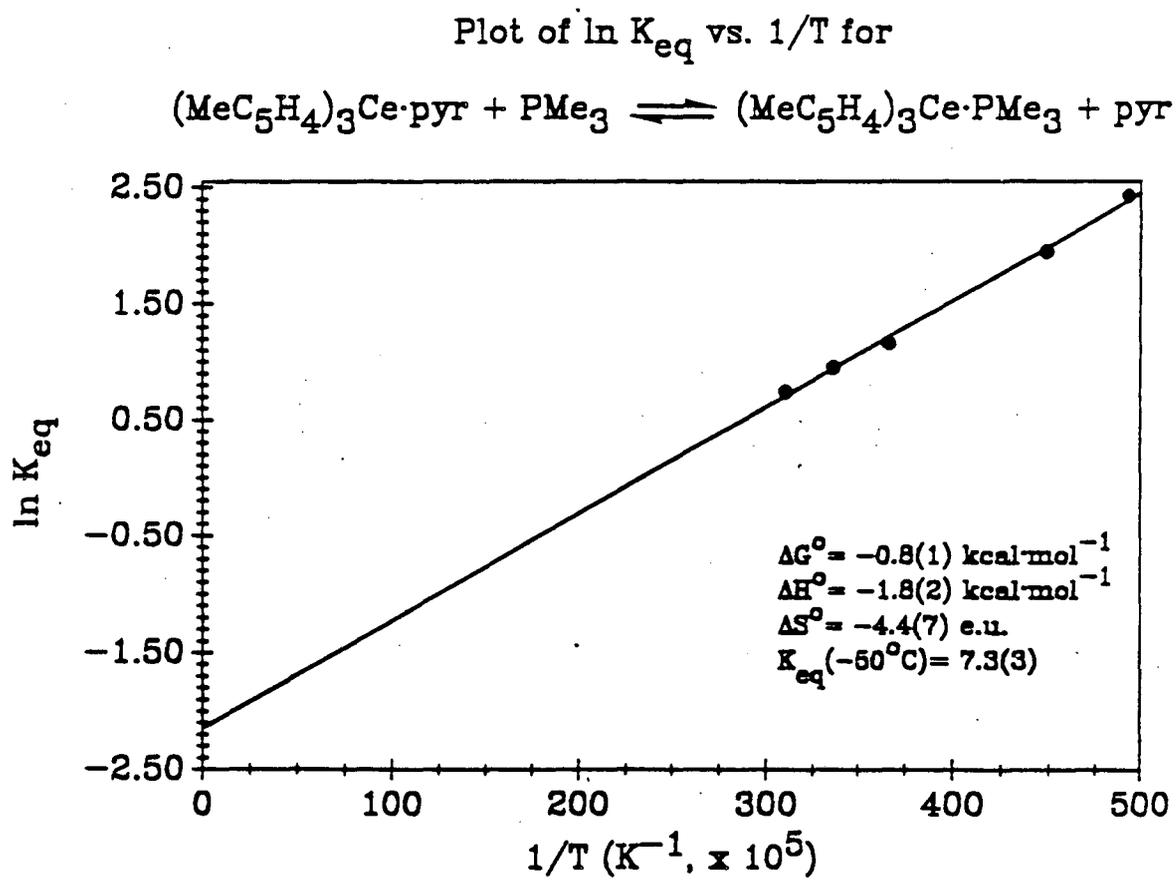
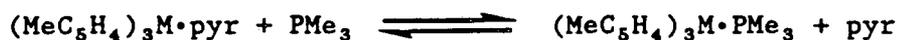


Table 1.20

Equilibrium Data for the Reaction



M	K_{eq}	ΔG° (kcal·mol ⁻¹)	ΔH° (kcal·mol ⁻¹)	ΔS° (e.u.)
Ce	7.3(3)	-0.8(1)	-1.8(2)	-4.4(7)
Nd	11(2)	-1.1(4)	-2.2(4)	-5(1)

coordination of PMe_3 and that the driving force of the equilibrium is the negative enthalpy of the reaction. The electronic contribution to M-L bond stability dominates the equilibrium as the more sterically congested $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{PMe}_3$ is preferentially formed. In view of the notion that cerium should form stronger bonds with the harder nitrogen ligands, the observation that the Ce-P bond is about $1.8 \text{ kcal}\cdot\text{mol}^{-1}$ more stable than the Ce-N bond is quite surprising. Similar results are observed in the analogous Nd system (Table 1.20).

All of the previously described ligand competition studies involved ligand pairs that differed both sterically and electronically. Since both steric and electronic factors play a role in determining a ligand's relative basicity toward a metal environment, it is desirable to eliminate or greatly reduce one of these factors when comparing basicity trends. Two ligands types that offer this luxury are nitriles and isocyanides. These "rod-like" ligands are sterically similar because the alkyl group is far removed from the coordinating atom. Electronically, however, the two are quite different. Nitriles are considered to be σ -donor ligands only while isocyanides are both good σ -donor and π -acceptor ligands. In

the evaluation of the competition between these two ligand types for a metal environment, the direction of the equilibrium should reflect differences in M-L, or electronic, interactions and not differences in intramolecular ligand-cyclopentadienyl, or steric, interactions.

The competition between ethylcyanide, EtCN, and ethylisocyanide, EtNC, for $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{M}$, where M is Ce or Nd, was measured as a function of temperature. Again plotting $\ln K_{\text{eq}}$ versus $1/T$ yields a straight line (Fig. 20).

Fig. 20

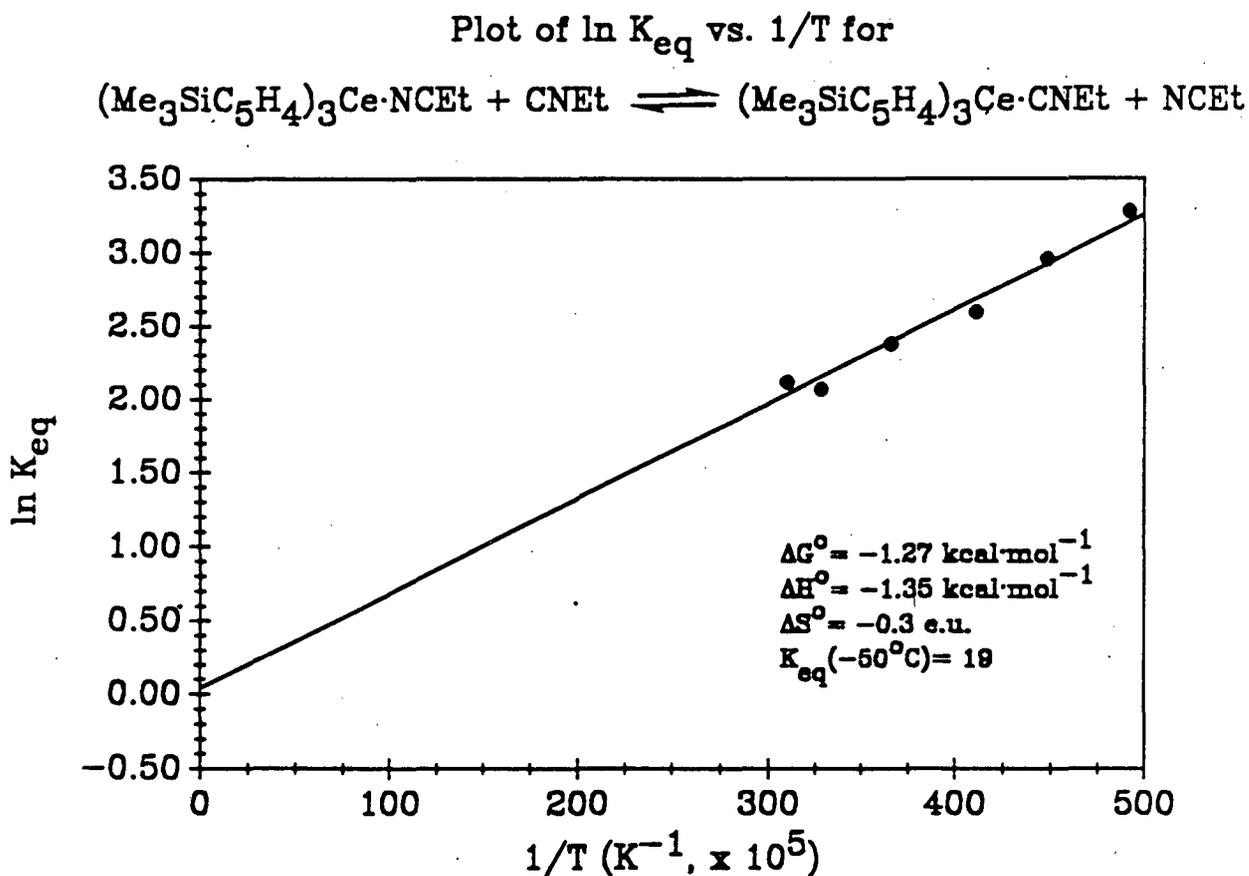


Table 1.21

K_{eq} and Thermodynamic Values for the Reaction



M	νCNR	νNCR	$K_{eq}(-50^\circ\text{C})$	$\Delta H^\circ (\text{kcal}\cdot\text{mol}^{-1})$	$\Delta S^\circ (\text{e.u.})$
Ce	2200	2260	32(1)	-1.8(2)	-1.3(7)
Nd	2200	2260	31(1)	-1.3(2)	-0.7(7)
EtNC	2151	--	--	----	----
EtCN	--	2255	--	----	----

The equilibrium constants reveal that both metal complexes show a greater coordinative affinity toward EtNC (Table 1.21). As expected, the entropy difference is very close to zero reflecting the similar steric demands of the ligands. The driving force of the equilibria is the negative enthalpy of reaction. This is consistent with the notion that isocyanides are better bases than nitriles toward the proton in the gas phase.⁴⁸ The increase in the CN stretching frequencies observed for the Ce and Nd isocyanide and nitrile complexes, relative to the free ligand, is consistent with a σ -only or electrostatic metal-ligand bonding interaction.⁴⁰

The relative basicity series established for $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ can be compared with the basicity trends measured for other Lewis acids. Table 1.22 lists gas phase enthalpies of formation for H^+ and AlMe_3 with a number of neutral bases. The data show that the trend in relative basicity toward $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ is similar to that observed for H^+ and AlMe_3 in the gas phase. The trends are not identical, however, and possible explanations for the discrepancies are difficult to rationalize. The chemical environments of $(\text{MeC}_5\text{H}_4)_3\text{Ce}$, H^+ , and AlMe_3 are very different, and steric and electronic contributions to M-L bond stability are inseparable in the set of ligands in Table 1.22.

Table 1.22

ΔH_f for Acid + L \longrightarrow Acid-L			
H^+		$AlMe_3$	
<u>L</u>	<u>$-\Delta H^{27}$</u>	<u>L</u>	<u>$-\Delta H^{27}$</u>
quin	228.7	PMe_3	22.1
PMe_3	223.5	NMe_3	19.8
py	218.1	py	17.4
$P(OR)_3$	208.0	thf	12.7
SEt_2	202.6	SEt_2	6.5
thf	196.4		

Furthermore, interaction between solvent and $(MeC_5H_4)_3Ce$ or free ligand may produce a significant effect in the competition equilibria that is not observed in gas phase enthalpy measurements.

Although relative acidity and basicity trends are difficult to compare accurately between chemically different Lewis acid environments, a reasonable and understandable comparison can often be made between Lewis acids that are sterically and electronically similar. The sizes of the Ce(III) and U(III) ions, 1.21Å and 1.18Å, respectively, are very similar. Consequently, the differences in the steric demands displayed by the $(MeC_5H_4)_3Ce$ and $(MeC_5H_4)_3U$ environments toward Lewis bases are negligible. The base competition reactions were measured in the same solvent, thereby eliminating any effects on relative basicity caused by solvent interactions. The oxidation state of both metals ions is +3, and, based on purely electrostatic arguments, the trends in relative basicity toward $(MeC_5H_4)_3Ce$ and $(MeC_5H_4)_3U$ should be identical. Table 1.23 shows that the qualitative trends in Lewis basicity toward the two metal

Table 1.23

Qualitative Ligand Displacement Series for Cp₃MCe:PMe₃ > pyr > P(OCH₂)₃CEt > thf ≈ quin > PEt₃ > P(OMe)₃ ≈ tht >>> NMe₃U:PMe₃ > pyr > tht ≈ thf ≈ quin >>> NMe₃; PEt₃ > P(OMe)₃ >>> NMe₃

environments are roughly identical. The only difference is the relative ordering of the tht ligand.

Closer examination of the equilibrium data, however, reveal significant differences in ligand basicity toward (MeC₅H₄)₃Ce and (MeC₅H₄)₃U. Although coordination of PMe₃ is thermodynamically favored over pyridine in both systems, (MeC₅H₄)₃U shows a much greater preference for coordination of PMe₃ (Table 1.24). The entropy terms reflect that formation of the more sterically congested (MeC₅H₄)₃M·PMe₃ complex results in a greater loss of entropy for the slightly smaller uranium environment. The more negative enthalpy of reaction for the uranium system reflects the difference in K_{eq} values and indicates that there is an additional source of bond stabilization energy available to uranium.

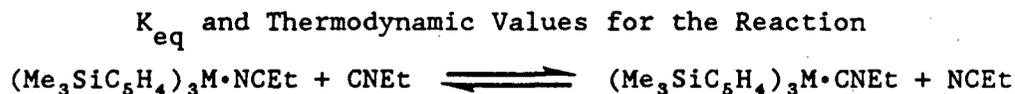
Table 1.24

Equilibrium Data for the Reaction



<u>M</u>	<u>K_{eq}</u>	<u>ΔG° (kcal·mol⁻¹)</u>	<u>ΔH° (kcal·mol⁻¹)</u>	<u>ΔS° (e.u.)</u>
Ce	7	-0.5(1)	-1.8(2)	-4.4(7)
U	190	-2.3(2)	-3.7(4)	-6.2(8)

Table 1.25



<u>M</u>	<u>νCNR</u>	<u>νNCR</u>	<u>K_{eq}</u>
Ce	2200	2260	32(1)
U	2160	2248	170(2)
EtNC	2151	--	
EtCN	--	2255	

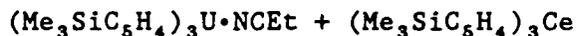
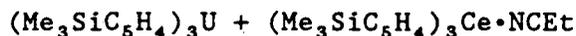
A similar situation exists in the isocyanide/nitrile competition studies. Both metal environments show greater coordinative affinity for the isocyanide ligand (Table 1.25). Again, $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ exhibits a much greater preference for coordination of EtNC. In this case, the extra bond stabilization energy available to uranium must be a reflection of differences in the electronic contribution to M-L bond stability because EtNC and EtCN have nearly identical steric properties. Examination of the CN stretching frequencies observed in the isocyanide complexes gives insight into the nature of this extra bond stabilization energy.

Upon coordination of an isocyanide to an electropositive metal, σ -donation, or a purely electrostatic interaction, increases the CN stretching frequency relative to free isocyanide.⁴⁰ A lowering of the CN stretching frequency is observed if the metal is capable of π -donation and the isocyanide accepts electron density into an accessible C-N antibonding orbital.⁴⁹ The CN stretching frequency in $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}\cdot\text{CNEt}$ is lower than that found in $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNEt}$. The same lowering of the CN stretching frequency in uranium complexes relative to lanthanide complexes has previously been observed and has been attributed to both a weaker uranium-ligand bond and π -donation

from uranium to isocyanide.⁵⁰ The observed K_{eq} values indicate that the U·CNET bond is stronger than the Ce·CNET bond, consistent with the observed shorter U-C bond length (p. 44). However, a weakening of the U·NCEt bond relative to the Ce·NCEt bond is also consistent with the K_{eq} data. Brennan has shown that dissolving equal amounts of $(Me_3SiC_5H_4)_3U$ and $(Me_3SiC_5H_4)_3Ce \cdot CNET$ in d^8 -toluene produces a 1H NMR spectrum containing resonances due only to $(Me_3SiC_5H_4)_3U \cdot CNET$ and $(Me_3SiC_5H_4)_3Ce$; no measurable amount of $(Me_3SiC_5H_4)_3Ce \cdot CNET$ is present in solution. This observation proves that the U·CNET bond is stronger than the Ce·CNET bond, and therefore, it is reasonable to suggest that π -bonding causes the relative lowering in CN stretching frequency in the uranium isocyanide complexes and stabilizes the U·CNET bond relative to the Ce·CNET bond.

Trialkylphosphines have been shown to act as π -acceptor ligands in transition metal complexes;⁵¹ therefore, metal to ligand π -bonding can also be used to explain the greater preference that $(MeC_5H_4)_3U$ displays for coordination of PMe_3 over pyridine. Further support for the claim that π -bonding is the source of the extra bond stabilization energy available to uranium and not to cerium is the observation that the CO stretching frequency in $(Me_3SiC_5H_4)_3U(CO)$ of 1976 cm^{-1} is ca. 170 cm^{-1} lower than that in free carbon monoxide.⁴⁴ Neither $(Me_3SiC_5H_4)_3Ce$ nor $(Me_3SiC_5H_4)_3Nd$ form complexes with CO.

Preliminary competition reactions of a ligand for $(RC_5H_4)_3Ce$ or $(RC_5H_4)_3U$ indicate that there is also a σ -only, or electrostatic, component that gives additional bond stabilization energy to the uranium compound. The equilibrium constant for the reaction



is 7 at 30°C. This result shows $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ has a greater coordinative affinity for EtCN, a σ -donor only ligand, than $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$. This preference, however, is not as profound as that found for the isocyanide, EtNC. The stronger U·NCeT bond relative to Ce·NCeT is not a reflection of the steric contribution to M-L bond stability because coordination of EtCN to the slightly larger, and therefore sterically less demanding, cerium environment should be more favorable. Unfortunately, we have not been able to isolate crystals of nitrile complexes that are suitable for X-ray crystallography study to study compare M-N distances.

The additional U-L bond stabilization energy observed in solution, when L is a π -accepting ligand, is also observed in the solid state, and a comparison of the structurally characterized $(\text{RC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ and $(\text{RC}_5\text{H}_4)_3\text{U}\cdot\text{L}$ complexes lends further support to the postulate of U-L π -bonding. Table 1.26 gives a list of average M-C and M-L bond distances in several known $(\text{RC}_5\text{H}_4)_3\text{M}\cdot\text{L}$ compounds. The contention that the Ce(III) and U(III) ions are similar in size is supported by the average M-C bond distances. In all cases, the average Ce-C distance is 0.02Å to 0.03Å longer than the corresponding average U-C distance. The parameter Δ , defined as $[(\text{U-C}) - (\text{U-L})] - [(\text{Ce-C}) - (\text{Ce-L})]$, can be used as a measure of the ability of ionic summation arguments to predict bond lengths between two compounds. Each set of metal values deletes the contribution of the metal radius to the M-L and M-C bond lengths. When $\Delta = 0$, the observed M-L bond

lengths are identical to those predicted by ionic summation methods. When $\Delta > 0$, the U-L bond length is shorter relative to the Ce-L distance than that predicted.

Table 1.26

The Effect of U→L π -Donation on U-L Bondlength

<u>Compound</u>	<u>M-C(Å)</u>	<u>M-L(Å)</u>	<u>Δ^1</u>	<u>Δ^2</u>	<u>Ref.</u>
$(C_5H_5)_3La \cdot thf$	2.82(4)	2.57(1)	-0.01	0.02	15a
$(C_5H_5)_3Pr \cdot thf$	2.80(2)	2.56(1)	0.00	0.01	15b
$(C_5H_5)_3Nd \cdot thf$	2.78(2)	2.54(1)	0.00	-0.01	15b
$(C_5H_5)_3U \cdot thf$	2.79(3)	2.55(1)			15e
$(MeC_5H_4)_3Ce \cdot quin$	2.85(3)	2.789(3)	0.00	0.03	32
$(MeC_5H_4)_3U \cdot quin$	2.82(3)	2.764(4)			32
$(MeC_5H_4)_3Ce \cdot NC_5H_4NMe_2$	2.85(3)	2.668(6)	-0.01	0.03	Ch. 1
$(MeC_5H_4)_3U \cdot NC_5H_4NMe_2$	2.82(4)	2.64(2)			35
$(MeC_5H_4)_3Ce \cdot PMe_3$	2.82(3)	3.074(6)	+0.07	+0.10	10
$(MeC_5H_4)_3U \cdot PMe_3$	2.79(3)	2.972(6)			28
$(MeC_5H_4)_3Ce \cdot P(OCH_2)_3CEt$	2.82(3)	3.093(3)	+0.09	+0.11	32
$(MeC_5H_4)_3U \cdot P(OCH_2)_3CEt$	2.80(5)	2.988(6)			32
$(C_5H_5)_3Pr \cdot CNC_6H_{11}$	2.78(2)	2.65(1)	+0.11	+0.08	43
$(MeC_5H_4)_3Ce \cdot CNCMe_3$	2.79(4)	2.71(2)	+0.16	+0.14	Ch. 1
$(Me_3SiC_5H_3)_3U \cdot CNEt$	2.81(3)	2.57(2)			44

$$\Delta^1 = [(U-C) - (U-L)] - [(M-C) - (M-L)]$$

$$\Delta^2 = (M-L) - (U-L)$$

Examination of the data in Table 1.26 shows that with first row nitrogen and oxygen donor ligands (class a or hard donors) the observed M-L distances can be rationalized by ionic summation methods since $\Delta = 0$. For ligands that are capable of acting as π -acceptors, isocyanides and second row phosphines and phosphites, $\Delta > 0$ indicating a relative shortening of the U-L bond. This perturbation is consistent with a stronger U-L bond, relative to Ce-L, which is consistent with the solution equilibrium studies.

Although the observed solution equilibria and solid state X-ray diffraction data may be rationalized by postulating that $(RC_5H_4)_3U$ is capable of engaging in π -backbonding with ligands that have available acceptor orbitals, little can be said about the relative contribution of π -bonding to overall U-L bond stability. The CO stretching frequency in $(Me_3SiC_5H_4)_3U \cdot CO$ is lowered relative to free carbon monoxide, but the U-CO interaction is very weak. The complex is not stable under reduced pressure and cannot be isolated in the solid state. Marks has estimated the U-CO bond strength to be 10 kcal·mol⁻¹.⁵² Fabiano has recently found that phosphine oxides and phosphine sulfides, ligands with relatively small steric demands, form the strongest M-L interactions of all bases studied.⁵⁴ A π -effect cannot be used to explain this trend in relative basicity.

The examination of additional head-to-head ligand competitions between $(RC_5H_4)_3Ce$ and $(RC_5H_4)_3U$ are needed in order to obtain further understanding about the nature and magnitude of the additional bond stabilization energy available to uranium. Presently, these studies are greatly limited by the need to have stable $(RC_5H_4)_3M \cdot L$ complexes whose corresponding base-free $(RC_5H_4)_3M$ complexes have solubility properties suitable for variable temperature equilibrium studies.

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CHAPTER TWO:

Reactions of Tris(cyclopentadienyl)cerium and -uranium Complexes with Protic Compounds: Synthesis and Structure of $[(RC_5H_4)_2CeER]_2$ and $(RC_5H_4)_3UER$ Complexes.

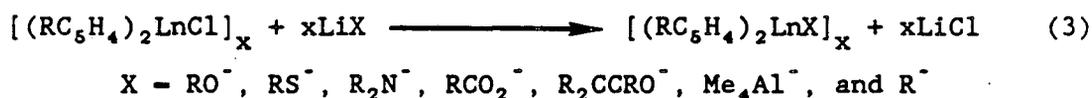
The bis(cyclopentadienyl)lanthanide chloride complexes, $[(RC_5H_4)_2LnCl]_2$, where R is Me or H, for the trivalent lanthanide ions of Sm through Lu were successfully synthesized by Dubeck and co-workers in 1962.¹ These complexes were isolated from the reaction of two equivalents of sodium cyclopentadienide with the anhydrous metal trichlorides in tetrahydrofuran followed by sublimation (Eq 1) or by treatment of the tris(cyclopentadienyl)lanthanide complex with the corresponding metal trichloride (Eq 2).



Ebulliometric molecular weight determinations show that the methylcyclopentadienyl derivatives are dimeric in benzene, presumably via a chloride ion bridge. This bridging interaction is weak enough to be cleaved by coordination of thf because molecular weight determinations show that the complexes are monomeric in that solvent. The unsubstituted-cyclopentadienyl complexes do not possess sufficient solubility in benzene or other non-polar solvents to determine their molecular weight in these solvents, though they are monomeric in thf. X-Ray diffraction studies of the $[(MeC_5H_4)_2YbCl]_2$ complex showed that it is dimeric in the solid state and confirmed that the chloride ions

form the bridging interaction between the two bis(cyclopentadienyl)-lanthanide moieties.²

Investigations into the reactivity of the $[(RC_5H_4)_2LnCl]_2$ complexes led to the synthesis of several new classes of lanthanide complexes. For example, alkoxide, thiolate, amide, carboxylate, enolate, trialkylaluminum, and alkyl complexes were synthesized by the metathetical displacement of the chloride ion (Eq 3).³



These complexes contained unique structure types and unique chemical reactivity. The alkyl complexes, $[(RC_5H_4)_2LnR]_2$, for example, are of particular interest because they have the ability to polymerize olefins,⁴ activate C-H bonds,⁵ and insert small unsaturated molecules.⁶

The $[(RC_5H_4)_2LnCl]_2$ complexes of the larger lanthanide ions, La through Nd, could not be prepared by the reaction shown in Eq 1. Addition of two equivalents of sodium cyclopentadienide to these anhydrous metal trichlorides in tetrahydrofuran resulted in the isolation of the $(RC_5H_4)_3Ln \cdot thf$ complex and $LnCl_3$. The larger size of these metal ions produces a more sterically unsaturated metal environment and presumably facilitates a ligand redistribution reaction in which the lanthanide ion increases its coordination number by two (Eq 4).

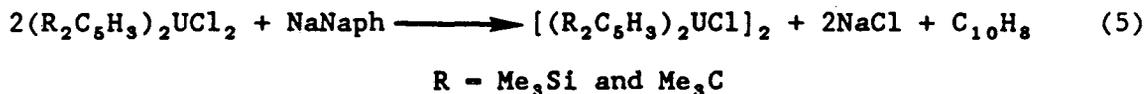


The preference of the early lanthanides to form the $(RC_5H_4)_3Ln \cdot thf$ complexes over the $[(RC_5H_4)_2LnCl]_2$ complexes is consistent with the solid-state structures of the base-free $(RC_5H_4)_3Ln$ complexes which show that coordination number and geometry about the metal ion change markedly with metal ion radius (Chapter 1).

It was of interest to develop the syntheses and study the reactivities of the early bis(cyclopentadienyl)lanthanide chloride complexes in order to explore and to expand the organometallic chemistry of these metal ions. From a synthetic standpoint, the synthesis of the early $[(RC_5H_4)_2LnCl]_2$ complexes is challenging. Furthermore, the larger size of these ions, which facilitates ligand redistribution reactions and prevents the isolation of $[(RC_5H_4)_2LnCl]_2$, may also render complexes with interesting structural and chemical properties. The polymerization of olefins, for example, may prove to be greatly enhanced relative to that observed in the smaller, more sterically congested $[(RC_5H_4)_2LnR']_2$ derivatives, because the larger analogues are more coordinatively unsaturated. The isolation of stable bis-cyclopentadienyl complexes of the early lanthanides also allows one to compare the reactivity properties between actinide and lanthanide environments. This is particularly significant for uranium and cerium, whose sizes are similar but whose chemical and physical properties are quite different.

The first stable $[(RC_5H_4)_2MCl]_2$ complexes of the early f-metals were uranium complexes. Their syntheses involved a more sterically demanding cyclopentadienyl ligand to prevent ligand redistribution reactions from occurring. The ability of uranium to form stable U(III) and U(IV) organometallic complexes was also crucial in the synthetic strategy. The reduction of the U(IV) complexes, $(R_2C_5H_3)_2UCl_2$, where R is Me_3Si and Me_3C , and $(Me_5C_5)_2U(CH_2SiMe_3)Cl$, in nonpolar solvents

leads to the relatively facile isolation of the $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{UCl}\}_2$ ⁷ and $[(\text{Me}_5\text{C}_5)_2\text{UCl}]_3$ ⁸ complexes, respectively (Eqs 5 and 6).



The X-ray crystal structure shows that the (Me₅C₅) derivative is trimeric in the solid state. Similar to the related complexes of the smaller lanthanides, the (R₂C₅H₃) derivatives are dimeric in the solid state.

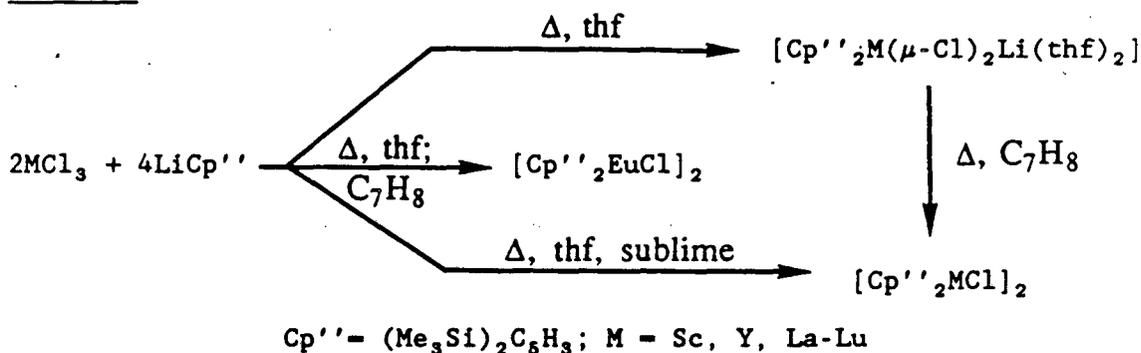
Sterically more demanding cyclopentadienyl ligands have also been employed in efforts to synthesize the analogous 4f-metal complexes. These efforts, however, have been less successful mainly due to the inability of the 4f-metal ions to form isolable organometallic Ln(IV) complexes and the need to carry out syntheses in polar, coordinating solvents. The former aspect eliminates the use of the redox reaction strategy, while the latter aspect enhances the formation of ionic species such as (RC₅H₄)₂Ln(Cl)₂ML₂, where M is an alkali metal and L is the coordinating solvent.⁹ Often mixtures of neutral and ionic species are formed and their separation is difficult.

The complexes (Me₅C₅)₂Ce(Cl)₂Li(OEt)₂¹⁰ and (Me₅C₅)₂Ce(Cl)₂K(dme)₂¹¹ have recently been synthesized according to Eq 7 and Eq 8, respectively.



These complexes, however, are not ideal starting materials for the study of the reactivity of the early $[(RC_5H_4)_2LnX]_2$ complexes. The latter complex, for example, is isolated in only 14% yield after seven days of stirring and refluxing in thf. The complex decomposes slowly at room temperature, and the isolation of pure crystalline material is very difficult. Another undesirable property of these two complexes is their propensity to lose coordinated ligand, Et_2O and dme , in the solid state and/or the alkali-metal halide in solution. Crystalline material readily converts into a powder upon standing or exposure to vacuum, and, as a result, control of stoichiometry in subsequent reactions becomes inaccurate.

Scheme 1



The first successful synthesis of a series of neutral hydrocarbon-soluble $[(Me_3Si)_2C_5H_3]_2LnCl)_2$ complexes for the lanthanide ions of La through Tb and Yb has been recently reported (Scheme 1).¹² The reported yields of these complexes are about 40%, and reaction times are on the order of two days. No detailed physical properties, except for the X-ray crystal structure of the Pr derivative, were reported, however.

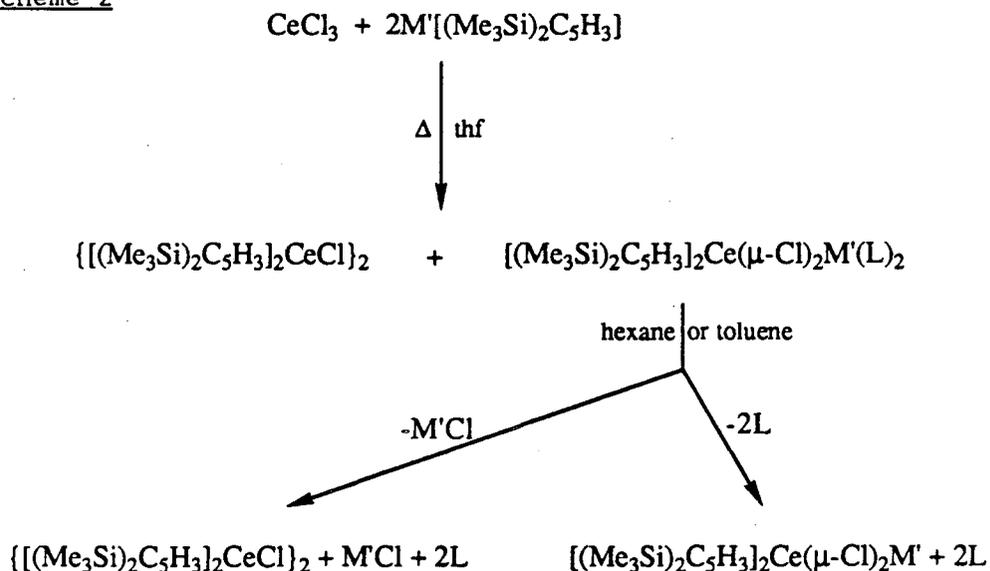
In view of these results, it seemed as though $[(Me_3Si)_2C_5H_3]_2CeCl)_2$ could serve as a useful starting material for

the study of the reactivity of the early bis(cyclopentadienyl)-lanthanide complexes. Furthermore, the successful isolation of pure $[(R_2C_5H_3)_2UCl]_2$, where R is Me_3Si and Me_3C , in our laboratories¹³ affords one the luxury of comparing the structural and chemical properties of the sterically similar but electronically different cerium and uranium environments.

Attempts to synthesize $\{[(Me_3Si)_2C_5H_3]_2CeCl\}_2$ by the synthetic route reported by Lappert met with little success, however. The yield is only about 10-15%, and the product is most likely a mixture of the neutral and anionic species, $\{[(Me_3Si)_2C_5H_3]_2CeCl\}_2$ and $[(Me_3Si)_2C_5H_3]_2Ce(\mu-Cl)_2Li(thf)_2$, respectively. Flame-tests on the isolated product indicate that Li is present. The reason for this result is still unclear. Slightly better, but still unacceptable, results are obtained from the reaction of two equivalents of $K(Me_3Si)_2C_5H_3$ with $CeCl_3$ in refluxing thf. A yellow powdery product is obtained in roughly 20-25% yield. The 1H NMR spectrum shows only the expected $ABB'X_9X'$ pattern for the ring protons. Further characterization of this product was not carried out due to the inability to isolate crystalline material.

The difficulties encountered in obtaining pure product in these syntheses is most prominent in the separation of the hexane or toluene soluble extract from the insoluble salts. Filtration of the clear, yellow extract inevitably produces a cloudy filtrate which contains lithium, as shown by flame-tests. Presumably the polar reaction conditions stabilize, at least to some extent, an alkali-metal chloride addition product. Extraction with a nonpolar solvent destabilizes this anionic species and results in the loss of $M'Cl$ and/or coordinated ligand and the formation of a precipitate (Scheme 2). This postulate is supported by the observation that anionic

Scheme 2

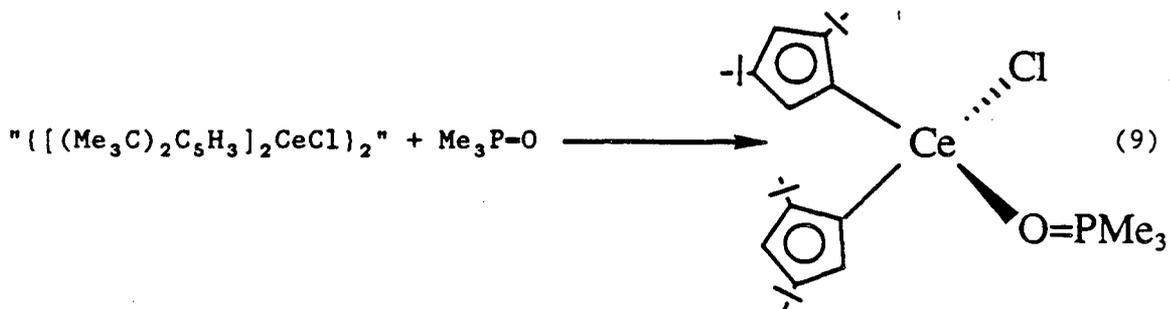


species are crystallized from diethyl ether and neutral complexes are crystallized from toluene in attempts to synthesize bis-(pentamethylcyclopentadienyl)lanthanide chloride complexes of Nd, Sm, and Yb.⁹

In studying the coordination chemistry of the tris-(cyclopentadienyl)cerium complexes, the t-butylcyclopentadienyl derivatives were much easier to purify than the analogous trimethylsilylcyclopentadienyl derivatives. Attempts were therefore made to isolate the $\{[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeCl}\}_2$ complex in hopes of obtaining pure crystalline material. After refluxing $\text{K}[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]$ and CeCl_3 in thf for 2 days, cooling, and allowing the insoluble material to settle for 6 h, the yellow-brown thf solution is filtered, and then the filtrate is taken to dryness. The yellow solid is extracted with toluene, and again the insoluble material is allowed to settle. In this case, only two filtrations of the toluene extract are needed to produce a precipitate-free filtrate. Cooling the filtrate

to -20°C , followed by cooling to -80°C , produces a yellow powder in ca. 40% yield. Again the ^1H NMR spectrum shows only the expected $\text{ABB}'\text{X}_9\text{X}'_9$ pattern for the ring protons. Often the yellow product does not completely redissolve, and cloudiness is sometimes observed in the extract. Since crystalline material again cannot be obtained, further characterization was not carried out. However, since the product yield is significantly greater than in the other syntheses, some attempts were made to isolate derivatives of " $\{[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeCl}\}_2$ ".

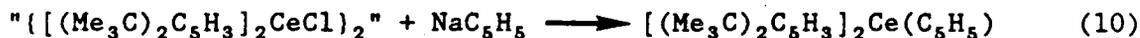
The study of the relative coordinative affinity of Lewis bases toward $(\text{RC}_5\text{H}_4)_3\text{M}$, where M is Ce or U, showed that $(\text{MeC}_5\text{H}_4)_3\text{M}$ complexes are capable of forming 2:1 adducts with relatively sterically undemanding isocyanide and nitrile ligands in solution, while the $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{M}$ complexes are not. The 2:1 complexes, $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{UCl}(\text{CNBu}^t)_2\}$ and $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{UCl}(\text{NCBu}^t)_2\}$, have been recently prepared and structurally characterized.¹⁴ It was of interest to see whether coordination compounds of " $\{[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeCl}\}_2$ " would form 1:1 or 2:1 adducts in the solid state. Addition of excess $\text{Me}_3\text{P}=\text{O}$, a relatively sterically undemanding ligand and one of the strongest Lewis bases toward $(\text{MeC}_5\text{H}_4)_3\text{Ce}$,¹⁵ to a hexane solution of " $\{[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeCl}\}_2$ ", followed by crystallizing from toluene, affords the yellow $\{[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeCl}(\text{O}=\text{PMe}_3)\}_2$ complex (Eq 9).



The ^1H NMR spectrum, elemental analysis, and mass spectrum confirm the 1:1 stoichiometry. Interestingly, the two cyclopentadienyl ligands are magnetically inequivalent in the ^1H NMR spectrum. Stopped ring rotation and/or chemical inequivalence of the rings cannot be invoked to explain this observation. The former phenomenon has never been observed in cyclopentadienyl complexes of the f-metals, and the latter cannot be rationalized, at least in solution, if one assumes a tetrahedral geometry about the cerium atom. This phenomenon is also observed in the analogous uranium complex.¹⁶ One explanation for the inequivalent cyclopentadienyl resonances involves the anisotropy of the molecule's magnetic tensor.¹⁷ Each cyclopentadienyl ligand "sees" this magnetic tensor differently, and therefore, each is magnetically unique. There are a few examples of this phenomenon in the literature.¹⁸

The E.I. mass spectrum contains a parent ion at $M/e = 529$ amu, corresponding to a monomeric species with loss of coordinated ligand. The loss of a neutral ligand in the gas phase is not surprising because all of the $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{L}$ complexes described in Chapter 1 give parent ions corresponding to $(\text{MeC}_5\text{H}_4)_3\text{Ce}$. The E.I. mass spectrum of the analogous uranium complex also shows a parent ion corresponding to a monomeric species with loss of $\text{Me}_3\text{P}=\text{O}$.¹⁶ Unfortunately, crystals suitable for X-ray diffraction studies could not be obtained in order to ascertain the solid state structure.

Since the goal behind the synthesis of the $[(\text{R}_2\text{C}_5\text{H}_3)_2\text{CeCl}]_2$ complexes was to investigate chloride ion displacement reactions, " $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeCl}$ " was allowed to react with NaC_5H_5 and MeLi . Addition of one equivalent of NaC_5H_5 to a diethyl ether solution of $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeCl}$ results in the formation of the mixed-cyclopentadienyl complex, $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{Ce}(\text{C}_5\text{H}_5)$, (Eq 10).



The compound gives a parent molecular ion at $M/e = 559$ amu in the E.I. mass spectrum, corresponding to a monomeric structure in the gas phase. The melting point, purple color, and extreme solubility in hexane indicate that the complex is also monomeric in solution and in the solid state, similar to $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$ and $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$. The analogous $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{U}(\text{C}_5\text{H}_5)^{16}$ and $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{U}(\text{C}_5\text{H}_5)^{14}$ complexes have also been prepared in a similar fashion. None of these complexes have been structurally characterized by X-ray diffraction to verify a monomeric solid-state structure, a important point given the polymeric structures of the C_5H_5 derivatives (Chapter 1).

In contrast to the reaction of " $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeCl}_2$ " with NaC_5H_5 , the addition of two molar equivalents of MeLi to a toluene, hexane, or diethyl ether solution of " $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeCl}_2$ " results only in the isolation of starting material even if the reaction time is for periods of up to five days. Similar results have been obtained in the $[(\text{R}_2\text{C}_5\text{H}_3)_2\text{UCl}]_2$ complexes.^{14,16} Furthermore, attempts to displace the chloride ion from $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{UCl}_2$ with LiNMe_2 , LiOBu^t , and, LiCH_2Ph have been unsuccessful (Eq 11).¹⁴



M = Ce, U; X = Me

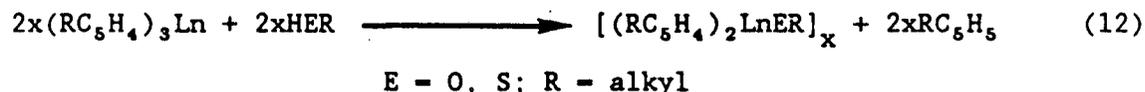
M = U; X = Me_2N^- , $^t\text{BuO}^-$, PhCH_2^-

In view of the difficulties encountered in obtaining satisfactory yields of crystalline $[(\text{R}_2\text{C}_5\text{H}_3)_2\text{CeCl}]_2$ complexes from reactions involving alkali-metal cyclopentadienides and CeCl_3 , and the reluctance of the complexes to undergo halide displacement reactions,

a new synthetic route for the early lanthanide and actinide $[(RC_5H_4)_2MX]_2$ complexes was clearly needed so that their reaction chemistry could be explored and compared.

Reactions of $(RC_5H_4)_3Ce$ Complexes with Protic Acids

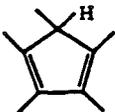
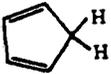
One logical approach toward the synthesis of $[(RC_5H_4)_2LnX]_2$ complexes is the reaction of the easily synthesized and well characterized tris(cyclopentadienyl)lanthanide complexes with protic reagents. The chemistry of the $(RC_5H_4)_3Ln$ complexes, especially for the early lanthanides, is limited for the most part to coordination compounds with Lewis bases. This is mainly due to the coordinatively saturated nature of these complexes and the inability of most lanthanides to form stable organometallic complexes in oxidation states other than the trivalent state. The tris(cyclopentadienyl)lanthanide complexes, however, are susceptible to hydrolysis, upon which ring protonation and eventual decomposition occurs. If less rigorous protolysis conditions are used, *i.e.* a stoichiometric amount of a weaker protic reagent, then the desired $[(RC_5H_4)_2CeX]_2$ complexes might be synthesized as depicted in Eq 12.



The simplest way to view this reaction is as a proton transfer from HER to $RC_5H_4^-$. Thus, a reaction is predicted to be thermodynamically feasible if the pKa of the protic substrate is less than that of RC_5H_5 . Table 2.1 gives pKa values for several protic acids¹⁹ and substituted-cyclopentadienes.²⁰

Table 2.1

pKa Values for Selected Organic Acids

<u>Compound</u>	<u>pKa</u> ^(a)	<u>Reference</u>
PhC≡CH	20	19
PhC≡CH	29 ^(b)	20a
Bu ^t OH	19.2	19
Pr ⁱ OH	17.1	19
HOH	15.74	19
MeOH	15.5	19
Bu ^t SH	11.2	19
Pr ⁱ SH	10.9	19
C ₆ H ₅ OH	10.0	19
C ₆ H ₅ SH	6.6	19
	26.1 ^(b)	20c
	18 ^(b)	20b
	16	20a
	15.4	20e
	9.8	20d

(a). measured in water

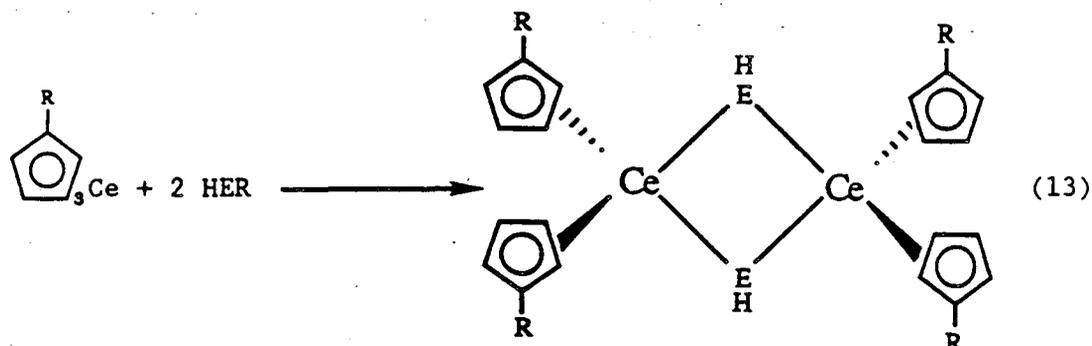
(b). measured in dms0

Previous studies have shown the utility of alcohols and thiols in forming novel complexes via ring protolysis reactions.^{21,31,36} The only reported $[(RC_5H_4)_2MX]_2$ complexes of the early f-metals that have been synthesized by this method are $[(C_5H_5)_2NdCN]_x$ ²² and $[(C_5H_5)_2UCl]_x$.²³ The isolation of these relatively sterically unsaturated complexes presumably results from their insolubility, which prevents ligand redistribution and eventual decomposition in solution.

Several factors must be considered when designing this synthetic scheme. Clearly, the thermodynamics of the reaction, not the kinetics, are governed by the pKa's of the cyclopentadienyl ligand and protic source. It should be kept in mind that the aqueous pKa values may not be transferable to non-aqueous media, and the values given in Table 2.1 should only be used as a qualitative guide in designing ring protolysis strategies. Furthermore, if substrate coordination occurs prior to ring protonation, the acidity of the substrate will change, probably getting lower. This rationale has been used to explain the observation that $PhC\equiv CH$ is capable of reacting as a protic acid toward several heavier tris(cyclopentadienyl)lanthanide complexes.²⁴ The $(C_5H_5)_3Yb \cdot NH_3$ complex is converted to the $[(C_5H_5)_2Yb-NH_2]_2$ complex at elevated temperatures.²⁵ This observation may reflect that the very weak "protic acid", NH_3 , is activated toward ring protolysis upon coordination to the Yb metal. One must also consider the steric demands of the protic substrate and the cyclopentadienyl ligand. Both of these factors involve the ability of the substrate to react for kinetic reasons, and the coordinative saturation, or the kinetic stability, of the resultant product. The ease with which the steric and electronic properties of the cyclopentadienyl ligand can be

modified provides one with a variety of starting materials so that the importances of these factors can be investigated.

The reaction of some tris(cyclopentadienyl)cerium complexes with several alcohols and thiols proceeds in ether or hydrocarbon solvents according to Eq 13 to yield $[(RC_5H_4)_2CeER]_2$ complexes.



All of the complexes readily crystallize from hexane and are isolated in good yield. The physical properties of these crystalline complexes are given in Table 2.2. Their intense colors depend on the identity of the heteroatom. The alkoxide complexes are yellow while the thiolate complexes are purple or pink. These colors may be due to a ligand lone pair to metal charge transfer absorption, and they suggest

Table 2.2 Physical Properties of $[(RC_5H_4)_2CeER]_2$ Compounds

<u>Compound</u>	<u>color</u>	<u>m.p. (°C)</u>	<u>yield</u>
$[(MeC_5H_4)_2CeSCMe_3]_2$	purple	139-142	30%
$[(Me_3CC_5H_4)_2CeSCHMe_2]_2$	magenta	266-268(dec)	70%
$[(Me_3CC_5H_4)_2CeSC_6H_5]_2$	pink	191-194	69%
$[(Me_3CC_5H_4)_2CeOCHMe_2]_2$	yellow	240-241	64%
$[(Me_3CC_5H_4)_2CeOC_6H_5]_2$	yellow	258-260	52%
$[(Me_3Si)_2C_5H_3]_2CeOH]_2$	yellow	229-232(dec)	71%

that the energy of this transition decreases in the order $O > S$. A similar relationship has been observed for the $(Me_5C_5)_2Yb(ER)(L)$ complexes.²⁶

The 1H NMR spectra show the expected $AA'BB'X_n$ or $AA'BX_9X'_9$ patterns for the ring protons along with the ligand resonances (Table 2.3). The ring-CH resonances are shifted downfield from the ring alkyl resonance, and the ligand resonances are, in most cases, shifted upfield from the alkyl resonance.

Information about the solution structure of these complexes was obtained from a crossover experiment between the $[(Me_3CC_5H_4)_2CeSPr^i]_2$ and $[(Me_3CC_5H_4)_2CeSPh]_2$ complexes. When equimolar amounts of the two complexes are mixed, the 1H NMR spectrum of the mixture, between $70^\circ C$ and $-70^\circ C$, reveals a mixture of the two starting materials plus the mixed-thiolate complex, $[(Me_3CC_5H_4)_2Ce(SPri)(SPh)]_2$, in a 1:1:2 statistical ratio as shown in Fig 1. If the complexes were monomeric species in solution, the 1H NMR spectrum of the mixture would either consist of one time-averaged set of cyclopentadienyl ligand resonances or two unique types of cyclopentadienyl ligand resonances, depending on the rate of ligand exchange relative to the NMR time-scale. Three unique cyclopentadienyl ligand resonances will be observed only if the complexes exist as dimeric or other oligomeric species in solution. The 1:1:2 product ratio and the integrated intensities of the thiolate ligand resonances support the claim that the complexes exist as dimers in solution.

Since the 1:1:2 product ratio is observed at all temperatures, the activation energy of the barrier to thiolate exchange cannot be obtained from the 1H NMR data. All that the spectrum reveals is that

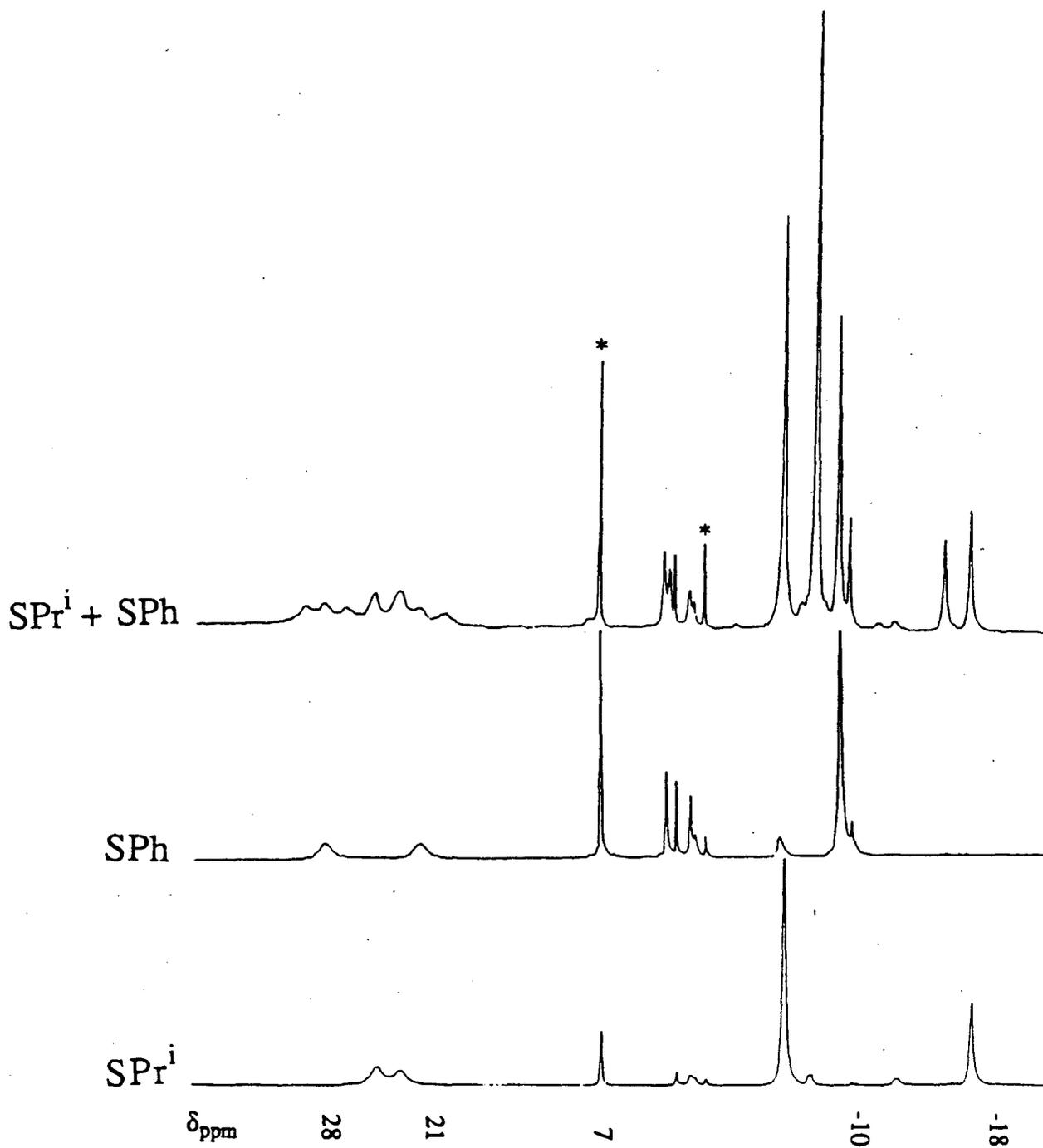
Table 2.3

 ^1H NMR Data for $[(\text{RR}'\text{C}_5\text{H}_9)_2\text{CeER}'']_2$

<u>ER''</u>	<u>δ CH(A)</u>	<u>δ CH(B)</u>	<u>δ R(X)</u>	<u>δ ligand</u>
<u>R=Me, R'=-H</u>				
SCMe ₃	20.54 (\approx 80 Hz)	18.79 (\approx 90 Hz)	4.71 (26 Hz)	-22.22 (9H, 20 Hz)
<u>R=Me₃C, R'=-H</u>				
SCHMe ₂	21.85 (50 Hz)	20.51 (45 Hz)	-4.96 (17 Hz)	-12.37 (1H) -17.49 (6H, 20 Hz)
SC ₆ H ₅	25.73 (77 Hz)	19.23 (74 Hz)	-8.97 (18 Hz)	2.69 (2H) 1.15 (1H) -4.67 (2H)
OCHMe ₂		16.90 (\approx 90 Hz)	0.84 (20 Hz)	-3.25 (1H, 17 Hz) -17.34 (6H, 34 Hz)
OC ₆ H ₅	21.52 (72 Hz)	14.98 (73 Hz)	-4.57 (16 Hz)	-3.41 (1H) -5.03 (2H, d, J=6.8 Hz) -16.23 (2H)
<u>R=R'=-SiMe₃</u>				
OH	--	--	-5.90 (22 Hz)	-----

The observed spectra show that A=A', B=B', and X=X' in the AA'BB'X₃, AA'BB'X₉, and ABB'X₉X₉' spin systems of these complexes. All spectra were recorded in C₆D₆ and referenced relative to tetramethylsilane, $\delta=0$. The A protons are arbitrarily assigned to those farthest downfield. Relative intensities and line-widths at half peak height are give in parentheses.

Fig 1

Crossover Experiment Between

the thiolate ligands exchange, and that once equilibrium is reached, the rate of exchange is either very fast or very slow relative to the NMR time-scale. Two possible pathways for the thiolate ligand exchange are shown in Scheme 3. In pathway A, the complexes completely dissociate to form the monomeric intermediates Cp_2CeSR and $\text{Cp}_2\text{CeSR}'$. These then combine to give the mixed-thiolate product. In pathway B, one Ce-S bond breaks to form the open dimeric intermediates RSCe_2SR and $\text{R}'\text{SCe}_2\text{SR}'$. Two of these then react to produce the mixed-thiolate complex.

The E.I. mass spectra of the SPr^{i} , OPr^{i} , and OH complexes give molecular ions which correspond to dimeric structures in the gas phase; consistent with the solution studies. The phenoxide and thiophenoxide complexes do not give molecular ions in the mass spectra. In order to elucidate their solid state structures, the SPr^{i} , OPr^{i} , and OH complexes were structurally characterized by X-ray diffraction. The structures show that the molecules are dimeric in the solid state as well.

The $[(\text{Me}_3\text{C}_5\text{H}_4)_2\text{CeOCHMe}_2]_2$ complex crystallizes from a saturated hexane solution at -20°C in the monoclinic space group, $\text{P2}_1/\text{c}$. ORTEP drawings viewed from the top and the side of the Ce_2O_2 ring are shown in Fig 2. Selected bond distances and angles are given in Table 2.4. The structure consists of centrosymmetric dimers with a pseudo-tetrahedral arrangement of two $\eta^5\text{-Me}_3\text{CC}_5\text{H}_4$ ligands and two bridging, oxygen-bound isopropoxide ligands about each cerium atom. The Ce_2O_2 ring is planar, with Ce-O-Ce' and O-Ce-O angles of $108.3(1)^\circ$ and $71.7(1)^\circ$, respectively. The Ce-O distances, $2.373(3)\text{\AA}$ and $2.369(3)$, are identical within 3σ . Since cerium is in the trivalent oxidation state, one would expect one dative Ce-O interaction and a one-electron

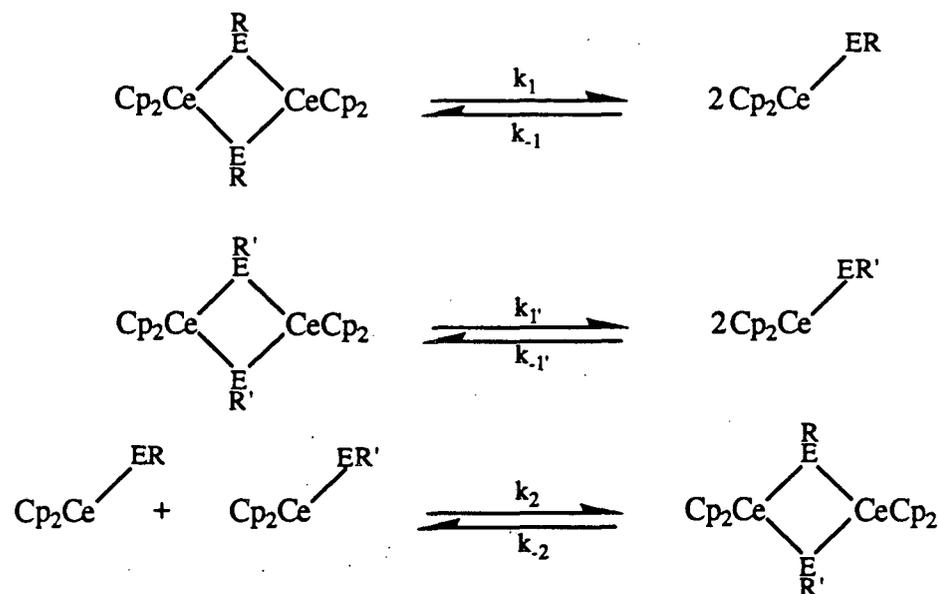
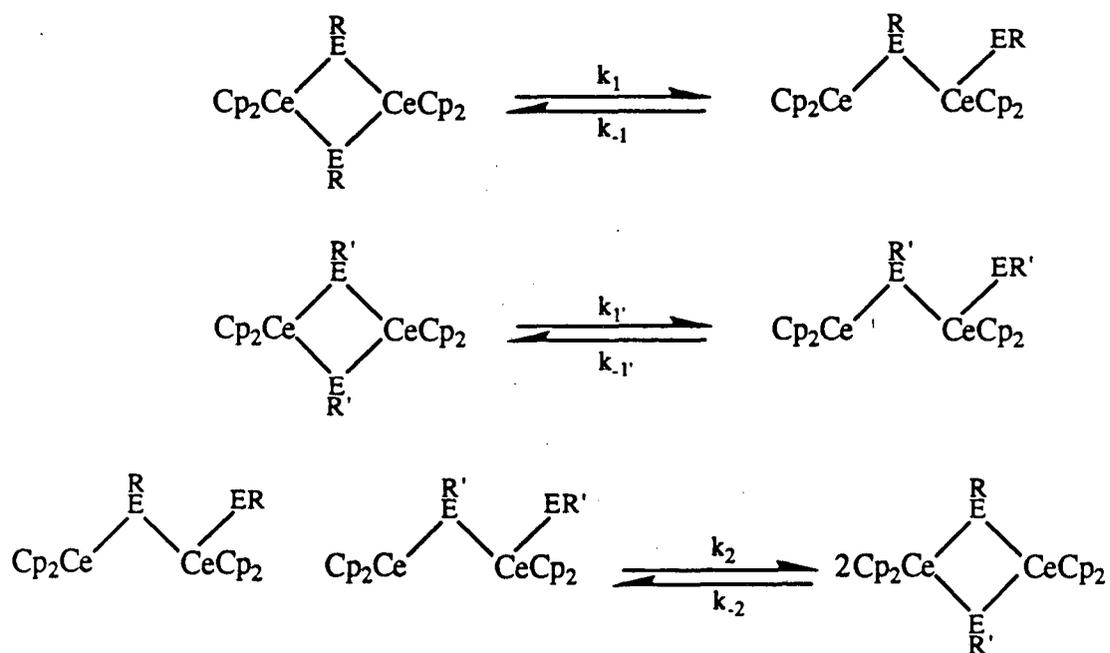
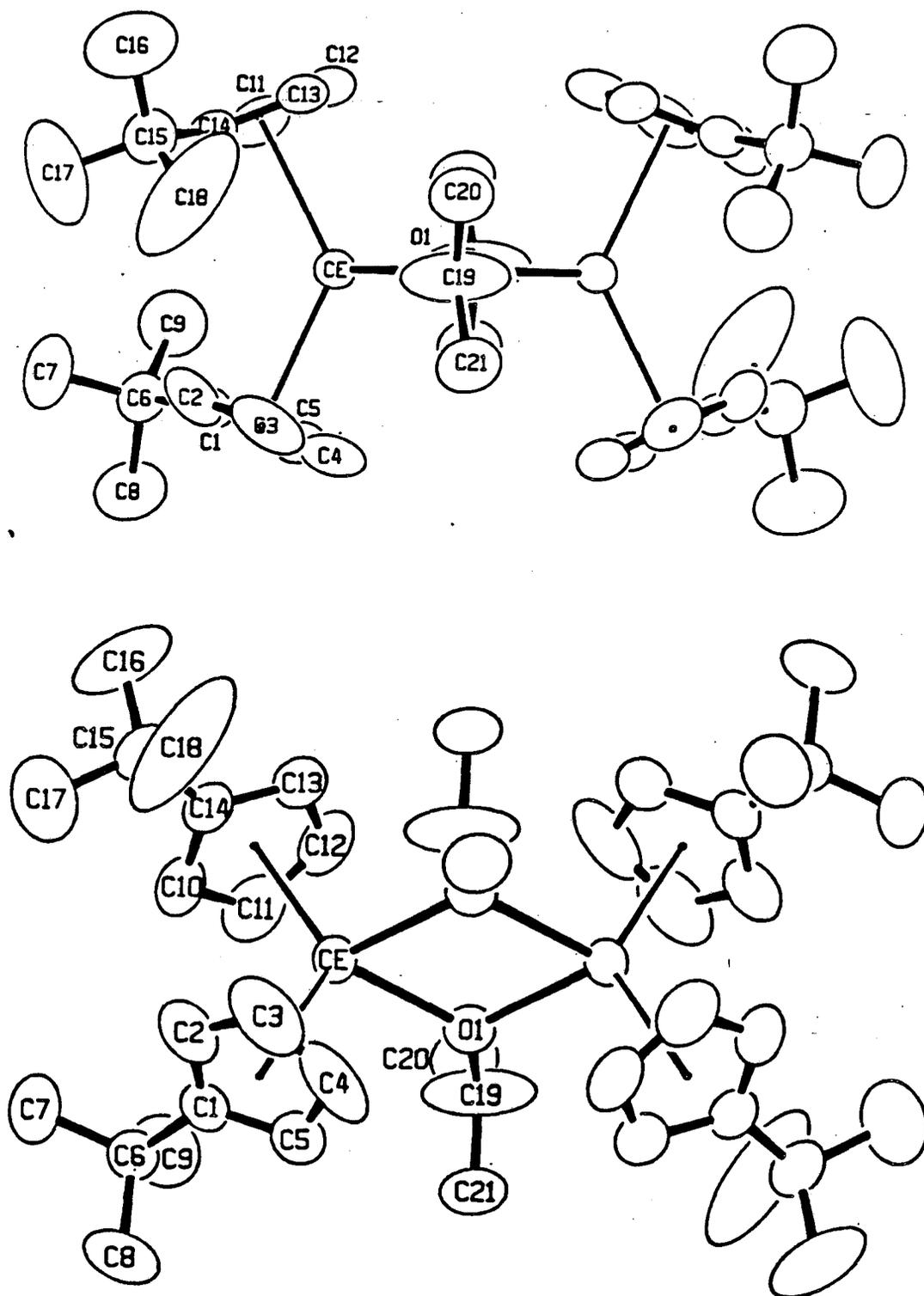
Scheme 3Mechanisms of Thiolate ExchangePathway A:Pathway B:

Fig 2

ORTEP Drawings of $[(\text{Me}_3\text{C}_5\text{H}_4)_2\text{CeOCHMe}_2]_2$ 

The average Ce-Cp distance is 2.51Å and the Cp-Ce-Cp angle is 128.5°. The view from the top of the plane shows that the cyclopentadienyl rings adopt a staggered configuration. The cyclopentadienyl rings are nearly planar, and the longest Ce-C distance is to the carbon atom which is attached to the t-butyl group. The last two observations presumably manifest themselves in order to relieve steric repulsions. One other bridging isopropoxide complex of cerium has been reported.²⁹ The $(C_8H_8)Ce(\mu-OCHMe_2)_2Al(C_2H_5)_2$ complex was not structurally characterized, however, and geometric comparisons cannot be made.

The $[(Me_3Si)_2C_5H_3]_2CeOH)_2$ complex crystallizes from hexane at -20°C in the monoclinic space group, P1. ORTEP drawings viewed down and from the side of the Ce_2O_2 ring are shown in Fig 3. Selected bond distance and angles are given in Table 2.5. The X-ray data were collected at -121°C to minimize thermal motion so that the hydroxide hydrogen atom could be located. It was clearly located in a later difference Fourier map and was refined isotropically. Similar to the $[(Me_3C_5H_4)_2CeOCHMe_2]_2$ complex, the structure consists of centrosymmetric dimers with a rigorously planar Ce_2O_2 moiety and nearly identical Ce-O distances. All bond distances, angles, and geometric features are similar to the isopropoxide complex. The most noticeable difference between the two structures is found in the Cp-Ce-Ce' angles, which differ by 7° in the hydroxide complex and by 4° in the isopropoxide complex. This 3° difference shows that the $(Me_3Si)_2C_5H_3$ rings open away from each other more than the $Me_3CC_5H_4$ rings, and it probably reflects the more sterically demanding nature of two Me_3Si groups, relative to one Me_3C group, on the cyclopentadienyl ring. No other structurally characterized f-metal hydroxide complexes have been reported.

Fig 3

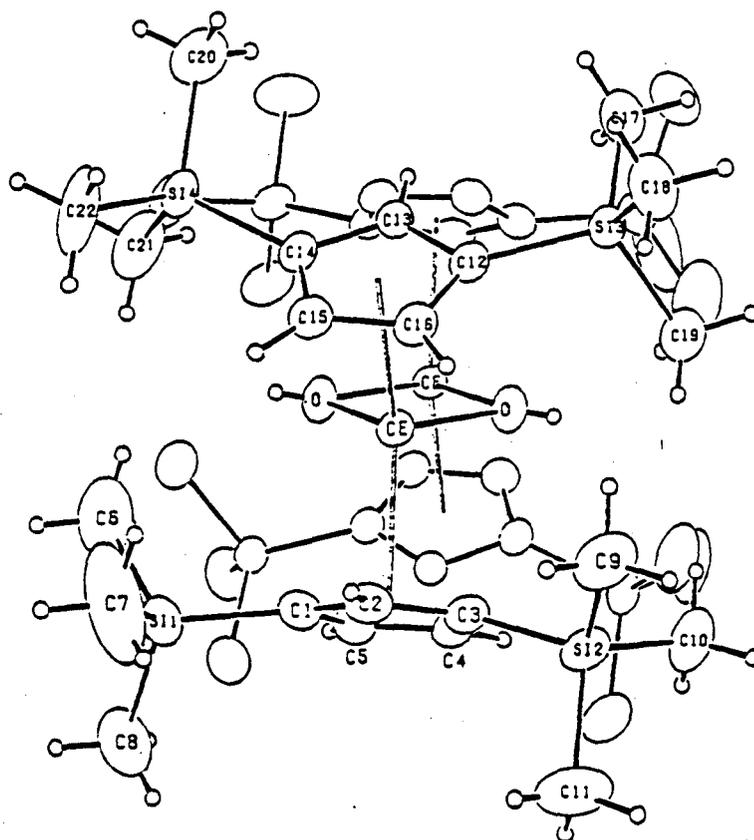
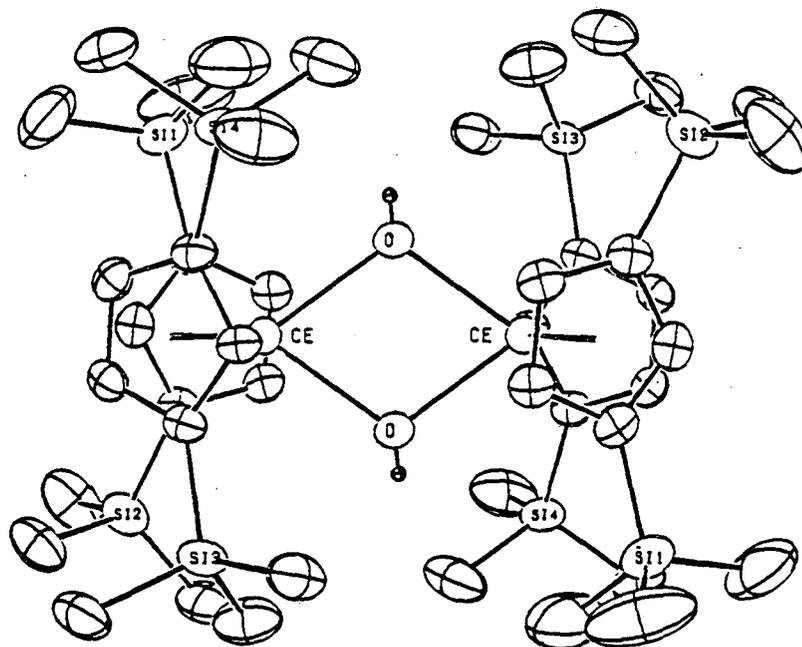
ORTEP Drawings of $\{[(\text{Me}_3\text{Si})_2\text{C}_6\text{H}_3]_2\text{CeOH}\}_2$ 

Table 2.5

Bond Distances (Å) and Intramolecular Angles (°) for
 $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeOH})_2$

Ce-C1	2.792(2)	Ce-C12	2.800(2)		
Ce-C2	2.794(2)	Ce-C13	2.829(2)	Ce-Ce'	3.826(1)
Ce-C3	2.825(2)	Ce-C14	2.860(2)	Ce-O	2.355(2)
Ce-C4	2.814(2)	Ce-C15	2.815(2)	Ce-O'	2.354(2)
Ce-C5	2.780(2)	Ce-C16	2.779(2)		
Ce-Cp1	2.531	Ce-Cp2	2.546		
Cp1-Ce-Cp2	128.89	Cp1-Ce-O	106.61	Cp2-Ce-O'	111.34
Cp1-Ce-Ce'	112.02	Cp2-Ce-O	115.18	Ce-O-Ce'	108.70(6)
Cp2-Ce-Ce'	119.06	Cp1-Ce-O'	108.88	O-Ce-O'	71.30(6)

Cp1 and Cp2 are the centroids of the rings comprised of C1-C5 and C12-C16, respectively. The data was collected at -121°C . The hydroxide hydrogen atom was located and refined isotropically.

Magenta crystals of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeSCHMe}_2]_2$ were grown from a saturated hexane solution cooled to -20°C . The complex crystallizes in the monoclinic space group, $P2_1/n$. An ORTEP drawing is shown in Fig 4. Selected bond distances and angles are given in Table 2.6. Similar to the isopropoxide and hydroxide complexes, the structure consists of centrosymmetric dimers with a distorted tetrahedral arrangement of two staggered $\eta^5\text{-Me}_3\text{CC}_5\text{H}_4$ rings and two bridging, sulfur-bound isopropylthiolate ligands about the cerium atom. The Ce_2S_2 ring is planar with Ce-S-Ce' and S-Ce-S' angles of $101.06(6)^\circ$ and $78.94(6)^\circ$, respectively.

Unlike the alkoxide dimers, the geometry about the bridging heteroatom is not planar. The geometry about sulfur is best described as pyramidal because the sum of the angles about sulfur is 347.8° . A pyramidal geometry about sulfur has been observed in several bridging thiolate complexes of transition-metals.³⁰ Generally, M-S π -bonding

Fig 4

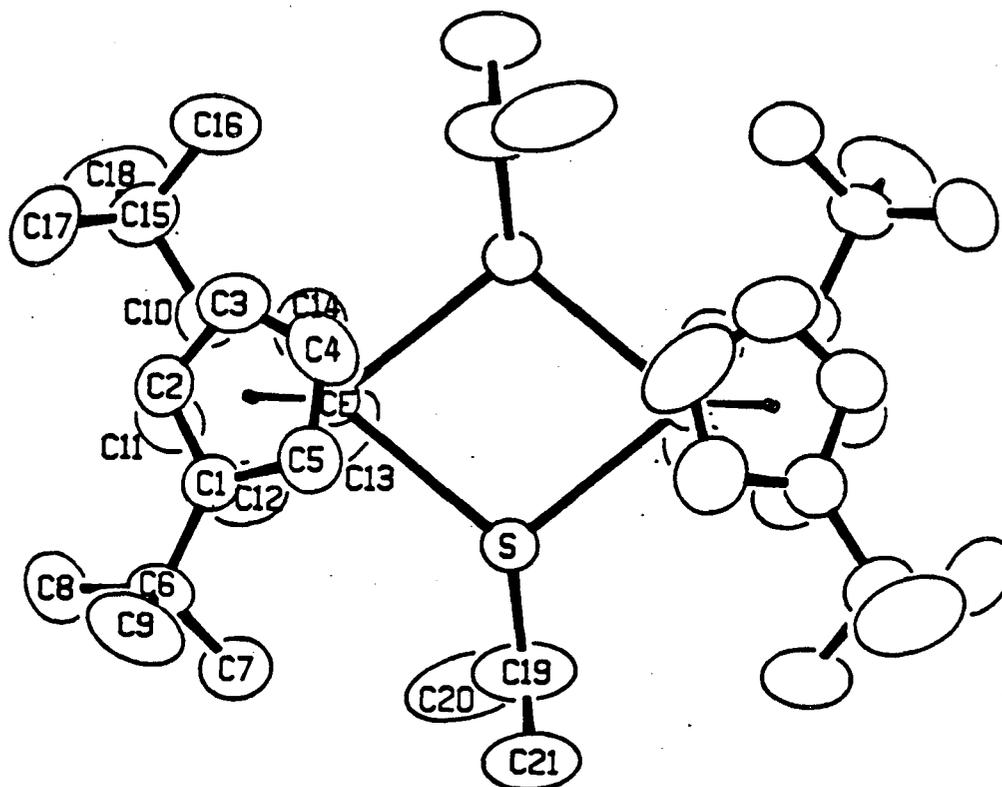
ORTEP Drawing of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeSCHMe}_2]_2$ 

Table 2.6

Bond Distances (Å) and Intramolecular Angles (°) for
 $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeSCHMe}_2]_2$

Ce-C1	2.805(6)	Ce-C10	2.849(6)	Ce-Ce	4.449(2)
Ce-C2	2.781(6)	Ce-C11	2.794(6)	Ce-S	2.894(2)
Ce-C3	2.772(6)	Ce-C12	2.751(7)	Ce-S'	2.870(2)
Ce-C4	2.765(6)	Ce-C13	2.740(7)	C19-S	1.838(8)
Ce-C5	2.789(6)	Ce-C14	2.793(6)		
Ce-Cp1	2.511	Ce-Cp2	2.517		
Cp1-Ce-Cp2	130.70	Cp1-Ce-S	108.15	S-Ce-S'	78.94(6)
Cp1-Ce-Ce'	114.4	Cp2-Ce-S	109.94	Ce-S-Ce'	106.06(6)
Cp2-Ce-Ce'	114.9	Cp1-Ce-S'	109.00	Ce-S-C19	128.5(3)
		Cp2-Ce-S'	108.03	Ce'-S-C19	118.2(4)
S-C19-C20	117.8(7)	S-C19-C21	111.4(6)	C20-C19-C21	118.9(9)

Cp1 and Cp2 are the centriods of the rings comprised of C1-C5 and C10-C14, respectively.

has been used to rationalize this observation. Metal-to-ligand π -bonding is not a likely mode of bonding available to the cerium atom, however. One rationalization for the pyramidal geometry in the cerium complex is that the more polarizable nature of sulfur, relative to oxygen, brings about the partial development of the lone pair of electrons, and thus, the pyramidal geometry. Of course, this geometry may be a reflection of the molecular geometry which best minimizes steric repulsions. A pyramidal bridging sulfur atom has also been observed in the lanthanide thiolate complexes

$\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{GdSCHMe}_2\}_2$ ³¹ and $\{[(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{AlMe}_3)_2(\mu\text{-S-p-C}_7\text{H}_7)]_2\cdot\text{C}_7\text{H}_8\}$ ³²

The Ce-S distances, 2.870(2)Å and 2.894(2)Å, are similar, but not as much as the two Ce-O distances in the alkoxide dimers. This observation may also be a reflection of the partial development of

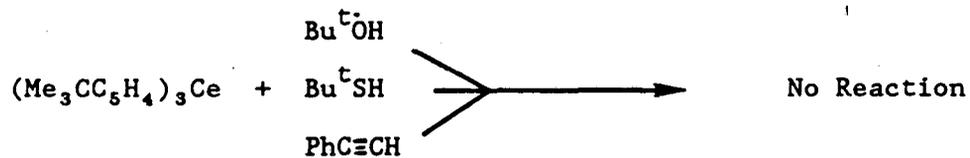
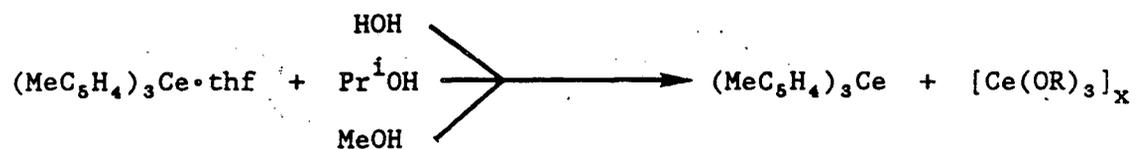
sulfur's lone pair of electrons. The ca. 0.50Å longer Ce-S distance, relative to the Ce-O distance, is consistent with the ca. 0.44Å larger size of sulfur relative to oxygen.³³ The slightly different angles about cerium between the thiolate and alkoxide complexes also consistently reflect the different sizes of the heteroatoms.

The synthesis and characterization of the $[(RC_5H_4)_2CeSR']_2$ complexes represents the first fully characterized cyclopentadienylcerium thiolate complexes. The tetravalent $(C_5H_5)_3CeSR$ complexes, where R is an alkyl, have been reported, but their characterization rests solely on IR analysis.³⁴ The synthesis of these complexes has since been refuted,³⁵ however, and one should be skeptical as to their existence.

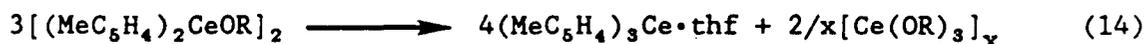
Not all of the attempted protolysis reactions yielded the desired $[(RC_5H_4)_2CeER]_2$ complex. Often the protic substrate reacted with $(RC_5H_4)_3Ce$, but the desired product readily decomposed, presumably via a ligand redistribution pathway. In other cases, no reaction was observed between the substrate and $(RC_5H_4)_3Ce$. The failure to synthesize $[(RC_5H_4)_2CeER]_2$ complexes from the protolysis reactions reflect the importance of kinetic and thermodynamic factors in governing the reaction products. The successful isolation of $[(RC_5H_4)_2CeER]_2$ complexes, however, illustrates how steric and/or electronic perturbations in the reaction system can be used to prepare the compounds of interest. Scheme 4 summarizes the types of reaction pathways that were encountered in the reactions involving protic substrates with $(RC_5H_4)_3Ce$ complexes.

The most common reason for the inability to isolate the desired $[(RC_5H_4)_2CeER]_2$ complex is ligand redistribution reactions. The pKa's of HOH, MeOH, and Pr^iOH are 15.4, 15.5, and 17.1, respectively. However, addition of one equivalent of HOH, MeOH, or Pr^iOH to an ether

Scheme 4

Pathways in the Reaction of $(RC_5H_4)_3Ce$ with Protic Reagents

solution of $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ results in the isolation of starting material and an insoluble white solid. Presumably the white solid is $[\text{Ce}(\text{OR})_3]_x$ which forms from the ligand disproportionation reaction of $[(\text{RC}_5\text{H}_4)_2\text{CeOR}]_2$ described by Eq 14.



The redistribution reactions of the $[(\text{MeC}_5\text{H}_4)_2\text{CeOR}]_2$ complexes are consistent with the observations by Dubeck and co-workers that the $[(\text{MeC}_5\text{H}_4)_2\text{LnCl}]_2$ complexes of the early lanthanides are not isolable.¹

Increasing the steric bulk of the protic substrate, and therefore, increasing the activation energy necessary to achieve ligand redistribution, leads to the successful isolation of $[(\text{MeC}_5\text{H}_4)_2\text{CeSBu}^t]_2$. This molecule is susceptible to ligand redistribution because isolated yields are relatively low (Table 2.2), elemental analysis is poor, and redissolving leads to the gradual formation of a lightly colored precipitate.

The isolation of several $[(\text{Bu}^t\text{C}_5\text{H}_4)_2\text{CeER}]_2$ complexes (Table 2.2) shows that the steric bulk of the cyclopentadienyl ligand plays a role in hindering ligand redistribution reactions. For example, $[(\text{Bu}^t\text{C}_5\text{H}_4)_2\text{CeOPr}^i]_2$ does not undergo ligand redistribution reactions to any observable extent, while $[(\text{MeC}_5\text{H}_4)_2\text{CeOPr}^i]_2$ is not isolable as $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ is observed. On the other hand, products obtained from the reaction of $(\text{Bu}^t\text{C}_5\text{H}_4)_3\text{Ce}$ and the smaller reagents, HOH and MeOH, are also unstable toward ligand redistribution. The rate of ligand redistribution in the $(\text{Bu}^t\text{C}_5\text{H}_4)_3\text{Ce}$ reactions are slower than those for the $(\text{MeC}_5\text{H}_4)_3\text{Ce}$, since an immediate change in the solution color from purple to yellow is observed upon addition of HOH or MeOH to $(\text{Bu}^t\text{C}_5\text{H}_4)_3\text{Ce}$. This yellow color is indicative of the $[(\text{RC}_5\text{H}_4)_2\text{CeOR}]_2$

complexes (Table 2.2). Within minutes the color reverts back to purple with the formation of a white precipitate. Attempts to isolate the $[(\text{Bu}^t\text{C}_5\text{H}_4)_2\text{CeOR}]_2$ complex by lowering the reaction temperature, and thereby inducing precipitation of the complex as it is formed, were not successful.

Using $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$ prevents ligand redistribution reactions even with HOH or MeOH. Addition of one equivalent of degassed water to a thf solution of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ results in a change of solution color from blue to yellow with no precipitate or reversion of solution color. The yellow $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeOH}$ complex is isolated in 71% yield and it gives another example of how to manipulate steric effects to give kinetic rather than thermodynamic products.

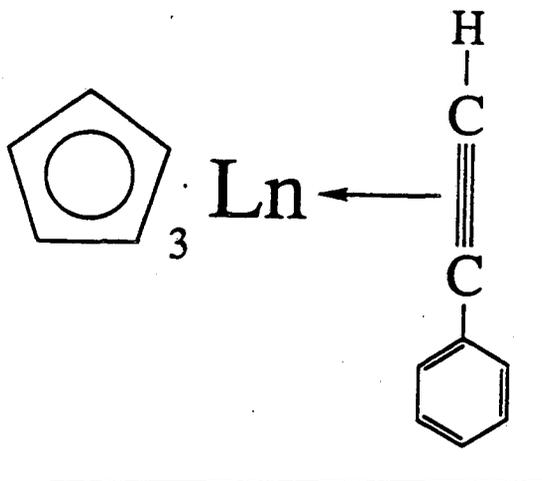
Along with the ability to form more kinetically inert $[(\text{RC}_5\text{H}_4)_2\text{CeER}]_2$ complexes, the bulky $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_4$ ligand changes the electronic properties of the ligand and the metal. The sequential replacement of H by an alkyl group raises the pKa of the cyclopentadienyl ligand. For example, the pKa of C_5H_6 is 16 while that of $\text{Me}_5\text{C}_5\text{H}$ is 26. The pKa's of several cyclopentadienes that are of interest to us are not known, such as $\text{Bu}^t\text{C}_5\text{H}_5$ and $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_4$, so it is difficult to be more quantitative. Experimentally, Bu^tOH does not react with $(\text{Bu}^t\text{C}_5\text{H}_4)_3\text{Ce}$, even when heated for periods of up to 5 days. The alcohol, pKa = 19.2, may or may not be a strong enough acid to successfully protonate the $\text{Bu}^t\text{C}_5\text{H}_4^-$ anion. On the other hand, the increased steric bulk of Bu^tOH , relative to HOH, MeOH, and Pr^iOH , may prevent the alcohol from approaching the metal because of intermolecular steric repulsions. Support for the latter postulate is found in the observation that Bu^tSH does not react with $(\text{Bu}^t\text{C}_5\text{H}_4)_3\text{Ce}$. *t*-Butylthiol (pKa = 11.2) is a stronger acid than $\text{Bu}^t\text{C}_5\text{H}_5$, and it should give $[(\text{Bu}^t\text{C}_5\text{H}_4)_2\text{CeSBU}^t]_2$. The isolation of $[(\text{Me}_3\text{C}_5\text{H}_4)_2\text{CeSBU}^t]_2$

proves that this thiolate is thermodynamically accessible and the lack of reaction of Bu^tSH with $(\text{Bu}^t\text{C}_5\text{H}_4)_3\text{Ce}$ must be kinetic probably due to the increased steric bulk of Bu^tEH and/or $\text{Bu}^t\text{C}_5\text{H}_4$ relative to Pr^iOH and/or MeC_5H_4 , respectively.

It has been suggested that the mechanism for ring protolysis involves the initial coordination of the protic substrate to the metal, followed by the ring protonation step.³⁶ No mechanistic studies have been made on the ring protolysis reactions of tris(cyclopentadienyl)lanthanide complexes, but the experimental results presented here are consistent with a mechanism involving initial coordination of the protic compound. If this is the case, then the relative Lewis basicity of the protic source toward $(\text{RC}_5\text{H}_4)_3\text{Ce}$ is an important property governing the ring protolysis reaction. The ligand basicity studies presented in Chapter 1 suggest that, within a given class of ligands, Lewis basicity toward $(\text{RC}_5\text{H}_4)_3\text{Ce}$ decreases with increased steric bulk of the ligand. For example, in the alcohol series, the Lewis basicity toward $(\text{RC}_5\text{H}_4)_3\text{Ce}$ should decrease in the order $\text{HOH} > \text{MeOH} > \text{Pr}^i\text{OH} > t\text{-BuOH}$. Thus, $t\text{BuOH}$ is less likely to protonate the ring relative to Pr^iOH because it has the highest pK_a and the weakest basicity toward $(\text{RC}_5\text{H}_4)_3\text{Ce}$. Qualitatively, the rates of the reactions between alcohols and $(\text{RC}_5\text{H}_4)_3\text{Ce}$ seem to support this postulate.

One of the most interesting protolysis reactions that has been observed for heavier $(\text{C}_5\text{H}_5)_3\text{Ln}$ complexes involves the $\text{PhC}\equiv\text{CH}$ substrate. The interest lies in the fact that the pK_a of $\text{PhC}\equiv\text{CH}$ is relatively high (21 in H_2O and 29 in dmsO) and it should not react with $(\text{C}_5\text{H}_5)_3\text{Ln}$. However, it does react with $(\text{C}_5\text{H}_5)_3\text{Ln}$ to yield $[(\text{C}_5\text{H}_5)_2\text{LnC}\equiv\text{CPh}]_2$. It is presumed that the acetylene weakly

Fig 5



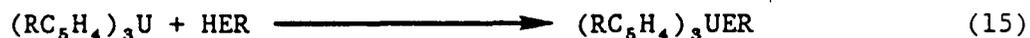
coordinates to the metal environment in the manner depicted in Fig 5 which results in a lowering of the pKa of the acetylene.³⁷

No reaction is observed between $\text{PhC}\equiv\text{CH}$ and either $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ or $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$; two complexes containing cyclopentadienyl ligands which are stronger bases than C_5H_5^- . The reason for this observation presumably reflects the poor Lewis basicity of $\text{PhC}\equiv\text{CH}$ toward $(\text{RC}_5\text{H}_4)_3\text{Ce}$ and the more sterically demanding nature of the *t*-butylcyclopentadienyl and bis-trimethylsilylcyclopentadienyl ligands relative to the unsubstituted cyclopentadienyl ligand. Competition studies have shown that the Lewis acidity of $(\text{RC}_5\text{H}_4)_3\text{Ce}$ toward a particular Lewis base decreases as the steric bulk of the cyclopentadienyl ligands increases (Chapter 1). The $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeCCPh}_2$ complex has been synthesized by another method (Chapter 3), but no attempt was made to synthesize a phenylacetylide complex, via the ring protolysis reaction, involving less bulky cyclopentadienyl ligands because such a product is probably unstable toward ligand redistribution.

Reactions of $(RC_5H_4)_3U$ Complexes with Protic Acids

In view of the success in synthesizing stable $[(RC_5H_4)_2CeER]_2$ complexes from the protolysis of $(RC_5H_4)_3Ce$ with protic acids, it seemed reasonable to extend this synthetic strategy to analogous uranium complexes. The majority of studies of organouranium complexes involve U(IV) species, e.g. the $(C_5H_5)_3UX$ and $(R_xC_5H_{5-x})_2UX_2$ complexes. Relatively few $[(RC_5H_4)_2UX]_2$ complexes have been reported in the literature, presumably because they easily undergo ligand redistribution and/or oxidation reactions. Kanellakopulos has reportedly synthesized the $[(C_5H_5)_2UCl]_x$ complex from a slow addition of anhydrous HCl to $(C_5H_5)_3U$.²³ The extreme insolubility of this complex, and the presence of an excess of $(C_5H_5)_3U$ at all times, probably prevents ligand redistribution and eventual decomposition from occurring. The majority of the reported $[(RC_5H_4)_2UX]_2$ complexes involve the sterically demanding Me_5C_5 and $(Me_3Si)_2C_5H_3$ ligands to stabilize the molecule with respect to ligand redistribution.

The reaction of one equivalent of the protic substrates, HER, with $(RC_5H_4)_3U$, however, does not yield the desired $[(RC_5H_4)_2UER]_2$ complex. Instead, the U(III) ion is oxidized to U(IV) and $(RC_5H_4)_3UER$ complexes are isolated as the major product (Eq 15). Other species are also formed in lower yield in this reaction, but they were not rigorously characterized due to their extreme insolubility.



The $(RC_5H_4)_3UER$ complexes are by no means novel. The method used to synthesize them, however, is novel. Usually, tris(cyclopentadienyl)uranium alkoxide and thiolate complexes are prepared metathetically from the reaction of $(RC_5H_4)_3UCl$ with the

Table 2.7

Physical Properties of $(RC_5H_4)_3UER$ Complexes

<u>Compound</u>	<u>Color</u>	<u>m.p. (°C)</u>	<u>yield</u>
$(MeC_5H_4)_3OMe$	green	274-275	30%
$(MeC_5H_4)_3UOPr^i$	green	196-200	37%
$(MeC_5H_4)_3UOPh$	green	127-128	34%
$(MeC_5H_4)_3USPr^i$	gold-brown	121-123	27%
$(MeC_5H_4)_3UOC_6F_5$	red-brown	120-122	29%
$(Me_3CC_5H_4)_3USC_6H_5$	red	142-143	22%

appropriate alkali-metal alkoxide or thiolate.^{38,39}

Very few physical properties of these complexes have been reported. Usually they are characterized by IR and elemental analyses only. There are a few reports where trends in the 1H NMR spectra of these complexes have been investigated.³⁸ Table 2.7 gives the physical properties of the $(RC_5H_4)_3UX$ complexes synthesized in this study from the reaction of $(RC_5H_4)_3U$ with alcohols and thiols. The complexes are extremely soluble in hydrocarbon solvents; they were crystallized from saturated hexane solutions as thin plates or needles. Unfortunately, crystals, suitable for X-ray diffraction studies, could not be obtained. No other tris(cyclopentadienyl)-uranium alkoxide or thiolate complexes have been structurally characterized. The complexes listed in Table 2.7 give molecular ions in the E.I. mass spectrum corresponding to a monomeric structure in the gas phase.

Table 2.8 gives data from the ^1H NMR spectra of several tris(cyclopentadienyl)uranium alkoxide and thiolate complexes. The ^1H NMR spectra of the $(\text{RC}_5\text{H}_4)_3\text{UER}$ complexes, where R is H, Me, or Me_3C , show the expected resonances for the A_5 , $AA'BB'X_3$, or $AA'BB'X_9$ spin systems. The line-widths at half-height range from 6 Hz to 12 Hz for the ring -CH- protons and from 2 Hz to 9 Hz for the ring-alkyl protons. These widths are indicative of U(IV) compounds and are narrower than the 15-30 Hz line-widths typically observed in U(III) complexes.⁴⁰ The ring -CH- resonances are shifted upfield from the ring-alkyl resonance in the alkoxide complexes. The alkoxide ligand resonances are shifted downfield from the ring-alkyl resonance, and the magnitude of this shift generally depends on the distance of the protons away from the paramagnetic U(IV) ion. This phenomenon has been observed in a number of paramagnetic f-metal complexes, including some the previously reported $(\text{RC}_5\text{H}_4)_3\text{UX}$ complexes, and presumably arises from the through-space pseudocontact term of the isotropic chemical shift.³⁸

The thiolate complexes show ring -CH- resonances flanking the ring-alkyl resonances and thiolate ligand resonances shifted upfield from the ring-alkyl resonances. The difference in the relative positions of the proton resonances between the alkoxide and thiolate complexes probably reflects the nature of the magnetic properties of the O and S heteroatoms; replacement of oxygen by sulfur presumably changes the sign of the magnetic anisotropy and therefore, the sign of the pseudocontact shift, resulting in a change of sign for the isotropic chemical shift.⁴¹

The difference in reactivity between $(\text{RC}_5\text{H}_4)_3\text{Ce}$ and $(\text{RC}_5\text{H}_4)_3\text{U}$ with protic acids probably reflects the accessible tetravalent oxidation state that is available to uranium and not to cerium. The

Table 2.8

 ^1H NMR Data of $(\text{RC}_5\text{H}_4)_3\text{UER}$ Complexes^a

<u>Compound</u>	<u>$\delta\text{CH(A)}$</u>	<u>$\delta\text{CH(B)}$</u>	<u>$\delta\text{(R)}$</u>	<u>δ ligand</u>
$(\text{MeC}_5\text{H}_4)_3\text{UOMe}$	-10.60 (6H, 12Hz)	-22.41 (6H, 11Hz)	-0.32 (9H, 8Hz)	45.13 (3H, 12Hz)
$(\text{MeC}_5\text{H}_4)_3\text{UOPr}^i$	-13.93 (6H, 8Hz)	-23.31 (6H, 8Hz)	-1.54 (9H, Hz)	55.5(1H, 20Hz) 15.7(6H, 8Hz)
$(\text{MeC}_5\text{H}_4)_3\text{UOPh}$	-4.75 (6H, 7Hz)	-11.97 (6H, 7Hz)	-3.11 (9H, 3Hz)	4.72(2H, t, J=8Hz) 3.96(2H, t, J=8Hz) -10.48 (1H)
$(\text{MeC}_5\text{H}_4)_3\text{USPr}^i$	-1.24 (6H, 7Hz)	-8.77 (6H, 7Hz)	-1.58 (9H, 3Hz)	-19.7(6H, d, 7Hz) -44.7(1H, m, 7Hz)
$(\text{MeC}_5\text{H}_4)_3\text{UOC}_6\text{F}_5$	3.55 (6H, 10Hz)	-9.92 (6H, 9Hz)	-5.14 (9H, 3Hz)	—————
$(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{USPh}$	3.64 (6H, 7Hz)	-12.16 (6H, 7Hz)	-2.43 27H, 4Hz)	-1.38 (2H) -8.43 (1H) -21.2(2H, t, 8Hz)

	<u>δ ring</u>	<u>δ ligand</u>
$(\text{C}_5\text{H}_5)_3\text{UOMe}$	-17.06 (5H)	52.5(3H)
$(\text{C}_5\text{H}_5)_3\text{UOPr}^i$	-25.8 (5H)	54.7(1H), 10.6(6H)
$(\text{C}_5\text{H}_5)_3\text{UOEt}$	-25.6 (5H)	51.8(2H), 9.6(3H)
$(\text{C}_5\text{H}_5)_3\text{UOPh}$	-8.85 (5H)	not reported
$(\text{C}_5\text{H}_5)_3\text{USEt}$	-4.53 (5H)	-33.78(2H), -18.85(3H)
$(\text{C}_5\text{H}_5)_3\text{USPh}$	-4.63 (5H)	not observed

(a) The spectra of the first six compounds were recorded in C_6D_6 and referenced relative to tetramethylsilane, $\delta=0.00$. The B protons are arbitrarily assigned to those farthest upfield.

Table 2.9

Redox Potentials for Actinide and Lanthanide Complexes

<u>Compound</u>	<u>$E_{1/2}$(a)</u>	<u>solvent</u>	<u>ref</u>
U(IV)	-0.64	1M HCl	42a
(C ₅ H ₅) ₄ U	-1.67	thf	42b
(C ₅ H ₅) ₃ UCl	-1.53	thf	42b
(MeC ₅ H ₄) ₃ UCl	-1.86	thf	42c
(Me ₅ C ₅) ₂ UCl ₂	-1.54	MeCN	42d
Ce(IV)	+1.61	1M HNO ₃	42a
(C ₈ H ₈) ₂ Ce	-1.28	thf	42e

(a) $E_{1/2}$ is the reversible half-wave potential vs. SHE for
 $M(IV) + 1e \text{ -----} \rightarrow M(III)$

U(IV)/U(III) redox potential, measured in aqueous acid, is -0.61 eV, while that of the Ce(IV)/Ce(III) couple is 1.61 eV.^{42a} These values should be used in a very qualitative sense because redox potentials are dependent on the solvent and on the ligand environment about the metal atom (Table 2.9).

As stated earlier, the reaction pathway for the reaction of (RC₅H₄)₃Ce with protic substrates probably involves initial coordination followed by ring protonation. The reaction pathway for the reaction of (RC₅H₄)₃U with protic substrates is difficult to understand because uncharacterized species were also formed. In particular, it is not clear whether oxidation takes place with or without ring protonation.

Some likely steps in the formation of (RC₅H₄)₃UER complexes from the reaction of (RC₅H₄)₃U with protic acids involve initial coordination of the substrate followed by oxidation of uranium and evolution of H₂ (Scheme 5). This process is clearly thermodynamically

avored since it involves the oxidation of U(III) to U(IV), formation of an H-H bond, formation of a U-X bond, and only the breaking of an H-X bond.⁴³ It has recently been shown that trivalent $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{NH}_2\text{R}$ complexes, where R is H, Me, Ph, p-C₇H₇, undergo oxidation with evolution of H₂ at elevated temperatures to quantitatively yield the tetravalent $(\text{MeC}_5\text{H}_4)_3\text{U-NHR}$ complexes.¹⁶ However, the reaction of $(\text{RC}_5\text{H}_4)_3\text{U}$ with protic acids does not result in any observable evolution of gas and the yield is not quantitative.

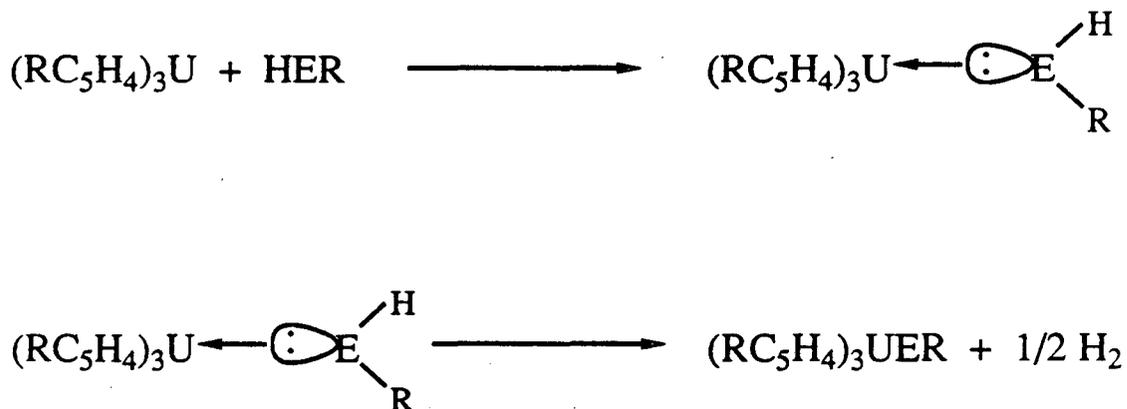
Another plausible reaction pathway involves the initial coordination of the substrate, followed by ring protonation, and then oxidation of the metal and ligand redistribution (Scheme 6). Direct chemical evidence for the formation of a $[(\text{RC}_5\text{H}_4)_2\text{UX}]_2$ complex would lend support to this latter pathway.

The $[(\text{RC}_5\text{H}_4)_2\text{CeSPh}]_2$ complex is the most insoluble of the $[(\text{RC}_5\text{H}_4)_2\text{CeER}]_2$ complexes prepared in this study; it forms as a precipitate during the course of the reaction between $(\text{RC}_5\text{H}_4)_3\text{Ce}$ and HSPH. If ring protonation were taking place at a rate faster than, or similar to, the oxidation step in the reaction of $(\text{RC}_5\text{H}_4)_3\text{U}$ with protic acids, then cooling the reaction temperature might lead to the formation of $[(\text{RC}_5\text{H}_4)_2\text{UX}]_2$ if the complex has low enough solubility to be instantly driven out of solution as it is formed, thus preventing oxidation and/or ligand redistribution from occurring.

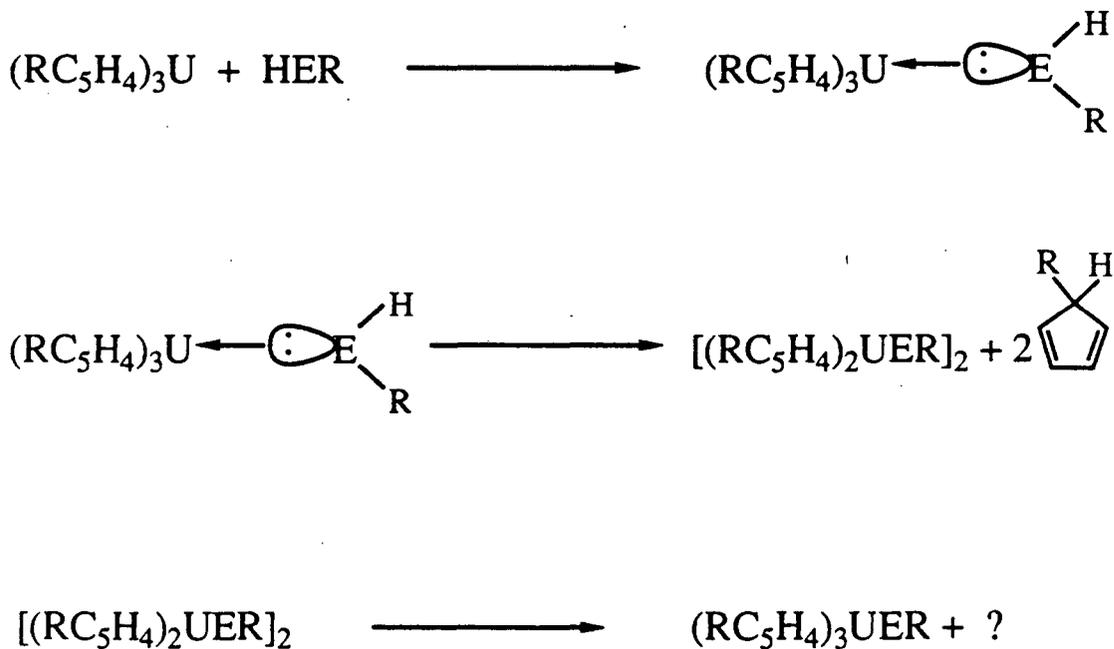
Addition of HSPH to a cooled (-25°C) hexane solution of $(\text{RC}_5\text{H}_4)_3\text{U}$ results in an initial solution color change from green to red, followed by the formation of a green precipitate. The red solution color is indicative of coordination complexes of $(\text{RC}_5\text{H}_4)_3\text{U}\cdot\text{L}$.⁴⁴ The hexane was removed by filtration, and the microcrystalline, green solid was washed with cold hexane and dried in vacuo. Dark green crystals can be isolated from a saturated toluene solution, but the

Reaction Steps in the Formation of $(RC_5H_4)_3UER$

Scheme 5:



Scheme 6:



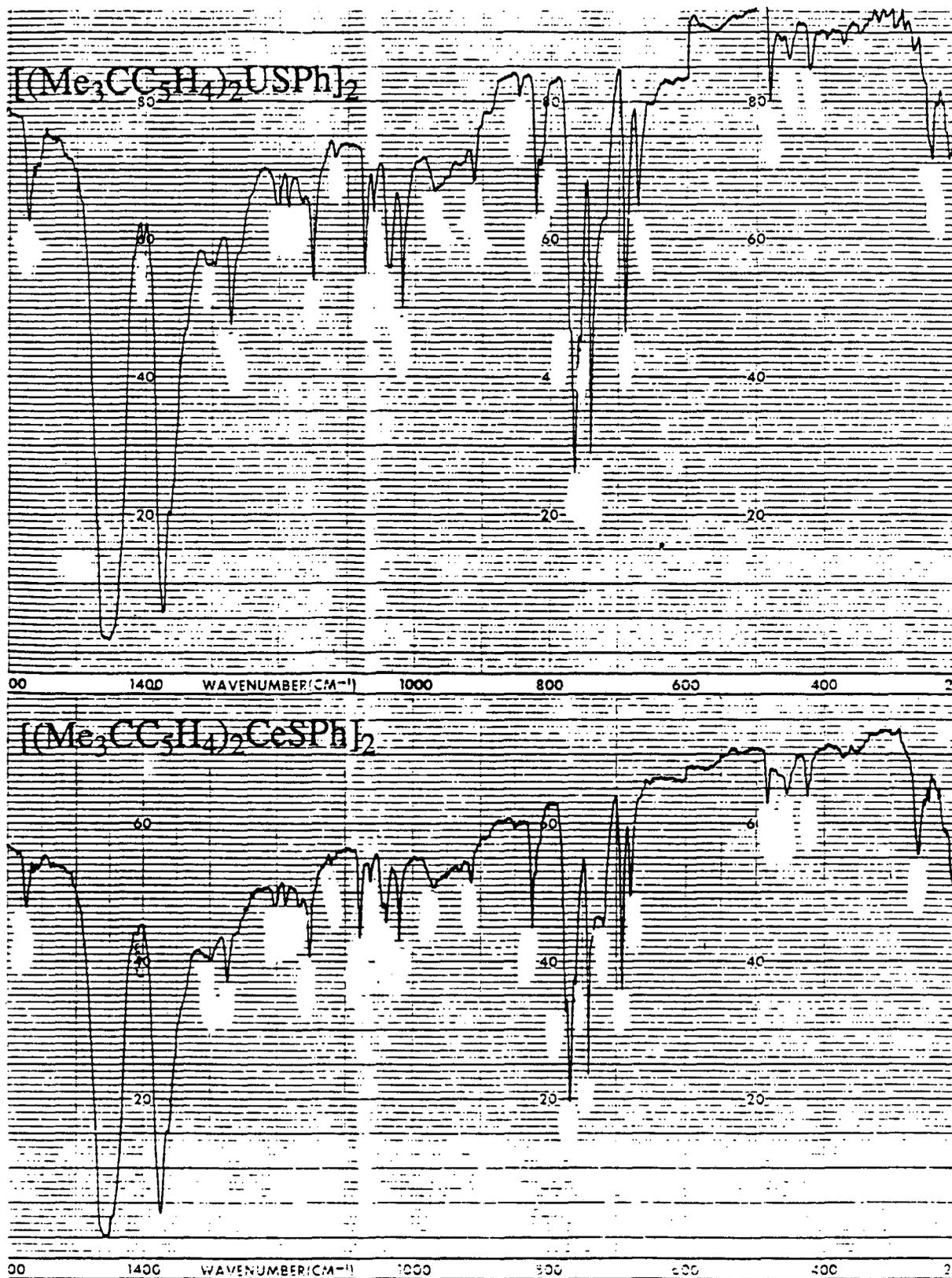
solution color gradually turns from green to red during work-up. Characterization of the green solid (or crystals) suggests the formulation of the ring protonation product, $[(RC_5H_4)_2USPh]_2$. The complex is very unstable toward oxidation and ligand redistribution, however.

The IR spectrum more closely resembles $[(RC_5H_4)_2CeSPh]_2$ than $(RC_5H_4)_3USPh$ (Fig 6). The E.I. mass spectrum gives a weak molecular ion at $M/e = 1178$ amu, corresponding to the trivalent bridging thiolate complex. The most intense peak in the mass spectrum, however, corresponds to the tetravalent $[(RC_5H_4)_2U]_2S$ complex ($M/e = 1024$ amu). The 1H NMR spectrum is contaminated with impurities presumably due to rapid oxidation and ligand redistribution in solution. The major features consist of a set of relatively broad resonances in a 9:2:2 ratio and a set of sharper resonances also in a 9:2:2 ratio. The latter resonances correspond to the $(RC_5H_4)_3USPh$ complex, and their integrated intensities increase with time relative to the broader set.

Unfortunately one cannot be more definitive about the constitution of $(RC_5H_4)_3UER$, but the postulate that ring protonation occurs prior to oxidation and ligand redistribution in the reaction between $(RC_5H_4)_3U$ and protic substrates is indicated as one possible explanation of several experimental observations. It by no means implies that this is the only pathway that will lead to the observed products. The formation of additional products, still uncharacterized, implies that the reaction is quite complex. Clearly, these products must be identified before any meaningful and detailed mechanisms are proposed.

The $\{[(Me_3Si)_2C_5H_3]_2UOH\}_2$ complex has recently been synthesized from the reaction of $[(Me_3Si)_2C_5H_3]_3U$ with water.¹⁴ In this example,

Fig 6

IR Spectra of $[(Me_3CC_6H_4)_2MSPh]_2$ M = U, Ce

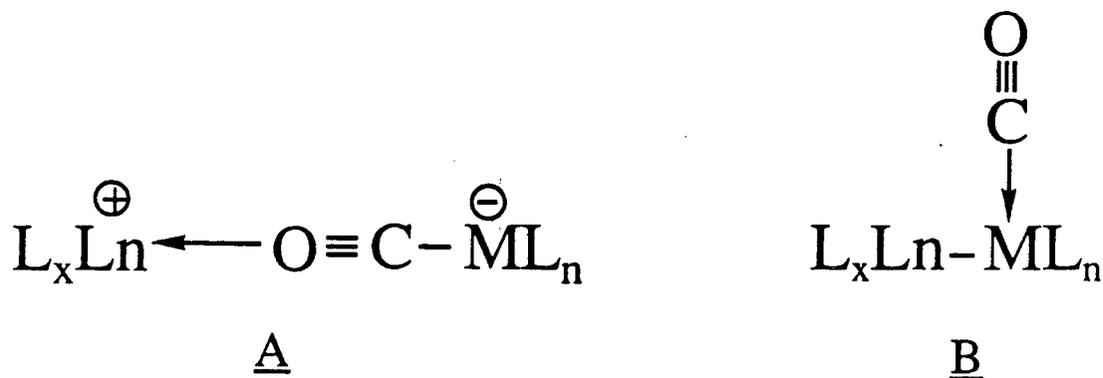
the increased steric bulk of the cyclopentadienyl ligand presumably makes the redox and/or ligand redistribution pathways less energetically favorable. This result supports the postulate that ring protonation is a key step in the reaction of $(RC_5H_4)_3U$ with protic acids.

Reactions of $(RC_5H_4)_3U$ Complexes with Transition-metal Hydrides

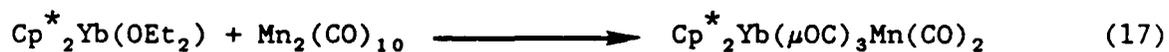
The driving force to form U(IV) species in the reaction of $(RC_5H_4)_3U$ with protic substrates suggests that the formation of mixed-metal complexes containing an actinide and a transition metal might be possible. Transition-metal hydride complexes can either function as proton or hydride donors in polar solvents. In general, the hydrides of early transition-metal cyclopentadienyl complexes exhibit hydridic behavior, while most hydride complexes of the later transition-metals act as proton donors.⁴⁵ Of particular interest are the 18-electron $(C_5H_5)M(CO)_3H$ complexes, where M is Cr, Mo, and W, which have been shown to act as moderately strong acids.⁴⁶ It seems reasonable that the reaction of $(RC_5H_4)_3U$ with a transition-metal hydride might lead to the formation of a complex with an actinide- and a transition-metal.

Two structure-types are envisioned for such a mixed-metal complex (Fig 6). Structure A contains an isocarbonyl group bridging the two metal fragments, while structure B contains a direct, unsupported, actinide to transition-metal bond. The former structure-type is quite common between highly oxophilic metal centers and transition-metal carbonyls.⁴⁷ Complexes of this type have been synthesized from the reaction of transition-metal hydrides with metal-alkyl complexes (Eq 16) or from the reductive cleavage of binuclear transition-metal carbonyls (Eq 17).

Fig 6

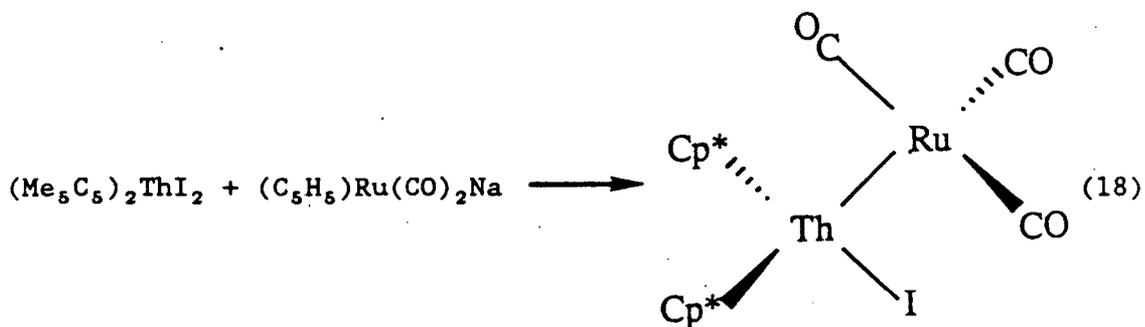
Two Possible Structures of Actinide-Transition Metalcarbonyl Complexes

Generally, the observed M-O-C angle is nearly linear, and the O-C-M' angle is bent. The most striking structural feature of these isocarbonyl-complexes is a lowered CO stretching frequency relative to that in the acid-free complex.



where Cp^* is Me_5C_5 and Cp is C_5H_5

Only one example of a direct, unsupported, actinide to transition-metal bond (structure B) has been reported.⁴⁸ The complex, $(\text{Me}_5\text{C}_5)\text{Th}(\text{I})\text{Ru}(\text{CO})_2(\text{C}_5\text{H}_5)$, was prepared according to Eq 18.



The X-ray crystal structure shows that a direct Th-Ru bond exists with no other atoms close enough to the thorium atom to form a bridging interaction.

The reaction of $(\text{RC}_5\text{H}_4)_3\text{U}$, where R is Me_3Si and Me_3C , with $(\text{C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$, where M is Mo and W, proceeds in hexane within minutes to yield red complexes. Some physical properties of these complexes are given in Table 2.10. The integrated intensities of the resonances in the ^1H NMR spectra are in a 27:6:6:5 ratio indicating that the complexes consist of $(\text{RC}_5\text{H}_4)_3\text{U}$ and $(\text{C}_5\text{H}_5)\text{M}(\text{CO})_3$ fragments in a 1:1 ratio. The line-widths at half-height of the uranium resonances, 2 to 7 Hz, are consistent with a tetravalent oxidation state for uranium.

The IR spectra give the most useful information about the molecular structure of these complexes. Most notable is a broad CO band at ca. 1500 cm^{-1} . This lowered CO stretching frequency is consistent with the isocarbonyl-bridging structure previously described (structure A, Fig 6). Presumably, the oxophilic nature of the uranium ion and/or ligand-ligand repulsions stabilize the isocarbonyl-structure relative to the actinide to transition-metal bond structure.

Table 2.10

Physical Properties of $(RC_5H_4)_3U(\mu-OC)M(CO)_2(R_5H_5)$ Complexes

<u>Compound</u>	<u>Color</u>	<u>1H NMR^a</u>	<u>ν_{CO} (cm⁻¹)^b</u>
$(Me_3SiC_5H_4)_3U(\mu-OC)Mo(CO)_2(C_5H_5)$	red	12.78 (6H, 6 Hz); -3.06 (5H, 2 Hz) -6.94 (27H, 2 Hz); -9.64 (6H, 6 Hz)	1923, 1832 1715, 1575
$(Me_3SiC_5H_4)_3U(\mu-OC)Mo(CO)_2(Me_5C_5)$	red	11.15 (6H, 7 Hz); -3.94 (15H, 3 Hz) -6.52 (27H, 2 Hz); -9.22 (6H, 6 Hz)	1928, 1845 1718, 1518
$(Me_3CC_5H_4)_3U(\mu-OC)W(CO)_2(C_5H_5)$	red	20.50 (6H, 6 Hz); -2.50 (5H, 2 Hz) -9.30 (27H, 3 Hz); -19.08 (6H, 6 Hz)	1920, 1831 1715, 1558

(a) Recorded in C_6D_6 at 30°C and referenced relative to $SiMe_4$, $\delta=0$.

Relative intensities and line-widths at half peak height are given in parentheses.

(b) Recorded as Nujol mulls between CsI windows.

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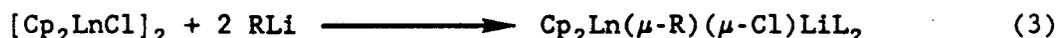
CHAPTER THREE: Preparation and Reactions of Cerium
and Uranium Alkyl Complexes

Compounds containing σ -alkyl groups have been of chemical and structural interest since trimethylaluminum was first structurally characterized by Lewis and Rundle in 1953.¹ The first alkyl complexes of the lanthanides were claimed to be monomeric,² but subsequent studies showed that they are dimeric and structurally similar to $[\mu\text{-Me}_2\text{AlMe}_2]_2$, i.e. they consist of electron-deficient, three center bonding involving two methyl groups bridging two metal atoms so that the carbon atom is five coordinate and the M-C-M angle is acute ($<100^\circ$).³⁻⁵ One exception is the $(\text{Me}_5\text{C}_5)_2\text{Lu}(\mu\text{-Me})\text{Lu}(\text{Me})(\text{Me}_5\text{C}_5)_2$ complex that contains one terminal methyl group and one methyl group that asymmetrically bridges the two Lu atoms in a nearly linear fashion.^{6a} This asymmetric geometry presumably reflects the sterically demanding nature of the Me_5C_5 ligand relative to C_5H_5 and the small ionic radius of Lu relative to the other lanthanides. Monomeric Cp_2LnR complexes, where Cp is used to represent the $\text{R}_n\text{C}_5\text{H}_{5-n}^-$ anion, can be prepared if more sterically demanding alkyl and/or cyclopentadienyl ligands are used.^{4a,6b,7} From a chemical reactivity point of view, the $[\text{Cp}_2\text{LnR}]_x$ complexes, where x is 1 or 2, are very interesting because they are capable of polymerizing olefins, activating C-H bonds, and inserting small unsaturated molecules.⁶

The synthesis of the heavier lanthanide alkyl complexes has been studied and developed over the last 15 years. The methods used to synthesize these complexes involve the displacement of AlMe_3 from $\text{Cp}_2\text{Ln}(\mu\text{-Me}_2\text{AlMe}_2)$ by Lewis bases (Eq 1) or the metathetical displacement of chloride from $[(\text{RC}_5\text{H}_4)_2\text{LnCl}]_2$ by alkyllithium reagents (Eq 2).



These synthetic methods are in no way general, and they often do not yield neutral, base-free alkyl complexes. For example, method 1 works for the lanthanides Gd through Lu to give dimeric methyl complexes, but it fails for scandium as a coordination complex; $(\text{C}_5\text{H}_5)_2\text{ScMe}(\text{py})$, is isolated.^{4a} A similar failure has been observed in attempts to prepare $[(\text{Me}_5\text{C}_5)_2\text{YbMe}]_2$ from the reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\mu\text{-Me}_2\text{AlMe}_2)$ with pyridine.⁸ Method 2 gives neutral products only when sterically demanding alkyls are used.⁷ Usually anionic addition products are isolated from this synthetic method presumably because the polar and coordinating nature of the reaction solvent stabilizes the anionic complex (Eq 3).⁹ An extended number of ligand displacement reactions are needed to remove the added LiCl and/or L moiety, and sometimes this process is very tedious.^{6a}

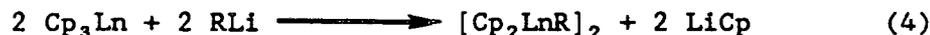


While the synthesis of the heavier lanthanide alkyl complexes has been somewhat developed, the synthesis of the lighter congeners has heretofore remained undeveloped. The reason for this mainly lies in the inability to synthesize stable, well-characterized $[(\text{RC}_5\text{H}_4)_2\text{LnCl}]_2$ complexes (Chapter 2). As a result, there are only a few reported σ -alkyl complexes of the early lanthanides,^{7a,9b-c} and only one reported cerium alkyl, $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4]\text{CeC}\equiv\text{CPh}$.¹⁰ Interestingly, the methods used to prepare La and/or Pr alkyls do not yield the cerium analogue. It was of interest to develop the synthesis of the early

$[(RC_5H_4)_2LnR]_2$ complexes, particularly for those of cerium, so that their structural and chemical properties could be compared to the analogous complexes of the later lanthanides and early actinides. Such a development might also lead to a more general, and less tedious, synthetic route to some of the heavier $[(RC_5H_4)_2LnR]_2$ complexes.

Reactions of Tris(cyclopentadienyl)cerium complexes with RLi

One approach toward this means involves the reaction of the base-free $(RC_5H_4)_3Ln$ complexes with alkyllithium reagents (Eq 4).



The work of Jonas has shown that the $C_5H_5^-$ anion acts as a leaving group in the reaction of transition-metal cyclopentadienyl compounds with alkyl-lithium reagents.¹¹ This synthetic strategy has been previously tested for a few tris(cyclopentadienyl)lanthanide and -actinide complexes.^{12,13} Reaction of $(C_5H_5)_3Pr$ and $(C_5H_5)_3U$ with alkyllithium reagents in thf gives the addition products, $[(C_5H_5)_3MR]Li$, and the reaction of $(C_5H_5)_3Ln \cdot thf$, where Ln is Nd or Lu, with Me_3CLi in thf/ Et_2O gives the Lewis base coordinated alkyl, $(C_5H_5)_3LnCMe_3(thf)$, but other alkyllithium reagents do not behave similarly.¹⁴ Addition products rather than substitution products are formed in these reactions, presumably because the lanthanide or actinide metallocene and the cyclopentadienyllithium complexes have similar solubility in the reaction solvent. The formation of neutral, base-free substitution products, such as $[Cp_2LnR]_2$, might be enhanced if the reaction is done in a solvent in which the cyclopentadienyllithium derivative is insoluble and in which the

lanthanide or actinide derivative is soluble. The hexane-soluble $(\text{Bu}^t\text{C}_5\text{H}_4)_3\text{Ce}$ and $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ complexes may serve as useful starting materials in this synthetic strategy because cyclopentadienyllithium derivatives are insoluble in hexane.

Addition of MeLi to a hexane solution of $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ at room temperature results in the formation of a light colored precipitate while the solution color changes from purple to orange. Removal of the solvent, followed by extraction with and crystallization from hexane affords the orange $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ complex in 67% yield.



The light colored precipitate gives a positive Li flame-test and is presumably $\text{Li}(\text{Me}_3\text{CC}_5\text{H}_4)$. If the reaction is done at -25°C , a yellow product, which is more difficult to crystallize, is also isolated. This product gives a positive Li flame-test and probably is the anionic addition product, $(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{Ce}(\mu\text{-Me})(\mu\text{-Cl})\text{Li}(\text{OEt}_2)_2$, although rigorous characterization was not performed due to the inability to obtain a crystalline product free from the neutral methyl complex.

Crystals of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ suitable for X-ray diffraction studies were obtained, and the solid-state structure was determined. The molecule crystallizes in the orthorhombic space group, Cmca , and consists of centrosymmetric dimers, as required by symmetry, with a pseudo-tetrahedral arrangement of two staggered $\eta^5\text{-}(\text{Me}_3\text{CC}_5\text{H}_4)$ ligands and two bridging, carbon-bound, methyl groups about each cerium atom. An ORTEP drawing is shown in Fig 1. Bond lengths and angles are given in Table 3.1. The methyl hydrogen atoms were located in a difference Fourier map and refined isotropically. No close, or agostic, interactions exist between these hydrogen atoms and the cerium atoms,

Fig 1

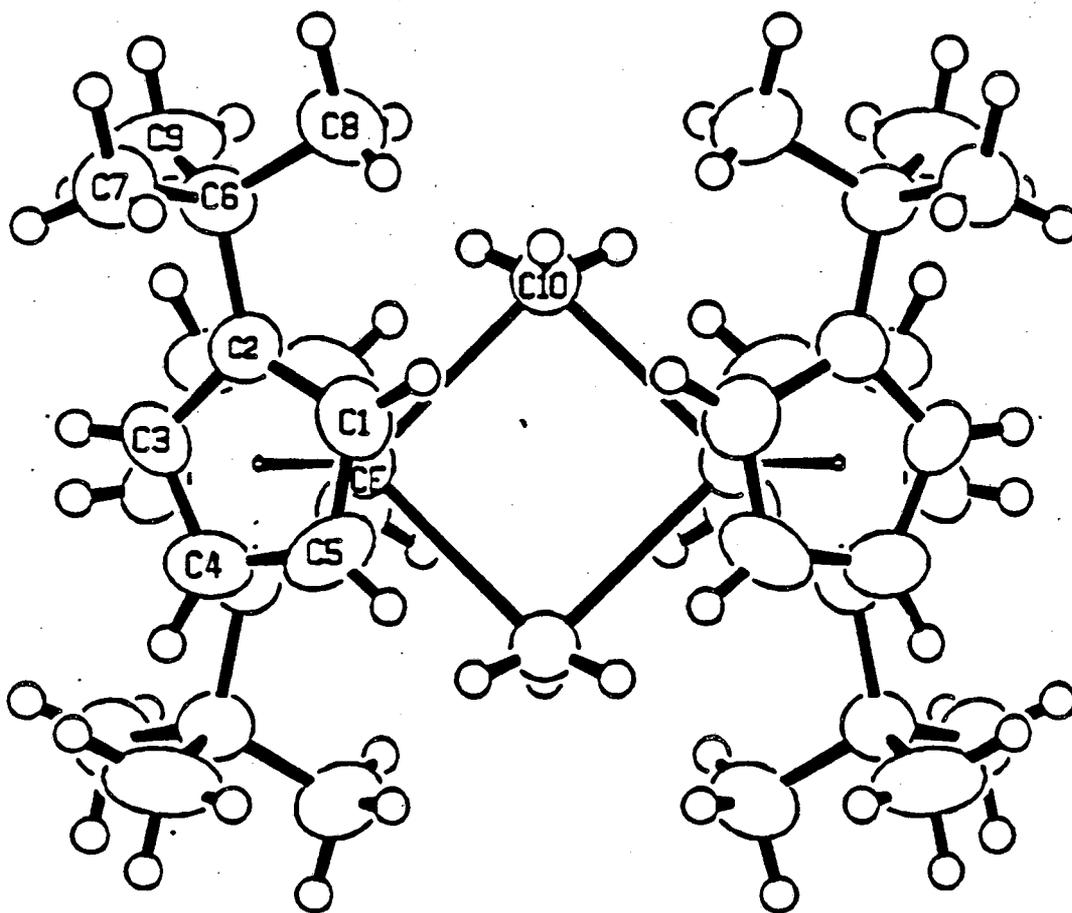
ORTEP Drawing of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ 

Table 3.1

Bond Distances (Å) and Angles (°) in

Ce-C1	2.838(4)	Ce-Cp	2.532
Ce-C2	2.859(5)	Ce-C10	2.665(6)
Ce-C3	2.779(5)	Ce-Ce'	3.805
Ce-C4	2.741(6)	Ce-Cavg	2.80(5)
Ce-C5	2.765(6)		
Cp-Ce-Cp'	130.4	Ce-C10-Ce'	88.9(3)
Cp-Ce-C10	108.3	C10-Ce-C10'	91.1(3)

Cp is the ring centroid comprised of atoms C1, C2, C3, C4, and C5.

which is consistent with the lack of any low energy C-H bands between 2800 cm^{-1} and 2600 cm^{-1} in the IR spectrum. The Ce_2C_2 ring is planar, with Ce-C-Ce' and C-Ce-C' angles of $88.9(3)^\circ$ and $91.1(3)^\circ$, respectively. The structure of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ is very similar to that of $[\mu\text{-Me}_2\text{AlMe}_2]_2$ and the related $[(\text{C}_5\text{H}_5)_2\text{LnMe}]_2$ complexes, where Ln is Y and Yb.^{1e,4} Any bond length and/or bond angle perturbations between these structures seem to reflect different sizes of the metal ions and the steric demands of the cyclopentadienyl ligands. For example, the Ce-C distance, $2.665(6)\text{Å}$, is comparable to the Al-C, Y-C, and Yb-C distances after accounting for differences in the ionic radii of the metal ions, and the M-C-M angles increase with increasing metal ion radius in order to relieve intramolecular ligand-ligand repulsions. Table 3.2 gives selected bond length and angle data of these structurally similar bridging methyl complexes. The structure of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ is also very similar to the structurally characterized alkoxide complexes described in Chapter 2. Any structural differences only reflect the different sizes of the bridging moiety. For example, the Ce-O distance, $2.355(2)\text{Å}$, in

Table 3.2

Selected Distances (Å) and Angles (°) in
[Cp₂M(μ-Me)]₂ Complexes

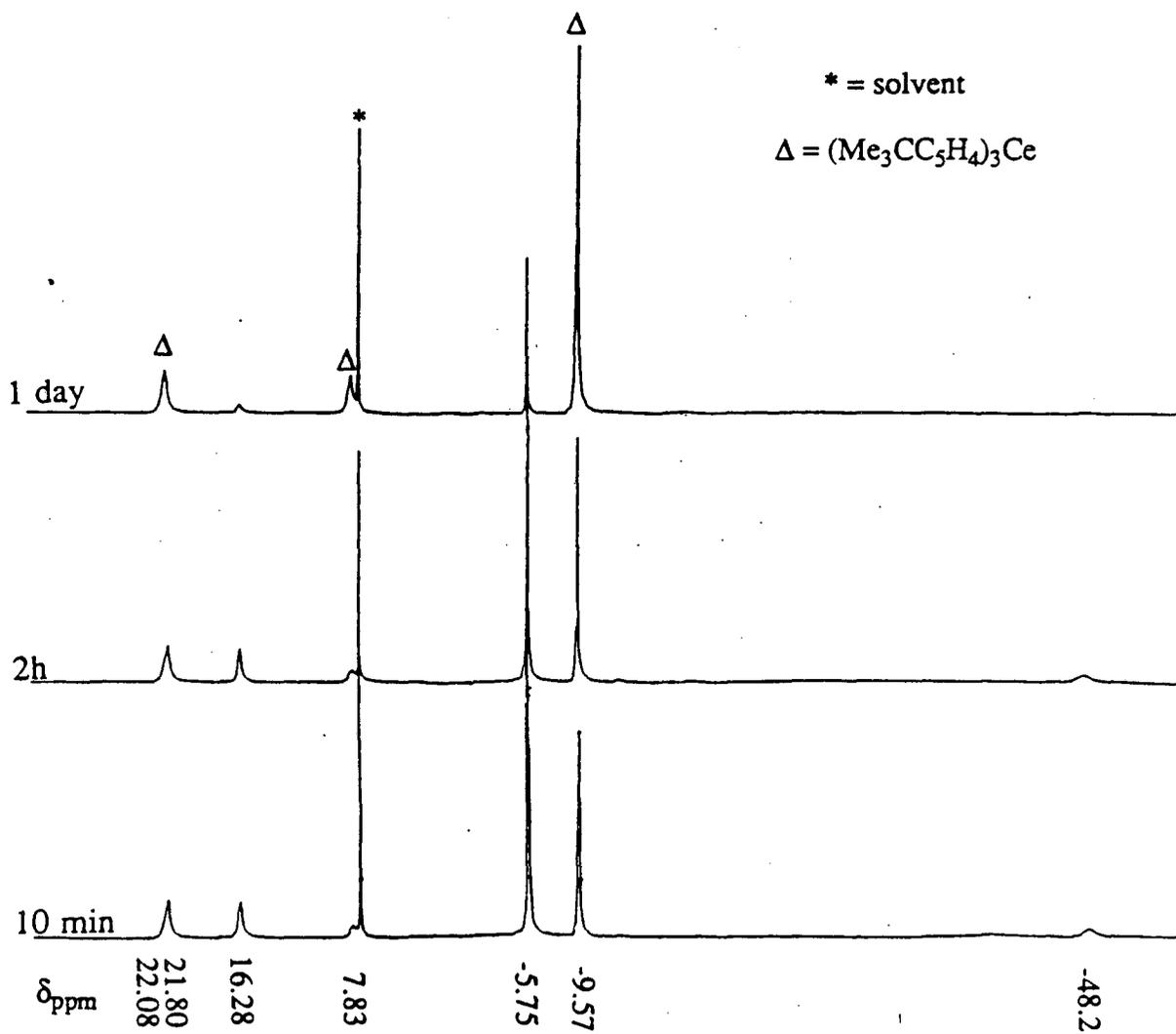
<u>Compound</u>	<u>Radius(Å)^a</u>	<u>M-(μ-C)(Å)</u>	<u>M-C-M(°)</u>	<u>C-M-C(°)</u>	<u>Ref</u>
[Me ₂ Al(μ-Me)] ₂	0.53	2.124(2)	75.7(1)	104.3(1)	1e
[(C ₅ H ₅) ₂ YbMe] ₂	0.99	2.51(4)	86.6(5)	93.4(5)	4a
[(C ₅ H ₅) ₂ YMe] ₂	1.02	2.55(1)	87.7(3)	92.3(3)	4b
[(Me ₃ CC ₅ H ₄) ₂ CeMe] ₂	1.14	2.665(6)	91.1(3)	88.9(3)	this work

(a) M(III) ion radius for coordination number eight

[[Me₃Si)₂C₅H₃]₂CeOH)₂ is 0.3Å larger than the Ce-C distance in [(Me₃CC₅H₄)₂CeMe]₂ reflecting the ca. 0.3Å larger size of oxygen relative to a sp³-hybridized carbon.¹⁵

The [(Me₃CC₅H₄)₂CeMe]₂ complex does not give a molecular ion in the E.I. mass spectrum, indicating that the dimer is not stable in the gas phase. The higher mass fragments correspond to (Me₃CC₅H₄)₃Ce (503 amu) and (Me₃CC₅H₄)₂Ce (382 amu). The cerium methyl complex is not stable in solution. Figure 2 shows the room temperature ¹H NMR spectrum in C₆D₆ as a function of time. The major features consist of one set of resonances in a 6:6:27:3 ratio at 21.8, 16.3, -5.8, and -48.2 ppm, respectively, corresponding to [(Me₃CC₅H₄)₂CeMe]₂ and another set of resonances in a 2:2:9 ratio, at 22.1, 7.8, and -9.6 ppm, respectively. The latter set, which corresponds to the base-free (Me₃CC₅H₄)₃Ce complex, grows with time relative to the former set. The half-life for this decomposition process is about 2-3 h. An unidentified yellow precipitate is the other decomposition product.

Fig 2

 ^1H NMR Spectrum of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ in C_6H_6 

Two processes that explain the decomposition of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ and the yellow solid are shown in Scheme 1.

Pathway A involves a simple ligand redistribution reaction similar to that observed in the kinetically unstable $[(\text{RC}_5\text{H}_4)_2\text{CeER}]_2$ complexes described in Chapter 2. Pathway B involves the activation of a C-D bond from the NMR solvent, followed by ligand redistribution of the resultant cerium phenyl complex. The $[(\text{Me}_5\text{C}_5)_2\text{LuMe}]_2$ complex has been shown to activate C-H bonds of benzene, pyridine, and methane,^{6a} thus it seems reasonable to suggest that such a process is available to the cerium methyl complex. Two experimental observations suggest that decomposition by pathway B is not occurring. Firstly, no resonances other than those attributed to $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ and $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ are observed in the ^1H NMR spectrum. If the C-H bond of benzene were being activated, one would expect to observe additional ring resonances due to the $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CePh}]_2$ complex. Secondly, the rate of decomposition is qualitatively the same in d^6 -benzene and d^{14} -methylcyclohexane. One would expect that activation of a sp^2 -hybridized C-H bond would be easier than that of a sp^3 -hybridized C-H bond, and therefore the rate of decomposition in the two solvents would differ. Consistent with this notion is the observation that C-H activation of arenes and olefins by $[(\text{Me}_5\text{C}_5)_2\text{LuMe}]_2$ is more rapid than activation of SiMe_4 .^{6g}

Increasing the steric demands of the cyclopentadienyl ligand led to the isolation of stable $[\text{Cp}_2\text{LnER}]_2$ complexes, where Cp is $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$ and $\text{Me}_3\text{CC}_5\text{H}_4$, which contained relatively small ER groups, and therefore it seems reasonable that this approach would also lead to the isolation of a more stable cerium methyl complex. The reaction of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ with one equivalent of MeLi proceeds as described by Eq 5 to yield orange crystals of the

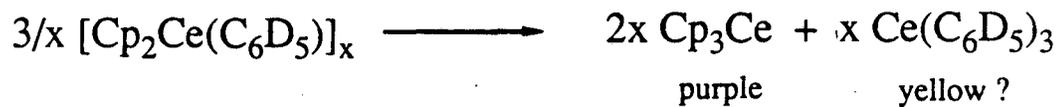
SCHEME 1

Possible Decomposition Pathways
of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ in C_6H_6

A: ligand redistribution only:



B: C-H activation and ligand redistribution:



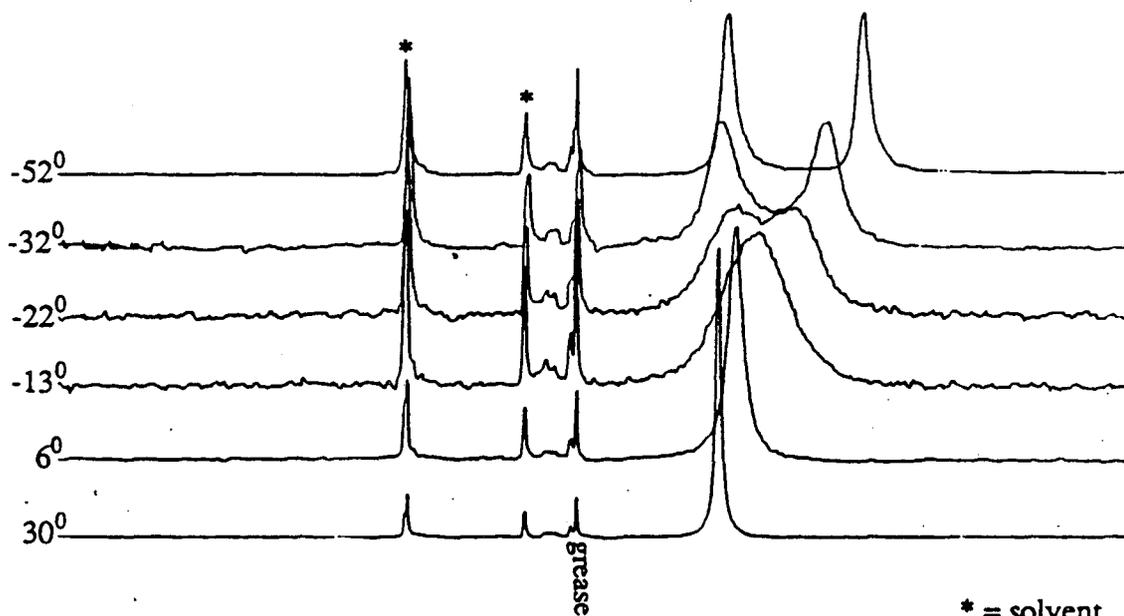
$\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeMe}\}_2$ complex. Examination of the room temperature ^1H NMR spectrum, as a function of time, shows that the more sterically demanding cyclopentadienyl ligands render this cerium methyl complex more stable toward ligand redistribution because the half-life for decomposition to $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ and a yellow solid is on the order of four days.

The $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeX}\}_2$ complexes, where X is Me and OH give ^1H NMR spectra containing ring SiMe_3 resonances which are not equivalent at all temperatures (Fig 3). Both complexes contain a single SiMe_3 resonance at room temperature which broadens and splits into two resonances in a 1:1 integrated ratio upon cooling. Using the two-site exchange equation¹⁶, the activation energy for the barrier to this process can be calculated as $13 \pm 2 \text{ kcal}\cdot\text{mol}^{-1}$ and $9 \pm 2 \text{ kcal}\cdot\text{mol}^{-1}$ for the methyl and hydroxide complexes, respectively.

Although stopped ring rotation has never been observed in cyclopentadienyl lanthanide complexes, the most plausible mechanism for the observed temperature dependence of the NMR spectra of the complexes is that at high temperature the rotation of the cyclopentadienyl rings is rapid on the NMR time-scale and at low temperature the rotation is slow or stopped. Figure 4 shows the molecular geometry of $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeOH}\}_2$ as determined by X-ray diffraction (Chapter 2). The Figure shows that the idealized geometry in this conformation is C_i and contains a mirror plane (σ_{xz}) which interconverts the SiMe_3 groups on a given ring. There is also an inversion center which interconverts Cp1 with $\text{Cp1}'$, but there is no symmetry element which will interconvert Cp1 with Cp2 . If the rings are allowed to freely rotate the idealized geometry becomes D_{2h} and additional symmetry elements are introduced, namely a mirror plane (σ_{xy}) and a two-fold axis of rotation (C_{2x}), which interconvert Cp1

Fig 3

VT ^1H NMR Spectra of $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeX}\}_2$ in C_7D_8 ,
 where X is OH^- , CH_3^-



* = solvent

$\Delta = [(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$

+ = $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeOH}\}_2$

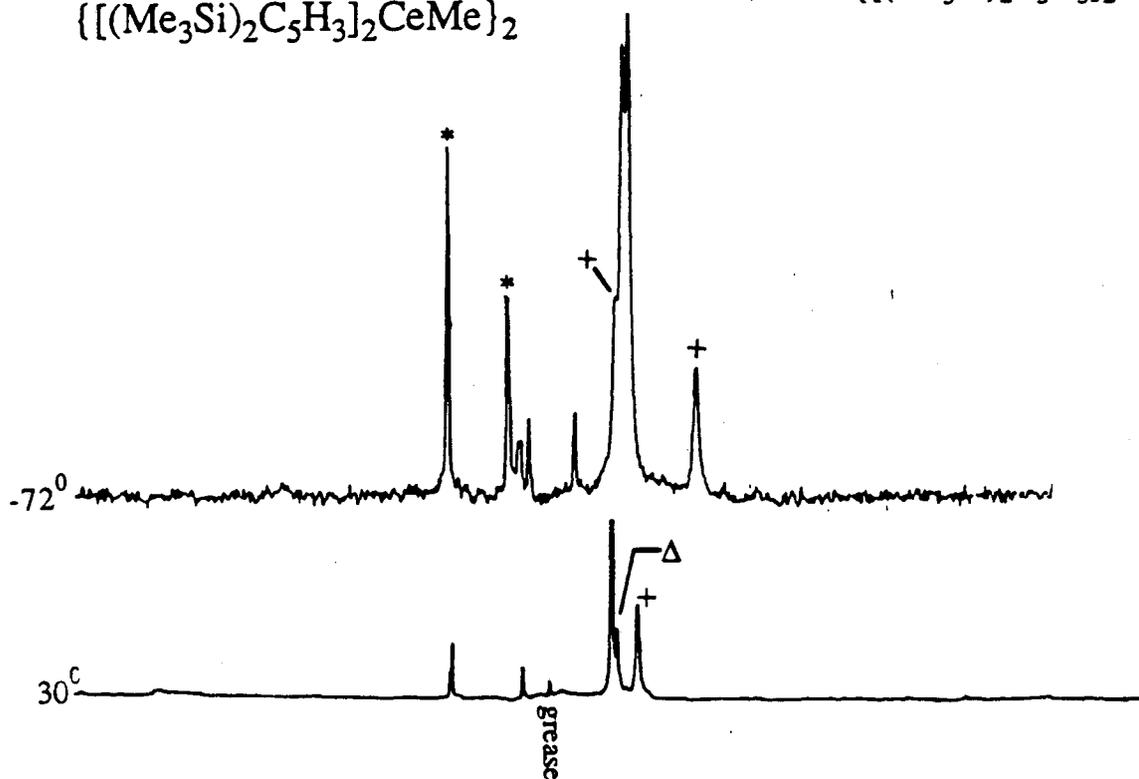
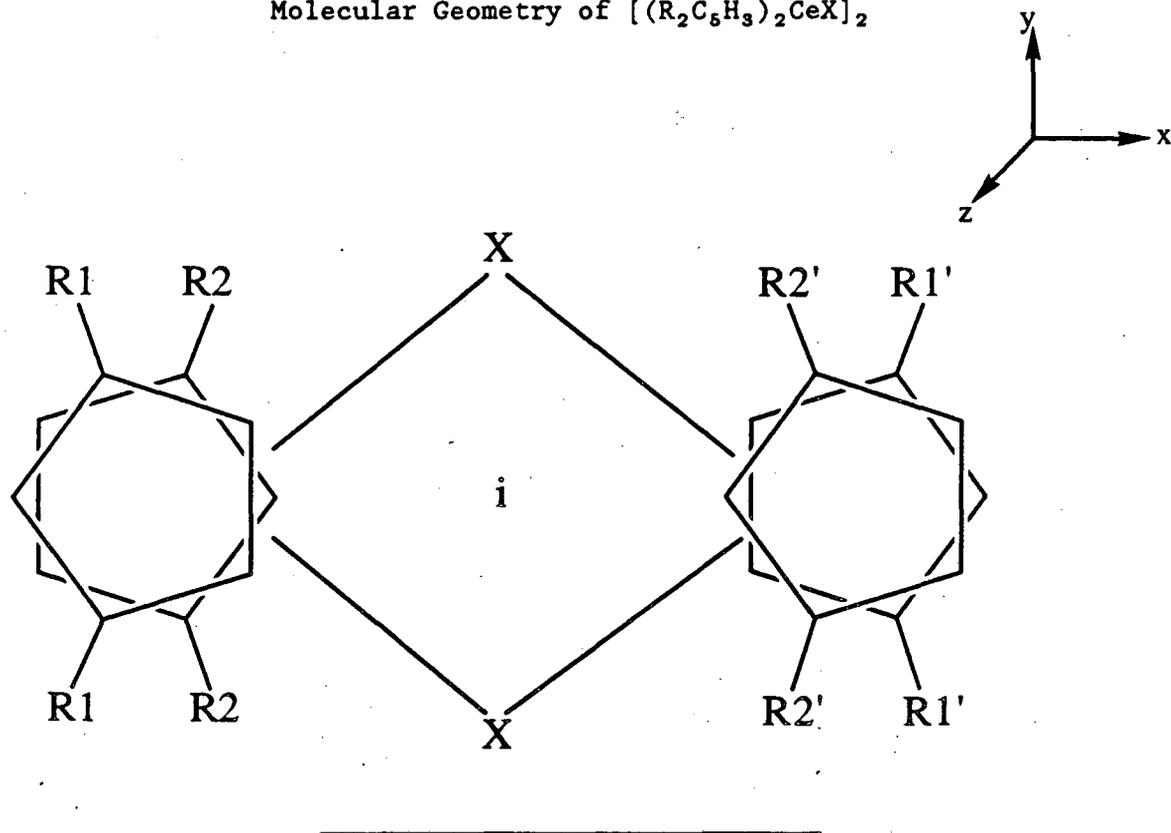


Fig 4

Molecular Geometry of $[(R_2C_5H_3)_2CeX]_2$ 

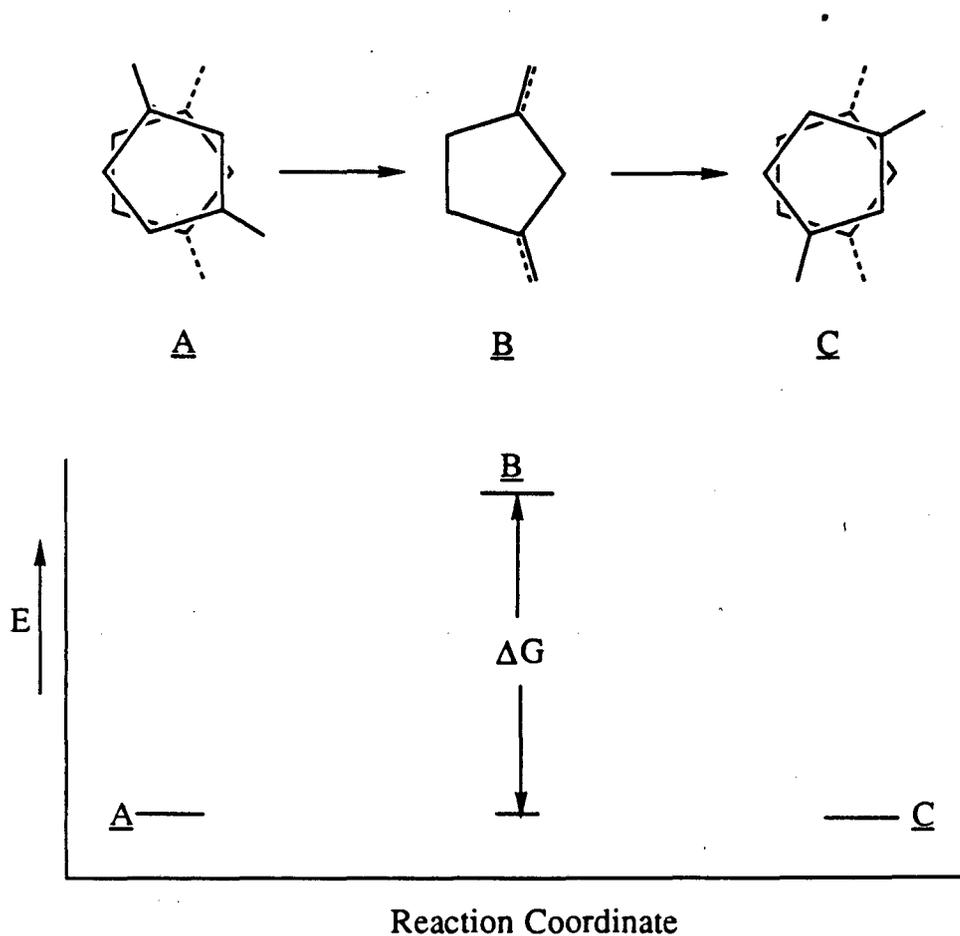
with Cp2. At low temperature the rigid conformation is present in solution, and two peaks of equal intensity are observed in the 1H NMR spectrum. As the temperature increases, ring rotation becomes fast on the NMR time-scale. Such rotation causes Cp1 and Cp2 to have equivalent chemical environments, and only one resonance is observed.

The magnitude of the activation energy to the barrier of ring rotation in the $[(Me_3Si)_2C_5H_3]_2CeX$ complexes can be rationalized in terms of intramolecular ligand-ligand repulsions and their relationship with the identity of X. A more sterically demanding environment about the metal environment will increase the barrier to ring rotation because repulsions will be greater when ring-alkyl substituents pass each other in the transition state of going from

conformation A to C (Fig 5). This assumes that the barrier of the top SiMe_3 group passing by the bottom CH group is very small. This notion is supported by the observation that the barrier to ring rotation in 1,1',3,3'-tetra-tert-butyluranocene, $8.3 \text{ kcal}\cdot\text{mol}^{-1}$ at -70°C , is lower than that in 1,1';3,3'-tetra-tert-butylferrocene, $13.1 \text{ kcal}\cdot\text{mol}^{-1}$ at -27.5°C , because the ring-ring distance is shorter in the latter.¹⁷ In the cerium complexes, replacing a carbon-bound ligand with an oxygen-bound ligand increases steric congestion about the metal environment and raises the barrier to ring rotation.

Fig 5

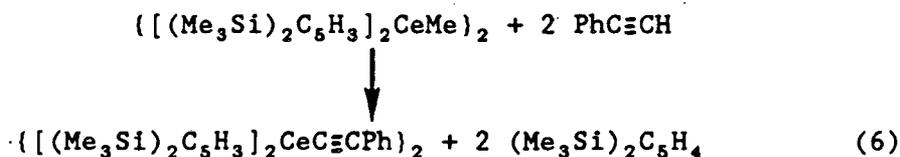
Mechanism of Ring Rotation



Although the reaction of MeLi with tris(cyclopentadienyl)cerium complexes readily leads to the formation of isolable cerium methyl compounds, the reaction is not a general method that can be used to prepare other alkyl complexes. A yellow oil and $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$, for example, are isolated from the reaction of Bu^tLi and $(\text{Me}_3\text{Si})_2\text{CHLi}$ with $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ in hexane. The yellow oil is insoluble in hexane, diethyl ether, and pyridine and was not characterized. Similarly, the reaction of the two alkyl lithium reagents with $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ affords a multicolored solid after removal of the reaction solvent. Attempts at separating the products by fractional crystallization result only in the isolation of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$. The reason for the inability to isolate these alkyl complexes by the described method is unclear. It may be a reflection of the synthetic method or a reflection of the instability of the desired products toward decomposition.

Reactions of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$

One additional cerium alkyl complex is prepared from the addition of phenylacetylene ($\text{pK}_a = 21$ in H_2O , 29 in DMSO)¹⁸ to a hexane solution of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeMe}_2$. A slight darkening of the orange solution color and the evolution of gas is observed upon addition. Solvent removal, followed by extraction with and crystallization from hexane affords the orange $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeC}\equiv\text{CPh}_2$ in 67% yield (Eq 6).

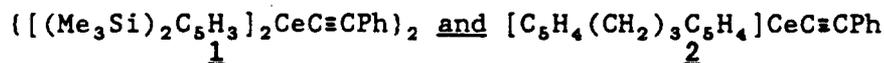


Although phenylacetylene is not thermodynamically and/or kinetically able to protonate a cyclopentadienyl ring in $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$, it is able to protonate the relatively strong base CH_3^- (the pK_a of $\text{CH}_4 \approx 49$ in H_2O)¹⁹ in $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeMe}$. The IR spectrum contains a sharp, moderately intense absorption at 2015 cm^{-1} which is characteristic of terminal acetylides and consistent with the $\text{C}\equiv\text{C}$ stretching frequency observed in several other bridging acetylide complexes of the lanthanides.⁵ From a structural point of view, bridging acetylide complexes of the lanthanides are interesting because all of the known ones contain an asymmetric bridge with different $\text{M}-\text{C}\equiv\text{C}$ angles. The difference ranges from 11° in $[(\text{C}_5\text{H}_5)_2\text{ErC}\equiv\text{CBu}^t]_2$ to 49° in $(\text{Me}_5\text{C}_5)_4\text{Yb}_3(\text{C}\equiv\text{CPh})_4$, and has been rationalized in terms of a π -interaction of the triple bond with one of the metal atoms.^{5g} The crystal structure of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeC}\equiv\text{CPh}$ would provide another datum in this class, but crystals suitable for X-ray diffraction could not be obtained.

The only other reported cerium alkyl complex is also a phenylacetylide complex, $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4]\text{CeC}\equiv\text{CPh}$.¹⁰ A comparison of the physical properties of the two complexes, however, reveals some striking differences (Table 3.3). The most notable difference is found in the ^1H NMR spectra. The ^1H NMR spectrum of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeC}\equiv\text{CPh}$ contains relatively broad resonances ($\nu_{1/2} = 50\text{-}75\text{ Hz}$ for the cyclopentadienyl ring CH protons and $\nu_{1/2} = 14\text{ Hz}$ for the ring SiMe_3 protons) with chemical shifts consistent with the many paramagnetic Ce(III) complexes described in this study. The ^1H NMR spectrum of the $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4]\text{CeC}\equiv\text{CPh}$ complex is diamagnetic in nature. Preparation of the latter complex by the reported synthetic method was not attempted, and thus the nature of the discrepancies in the physical properties remains a mystery.

Table 3.3

Physical Properties of

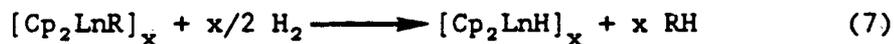


	<u>color</u>	<u>m.p. (°)</u>	<u>$\nu_{\text{C-C}} (\text{cm}^{-1})$</u>	<u>δ_{ring}</u> ^{<u>$^1\text{H NMR}$</u>}	<u>$\delta_{\text{C}_6\text{H}_5}$</u>
<u>1</u>	orange	193-195(dec)	2015(sharp)	33.6(4H, 50Hz) ^a 16.7(2H, 75Hz) -3.23(36H, 14Hz)	2.10(1H) 1.61(2H) -2.65(2H)
<u>2</u>	brown	150(dec)	2050(broad)	7.29-7.59(8H) ^b	9.16(s, 5H)

(a) 30°C, C₆D₆; chemical shifts are in ppm relative to tetramethylsilane, $\delta=0.00$. Relative intensities and peak width at half-height are given in parentheses.

(b) 25°C; chemical shifts are in ppm relative to thf, $\delta=1.79$. Relative intensities are given in parentheses.

Hydride complexes of the lanthanides are less common than alkyl complexes. Those that have been reported are prepared from the hydrogenation of an alkyl to afford the hydride complex and alkane (Eq 7).^{7a,d,20}



Similar results are found from the hydrogenation of $\left[\left(\text{Me}_3\text{Si} \right)_2 \text{C}_5\text{H}_3 \right]_2 \text{CeMe} \right]_2$. Upon stirring a hexane solution of the methyl complex in an atmosphere of H₂(D₂), the solution color changes from orange to cherry red. Solvent removal, followed by extraction with and crystallization from hexane affords $\left[\left(\text{Me}_3\text{Si} \right)_2 \text{C}_5\text{H}_3 \right]_2 \text{CeH} \right]_2$ or $\left[\left(\text{Me}_3\text{Si} \right)_2 \text{C}_5\text{H}_3 \right]_2 \text{CeD} \right]_2$ in 47% yield. Stirring a hexane solution of

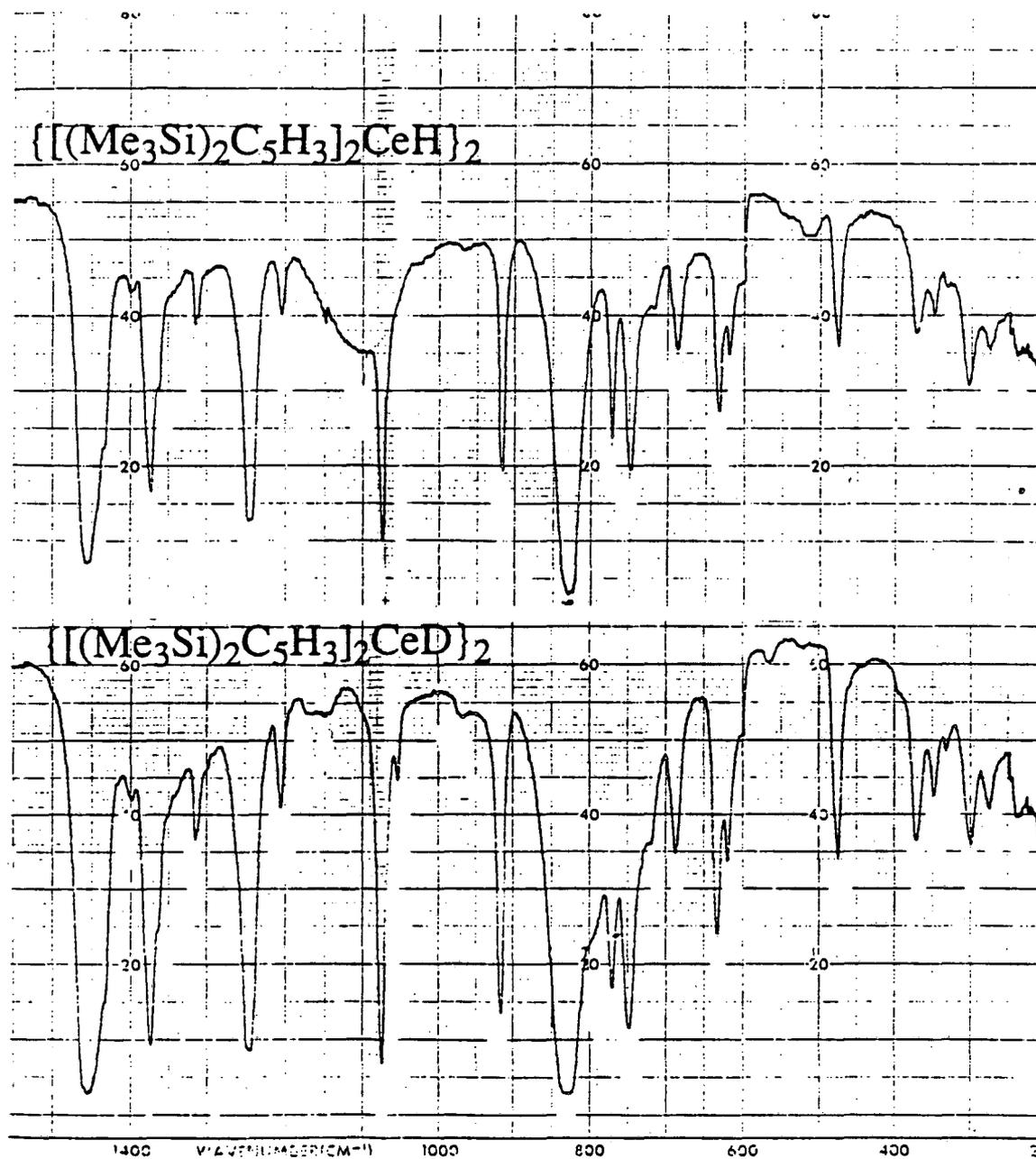
$[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ in a hydrogen atmosphere does not afford the $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeH}]_2$ complex, as $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ and an insoluble yellow solid are formed. Presumably these species are formed from the decomposition of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeH}]_2$ via a ligand redistribution pathway.

The IR spectra (Fig 6) of the hydride and deuteride complexes are superimposable except for a broad absorption at 1095 cm^{-1} ($\nu_{1/2} \approx 100\text{ cm}^{-1}$) in the hydride complex that shifts to 805 cm^{-1} upon deuteration ($\nu_{\text{Ce-H}}/\nu_{\text{Ce-D}} = 1.36$). This band is comparable to that observed in the $[(\text{Me}_5\text{C}_5)_2\text{LnH}]_2$ complexes, where Ln is La, Nd, and Sm, and is attributable to the asymmetric M-H stretching mode.^{7a} The symmetric stretching mode is also reportedly observed in the latter complexes, but cannot be identified in the cerium hydride. The hydride resonance and the ring CH resonances are not observed in the ^1H NMR spectrum between 70°C and 30°C .

The reaction of $([(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeMe})_2$ with ammonia ($\text{pK}_a \approx 35$)²¹ in hexane causes the orange solution color to change to yellow. Yellow crystals of $([(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeNH}_2)_2$ can be isolated from hexane. The IR spectrum contains two weak absorptions at 3350 and 3285 cm^{-1} which are attributed to N-H stretching modes and are comparable to N-H stretching frequencies observed in reported transition-metal complexes containing bridging NH_2 groups.²² The complex gives a molecular ion in the E.I. mass spectrum and fragments at 939 amu and 923 amu which correspond to loss of ring and/or NH_2 . The chemical shift of the ring SiMe_3 protons occurs at -3.66 ppm in the room temperature ^1H NMR spectrum. The ring CH protons and the NH_2 protons are not observed at this temperature. Further studies of the $([(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeNH}_2)_2$ complex were not carried out because it is always contaminated with variable amounts of $([(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeOH})_2$ as

Fig 6

IR Spectra^(a) of $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeX}\}_2$,
where X is H⁻ and D⁻



evident from the IR spectrum ($\nu_{\text{OH}} = 3650 \text{ cm}^{-1}$), ^1H NMR spectrum ($\delta \text{ SiMe}_3 = -5.89 \text{ ppm}$).

The most interesting feature of lanthanide carbon bonds is their ability to act as homogeneous catalysts in the polymerization of olefins and to insert small unsaturated molecules.⁶ Addition of ethylene (1-10 atm) at room temperature to a hexane solution of either $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$, $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeMe}\}_2$, or $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeH}\}_2$ leads to the rapid formation of polyethylene. In the $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$ case, the efficiency of polymerization is qualitatively lower because the complex gradually decomposes to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ and a yellow solid. In the other two cases, starting material can be isolated from the polymer after the reaction is quenched. No kinetic studies on the polymerization reaction or rigorous characterization of the polymer were performed. None of the cerium complexes polymerize propylene. However, the reaction of propylene with $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeMe}\}_2$ and $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeH}\}_2$ results in a solution color change to red-brown, but the extremely soluble products were not characterized. The reaction of CO with these two complexes also results in a solution color change to brown and the formation of a very soluble, often oily, product.

Reactions of MeLi with $(\text{RC}_5\text{H}_4)_3\text{U}$

There are only a limited number of reported U(III) alkyl complex in the literature, and none of them contain bridging methyl groups.²³ It is of interest to study the synthesis and reactivity of U(III) alkyl complexes because the accessible tetravalent oxidation state may lead to interesting and novel reactivity patterns not found in the related lanthanide complexes.

Addition of MeLi to a hexane solution of $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{U}$ at -20°C results in the formation of white and green precipitates. Solvent removal, followed by extraction with and crystallization from hexane affords dark green crystals of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{UMe}]_2$. The physical properties of this complex are similar to the cerium analogue. The IR spectra are virtually superimposable (Fig 7). The melting points are similar, and the ^1H NMR spectra are similar; i.e. $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{UMe}]_2$ is not stable toward decomposition in solution. Figure 8 shows the ^1H NMR spectra as a function of time. The major features contain one set of resonances in a 6:6:27:3 ratio at 8.08, 1.11, -20.02, and -139.3 ppm, respectively, corresponding to the uranium methyl complex. Another set of resonances in the zero time spectrum are also observed in a 2:9:2 ratio at 9.06, -21.00, and -24.17 ppm, respectively. The latter set, which corresponds to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{U}$, grows with time relative to the former set. The line-widths at half-height of these ring resonances range from 15 to 50 Hz and are consistent with U(III) complexes. Additional sharper lines also grow in with time. These resonances are presumably U(IV) species that result from ligand redistribution and oxidation reactions. The complex does not give a molecular ion in the E.I. mass spectrum, but a fragment corresponding to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{U}_2\text{Me}$ (975 amu) is observed. Crystals suitable for X-ray diffraction could not be obtained.

The $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{thf}$ complex behaves differently; addition of one equivalent of MeLi to $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{thf}$ in diethyl ether in the presence of one equivalent of tmed at -30°C gives a red precipitate which upon crystallization from diethyl ether affords red needles that melt at $81-85^\circ\text{C}$ (dec). The crystals give a positive Li flame-test. The room temperature ^1H NMR spectrum contains four broad features, half-width at half-height ≈ 100 Hz, at 6.11, 2.23, -5.42, and -10.8 ppm of

Fig 7

IR Spectra^(a) of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{M}(\mu\text{-Me})_2]$,
where M is U and Ce

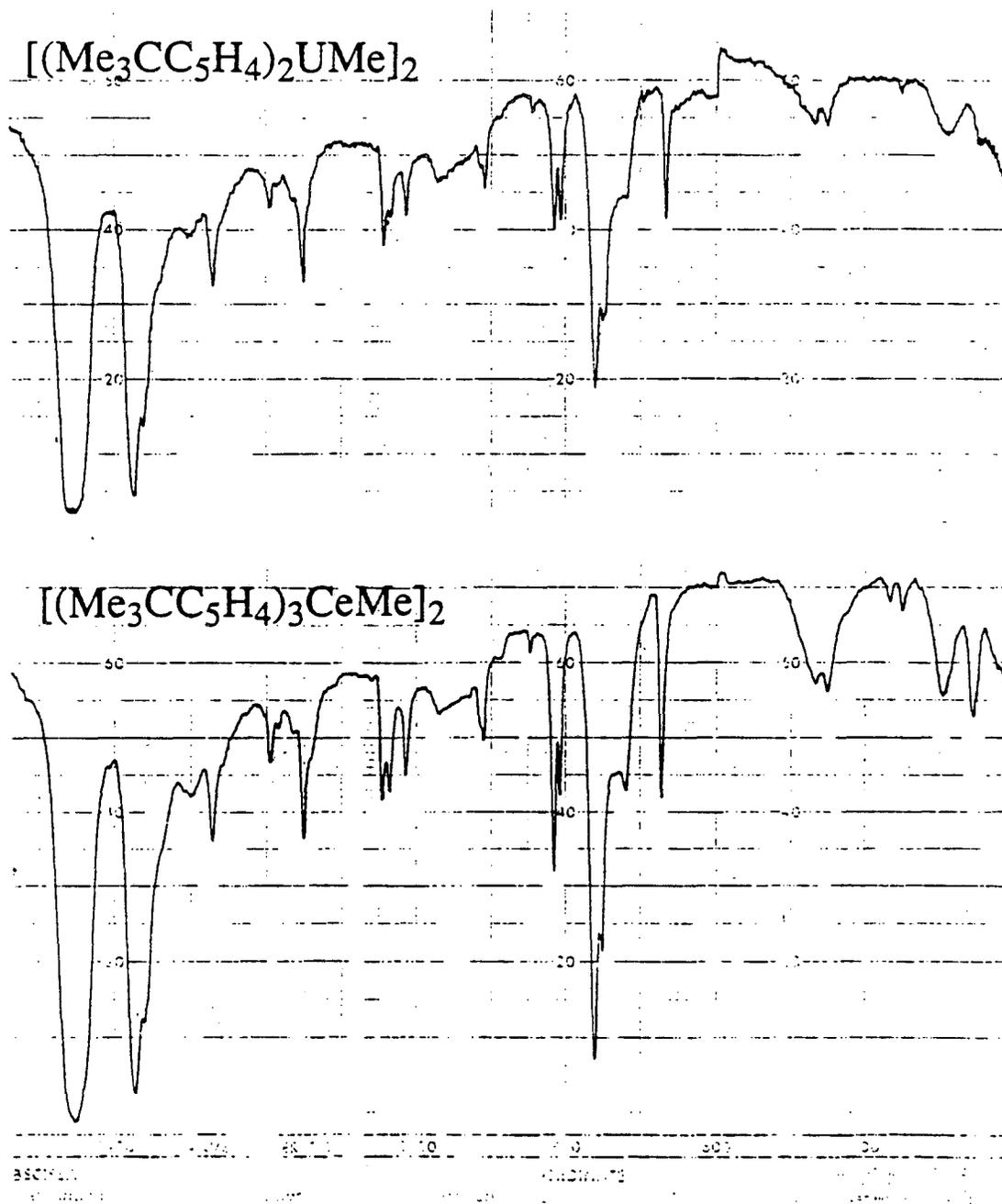
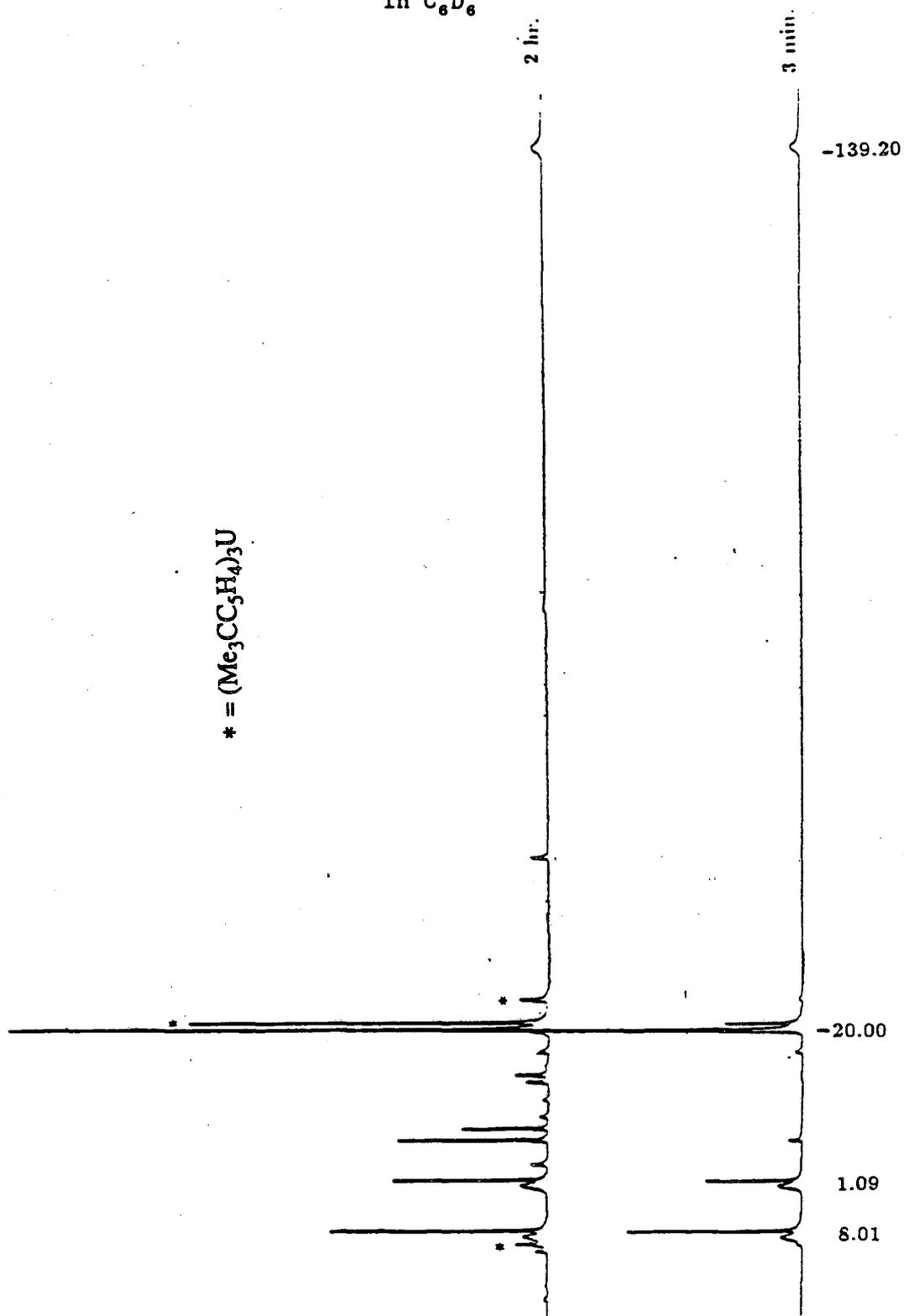


Fig 8

Room Temperature ^1H NMR Spectra of $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{U}(\mu\text{-Me})_2]$ in C_6D_6 

approximate area ratio of 1.5:3:1:1. The low temperature (-70°C) spectrum is better resolved and consists of a set of resonances at 14.4, -8.1, -18.7 ppm in a 12:18:12 area ratio, a set of resonances in the diamagnetic region of the spectrum at 2.63, 2.35, 2.10, and 1.50 ppm in a 4:4:12:12 area ratio, and a resonance at -284 ppm. These groups of resonances correspond to the cyclopentadienyl protons, the tmed protons, and methyl protons, respectively, and the integrated intensities indicate that the molecule contains six rings, two tmed groups, and one methyl group. The methyl resonance follows Curie behavior and the extrapolated chemical shift at +30°C is -185 ppm, consistent with that found in other uranium methyl complexes.^{13a,24}

In order to elucidate the composition of the complex the X-ray crystal structure was determined. The complex crystallizes in the monoclinic space group, C2/c, and the structure consists of two molecules of the [(MeC₅H₄)₃UMeU(MeC₅H₄)₃] fragment and one molecule each of the [Li(Me₂NCH₂CH₂NMe₂)]₂[μ-MeC₅H₄] and [Li(Me₂NCH₂CH₂NMe₂)₂] fragments. ORTEP drawings are shown in Fig 9. Selected bond distances and angles are given in Table 3.4. The Li(tmed) fragments are not unusual in any way.²⁵

The most interesting feature of the anionic fragment is the near-linear U-C(53)-U angle of 176.9(11)°. Only a few structures have revealed bridging methyl groups in which the angle about carbon is near-linear, and this represents the first such structure involving uranium.^{6a,26} The U-C(53) distances, 2.71(3) and 2.74(2)Å, are longer than that found in (C₅H₅)₃U(n-Bu), 2.43(2)Å,²⁷ and in [(C₅H₅)₃U(n-Bu)]⁻, 2.56(1)Å.^{13a} This is expected since the linear bridged bonds are ca. 10% longer than the terminal one in (Me₅C₅)₂Lu(μ-Me)Lu(Me)(C₅Me₅)₂.^{6a} The averaged U-C(Cp) distance, 2.82(4)Å, and the averaged Cp-U-Cp angle, 117°, are identical to those found in

Fig 9

ORTEP Drawings of

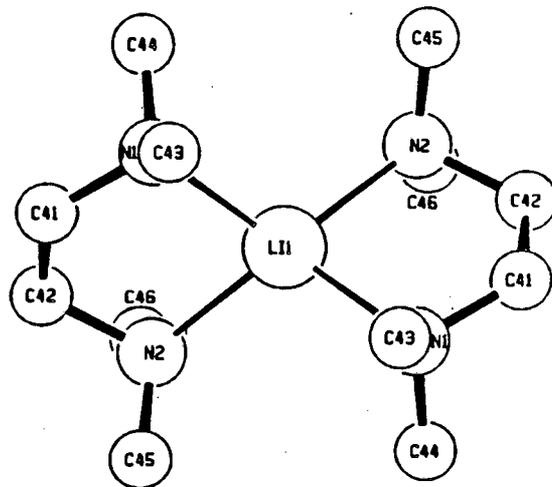
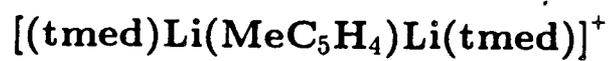
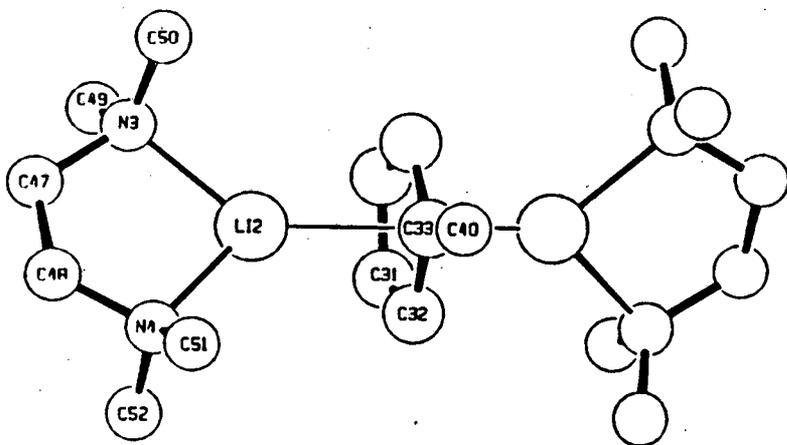
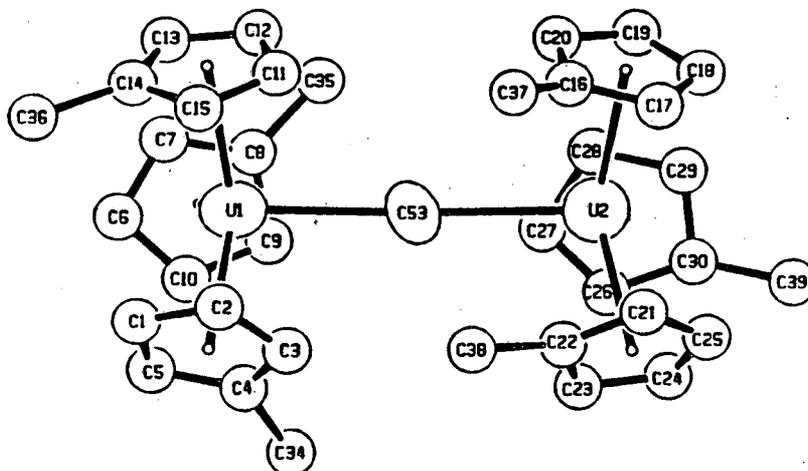
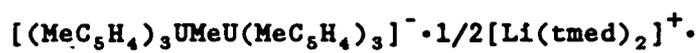


Table 3.4

Bond Distances (Å) and Angles (°) in
 $[(\text{MeC}_5\text{H}_4)_3\text{UMeU}(\text{MeC}_5\text{H}_4)_3]^- \cdot 1/2[\text{Li}(\text{tmed})_2]^+$
 $1/2[(\text{tmed})\text{Li}(\text{MeC}_5\text{H}_4)\text{Li}(\text{tmed})]^+$

U1-Cp1	2.56	U-Cavg	2.82(4)	N2-C42	1.46(2)	Li2-Cp7	2.00
U1-Cp2	2.60	U1-C53	2.71(3)	C41-C42	1.52(2)	Li2-N3	2.10(5)
U1-Cp3	2.56	U2-C53	2.74(2)	Li2-C31	2.29(6)	Li2-N4	2.08(5)
U2-Cp4	2.61	Li1-N1	2.07(3)	Li2-C31'	2.26(6)	N3-C47	1.48(2)
U2-Cp5	2.56	Li1-N2	2.21(4)	Li2-C32	2.33(6)	N4-C48	1.46(2)
U2-Cp6	2.56	N1-C41	1.47(2)	Li2-C33	2.33(5)	C47-C48	1.52(2)
Cp1-U1-Cp2	120.3	Cp5-U2-C53	101.6	N1-C41-C42	123(4)		
Cp1-U1-Cp3	117.3	Cp6-U2-C53	98.2	Li2-Cp7-Li2	175.4		
Cp2-U1-Cp3	115.2	U1-C53-U2	176.9(11)	N3-Li2-Cp7	134.2		
Cp4-U2-Cp5	115.5	N1-Li1-N2	89(1)	N4-Li2-Cp7	138.6		
Cp4-U2-Cp6	120.6	N1-Li1-N1'	130(3)	N3-Li2-N4	87(2)		
Cp5-U2-Cp6	114.2	N1-Li1-N2'	115(1)	Li2-N3-C47	105(2)		
Cp1-U1-C53	98.3	N2-Li1-N2'	123(3)	Li2-N4-C48	110(2)		
Cp2-U1-C53	99.4	Li1-N1-C41	103(2)	N3-C47-C48	118(3)		
Cp3-U1-C53	99.4	Li1-N2-C42	105(3)	N4-C48-C47	113(3)		
Cp4-U2-C53	101.6	N2-C42-C41	113(4)				

Cp1, Cp2, Cp3, Cp4, Cp5, and Cp6 are the rings comprised of C1-C5, C6-C10, C11-C15, C16-C20, C21-C25, and C26-C30, respectively. Cp7 is the centroid comprised of C31-C33 and the symmetrically related atoms of C32 and C33.

$(\text{C}_5\text{H}_5)_3\text{U}(\text{n-Bu})$ and $[(\text{C}_5\text{H}_5)_3\text{U}(\text{n-Bu})]^-$. Unfortunately, the hydrogen atoms on the bridging methyl group could not be located in the X-ray study, but the symmetry requires that the geometry about the carbon atom is trigonal bipyramidal. Attempts at obtaining a low temperature data set were unsuccessful as the crystal underwent an unresolved transformation upon cooling and it diffracted X-rays poorly.

The $[\text{Li}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)]_2[\mu\text{-MeC}_5\text{H}_4]$ fragment consists of the cyclopentadienyl ring symmetrically bridging between two $\text{Li}(\text{tmed})$ moieties that are oriented perpendicular to each other. The averaged Li-C distance, 2.31(3)Å, and the Li-Cp distance, 2.00Å,²⁸ are similar to those found in $[(\text{Me}_3\text{Si})_3\text{C}_5\text{H}_2]\text{Li}(\text{tmed})$, 2.33(3)Å, and

(Me₃SiC₅H₄)Li(tmed), 2.28(1)Å.²⁹ The Li-Cp-Li angle is 175°, and the MeC₅H₄ ring is the perpendicular bisector of the Li--Li vector, consistent with theoretical calculations which show the most stable geometry in LiCp is one in which the Li atom is situated over the center of the cyclopentadienyl ring.³⁰

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CHAPTER FOUR:

Experimental Details

General

The compounds described within are air and moisture sensitive. All work was conducted under inert atmosphere (N_2 or Ar) using standard Schlenk techniques, or in an inert atmosphere glovebox. All solvents (except CH_2Cl_2) were dried and deoxygenated by distillation from sodium benzophenone ketyl under N_2 prior to use. Dichloromethane was dried by distillation from CaH under N_2 prior to use.

The infrared spectra were recorded on a Perkin-Elmer 297 spectrometer, as Nujol mulls between CsI windows. Nuclear magnetic resonance spectra were recorded on a JEOL FX90Q FT 90 MHz spectrometer in deuterated-benzene or -toluene dried over and distilled from sodium or potassium metal. Mass spectra and elemental analyses were performed by the University of California, Berkeley mass spectral and microanalytical laboratories. The isotopic cluster of the parent molecular ion was simulated for several of the complexes and is compared to the observed ion. Melting points were measured in sealed capillaries and are uncorrected.

Cerium trichloride, $NdCl_3$, and UCl_4 were treated with refluxing $SOCl_2$ for ca. 7 days, followed by extraction of the finely ground solid with CH_2Cl_2 until the extract was colorless, and heating the powder under reduced pressure (1 mtorr) at ca. $150^\circ C$ for 12 hours.

The starting materials $(MeC_5H_4)_3U \cdot thf$,¹ $(Me_3SiC_5H_4)_3U$,² $(Me_3CC_5H_4)_3U$,³ and $Ce[N(SiMe_3)_2]_3$ ⁴ were prepared as previously described. The carbonyl hydrides $(C_5H_5)Mo(CO)_3H$, $(C_5H_5)W(CO)_3H$, and $(Me_5C_5)Mo(CO)_3H$ were prepared by literature methods and sublimed prior to use.⁵

Methylcyclopentadienide anion was prepared from freshly cracked MeC_5H_5 monomer as the Na salt in tetrahydrofuran. Trimethylsilylcyclopentadiene was prepared as described by Brennan⁶ and used as the K salt in tetrahydrofuran. *t*-Butylcyclopentadiene was prepared by a literature method⁷ from CpMgBr and *t*-BuCl in diethyl ether and also used as the potassium salt in thf.

All ligands and reagents were purified under inert atmosphere prior to use. Pyridine and tetrahydrothiophene were pre-dried over KOH, followed by refluxing over and distillation from sodium. Phenol, quinuclidine, Verkade's phosphite, and *p*-dimethylaminopyridine were sublimed. Trimethylphosphite was dried over and distilled from sodium. Propionitrile and *t*-butylisocyanide were distilled under N_2 , as were the thiols (PhSH , Bu^tSH , and Pr^iSH). Methanol and isopropanol were dried over Mg/Mg(OR)_2 and distilled. Ethylisocyanide⁸ and trimethylphosphine⁹ were prepared by literature methods and distilled under N_2 .

Chapter One:

$(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$

Sodium cyclopentadienide (26.4 mL of a 1.25M solution in tetrahydrofuran, 33.0 mmol) was added to a suspension of cerium trichloride (2.71 g, 11.0 mmol) in tetrahydrofuran (60 mL). The yellow suspension was stirred for 12h, then the solvent was removed under reduced pressure. The yellow residue was extracted with diethyl ether (150 mL), filtered, and the filtrate was concentrated to ca. 80 mL. Cooling the extract to -20°C afforded yellow needles (2.8g, 57% yield), m.p. $142\text{-}146^\circ\text{C}$ (dec). Concentrating the mother liquor to ca. 30 mL and cooling to -20°C affords an additional 0.95g (19%) of

product. Anal. Calcd. for $C_{22}H_{29}CeO$: C, 58.8; H, 6.50. Found: C, 58.7; H, 6.42. IR: 1320w, 1260m, 1238w, 1165m, 1075m, 1045s, 1030s, 1015s, 970w, 927m, 860s, 820s, 750s, 665m, 610m, 550w, 470w, 400w, 320m, 210s cm^{-1} . 1H NMR (C_6D_6 , $36^\circ C$): 10.19 (6H, $\nu_{1/2} = 20$ Hz), 8.66 (6H, $\nu_{1/2} = 20$ Hz), -1.41 (9H, $\nu_{1/2} = 5$ Hz), -4.93 (4H, $\nu_{1/2} = 8$ Hz), -11.26 (4H, $\nu_{1/2} = 20$ Hz). The last two resonances shift toward the diamagnetic region of the spectrum upon addition of tetrahydrofuran.

$(MeC_5H_4)_3Ce$

Method A:

To $(MeC_5H_4)_3Ce \cdot thf$ (1.35g, 3.00 mmol) dissolved in toluene (30 mL) was added, via syringe, $AlMe_3$ (3.13 mL of a 0.96M solution in hexane, 3.0 mmol). The yellow-green solution turned bright green upon addition. The solution was stirred for 1 hr, then the solvent was removed under reduced pressure. The yellow solid was extracted with toluene (50 mL, $50^\circ C$), filtered, and the filtrate was concentrated to ca. 20 mL ($50^\circ C$). Cooling the extract to $-20^\circ C$ for 3 hr, followed by cooling to $-80^\circ C$ afforded yellow-orange crystals (0.65g, 57%), m.p. $152-153^\circ C$. Anal. Calcd. for $C_{18}H_{21}Ce$: C, 57.3; H, 5.61. Found: C, 57.2; H, 5.69. IR: 1315w, 1305w, 1237mw, 1115w, 1102w, 1032m, 970w, 928mw, 882w, 870w, 830s, 790w, 760s, 742s, 615ms, 510w, 328m, 230m cm^{-1} . 1H NMR (C_6D_6 , $29^\circ C$): 13.02 (2H, $\nu_{1/2} = 43$ Hz), 10.56 (2H, $\nu_{1/2} = 58$ Hz), -4.52 (3H, $\nu_{1/2} = 20$ Hz). The E.I. mass spectrum showed a molecular ion at $M/e = 377$ amu corresponding to the $(MeC_5H_4)_3Ce$ monomer. No higher masses were found, but sequential ring loss was observed. The molecular ion isotopic cluster was simulated: M/e (calcd.%, obsvd.%); 377 (100, 100); 378 (19.97, 18.49); 379 (14.44, 15.07).

Method B: Toluene reflux

To $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ (1.52g, 3.38 mmol) was dissolved in toluene (150 mL) to give a yellow solution. This solution was heated to ca. 100°C, then the solvent removed very slowly under reduced pressure (over ca. 2-3 hr). As the thf was removed with the toluene, the solution turned greenish-blue. The yellow-orange residue was dissolved in an additional 150 mL of toluene, and the toluene reflux process was repeated. The solid residue was extracted with toluene (60 mL, 50°C), filtered, and the filtrate was concentrated to ca. 35 mL. Cooling to -20°C for 3 hr, followed by cooling to -80°C afforded yellow orange crystals (0.93g, 73%) whose physical properties were identical to those obtained from Method A.

 $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{PMe}_3$

Trimethylphosphine (0.23 mL, 2.3 mmol) was added, via syringe, to $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ (1.03g, 2.29 mmol) dissolved in diethyl ether (50 mL). There was no observable color change upon addition. The yellow solution was stirred for 30 min, then the diethyl ether was removed under reduced pressure. The yellow-green residue was dissolved in diethyl ether (60 mL), filtered, and the filtrate was concentrated to ca. 25 mL. Cooling the extract to -20°C afforded yellow crystals (0.88g, 82% yield), m.p. 176-179°C (dec). Anal. Calcd. for $\text{C}_{21}\text{H}_{30}\text{CeP}$: C, 55.6; H, 6.67; P, 6.83. Found: C, 55.5; H, 6.70; P, 6.79. IR: 1305w, 1280w, 1235w, 1150w, 1118w, 1042m, 1035s, 957s, 940m, 835w, 818s, 778m, 750s, 720m, 617w, 485w, 330m, 220s cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 25°C): 11.29 (6H, $\nu_{1/2}$ -26 Hz), 8.64 (6H, $\nu_{1/2}$ -26 Hz), -2.64 (9H, $\nu_{1/2}$ -8 Hz), -8.40 (9H, $\nu_{1/2}$ -8 Hz). The last resonance shifts toward the diamagnetic region of the spectrum upon addition of trimethylphosphine.

$(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{PEt}_3$

To $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ (0.20 mL, 0.53 mmol) dissolved in toluene (20 mL, 40°C) was added, via syringe, triethylphosphine (0.15 mL, 1.0 mmol). The green-blue solution immediately turned yellow upon addition. The solution was stirred for 5 min, then the solvent was removed under reduced pressure. The yellow residue was extracted with diethyl ether (30 mL), filtered, and the filtrate was concentrated to ca. 10 mL. Cooling the extract to -20°C afforded green-yellow crystals (0.12g, 46%), m.p. 117-119°C. Anal. Calcd. for $\text{C}_{24}\text{H}_{36}\text{CeP}$: C, 58.2; H, 7.32; P, 6.25. Found: C, 58.6; H, 7.31; P, 5.34. IR: 2320w, 2280w, 2160w, 2005w, 1300w, 1258w, 1232w, 1165m, 1150m, 1060w, 1042s, 1032s, 975m, 925m, 890w, 846m, 813s, 746s, 738s, 695m, 670m, 608m, 515w, 462w, 410w, 320s, 240m, 218s cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 26°C): 12.62 (6H, $\nu_{1/2}$ -30 Hz), 8.76 (6H, $\nu_{1/2}$ -28 Hz), -3.04 (9H, $\nu_{1/2}$ -10 Hz), -4.14 (9H, $\nu_{1/2}$ -16 Hz), -7.81 (6H, $\nu_{1/2}$ -22 Hz). The last two resonances shift toward the diamagnetic region of the spectrum upon addition of triethylphosphine.

 $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{NC}_5\text{H}_5$

Pyridine (0.20 mL, 2.5 mmol) was added, via syringe, to $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ (1.10g, 2.45 mmol) dissolved in diethyl ether (60 mL). The solution color turned from yellow to yellow-orange upon addition. This solution was stirred for 30 min, filtered, and the filtrate was concentrated to ca. 20 mL. Cooling the extract to -20°C yielded yellow-orange crystals (0.81g, 72 % yield), m.p. 132-134°C (dec). Anal. Calcd. for $\text{C}_{23}\text{H}_{26}\text{CeN}$: C, 60.5; H, 5.74; N, 3.07. Found: C, 60.3; H, 5.78; N, 3.14. IR: 1622w, 1594s, 1480w, 1430m, 1350w, 1238w, 1212m, 1150w, 1071w, 1060m, 1040m, 1030m, 1000m, 974w, 929w, 850w, 820s, 768m, 748s, 700s, 618m, 480w, 420w, 322m, 220s cm^{-1} . ^1H

NMR (C_6D_6 , $36^\circ C$): 9.28 (6H, $\nu_{1/2}$ -16 Hz), 8.98 (6H, $\nu_{1/2}$ -16 Hz), 3.26 (1H, t, $J=7$ Hz), 1.56 (2H, d, $J=7$ Hz), -1.05 (9H), -6.99 (2H, $\nu_{1/2}$ -20 Hz). The third, fourth, and sixth resonances exchange with added pyridine.

$(MeC_5H_4)_3Ce \cdot NC_5H_4NMe_2$

To $(MeC_5H_4)_3Ce \cdot thf$ (0.59g, 1.3 mmol) dissolved in diethyl ether (25 mL) was added, via syringe, p-dimethylaminopyridine (0.16g, 1.3 mmol) dissolved in diethyl ether (10 mL). A yellow precipitate formed in the yellow solution upon addition. The suspension was stirred for 30 min, then the solvent was removed under reduced pressure. The yellow solid was extracted with diethyl ether (65 mL), filtered, and the filtrate was concentrated to ca. 55 mL. Cooling the extract to $-20^\circ C$ afforded yellow crystals (0.40g, 61% yield), m.p. $173-175^\circ C$. An additional 0.10g (15%) of product can be obtained by concentrating the mother liquor to ca. 25 mL and cooling to $-20^\circ C$. Anal. Calcd. for $C_{25}H_{31}CeN_2$: C, 60.1; H, 6.25; N, 5.61. Found: C, 59.8; H, 6.10; N, 5.64. IR: 1595s, 1525m, 1455s, 1410w, 1372s, 1360m, 1340w, 1300w, 1272w, 1225m, 1218w, 1168w, 1056m, 1042w, 1020m, 997s, 970w, 945w, 925w, 850w, 834w, 810m, 772m, 750s, 612m, 545m, 325m, 240w, 220m cm^{-1} . 1H NMR (C_6D_6 , $30^\circ C$): 8.86 (6H, $\nu_{1/2}$ -18 Hz), 8.32 (6H, $\nu_{1/2}$ -17 Hz), 1.05 (2H, $\nu_{1/2}$ -6 Hz), -0.06 (6H, $\nu_{1/2}$ -3 Hz), -0.53 (9H, $\nu_{1/2}$ -8 Hz), -7.28 (2H, $\nu_{1/2}$ -15 Hz). The third, fourth, and sixth resonances exchange at room temperature with added p-dimethylaminopyridine.



Toluene (60 mL) was added to quinuclidine (0.19g, 1.7 mmol) and $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ (0.75g, 1.7 mmol). The yellow solution was stirred for 2h. During this time the solution became yellow-green. The toluene was removed slowly (ca. 45 min.) under reduced pressure. The yellow-green residue was dissolved in toluene (60mL), filtered, and the filtrate was concentrated to ca. 50 mL. Cooling the extract to -20°C afforded yellow needles (0.50g, 53 % yield), m.p. 156-159° (dec). Anal. Calcd. for $\text{C}_{25}\text{H}_{34}\text{CeN}$: C, 61.5; H, 7.01; N, 2.87. Found: C, 61.5; H, 7.03; N, 2.93. IR: 1310m, 1272w, 1235w, 1198m, 1150w, 1112w, 1043s, 1035m, 1030m, 1010w, 990m, 973m, 927m, 895w, 853w, 822s, 820m, 810s, 780s, 750s, 610m, 570w, 540w, 475w, 400w, 323m, 220s cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 28°C): 12.16 (6H, $\nu_{1/2}$ -15 Hz), 6.90 (6H, $\nu_{1/2}$ -15 Hz), -1.95 (9H, $\nu_{1/2}$ -5 Hz), -3.48 (1H, $\nu_{1/2}$ -9 Hz), -4.32 (6H, $\nu_{1/2}$ -12 Hz), -11.14 (6H, $\nu_{1/2}$ -23 Hz).



To the phosphite (0.20g, 1.2 mmol) and $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ (0.55g, 1.2 mmol) was added toluene (60 mL). The yellow-green solution was stirred for 2h, then the toluene was removed slowly under reduced pressure. The yellow-green residue was dissolved in diethyl ether (50 mL), filtered, and the filtrate was concentrated to ca. 30 mL. Cooling the extract to -20°C afforded yellow bricks (0.31g, 47% yield), m.p. 170-171°C. Anal. Calcd. for $\text{C}_{24}\text{H}_{32}\text{CeO}_3\text{P}$: C, 53.4; H, 5.98; P, 5.74. Found: C, 53.4; H, 6.12; P, 5.99. IR: 1690m, 1610w, 1300m, 1260w, 1237w, 1188m, 1170w, 1150s, 1060w, 1040s, 970m, 955s, 860w, 848s, 820s, 760s, 730s, 642s, 620m, 565w, 532m, 497m, 468m, 420w, 409m, 370m, 350m, 330s, 250m, 230s cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 33°C): 10.28 (12H, $\nu_{1/2}$ -40 Hz), -1.64 (6H, $\nu_{1/2}$ -4 Hz), -1.92 (3H, t, J=7 Hz),

-2.28 (9H, $\nu_{1/2}$ -8 Hz), -2.51 (2H,q, J=7 Hz). The first resonance splits into two peaks of equal intensity in the variable temperature ^1H NMR analysis. The second, third, and fifth resonances exchange with added phosphite.

$(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{P}(\text{OMe})_3$

To $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ (0.73g, 1.93 mmol) dissolved in diethyl ether (30 mL) was added, via syringe, trimethylphosphite (0.50 mL, 4.1 mmol). The yellow solution stayed yellow with no precipitate upon addition. The solution was stirred for 30 min, then the solvent was removed under reduced pressure. The yellow solid was dissolved in diethyl ether (25 mL), filtered, and the filtrate was concentrated to ca. 10 mL. Cooling to -20°C afforded a yellow micro-crystalline solid (0.58g, 66%), m.p. $73\text{-}76^\circ\text{C}$ (dec). Anal. Calcd. for $\text{C}_{21}\text{H}_{30}\text{CeO}_3\text{P}$: C, 50.3; H, 6.03; P, 6.17. Found: C, 50.8; H, 6.06; P, 5.47. IR: 1300w, 1232w, 1168m, 1150w, 1052m, 1030s, 1015s, 970w, 925w, 847w, 820m, 748s, 610m, 516m, 375w, 325m, 220m cm^{-1} . ^1H NMR (C_6D_6 , 30°C): 11.08 (6H, $\nu_{1/2}$ -38 Hz), 9.82 (6H, $\nu_{1/2}$ -34 Hz), -2.26 (9H, $\nu_{1/2}$ -6 Hz), -2.76 (9H, $\nu_{1/2}$ -16 Hz). The fourth resonance shifts toward the diamagnetic region of the spectrum with added trimethylphosphite.

$(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{THT}$

To $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ (0.30g, 0.79 mmol) dissolved in toluene (20 mL, 40°C) was added, via syringe, tetrahydrothiophene (0.15 mL, 1.7 mmol). The green-blue color immediately turned yellow upon addition of the ligand. The solution was stirred for 10 min, then the solvent was removed under reduced pressure. The yellow residue was extracted with diethyl ether (30 mL), filtered, and the filtrate was concentrated to ca. 10 mL. Cooling the extract to -20°C afforded yellow-green

crystals (0.23 g, 63%), m.p. 112-115°C (dec). Anal. Calcd. for $C_{22}H_{29}CeS$: C, 56.8; H, 6.28; S, 6.89. Found: C, 56.8; H, 6.31; S, 5.85. IR: 1300w, 1260w, 1235w, 1210w, 1170w, 1153w, 1043m, 1030m, 1015m, 958w, 928w, 850w, 820s, 750s, 720m, 670w, 613w, 460w, 400w, 330s, 242m, 220s cm^{-1} . 1H NMR (C_6D_6 , 27°C): 11.11 (6H, $\nu_{1/2}$ =30 Hz), 10.14 (6H, $\nu_{1/2}$ =36 Hz), -2.48 (9H, $\nu_{1/2}$ =11 Hz), -4.93 (4H, $\nu_{1/2}$ =11 Hz), -8.35 (4H, $\nu_{1/2}$ =15 Hz). The fourth and fifth resonances shift toward the diamagnetic region with added tetrahydrothiophene.

$(MeC_5H_4)_3Ce \cdot NCEt$

To $(MeC_5H_4)_3Ce \cdot thf$ (0.76g, 1.7 mmol) dissolved in diethyl ether (30 mL) was added, via syringe, propionitrile (0.14 mL, 3.5 mmol). There was no observable color change upon addition. The yellow solution was stirred for 30 min, then the solvent was removed under reduced pressure. The yellow solid was dissolved in diethyl ether (30 mL), filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the extract to -20°C afforded yellow crystals (0.44g, 60%), m.p. 62-65°C. Anal. Calcd. for $C_{21}H_{26}CeN$: C, 58.3; H, 6.06; N, 3.24. Found: C, 58.0; H, 6.01; N, 3.18. IR: 2350w(br), 2260s, 2160w, 2110w, 1410m, 1375s, 1365mw, 1310m, 1260w, 1235m, 1170w, 1092w, 1070m, 1061w, 1045m, 1030s, 1020w, 975w, 928m, 885w, 850m, 822s, 765s, 740s, 617m, 563w, 330s, 240s, 220s cm^{-1} . 1H NMR (C_6D_6 , 34°C): 11.04 (6H), 7.86 (6H), -0.65 (9H), -3.81 (3H, t, J=6.8 Hz), -7.24 (2H, q, J=6.8 Hz). The last two resonances shift toward the diamagnetic region of the spectrum upon addition of excess propionitrile. Variable temperature 1H NMR indicates the presence of a bis-ligand adduct in solution; however, no 1:2 adduct was isolated when excess base was used.

$(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNEt}$

To $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ (0.44g, 0.98 mmol) dissolved in diethyl ether (30 mL) was added, via syringe, ethylisocyanide (0.08 mL, 0.98 mmol). There was no observable color change in the yellow solution upon addition. The solution was stirred for 20 min, then the solvent was removed under reduced pressure. The yellow residue was dissolved in hexane (75 mL, 50°C) and the solution was filtered. Cooling the extract to -20°C afforded small yellow crystals (0.25g, 58%), m.p. 60-61°C. Anal. Calcd. for $\text{C}_{21}\text{H}_{26}\text{CeN}$: C, 58.3; H, 6.06; N, 3.24. Found: C, 58.5; H, 6.09; N, 3.37. IR: 2320w(br), 2200s, 2070w, 1342m, 1302w, 1235w, 1160w, 1140w, 1092m, 1060w, 1045m, 1030m, 1008w, 975w, 929m, 850w, 822s, 765s, 743s, 618m, 500w, 330m, 245m, 223m cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 34°C): 10.38 (6H), 8.31 (6H), -0.73 (9H), -3.61 (3H), -5.86 (2H, d, J=6 Hz). The last two resonances shift toward the diamagnetic region of the spectrum upon addition of excess ethylisocyanide. Variable temperature $^1\text{H NMR}$ indicates the presence of a bis-ligand adduct in solution; however, no 1:2 adduct was isolated when excess base was used.

 $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNCMe}_3$

To $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ (0.56g, 1.2 mmol) dissolved in diethyl ether (30 mL) was added, via syringe, t-butylisocyanide (0.14 mL, 1.2 mmol). There was no observable change in the yellow solution upon addition. The solution was stirred for 20 min, then the solvent was removed under reduced pressure. The yellow solid was extracted with hexanes (60 mL), filtered, and the filtrate was concentrated to ca. 50 mL. Cooling the extract to -20°C afforded yellow needles (0.36g, 63%), m.p. 108-110°C. Concentrating the mother liquor to ca. 25 mL and cooling to -20°C affords an additional 0.06g (11%). If an excess of

base was used the same product was isolated, i.e. no 1:2 adduct could be isolated. Anal. Calcd. for $C_{23}H_{30}CeN$: C, 60.0; H, 6.16; N, 2.85. Found: C, 60.4; H, 6.43; N, 3.13. IR: 2175s, 2060w, 1670w(br), 1300w, 1233m, 1195m, 1165w, 1150w, 1060w, 1042m, 1028m, 970m, 925m, 888w, 848m, 812s, 748s, 720m, 697w, 612m, 567w, 525m, 417w, 411m, 322s, 240m, 218s cm^{-1} . 1H NMR (C_6D_6 , 30°C): 10.53 (6H, $\nu_{1/2}$ -24 Hz), 7.99 (6H, $\nu_{1/2}$ -28 Hz), -0.57 (9H, $\nu_{1/2}$ -10 Hz), -4.13 (9H, $\nu_{1/2}$ -5 Hz). The last resonance shifts toward the diamagnetic region of the spectrum upon addition of t-butylisocyanide.

$(Me_3SiC_5H_4)_3Ce$

Potassium trimethylsilylcyclopentadienide (40.3 mL of a 0.74M solution in tetrahydrofuran, 30.0 mmol) was added to a suspension of cerium trichloride (2.45g, 9.94 mmol) in tetrahydrofuran (50 mL). The suspension became yellow after ca. 15 min and was stirred for 18h. The solvent was removed under reduced pressure. The yellow residue was extracted with hexane (120 mL) and the blue-green solution was filtered. While concentrating the filtrate a yellow solid began to crystallize which is presumably the thf adduct. All of the hexane was removed under reduced pressure and the yellow-green residue was melted in a water bath (85°C) under dynamic vacuum which produced a viscous, dark blue solution. The solution was cooled to room temperature, and the blue solid was dissolved in hexane (15 mL), filtered, and the filtrate was concentrated to ca. 3 mL. Cooling the filtrate to -80°C yielded a royal blue solid (3.7g, 68% yield), m.p. 69-70°C. Anal. Calcd. for $C_{24}H_{39}CeSi_3$: C, 52.2; H, 7.12. Found: C, 51.9; H, 7.33. IR: 1360m, 1310w, 1245s, 1058w, 1039s, 975w, 950w, 900s, 830s, 780w, 765s, 750m, 720w, 698w, 685m, 630w, 622m, 420m, 340m, 310m, 250w, 220m cm^{-1} . 1H NMR (C_6D_6 , 32°C): 24.15 (2H, $\nu_{1/2}$ -34 Hz), 5.15 (2H, $\nu_{1/2}$ -34

Hz), -8.30 (9H, $\nu_{1/2}$ -8 Hz). The mass spectrum showed a molecular ion at $M/e = 551$, successive ring loss, and ring fragmentation. The molecular ion isotopic cluster was simulated: M/e (calcd.%, obsvd.%); 551 (100, 100); 552 (41.98, 28.30); 553 (30.92, 16.78); 554 (---, 10.01). The compound sublimes at $60^\circ\text{C}/10^{-5}\text{mm}$.

$(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}\cdot\text{NCEt}$

Propionitrile (0.03 mL, 0.83 mmol) was added, via syringe to $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$ (0.46g, 0.83 mmol) dissolved in hexane (30 mL). The dark blue solution immediately turned yellow. The solution was stirred for 30 min, then the solvent was removed under reduced pressure. The yellow residue was dissolved in hexane (50 mL) and the solution was filtered. Cooling the filtrate to -20°C yielded small yellow needles (0.34g, 67% yield), m.p. $126\text{-}128^\circ\text{C}$. If an excess of base was used the same product was isolated, i.e. no 1:2 adduct could be isolated. Variable temperature ^1H NMR indicates there is not a bis-ligand species present in solution. Anal. Calcd. for $\text{C}_{27}\text{H}_{44}\text{CeNSi}_3$: C, 53.4; H, 7.31; N, 2.31. Found: C, 52.3; H, 7.07; N, 2.80. IR: 2260s, 1360m, 1308m, 1242s, 1178s, 1070w, 1060w, 1038s, 970w, 900s, 830s, 785w, 750m, 720m, 685m, 638s, 632m, 620s, 560w, 420s, 320s, 250w, 220s cm^{-1} . ^1H NMR (C_6D_6 , 30°C): 13.63 (6H, $\nu_{1/2}$ -21 Hz), 6.59 (6H, $\nu_{1/2}$ -21 Hz), -2.25 (27H, $\nu_{1/2}$ -4 Hz), -3.61 (3H, t, $J=7$ Hz), -6.86 (2H, q, $J=7$ Hz). The last two resonances shift toward the diamagnetic region of the spectrum with addition of propionitrile.

$(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNEt}$

Ethylisocyanide (0.07 mL, 0.91 mmol) was added, via syringe to $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$ (0.50g, 0.91 mmol) dissolved in hexane (20 mL). The dark blue solution immediately turned yellow and some precipitate

formed. The solution was stirred for 30 min, then the solvent was removed under reduced pressure. The yellow residue was dissolved in hexane (45 mL), filtered, and the filtrate was concentrated to ca. 30 mL. Cooling the filtrate to -20°C yielded small yellow crystals (0.35g, 63% yield), m.p. $121-123^{\circ}\text{C}$. If an excess of base was used the same product was isolated, i.e. no 1:2 adduct was isolated. Variable temperature ^1H NMR indicates there is no bis-ligand species present in solution. Anal. Calcd. for $\text{C}_{27}\text{H}_{44}\text{CeNSi}_3$: C, 53.4; H, 7.31; N, 2.31. Found: C, 52.5; H, 7.37; N, 2.11. IR: 2200m, 1310w, 1257w, 1245s, 1175m, 1090w, 1060w, 1040s, 937w, 900s, 830s, 765s, 750m, 720w, 685w, 640w, 623m, 605w, 422m, 320 cm^{-1} . ^1H NMR (C_6D_6 , 28°C): 13.71 (6H, $\nu_{1/2}=30$ Hz), 6.13 (6H, $\nu_{1/2}=30$ Hz), -2.17 (27H, $\nu_{1/2}=6$ Hz), -3.91 (3H, $\nu_{1/2}=16$ Hz), -6.52 (2H, $\nu_{1/2}=23$ Hz). The last two resonances shift toward the diamagnetic region of the spectrum upon addition of ethylisocyanide.

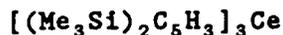
$(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}\cdot\text{CNCMe}_3$

To $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$ (0.64g, 1.2 mmol) dissolved in hexane (30 mL) was added, via syringe, t-butylisocyanide (0.14 mL, 1.2 mmol). The blue solution turned yellow upon addition. The solution was stirred for 20 min, then the solvent was removed under reduced pressure. The yellow solid was extracted with hexane (30 mL), filtered, and the filtrate was concentrated to ca. 25 mL. Cooling to -20°C afforded yellow crystalline hairs (0.56g, 76%), m.p. $111-113^{\circ}\text{C}$. If an excess of base was used the same product was isolated, i.e. no 1:2 adduct could be isolated. Anal. Calcd. for $\text{C}_{29}\text{H}_{48}\text{CeNSi}_3$: C, 54.8; H, 7.62; N, 2.21. Found: C, 54.1; H, 7.32; N, 2.30. IR: 2170s, 1370s, 1360m, 1305w, 1240s, 1188w, 1172m, 1058w, 1038s, 900s, 828s, 781m, 762s, 745m, 718w, 686m, 638w, 620m, 525w, 420m, 330w, 315m, 240 cm^{-1} .

$^1\text{H NMR}$ (C_6D_6 , 30°C): 13.25 (6H, $\nu_{1/2}=22$ Hz), 6.52 (6H, $\nu_{1/2}=26$ Hz), -2.14 (27H, $\nu_{1/2}=6$ Hz), -3.80 (9H, $\nu_{1/2}=5$ Hz). The last resonance shifts toward the diamagnetic region of the spectrum upon addition of *t*-butylisocyanide.

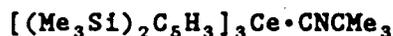
$(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_4$

Potassium metal (47g, 1.2 mol) was placed in a 5-liter flask equipped with a 500 mL addition funnel, reflux condenser, and an overhead stirrer. The metal was washed with hexane and degassed. Diethyl ether (1.5 l) was added. The addition funnel was charged with freshly distilled $\text{Me}_3\text{SiC}_5\text{H}_5$ (173.7g, 1.25 mol) and diethyl ether (200 mL). The solution was degassed and then added dropwise to the stirred potassium at rate such that a slight reflux was maintained. After addition of the diene, stirring was continued until all the potassium had been consumed. Trimethylsilylchloride (130.3g, 1.2 mol) and diethyl ether (200 mL) were placed in the addition funnel and degassed. The solution was added dropwise to the $\text{K}(\text{Me}_3\text{SiC}_5\text{H}_4)$ at a rate such that a moderate reflux was maintained. A white precipitate formed and the stirring was continued for 24 h. The suspension was carefully poured into distilled water (1.5 l). The organic layer was collected and dried over MgSO_4 . The ether was removed by distillation, and the remaining yellow liquid was vacuum distilled ($45\text{-}50^\circ\text{C}$, 5 mm), affording $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_4$ as a colorless liquid (1.1 mol, 88%). $^1\text{H NMR}$ (C_6D_6 , 30°C): 6.76 (-CH-), 6.71 (-CH-), 6.46 (-CH-), 6.41 (-CH-), -0.04 (-SiMe₃), -0.10 (-SiMe₃).



To $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ce}$ (0.85g, 1.4 mmol) dissolved in diethyl ether (30 mL) was added, via syringe, bis(trimethylsilyl)cyclopentadiene (1.04 mL, 4.2 mmol). The solution was stirred for 15 h. During this time the solution color gradually turned from yellow to green and finally to blue with the presence of a small amount of white precipitate. The diethyl ether was removed under reduced pressure. The blue solid was dissolved in hexane (30 mL), filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the extract to -20°C followed by further cooling to -80°C afforded blue crystals (0.33g, 31%). Concentrating the mother liquor to ca. 5 mL and cooling to -20°C afforded an additional 0.19g (18%) of product, m.p. $210\text{-}213^\circ\text{C}$.

Anal. Calcd. for $\text{C}_{33}\text{H}_{83}\text{CeSi}_6$: C, 51.6; H, 8.26. Found: C, 49.3; H, 8.18. IR: 1372s, 1360m, 1315w, 1241s, 1205w, 1150w, 1073s, 1012w, 970w, 915s, 830s, 771m, 745m, 718w, 684m, 632m, 612w, 475m, 371w, 348w, 295w, 270m cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 30°C): 26.88 (1H, $\nu_{1/2}=30$ Hz), 17.16 (2H, $\nu_{1/2}=36$ Hz), -4.48 (18H, $\nu_{1/2}=7$ Hz). The E.I. mass spectrum showed a molecular ion at $M/e = 767$ amu, as well as sequential ring loss and ring fragmentation. The molecular ion isotopic cluster was simulated: M/e (calcd.%, obsvd.%); 767 (100, 100), 768 (67.3, 68.5), 769 (54.3, 47.8), 770 (25.4, 24.2), 771 (11.3, 9.8).



To $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ (0.48g, 0.56 mmol) dissolved in hexane (30 mL) was added, via syringe, *t*-butylisocyanide (0.13 mL, 1.12 mmol). The blue solution immediately turned yellow upon addition. A yellow precipitate formed after ca. two minutes. The suspension was stirred for 20 min, then the solvent was removed under reduced pressure. The

yellow residue was extracted with diethyl ether (60 mL), filtered, and the filtrate was concentrated to ca. 50 mL. Cooling the extract to -20°C afforded yellow bricks (0.27g, 57%), m.p. $223-226^{\circ}\text{C}$ (upon heating the yellow solid turns green then blue from $150-190^{\circ}\text{C}$, probably due to loss of isocyanide). Concentrating the mother liquor to ca. 20 mL and cooling to -20°C affords an additional 0.10g (21%) of product. IR: 2205w, 2170s, 2065w, 1402w, 1372s, 1363mw, 1315mw, 1243s, 1203m, 1072s, 1055mw, 970vw, 918s, 831s, 815s, 771m, 750ms, 720w, 681m, 632ms, 617m, 521w, 480ms, 368m, 350w, 325w, 295m, 230vw cm^{-1} . Anal. Calcd. for $\text{C}_{38}\text{H}_{72}\text{CeNSi}_6$: C, 53.6; H, 8.52; N, 1.64. Found: C, 53.4; H, 8.60; N, 1.62. $^1\text{H NMR}$ (C_6D_6 , 30°C): 12.76 (1H, very broad; $\nu_{1/2} \approx 150$ Hz), 11.68 (2H, $\nu_{1/2} \approx 50$ Hz), -0.94 (18H, $\nu_{1/2} = 8$ Hz), -3.11 (3H, $\nu_{1/2} = 15$ Hz). No bis-isocyanide adduct could be isolated.

$(\text{MeC}_5\text{H}_4)_3\text{Nd}\cdot\text{thf}$

Sodium cyclopentadienide (27.0 mL of a 0.88M solution in tetrahydrofuran, 24. mmol) was added to a suspension of neodymium trichloride (2.0g, 8.1 mmol) in tetrahydrofuran (100 mL). The aqua-blue suspension was stirred for 19 h, then the solvent was removed under reduced pressure. The light blue residue was extracted with diethyl ether (150 mL), filtered, and the filtrate was concentrated to ca. 70 mL. Cooling the filtrate to -20°C yielded blue-lavender needles (1.7g, 48% yield), m.p. $148-152^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{22}\text{H}_{29}\text{NdO}$: C, 58.2; H, 6.44. Found: C, 57.8; H, 6.48. IR: 1403w, 1258w, 1233m, 1165m, 1060w, 1040s, 1030s, 1010s, 970w, 925m, 860m, 845m, 821s, 750s, 665m, 610m, 470w, 420w, 320m, 215s cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 30°C): 6.11 (6H, $\nu_{1/2} = 26$ Hz), 5.94 (6H, $\nu_{1/2} = 25$ Hz), -1.83 (9H, $\nu_{1/2} = 4$ Hz), -9.15 (4H, $\nu_{1/2} = 12$ Hz), -19.44 (4H, $\nu_{1/2} = 40$ Hz). The

last two resonances shift toward the diamagnetic region of the spectrum upon addition of tetrahydrofuran.

$(\text{MeC}_5\text{H}_4)_3\text{Nd}\cdot\text{PMe}_3$

Trimethylphosphine (0.06 mL, 0.75 mmol) was added, via syringe, to $(\text{MeC}_5\text{H}_4)_3\text{Nd}\cdot\text{thf}$ (0.34g, 0.75 mmol) dissolved in diethyl ether (30 mL). No color change was observed. The light blue solution was stirred for 30 min, then the diethyl ether was removed under reduced pressure. The light blue residue was dissolved in diethyl ether (30 mL), filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the filtrate to -20°C gave blue-lavender crystals (0.34g, 65 % yield), m.p. $202\text{-}205^\circ\text{C}$. Anal. Calcd. for $\text{C}_{21}\text{H}_{30}\text{NdP}$: C, 55.1; H, 6.61; P, 6.77. Found: C, 53.4; H, 6.53; P, 6.76. IR: 1305w , 1285m , 1260w , 1235w , 1155m , 1060w , 1042m , 1035s , 958s , 850w , 822s , 770m , 758s , 752s , 742m , 615m , 470w , 328m , 225m cm^{-1} . $^1\text{H MNR}$ (C_6D_6 , 32°C): 7.15 (6H, $\nu_{1/2} = 28$ Hz), 4.78 (6H, $\nu_{1/2} = 28$ Hz), -3.74 (9H, $\nu_{1/2} = 8$ Hz), -13.73 (9H, $\nu_{1/2} = 12$ Hz). The last resonance shifts toward the diamagnetic region of the spectrum upon addition of trimethylphosphine.

$(\text{MeC}_5\text{H}_4)_3\text{Nd}\cdot\text{NC}_5\text{H}_5$

Pyridine (0.10 mL, 1.3 mmol) was added, via syringe, to $(\text{MeC}_5\text{H}_4)_3\text{Nd}\cdot\text{thf}$ (0.57g, 1.3 mmol) dissolved in diethyl ether (50 mL). The bluish solution lightened slightly. This solution was stirred for 30 min, then the solvent was removed under reduced pressure. The light blue residue was dissolved in diethyl ether (50 mL), filtered, and the filtrate was concentrated to ca. 20 mL. Cooling the filtrate to -20°C yielded lavender needles (0.37g, 64 % yield), m.p. $127\text{-}129^\circ\text{C}$. Anal. Calcd. for $\text{C}_{23}\text{H}_{26}\text{NNd}$: C, 60.0; H, 5.69; N, 3.04. Found: C, 59.9; H,

5.94; N, 3.08. IR: 1625w, 1595s, 1482m, 1432s, 1350w, 1240w, 1225w, 1213s, 1170w, 1150m, 1075w, 1060s, 1042s, 1030s, 1000s, 970w, 930m, 880w, 865w, 850m, 822s, 770s, 748s, 700s, 650w, 618s, 422m, 321s, 220s cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 36°C): 6.75 (6H, $\nu_{1/2}=30$ Hz), 3.52 (6H, $\nu_{1/2}=35$ Hz), -0.65 (9H, $\nu_{1/2}=9$ Hz), -2.49 (2H, d, $J=8$ Hz), -18.08 (2H, $\nu_{1/2}=45$ Hz), the other pyridine resonance is at ca. 2.1 ppm and is very broad ($\nu_{1/2}=40$ Hz). The last two resonances and the one at 2.1 undergo exchange with added pyridine.

$(\text{MeC}_5\text{H}_4)_3\text{Nd}\cdot\text{NCEt}$

To $(\text{MeC}_5\text{H}_4)_3\text{Nd}\cdot\text{thf}$ (0.43g, 0.95 mmol) dissolved in diethyl ether (30 mL) was added, via syringe, propionitrile (0.08 mL, 1.9 mmol). There was a very slight change in the hue of the blue solution upon addition. The solution was stirred for 30 min, then the solvent was removed under reduced pressure. The light blue solid was dissolved in diethyl ether (20 mL), filtered, and the filtrate was concentrated to ca. 5 mL. Cooling the extract to -20°C affords blue crystals (0.14g, 34%), m.p. $62\text{-}65^\circ\text{C}$ (the compound turns purple upon melting). The low yield is a result of the compound's extreme solubility in diethyl ether and low solubility in hexane. A larger crystallized yield probably can be obtained by using an ether/hexane mixture. Anal. Calcd. for $\text{C}_{21}\text{H}_{26}\text{NNd}$: C, 57.8; H, 6.00; N, 3.21. Found: C, 58.1; H, 5.92; N, 3.05. IR: 2265s, 1375s, 1365mw, 1308w, 1260w, 1238w, 1160w, 1070mw, 1046m, 1030ms, 1012w, 972w, 928m, 850mw, 828ms, 768s, 745s, 722mw, 615m, 328ms, 245w, 220m cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32°C): 10.28 (6H, $\nu_{1/2}=40$ Hz), 0.28 (9H, $\nu_{1/2}=14$ Hz), -0.48 (6H, $\nu_{1/2}=40$ Hz), -8.43 (3H, t, $J=6.8$ Hz), -16.78 (2H, q, $J=6.8$ Hz). The last two resonances shift toward the diamagnetic region of the spectrum upon addition of excess propionitrile. Variable temperature $^1\text{H NMR}$ indicates the

presence of a bis-ligand adduct in solution; however, no 1:2 adduct could be isolated when excess base was used.

$(\text{MeC}_5\text{H}_4)_3\text{Nd}\cdot\text{CNEt}$

To $(\text{MeC}_5\text{H}_4)_3\text{Nd}\cdot\text{thf}$ (0.35g, 0.77 mmol) dissolved in diethyl ether (30 mL) was added, via syringe, ethylisocyanide (0.06 mL, 0.81 mmol). There was a very slight change in the hue of the blue solution upon addition. The solution was stirred for 30 min, then the solvent was removed under reduced pressure. The light blue solid was dissolved in diethyl ether (30 mL), filtered, and the filtrate was concentrated to ca. 5 mL. Cooling the extract to -20°C affords blue micro-crystals (0.10g, 30%), m.p. $60-62^\circ\text{C}$ (the compound turns purple upon melting). The low yield is a result of the compound's extreme solubility in diethyl ether and low solubility in hexane. A larger crystallized yield probably can be obtained by using an ether/hexane mixture.

Anal. Calcd. for $\text{C}_{21}\text{H}_{26}\text{NNd}$: C, 57.8; H, 6.00; N, 3.21. Found: C, 58.1; H, 6.37; N, 3.17. IR: 2200s, 1375s, 1365mw, 1342m, 1305w, 1258w, 1235w, 1160w, 1138w, 1092m, 1060w, 1042m, 1030ms, 1005w, 970w, 928m, 850mw, 825s, 800w, 768s, 740s, 612m, 500w, 328ms, 245w, 220m cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32°C): 8.40 (6H, $\nu_{1/2} = 36$ Hz), 0.54 (6H, $\nu_{1/2} = 30$ Hz), -0.90 (9H, $\nu_{1/2} = 10$ Hz), -8.07 (3H, $\nu_{1/2} = 18$ Hz), -15.57 (2H, $\nu_{1/2} = 23$ Hz). The last two resonances shift toward the diamagnetic region of the spectrum upon addition of excess ethylisocyanide.

Variable temperature $^1\text{H NMR}$ indicates the presence of a bis-ligand adduct in solution; however, no 1:2 adduct could be isolated when excess base was used.

$(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Nd}$

Potassium trimethylsilylcyclopentadienide (27.5 mL of a 0.90M solution in tetrahydrofuran, 25 mmol) was added to a suspension of neodymium trichloride (2.05g, 8.18 mmol) in tetrahydrofuran (50 mL). The suspension became reddish after ca. 15 min and purple-gray after ca. 2h. The suspension was stirred for 16 h, then the solvent was removed under reduced pressure. The pink-purple residue was extracted with hexane (120 mL) and the green solution was filtered. The filtrate was evaporated to dryness under reduced pressure, melted in a water bath (85°C) under dynamic vacuum, then cooled to room temperature. The green residue was dissolved in hexane (15 mL), filtered, and the filtrate was concentrated to ca. 3 mL. Cooling the filtrate to -80°C yielded a green solid (3.3g, 74% yield), m.p. 63-69°C. Anal. Calcd for $\text{C}_{24}\text{H}_{39}\text{NdSi}_3$: C, 51.9; H, 7.07. Found: C, 50.6; H, 6.82. IR: 1360m, 1310w, 1258w, 1245s, 1128m, 1058w, 1039s, 970w, 950w, 900s, 830s, 780w, 770s, 750m, 720m, 686m, 622m, 550w, 470w, 418m, 380w, 335m, 308w, 250w, 220m cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 34°C): 27.10 (2H, $\nu_{1/2}$ -30 Hz), -2.44 (2H, $\nu_{1/2}$ -30 Hz), -14.22 (9H, $\nu_{1/2}$ -6 Hz). The E.I. mass spectrum showed a molecular ion at $M/e = 555$ amu, successive ring loss, and ring fragmentation. The parent molecular ion isotopic cluster was simulated: M/e (calcd.%, obsvd.%); 553 (80.20, 70.25); 554 (69.64, 56.25); 555 (100, 100); 556 (64.34, 49.06); 557 (76.42, 71.25); 558 (29.61, 19.88); 559 (28.07, 23.88); 560 (9.81, 7.72); 561 (20.15, 18.31); 562 (7.80, 1.41).

 $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Nd}\cdot\text{NCEt}$

Propionitrile (0.04 mL, 0.94 mmol) was added, via syringe to $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Nd}$ (0.51g, 0.92 mmol) dissolved in hexane (25 mL). The green solution immediately turned to an aqua-color and some

precipitate formed. The solution was stirred for 30 min, then the solvent was removed under reduced pressure. The blue residue was dissolved in diethyl ether (50 mL), filtered, and the blue filtrate was concentrated to ca. 25 mL. Cooling the filtrate to -20°C yielded blue-lavender crystals (0.27g, 48 % yield), m.p. $126-128^{\circ}\text{C}$. If an excess of base was used the same product was isolated. Variable temperature ^1H NMR indicates there is no bis-ligand species present in solution. Anal. Calcd. for $\text{C}_{27}\text{H}_{44}\text{NNdSi}_3$: C, 53.1; H, 7.26; N, 2.29. Found: C, 52.6; H, 6.98; N, 2.15. IR: 2260s, 1308m, 1240s, 1190w, 1178s, 1070w, 1060w, 1040s, 970w, 900s, 830s, 785m, 768s, 750s, 720m, 682m, 638s, 630w, 620s, 560w, 420s, 320s, 250m, 220s cm^{-1} . ^1H NMR (C_6D_6 , 34°C): 12.38 (6H, $\nu_{1/2}=34$ Hz), 0.50 (6H, $\nu_{1/2}=34$ Hz), -4.34 (27H, $\nu_{1/2}=4$ Hz), -7.62 (3H,t), -15.00 (2H,q). The last two resonances shift toward the diamagnetic region of the spectrum upon addition of propionitrile.

$(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Nd}\cdot\text{CNEt}$

Ethylisocyanide (0.08 mL, 0.98 mmol) was added, via syringe, to $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Nd}$ (0.54g, 0.98 mmol) dissolved in hexane (15 mL). No apparent color change was observed. After 15 min a bluish solid was observed on the edge of the green solution. More hexane (15 mL) was added and all of the precipitate dissolved. The solution was stirred an additional 2h, then the solvent was removed under reduced pressure. The blue residue was dissolved in hexane (30 mL), filtered, and the filtrate was concentrated to ca. 20 mL. Cooling the filtrate to -20°C yielded blue-lavender crystals (0.35g, 58%), m.p. $111-114^{\circ}\text{C}$. If an excess of base was used the same product was isolated. Variable temperature ^1H NMR indicates there is no bis-ligand species present in solution. Anal. Calcd. for $\text{C}_{27}\text{H}_{44}\text{NNdSi}_3$: C, 53.1; H, 7.26; N, 2.29.

Found: C, 52.8; H, 7.59; N, 2.31. IR: 2200m, 1308w, 1245s, 1190w, 1060w, 1040s, 1008w, 975w, 902m, 880s, 770s, 750m, 720w, 700w, 685m, 632w, 622m, 422s, 320s, 250w cm^{-1} . ^1H NMR (C_6D_6 , 34°C): 11.69 (6H, $\nu_{1/2}=34$ Hz), 0.24 (6H, $\nu_{1/2}=34$ Hz), -4.23 (27H, $\nu_{1/2}=3$ Hz), -7.54 (3H, $\nu_{1/2}=16$ Hz), -14.57 (2H, $\nu_{1/2}=21$ Hz). The last two resonances shift toward the diamagnetic region of the spectrum upon addition of ethylisocyanide.

CHAPTER TWO:" $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeCl}$ "

To CeCl_3 (2.32g, 9.41 mmol) and $\text{K}[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]$ (4.07g, 18.8 mmol) was added tetrahydrofuran (60 mL). The suspension was heated to reflux and stirred for 2 days. The suspension was cooled to room temperature and the insoluble solid was allowed to settle for 10 h. The yellow-brown solution was filtered and the solvent was removed from the filtrate under reduced pressure. The yellow solid was extracted with toluene (60 mL), filtered twice, and the filtrate was concentrated to ca. 40 mL. Cooling to -20°C afforded a yellow powder. Additional product can be obtained from repeated concentration of the mother liquor and cooling to -20°C . The total yield was 2.5g (50%). $^1\text{H NMR}$ (C_6D_6 , 29°C): 42.0 (1H, $\nu_{1/2} \approx 150$ Hz), 11.4 (2H, $\nu_{1/2} \approx 180$ Hz), -3.94 (18H, $\nu_{1/2} = 11$ Hz). The product was not characterized further because crystalline material could not be obtained and sometimes the solid does not completely redissolve.

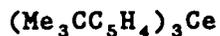
 $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{Ce}(\text{Cl})\text{OPMe}_3$

To " $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeCl}$ " (0.48g, 0.90 mmol) and Me_3PO (0.13g, 1.4 mmol) was added toluene (30 mL). The bright yellow solution was stirred for 4 h, then the solvent was removed under reduced pressure. The canary-yellow solid was heated (50°C) under reduced pressure for 45 min to remove any excess Me_3PO . The solid was extracted with toluene (30 mL), filtered, and the filtrate was concentrated to ca. 10 mL. Cooling the extract to -20°C afforded large canary-yellow crystals that collapsed to a powder upon exposure to vacuum (0.22g, 39%), m.p. $221\text{--}222^\circ\text{C}$. An additional 0.10g (18%) of product can be obtained by concentrating the mother liquor to ca. 5 mL and cooling to

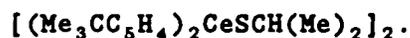
-20°C. Anal. Calcd. for $C_{29}H_{51}CeClOP$: C, 55.5; H, 8.26; Cl, 5.70; P, 4.98. Found: C, 54.5; H, 8.03; Cl, 5.48; P, 4.69. IR: 1310m, 1298m, 1249m, 1200mw, 1162w, 1103s, 1050w, 1020w, 950s, 859mw, 852mw, 811m, 801s, 740s, 680m, 660w, 420w, 373w, 360m cm^{-1} . 1H NMR (C_6D_6 , 29°C): 16.30 (4H, $\nu_{1/2}$ -30 Hz), 13.83 (2H, broad), 5.86 (9H, $\nu_{1/2}$ -55 Hz), -4.01 (18H, $\nu_{1/2}$ ≈25 Hz), -4.60 (18H, $\nu_{1/2}$ ≈25 Hz). The E.I. mass spectrum showed a molecular ion at $M/e = 529$ amu.



To " $[(Me_3C)_2C_5H_3]_2CeCl$ " (0.97g, 1.8 mmol) dissolved in tetrahydrofuran (30 mL) was added, via syringe, NaC_5H_5 (1.40 mL of a 1.13M solution in thf, 1.83 mmol). The yellow solution darkened and re-lightened slightly upon addition, then the solution color turned purple after ca. 15 min. The solution was stirred for 4 h, then the solvent was removed under reduced pressure. The purple and white solids were extracted with hexane (45 mL), filtered, and the filtrate was concentrated to ca. 10 mL. Cooling the extract to -20°C afforded purple crystals (0.40g, 39%), m.p. 140-144°C. An additional 0.17g (17%) of product can be obtained by concentrating the mother liquor to ca. 5 mL and cooling to -20°C. Anal. Calcd. for $C_{31}H_{47}Ce$: C, 66.5; H, 8.46. Found: C, 65.9; H, 8.39. IR: 1370m, 1360s, 1298w, 1257m, 1248m, 1230w, 1198mw, 1163mw, 1085w, 1052m, 1012s, 972w, 890w, 857w, 805s, 760s, 720mw, 675mw, 658w, 640w, 605w, 562w, 485w, 425w, 388w, 348mw, 260w, 215m cm^{-1} . 1H NMR (C_6D_6 , 30°C): 23.76 (2H, $\nu_{1/2}$ -21 Hz), 19.06 (4H, $\nu_{1/2}$ -35 Hz), 13.01 (5H, $\nu_{1/2}$ -24 Hz), -8.24 (36H, $\nu_{1/2}$ -9 Hz). The E.I. mass spectrum showed a molecular ion at 559 amu.



Potassium t-butylcyclopentadienide (43 mL of a 0.66M solution in thf, 28 mmol) was added, via syringe, to CeCl_3 (2.34g, 9.49 mmol) suspended in thf (50 mL). The suspension turned greyish-purple after ca. 30 min. The suspension was stirred for 18 h, then the solvent was removed under reduced pressure. The purple residue was extracted with hexane (1x90 mL, 1x30 mL, 50°C), filtered, and the filtrate was concentrated to ca. 10 mL. Cooling the extract to -80°C afforded a purple solid (3.7g, 78%), m.p. 85°C. In order to obtain a solid product, it is sometimes necessary to melt the crude product under vacuum to remove all of the thf. Anal. Calcd. for $\text{C}_{27}\text{H}_{39}\text{Ce}$: C, 64.4; H, 7.80. Found: C, 64.8; H, 7.85. IR: 1360s, 1267s, 1200m, 1189w, 1155s, 1045s, 1040s, 1017m, 975w, 912m, 850w, 818s, 710m, 670s, 610w, 587w, 448m, 370m, 350m, 257m cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 33°C): 21.80 (2H, $\nu_{1/2}$ -31 Hz), 7.74 (2H, $\nu_{1/2}$ -30 Hz), -9.35 (9H, $\nu_{1/2}$ -10 Hz). The E.I. mass spectrum showed a molecular ion at M/e = 803 amu.



Isopropylthiol (1.00 mL, 10.8 mmol) was added, via syringe, to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ (1.70g, 3.37 mmol) dissolved in hexane (30 mL). The purple solution was stirred for 18 h during which time the color gradually turned to magenta. The solvent was removed under reduced pressure. The pink solid was dissolved in hexane (30 mL), filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the extract to -20°C afforded magenta crystals (0.84g, 55%), m.p. 139-142°C. An additional 10-20% can be obtained by concentrating the mother liquor to ca. 7 mL and cooling to -20°C. Anal. Calcd for $\text{C}_{42}\text{H}_{66}\text{Ce}_2\text{S}_2$: C, 55.1; H, 7.27; S, 7.00. Found: C, 55.3; H, 7.28; S, 6.95. IR: 1272m, 1248w, 1200w, 1152s, 1045m, 1038m, 970w, 910w, 820s, 753s,

672m, 605m, 452w, 353w, 260w cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 32°C): 21.85 (4H, $\nu_{1/2} = 50$ Hz), 20.51 (4H, $\nu_{1/2} = 45$ Hz), -4.96 (18H, $\nu_{1/2} = 17$ Hz), -12.37 (1H), -17.49 (6H, $\nu_{1/2} = 20$ Hz). The E.I. mass spectrum showed a molecular ion at $M/e = 914$ amu. The molecular ion isotopic cluster was simulated: M/e (calcd.%, obsvd.%); 914 (100,100); 915 (48.4, 49.4); 916 (45.4, 44.6); 917 (18.1, 17.7); 918 (8.1, --).

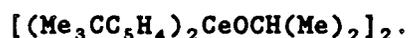
$[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeSC}_6\text{H}_5]_2$.

To $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ (0.91g, 1.8 mmol) dissolved in hexane (30 mL) was added, via syringe, thiophenol (0.12 mL, 1.7 mmol). After ca. one min a pink precipitate began to form in the purple solution. The mixture was stirred for 12 h, then the solvent was removed under reduced pressure. The pink residue was dissolved in toluene (30 mL), filtered, and the filtrate was concentrated to ca. 25 mL. Cooling the extract to -20°C afforded pink crystals that became a powder when exposed to vacuum (0.61g, 69%), m.p. $191-194^\circ\text{C}$. Anal. Calcd. for $\text{C}_{48}\text{H}_{62}\text{Ce}_2\text{S}_2$: C, 58.6; H, 6.34; S, 6.52. Found: C, 59.1; H, 6.47; S, 6.12. IR: 1570w, 1407w, 1300w, 1273m, 1200w, 1187w, 1165w, 1151m, 1120w, 1078m, 1060w, 1045m, 1038w, 1020m, 970w, 912w, 822m, 775m, 768s, 757mw, 740s, 720mw, 690s, 680m, 483w, 455w, 425w, 258m cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 28°C): 25.73 (4H, $\nu_{1/2} = 77$ Hz), 19.23 (4H, $\nu_{1/2} = 74$ Hz), 2.69 (2H), 1.14 (1H), -4.67 (2H), -8.79 (18H, $\nu_{1/2} = 18$ Hz). The E.I. mass spectrum did not give a molecular ion at $M/e = 983$ amu. The observed parent ion corresponds to $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeS}]_2$, $M^+ = 796$ amu.

$[(\text{MeC}_5\text{H}_4)_2\text{CeSCCMe}]_2$.

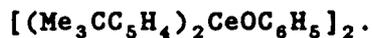
To $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{thf}$ (0.84g, 3.4 mmol) dissolved in diethyl ether (40 mL) was added, via syringe, t-butylthiol (0.38 mL, 3.4 mmol). The solution gradually turned from yellow to brown then to purple. The

solution was stirred for 12 h, then the solvent was removed in vacuo. The purple solid was extracted with hexane (2x30 mL), filtered, and the filtrate was concentrated to ca. 50 mL. Cooling the extract to -20°C afforded purple crystals (0.31 g, 24%), m.p. 266-268°C (dec). Anal. Calcd. for $C_{32}H_{48}Ce_2S_2$: C, 49.6; H, 5.98; S, 8.27. Found: C, 49.7; H, 5.81; S, 5.92. IR: 1300w, 1232w, 1205w, 1168w, 1142s, 1060w, 1040w, 1028m, 970w, 928m, 850w, 820s, 765s, 618m, 588m, 390m, 325m, 250s, 220w cm^{-1} . 1H NMR (C_6D_6 , 29°C): 20.54 (4H, $\nu_{1/2} \approx 80$ Hz), 18.79 (4H, $\nu_{1/2} \approx 90$ Hz), 4.71 (6H, $\nu_{1/2} = 26$ Hz), -22.22 (9H, $\nu_{1/2} = 20$ Hz).

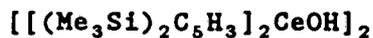


To $(Me_3CC_5H_4)_3Ce$ (1.78g, 2.96 mmol) dissolved in hexane (30 mL) was added, via syringe, isopropanol (0.23 mL, 3.0 mmol). The solution color gradually turned from purple to brown to green and finally to yellow, and a yellow precipitate was observed. The suspension was stirred for 6 h, then the solvent was removed under reduced pressure. The yellow solid was dissolved in toluene (50 mL), filtered, and the filtrate was concentrated to ca. 30 mL. Cooling the extract to -20°C for 3 hours, followed by cooling to -80°C yielded yellow micro-crystals (0.83g, 64%), m.p. 240-241°C. Anal. Calcd. for $C_{42}H_{66}Ce_2O_2$: C, 57.1; H, 7.53. Found: C, 56.9; H, 7.64. IR: 1270s (br), 1155m, 1110m, 1070w, 1048w, 1033w, 950m, 850w, 822m, 810w, 755s, 735m, 673m, 530w, 440w, 335m (br), 258w cm^{-1} . 1H NMR (C_6D_6 , 70°C): 16.90 (8H, $\nu_{1/2} \approx 90$ Hz), 0.84 (18H, $\nu_{1/2} = 20$ Hz), -3.25 (1H, $\nu_{1/2} = 17$ Hz), -17.34 (6H, $\nu_{1/2} = 34$ Hz). 1H NMR (C_6D_6 , 32°C): 18.4 (8H, $\nu_{1/2} \approx 110$ Hz), 0.98 (18H, $\nu_{1/2} = 28$ Hz), -3.87 (1H, $\nu_{1/2} = 25$ Hz), -19.90 (6H, $\nu_{1/2} = 67$ Hz). The E.I. mass spectrum showed a molecular ion at $M/e = 882$ amu. The

molecular ion isotopic cluster was simulated: M/e (calcd.%, obsvd.%); 882 (100,100); 883 (46.9, 22.3); 884 (36.2, 10.3); 885 (13.6, 28.0).



To $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ (0.70g, 1.4 mmol) dissolved in hexane (30 mL) was added, via cannula, phenol (0.13g, 1.4 mmol) dissolved in hexane (10 mL). The purple solution turned yellow upon addition with formation of a yellow precipitate. The suspension was stirred for 4 h, then the solvent was removed under reduced pressure. The yellow solid was extracted with toluene (45 mL), filtered, and the filtrate was concentrated to ca. 20 mL. Cooling the extract to -20°C afforded yellow crystals (0.33g, 50%), m.p. $258-260^\circ\text{C}$. Anal. Calcd. for $\text{C}_{48}\text{H}_{62}\text{Ce}_2\text{O}_2$: C, 60.6; H, 6.57. Found: C, 61.2; H, 6.59. IR: 1588s, 1575m, 1273m, 1222s, 1160m, 1150w, 1065m, 1048m, 1035m, 1015m, 975w, 915w, 890w, 835m, 818s, 810m, 760s, 735m, 720m, 692m, 672m, 567m, 448m, 350m, 262m cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 30°C): 21.52 (4H, $\nu_{1/2}=72$ Hz), 14.98 (4H, $\nu_{1/2}=73$ Hz), -3.41(1H), -4.57 (18H, $\nu_{1/2}=16$ Hz), -5.03 (2H, d, $J=6.8$ Hz), -16.23 (2H). The E.I. mass spectrum did not show a molecular ion at M/e = 950 amu. The observed parent ion was M/e = 503 which corresponds to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$



To $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ (0.49g, 0.64 mmol) dissolved in tetrahydrofuran (20 mL) was added, via micro-liter syringe, degassed H_2O (11.5 μL , 0.64 mmol). The blue solution turned yellow upon addition. The solution was stirred for 20 min, then the solvent was removed under reduced pressure. The yellow residue was dissolved in hexane (45 mL), filtered, and the filtrate was concentrated to ca. 25 mL. Cooling the extract to -20°C afforded gold crystals, (0.21g,

57%), m.p. 229-232°C (dec). Concentrating the mother liquor to ca. 7 mL and cooling the extract to -20°C affords an additional 0.10g (14%) of product. Anal. Calcd. for $C_{44}H_{86}Ce_2O_2Si_8$: C, 45.9; H, 7.52. Found: C, 42.5; H, 7.66. IR: 3655m, 1372s, 1365m, 1318mw, 1249s, 1240s, 1208mw, 1075s, 1052w, 970w, 918ms, 835s, 822s, 770m, 750ms, 720w, 688m, 632m, 620mw, 600m, 475m, 387mw, 370mw, 354m, 305m, 290w, 270w cm^{-1} . 1H NMR (C_6D_6 , 29°C): -5.90 (36H, $\nu_{1/2}$ -22 Hz), no other resonances could be located between 70°C and -70°C. However, the variable temperature 1H NMR spectra show that the ring $SiMe_3$ resonance broadens with cooling and splits into two peaks of equal intensity below -18°C. The activation energy of this barrier is calculated to be 13 ± 3 kcal·mol $^{-1}$. The E.I. mass spectrum showed a molecular ion at $M/e = 1132$ amu ($M^+ - H_2O$). The molecular ion isotopic cluster was simulated: M/e (calcd%, obsvd%); 1132 (100, 100); 1133 (89.9, 89.0); 1134 (91.3, 93.1); 1135 (56.5, 71.3); 1136 (33.0, 53.8); 1137 (15.3, 28.6).



$(\text{MeC}_5\text{H}_4)_3\text{UOMe}$

Methanol (0.08 mL, 2.0 mmol) was added, via syringe, to $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{thf}$ (1.15g, 2.10 mmol) dissolved in diethyl ether (30 mL). The red solution slowly turned green after addition. The solution was stirred for 20 h, then the solvent was removed under reduced pressure. The green solid was dissolved in hexane (40 mL), filtered, and the filtrate was concentrated to ca. 10 mL. Cooling the extract to -20°C afforded green micro crystals (0.32g, 30%), m.p. $274-275^\circ\text{C}$ (turns brown at 120°C). Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{OU}$: C, 45.1; H, 4.78. Found: C, 44.8; H, 4.78. IR: 1260w, 1248w, 1168w, 1150w, 1070w, 1045w, 1030w, 970w, 930m, 890w, 820s (br), 760s, 608m, 422s, 330s, 225s cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 29°C): 45.13 (3H, $\nu_{1/2}=12$ Hz), -0.32 (9H, $\nu_{1/2}=8.5$ Hz), -10.60 (6H, $\nu_{1/2}=12$ Hz), -22.41 (6H, $\nu_{1/2}=11$ Hz). The E.I. mass spectrum showed a molecular ion at $M/e = 506$ amu.

 $(\text{MeC}_5\text{H}_4)_3\text{UOCHMe}_2$

Isopropanol (0.13 mL, 1.7 mmol) was added, via syringe, to $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{thf}$ (0.90g, 1.6 mmol) dissolved in diethyl ether (40 mL). The red solution color turned green upon addition. The solution was stirred for 5 h, then the solvent removed under reduced pressure. The green solid was dissolved in hexane (40 mL), filtered, and the filtrate was concentrated to ca. 10 mL. Cooling the extract to -20°C yielded flaky-green needles (0.32g, 37%), m.p. $196-200^\circ\text{C}$. Anal. Calcd. for $\text{C}_{21}\text{H}_{28}\text{OU}$: C, 47.2; H, 5.28. Found: C, 47.0; H, 5.11. IR: 1330m, 1240w, 1160m, 1130s, 1165w, 1045m, 1035m, 1030m, 990s, 930w, 885w, 842s, 820m, 760s, 605m, 550s, 450m, 421m, 330s, 228s cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 28°C): 55.51 (1H, $\nu_{1/2}=20$ Hz), 15.65 (6H, $\nu_{1/2}=8$ Hz), -1.54 (9H, $\nu_{1/2}=3$ Hz), -13.93 (6H, $\nu_{1/2}=8$ Hz), -23.31 (6H, $\nu_{1/2}=8$ Hz). The E.I. mass spectrum showed a molecular ion at $M/e = 534$ amu.

$(\text{MeC}_5\text{H}_4)_3\text{UOC}_6\text{H}_5$

To $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{thf}$ (0.81g, 1.5 mmol) dissolved in diethyl ether (40 mL) was added, via cannula, $\text{C}_6\text{H}_5\text{OH}$ (0.14g, 1.5 mmol) dissolved in diethyl ether (10 mL). The red solution color became green upon addition with some green precipitate. The solution was stirred for 3 h, then the solvent was removed under reduced pressure. The green solid was dissolved in hexane (40 mL, 50°C) and filtered. Cooling the filtrate to -20°C afforded green crystals (0.29g, 34%), m.p. 127-128°C. Anal. Calcd. for $\text{C}_{24}\text{H}_{26}\text{OU}$: C, 50.7; H, 4.61. Found: C, 50.6; H, 4.53. IR: 1580s, 1300w, 1258s, 1158m, 1150w, 1065w, 1049w, 1029w, 1018w, 995w, 973w, 931w, 884w, 861s, 845w, 838w, 812w, 775m, 762s, 720m, 690m, 600m, 520w, 442w, 337w, 238w cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 29°C): 4.72 (2H, t, J=7.8 Hz); 3.96 (2H, t, J=7.8 Hz); -3.11 (9H, $\nu_{1/2}$ -3 Hz), -4.75 (6H, $\nu_{1/2}$ -7 Hz), -10.48 (1H, $\nu_{1/2}$ ≈10 Hz), -11.97 (6H, $\nu_{1/2}$ -7 Hz). The E.I. mass spectrum showed a molecular ion at M/e = 569 amu.

 $(\text{MeC}_5\text{H}_4)_3\text{USCHMe}_2$

Isopropylthiol (0.15 mL, 1.6 mmol) was added, via syringe, to $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{thf}$ (0.84g, 1.5 mmol) dissolved in diethyl ether (30 mL). The red solution color became brown-green upon addition. The solution was stirred for 30 min, then the solvent was removed under reduced pressure. The brown-green solid was extracted with hexane (2 x 25 mL), filtered, and the filtrate was concentrated to ca. 35 mL. Cooling the extract to -20°C yielded golden-brown flakes (0.23g, 27%), m.p. 121-123°C. Anal. Calcd for $\text{C}_{21}\text{H}_{28}\text{SU}$: C, 45.8; H, 5.13; S, 5.82. Found: C, 44.8; H, 5.13; S, 5.31. IR: 1305w, 1260w, 1235w, 1142m, 1070w, 1045w, 1032m, 972w, 928w, 890w, 863m, 851m, 847m, 795m, 775s, 720s, 624m, 605m, 570w, 440mw, 363mw, 341m, 331m, 242m cm^{-1} . $^1\text{H NMR}$

(C₆D₆, 28°C): -1.24 (6H, $\nu_{1/2}$ -7 Hz), -1.58 (9H, $\nu_{1/2}$ -3 Hz), -8.77 (6H, $\nu_{1/2}$ -7 Hz), -19.67 (6H, d, J=7 Hz), -44.72 (1H, sept, J=7 Hz; only 3 of the 7 lines are observed). The E.I. mass spectrum showed a molecular ion at M/e = 550 amu.

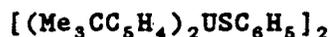
(MeC₅H₄)₃UOC₆F₅

To (MeC₅H₄)₃U·thf (0.69g, 1.3 mmol) dissolved in diethyl ether (30 mL) was added, via cannula, C₆F₅OH (0.24g, 1.3 mmol) dissolved in diethyl ether (10 mL). The red solution color turned red-brown upon addition. The solution was stirred for 3 h, then the solvent was removed under reduced pressure. The red-brown solid was extracted with hexane (30 mL, 50°C), filtered, and the filtrate was concentrated to ca. 20 mL. Cooling the extract to -20°C afforded red-brown needles (0.24g, 29%), m.p. 120-122°C. Anal. Calcd. for C₂₄H₂₁F₅OU: C, 43.8; H, 3.21. Found: C, 44.0; H, 3.20. IR: 1645mw, 1620w, 1578w, 1372s, 1308m, 1258w, 1245w, 1169s, 1065w, 1018s, 995w, 970ms, 930w, 845m, 775s, 719m, 650m, 605w, 478m, 340m, 240m cm⁻¹. ¹H NMR (C₆D₆, 31°C): 3.55 (2H, $\nu_{1/2}$ -10 Hz), -5.14 (3H, $\nu_{1/2}$ -8 Hz), -9.92 (2H, $\nu_{1/2}$ -9 Hz). The E.I. mass spectrum showed a parent ion at M/e = 658 amu.

(Me₃CC₅H₄)₃USC₈H₅

To (Me₃CC₅H₄)₃U (1.07g, 1.76 mmol) dissolved in hexane (30 mL) was added, via syringe, thiophenol (0.18 mL, 1.8 mmol). The green solution color turned red with a light red-brown precipitate. The solution was stirred for 5 h, then the solvent was removed under reduced pressure. The red solid was extracted with hexane (30 mL), filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the extract to -20°C afforded red crystals (0.28g, 22%), m.p. 142-143°C. Anal. Calcd. for C₃₃H₄₄SU: C, 55.8; H, 6.24; S, 4.51. Found: C,

52.7; H, 6.32; S, 4.65. IR: 1575m, 1300w, 1272m, 1198w, 1168w, 1155ms, 1070mw, 1052w, 1040w, 1021m, 970m, 838m, 798m, 788m, 772ms, 765s, 739s, 720m, 698m, 678mw, 611m, 482w, 418w, 238mw cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 28°C): 3.64 (6H, $\nu_{1/2} \approx 7$ Hz), -1.38 (2H), -2.43 (27H, $\nu_{1/2} \approx 4$ Hz), -8.43 (1H), -12.16 (6H, $\nu_{1/2} \approx 7$ Hz), -21.23 (2H, d, $J=7.8$ Hz). The E.I mass spectrum showed a weak parent ion at $M/e = 710$ amu.



To $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{U}$ (1.07g, 1.78 mmol) dissolved in hexane (15 mL) and cooled to -25°C was added, via syringe $\text{C}_6\text{H}_5\text{SH}$ (0.18 mL, 1.8 mmol). The solution color turned from green to red upon addition. After ca. 2 min a green precipitate began forming. The suspension was stirred for an additional 15 min, and the precipitate was allowed to settle. The hexane was removed by filtration. The remaining green, microcrystalline solid was washed with hexane (2x10 mL, -25°C). The solid was extracted with toluene (45 mL, -30°C). This caused the solution color to become red. The solution was filtered, and the filtrate was concentrated to ca. 30 mL. Cooling to -20°C afforded dark green crystals (0.25g, 24%), m.p. $112-113^\circ\text{C}$ (dec). Anal. Calcd. for $\text{C}_{48}\text{H}_{62}\text{S}_2\text{U}_2$: C, 48.9; H, 5.30; S, 5.44. Found: C, 48.5; H, 5.05; S, 4.24. IR: 1570m, 1405w, 1300w, 1272m, 1200w, 1186w, 1165w, 1150m, 1118w, 1075m, 1062w, 1038m, 1018m, 970w, 912mw, 845w, 821m, 812w, 772m, 763s, 757mw, 740s, 718mw, 690s, 672m, 481mw, 453w, 424w, 239mw cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 28°C): 6.28 (4H, $\nu_{1/2} \approx 50$ Hz), -0.87 (1H), -1.92 (2H, d, $J=6.8$ Hz), -7.58 (4H, $\nu_{1/2} \approx 58$ Hz), -17.63 (18H, $\nu_{1/2} \approx 13$ Hz), -21.07 (2H). The NMR solution color gradually turned red with time. The $^1\text{H NMR}$ spectrum contained $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{USC}_6\text{H}_5$ impurities presumably because of ligand redistribution and/or oxidation. The integrated

intensity of these resonances grew with time relative to those of the $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{USC}_6\text{H}_5]_2$ complex.



To $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ (0.75g, 1.2 mmol) dissolved in hexane (15 mL) was added, via cannula, $(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{H}$ (0.28g, 1.2 mmol) dissolved in hexane (15 mL). The green solution color turned red with formation of a red precipitate upon addition. After stirring for 30 min the red precipitate re-dissolved. The red solution was filtered at which point red plates crystallized out. These were redissolved with an additional 60 mL hexane. Cooling the solution to -20°C afforded red needles (0.62g, 60%), m.p. $150\text{-}152^\circ\text{C}$. Anal. Calcd. for $\text{C}_{38}\text{H}_{44}\text{MoO}_3\text{Si}_3\text{U}$: C, 42.9; H, 4.96. Found: C, 43.8; H, 5.13. IR: 1923s, 1832s, 1575s (br), 1308w, 1247s, 1170m, 1115w, 1070w, 1041m, 1005w, 975w, 895m, 833s, 813m, 805m, 794m, 782m, 750m, 688m, 632m, 621m, 610m, 590m, 495s, 415s, 330m, 310m, 270w, 240m cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 29°C): 12.78 (6H, $\nu_{1/2} = 6$ Hz), -3.06 (5H, $\nu_{1/2} = 2$ Hz), -6.94 (27H, $\nu_{1/2} = 2$ Hz), -9.64 (6H, $\nu_{1/2} = 6$ Hz). X-ray quality crystals were grown from diethyl ether (-20°C). Data was collected, but the structure could not be solved because of disorder and/or twinning. The molecule crystallizes in the monoclinic space group, $\text{P}2_1$; $a = 13.458\text{\AA}$, $b = 12.842\text{\AA}$, $c = 10.982\text{\AA}$, $\beta = 101.7^\circ$. Preliminary refinement confirms a $\mu\text{-CO}$ structure with U-O-C and O-C-Mo angles of 157° and 180° , respectively.



To $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ (0.83g, 1.3 mmol) dissolved in hexane (15 mL) was added, via cannula, $(\text{Me}_5\text{C}_5)\text{Mo}(\text{CO})_2\text{H}$ (0.40g, 1.3 mmol) dissolved in hexane (15 mL). The green solution color immediately turned red upon

addition. No precipitate formed. The solution was stirred for 14 h, then the solvent was removed under reduced pressure. A red oily solid remained. All attempts at solidifying this material failed, and therefore it was characterized only by ^1H NMR and IR spectroscopy. ^1H NMR (C_6D_6 , 29°C): 11.51 (6H, $\nu_{1/2} = -7$ Hz), -3.94 (15H, $\nu_{1/2} = -3$ Hz), -6.52 (27H, $\nu_{1/2} = -2$ Hz), -9.22 (6H, $\nu_{1/2} = -6$ Hz). IR: 2010mw, 1928s, 1845s, 1718m (br), 1518s (br), 1247m, 1172w, 1112mw, 1065w, 1040mw, 900w, 835m, 805w, 795w, 782w, 755w, 690w, 632w, 618w, 590w, 490w, 420w, 270w cm^{-1} .



To $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{U}$ (0.65g, 1.1 mmol) dissolved in hexane (15 mL) was added, via cannula, $(\text{C}_5\text{H}_5)\text{W}(\text{CO})_2\text{H}$ (0.36g, 1.1 mmol) dissolved in hexane (15 mL). The green solution color turned red with formation of a red precipitate upon addition. The suspension was stirred for 8 h, then the solvent was removed under reduced pressure. The red-brown solid was dissolved in diethyl ether (60 mL), filtered, and the filtrate was concentrated to ca. 50 mL. Cooling to -20°C , followed by cooling to -80°C afforded thin red needles (0.62g, 60%). ^1H NMR (C_6D_6 , 28°C): 20.50 (6H, $\nu_{1/2} = -6$ Hz), -2.50 (5H, $\nu_{1/2} = -2$ Hz), -9.30 (27H, $\nu_{1/2} = -3$ Hz), -19.08 (6H, $\nu_{1/2} = -6$ Hz). IR: 1920s, 1831s, 1715m (br), 1558s (br), 1265m, 1150w, 1112w, 1065w, 1050w, 1038w, 1002w, 972w, 890w, 850w, 810w, 800mw, 788m, 775mw, 735w, 720m, 675w, 665, 628m, 595m, 505m, 485mw cm^{-1} . Further characterization was not carried out as the IR spectrum is consistent with an isocarbonyl structure.

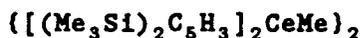
CHAPTER THREE

$[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeMe}]_2$.

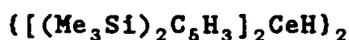
Method A: To $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ (1.22g, 2.42 mmol) dissolved in hexane (25 mL) was added, via syringe, MeLi (2.60 mL of a 0.91M solution in hexane, 2.4 mmol). The purple solution color immediately turned brown and then orange with the formation of a light-colored precipitate. The solution was stirred for 45 min, then the solvent was removed under reduced pressure. The orange solid was extracted with hexane (60 mL), filtered, and the filtrate was concentrated to ca. 45 mL. Cooling the extract to -20° for two hours followed by cooling to -80°C for 6-8 hours yielded orange crystals (0.64g, 67%), m.p. $125\text{-}129^\circ\text{C}$. Anal. Calcd. for $\text{C}_{38}\text{H}_{58}\text{Ce}_2$: C, 57.4; H, 7.35. Found: C, 57.6; H, 7.37. IR: 1300w, 1272m, 1195w, 1150m, 1045m, 1035m, 1012m, 970w, 910w, 848w, 815s, 808m, 760s, 750s, 720m, 672s, 465m, 450m, 367w, 350w, 295m, 255m cm^{-1} . ^1H NMR (C_6D_6 , 30°C): 21.80 (4H, $\nu_{1/2} = 20$ Hz), 16.28 (4H, $\nu_{1/2} = 20$ Hz), -5.75 (18H, $\nu_{1/2} = 7$ Hz), -48.23 (3H, $\nu_{1/2} = 70$ Hz). This compound decomposes to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ and an uncharacterized yellow solid in solution. The E.I. mass spectrum does not give a parent molecular ion; the highest mass fragment corresponds to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ ($M/e = 503$ amu).

Method B: To $[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeSCH}(\text{Me})_2]_2$ (1.30g, 1.42 mmol) dissolved in hexane (50 mL) was added, via syringe, MeLi (3.12 mL of a 0.91M solution in diethyl ether, 2.8 mmol). The magenta solution color turned orange with the formation of a light-colored precipitate. The solution was stirred for 30 min, then the solvent was removed under reduced pressure. The orange solid was extracted with hexane (50 mL), filtered, and the filtrate was concentrated to ca. 40 mL. Cooling the extract to -20°C followed by cooling to -80°C afforded

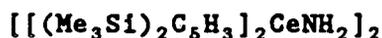
orange crystals (0.73g, 65%). All physical properties and analytical results were identical to those observed in Method A.



To $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ (1.16g, 1.51 mmol) dissolved in hexane (30 mL) was added, via syringe, MeLi (1.54 mL of a 0.98M solution in diethyl ether, 1.51 mmol). The blue solution color gradually turned orange over a period of ca. 30 min with the formation of a white precipitate. The suspension was stirred for 1 h, then the solvent was removed under reduced pressure. The orange residue was extracted with hexane (2x30 mL), filtered, and the filtrate was concentrated to ca. 40 mL. Cooling the extract to -20°C for 6-8 h, followed by cooling to -80°C afforded orange crystals (0.48g, 55%), m.p. $152-154^\circ\text{C}$ (with evolution of gas and decomposition). An additional 0.08g (9%) can be isolated by concentrating the mother liquor to ca. 15 mL and cooling to -80°C . Anal. Calcd. for $\text{C}_{46}\text{H}_{90}\text{Ce}_2\text{Si}_8$: C, 48.1; H, 7.90. Found: C, 43.8; H, 8.12. IR: 1372s, 1360m, 1312w, 1241s, 1205mw, 1168w, 1149w, 1072s, 1050w, 965w, 918s, 830s, 775m, 750ms, 720mw, 685m, 635m, 619m, 478m, 370m, 348w, 328w, 300m, 278m, 235w cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 30°C): 26.2 (6H, $\nu_{1/2} \approx 100$ Hz), -4.10 (36H, $\nu_{1/2} = 7$ Hz), -33 (3H, $\nu_{1/2} > 100$ Hz). The ring CH protons and the bridging CH_3 protons could not be resolved between 70° and -70°C . At -72°C there are two SiMe_3 resonances in a 1:1 ratio at -7.43 and -7.92 ppm. Resonances due to $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeOH}_2$ (-5.89 ppm) and $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ (-4.48 ppm) impurities are often observed in the spectrum, in variable amounts; the resonance due to $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ usually increases with time and the resonance due to the hydroxide does not.

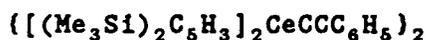


$(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeMe})_2$ (0.20g, 0.17 mmol) was dissolved in hexane (30 mL) and transferred to a high pressure flask (Fisher-Porter bottle) via cannula. The flask was charged with H_2 to a pressure of ca. 10 atm. The orange solution color gradually turned cherry red after about 5 min. The solution was stirred for 90 min, transferred to a Schlenk tube, and the solvent was removed under reduced pressure. The pink residue was dissolved in hexane (30 mL), filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the extract to -20°C afforded red-pink crystals (0.08g, 41%), m.p. $180\text{-}183^\circ\text{C}$. An additional 0.04g (20%) of product can be obtained by concentrating the mother liquor to ca. 5 mL and cooling to -20°C . Anal. Calcd. for $\text{C}_{44}\text{H}_{86}\text{Ce}_2\text{Si}_8$: C, 47.2; H, 7.74. Found: C, 47.5; H, 7.87. IR: 1400w, 1372s, 1360m, 1314mw, 1245s, 1205mw, 1149w, $\approx 1095\text{s}$ (very broad), 1072s, 965vw, 915s, 830s, 771m, 748m, 718w, 685m, 631ms, 619m, 515w, 475ms, 371m, 349w, 331vw, 302m, 275w, 237w cm^{-1} . IR spectrum of the deuteride: 1400w, 1314mw, 1245s, 1205mw, 1170w, 1150w, 1072s, 1051w, 968w, 915s, 830s, 805s (very broad), 770m, 748s, 718w, 685m, 631ms, 619m, 565w, 520w, 475ms, 321m, 349mw, 331w, 300m, 275mw, 235w cm^{-1} ($\nu\text{Ce-H} / \nu\text{Ce-D} = 1.36$). $^1\text{H NMR}$ (C_6D_6 , 30°C): -6.47 (ring SiMe_3 , $\nu_{1/2} = 16$ Hz). The ring CH protons and the bridging hydride proton are not observed between 70° and 30°C . Resonances due to $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeOH})_2$ (-5.89 ppm) and $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ (-4.48 ppm) impurities are always observed in the spectrum. An unidentified compound gives rise to a peak at -7.02 ppm.



To $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeMe})_2$ (0.28g, 0.24 mmol) dissolved in hexane (25 mL) was added, via cannula, an ammonia saturated hexane solution

(20 mL). The orange solution color turned yellow; the solution was stirred for 10 min, then the solvent was removed under reduced pressure. The yellow solid was dissolved in hexane (30 mL), filtered, and the filtrate was concentrated to ca. 25 mL. Cooling the extract to -20°C afforded yellow crystals (0.20g, 73%). The melting point was not taken since the compound is impure. Anal. Calcd. for $\text{C}_{44}\text{H}_{88}\text{Ce}_2\text{N}_2\text{Si}_8$: C, 45.9; H, 7.71; N, 2.44. Found: C, 39.2; H, 7.47; N, 1.24. IR: 3350w, 3285w, 1374s, 1362m, 1310w, 1245m, 1240m, 1211w, 1205w, 1150w, 1075ms, 1050w, 972w, 918ms, 825sm, 770m, 745ms, 718m, 685m, 635m, 620mw, 590m, 475m, 368mw, 342mw, 295mw cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 29°C): -3.67 (ring SiMe_3 , $\nu_{1/2} = 20$ Hz). Resonances due to the $([(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeOH})_2$ (-5.89 ppm) impurity are always observed in the spectrum, sometimes to the extent of ca. 30%. The E.I. mass spectrum shows a molecular ion at $M/e = 1148$ amu and fragments due to successive ring and/or NH_2 loss. The molecular ion isotopic cluster was simulated: M/e (calcd.%, obsvd.%); 1148 (100, 100); 1149 (90.6, 88.4); 1150 (91.7, 92.5); 1151 (57.0, 59.5); 1152 (33.3, 31.3).

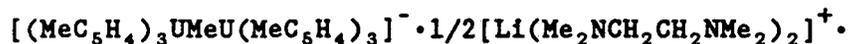


To $([(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeMe})_2$ (0.20g, 0.17 mmol) dissolved in hexane (30 mL) was added, via syringe, phenylacetylene (38 μL , 0.35 mmol). The orange solution color darkened slightly and gas evolution was observed. The solution was stirred for 2 h, then the solvent was removed under reduced pressure. The orange residue was extracted with hexane (30 mL), filtered, and the filtrate was concentrated to ca. 20 mL. Cooling the extract to -20°C afforded orange crystals (0.10g, 45%), m.p. $193\text{-}195^{\circ}\text{C}$ (dec). An additional 0.05g (22%) of compound can be isolated by concentrating the mother liquor to ca. 7 mL and cooling to -20°C . Anal. Calcd. for $\text{C}_{60}\text{H}_{94}\text{Ce}_2\text{Si}_8$: C, 54.6; H, 7.18. Found:

C, 51.3; H, 7.62. IR: 2015mw, 1370s, 1310w, 1242m, 1202w, 1115w, 1105w, 1072ms, 1018w, 968w, 918ms, 820s, 768mw, 765w, 745ms, 718m, 678m, 630m, 615m, 550mw, 472m, 370mw, 345w, 300ms cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 30°C): 33.6 (4H, $\nu_{1/2} = -50$ Hz), 16.7 (2H, $\nu_{1/2} = -75$ Hz), 2.01 (1H), 1.61 (2H), -2.65 (2H), -3.23 (36H, $\nu_{1/2} = -14$ Hz). Resonances due to $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{CeOH}\}_2$ (-5.89 ppm) and $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ (-4.48 ppm) impurities are often observed in the spectrum. The E.I. mass spectrum does not give a molecular ion.

$[(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{UMe}]_2$.

To $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{U}$ (0.92g, 1.5 mmol) dissolved in hexane (30 mL) was added, via syringe, MeLi (1.68 mL of a 0.91M solution in hexane, 1.53 mmol). The green solution color lightened slightly upon addition, and a green precipitate formed. The suspension was stirred for 40 min, then the solvent was removed under reduced pressure. The dark green solid was extracted with hexane (25 mL), filtered, and the filtrate was concentrated to ca. 20 mL. Cooling the extract to -20° afforded dark green crystals (0.25g, 33%), m.p. $111-115^\circ\text{C}$. An additional 0.13g (17%) of product can be obtained by concentrating the mother liquor to ca. 10 mL and cooling to -20°C . Anal. Calcd. for $\text{C}_{38}\text{H}_{58}\text{U}_2$: C, 46.1; H, 5.90. Found: C, 46.5; H, 5.98. IR: 1300w, 1270m, 1195w, 1150m, 1041mw, 1032mw, 1012mw, 970w, 908mw, 848w, 812m, 806m, 760s, 750s, 718m, 667s, 468w, 450w, 350w, 288m, 245w cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 30°C): 8.08 (4H, $\nu_{1/2} = -50$ Hz), 1.11 (4H, $\nu_{1/2} = -50$ Hz), -20.02 (18H, $\nu_{1/2} = -11$ Hz), -139.25 (3H, $\nu_{1/2} = -68$ Hz). This compound decomposes to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{U}$ and other uncharacterized products in solution.



To $(\text{MeC}_5\text{H}_4)_3\text{U} \cdot \text{thf}$ (0.91g, 1.66 mmol) dissolved in diethyl ether (30 mL) and cooled to -30°C was added, via syringe, tmed (0.25 mL, 1.66 mmol). There was no observable change upon addition. Then, MeLi (1.70 mL of a 0.97M solution in diethyl ether, 1.65 mmol) was added. A red precipitate formed instantly upon addition. The suspension was stirred for 30 min at -10°C , then the solvent was removed under reduced pressure. The red solid was extracted with diethyl ether (100 mL), filtered, and the filtrate was concentrated to ca. 80 mL. Cooling the extract to -20°C afforded red crystals (0.20g, 19%), m.p. $81-85^\circ\text{C}$. An additional 0.07g (7%) can be obtained by concentrating the mother liquor to ca. 25 mL and re-cooling to -20°C . Anal. Calcd. for $\text{C}_{103}\text{H}_{161}\text{Li}_3\text{N}_8\text{U}_4$: C, 50.0; H, 6.50; N, 4.49. Found: C, 49.4; H, 7.26; N, 6.49. IR: 1285s, 1246m, 1180mw, 1155m, 1125m, 1095mw, 1060m, 1040m, 1028s, 1010m, 970w, 942s, 925m, 846mw, 810s, 735s, 638w, 608m, 593w, 500m (br), 445mw, 353m, 325m (br), 272 cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 30°C): 6.11 (12H, $\nu_{1/2}=100\text{ Hz}$), 2.23 (broad), -5.42 (18H, $\nu_{1/2}=109\text{ Hz}$), -10.78 (12H, $\nu_{1/2}=100\text{ Hz}$). $^1\text{H NMR}$ (C_7D_8 , -70°C): 14.43 (12H), 6.17 (2H), 3.21 (1.5H), 2.63 (4H), 2.35 (4H), 2.10 (12H), 1.50 (12H), -8.08 (18H), -18.70 (12H), -284.66 (3H). The E.I. mass spectrum shows fragments at 489 amu $[(\text{MeC}_5\text{H}_4)_3\text{UMe} - 1]$, 475 amu $[(\text{MeC}_5\text{H}_4)_3\text{U}]$, 396 amu $[(\text{MeC}_5\text{H}_4)_2\text{U}]$, and 316 amu $[(\text{MeC}_5\text{H}_4)\text{U}]$.

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