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Authors
Windorff, Cory J
MacDonald, Matthew R
Meihaus, Katie R
et al.

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Uranium Complexes

Expanding the Chemistry of Molecular U^{2+} Complexes: Synthesis, Characterization, and Reactivity of the $\{[C_5H_3(SiMe_3)_2]_3U\}^-$ Anion

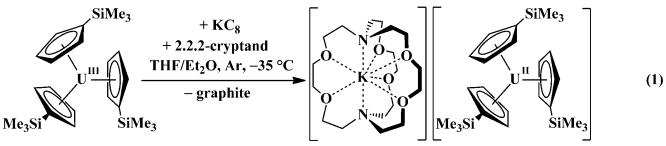
Cory J. Windorff,[a] Matthew R. MacDonald,[a] Katie R. Meihaus,[b] Joseph W. Ziller,[a] Jeffrey R. Long,*[b] and William J. Evans*[a]

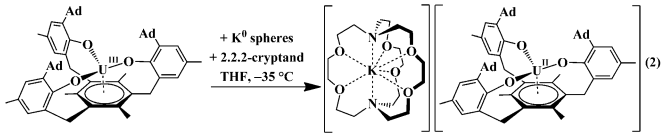
Abstract: The synthesis of new molecular complexes of U^{2+} has been pursued to make comparisons in structure, physical properties, and reactivity with the first U^{2+} complex, [K(2.2.2-cryptand)][Cp′$_3$U], **1** (Cp′ = $C_5H_4SiMe_3$). Reduction of Cp″$_3$U [Cp″ = $C_5H_3(SiMe_3)_2$] with KC_8 in the presence of 2.2.2-cryptand or 18-crown-6 generates [K(2.2.2-cryptand)][Cp″$_3$U], **2-K(crypt)**, or [K(18-crown-6)(THF)$_2$][Cp″$_3$U], **2-K(18c6)**, respectively. The UV/Vis spectra of **2-K** and **1** are similar, and they are much more intense than those of U^{3+} analogues. Variable temperature magnetic susceptibility data for **1** and **2-K(crypt)** reveal lower room temperature $\chi_M T$ values relative to the experimental values for the $5f^3$ U^{3+} precursors. Stability studies monitored by UV/Vis spectroscopy show that **2-K(crypt)** and **2-K(18c6)** have $t_{1/2}$ values of 20 and 15 h at room temperature, respectively, vs. 1.5 h for **1**. Complex **2-K(18c6)** reacts with H_2 or $PhSiH_3$ to form the uranium hydride, [K(18-crown-6)(THF)$_2$][Cp″$_3$UH], **3**. Complexes **1** and **2-K(18c6)** both reduce cyclooctatetraene to form uranocene, $(C_8H_8)_2U$, as well as the U^{3+} byproducts [K(2.2.2-cryptand)][Cp′$_4$U], **4**, and Cp″$_3$U, respectively.

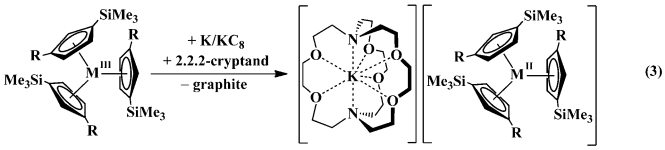
Introduction

A critical aspect for understanding the chemistry of an element and the reactivity of its molecules is the range of available oxidation states. Accordingly, extensive studies have been made to establish the limits of oxidation states for all the elements in the periodic table. Although uranium has received extra scrutiny because of its applications in nuclear energy, the number of oxidation states found in isolable molecular species was limited to +3 through +6 for many years.

Recently, however, the organometallic chemistry of uranium has revealed that the +2 oxidation state is accessible for uranium in the proper ligand environment. The first example of a crystallographically characterized, molecular, U^{2+} complex, [K(2.2.2-cryptand)][Cp′$_3$U], **1**, was obtained by reduction of Cp′$_3$U (Cp′ = $C_5H_4SiMe_3$) with potassium graphite (KC_8) in the presence of 2.2.2-cryptand at −35 °C [Eq. (1)].[1] Subsequently, a second example was obtained by Meyer and co-workers in a tris(aryloxide)arene ligand environment by potassium reduction of [(^{Ad,Me}ArO)$_3$mes]U [Eq. (2)].[2] These reactions are variations of reductions examined with Cp″$_3$M [Cp″ = $C_5H_3(SiMe_3)_2$; M = La[3] and Th[4]] and with Cp′$_3$Ln[5] to make new +2 ions of the rare earth metals and thorium as depicted in Equation (3).







R = $SiMe_3$; M = La, Th

R = H; M = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu, U

The existence of the $(Cp''_3M)^-$ anions for M = La and Th [Eq. (3)], and of $(Cp'_3U)^-$, [Eq. (1)], suggested that the analogous Cp″ complex of U^{2+}, namely $(Cp''_3U)^-$, **2**, was a reasonable synthetic target. The reactivity/stability of **2** was of particular interest since **1** is so reactive that it is difficult to characterize its physical properties. We report here that the reduction

[a] C. J. Windorff, Dr. M. R. MacDonald, Dr. J. W. Ziller, Prof. W. J. Evans
Department of Chemistry, University of California–Irvine
Irvine, CA 92697 (USA)
E-mail: wevans@uci.edu

[b] Dr. K. R. Meihaus, Prof. J. R. Long
Department of Chemistry, University of California–Berkeley
Berkeley, CA 94720 (USA)
E-mail: jrlong@berkeley.edu

Supporting information and ORCIDs for some of the authors for this article are available on the WWW under http://dx.doi.org/10.1002/chem.201503583: NMR, UV/Vis & NIR spectra, selected bond lengths, additional magnetic data and crystallographic data (CIF) for **4**, **5**, Cp′$_2$Pb and Cp′$_3$U(THF).

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chemistry of Cp''_3U leads to new examples of U^{2+} complexes. The spectroscopic and magnetic properties of the new U^{2+} complexes are described and compared to those of **1** and reactivity studies on both **1** and **2** are presented to allow further elaboration of the chemistry of U^{2+}.

Results

New U^{2+} Complexes

Synthesis of [M(chelate)][Cp''$_3$U] (M = K, Na)

Addition of KC_8 under an atmosphere of argon or dinitrogen to a stirred dark green/brown THF solution of Cp''_3U and 18-crown-6 at room temperature caused an immediate color change to black. After the reaction mixture was stirred for 4 min, solids were removed by filtration. The solvent was removed under reduced pressure and the resulting solid was washed and crystallized from THF/hexane. Black crystals of [K(18-crown-6)(THF)$_2$][Cp''$_3$U], **2-K(18c6)**, were isolated in 90% yield and crystallographically characterized, see Figure 1.

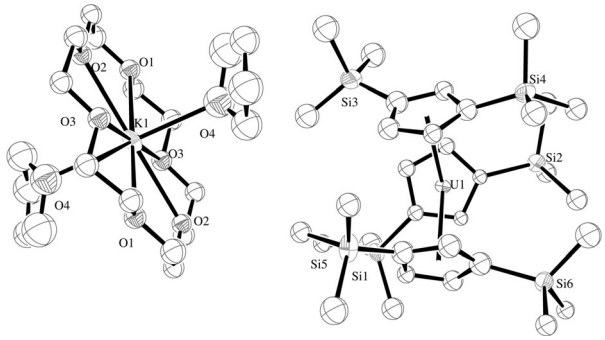
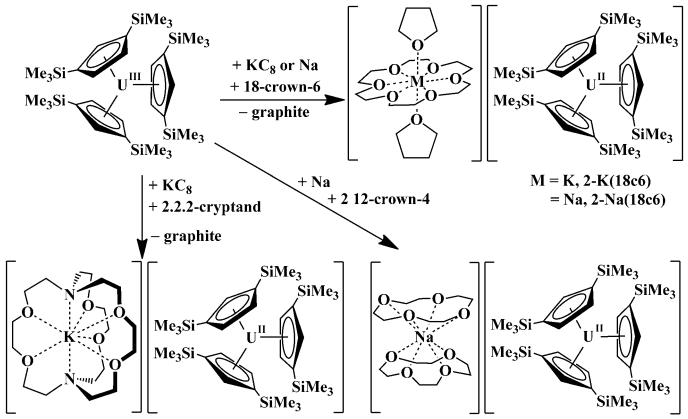


Figure 1. Connectivity structure of [K(18-crown-6)(THF)$_2$][Cp''$_3$U], **2-K(18c6)**, drawn at the 30% probability level. Hydrogens have been omitted for clarity.

Since the quality of the crystal structure of **2-K(18c6)** did not allow a discussion of metrical parameters, the synthesis of a variant was pursued. Addition of solid Cp''_3U to a THF solution of 18-crown-6 stirred over a smear of sodium metal at room temperature also quickly generated a black solution. After 30 min, work-up of the reaction mixture provided black crystals of [Na(18-crown-6)(THF)$_2$][Cp''$_3$U], **2-Na(18c6)** (see Supporting Information). Unfortunately, crystallographic characterization of **2-Na(18c6)** showed high disorder in one of the Cp'' rings and, like **2-K(18c6)**, detailed metrical data cannot be discussed, see Figure S11–S12. Sodium reduction of Cp''_3U in the presence of 12-crown-4 was also conducted and solids with properties consistent with [Na(12-crown-4)$_2$][Cp''$_3$U], **2-Na(12c4)**, were isolated, but provided no better crystallographic data. Reaction of Cp''_3U with KC_8 in the presence of 2.2.2-cryptand also yielded a product consistent with [K(2.2.2-cryptand)][Cp''$_3$U], **2-K(crypt)**. However, X-ray quality crystals could not be isolated. The reactions are summarized in Scheme 1.



Scheme 1. Synthesis of [K(18-crown-6)(THF)$_2$][Cp''$_3$U], **2-K(18c6)**, [K(2.2.2-cryptand)][Cp''$_3$U], **2-K(crypt)**, [Na(18-crown-6)(THF)$_2$][Cp''$_3$U], **2-Na(18c6)** and [Na(12-crown-4)][Cp''$_3$U], **2-Na(12c4)**.

Structural Data

The crystallographic data on **2-K(18c6)** and **2-Na(18c6)** showed, in each case, a trigonal planar arrangement of the Cp'' ring centroids about the uranium center. The structure of **2-K(18c6)** is not isomorphous with the thorium complex of the same formula, [K(18-crown-6)(THF)$_2$][Cp''$_3$Th].[4] The [K(18-crown-6)(THF)$_2$]$^+$ and [Na(18-crown-6)(THF)$_2$]$^+$ cations in each example of **2** are well-separated from the anion, showing no cation-Cp'' interaction, which contrasts with the rare earth complexes, [K(18-crown-6)][Cp'$_3$Ln] (Ln = Y, Ho, Er), in which the [K(18-crown-6)]$^+$ cation is located next to one of the Cp' rings.[5a,b] Unfortunately, the crystal data were not of high enough quality for any additional analyses.

NMR Data

The ^{1}H NMR spectra of **2-K(18c6)**, **2-K(crypt)**, **2-Na(18c6)**, and **2-Na(12c4)** in [D$_8$]THF are nearly identical and show paramagnetically broadened resonances around δ −4 ppm for the $C_5H_3(Si\mathit{Me}_3)_2$ protons, and around 11 and −12 ppm for the $C_5\mathit{H}_3(SiMe_3)_2$ protons in a 1:2 ratio, respectively. There is less than 0.25 ppm difference in resonance shifts among the four complexes (Supporting Information, Figure S1). All of these resonances are shifted compared to the U^{3+} precursor, Cp''_3U, in [D$_8$]THF, which has the trimethylsilyl protons at δ −9 and the cyclopentadienyl protons at 20 and −6 ppm (Supporting Information, Figure S1).

The greater thermal stability of the new U^{2+} complexes allowed ^{29}Si NMR spectroscopy at room temperature for the first time on this new oxidation state. Previously, complex **1** was found to have a ^{29}Si resonance at δ −322.4 ppm at 170 K. The low temperature of this NMR experiment was necessary due to the limited thermal stability of **1**. The ^{29}Si NMR spectra of **2-K(18c6)**, **2-K(crypt)**, **2-Na(18c6)**, and **2-Na(12c4)** at room temperature contained broad ($\nu_{1/2}$ ≥ 120 Hz) resonances at δ −327.3, −329.5, −328.6 and −329.9 ppm, respectively. These are significantly shifted upfield from those of Cp''_3U in THF at δ −162.9 ppm[6] and are the most negative shifts ever observed for uranium complexes containing silicon.

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When **2-K(18c6)** and Cp''_3U were mixed together in an approximately 1:1 ratio, a single set of ^1H NMR resonances was observed with shifts intermediate between the resonances for the two isolated complexes. This suggests that on the NMR time scale there is electron exchange between the complexes of the U^{2+} and U^{3+} ions. Exchange of this type has been observed in non-aqueous systems with $U^{3+/4+}$ cation/neutral and neutral/anion pairs[7] and has been examined for $U^{3+/4+/5+/6+}$ ions in aqueous solution.[8] The principal resonance assigned to the $SiMe_3$ units remains sharp at room temperature, but it becomes broad below −50 °C and becomes too broad to be unambiguously identified at −100 °C. Separate resonances were not observed at low temperature.

Optical spectra

The UV/Vis spectra of **1**, **2-K(crypt)**, and Cp''_3U in THF are shown in Figure 2. Due to the highly absorbing nature of compounds **1** and **2**, UV/Vis samples were recorded as 1.5 mM solutions in 1 mm cuvettes. The spectra of **2-Na(18c6)**, **2-Na(12c4)**, and **2-K(18c6)** are nearly identical to that of **2-K(crypt)**, Figure S2, and all of these are similar to that of **1**. The spectrum of Cp''_3U in THF is similar to those of Cp''_3U and Cp'_3U in hexane, but differs from that of Cp'_3U in THF because the latter compound forms a THF adduct as confirmed by X-ray crystallography [see Supporting Information for optical spectra Figure S4 and for structural details on Cp'_3U(THF) Figure S13].

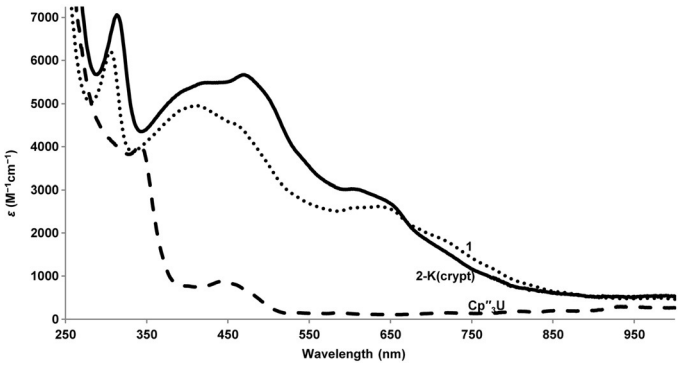

Figure 2. Experimental UV/Vis spectra of [K(2.2.2-cryptand)][Cp''_3U], **2-K(crypt)** (solid line), [K(2.2.2-cryptand)][Cp'_3U], **1** (dotted line), and Cp''_3U (dashed line) in THF at 298 K.

The 3000 to 7500 $M^{-1}cm^{-1}$ extinction coefficients of the U^{2+} complexes are much larger than those of the U^{3+} compounds. This difference is similar to the larger intensities observed for other Ln^{2+} and An^{2+} complexes, [K(2.2.2-cryptand)][Cp'_3Ln] [Ln = Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu],[5] [K(2.2.2-cryptand)][Cp''_3M] [M = La, Th],[3–4] and [K(2.2.2-cryptand)][Cp'_3U], **1**,[1] compared to their +3 analogues, Cp'_3Ln, Cp''_3La and Cp''_3Th, and Cp'_3U, respectively.

Near infrared (NIR) spectra were also obtained on **1**, **2** and Cp''_3U, Figure 3 and Figure S3. NIR spectra were recorded in 1 cm cuvettes at 2–3 mM concentration for U^{2+} and U^{3+} complexes. Numerous absorptions were observed in the 900–1600 nm range which was limited by the highly absorbing nature of THF;[9] see Figure S3 for NIR spectra of **2-K(18c6)**, **2-Na(18c6)**, and **2-Na(12c4)**.

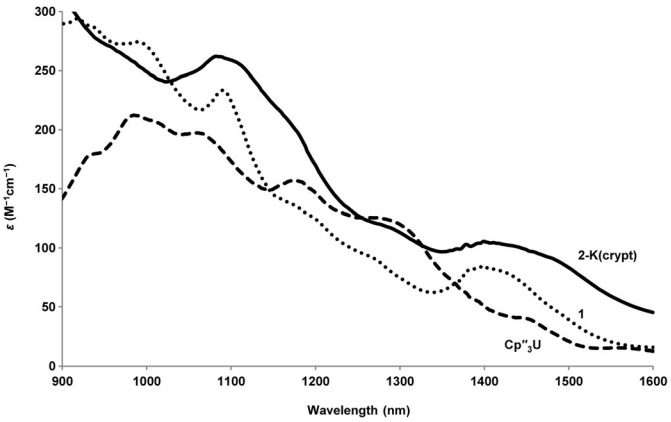

Figure 3. Experimental NIR spectra of [K(2.2.2-cryptand)][Cp''_3U], **2-K(crypt)** (solid line), [K(2.2.2-cryptand)][Cp'_3U], **1** (dotted line), and Cp''_3U (dashed line) in THF at 298 K.

Magnetic susceptibility

DC magnetic susceptibility data were collected for **1**, **2-K(crypt)**, and Cp'_3U over the temperature range 1.8 to 300 K under an applied field of 1000 Oe, Figure 4. At 300 K, the values of the molar magnetic susceptibility times temperature, $\chi_M T$ (and μ_{eff}), for **1** and **2-K(crypt)** are 0.98 and 0.64 emu K mol^{-1} (2.8 and 2.26 μ_B), respectively. These are considerably lower than the room temperature $\chi_M T$ value of 1.33 emu K mol^{-1} (3.26 μ_B) observed for the representative U^{3+} complex, Cp'_3U, which is consistent with a different oxidation state for **1** and **2-K(crypt)**.[10] The data on Cp'_3U are similar to those on Cp''_3U: $\chi_M T = 1.38$ emu K mol^{-1} (3.32 μ_B) at 300 K and 0.51 emu K mol^{-1} at 5 K.[11] Field-dependent $\chi_M T$ data for **1** (Figure S10, top) suggest that the larger moment is likely due to a temperature-independent paramagnetic contribution that is not exhibited by **2-K(crypt)** (Figure S10, bottom). With decreasing temperature, $\chi_M T$ declines gradually for **1** and **2-K(crypt)** and reaches values of 0.12 and 0.04 emu K mol^{-1}, respectively, at 1.8 K.

Reactivity

Formation of a U^{3+} hydride complex from 2-K(18c6)

To make the claim that [K(2.2.2-cryptand)][Cp'_3U], **1**, was the first unequivocal example of a U^{2+} complex, it was necessary to characterize the corresponding U^{3+} hydride, [K(2.2.2-cryptand)][Cp'_3UH], to demonstrate that **1** did not contain a crystallographically undetected hydride.[1] This hydride was made in two ways: by adding KH to Cp'_3U in the presence of 2.2.2-cryptand and by reacting **1** with H_2.[1] When similar experiments were attempted with **2-K(crypt)**, an analogous compound, [K(2.2.2-cryptand)][Cp''_3UH], was formed, but it was iso-

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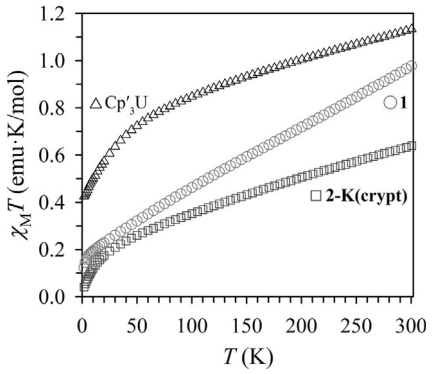
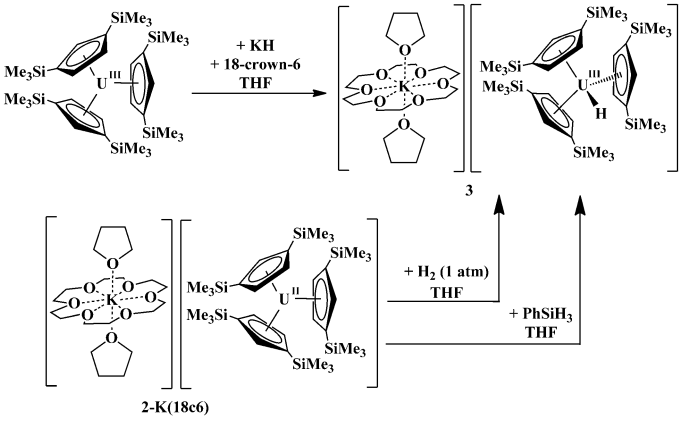


Figure 4. Plot of the static molar magnetic susceptibility times temperature ($\chi_M T$) versus T collected at 0.1 T for Cp'_3U (triangles), [K(2.2.2-cryptand)][Cp'_3U], **1** (circles), [K(2.2.2-cryptand)][Cp''_3U], **2-K(crypt)** (squares).

lated as a red oil. The analogous 18-crown-6 compound, [K(18-crown-6)$(THF)_2$][Cp''_3UH], **3**, was synthesized from **2-K(18c6)** and isolated as a dark red solid.

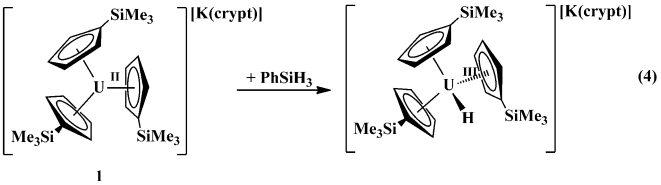
Complex **3** can be generated in several ways, Scheme 2. Addition of KH and 18-crown-6 to a solution of Cp''_3U in THF quickly forms a dark red solution from which **3** could be isolated as a dark red powder. The compound has a UV/Vis spectrum in THF at 298 K that is nearly identical to that of [K(2.2.2-cryptand)][Cp'_3UH][1] (Supporting Information, Figure S6). Complex **3** can also be synthesized from the reaction of **2-K(18c6)** with H_2 (1 atm) or with $PhSiH_3$ (Scheme 2).



Scheme 2. Syntheses of [K(18-crown-6)$(THF)_2$][Cp''_3UH], **3**.

Both methods are preferable to the KH reaction which requires crystallization to obtain pure product. The H_2 reaction works best for large scale preparations and the $PhSiH_3$ reaction is most convenient for smaller reactions. After it was determined that **2-K(18c6)** reacts with $PhSiH_3$, the analogous reaction with **1** was conducted to show that it reacts similarly to make [K(2.2.2-cryptand)][Cp'_3UH],[1] see Equation (4).

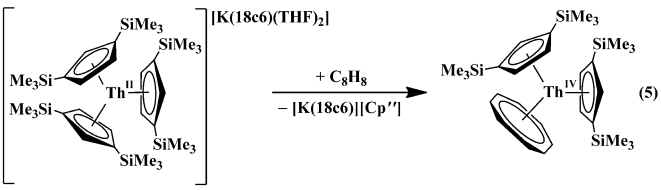
The ^1H and ^{13}C NMR spectra of **3** show paramagnetically broadened peaks ranging from 8 to −4 ppm in the ^1H NMR spectrum, which is consistent with two of the three resonances expected for the $[C_5H_3(SiMe_3)_2]^-$ ligand. In addition, there is

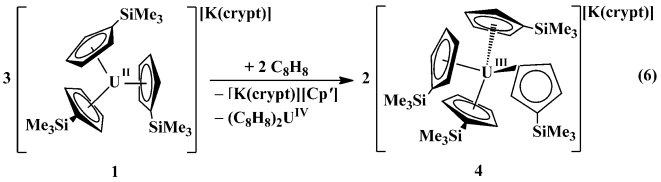


a broad resonance in the ^1H NMR spectrum at δ 601 ppm ($\nu_{1/2}$ = 250 Hz), which is consistent with other monomeric anionic U^{3+} hydride compounds (δ U–H, $\nu_{1/2}$), [K(2.2.2-cryptand)][Cp'_3UH] (560, 175 Hz),[1] [Na(18-crown-6)$(THF)_2$][Cp'_3UH] (547, 220 Hz),[7b,12] [Na(18-crown-6)$(THF)_2$][$(C_5H_4tBu)_3UH$] (521, 160 Hz).[12] When the reaction of **2-K(18c6)** with H_2 was repeated with D_2, the product had an identical ^1H NMR spectrum except the resonance at 601 ppm was no longer present. The ^2H NMR spectrum contained only one resonance at 601 ppm.

Cyclooctatetraene reactions

Reactions of the U^{2+} complexes **1** and **2-K(18c6)** with 1,3,5,7-cyclooctatetraene, C_8H_8, were conducted to determine if they could function as two electron reductants and generate a $(C_8H_8)^{2-}$ product as was found for Th^{2+} [Eq. (5)].[4] A cold THF solution of **1** reacted with C_8H_8 over one hour and crystallization of the crude mixture yielded $(C_8H_8)_2U$ by ^1H NMR analysis[13] and unit cell determination.[14] The brown-red mother liquor was reduced in volume and crystallization from THF/Et_2O yielded a mixture of [K(2.2.2-cryptand)][Cp′] and [K(2.2.2-cryptand)][Cp'_4U], **4**, both of which were identified by X-ray crystallography and NMR spectroscopy[15] [see Equation (6), Figure 5]. This result contrasts with the reaction of Cp'_3U with C_8H_8 which forms $Cp'_2U(C_8H_8)$.[16]





The reaction of **2-K(18c6)** with excess C_8H_8 also produces $(C_8H_8)_2U$ and the potassium salt of the cyclopentadienyl ligand, [K(18-crown-6)][Cp″]. However with this larger cyclopentadienyl ring, the neutral tris(cyclopentadienyl) U^{3+} complex, Cp''_3U, was isolated [Eq. (7)], instead of the tetrakis(cyclopentadienyl) product shown in Equation (6). Reaction of either **1** or **2** with one equivalent of C_8H_8 produced the same products in re-

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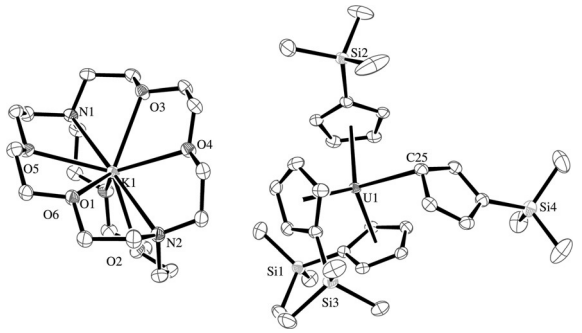
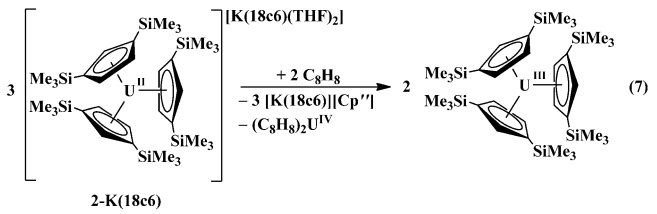


Figure 5. Thermal ellipsoid plot of [K(2.2.2-cryptand)][Cp′$_4$U], **4**, drawn at the 50% probability level. Hydrogen atoms and a co-crystallized diethyl ether molecule have been omitted for clarity.



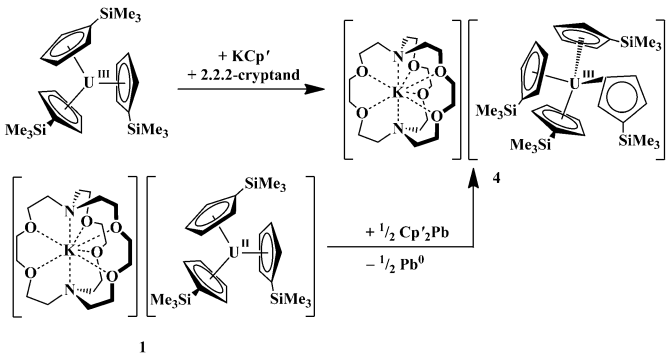
duced yield. Reaction of Cp′′$_3$U with C_8H_8 gave no reaction at room temperature over one week.

Complex **4** is the first crystallographically characterized example of a tetrakis(cyclopentadienyl) U^{3+} complex, although several U^{4+} examples have been synthesized through direct synthesis or isolation as a side product: Cp_4U[17] ($Cp = C_5H_5$), $(C_5H_4Me)_4U$,[18] $[C_5H_4CH(Me)CH_2C_5H_4]UCp_2$,[19] $(C_5H_4PPh_2)_4U$[20] and $(C_5H_4PPh_2)_2U(C_5H_4PPh_2)_2M(CO)_4$ (M = Cr, Mo).[20] The only crystallographically characterized tetrakis(cyclopentadienyl) U^{4+} complex is Cp_4U.[21]

An yttrium analogue of **4** is known[15] that is not isomorphous but has the same coordination environment containing three η^5-Cp′ rings and one η^1-Cp′ ligand. The ^{1}H NMR spectrum of **4** contains a single set of resonances from room temperature down to −90 °C suggesting that all of the rings are bound η^5 in solution. This contrasts with the yttrium analogue that shows two different $SiMe_3$ resonances in a 1:3 ratio at low temperature.[15] The 2.56(2) Å U–(η^5-Cp′ ring centroid) average distance and the 2.776(2) Å U–C25(η^1-Cp′) distance in **4** are numerically larger than those in the yttrium complex, 2.48(1) and 2.680(2) Å,[15] respectively, which is consistent with the larger ionic radius of U^{3+} versus Y^{3+} (1.025 Å vs 0.900 Å, respectively, using the Shannon radii available only for six coordinate species).[22]

Independent syntheses of [K(2.2.2-cryptand)][Cp′$_4$U], 4

To obtain useful quantities of **4** in pure form for full characterization, direct syntheses were pursued. Complex **4** can be made in 85% yield from 2.2.2-cryptand, KCp′, and Cp′$_3$U in THF. It can also be obtained in 64% yield by reacting the U^{2+} complex, [K(2.2.2-cryptand)][Cp′$_3$U], **1**, with Cp′$_2$Pb in THF (Scheme 3). The Cp′$_2$Pb used in Scheme 3 was obtained by a modification of the previous reported synthesis from $PbCl_2$ and KCp′ with vacuum distillation and a 7% yield.[23] In this study, Cp′$_2$Pb was obtained in 86% yield from PbI_2 and KCp′ in THF followed by extraction into hexane. Cp′$_2$Pb was characterized by X-ray crystallography and shows an infinite polymeric zigzag chain, which is similar to that of Cp_2Pb.[24] Details are in the Supporting Information Figure S14.



Scheme 3. Syntheses of [K(2.2.2-cryptand)][Cp′$_4$U], **4**.

Decomposition studies of 2-K versus 1

It was previously reported that **1** decomposes in THF at room temperature with first order kinetics and a $t_{1/2}$ of 1.5 h as measured in 3 mM solutions,[1] but the mechanism of the decomposition is not known. Decomposition studies were conducted on **2-K(crypt)** and **2-K(18c6)** to see how they compared with **1**. Visually, both Cp′′ complexes display much greater thermal stability than **1** since they maintain their intense U^{2+} colors at room temperature over several days. The **2-K** complexes also differ from **1** in that they turn light yellow-brown rather than dark red upon decomposition (see below). Quantitative measurements were done by UV/Vis spectroscopy monitoring the reduction of the absorption at 470 nm. The data collected from scans taken every 15 min over 17 h using 1.5 mM solutions appear to be first order with respect to **2-K** with $t_{1/2}$ of 20(1) and 15(1) h for **2-K(crypt)** and **2-K(18c6)**, respectively (Figure 6).

Decomposition of the sodium salts, **2-Na(18c6)** and **2-Na(12c4)**, was also examined by UV/Vis spectroscopy, but these complexes appear to be more complicated since the data fit neither first nor second order models. These sodium salts also have higher thermal stability than **1**, as solutions of the sodium salts maintain their U^{2+} color for days standing at room temperature.

In the course of studying the thermal stability of these complexes, a synthesis of the 18-crown-6 analogue of **1**, namely "[K(18-crown-6)(THF)$_2$][Cp′$_3$U]," gave an isolable decomposition product. Potassium-graphite reduction of Cp′$_3$U at −35 °C gave a dark green color, consistent with the formation of "[Cp′$_3$U]$^-$" but the sample quickly turned dark red, consistent with the decomposition of **1**. The solution was placed in a −30 °C freezer and yielded a crystallographically-characterizable decomposition product identified as the bimetallic U^{3+} hydride [K(18-

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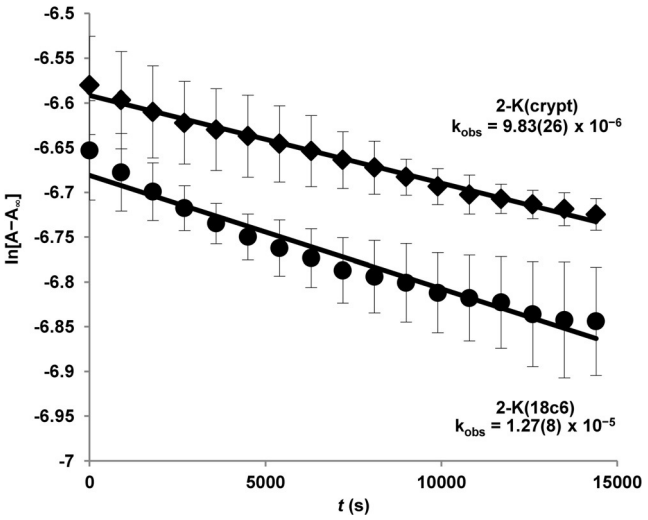

Figure 6. Decrease in absorbance at 470 nm for [K(2.2.2-cryptand)][Cp″$_3$U], **2-K(crypt)** (diamonds, top) and [K(18-crown-6)(THF)$_2$][Cp″$_3$U], **2-K(18c6)** (circles, bottom), recorded at 298 K in THF in 15 min intervals.

crown-6)(OEt$_2$)][(Cp′$_3$U)$_2$(μ-H)], **5** (Figure 7). This complex is similar to the previously identified bridging hydrides, [Na(THF)$_2$][(Cp$_3$U)$_2$(μ-H)][25] and [Na(18-crown-6)(THF)$_2$][(Cp′$_3$U)$_2$(μ-H)].[12] A structural comparison is given in the Supporting Information, Table S2. The origin of the hydride is unknown, but it is likely the solvent.[26]

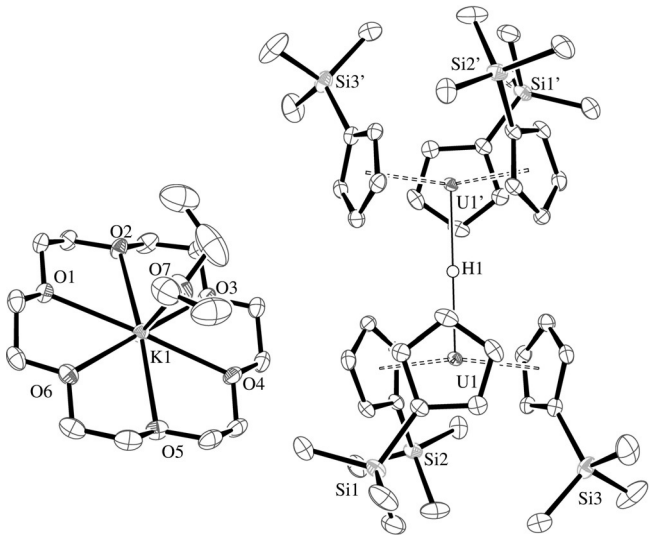

Figure 7. Thermal ellipsoid plot of [K(18-crown-6)(OEt$_2$)][(Cp′$_3$U)$_2$(μ-H)], **5**, drawn at the 50% probability level with co-crystallized diethyl ether and all hydrogen atoms except H1 removed for clarity.

Discussion

The synthesis and isolation of [K(2.2.2-cryptand)][Cp″$_3$U], **2-K(crypt)**, and [K(18-crown-6)(THF)$_2$][Cp″$_3$U], **2-K(18c6)**, by reduction of Cp″$_3$U demonstrates that the generation of cyclopentadienyl U^{2+} complexes is not limited to the Cp′ ligand in [K(2.2.2-cryptand)][Cp′$_3$U], **1**. The fact that [Na(18-crown-6)(THF)$_2$][Cp″$_3$U], **2-Na(18c6)**, and [Na(12-crown-4)$_2$][Cp″$_3$U], **2-Na(12c4)**, can be synthesized demonstrates that the reduction of U^{3+} to U^{2+} in molecular complexes can be accomplished with Na (−2.7 V vs. SHE) as well as by K (−2.9 V vs. SHE) and that the countercations for these anionic complexes can contain Na^+ as well as K^+ ions. These studies also show that alkali metal reduction of Cp″$_3$U to generate **2** does not form reduced dinitrogen products. This is similar to the reduction of Cp″$_3$La to form [Cp″$_3$La]$^-$ which can be done under N_2.[3,5a] Both **1** and **2** have the U^{2+} center surrounded by three cyclopentadienyl rings, a coordination geometry that has been a common denominator for new M^{2+} ions of the lanthanides and actinides [see Eq. (1) and (3)].[1,3–5] The only other coordination environment observed for these new ions is the arene tris(aryloxide) ligand system in [K(2.2.2-cryptand)]{[(^{Ad,Me}ArO)$_3$mes]U} [see Equation (2)].[2]

In general, the Cp″ complexes **2** are more thermally stable than the Cp′ complex **1** which makes both synthesis and characterization less difficult. In contrast to the synthesis of **1** that requires low temperatures from start to finish, the first order $t_{1/2}$ values of 20 h and 15 h for **2-K(crypt)** and **2-K(18c6)**, respectively, allow the syntheses to be done at room temperature. This enhanced stability also allows the ^{29}Si NMR spectra to be obtained at room temperature instead of at −103 °C as previously necessary for **1**.[6] The −322 ppm shift originally found for **1** at low temperature was the lowest shift ever observed in the ^{29}Si NMR spectrum of a uranium complex. The −327, −329, −329 and −330 ppm shifts observed for **2-K(18c6)**, **2-K(crypt)**, **2-Na(18c6)** and **2-Na(12c4)**, respectively, are consistent with this low value observed for **1** and fit with the observed trend for +4, +3, and +2 uranium complexes that the shifts become increasingly negative as the oxidation state decreases.[6]

Although the complexes **2** are more thermally stable than **1**, their spectroscopic and magnetic properties are similar. Both **1** and **2** have UV/Vis spectra (see Figure 2) with intensities much higher than those of the trivalent analogues, Cp″$_3$U and Cp′$_3$U(THF), respectively. The NIR spectra of **1** and **2** also have a similar appearance (see Figure 3).

The similarities in physical properties of **1** and **2-K(crypt)** extend also to their magnetic susceptibility data (see Figure 4). Variable-temperature data collected at 0.1 T reveal room temperature $\chi_M T$ values of 0.98 and 0.64 emu K mol^{-1}, respectively, lower than the values of 1.33 and 1.38 emu K mol^{-1} found for Cp′$_3$U and Cp″$_3$U,[11] respectively, and the theoretical value of 1.64 emu K mol^{-1} for a 5f^3 ion. The lower magnetic susceptibilities of **1** and **2** are therefore consistent with the presence of a different oxidation state from that of Cp′$_3$U and Cp″$_3$U.[10] The slightly larger room temperature $\chi_M T$ value for **1** compared to **2-K(crypt)** can be ascribed in part to a temperature-independent paramagnetic contribution that is not exhibited in the latter (Supporting Information, Figure S10). With decreasing temperature the $\chi_M T$ versus T curves decline gradually due to the presence of magnetic anisotropy and/or the depopulation of crystal field levels (see Figure 4), and at 1.8 K, the value of $\chi_M T$ is 0.12 emu K mol^{-1} and 0.04 emu K mol^{-1} for **1** and **2-K(crypt)**, respectively. The recently reported divalent complex

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[K(2.2.2-cryptand)]{[(^{Ad,Me}ArO)$_3$mes]U} exhibited similar static susceptibility data, with a room temperature $\chi_M T$ value of 0.63 emu K mol^{-1} (1 T) that decreased to 0.07 emu K mol^{-1} at 2 K.[2] However, physical characterization data supported a 5f^4 configuration[2] in contrast to the 5f^{3}6d^1 (6d$_{z^2}$) electron configuration previously postulated for **1** on the basis of DFT and UV-visible spectroscopy.[1]

For lanthanides in the analogous divalent series [K(2.2.2-cryptand)][Cp′$_3$Ln], it was possible to rationalize the experimentally-determined isoelectronic 4f^{n}5d^1 (5d$_{z^2}$) configuration, using static susceptibility data and *LS* coupling rules.[27] However, an *LS* coupling rationale is not straightforward when analyzing static magnetic susceptibility data for **1** or **2-K(crypt)** because it relies on the assumption that orbital angular momentum remains unquenched in the presence of a ligand field, which is not necessarily true for uranium. Furthermore, *LS* coupling predicts the same theoretical room temperature $\chi_M T$ value of 0.9 emu K mol^{-1} for both 5f^{3}6d^1 (6d$_{z^2}$) and 5f^4 configurations. However in conjunction with the comprehensive physical characterization data presented here and previous characterization of **1**[1] and [K(2.2.2-cryptand)][Cp′$_3$Ln],[27] we believe these magnetic data are consistent with a 5f^{3}6d^1 electron configuration for **1** and **2-K(crypt)**.

Reactivity studies on **1** and **2-K(18c6)** show that they each react with both H_2 and $PhSiH_3$ to make the U^{3+} hydrides, [K(2.2.2-cryptand)][Cp′$_3$UH] and [K(18-crown-6)(THF)$_2$][Cp″$_3$UH], **3**, respectively. The existence of **3** as a distinct complex from [K(18-crown-6)(THF)$_2$][Cp″$_3$U], **2-K(18c6)**, is evidence that the crystal structures of the (Cp″$_3$U)$^-$ anions, **2**, contain U^{2+} and not (U^{III}-H)$^{2+}$. The formation of the bridged U^{3+} hydride, [K(18-crown-6)(OEt$_2$)][(Cp′$_3$U)$_2$(μ-H)], **5**, in the decomposition of an 18-crown-6 salt of (Cp′$_3$U)$^-$ suggests there are other routes to make uranium hydrides from these U^{2+} compounds. Lappert has previously found hydride products in attempts to make Y^{2+}, La^{2+} and Ce^{2+} complexes.[26]

Complexes **1** and **2** reduce 1,3,5,7-cyclooctatetraene to $(C_8H_8)^{2-}$ and form the extensively studied U^{4+} complex, uranocene $(C_8H_8)_2U$.[13–14,28] This U^{2+} reactivity differs from that of the Th^{2+} analog, (Cp″$_3$Th)$^-$, in which the $(C_8H_8)^{2-}$ reduction product retains cyclopentadienyl ligands, Cp″$_2$Th(C_8H_8) [Eq. (5)].[4] It also differs from the reactivity of the U^{3+} complexes, Cp′$_3$U and Cp″$_3$U. The former reacts with C_8H_8 to form Cp′$_2$U(C_8H_8)[16] and the latter does not react.

In the cyclooctatetraene reactions, both U^{2+} and Th^{2+} effect the two electron reduction of C_8H_8 to $(C_8H_8)^{2-}$ and the formation of U^{4+} products that are observed consistent with $An^{2+} \rightarrow An^{4+} + 2e^-$ half-reactions (An = U, Th). However, the uranium reactions are more complicated since U^{3+} complexes are formed as byproducts. In the case of U^{2+} with Cp′, this byproduct is formed as the tetrakis(cyclopentadienyl) complex, [K(2.2.2-cryptand)][Cp′$_4$U], **4**. An analogous tetrakis(cyclopentadienyl) complex apparently is not favored with the larger Cp″ ligand and the byproduct is the tris(cyclopentadienyl) complex Cp″$_3$U. In each of these cases, these U^{3+} products indicate that some $U^{2+} \rightarrow U^{3+} + e^-$ processes are also occurring. Since U^{3+} is more accessible than Th^{3+}, it is possible that these one electron processes will be more facile with U^{2+} than with Th^{2+} complexes. Another difference between Th and U is the larger size of Th^{4+} compared to U^{4+}, 1.21 versus 1.17 Å, respectively, for 12-coordinate radii.[22] Cp″$_2$U(C_8H_8) would be more sterically crowded than Cp″$_2$Th(C_8H_8).[29]

The origin of the greater stability of (Cp″$_3$U)$^-$, **2**, vs. (Cp′$_3$U)$^-$, **1**, is not clear. The larger (Cp″)$^-$ ligand does provide more steric protection of the metal center. In addition, the di-silyl substituted ligand could reduce the electron density on the metal center if the $SiMe_3$ group is electron withdrawing with respect to H in this system.[26a,30] In any case, the observed greater reactivity of **1** vs. **2** is consistent with data on U^{3+} analogs where more reactivity has been reported for Cp′$_3$U than for Cp″$_3$U.[12,16,31]

Conclusions

Crystallographically characterizable complexes of U^{2+} are accessible not only using the mono-silyl Cp′ ligand as found previously with [K(2.2.2-cryptand)][Cp′$_3$U], **1**, but also with the bulkier di-silyl Cp″ ligand. The new examples of U^{2+} complexes, [K(2.2.2-cryptand)][Cp″$_3$U], **2-K(crypt)**, [K(18-crown-6)(THF)$_2$][Cp″$_3$U], **2-K(18c6)**, [Na(18-crown-6)(THF)$_2$][Cp″$_3$U], **2-Na(18c6)**, and [Na(12-crown-4)$_2$][Cp″$_3$U], **2-Na(12c4)**, demonstrate that sodium metal can be used as a reductant and a variety of countercations will form isolable complexes. The complexes **2** also show that U^{2+} compounds more thermally stable than **1** can be synthesized. The magnetic susceptibility data on **1** and **2-K(crypt)** are similar as are the UV/Vis-NIR and ^{29}Si NMR spectra and are consistent with the +2 oxidation state for uranium. Both **1** and **2** react with H_2 and $PhSiH_3$ to form U^{3+} hydrides which establish that the U^{2+} complexes are not (U^{III}-H)$^{2+}$ compounds. Cyclooctatetraene is reduced to $(C_8H_8)^{2-}$ by **1** and **2**, a formal two electron redox process, but the presence of U^{3+} byproducts, (Cp′$_4$U)$^-$ and Cp″$_3$U, suggest that one-electron pathways may also be traversed in these reactions. A difference in reactivity between **1** and **2** is that in the sterically bulkier Cp″ system, the tetrakis(cyclopentadienyl) byproduct does not form. The existence of the U^{2+} anion, (Cp″$_3$U)$^-$, **2**, demonstrates that, along with (Cp′$_3$U)$^-$ and the Meyer complex, [K(2.2.2-cryptand)]{[(^{Ad,Me}ArO)$_3$mes]U}, there are at least three coordination environments that can be used to investigate the chemistry of this new oxidation state of uranium.

Experimental Section

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over sodium benzophenone ketyl or sodium/potassium alloy, degassed by three freeze–pump–thaw cycles, and vacuum transferred before use. ^{1}H, ^{2}H, ^{13}C, ^{29}Si and ^{207}Pb NMR spectra were recorded on a Bruker GN500 or CRYO500 MHz spectrometer operating at 499.3, 76.8, 125.6, 99.2 and 103.3 MHz, respectively, at 298 K unless otherwise stated. ^{1}H, ^{2}H and ^{13}C NMR spectra were referenced internally to solvent resonances. ^{29}Si and ^{207}Pb NMR spectra were referenced ex-

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ternally to $SiMe_4$ and $Pb(NO_3)_2$, respectively. Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS elemental analyzer. IR spectra were recorded as KBr pellets on a JASCO 4700 FTIR. UV/Vis spectra were collected in THF or hexane at 298 K using a Varian Cary 50 Scan UV/Vis spectrophotometer in a 1 mm cuvette. Near IR spectra were collected in THF or hexane at 298 K using a PerkinElmer Lambda 900 UV/Vis/NIR spectrometer in a 1 cm cuvette. All optical spectra were recorded as 1.5–2 mM solutions except NIR of U^{3+} compounds which were recorded in 3 mM solutions. Samples for magnetic susceptibility measurements were prepared by adding the powdered crystalline compound to a 5 mm inner diameter quartz tube with a quartz platform $^3/_4$ down the length of the tube. Solid eicosane was then added to prevent crystallite torqueing and provide good thermal contact between the sample and the bath. The tubes were fitted with Teflon sealable adapters, evacuated using a glove box vacuum pump, and flame sealed under static vacuum. Following flame sealing, the solid eicosane was melted in a water bath held at 40 °C. Magnetic susceptibility measurements were performed using a Quantum Design MPMS2 SQUID magnetometer. DC susceptibility data were collected at temperatures ranging from 1.8 to 300 K, using applied fields of 1.0, 0.5, and 0.1 T. All data were corrected for diamagnetic contributions from the core diamagnetism estimated using Pascal's constants.[32,33] Evans method[34] samples were weighed directly into a tared NMR tube, and charged with THF and a flame sealed capillary tube containing a sample of neat THF. The NMR sample was removed from the glovebox and recorded on a Bruker GN500 NMR at room temperature (298 K).

H_2 (99.99%, Praxair) and D_2 (99.98%, Cambridge Isotope Laboratories) gases were used as received. KH (30% wt dispersion in mineral oil, Aldrich) was washed several times with hexane, filtered, and dried under vacuum before use. Potassium and sodium metals (Aldrich) were washed with hexane and scraped to provide fresh surfaces before use. 12-Crown-4 (Aldrich) was dried over activated molecular sieves and degassed by three freeze-pump-thaw cycles before use. PbI_2 (Aldrich), 18-crown-6 (Aldrich), and 2.2.2-cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, Aldrich) were placed under vacuum (10^{-3} Torr) for 12 h before use. $PhSiH_3$ (Aldrich) was dried over 4 Å activated molecular sieves, and degassed by three freeze-pump-thaw cycles. C_8H_8 (Aldrich) was distilled, dried over 4 Å activated molecular sieves, and degassed by three freeze-pump-thaw cycles. The following compounds were prepared following literature procedures: KCp′,[35] UI_3,[36] Cp'_3U,[1] Cp''_3U,[6] and KC_8.[37] KCp″ was made analogously to KCp′.[35]

[K(18-crown-6)(THF)$_2$][Cp″$_3$U], 2-K(18c6): In a glovebox, addition of solid KC_8 (70 mg, 0.50 mmol) to a vigorously stirred green solution of Cp''_3U (204 mg, 0.236 mmol) and 18-crown-6 (68 mg, 0.26 mmol) in THF (3 mL) caused the mixture to immediately turn black. After stirring 4 min, the reaction was filtered to remove black solids, presumably graphite, and the solvent was removed under reduced pressure. The black solids were washed with hexane and crystallized from THF layered with hexane at −30 °C (310 mg, 90%). X-ray quality crystals were grown from a 1:1 THF/Et_2O solution at −30 °C. ^{1}H NMR ([D$_8$]THF): δ = 11.16 (s, $C_5H_3(SiMe_3)_2$, 3H), 3.78 (s, $C_{12}H_{24}O_6$, 24H), −4.46 (s, $C_5H_3(SiMe_3)_2$, 54H), −12.30 (s, $C_5H_3(SiMe_3)_2$, 6H); ^{29}Si NMR ([D$_8$]THF): δ = −327.3 (br, $\nu_{1/2}$ = 150 Hz, $C_5H_3(SiMe_3)_2$). Evans method (THF, 298 K): 2.9 μ_B. UV/Vis/NIR (THF, ε, $M^{-1}cm^{-1}$): λ_{max} = 315 (7500), 470 (6000), 605 (3200 shoulder), 926 (400), 982 (400), 1075 (300, shoulder), 1382 nm (100, shoulder). FTIR: ν = 3043w, 2948s, 2892s, 1472m, 1454m, 1434m, 1396w, 1351m, 1314w, 1283w, 1244s, 1201m, 1110vs, 1077s, 962s, 921s, 830vs, 749s, 681m, 635m cm^{-1}. Elemental analysis calculated (%) for $C_{53}H_{103}O_8Si_6KU$: C 48.44, H 7.90; found: C 48.13, H 7.88.

[K(2.2.2-cryptand)][Cp″$_3$U], 2-K(crypt): In a glovebox, addition of solid KC_8 (47 mg, 0.35 mmol) to a 2:1 Et_2O/THF (3 mL) solution of Cp''_3U (210 mg, 0.243 mmol) and 2.2.2-cryptand (93 mg, 0.25 mmol) caused the mixture to immediately turn black. After stirring 4 min, the reaction was filtered and the solvent was removed under reduced pressure. The black solid was triturated with hexane to yield **2-K(crypt)** as a black powder (270 mg, 87%). ^{1}H NMR ([D$_8$]THF): δ = 11.14 (s, $C_5H_3(SiMe_3)_2$, 3H), 3.71 (s, OCH_2CH_2O, 12H), 3.65 (t, $^3J_{HH}$ = 4.5 Hz, NCH_2CH_2O, 12H), 2.62 (t, $^3J_{HH}$ = 4.5 Hz, NCH_2CH_2O, 12H), −4.38 (s, $C_5H_3(SiMe_3)_2$, 54H), −12.35 (s, $C_5H_3(SiMe_3)_2$, 6H); ^{29}Si NMR ([D$_8$]THF): δ = −329.5 (br, $\nu_{1/2}$ = 120 Hz, $C_5H_3(SiMe_3)_2$). Evans method (THF, 298 K): 2.4 μ_B. UV/Vis/NIR (THF, ε, $M^{-1}cm^{-1}$): λ_{max} = 315 (7500), 470 (6000), 605 (3200 shoulder), 1086 (300), 1382 nm (100 shoulder). FTIR: ν = 2949s, 2887s, 2815m, 1738s, 1447w, 1446m, 1355s, 1297w, 1234s, 1201m, 1134m, 1106vs, 1078s, 951s, 921s, 829vs, 748m, 663w, 632w cm^{-1}. Elemental analysis calculated (%) for $C_{51}H_{99}N_2O_6Si_6KU$: C 47.78, H 7.78, N 2.19; found: C 47.25, H 7.86, N 2.22.

[Na(18-crown-6)(THF)$_2$][Cp″$_3$U], 2-Na(18c6): In a glovebox, solid Cp''_3U (290 mg, 0.335 mmol) was added to a stirred solution of 18-crown-6 (100 mg, 0.371 mmol) in THF (5 mL) in a scintillation vial with sodium metal (50 mg, 2.0 mmol) smeared on the walls. The green solution quickly turned black and was stirred for 30 min. The solution was filtered and the solvent was removed under reduced pressure. The resulting black solids were washed with hexane and dried under reduced pressure to yield **2-Na(18c6)** (365 mg, 84%). X-ray quality crystals were grown from a 1:1 THF/Et_2O solution at −30 °C. ^{1}H NMR ([D$_8$]THF): δ = 11.33 (s, $C_5H_3(SiMe_3)_2$, 3H), 3.73 (s, $C_{12}H_{24}O_6$, 24H), −4.49 (s, $C_5H_3(SiMe_3)_2$, 54H), −12.39 (s, $C_5H_3(SiMe_3)_2$, 6H); ^{29}Si NMR ([D$_8$]THF): δ = −328.6 (br, $\nu_{1/2}$ = 120 Hz, $C_5H_3(SiMe_3)_2$). Evans method (THF, 298 K): 2.9 μ_B. UV/Vis/NIR (THF, ε, $M^{-1}cm^{-1}$): λ_{max} = 315 (6000), 470 (5000), 605 (2500 shoulder), 978 (300), 1082 (300), 1382 nm (100 shoulder). FTIR: ν = 2953s, 2898s, 1558w, 1451m, 1456m, 1353s, 1270w, 1249s, 1114vs, 1076m, 965m, 923s, 832vs, 753m cm^{-1}. Elemental analysis calculated (%) for $C_{53}H_{103}O_8Si_6NaU$: C 49.05, H 8.00; found: C 49.45, H 8.11.

[Na(12-crown-4)$_2$][Cp″$_3$U], 2-Na(12c4): In a glovebox, solid Cp''_3U (114 mg, 0.132 mmol) was added to a stirred solution of 12-crown-4 (80 µL, 0.49 mmol) in THF (5 mL) in a scintillation vial with sodium metal (70 mg, 3.0 mmol) smeared on the walls. The green solution quickly turned black and was stirred for 30 min. The solution was filtered and the volatiles were removed under reduced pressure. The resulting black solids were washed with hexane and dried under reduced pressure to yield **2-Na(12c4)** (155 mg, 95%). ^{1}H NMR ([D$_8$]THF): δ = 11.09 (s, $C_5H_3(SiMe_3)_2$, 3H), 3.70 (s, $C_8H_{16}O_4$, 32H), −4.39 (s, $C_5H_3(SiMe_3)_2$, 54H), −12.23 (s, $C_5H_3(SiMe_3)_2$, 6H); ^{13}C NMR ([D$_8$]THF): δ = 195.4 ($C_5H_3(SiMe_3)_2$), 194.3 ($C_5H_3(SiMe_3)_2$), 76.7 ($C_5H_3(SiMe_3)_2$), 67.4 ($C_8H_{16}O_4$), −111.0 ($C_5H_3(SiMe_3)_2$); ^{29}Si NMR ([D$_8$]THF): δ = −329.9 (br, $\nu_{1/2}$ = 120 Hz, $C_5H_3(SiMe_3)_2$). Evans method (THF, 298 K): 2.6 μ_B. UV/Vis/NIR (THF, ε, $M^{-1}cm^{-1}$): λ_{max} = 315 (6000), 470 (4500), 605 (2300 shoulder), 1086 (300), 1382 nm (100 shoulder). FTIR: ν = 2951s, 2909s, 2871s, 1471m, 1454m, 1446m, 1391w, 1365m, 1286w, 1291m, 1239s, 1137s, 1098vs, 1023s, 958w, 919vs, 833vs, 748s, 687w, 634w cm^{-1}. Elemental analysis calculated (%) for $C_{49}H_{95}O_8Si_6NaU$: C 47.39, H 7.71; found: C 47.17, H 7.93.

[K(18-crown-6)(THF)$_2$][Cp″$_3$UH], 3, From 2-K(18c6) and H_2: A 30 mL Schlenk flask fitted with a high vacuum greaseless stopcock was charged with a solution of **2-K(18c6)** (184 mg, 0.140 mmol) in THF (5 mL), sealed, removed from the glovebox, and placed in a 0 °C ice bath. The flask was attached to a high vacuum line and

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briefly degassed three times to the solvent pressure. The flask was charged with H_2 (1 atm), sealed, and allowed to warm to 25 °C. After stirring overnight, the dark red solution was dried under reduced pressure, the flask was brought into the glovebox, and the solids were washed with hexane. The product was crystalized from a THF solution layered with hexane at −30 °C and isolated as a dark red crystalline solid (175 mg, 95%). ^{1}H NMR ([D$_8$]THF): δ = 601 (br s, $\nu_{1/2}$ = 250 Hz, U*H*, 1 H), 7.54 (s, $C_5H_3(SiMe_3)_2$, 3 H), 3.84 (s, $C_{12}H_{24}O_6$, 24 H), −3.92 (s, $C_5H_3(SiMe_3)_2$, 54 H). ^{13}C NMR ([D$_8$]THF): δ = 274.7 ($C_5H_3(SiMe_3)_2$), 249.8 ($C_5H_3(SiMe_3)_2$), 71.3 ($C_{12}H_{24}O_8$), −9.7 ($C_5H_3(SiMe_3)_2$); no ^{29}Si NMR resonance was observed. Evans method (THF, 298 K): 3.3 μ_B. UV/Vis/NIR (THF, ε, M^{-1}cm^{-1}): λ_{max} = 504 (1000), 561 (700 shoulder), 686 (300), 932 (200 shoulder), 976 (300), 1026 (200 shoulder), 1072 (200), 1230 (100), 1290 (100), 1380 nm (100). FTIR: ν = 2043w, 2950s, 2894s, 2822m, 1451m, 1454m, 1435m, 1395w, 1352s, 1267w, 1248s, 1160w, 1115vs, 1077s, 1033w, 964s, 930m, 924s, 830vs, 750s, 688w, 636w cm^{-1}. Elemental analysis calculated (%) for $C_{53}H_{104}O_8Si_6KU$: C 48.41, H 7.97; found: C 47.30, H 7.96. The low carbon content is sometimes observed in complexes with high silicon content.[3]

[K(18-crown-6)(THF)$_2$][Cp″$_3$UD], 3D, from 2-K(18c6) and D$_2$: The deuterium analogue of **3** was prepared in 79% yield as described above but using D_2 instead of H_2. ^{1}H NMR ([D$_8$]THF): δ = 7.54 (s, $C_5H_3(SiMe_3)_2$, 3 H), 3.84 (s, $C_{12}H_{24}O_6$, 24 H), −3.92 (s, $C_5H_3(SiMe_3)_2$, 54 H); ^{2}H NMR ([D$_8$]THF): δ = 601 (br s, $\nu_{1/2}$ = 250 Hz, U*H*, 1 H).

[K(18-crown-6)(THF)$_2$][Cp″$_3$UH], 3, from 2-K(18c6) and PhSiH$_3$: In a glovebox, addition of solid KC_8 (50 mg, 0.37 mmol) to a vigorously stirred green solution of Cp″$_3$U (194 mg, 0.224 mmol) and 18-crown-6 (60 mg, 0.23 mmol) in THF (4 mL) caused the mixture to immediately turn black. After stirring 4 min, the reaction was filtered into a colorless stirred solution of $PhSiH_3$ (30 mg, 0.290 mmol) in THF (2 mL). The mixture turned red over the next 30 min and was stirred overnight. The volatiles were removed under reduced pressure and the product was washed with hexane leaving **3** as a dark red powder (232 mg, 79%, based on Cp″$_3$U) identified by ^{1}H NMR spectroscopy. Complex **3** can also be made from isolated **2-K(18c6)** (17 mg, 0.013 mmol) in ([D$_8$]THF) and 1 drop of $PhSiH_3$. The NMR tubed was briefly vortexed and taken to the NMR spectrometer. ^{1}H NMR analysis showed full conversion to **3** within 30 min.

[K(18-crown-6)(THF)$_2$][Cp″$_3$UH], 3, from Cp″$_3$U and KH: Solid KH (20 mg, 0.50 mmol) was added to a solution of Cp″$_3$U (99 mg, 0.11 mmol) and 18-crown-6 (32 mg, 0.12 mmol) in THF (4 mL). After stirring for 6 h, the solvent was removed under reduced pressure. The solids were washed with hexane and extracted with Et_2O. The product was crystalized from an Et_2O solution layered with hexane at −30 °C and isolated as a dark red crystalline solid (115 mg, 77%), identified by ^{1}H NMR spectroscopy.

[K(2.2.2-cryptand)][Cp′$_3$UH], from 1·THF and PhSiH$_3$: In the glovebox, solid [K(2.2.2-cryptand)][Cp′$_3$U]·THF, **1·THF**, (41 mg, 0.036 mmol) was tapped into a stirred solution of $PhSiH_3$ (47 mg, 0.43 mmol) in THF (3 mL), the reaction quickly turned dark red. After 3 h the mixture was filtered and the volatiles were removed under reduced pressure to produce a red oil. The oil was dissolved in minimal 1:1 THF/Et_2O and an additional 5 mL of Et_2O was added and the solution was cooled to −35 °C and layered with hexane. Dark red solids deposited (30 mg, 79%) and were identified as [K(2.2.2-cryptand)][Cp′$_3$UH] by ^{1}H NMR spectroscopy.[1]

Reaction of [K(2.2.2-cryptand)][Cp′$_3$U]·THF, 1·THF, with cyclooctatetraene: In a glovebox, a solution of cyclooctatetraene (73 mg, 0.70 mmol) in THF (2 mL) was quickly added to a cold stirred solution of [K(2.2.2-cryptand)][Cp′$_3$U]·THF, **1·THF**, (90 mg, 0.085 mmol) in THF (5 mL, −35 °C). The mixture was stirred for 1 h as it warmed to room temperature. The resulting brown-red/green solution was concentrated to 4 mL, layered with Et_2O, and stored at −35 °C overnight. The dark amber red mother liquor was decanted and the resulting green crystalline solids were dried under reduced pressure and identified as $(C_8H_8)_2U$ by ^{1}H NMR spectroscopy[13,38] and single crystal X-ray diffraction[14] (7 mg, 30%). The solvent was removed from the mother liquor until a dark red-brown oil remained. The oil was dissolved in Et_2O (5 mL), layered with hexane (5 mL), and stored at −35 °C for 2 d to yield a mixture of colorless and dark red crystals that were determined by X-ray diffraction and ^{1}H NMR spectroscopy to be [K(2.2.2-cryptand)][Cp′][15] and [K(2.2.2-cryptand)][Cp′$_4$U], **4**, respectively in a 1:5 ratio by ^{1}H NMR analysis (see below).

Independent synthesis of [K(2.2.2-cryptand)][Cp′$_4$U], 4, from Cp′$_3$U: In a glovebox, a solution of KCp′ (35 mg, 0.20 mmol) and 2.2.2-cryptand (75 mg, 0.20 mmol) in THF (2 mL) was added to a stirred solution of Cp′$_3$U (130 mg, 0.200 mmol) in THF (2 mL). After 10 min, the solvent was removed from the dark red solution under vacuum until a dark red oily residue formed. The oil was dissolved in Et_2O (6 mL) and stored at −35 °C for 2 d to produce dark red crystals suitable for X-ray diffraction. The mother liquor was decanted and the crystals were dried under vacuum to yield **4** as a dark red crystalline solid (204 mg, 85%). ^{1}H NMR ([D$_8$]THF, 298 K): δ = 3.08 (s, OCH_2CH_2O, 12 H), 3.04 (t, $^3J_{HH}$ = 4.5 Hz, NCH_2CH_2O, 12 H), 2.07 (t, $^3J_{HH}$ = 4.5 Hz, NCH_2CH_2O, 12 H), −2.42 (br s, $C_5H_4SiMe_3$, 36 H), −9.69 (br s, $C_5H_4SiMe_3$, 8 H), −25.50 (br s, $C_5H_4SiMe_3$, 8 H); ^{1}H NMR ([D$_8$]THF, 238 K): δ = 2.87 (s, OCH_2CH_2O + NCH_2CH_2O, 24 H), 2.07 (s, NCH_2CH_2O, 12 H), −3.15 (br s, $C_5H_4SiMe_3$, 36 H), −13.82 (br s, $C_5H_4SiMe_3$, 8 H), −32.94 (br s, $C_5H_4SiMe_3$, 8 H); ^{1}H NMR ([D$_8$]THF, 183 K): δ = 2.69 (br s, $C_{18}H_{36}N_2O_6$, 6 H), 2.53 (br s, $C_{18}H_{36}N_2O_6$, 6 H), 2.14 (br s, $C_{18}H_{36}N_2O_6$, 12 H), 2.05 (br s, $C_{18}H_{36}N_2O_6$, 6 H), 0.90 (br s, $C_{18}H_{36}N_2O_6$, 6 H), −4.38 (br s, $C_5H_4SiMe_3$, 36 H), −20.93 (br s, $C_5H_4SiMe_3$, 8 H), −43.70 (br s, $C_5H_4SiMe_3$, 8 H); ^{29}Si NMR ([D$_8$]THF), 298 K): δ −121.8 ($C_5H_4SiMe_3$). Evans method (THF, 298 K): 3.0 μ_B. UV/Vis/NIR (THF, ε, M^{-1}cm^{-1}): λ_{max} = 370 (1500), 470 (1300), 580 (600), 656 (300), 740 (300), 940 (200), 1000 (200), 1096 (100), 1202 (100), 1426 nm (100). FTIR: ν = 3083w, 3033w, 2951m, 2888m, 2818m, 2763w, 2732w, 2362w, 1927w, 1480m, 1444m, 1400w, 1356m, 1301m, 1260m, 1246s, 1177m, 1134m, 1105s, 1082m, 1037m, 949s, 933m, 903m, 831s, 778m, 748s, 699m, 683m, 637m, 628m, 605m, 571w cm^{-1}. Elemental analysis calculated (%) for $C_{50}H_{88}N_2O_6Si_4KU$: C 49.93, H 7.37, N, 2.33; found: C 49.69, H 7.46, N 2.25.

Synthesis of [K(2.2.2-cryptand)][Cp′$_4$U], 4, from [K(2.2.2-cryptand)][Cp′$_3$U]·THF, 1·THF, and Cp′$_2$Pb: In a glovebox, a cold yellow solution of Cp′$_2$Pb (11 mg, 0.023 mmol) in THF (2 mL, −35 °C) was added to a stirred cold solution of **1·THF**, (49 mg, 0.043 mmol) in THF (5 mL, −35 °C). As the stirred solution warmed to room temperature over 15 min, the color changed from black-green to red-brown. The solvent was removed under reduced pressure and the resulting tacky red-brown residue was dissolved in Et_2O (3 mL) and stored at −35 °C for 4 h. The mother liquor was decanted and the resulting dark red crystals were rinsed with cold Et_2O (1 mL, −35 °C) and dried under vacuum to yield **4** as a red crystalline solid (33 mg, 64%). Identified by ^{1}H NMR spectroscopy.

Reaction of [K(18-crown-6)(THF)$_2$][Cp″$_3$U], 2-K(18c6), with cyclooctatetraene: In a glovebox, **2-K(18c6)** (21 mg, 0.016 mmol) was added as a solid to a solution of C_8H_8 (14 mg, 0.93 mmol) in THF (4 mL). After stirring 3 h, the volatiles were removed under reduced pressure. The solids were washed with hexane and extracted with THF. Solvent was removed to give a green powder identified as a mixture of $(C_8H_8)_2U$ and K(18-crown-6)Cp″ (7 mg) by ^{1}H NMR spectroscopy.[13,38] Under reduced pressure, the solvent was re-

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moved from the hexane washes to yield green-brown Cp''_3U (12 mg) as determined by ^1H NMR spectroscopy.[31h]

Cp'_2Pb:[23] In a glovebox, a solution of KCp′ (500 mg, 2.83 mmol) in THF (10 mL) was added to a stirred yellow slurry of PbI_2 (638 mg, 1.38 mmol) in THF (10 mL). Within 1 min, the mixture became bright yellow. After stirring overnight in the dark, the bright yellow mixture was centrifuged to remove white solids, presumably KI, and the solvent was removed under reduced pressure. The bright yellow residue was dissolved in hexane (20 mL), stirred for 2 h, and filtered to remove more white precipitate, presumably excess KCp′. Removal of solvent from the filtrate yielded Cp'_2Pb as a bright microcrystalline solid (572 mg, 86%). Bright yellow, needle-like crystals of Cp'_2Pb suitable for X-ray diffraction were grown from a pentane solution at −35 °C. ^1H NMR ([D$_6$]benzene): $\delta = 6.05$ (m, $C_5H_4SiMe_3$, 4H), 5.98 (m, $C_5H_4SiMe_3$, 4H), 0.24 (s, $C_5H_4SiMe_3$, 18H); ^{13}C NMR ([D$_6$]benzene): $\delta = 122.6$ ($C_5H_4SiMe_3$), 118.2 ($C_5H_4SiMe_3$), 115.2 ($C_5H_4SiMe_3$), 1.33 ($C_5H_4SiMe_3$); ^{29}Si NMR ([D$_6$]benzene): $\delta = -11.27$ ($C_5H_4SiMe_3$); ^{207}Pb NMR ([D$_6$]benzene): $\delta = -4970$. FTIR: $\nu = 3075$w, 2951m, 2890w, 2361w, 1436w, 1400w, 1349w, 1301w, 1241s, 1195w, 1172m, 1035m, 900s, 834s, 766s, 750s, 688m, 622s, 593w, 539s cm^{-1}. Elemental analysis calculated (%) for $C_{16}H_{26}Si_2Pb$: C 39.89, H 5.44; found: C 39.62, H 5.41.

Decomposition studies: In a glovebox, compounds were weighed into a scintillation vial then washed into a 10 mL volumetric flask and diluted to the mark with THF to form a 1.5 mM solution. The solution was added to a 1 mm cuvette fitted with a high vacuum greaseless stopcock. The sample was sealed and taken from the glovebox to the UV/Vis spectrometer. Spectra were recorded in 15 min intervals over the course of 17 h. A_∞ was measured after one month on a sample that remained in the UV/Vis cell with periodic recording of spectra until the spectrum no longer changed.

X-ray crystallographic data: Crystallographic details for complexes **4**, **5**, and Cp'_2Pb, as well as $Cp'_3U(THF)$ are given in the Supporting Information.

CCDC 1422622, 1422621, 1422623 and 1422620, **4**, **5**, Cp'_2Pb, [$Cp'_3U(THF)$], respectively, contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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