## ORGANOMETALLICS-

# Thorium(IV) and Uranium(IV) Halide Complexes Supported by Bulky $\beta$ -Diketiminate Ligands

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**S** Supporting Information



**ABSTRACT**: The coordination behavior of the bulky  $\beta$ -diketiminate ligands N,N'-bis(2,6-diisopropylphenyl)pentane-2,4diiminate  $(L^{Me})$  and N,N'-bis(2,6-diisopropylphenyl)-2,2-6,6-tetramethylheptane-3,5-diiminate  $(L^{tBu})$  toward ThX<sub>4</sub>(THF)<sub>4</sub> (X = Br, I) and UCl<sub>4</sub> has been investigated. The reaction between  $K[L^{Me}]$  and  $ThX_4(THF)_4$  (X = Br, I) afforded the mono( $\beta$ -diketiminate)thorium(IV) halide complexes (L<sup>Me</sup>)ThX<sub>3</sub>(THF) (X = Br (7), I (8)). The same reaction carried out with the more sterically demanding  $K[L^{Bu}]$  gave (L<sup>Hbu</sup>)ThBr<sub>3</sub>(THF) (9) and (L<sup>Hbu</sup>)ThI<sub>3</sub> (11). All attempts to install two  $\beta$ -diketiminate ligands on thorium(IV) were unsuccessful, giving the mono( $\beta$ -diketiminate)thorium(IV) halide complex and unreacted K[L<sup>Me</sup>] or  $K[L^{tBu}]$ . However, complex 9 was shown to react with smaller anions such as  $K[C_5H_4Me]$  to give the mixed-ligand methylcyclopentadienyl  $\beta$ -diketiminate complex (L<sup>tBu</sup>)Th(C<sub>5</sub>H<sub>4</sub>Me)Br<sub>2</sub> (10). Complexes 7–11 represent rare examples of thorium complexes featuring only one  $\beta$ -diketiminate ligand, and complexes 9-11 are the first examples of thorium and halide complexes supported by the L<sup>Bu</sup> framework. In a similar manner, both  $K[L^{Me}]$  and  $K[L^{Bu}]$  were shown to react with UCl<sub>4</sub> to give the corresponding mono( $\beta$ -diketiminate)uranium(IV) chloride complexes (L<sup>Me</sup>)UCl<sub>3</sub>(THF) (12) and (L<sup>Eb</sup>u)UCl<sub>3</sub> (13). Complex 13 represents the first example of a uranium complex featuring the L<sup>Eb</sup>u framework. Efforts to prepare the bis( $\beta$ diketiminate)uranium(IV) complex  $(L^{Me})_2UCl_2$  by reacting 2 equiv of  $K[L^{Me}]$  with  $UCl_4$  led instead to the interesting cationic diuranium complex  $[{(L^{Me})(Cl)U}_2(\mu-Cl)_3][Cl]$  (14). Complexes 7–14 have been characterized by a combination of <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, elemental analysis, electrochemistry, and UV-visible-near-IR spectroscopy. Several complexes have also been characterized by X-ray crystallography, and a discussion of their structures is presented. NMR spectroscopy and the X-ray structures demonstrate that the  $\beta$ -diketiminate ligand is symmetrically bound to the actinide metal in the L<sup>Me</sup> complexes and is asymmetrically bound to the actinide metal in the L<sup>tBu</sup> complexes. In all cases the actinide(IV) metal centers lie out of the plane of the  $\beta$ -diketiminate ligand NCCCN backbone by  $\sim 1-2$  Å. The electronic spectroscopy data on K[L<sup>Me</sup>],  $(L^{Me})$ ThI<sub>3</sub>(THF) (8), and  $(L^{Me})$ UCl<sub>3</sub>(THF) (12) suggest relatively weak metal–( $\beta$ -diketiminate) ligand bonding interactions, although small perturbations in the characteristics of the  $\beta$ -diketiminate  $\pi - \pi^*$  bands with changes in the the metal ion are consistent with some metal-ligand orbital interactions. This new class of mono( $\beta$ -diketiminate)thorium and -uranium halide complexes promises to provide a robust platform for developing new chemistry of the actinides.

#### INTRODUCTION

Cyclopentadienyl-based ligand sets have dominated the landscape of actinide chemistry since Reynolds and Wilkinson reported the synthesis of the first organometallic actinide complex,  $(C_5H_5)_3UCl$ , in 1956.<sup>1</sup> In this context, both the tris(cyclopentadienyl)  $((C_5H_5)_3)$  and bis(pentamethylcyclopentadienyl)  $((C_5Me_5)_2)$  ligand sets have been enormously successful frameworks for actinide chemistry.<sup>2</sup> These ligand sets support a variety of oxidation states and coordination environments, which has enabled the discovery of reaction chemistry unique to the actinides<sup>3</sup> and a better understanding of covalency in actinide–ligand bonding interactions<sup>4</sup> and 5f orbital involvement in bonding and reactivity.<sup>5</sup>

In recent years, there has been a shift toward using noncyclopentadienyl, monoanionic, multidentate ligand sets with

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nitrogen donor atoms to stabilize actinide metal centers.<sup>4a,6</sup> Several years ago, we initiated studies to investigate the chemistry of actinide halide complexes supported by  $\beta$ -diketiminate ligands. We communicated that  $\beta$ -diketiminate ligands can support monometallic low-coordinate uranium(III) metal complexes such as  $(L^{Me})_2$ UI (1), which was readily accessed from the reaction between 2 equivalents of K[ $L^{Me}$ ]  $(L^{Me} = (Ar)NC(Me)CHC(Me)N(Ar), Ar = 2,6-iPr_2C_6H_3)$  and the trivalent uranium precursor UI<sub>3</sub>(THF)<sub>4</sub>.<sup>7</sup> As illustrated in Chart 1, this interesting molecule featured a  $\beta$ -diketiminate

### Chart 1. Examples of Known Actinide $\beta$ -Diketiminate Complexes<sup>a</sup>



ligand bound to uranium(III) in an unusual  $\eta^3(N,C,C')$ -1azaallyl mode with close U···C<sub>alkene</sub> contacts. In other work, we reported that the reaction between  $K[L^{Me}]$  and the thorium iodobutoxide complex  $ThI_3[O(CH_2)_4I](THF)_3$  afforded the first mono( $\beta$ -diketiminate)thorium complex 2.<sup>8</sup> The  $\beta$ diketiminate ligand was introduced into 5f-element chemistry by Lappert and co-workers, who reported the thorium dichloride complex 3 and the mixed-valence  $[{U^{VI}}_2][U^{III}]_2$ salt 4, which were prepared from the reaction of ThCl<sub>4</sub> and UCl<sub>4</sub> with Li[(SiMe<sub>3</sub>)NC(Ph)CHC(Ph)N(SiMe<sub>3</sub>)], respectively.9 More recently, Hayton and co-workers have exploited the voluminous  $\beta$ -diketiminate framework to kinetically stabilize a series of pentavalent uranyl complexes, typified by 5 and 6.<sup>10</sup> In these systems, the  $\beta$ -diketiminate ligands prevent dimerization of the UO2<sup>+</sup> fragment by providing steric protection both in the uranyl equatorial plane and along the O = U = O axis.

Our recent illustration that the monoanionic PNP pincer ligand (PNP =  $N[2-P(^{i}Pr)_2-4-Me-C_6H_3]_2^{-})$  supports a range of

low- and high-valent uranium complexes and enables reaction chemistry not available for the  $C_sMe_s$  ligand set<sup>6r,s</sup> prompted us to continue to explore the ability of the bulky  $\beta$ -diketiminate ligands given in Figure 1 to serve as platforms for developing



**Figure 1.** Bulky  $\beta$ -diketiminate ligands featured in this work: R = methyl, L<sup>Me</sup>; R = *tert*-butyl, L<sup>IBu</sup>.

new actinide chemistry. In this contribution, we describe the synthesis and characterization of a series of new uranium(IV) and thorium(IV) halide complexes supported by the  $\beta$ -diketiminate ligand sets  $L^{Me} = (2,6^{-i}Pr_2C_6H_3)NC(Me)CHC-(Me)N(2,6^{-i}Pr_2C_6H_3)$  and  $L^{tBu} = (2,6^{-i}Pr_2C_6H_3)NC(^{t}Bu)-CHC(^{t}Bu)N(2,6^{-i}Pr_2C_6H_3)$ , which form a new class of starting materials for actinide chemistry. In addition, we discuss the electronic and structural consequences of installing the  $\beta$ -diketiminate ligand on thorium and uranium.

#### RESULTS AND DISCUSSION

**Synthesis and Structural Chemistry.** Scheme 1 presents the synthetic methods used and the yields obtained in the preparation of the thorium(IV)  $\beta$ -diketiminate complexes. Treatment of a toluene solution of ThX<sub>4</sub>(THF)<sub>4</sub> (X = Br,

Scheme 1. Synthetic Routes to Thorium Bromide and Iodide  $\beta$ -Diketiminate Complexes 7–11<sup>*a*</sup>



 $^{a}$ Ar = 2,6 $^{i}$ Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>

I)<sup>11</sup> with 1 equiv of K[L<sup>Me</sup>] at room temperature produces the corresponding thorium(IV)  $\beta$ -diketiminate complexes 7 (X = Br) and 8 (X = I) as yellow solids in 56% and 39% isolated yields, respectively. Following workup by filtration through Celite and crystallization, the complexes were reproducibly isolated as analytically pure solids and were characterized by a combination of <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, elemental analysis, and X-ray crystallography. Alternatively, complex 8 can be prepared using the thorium(IV) tetraiodide complex ThI<sub>4</sub>(DME)<sub>2</sub>.<sup>8</sup> In THF solution, ThI<sub>4</sub>(DME)<sub>2</sub> generates ThI<sub>4</sub>(THF)<sub>4</sub>; subsequent addition of toluene and 1 equiv of K[L<sup>Me</sup>] at room temperature affords (L<sup>Me</sup>)ThI<sub>3</sub>(THF) (8) in 40% isolated yield.

Complexes 7 and 8 represent members of a new class of thorium halide complexes that feature only one bulky  $\beta$ -diketiminate ligand  $(2,6^{-i}Pr_2C_6H_3)NC(Me)CHC(Me)N-(2,6^{-i}Pr_2C_6H_3)$  (L<sup>Me</sup>). The only other example is the thorium iodobutoxide complex 2. Efforts were made to prepare the bis( $\beta$ -diketiminate) systems; however, addition of 2 equiv of K[L<sup>Me</sup>] to ThX<sub>4</sub>(THF)<sub>4</sub> (X = Br, I) yielded only (L<sup>Me</sup>)-ThX<sub>3</sub>(THF) (X = Br (7), I (8)), even upon heating. Given the large ionic radius of thorium(IV) (1.05 Å)<sup>12</sup> and the previously reported bis( $\beta$ -diketiminate) complex [(Me<sub>3</sub>Si)NC(Ph)CHC-(Ph)N(SiMe<sub>3</sub>)]<sub>2</sub>ThCl<sub>2</sub> (3),<sup>9a</sup> this result is somewhat surprising. However, it underscores the fact that the [(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NC-(Me)CHC(Me)N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)] (L<sup>Me</sup>) framework provides a larger steric profile than Lappert's [(Me<sub>3</sub>Si)NC(Ph)CHC(Ph)-N(SiMe<sub>3</sub>)]  $\beta$ -diketiminate ligand.

The <sup>1</sup>H NMR spectra of 7 and 8 are consistent with those reported for other diamagnetic transition-metal and lanthanide complexes possessing the methyl-substituted ( $L^{Me}$ )  $\beta$ -diketiminate ligand. For instance, the <sup>1</sup>H NMR spectrum of complex 7 in  $C_6D_6$  exhibits multiplets between 7.16 and 7.22 ppm assignable to the six aromatic protons on the terminal aryl groups, a singlet at 5.21 ppm for the unique  $\gamma$ -H of the NCCCN backbone, and two broad singlets at 4.07 and 1.23 ppm corresponding to the  $\alpha$  (4H) and  $\beta$  (4H) protons, respectively, of the coordinated THF. The two diastereotopic methyl groups of the isopropyl substituents appear as doublets at 1.17 and 1.66 ppm. A single resonance at 1.64 ppm, corresponding to the two methyl groups on the NCCCN backbone, and a single septet at 3.60 ppm, corresponding to the four isopropyl methine protons, are consistent with a  $C_{2\nu}$ symmetric structure relating the halves of the  $\beta$ -diketiminate ligand.

Complex 8 displays a similar spectrum, but a wholesale shift of the resonances to downfield is observed. This is a consequence of the weaker  $\pi$  donating ability of the iodide versus the bromide ligand. We and others have noted this phenomenon for a variety of uranium metallocene complexes.<sup>4b,13</sup> The poorer the  $\pi$  donor (I < Br), the more electron deficient the actinide metal center, which results in less shielding and a downfield shift of the auxiliary ligand protons. In the present case, (L<sup>Me</sup>)ThX<sub>3</sub>(THF) (X = Br (7), I (8)), the auxiliary ligands are the  $\beta$ -diketiminate and the THF.

Under conditions identical with those employed for the synthesis of complexes 7 and 8, complexes supported by the more sterically demanding *tert*-butyl-substituted  $\beta$ -diketiminate ligands were prepared. As illustrated in Scheme 1, K[L<sup>tBu</sup>] reacts with ThX<sub>4</sub>(THF)<sub>4</sub> (X = Br, I) at room temperature in toluene to provide (L<sup>tBu</sup>)ThBr<sub>3</sub>(THF) (9) and (L<sup>tBu</sup>)ThI<sub>3</sub> (11), respectively, in 74% and 45% yields. Both complexes were characterized by a combination of <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR

spectroscopy, elemental analysis, and X-ray crystallography. Complex 9 contains a coordinated THF, whereas complex 11 does not, which is most likely a consequence of the smaller ionic radius of bromide (1.96 Å) in comparison to iodide (2.20 Å).<sup>12</sup>

Unlike their  $L^{Me}$  counterparts  $(L^{Me})ThX_3(THF)$  (X = Br (7), I (8)), the <sup>1</sup>H NMR spectra of complexes  $(L^{tBu})$ -ThBr<sub>3</sub>(THF) (9) and  $(L^{tBu})ThI_3$  (11) reveal that the two arms of the  $\beta$ -diketiminate are inequivalent in solution. Consistent with the greater steric demands of the  $L^{tBu}$  ligand, each complex displays two septets (9, 3.71, 2.49 ppm; 11, 3.68, 2.50 ppm), corresponding to the two sets of methine protons of the isopropyl substituents, and four doublets (9, 1.73, 1.41, 0.98, 0.83 ppm; 11, 1.73, 1.40, 0.97, 0.81 ppm), corresponding to the four diastereotopic methyl groups of the isopropyl substituents.

As with the L<sup>Me</sup> framework, all attempts to install two L<sup>tBu</sup> ligands on thorium were unsuccessful and yielded only  $(L^{tBu})ThBr_3(THF)$  (9) or  $(L^{tBu})ThI_3$  (11). This is not unexpected, given the larger steric profile of the L<sup>tBu</sup> ligand in comparison to the L<sup>Me</sup> ligand. Although no reaction was observed with K[C<sub>5</sub>Me<sub>5</sub>], treatment of ( $L^{tBu}$ )ThBr<sub>3</sub>(THF) (9) with 1 equiv of  $K[C_{s}H_{4}Me]$  in toluene afforded a mixed-ligand thorium cyclopentadienyl  $\beta$ -diketiminate complex (10) in 74% isolated yield (Scheme 1). Efforts to replace a second bromine atom with a C5H4Me group failed, even with prolonged reaction times and heating.  $(L^{tBu})Th(C_5H_4Me)Br_2$  (10) is a unique example of a complex possessing both cyclopentadienyl and  $\beta$ -diketiminate ligands. To date, cyclopentadienyl  $\beta$ diketiminate mixed-ligand complexes have only been reported for chromium,<sup>14</sup> nickel,<sup>15</sup> and ytterbium.<sup>16</sup> The synthesis of  $(L^{tBu})Th(C_5H_4Me)Br_2$  (9) demonstrates that the mono( $\beta$ diketiminate) halide complexes can support organometallic chemistry.

Because of these promising results obtained for thorium(IV), we next turned our efforts toward uranium. A stable mono( $\beta$ -diketiminate)uranium(IV) trihalide complex would be a useful addition to the known tris(pyrazolylborate), pentamethylcyclopentadienyl, and PNP systems [HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]-UCl<sub>3</sub>(THF),<sup>17</sup> (C<sub>5</sub>Me<sub>5</sub>)UCl<sub>3</sub>(THF)<sub>2</sub>,<sup>2b,18</sup> and (PNP)-UCl<sub>3</sub>(THF)/(PNP)UCl<sub>3</sub>(O=PMe<sub>3</sub>)<sub>2</sub>/(PNP)UCl<sub>3</sub>(O=PMh<sub>3</sub>), respectively, which are rare examples of uranium trihalide complexes supported by a single monoanionic ligand set. In general, mono(ligand)actinide complexes are coordinatively unsaturated and prone to redistribution, but they are stable as adducts with one or two additional donor ligands.<sup>6j,18,19</sup>

As outlined in Scheme 2, treatment of UCl<sub>4</sub> with 1 equiv of either K[L<sup>Me</sup>] or K[L<sup>tBu</sup>] in THF at room temperature gives the corresponding mono( $\beta$ -diketiminate)uranium(IV) chloride complexes (L<sup>Me</sup>)UCl<sub>3</sub>(THF) (12) and (L<sup>tBu</sup>)UCl<sub>3</sub> (13) as red solids, respectively, in 72% and 66% isolated yields. Unlike thorium, the uranium chemistry requires THF to dissolve UCl<sub>4</sub>, which is insoluble in toluene. Following workup by filtration through Celite and crystallization, both complexes were reproducibly isolated as analytically pure solids and were characterized by a combination of <sup>1</sup>H NMR spectroscopy, elemental analysis, electronic absorption spectroscopy, and Xray crystallography.

As noted above, Hayton and co-workers have used the  $L^{Me}$  ligand in the preparation of a variety of uranyl complexes (e.g., 5 and 6),<sup>10</sup> and we have used it as a supporting ligand for trivalent uranium (e.g., complex 3).<sup>7</sup> The synthesis of

Scheme 2. Synthetic Routes to the Uranium Chloride  $\beta$ -Diketiminate Complexes  $12-14^{a}$ 



 $^{a}$ Ar = 2,6 $^{-i}$ Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

 $(L^{Me})UCl_3(THF)$  (12) demonstrates that this ligand set can also be used as a framework for tetravalent uranium, and  $(L^{tBu})UCl_3$  (13) represents the first example of a uranium complex featuring the  $L^{tBu}$  framework.

Typical of 5f<sup>2</sup> uranium(IV) species, the <sup>1</sup>H NMR spectra of complexes 12 and 13 exhibit sharp but paramagnetically shifted

resonances; the spectrum of complex 12 is representative and is shown in Figure 2. Complex 12 displays singlets downfield at 13.20 ppm and upfield at -0.89 ppm corresponding to the  $\gamma$ -H and methyl groups, respectively, of the NCCCN backbone. Broad singlets for the coordinated THF are observed upfield at -1.54 and -7.52 ppm. As observed for the thorium counterparts (complexes 7 and 8), there is a mirror plane relating both arms of the L<sup>Me</sup> ligand, as evidenced by the two doublets at 0.27 and -4.97 ppm for the two diastereotopic methyl groups of the isopropyl substituents and the singlet at -6.26 ppm for the four isopropyl methane protons. As with the thorium systems 9-11, the <sup>1</sup>H NMR spectrum of complex 13 clearly shows the asymmetric binding of the LtBu ligand to the uranium metal center, with two signals at 28.44 and -13.79 ppm for the four isopropyl methine protons and four sets of resonances at 9.78, 5.79, -0.77, and -24.22 ppm corresponding to the four sets of diastereotopic methyl groups of the isopropyl substituents. The  $\gamma$ -H and *tert*-butyl groups on the NCCCN backbone appear as singlets at -56.35 and -3.79 ppm, respectively.

We also attempted to prepare the bis( $\beta$ -diketiminate)uranium(IV) complex  $(L^{Me})_2UCl_2$ . However, as shown in Scheme 2, reaction of 2 equiv of  $K[L^{Me}]$  with  $UCl_4$  led instead to the cationic diuranium complex  $[\{(L^{Me})(Cl)U\}_2(\mu$ -Cl)\_3]-[Cl] (14), which was isolated as a dark brown solid in a modest 33% yield. The dimer's mode of formation is unclear; however, the reaction of  $(L^{Me})UCl_3(THF)$  (12) with another 1 equiv of  $K[L^{Me}]$  does not afford  $[\{(L^{Me})(Cl)U\}_2(\mu$ -Cl)\_3][Cl] (14), suggesting that 12 is not an intermediate in the formation of 14.

Compound 14 joins a small group of diuranium(IV) bridging chloride (where  $\mu$ -Cl > 1) complexes reported in the literature. In 1985, Cotton and Schwotzer reported the cationic



Figure 2. <sup>1</sup>H NMR spectrum of (L<sup>Me</sup>)UCl<sub>3</sub>(THF) (12) in C<sub>6</sub>D<sub>6</sub>. Peaks marked with asterisks denote the residual solvent of crystallization hexane.



Figure 3. X-ray crystal structures of  $(L^{Me})$ ThBr<sub>3</sub>(THF) (7),  $(L^{tBu})$ ThBr<sub>3</sub>(THF) (9; a <sup>t</sup>Bu group on one aryl ring was removed for clarity), and  $(L^{tBu})$ Th $(C_5H_4Me)Br_2$  (10).

	7	9	10	12	13	14
formula	$C_{41}H_{65}Br_3N_2O_3ThU$	$\mathrm{C}_{43}\mathrm{H}_{69}\mathrm{Br}_{3}\mathrm{N}_{2}\mathrm{O}_{2}\mathrm{Th}$	$C_{41}H_{60}Br_2N_2Th$	$C_{39}H_{63}Cl_3N_2OU$	$C_{35}H_{53}Cl_{3}N_{2}U$	$C_{68.50}H_{94}Cl_6N_4U_2$
a (Å)	36.731(9)	25.940(5)	10.62080(10)	35.507(8)	10.2148(4)	15.000(3)
b (Å)	12.654(3)	21.300(4)	20.3151(2)	12.576(3)	10.6827(4)	19.922(3)
c (Å)	22.999(6)	17.171(3)	18.8606(2)	22.923(5)	18.9861(8)	23.849(4)
$\alpha$ (deg)	90	90	90	90	83.799(1)	90
$\beta$ (deg)	124.220(4)	115.181(3)	105.5221(4)	124.222(3)	82.505(1)	91.273(3)
γ (deg)	90	90	90	90	61.941(1)	90
V (Å <sup>3</sup> )	8839(4)	8586(3)	3920.99(7)	8464(3)	1810.08(12)	7125(2)
Ζ	8	8	4	8	2	4
fw	1105.72	1117.77	972.77	920.29	846.17	1662.24
space group	C2/c	C2/c	$P2_{1}/c$	C2/c	$P\overline{1}$	$P2_1/n$
T(K)	140(2)	141(2)	141(2)	141(2)	141(2)	141(2)
$\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$D_{\rm calcd}~({\rm Mg}~{\rm m}^{-3})$	1.662	1.729	1.648	1.444	1.553	1.550
$\mu \ (\mathrm{mm}^{-1})$	6.123	6.303	5.871	4.054	4.730	4.805
R1 $(I > 2\sigma(I))$	0.0425	0.0347	0.0176	0.0602	0.0145	0.0652
wR2 (all data)	0.1051	0.0876	0.0493	0.1431	0.0390	0.1199

Table 1. Crystallographic Experimental Parameters for Complexes 7, 9, 10, and 12-14

compound {[U- $(\eta^6-C_6Me_6)Cl_2]_2(\mu-Cl)_3$ }AlCl<sub>4</sub>, which is quite similar to 14. This compound was formed using a variation of Fischer's reductive Friedel-Crafts reaction: the authors combined UCl<sub>4</sub>, AlCl<sub>3</sub>, and hexamethylbenzene in refluxing hexane for 12 h, replaced the solvent with CH<sub>2</sub>Cl<sub>2</sub>, and added zinc; after workup, yellow crystals of the cationic compound were isolated.<sup>20</sup> Subsequently,  $[UCl_3(THF)_2]_2(\mu$ -Cl)<sub>2</sub>, reported by Rebizant and co-workers, was synthesized from UCl<sub>4</sub> and THF in pentane at room temperature.<sup>21</sup> In 1994, Scott and Hitchcock prepared the first tripodal amido complex of uranium,  $[U(N'_{3}N)]_{2}(\mu-Cl)_{2}$   $(N'_{3}N = N[CH_{2}CH_{2}N-CH_$  $(SiMe_3)]_3$ ), by sublimation of the product of UCl<sub>4</sub> and Li<sub>3</sub>[N'<sub>3</sub>N] combined in cold THF, UCl(N'<sub>3</sub>N)(THF)<sub>x</sub> ( $x \leq$ 1).<sup>22</sup> In that same year, Arliguie and co-workers reported a cation-anion pair in which both ions were multinuclear in uranium; in this case, the anion was diuranium(IV):  $\{[UCl_2(Cp)]_2(\mu-Cl_3)\}^{-23}$  More recently, Coles and colleagues reported the structures  $[UCl(N(CH_2CH_2PR_2)_2)_2]_2(\mu-Cl_2)$  (R = Et, <sup>i</sup>Pr), in which each uranium(IV) has one tridentate and one bidentate phosphinoamide ligand.<sup>24</sup> The Evans group

described the synthesis of  $[UCl(O^{i}Pr)_{2}(DME)]_{2}(\mu-Cl)_{2}$  as a ligand redistribution product, which formed in low yield during an attempt to synthesize a mixed-metal zirconium–uranium-(IV) complex; this compound is very similar to the Rebizant structure, with the axial chlorides replaced by isopropoxides and the THF ligands replaced by DME.<sup>25</sup> Finally, the Liddle group reported several diuranium(IV) bridging chloride complexes,  $[UCl_{2}(BIPM^{TMS}H)]_{2}(\mu-Cl_{2})$  (BIPM<sup>TMS</sup> =  $C(PPh_{2}NSiMe_{3})_{2})$ ,  $[UCl(BIPM^{TMS})UCl(BIPM^{TMS}H)](\mu-Cl_{3})$ , and  $[UCl-(BIPM^{TMS})(THF)]_{2}(\mu-Cl_{2})$ , which were prepared en route to an arene-bridged diuranium single-molecule magnet.<sup>26</sup>

On the basis of our unsuccessful attempts to install two bulky  $\beta$ -diketiminate ligands on Th and U, we conclude that the combination of steric bulk and rigidity of these particular ( $\beta$ -diketiminate) ligands prevents the bis( $\beta$ -diketiminate) Th and U complexes from forming. In contrast, others have prepared bis(ligand) Th(IV) and U(IV) complexes with bulky but more flexible ligands, such as PNP,<sup>6s</sup> tris(pyrazolylborate),<sup>2a,6o,q</sup> cyclopentadienyl,<sup>2a,4e,27</sup> amidinate,<sup>6b,e,28</sup> and ferrocene diamide.<sup>29</sup> However, bis(ligand) complexes can be a dead end



Figure 4. X-ray crystal structures for  $(L^{Me})UCl_3(THF)$  (12),  $(L^{tBu})UCl_3$  (13), and  $[\{(L^{Me})(Cl)U\}_2(\mu-Cl)_3][Cl]$  (14). The 'Bu groups on the aryl rings in all three structures and Me groups on the NCCCN backbone of 14 were removed for clarity.

with respect to further reactivity, in that they tend to be thermodynamically and kinetically stable and can form as the majority product when the monoligand complex is the desired target. In comparison to their mono(ligand) counterparts, they can have reduced reactivity due to blocked access to the reactive electrophilic actinide center, as well as reduced electrophilicity at the actinide center due to twice the electron donation.

X-ray Crystallography. The X-ray crystal structures for the thorium bromide complexes (L<sup>Me</sup>)ThBr<sub>3</sub>(THF) (7), (L<sup>tBu</sup>)-ThBr<sub>3</sub>(THF) (9), and  $(L^{tBu})$ Th $(C_5H_4Me)$ Br<sub>2</sub> (10) are shown in Figure 3; crystal experimental parameters are given in Table 1. The average Th–Br distances in complex 7 (2.819 Å), complex 9 (2.841 Å), and complex 10 (2.833 Å) are similar, spanning a range of only 0.023 Å. These distances are comparable to those presented by the other reported thorium(IV) bromide complexes.<sup>30</sup> Substitution of a bromide ligand and a THF ligand (9) with a cyclopentadienyl ligand does not significantly affect the Th-Br distance in complex 10. The average Th-N distances also have a narrow range (0.054 Å), 2.444 Å (complex 7), 2.453 Å (complex 9), and 2.498 Å (complex 10), and provide a close match to those observed in the previously reported thorium  $\beta$ -diketiminate complexes  $[(2_{,6}-{}^{i}Pr_{2}C_{6}H_{3})NC(Me)CHC(Me)N(2_{,6}-{}^{i}Pr_{2}C_{6}H_{3})]ThI_{2}[O (CH_2)_4 I (THF)$  (2; Th-N(av) = 2.468 Å)<sup>8</sup> and [(Me\_3Si)- $NC(Ph)CHC(Ph)N(SiMe_3)$ ]<sub>2</sub>ThCl<sub>2</sub> (3; Th-N(av) = 2.467 Å).<sup>9a</sup> Finally, the Th–O distance is 2.467(4) Å in complex 7 and 2.520(3) Å in complex 9, while the Th $-C_{s}H_{4}Me$ (centroid) distance in complex 10 is 2.542(2) Å. Although these combined data show that moving from the smaller methyl substituent on the NCCCN backbone to the larger <sup>t</sup>Bu does not significantly lengthen the Th–N, Th–O, or Th–Br bond distances, the <sup>t</sup>Bu groups do cause the N-Th-N angles to widen: 74.43(15)° in complex 7, 82.94(11)° in complex 9, and 78.42(7)° in complex 10.

The X-ray crystal structures of the uranium chloride complexes  $(L^{Me})UCl_3(THF)$  (12),  $(L^{tBu})UCl_3$  (13), and  $[\{(L^{Me})(Cl)U\}_2(\mu-Cl)_3][Cl]$  (14) are shown in Figure 4; crystal experimental parameters are given in Table 1. As in the thorium counterparts, the average actinide—halide distances in the monometallic uranium complexes are very similar, at 2.594

Å for complex 12 and 2.578 Å for complex 13. These distances are comparable to those reported for other structurally characterized uranium(IV) chloride complexes.<sup>31</sup> In the cationic bimetallic complex 14, however, the terminal uranium chloride distances are slightly longer, at U-Cl(av) = 2.639 Å. Also, as is typical for complexes containing both bridging and terminal ligands, the U-( $\mu$ -Cl) distances are longer than the terminal U–Cl distances: the U– $(\mu$ -Cl)(av) distance in 14 is 2.827 Å. This U–( $\mu$ -Cl) distance is average for dinuclear U(IV) complexes with bridging chlorides.<sup>32</sup> The U…U distance in complex 14 is 4.0389(7) Å, which is at the low end of the range of other similar complexes.<sup>33</sup> The U–N(av) distances and N– U-N angles are nearly the same in the two monometallic uranium complexes (2.391 Å and 76.9(3)° for 12; 2.3576 Å and  $76.79(5)^{\circ}$  for 13) and are comparable to those observed for other known uranium  $\beta$ -diketiminate complexes (e.g.: 5, U-N(av) = 2.417 Å and  $N-U-N = 72.4(2)^{\circ}$ ;<sup>10b</sup> 6, U-N(av) =2.48 Å and N–U–N = 72.6(5) $^{\circ 10a}$ ). Neither the N–U–N angles nor the U-N or U-Cl distances show even the small differences seen in the thorium complexes as a result of moving from methyl to *tert*-butyl groups.

In all the thorium and uranium  $\beta$ -diketiminate complexes, the actinide metal ion is situated above the plane defined by the NCCCN ligand backbone. This distance is greater in the monometallic L<sup>tBu</sup> complexes (~1.7–1.9 Å) than in the L<sup>Me</sup> complexes (~0.82–0.89 Å). As noted earlier, this difference is also observed in solution by <sup>1</sup>H NMR spectroscopy, with the appearance of inequivalent <sup>tBu</sup> groups in the L<sup>tBu</sup> complexes but equivalent Me groups in the L<sup>Me</sup> complexes. Overall, these compounds can be considered to exhibit electron delocalization over the  $\beta$ -diketiminate ligand, and interestingly, their An–N distances compare well to those within actinide bis(ketimide) complexes.<sup>4e,27b,34</sup>

Electrochemistry and Electronic Spectroscopy. To assess and compare the electronic structures in the mono( $\beta$ -diketiminate) complexes to those in similar thorium(IV) and uranium(IV) systems electrochemical and UV–visible–near-infrared absorption spectroscopic studies were undertaken. Voltammetric data of K[L<sup>Me</sup>] and complex 12 were obtained in [Pr<sub>4</sub>N][B{3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>}<sub>4</sub>]/1,1,1-trifluorotoluene solutions (see the Supporting Information for details). Complex 12 was

determined to rapidly degrade in electrolyte solutions of THF, necessitating the switch to the less coordinating solvent 1,1,1trifluorotoluene. The voltammetric behavior of K[L<sup>Me</sup>] was fairly straightforward, exhibiting a single irreversible oxidation wave at  $\sim +0.55$  V (all potentials are referenced to the  $[(C_5H_5)_2Fe]^{+/0}$  couple) and no observable reductive electrochemical processes within the available cathodic potential limit  $(\sim -2.8 \text{ V})$  of this solvent/electrolyte system. In contrast, the voltammetric behavior of 12, while reproducible, was quite complex. Two irreversible oxidation processes were observed at ~+0.53 and +0.65 V, which we ascribe to a ligand-based oxidation comparable to that for the free ligand and probable oxidation of one or more of the bound chloride ions. In addition, 12 exhibited a total of three irreversible reduction waves in the range from -1.84 to -2.34 V. On the basis of previous studies by us and others,<sup>4d</sup> this is the proper potential range to anticipate a U(VI)/U(III) reduction process for this coordination environment, but the appearance of three discrete reduction steps (and the absence of reductive voltammetry for the free ligand) suggests there are some coupled chemical transformations in concert with metal-based reduction that lead to additional reduction waves. Electrochemical studies of the analogous Th(IV) complexes (e.g., 8) were not attempted.

The UV–visible–near-infrared absorption spectral data for  $K[L^{Me}]$  and complexes 8 and 12 in toluene solution are illustrated in Figure 5. There is an excellent correlation in the



Figure 5. UV–visible–near-infrared electronic absorption spectral data of  $K[L^{Me}]$ ,  $(L^{Me})ThI_3(THF)$  (8), and  $(L^{Me})UCl_3(THF)$  (12) in toluene solution at room temperature.

most intense absorption bands among all three systems in the UV-visible region. In particular, each system exhibits two intense high-energy bands above  $\sim 25000 \text{ cm}^{-1}$  (400 nm). The energetically higher lying of these two bands appears at nearly identical energies for all three systems ( $\sim$ 31000 cm<sup>-1</sup>), whereas the lower lying of the two bands shows substantial variation among the free ligand anion  $K[L^{Me}]$ , the Th(IV) complex 8, and the U(IV) complex 12. As shown in Figure 5, the U(IV)complex 12 also exhibits two additional broad, low-intensity features (illustrated by dotted lines from spectral fitting) in the visible region, attributed to charge transfer transitions (likely ligand to metal on the basis of the electrochemical data, indicating relative ease of oxidation of the ligand and reduction of the U(IV) center) as well as a host of narrow, very low intensity features in the near-infrared attributable to f-f transitions arising from the <sup>3</sup>H<sub>4</sub> manifold of the 5f<sup>2</sup> valence electronic configuration on the  $U(\ensuremath{\mathrm{IV}})$  metal ion.

The assignment of these electronic transitions merits some additional discussion because of the insight it may provide into the electronic structure and metal-ligand interactions in these  $\beta$ -diketiminate complexes of the tetravalent actinides. In this regard, a previous experimental and theoretical study of Cu(II) complexes containing  $\beta$ -diketiminate ligands is particularly relevant.<sup>35</sup> In this study involving  $(L^{Me})$ CuSCPh<sub>3</sub>, the  $\beta$ diketiminate ligand was modeled in density functional theory calculations as a simplified C<sub>3</sub>N<sub>2</sub>H<sub>5</sub> group to arrive at a description of the orbital character and relative energetics of the highest lying occupied (HOMO) and lowest lying unoccupied (LUMO) molecular orbitals of the free  $\beta$ -diketiminate ligand. In particular, the HOMO is defined as a combination of out-ofplane p orbitals on the two nitrogen atoms and the central carbon atom, whereas the next lowest lying molecular orbital (HOMO-1; only 0.2 eV lower in energy) is defined as an inplane, out-of-phase combination of p orbitals on the two nitrogen atoms. The LUMO is described as an out-of-plane combination of p orbitals on the two nitrogen atoms and the two  $\alpha$ -carbon atoms. Experimentally, for this Cu(II) complex there are two high-energy  $\pi - \pi^*$  transitions observed at 28500  $cm^{-1}$  ( $\varepsilon = 16360 \text{ M}^{-1} \text{ cm}^{-1}$ ) and ~30500  $cm^{-1}$  ( $\varepsilon = ~13000$  $M^{-1}$  cm<sup>-1</sup>) that are assigned to the  $\beta$ -diketiminate localized HOMO  $\rightarrow$  LUMO and HOMO-1  $\rightarrow$  LUMO transitions. These results are in excellent agreement with those observed in the present study for  $K[L^{Me}]$  and complexes 8 and 12 for the two highest energy bands illustrated in Figure 5, strongly suggesting that these bands have very similar  $\beta$ -diketiminate orbital origins in our actinide systems.

As noted above, the higher energy putative  $\pi - \pi^*$  band in our systems (Figure 5) is nearly insensitive to the metal ion identity. In contrast, the lower energy putative HOMO  $\rightarrow$ LUMO band in our systems is quite sensitive to the identity of the coordinating (Th(IV) vs U(IV)) or counter metal ion  $(K^+)$ . Recall that the structural data for the actinide(IV) complexes (vide supra) shows that the metal ion lies substantially out of the plane of the NCCCN backbone. Thus, direct  $\sigma$ -bonding interactions between the in-plane ligand orbitals in HOMO-1 and the metal orbitals should be diminished relative to the expected interaction for coplanarity in metal-ligand bonding. However, because of the much greater angular distribution of the frontier f orbitals in these actinides, there should be potential for relatively more interaction between the out-ofplane ligand orbitals in the HOMO and the metal f orbitals that could lead to the observed variability in the behavior of the lower-lying electronic transition. The relative energies of the metal f and d orbitals for U(IV) vs Th(IV) with respect to those of the ligand orbitals are also clearly contributing to the observed differences in these spectral band energies and intensities.

A final interesting observation regarding the electronic spectral data in these mono( $\beta$ -diketiminate) complexes pertains to the intensity in the f–f electronic bands in the near-infrared spectral region for **12**. We have reported a strong correlation for U(IV) and U(V) complexes in the intensity of the f–f transitions and the extent of covalency in the metal–ligand bonding.<sup>4b,d,e,5a,27b,36</sup> For example, in the bis(ketimide) complexes of U(IV) for which there is evidence of partial multiple-bond character in the metal–ketimide bonding, the f–f transition intensities are typically ~100–200 M<sup>-1</sup> cm<sup>-1</sup>. For **12** we find the f–f bands have intensities of only ~5–10 M<sup>-1</sup> cm<sup>-1</sup>. These are among some of the smallest values we have observed for f–f bands in organouranium complex-

es.<sup>4b,d,e,5a,13f,27b,36</sup> Thus, although the  $\beta$ -diketiminate ligand may be formally akin to a bis(ketimide) in its coordination environment, it is clear that the metal–ligand coordination geometry induced by the  $\beta$ -diketiminate precludes strong metal–ligand bonding interactions. This observation reinforces the value of f–f intensities as a qualitative means to assess metal–ligand bonding interactions in organoactinide complexes.

#### CONCLUSIONS

In summary, the first thorium(IV) and uranium(IV) halide complexes supported by the ligands N,N'-bis(2,6diisopropylphenyl)pentane-2,4-diiminate  $(L^{Me})$  and N,N'-bis-(2,6-diisopropylphenyl)-2,2-6,6-tetramethylheptane-3,5-diiminate  $(L^{tBu})$  have been prepared. The mono( $\beta$ -diketiminate) halide complexes  $(L^{Me})AnX_3(THF)$  (An = Th, X = Br, I; An = U, X = Cl) and  $(L^{tBu})AnX_3(THF)$  (An = Th, X = Br, I; An = U, X = Cl) were synthesized, as well as a mixed-ligand methylcyclopentadienyl  $\beta$ -diketiminate complex, (L<sup>tBu</sup>)Th- $(C_5H_4Me)Br_2$ . We anticipate that this new class of actinide compounds will be useful as starting materials for future thorium and uranium  $\beta$ -diketiminate reactivity studies. Interestingly, the corresponding  $bis(\beta$ -diketiminate) halide complexes could not be prepared, and for uranium, the cationic diuranium complex  $[{(L^{Me})(Cl)U}_2(\mu-Cl)_3][Cl]$  was isolated instead. To gain information about the electronic and structural consequences of installing the  $\beta$ -diketiminate ligand on thorium and uranium, we performed a combination of <sup>1</sup>H and  ${}^{13}C{}^{1}H$ NMR spectroscopy, elemental analysis, X-ray crystallography, and UV-visible-near-IR spectroscopy. Due to the large ionic radius of the actinide metal centers, in all cases, the actinide(IV) metal centers lie out of the plane of the  $\beta$ diketiminate ligand NCCCN backbone by  $\sim 1-2$  Å. The UVvisible-near-infrared electronic spectroscopic data for complexes  $(L^{Me})ThI_3(THF)$  (8) and  $(L^{Me})UCl_3(THF)$  (12) reflect this interesting metal-ligand bonding motif in the mono( $\beta$ diketiminate) halide complexes. Specifically, perturbations in ligand-based transitions in the UV region are consistent with the out-of-plane metal binding, while the intensities in the f-f transitions in the near-IR region for  $(L^{Me})UCl_3(THF)$  (12) demonstrate that the covalent bonding interaction is relatively weak.

#### EXPERIMENTAL SECTION

Instrumentation and Sample Protocols. Electronic absorption spectral data were obtained for toluene solutions of complexes over the wavelength range 300–1600 nm on a Perkin-Elmer Model Lambda 950 UV–visible–near-infrared spectrophotometer. All data were collected in 1.0 or 0.1 cm path length cuvettes loaded in a recirculating Vacuum Atmospheres NEXUS model inert-atmosphere (N<sub>2</sub>) drybox equipped with a 40CFM Dual Purifier NI-Train. Sample concentrations ranged from ~0.05 to ~20 mM, to optimize absorbance in the UV–visible and near-infrared regions. Spectral resolution was typically 2 nm in the visible region and 4–6 nm in the near-infrared region. Sample spectra were obtained versus air and corrected for solvent absorption subsequent to data acquisition.

Cyclic and square wave voltammetric data were obtained in the Vacuum Atmospheres drybox system described above. All data were collected using a Princeton Applied Research Corp. (PARC) Model 263 potentiostat under computer control with PARC Model 270 software. All sample solutions were ~2–3 mM in complex with 0.1 M [Pr<sub>4</sub>N][B{3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}] supporting electrolyte in 1,1,1-trifluorotoluene solvent. All data were collected with the positive-feedback IR compensation feature of the software/potentiostat activated to ensure minimal contribution to the voltammetric waves from uncompensated

solution resistance (typically ~1000  $\Omega$  under the conditions employed). Solutions were contained in PARC Model K0264 microcells consisting of a ~3 mm diameter Pt-disk working electrode, a Pt-wire counter electrode, and a silver-wire quasi-reference electrode. Scan rates from 20 to 5000 mV/s were employed in the cyclic voltammetry scans to assess the chemical and electrochemical reversibility of the observed redox transformations. Half-wave potentials were determined from the peak values in the square-wave voltammograms or from the average of the cathodic and anodic peak potentials in the reversible cyclic voltammograms. Potential calibrations were performed at the end of each data collection cycle using the ferrocenium/ferrocene couple as an internal standard. Electronic absorption and cyclic voltammetric data were analyzed using Wavemetrics IGOR Pro (Version 4.0) software on a Macintosh platform.

**General Synthetic Considerations.** Unless otherwise noted, reactions and manipulations were performed at ambient temperatures in a recirculating Vacuum Atmospheres Model HE-553-2 inert-atmosphere (He or  $N_2$ ) drybox equipped with a MO-40-2 Dri-Train, a Vacuum Atmospheres NEXUS model inert-atmosphere ( $N_2$ ) drybox equipped with a 40CFM Dual Purifier NI-Train, or using standard Schlenk techniques. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra are reported in parts per million (ppm) and were referenced to tetramethylsilane. <sup>13</sup>C{<sup>1</sup>H} NMR assignments were confirmed through the use of DEPT-135 experiments. Elemental analyses were performed at the University of California, Berkeley, Microanalytical facility on a Perkin-Elmer Series 2400 CHNS Analyzer.

**Materials.** Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich), alumina (Brockman I, Aldrich), and 3 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. All solvents (Aldrich) were purchased anhydrous and were dried over KH for 24 h, passed through a column of activated alumina, and stored over activated 3 Å molecular sieves prior to use. Benzene-*d*<sub>6</sub> (Aldrich) and tetrahydrofuran-*d*<sub>8</sub> (Cambridge Isotope Laboratories) were purified by storage over activated 3 Å molecular sieves prior to use. Iodine was purchased from Sigma Aldrich and used as received. K[L<sup>Me</sup>], K[L<sup>Hbu</sup>], and K[C<sub>5</sub>H<sub>4</sub>Me] were prepared as detailed below. H[(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NC(Me)CHC(Me)N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)],<sup>37</sup> H-[(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NC(<sup>t</sup>Bu)CHC(<sup>t</sup>Bu)N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)],<sup>38</sup> ThBr<sub>4</sub>(THF)<sub>4</sub>,<sup>11</sup> ThI<sub>4</sub>(THF)<sub>4</sub>,<sup>11</sup> ThI<sub>4</sub>(DME)<sub>2</sub><sup>8</sup> and UCl<sub>4</sub><sup>19e</sup> were prepared according to literature procedures.

*Caution*! Depleted uranium (primarily isotope <sup>238</sup>U) and natural thorium (isotope <sup>232</sup>Th) are both weak  $\alpha$ -emitters with half-lives of 4.47 × 10<sup>9</sup> and 1.41 × 10<sup>10</sup> years, respectively. Manipulations and reactions should be carried out in monitored fume hoods or in an inert-atmosphere drybox in a radiation laboratory equipped with  $\alpha$ - and  $\beta$ -counting equipment.

Synthesis of K[L<sup>Me</sup>]. A 50 mL round-bottomed flask equipped with a stir bar was charged with H[( $2,6^{-i}Pr_2C_6H_3$ )NC(Me)CHC-(Me)N( $2,6^{-i}Pr_2C_6H_3$ )] (1.20 g, 2.87 mmol) and diethyl ether (20 mL). To this clear brown solution was added K[N(SiMe\_3)\_2] (0.573 g, 2.87 mmol), causing the solution to become darker brown. The reaction mixture was stirred at room temperature. After 18 h, the reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter, and the volatiles were removed under reduced pressure. The resulting solid was scraped and transferred to a medium-porosity fritted filter and washed with hexane (3 × 10 mL). The washed solid was dried under reduced pressure to give K[L<sup>Me</sup>] as an off-white solid (1.268 g, 2.78 mmol, 97%). <sup>1</sup>H NMR ( $C_6D_6$ , 298 K):  $\delta$  7.06–7.01 (m, 6H, Ar-H), 4.82 (s, 1H,  $\gamma$ -C-H), 3.36 (sept, J = 27 Hz, 4H, CHMe<sub>2</sub>), 1.89 (s, 6H, C(CH<sub>3</sub>)), 1.26 (d, J = 6 Hz, 12H, CHMe<sub>2</sub>), 1.07 (d, J = 6Hz, 12H, CHMe<sub>5</sub>).

Synthesis of  $K[L^{tBu}]$ . A 250 mL side-arm flask equipped with a stir bar was charged with  $H[(2,6^{-i}Pr_2C_6H_3)NC({}^tBu)CHC({}^tBu)N-(2,6^{-i}Pr_2C_6H_3)]$  (2.50 g, 4.97 mmol) and THF (75 mL). To this was added KH (0.400 g, 9.97 mmol). The reaction mixture was stirred at reflux temperature. After 1 h, the heat was turned off and the reaction mixture stirred at room temperature. After 18 h, the reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter, and the volatiles were removed under reduced pressure. The resulting yellow solid was scraped and transferred to a medium-porosity fritted filter and washed with pentane (75 mL). The washed solid was dried under reduced pressure to give K[L<sup>tBu</sup>] as a pale yellow solid (1.90 g, 3.51 mmol, 71%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.00 (d, *J* = 9 Hz, 4H, *m*-Ar-H), 6.82 (t, *J* = 6 Hz, 2H, *p*-Ar-H), 4.94 (s, 1H,  $\gamma$ -C-H), 3.27 (sept, *J* = 39 Hz, 4H, CHMe<sub>2</sub>), 1.38 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.34 (d, *J* = 9 Hz, 12H, CHMe<sub>2</sub>), 0.94 (d, *J* = 6 Hz, 12H, CHMe<sub>2</sub>).

**Synthesis of K[C<sub>5</sub>H<sub>4</sub>Me].** A 250 mL side-arm flask equipped with a stir bar was charged with K[N(SiMe<sub>3</sub>)<sub>2</sub>] (9.52 g, 47.7 mmol) and diethyl ether (200 mL). To this stirred slurry was added portionwise  $C_5H_5Me$  (4.99 g, 62.2 mmol) over the course of 15–30 min. The resulting pale yellow slurry was stirred at room temperature. After 18 h, the volatiles were removed under reduced pressure. Hexanes (75 mL) was added to the resulting off-white solid residue, and the mixture was stirred at room temperature. After 12 h, the slurry was filtered through a coarse-porosity fritted filter. The solid was washed with hexanes (3 × 20 mL) and dried under reduced pressure to give K[C<sub>5</sub>H<sub>4</sub>Me] as an off-white solid (5.21 g, 44.1 mmol, 92%). <sup>1</sup>H NMR (THF- $d_{sy}$  298 K):  $\delta$  5.33 (s, 2H,  $C_5H_4Me$ ), 5.29 (s, 2H,  $C_5H_4Me$ ), 2.09 (s, 3H, CH<sub>3</sub>).

Synthesis of (L<sup>Me</sup>)ThBr<sub>3</sub>(THF) (7). A 125 mL side-arm flask equipped with a stir bar was charged with  $K[L^{Me}]$  (0.300 g, 0.657 mmol), ThBr<sub>4</sub>(THF)<sub>4</sub> (0.546 g, 0.653 mmol), and toluene (60 mL). The reaction mixture was stirred at room temperature. After 15 h, the reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter and the volatiles were removed under reduced pressure. The resulting yellow solid residue was extracted with hexanes  $(2 \times 25)$ mL). The yellow extracts were combined and filtered through a Celitepadded coarse-porosity fritted filter. The yellow filtrate was concentrated under reduced pressure to ~20 mL and placed in a -35 °C freezer to afford 7 as a yellow crystalline (X-ray quality) solid (0.350 g, 0.364 mmol, 56%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.16–7.22 (m, 6H, Ar-H), 5.21 (s, 1H,  $\gamma$ -C-H), 4.07 (bs, 4H, OCH<sub>2</sub>), 3.60 (sept, J = 6.9 Hz, 4H, CHMe<sub>2</sub>), 1.66 (d, J = 6.9 Hz, 12H, CHMe<sub>2</sub>), 1.64 (s, 6H, CH<sub>3</sub>), 1.23 (bs, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.17 (d, J = 6.9 Hz, 12H, CHMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  168.25 (C=N), 145.56  $(Ar_{dipp}-C_o)$ , 141.42  $(Ar_{dipp}-C_{ipso})$ , 128.65  $(Ar_{dipp}-C_p)$ , 125.72  $(Ar_{dipp}-C_p)$  $C_m$ ), 105.42 ( $\gamma$ -CH), 77.63 (OCH<sub>2</sub>CH<sub>2</sub>), 30.01 (CHMe<sub>2</sub>), 26.32 (OCH<sub>2</sub>CH<sub>2</sub>), 25.98 (CHMe<sub>2</sub>), 25.27 (CH<sub>3</sub>), 25.16 (CHMe<sub>2</sub>). Anal. Calcd for C33H49Br3N2OTh (mol wt 961.51): C, 41.22; H, 5.14; N, 2.91. Found: C, 41.00; H, 4.92; N, 2.85.

Synthesis of (L<sup>Me</sup>)Thl<sub>3</sub>(THF) (8). Method A: From Thl<sub>4</sub>(THF)<sub>4</sub>. A 125 mL side-arm flask equipped with a stir bar was charged with K[L<sup>Me</sup>] (0.229 g, 0.501 mmol), ThI<sub>4</sub>(THF)<sub>4</sub> (0.513 g, 0.501 mmol), and toluene (25 mL). The reaction mixture was stirred at room temperature. After 15 h, the reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter and the volatiles were removed under reduced pressure. The resulting yellow solid residue was washed with hexanes  $(2 \times 25 \text{ mL})$ . The yellow washings were decanted, and the remaining solid was dried under reduced pressure to give analytically pure 8 as a yellow solid (0.215 g, 0.649 mmol, 39%). X-ray-quality crystals of 8 were obtained by slow diffusion of hexanes into a concentrated THF solution at ambient temperature. <sup>1</sup>H NMR  $(C_6 D_{6^{\prime}} 298 \text{ K}): \delta 7.16 - 7.28 \text{ (m, 6H, Ar-H), 5.31} (s, 1H, \gamma-C-H), 4.37$ (bs, 4H, OCH<sub>2</sub>), 3.53 (sept, J = 6.9 Hz, 4H, CHMe<sub>2</sub>), 1.63 (d, J = 6.9Hz, 12H, CHMe<sub>2</sub>), 1.60 (s, 6H, CH<sub>3</sub>), 1.23 (bs, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.13  $(d, J = 6.9 \text{ Hz}, 12\text{H}, \text{CHM}e_2)$ . <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  168.56 (C=N), 143.90  $(Ar_{dipp}-C_o)$ , 142.80  $(Ar_{dipp}-C_{ipso})$ , 125.28  $(Ar_{dipp}-C_m)$ , 105.94 (γ-CH), 29.92 (CHMe<sub>2</sub>), 26.23 (CH<sub>3</sub>), 25.41 (CHMe<sub>2</sub>), 24.97 (CHMe<sub>2</sub>). The  ${}^{13}C{}^{1}H$  resonances for the coordinated THF and the  $Ar_{dipp}$ - $C_p$  were not observed. Anal. Calcd for  $C_{33}H_{49}I_3N_2OTh$  (mol wt 1102.51): C, 35.95; H, 4.48; N, 2.54. Found: C, 35.67; H, 4.61; N, 2.49

Method B: From  $Thl_4(DME)_2$ . A 20 mL scintillation vial was charged with  $ThI_4(DME)_2$  (0.1107 g, 0.1203 mmol), THF (5 mL), and a stir bar. This reaction mixture was stirred for 20 min at -35 °C, and then the volatiles were removed under reduced pressure. (A <sup>1</sup>H NMR spectrum acquired at this point showed the two DME ligands displaced by four THF ligands, with peaks at 4.30 and 1.30 ppm.) A toluene solution of  $K[L^{Me}]$  (0.0550 g in 5 mL) was prepared and cooled to -35 °C. Cold toluene (6 mL, -35 °C) was added to the dried reaction mixture, followed by the addition of the cooled toluene solution of  $K[L^{Me}]$ . The reaction mixture was stirred at room temperature for 1 h, and then the volatiles were removed under reduced pressure. The dried reaction mixture was extracted with pentane, and the pentane extract was filtered through a pipet equipped with a fiberglass plug and packed with Celite. The pentane filtrate was discarded, and the reaction mixture was then extracted with toluene and the extract filtered through the same Celite pipet. The toluene filtrate was dried, giving pure 8 (by <sup>1</sup>H NMR; shifts identical with those listed above) as a yellow solid (0.0544 g, 0.0487 mmol, 40%).

Synthesis of (L<sup>tBu</sup>)ThBr<sub>3</sub>(THF) (9). A 125 mL side-arm flask equipped with a stir bar was charged with K[L<sup>tBu</sup>] (1.00 g, 1.85 mmol), ThBr<sub>4</sub>(THF)<sub>4</sub> (1.63 g, 1.94 mmol), and toluene (75 mL). The reaction mixture was stirred at room temperature. After 15 h, the reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter and the volatiles were removed under reduced pressure. The resulting yellow solid residue was washed with hexanes  $(2 \times 25)$ mL). The yellow washings were decanted, and the remaining solid was dried under reduced pressure to give analytically pure 9 as a yellow solid (1.51 g, 1.44 mmol, 74%). X-ray-quality crystals of 9 were obtained by recrystallization from a concentrated toluene solution at  $-35 \,^{\circ}$ C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.05–7.02 (m, 2H, Ar-H), 6.96– 6.88 (m, 4H, Ar-H), 6.66 (s, 1H, γ-C-H), 4.31 (m, 4H, OCH<sub>2</sub>), 3.71 (sept, J = 6.9 Hz, 2H, CHMe<sub>2</sub>), 2.49 (sept, J = 6.9 Hz, 2H, CHMe<sub>2</sub>), 1.73 (d, J = 6.9 Hz, 6H, CHMe<sub>2</sub>), 1.41 (d, J = 6.9 Hz, 6H, CHMe<sub>2</sub>), 1.30 (m, 4H,  $OCH_2CH_2$ ), 1.09 (s, 18H,  $CMe_3$ ), 0.98 (d, J = 6.9 Hz, 6H, CHMe<sub>2</sub>), 0.83 (d, J = 6.9 Hz, 6H, CHMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) 298 K): 5 171.28 (C=N), 144.32 (Ar<sub>dipp</sub>-C<sub>o</sub>), 142.45 (Ar<sub>dipp</sub>-C<sub>o</sub>), 138.20 (Ar<sub>dipp</sub>- $C_{ipso}$ ), 126.55 (Ar<sub>dipp</sub>- $C_p$ ), 126.10 (Ar<sub>dipp</sub>- $C_m$ ), 125.14 ( $\gamma$ -CH), 44.89 (CMe<sub>3</sub>), 34.27 (CHMe<sub>2</sub>), 30.02 (CMe<sub>3</sub>), 28.29 (CHMe<sub>2</sub>), 27.39 (CHMe<sub>2</sub>), 26.87 (CHMe<sub>2</sub>), 26.82 (CHMe<sub>2</sub>), 25.17 (CHMe<sub>2</sub>). The  ${}^{13}C{}^{1}H$  resonances for the coordinated THF were not observed. Anal. Calcd for C<sub>39</sub>H<sub>61</sub>Br<sub>3</sub>N<sub>2</sub>OTh (mol wt 1045.66): C, 44.80; H, 5.88; N, 2.68. Found: C, 44.91; H, 6.13; N, 2.69.

Synthesis of  $(L^{tBu})(C_5H_4Me)ThBr_2$  (10). A 125 mL side-arm flask equipped with a stir bar was charged with (LtBu)ThBr<sub>3</sub>(THF) (9; 0.451 g, 0.431 mmol), K[C5H4Me] (0.105 g, 0.888 mmol), and toluene (55 mL). The reaction mixture was brought to a mild reflux for 5 min and then cooled to room temperature with stirring. After 12 h, the reaction mixture was filtered through a Celite-padded coarseporosity fritted filter and the volatiles were removed under reduced pressure. The resulting yellow solid residue was washed with hexanes  $(2 \times 20 \text{ mL})$  and dried under reduced pressure. Analytically pure 10 was obtained by recrystallization from a saturated hexanes/toluene (80/20) solution at -35 °C (0.310 g, 0.319 mmol, 74%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 7.12–7.09 (m, 2H, Ar-H), 6.97 (m, 4H, Ar-H), 6.73 (m, 2H,  $C_5H_4Me$ ), 6.56 (s, 1H,  $\gamma$ -C-H), 5.84 (m, 2H,  $C_5H_4Me$ ), 3.41 (sept, J = 6.9 Hz, 2H, CHMe<sub>2</sub>), 2.89 (s, 3H, C<sub>5</sub>H<sub>4</sub>Me), 2.67 (sept, J =6.9 Hz, 2H, CHMe<sub>2</sub>), 1.60 (d, J = 6.9 Hz, 6H, CHMe<sub>2</sub>), 1.42 (d, J =6.9 Hz, 6H, CHMe<sub>2</sub>), 1.18 (s, 18H, CMe<sub>3</sub>), 1.04 (d, J = 6.9 Hz, 6H, CHMe<sub>2</sub>), 0.89 (d, J = 6.9 Hz, 6H, CHMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  174.11 (C=N), 146.27 (Ar<sub>dipp</sub>-C<sub>ipso</sub>), 140.56 (Ar<sub>dipp</sub>-C<sub>o</sub>), 139.07 (Ar<sub>dipp</sub>-C<sub>o</sub>), 136.67 (C<sub>4</sub>H<sub>4</sub>C-Me), 125.69 (Ar<sub>dipp</sub>-C<sub>p</sub>), 125.53 (Ar<sub>dipp</sub>-C<sub>o</sub>), 125.5  $C_m$ ), 124.38 (Ar<sub>dipp</sub>- $C_m$ ), 122.97 ( $\gamma$ -CH), 120.33 ( $C_4H_4CMe$ ), 98.49 (C<sub>4</sub>H<sub>4</sub>CMe), 44.66 (CMe<sub>3</sub>), 31.43 (CHMe<sub>2</sub>), 30.88 (CMe<sub>3</sub>), 27.69 (CHMe<sub>2</sub>), 27.21 (CHMe<sub>2</sub>), 26.86 (CHMe<sub>2</sub>), 26.44 (CHMe<sub>2</sub>), 24.29 (CHMe<sub>2</sub>), 17.19 (C<sub>5</sub>H<sub>4</sub>Me). Anal. Calcd for C<sub>41</sub>H<sub>60</sub>Br<sub>2</sub>N<sub>2</sub>Th (mol wt 972.77): C, 50.62; H, 6.22; N, 2.88. Found: C, 50.91; H, 6.43; N, 2.83.

**Synthesis of (L<sup>tBu</sup>)Thl<sub>3</sub> (11).** A 125 mL side-arm flask equipped with a stir bar was charged with K[L<sup>tBu</sup>] (0.270 g, 0.500 mmol), ThI<sub>4</sub>(THF)<sub>4</sub> (0.513 g, 0.500 mmol) and toluene (25 mL). The reaction mixture was stirred at room temperature. After 15 h, the reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter and the volatiles were removed under reduced pressure. The resulting yellow solid residue was washed with hexanes (2 × 15 mL). The yellow washings were decanted and the remaining solid was

dried under reduced pressure to give analytically pure **11** as a yellow solid (0.251 g, 0.225 mmol, 45%). <sup>1</sup>H NMR ( $C_6D_6$ , 298 K):  $\delta$  7.04–7.02 (m, 2H, Ar-H), 6.93–6.88 (m, 4H, Ar-H), 6.74 (s, 1H,  $\gamma$ -C-H), 3.68 (sept, J = 6.9 Hz, 2H, CHMe<sub>2</sub>), 2.50 (sept, J = 6.9 Hz, 2H, CHMe<sub>2</sub>), 1.73 (d, J = 6.9 Hz, 6H, CHMe<sub>2</sub>), 1.40 (d, J = 6.9 Hz, 6H, CHMe<sub>2</sub>), 1.08 (s, 18H, CMe<sub>3</sub>), 0.97 (d, J = 6.9 Hz, 6H, CHMe<sub>2</sub>), 0.81 (d, J = 6.9 Hz, 6H, CHMe<sub>2</sub>), 1.36 (Ar<sub>dipp</sub>-C<sub>o</sub>), 140.21 (Ar<sub>dipp</sub>-C<sub>o</sub>), 137.76 (Ar<sub>dipp</sub>-C<sub>ipso</sub>), 126.20 (Ar<sub>dipp</sub>-C<sub>o</sub>), 125.69 (Ar<sub>dipp</sub>-C<sub>p</sub>), 124.76 ( $\gamma$ -CH), 44.31 (CMe<sub>3</sub>), 33.88 (CHMe<sub>2</sub>), 29.68 (CMe<sub>2</sub>), 27.92 (CHMe<sub>2</sub>), 26.94 (CHMe<sub>2</sub>), 26.46 (CHMe<sub>2</sub>), 26.45 (CHMe<sub>2</sub>), 24.81 (CHMe<sub>2</sub>). Anal. Calcd for C<sub>35</sub>H<sub>53</sub>I<sub>3</sub>N<sub>2</sub>Th (mol wt 1114.17): C, 37.72; H, 4.79; N, 2.51. Found: C, 37.91; H, 4.80; N, 2.36.

C, 37.91; H, 4.80; N, 2.36. Synthesis of (L<sup>Me</sup>)UCl<sub>3</sub>(THF) (12). A 50 mL side-arm flask equipped with a stir bar was charged with  $K[L^{\rm Me}]$  (0.200 g, 0.438 mmol), UCl<sub>4</sub> (0.148 g, 0.390 mmol), and tetrahydrofuran (20 mL). The reaction mixture was stirred at room temperature. After 15 h, the reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter and the volatiles were removed under reduced pressure. The resulting red residue was extracted with toluene  $(2 \times 15 \text{ mL})$ . The red extracts were combined and filtered through a Celite-padded coarse-porosity fritted filter. The volatiles were removed under reduced pressure, and the resulting red solid was washed with hexanes  $(2 \times 10 \text{ mL})$ . The washings were decanted, and the remaining solid was dried under reduced pressure to give 12 as a red solid (0.235 g, 0.282 mmol, 72%). X-ray-quality crystals of 12 were obtained by slowly cooling a hot hexanes solution (over 3 h) to ambient temperature. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 13.20 (s, 1H, γ-C-H), 4.40 (t, J = 7.75 Hz, 2H, Ar- $H_p$ ), 3.60 (d, J = 7.75 Hz, 4H, Ar- $H_m$ ), 0.27 (d, J = 7.75 Hz, 4H 6.0 Hz, 12H, CHMe<sub>2</sub>), -0.89 (s, 6H, CH<sub>3</sub>), -1.54 (bs, 4H, CH<sub>2</sub>O), -4.97 (d, J = 6.0 Hz, 12H, CHMe<sub>2</sub>), -6.26 (b, 4H, CHMe<sub>2</sub>), -7.52(bs, 4H, CH<sub>2</sub>CH<sub>2</sub>O). Anal. Calcd for C<sub>33</sub>H<sub>49</sub>Cl<sub>3</sub>N<sub>2</sub>OTh•C<sub>6</sub>H<sub>14</sub> (mol wt 920.32): C, 50.90; H, 6.90; N, 3.04. Found: C, 51.00; H, 6.85; N, 3.15.

Synthesis of  $(L^{tBu})UCl_3$  (13). A 50 mL side-arm flask equipped with a stir bar was charged with  $K[L^{tBu}]$  (0.250 g, 0.462 mmol),  $UCl_4$ (0.159 g, 0.419 mmol), and tetrahydrofuran (20 mL). The reaction mixture was stirred at room temperature. After 15 h, the volatiles from the reaction mixture were removed under reduced pressure. Toluene (30 mL) was added to the resulting red residue. After mixing, the slurry was filtered through a Celite-padded coarse-porosity fritted filter. The filtrate was collected, and the volatiles were removed under reduced pressure. The resulting orange residue was washed with hot hexanes  $(2 \times 15 \text{ mL})$  and dried under reduced pressure to give 13 as a pale red solid (0.225 g, 0.275 mmol, 66%). X-ray-quality crystals of 13 were obtained by slowly cooling a hot hexanes solution to ambient temperature. <sup>1</sup>H NMR ( $C_6D_6$ , 298 K):  $\delta$  28.44 (bs, 2H, CHMe<sub>2</sub>), 11.59 (m, 2H, Ar-H), 9.78 (s, 6H, CHMe<sub>2</sub>), 5.79 (s, 6H, CHMe<sub>2</sub>), 5.59 (m, 4H, Ar-H), -0.77 (s, 6H, CHMe<sub>2</sub>), -3.79 (s, 18H, CMe<sub>3</sub>), -13.79 (bs, 2H, CHMe<sub>2</sub>), -24.22 (s, 6H, CHMe<sub>2</sub>), -56.35 (s, 1H, γ-C-H). Anal. Calcd for C<sub>35</sub>H<sub>53</sub>Cl<sub>3</sub>N<sub>2</sub>U<sup>1</sup>/<sub>4</sub>C<sub>6</sub>H<sub>14</sub> (mol wt 867.74: C, 50.52; H, 6.56; N, 3.23. Found: C, 50.63; H, 6.49; N, 3.15.

Synthesis of [{(L<sup>Me</sup>)(Cl)U}<sub>2</sub>(µ-Cl)<sub>3</sub>][Cl] (14). A 20 mL scintillation vial equipped with a stir bar was charged with  $K[L^{Me}]$  (0.300 g, 0.657 mmol), UCl<sub>4</sub> (0.124 g, 0.326 mmol), and tetrahydrofuran (15 mL). The reaction mixture was stirred at room temperature. After 15 h, the reaction mixture was filtered through a Celite-padded coarse-porosity fritted filter and the volatiles were removed under reduced pressure. The resulting red residue was extracted with hexanes  $(2 \times 10 \text{ mL})$ . The extracts were combined and filtered through a Celite-padded coarse-porosity fritted filter. The red filtrate was concentrated under reduced pressure to  ${\sim}10$  mL and placed in a -35 °C freezer to afford 14 as a dark brown/black crystalline solid (0.081 g, 0.053 mmol, 33%). X-ray-quality crystals of 14 were obtained by slow (2 days) evaporation of a toluene solution (5 mL) at ambient temperature. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  18.16 ( $\nu_{1/2}$  = 285 Hz), 14.00 ( $\nu_{1/2}$  = 48 Hz), 4.11 ( $\nu_{1/2}$  = 147 Hz), -7.32 ( $\nu_{1/2}$  = 540 Hz), -13.66 ( $\nu_{1/2}$  = 198 Hz),  $-39.31 (\nu_{1/2} = 90 \text{ Hz})$ . Anal. Calcd for  $C_{58}H_{82}Cl_6N_4U_2 \cdot 1.5C_7H_8$ (mol wt 1662.28: C, 49.49; H, 5.70; N, 3.37. Found: C, 49.62; H, 5.56; N, 3.18.

X-ray Crystallography. Crystals of 10 and 13 were mounted in a nylon cryoloop from Paratone-N oil. The data were collected on a Bruker D8 diffractometer, with an APEX II charge-coupled-device (CCD) detector and Cryo Industries of America Cryocool G2 lowtemperature device (120 K). The instrument was equipped with a graphite-monochromated Mo K $\alpha$  X-ray source ( $\lambda = 0.71073$  Å) and a 0.5 mm monocapillary. A hemisphere of data was collected using  $\omega$ scans, with 10 s frame exposures and 0.5° frame widths. Data collection and initial indexing and cell refinement were handled using APEX II software.<sup>39</sup> Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.<sup>40</sup> The data were corrected for absorption using redundant reflections and the SADABS program.<sup>41</sup> Decay of reflection intensity was not observed, as monitored by analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. Unless otherwise noted, non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL NT.4

The crystal structures of 7, 9, 12, and 14 were determined as follows: A crystal was mounted in a nylon cryoloop from Paratone-N oil. The crystal was placed in a Bruker P4/CCD diffractometer and cooled to 140(2) K using a Bruker LT-2 low-temperature device. The instrument was equipped with a sealed, graphite-monochromated Mo K $\alpha$  X-ray source ( $\lambda$ = 0.71073 Å). A hemisphere of data was collected using  $\varphi$  scans, with 30 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART software.43 Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT software.<sup>44</sup> The data were corrected for absorption using the SADABS program.<sup>45</sup> Decay of reflection intensity was monitored by analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. Unless otherwise noted, non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. For the following structures the program PLATON/SQUEEZE was used to treat contributions from disordered solvent molecules: 7 and 9 (THF); 12 (hexane).<sup>46</sup> Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL NT.<sup>42</sup> Additional details of data collection and structure refinement are given in Table 1.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

CIF files giving crystallographic information for complexes 7, 9, 10, and 12–14 and a figure giving spectral fitting results for the electronic spectral data for  $K[L^{Me}]$ ,  $(L^{Me})ThI_3(THF)$  (8), and  $(L^{Me})UCl_3(THF)$  (12) and electrochemical data for  $K[L^{Me}]$  and  $(L^{Me})UCl_3(THF)$  (12). This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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