isolated lanthanide chlorotrialkylmetallate complexes $[Li(THF)_4][MCl\{CH(SiMe_3)_2\}_3]$, where M = Er and Yb, using a similar preparative procedure.[27]

Single crystals of $1 \cdot C_6H_{14}$ were grown from a concentrated hexane solution at −40 °C and the structure determined from diffraction data collected at −70 °C.[28] The structure consists of ordered trigonal-pyramidal $UR_3$ units which lie on a crystallographic threefold axis of symmetry, imparting rigorous $C_3$ symmetry to the molecule. The solvent molecules are disordered about a threefold axis (0, 0, *z*) in the unit cell. An ORTEP drawing of the $UR_3$ unit is shown in Figure 1. The uranium is 0.90 Å out of the plane of the methyne carbon atoms, and the C(4)–U(1)–C(4′) angle is 107.7 (4)°. The U(1)–C(4) distance is 2.48 (2) Å, which may be compared to the U–C(alkyl) bond length of 2.43 (2) Å in the U(IV) complex $Cp_3U(n\text{-}C_4H_9)$[29] and the U–N bond length of 2.320 (4) Å in the U(III) monomer $U[N(SiMe_3)_2]_3$.[30] The hydrogen atoms were not located in the final difference Fourier map.

The molecular structure also features short contacts to three symmetry related silyl methyl groups [U(1)–C(7) = 3.09 (2) Å; all other U–C contacts ≥4.31 (2) Å]. Similar γ-agostic interactions have been observed previously in f-element complexes containing $(SiMe_3)_2N^-$ and $(SiMe_3)_2CH^-$ ligands. These interactions are weak, and static structures have not been observed in solution via low-temperature NMR techniques.[31]

Further research on the chemistry and spectroscopic properties of 1 is in progress.

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**Supplementary Material Available:** Tables of crystal data (Table S1), atomic positional and isotropic equivalent thermal parameters (Table S2), anisotropic thermal parameters (Table S3), and selected distances and angles (Table S4) for 1 (4 pages); a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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(26) $^1H$ NMR in benzene-$d_6$ (22 °C): δ −3.8 (s, $Si(CH_3)_3$), δ −1.6 (s, THF), −0.7 (s, THF). Anal. Calcd for $UO_3LiClSi_6C_{33}H_{81}$: C, 40.6; H, 8.4; Li, 0.7; Cl, 3.6. Found: C, 39.5; H, 8.1; Li, 0.7; Cl, 3.5.

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(28) $1 \cdot C_6H_{14}$ crystallizes in the trigonal space group *P*31*c* with $a = b$ = 16.389 (7) Å, $c$ = 8.575 (9) Å, $V$ = 1995 (4) Å³, $Z$ = 2, and $d_{calcd}$ = 1.34 g cm⁻³. The data were collected at −70 °C to a 2θ angle of 45° on an Enraf-Nonius CAD4 automated diffractometer using Mo Kα radiation. The data were corrected empirically for absorption by using the average relative intensity curve of azimuthal scan data. The structure was solved by using standard Fourier techniques and refined by full-matrix least squares by using anisotropic thermal parameters on uranium, carbon (ligand), and silicon. The disordered solvent molecule was modeled by defining an idealized hexane molecule (C–C = 1.54 Å and C–C–C = 109.5°) and allowing the rigid body to refine to its preferred orientation. The position of the hexane was then fixed, with isotropic thermal parameters approximately equal to the largest equivalent isotropic thermal parameter for a carbon atom in the $UR_3$ molecule. The solvent molecule was included in the structure factor calculation in the final least-squares cycle, but not refined. Hydrogen atoms were not located. The final residuals for 876 reflections with $I \geq 2\sigma(I)$ were $R_F$ = 0.041 and $R_{wF}$ = 0.049.

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# Synthesis of Mixed-Ring Organoactinide Complexes: $[(C_8H_8)(C_5Me_5)ThCl]_2$ and Its Derivatives

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*Summary:* The "half-sandwich" thorium(IV) complex $(C_8H_8)ThCl_2(THF)_2$ (**1**) reacts with $(C_5Me_5)MgCl \cdot THF$ in toluene at 100 °C to give the white, air-sensitive, mixed-ring complex $(C_8H_8)(C_5Me_5)ThCl(THF)_x$ (**2**·THF ($x \leq 1$). Treatment of **2**·THF with $Me_3CCH_2MgCl$ in THF/$Et_2O$ gives the ten-coordinate Grignard addition product $(C_8H_8)(C_5Me_5)Th(\mu\text{-}Cl)_2Mg(CH_2CMe_3)(THF)$ (**3**). The adduct **2**·THF loses THF quantitatively at 100 °C under high vacuum, providing the base-free dimer $[(C_8H_8)(C_5Me_5)ThCl]_2$ (**2**). Metathesis of the chloride ligand in **2** with $LiCH(SiMe_3)_2$ gives the monomeric alkyl complex $(C_8H_8)(C_5Me_5)Th[CH(SiMe_3)_2]$ (**4**). The analogous amido complex $(C_8H_8)(C_5Me_5)Th[N(SiMe_3)_2]$ (**5**) was prepared from **2** and $NaN(SiMe_3)_2$ in toluene at 100 °C. Alkyl complex **4** reacts slowly with $H_2$ in alkane solvents to yield a sparingly soluble compound formulated as the oligomeric hydride $[(C_8H_8)(C_5Me_5)ThH]_x$ (**6**). The X-ray structures of **3** and **4** are described.

The cyclooctatetraenyl ($C_8H_{8-x}R_x^{2-}$) and cyclopentadienyl ($C_5H_{5-x}R_x^{1-}$) ligands have each played a major role in the development of actinide organometallic chemistry,[1] but, surprisingly, these two ring systems have never been used in combination on a single 5f-metal center.[2] We are interested in early actinide (An) complexes of the type $(C_8H_{8-x}R_x)(C_5H_{5-x}R_x)AnX$ (X = halide, alkyl, hydride, etc.) because they present a new opportunity to study reactions at a single site,[3] i.e., at the X ligand, on an actinide(IV) center. We report here our preliminary results on the synthesis and characterization of the first mixed-ring

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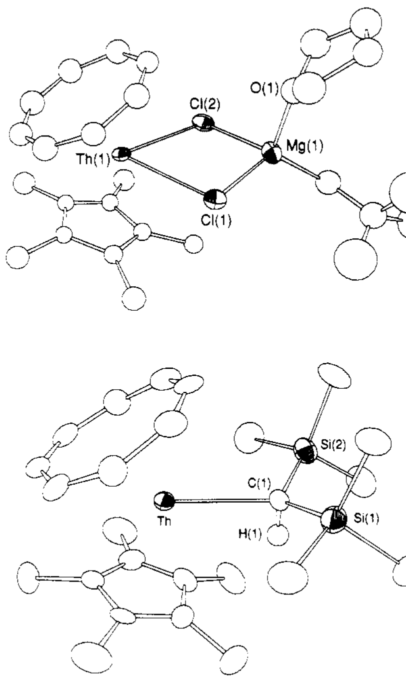

**Figure 1.** Top: ORTEP drawing (50% probability ellipsoids) of one of the independent molecules of $(C_8H_8)(C_5Me_5)Th(\mu\text{-}Cl)_2Mg(CH_2CMe_3)(THF)\cdot 0.5C_6H_5CH_3$. Selected distances and angles: Th(1)–$C_8H_8$(1)(centroid), 2.02 Å; Th(1)–$C_5Me_5$(1)(centroid), 2.54 Å; Th(1)–Cl(1)–Mg(1), 96.0 (3)°; Th(1)–Cl(2)–Mg(1), 95.7 (3)°. Bottom: ORTEP drawing (50% probability ellipsoids) of $(C_8H_8)(C_5Me_5)Th[CH(SiMe_3)_2]$. Selected distances and angles: Th–$C_8H_8$(centroid), 2.03 Å; Th–$C_5Me_5$(centroid), 2.54 Å; C(1)–Si(1,2), 1.86 (1) Å; Si(1)–C(1)–Si(2), 119.6 (5)°.

thorium(IV) complexes of this class.

Treatment of the "half-sandwich" complex $(C_8H_8)ThCl_2(THF)_2$ (**1**)[4] with $(C_5Me_5)MgCl\cdot THF$[5] in toluene at 100 °C provides, after unexceptional workup, the white, air-sensitive complex $(C_8H_8)(C_5Me_5)ThCl(THF)_x$ (**2**·THF ($x \le 1$)) in high yield (eq 1). We believe this complex is

$$\underset{\mathbf{1}}{(C_8H_8)ThCl_2(THF)_2} + (C_5Me_5)MgCl\cdot THF \xrightarrow[\Delta]{PhMe} \underset{\mathbf{2}\cdot THF}{(C_8H_8)(C_5Me_5)ThCl(THF)_x} + MgCl_2 \quad (1)$$

monomeric because the base-free complex **2** is dimeric (see below). The solubility of **2**·THF in hydrocarbon solvents depends on the value of $x$, decreasing as $x$ decreases. In addition, the ring resonances in the $^1H$ NMR spectrum vary with $x$.[6] We do not observe separate resonances for $(C_8H_8)(C_5Me_5)ThCl(THF)$ and $[(C_8H_8)(C_5Me_5)ThCl]_2$, which suggests that THF dissociates and intermolecularly recoordinates (with concomitant dimerization/monomerization of the thorium complex) rapidly on the room-temperature NMR time scale.

**2**·THF does not react cleanly with alkyllithium reagents; no spectroscopically observable $(C_8H_8)(C_5Me_5)ThR$ complexes are obtained in these reactions. Treatment of **2**·THF with a milder alkylating agent, $Me_3CCH_2MgCl$, in THF/$Et_2O$ at 25 °C followed by solvent removal and recrystallization of the solid residue from toluene at −40 °C yields a white, crystalline solid, **3**, in ca. 20% yield.[6b]

The structure of **3** was determined from diffraction data collected at 0 °C.[7] There are two crystallographically independent, structurally very similar, thorium complexes and one molecule of toluene in the asymmetric unit. An ORTEP drawing of one of the former is shown in Figure 1. This formally ten-coordinate[8] thorium compound is best described as a "Grignard adduct" of $(C_8H_8)(C_5Me_5)ThCl$. We are unaware of any transition-metal, lanthanide, or other actinide complexes of this type, although alkali-metal halide adducts of lanthanide (Ln) organometallics, e.g., $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li(OEt_2)_2$, are well-known.[9] The formation of a Grignard adduct is surprising given the fact that that many $(C_5H_5)_3ThR$ complexes are readily prepared from RMgX and $(C_5H_5)_3ThCl$.[1c,10]

The $C_8H_8$ and $C_5Me_5$ ligations in **3** are unexceptional compared to those of $(C_5Me_5)_2Th(X)Y$,[11] $(C_5Me_5)Th(CH_2Ph)_3$,[12] $(C_8H_8)_2Th$,[13] and **1**,[4b] and the $C_5Me_5$(centroid)–Th–$C_8H_8$(centroid) angle is 138.0°. The Th–Cl bond lengths of 2.884 (7) and 2.895 (7) Å are ca. 0.2 Å longer than those found in several $(C_5Me_5)_2Th(X)Cl$ systems[1a,11d,e] and in **1** but are comparable to the four "long" Th–Cl distances (2.907 (3) Å) in $ThCl_4$, where thorium is dodecahedrally coordinated.[14] The Cl(1)–Th–Cl(2) and Cl(1)–Mg–Cl(2) angles are 74.4 (2)° and 92.8 (4)°, respectively; the planes defined by these sets of atoms are nearly coincident, with a dihedral angle of 10.9°. The geometry about magnesium approximates a distorted tetrahedron; the Mg–Cl(1,2), Mg–O(1), and Mg–$C_\alpha$ bond distances are 2.41 (1), 2.05 (2), and 2.10 (3) Å, respectively. Treatment of toluene solutions of **3** with dioxane does *not* result in clean loss of $MgCl_2$(dioxane) and formation of $(C_8H_8)(C_5Me_5)Th(CH_2CMe_3)$.

**2**·THF slowly desolvates at 100 °C under high vacuum, yielding the base-free dimer $[(C_8H_8)(C_5Me_5)ThCl]_2$ (**2**) (ca. 70% overall yield based on **1**). This material is best purified by Soxhlet extraction with toluene. Elemental analyses of samples of **2** purified in this way demonstrate that only trace amounts (≤0.01%) of magnesium are

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[6] Complexes **2–6** gave satisfactory elemental analyses. Freshly prepared samples of **2**·THF show approximately one THF per $C_8H_8$ by $^1H$ NMR spectral integration. Selected $^1H$ NMR data (ppm, 25 °C, 200 MHz): (a) for **2**·THF ($C_6D_6$), δ 6.60 (s, $C_8H_8$), 2.00 (s, $C_5Me_5$), 3.66 (m, THF), 1.35 (m, THF); (b) For **3** ($C_6D_6$), δ 6.59 (s, $C_8H_8$), 1.97 (s, $C_5Me_5$), 1.43 (s, $CMe_3$), 0.38 (s, $CH_2$), 3.55 (m, THF), 1.13 (m, THF); (c) For **2** ($CD_2Cl_2$); δ 6.62 (s, $C_8H_8$), 2.03 (s, $C_5Me_5$); (d) for **4** ($C_6D_6$), δ 6.45 (s, $C_8H_8$), 1.77 (s, $C_5Me_5$), 0.27 (s, $SiMe_3$), −0.59 (s, CH); (e) for **5** ($C_6D_6$), δ 6.38 (s, $C_8H_8$), 1.84 (s, $C_5Me_5$), 0.25 (s, $SiMe_3$); (f) for **6** ($C_6D_6$), δ 6.45 (s, $C_8H_8$), 1.85 (s, $C_5Me_5$). See supplementary material for $^{13}C\{^1H\}$ NMR data.

[7] **3** crystallizes in the monoclinic space group $P2_1/n$ with $a$ = 19.726 (4) Å, $b$ = 13.232 (4) Å, $c$ = 25.328 (5) Å, $\beta$ = 97.30 (2)°, $V$ = 6557.6 Å$^3$, $d_{calcd}$ = 1.53 g cm$^{-3}$, and $Z$ = 8. The limits of data collection were $0 \le 2\theta \le 45°$ (Mo K$\alpha$). The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares. Final discrepancy indices were $R_F$ = 6.3% and $R_{wF}$ = 8.5%. The high $R$ values are likely a result of absorption effects; no disorder problems were encountered.

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present. In $CD_2Cl_2$, **2** shows only $^1H$ NMR resonances appropriate for the $C_8H_8$ and $C_5Me_5$ rings.[6c] The dimeric formulation is based on an isopiestic molecular weight determination[15a] and on a cryoscopic molecular weight determination in benzene of the more soluble analogue $[(C_8H_7SiMe_3)(C_5Me_5)ThCl]_2$.[15b]

Metathesis of the chloride ligand of **2** in toluene at 100 °C with [bis(trimethylsilyl)methyl]lithium,[16] gives the monomeric, heptane-soluble alkyl $(C_8H_8)(C_5Me_5)Th[CH(SiMe_3)_2]$ (**4**) in ca. 50% yield (eq 2). Spectroscopic data[6d]

$$\underset{\mathbf{2}}{[(C_8H_8)(C_5Me_5)ThCl]_2} + 2LiCH(SiMe_3)_2 \xrightarrow[\Delta]{PhMe} \underset{\mathbf{4}}{2(C_8H_8)(C_5Me_5)Th[CH(SiMe_3)_2]} + 2LiCl \quad (2)$$

are consistent with a pseudo-nine-coordinate formulation, and elemental analyses demonstrate the lack of lithium and chlorine. A single-crystal X-ray diffraction study has confirmed both the monomeric formulation and the presence of a $\sigma$-bound alkyl group.

The structure of **4** was determined from diffraction data collected at −50 °C,[17] and an ORTEP drawing of the molecule is shown in Figure 1. The $C_8H_8$ and $C_5Me_5$ ligations in **4** are very similar to those found in **3**, and the $C_8H_8$(centroid)–Th–$C_5Me_5$(centroid) angle is essentially identical at 138.1°. We note that the thorium–$\alpha$-carbon distance (Th–C(1) = 2.54 (1) Å) is comparable to the thorium–alkyl carbon bond lengths in, for example, $(C_5Me_5)Th(CH_2Ph)_3$ (2.58 (2) Å),[12] $(C_5Me_5)_2Th(CH_2Bu^t)_2$ (2.478 (4) and 2.546 (4) Å),[18] and $Th(CH_2Ph)_4(dmpe)_2$ (2.55 (2) Å).[19] The primary Th–hydrocarbyl interaction in **4** is supplemented by a secondary interaction to the $\alpha$-hydrogen H(1), which is distorted toward the thorium with a Th–C(1)–H(1) angle of 91 (6)°. This arrangement results in a Th–H(1) distance of 2.71 (9) Å. The present case differs somewhat from that of $(C_5Me_5)Nd[CH(SiMe_3)_2]$,[9c,20] where the secondary interaction involves one of the silyl methyl groups. In **4**, the Th–C(1)–Si(1,2) angles are nearly equal at 116.9 (5)° and 115.6 (5)°, respectively.

An analogous amido complex, $(C_8H_8)(C_5Me_5)Th[N(SiMe_3)_2]$ (**5**), has been prepared (50% yield) from **2** and $NaN(SiMe_3)_2$ in toluene at 100 °C (eq 3).[6e] Data from an

$$\underset{\mathbf{2}}{[(C_8H_8)(C_5Me_5)ThCl]_2} + 2NaN(SiMe_3)_2 \xrightarrow[\Delta]{PhMe} \underset{\mathbf{5}}{2(C_8H_8)(C_5Me_5)Th[N(SiMe_3)_2]} + 2NaCl \quad (3)$$

X-ray diffraction study[21] confirm the monomeric formulation.

Alkane solutions of alkyl complex **4** react slowly with $H_2$ to yield a sparingly soluble, diamagnetic white compound formulated as an oligomeric hydride, $[(C_8H_8)(C_5Me_5)ThH]_x$ (**6**) (eq 4). The IR spectrum of **6**

$$\underset{\mathbf{4}}{(C_8H_8)(C_5Me_5)Th[CH(SiMe_3)_2]} + H_2 \xrightarrow{C_6H_{14}} \underset{\mathbf{6}}{[(C_8H_8)(C_5Me_5)ThH]_x} + CH_2(SiMe_3)_2 \quad (4)$$

is complex; we tentatively assign a broad band at 1147 $cm^{-1}$, which shifts to 843 $cm^{-1}$ upon deuteration ($\nu_H/\nu_D$ = 1.36) to an antisymmetric Th–H–Th stretching mode. No bands corresponding to Th–H(terminal) modes were detected. We have not been able to locate a hydride resonance in $^1H$ NMR experiments.[6f] One possibility is that the hydride ligand in **6** exchanges rapidly with the deuteria of NMR solvents. This problem has been encountered with $(C_5Me_5)_2LnH$[9c] and $Me_2Si(C_5Me_4)_2LnH$ complexes.[22] An alternative explanation, suggested by a reviewer, is broadening of the hydride resonance due to the presence of a monomer–dimer (or monomer–trimer etc.) equilibrium of appropriate rate.

Experiments concerned with insertion of small organic molecules into the thorium–$\sigma$-ligand bonds, as well as the use of substituted cyclooctatetraenyl ligands to improve the solubility characteristics of selected derivatives, are in progress.

**Acknowledgment.** This work was performed under the auspices of the U.S. Department of Energy and the Office of Energy Research, Division of Chemical Sciences, U.S. Department of Energy. We thank Mr. Kenneth Salazar for skilled technical assistance.

**Supplementary Material Available:** Proton and $^{13}C\{^1H\}$ NMR data for **2**–**6** and tables of crystal data, positional and equivalent isotropic thermal parameters, and anisotropic thermal parameters and fully labeled ORTEP drawings for **3** and **4** (16 pages); listings of structure factor amplitudes for **3** and **4** (33 pages). Ordering information is given on any current masthead page.

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[17] **4** crystallizes in the monoclinic space group $P2_1/n$ with $a$ = 8.945 (2) Å, $b$ = 30.644 (3) Å, $c$ = 9.633 (1) Å, $\beta$ = 95.15 (1)°, $V$ = 2629.9 Å$^3$, $d_{calcd}$ = 1.59 g cm$^{-3}$, and $Z$ = 4. The limits of data collection were $0 \leq 2\theta \leq 45°$ (Mo K$\alpha$). Diffraction data were corrected for absorption effects. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares. The position of H(1) was clearly indicated in the Fourier difference maps and refined to a reasonable position and isotropic temperature factor. Final discrepancy indices were $R_F$ = 3.0% and $R_{wF}$ = 3.9%.

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