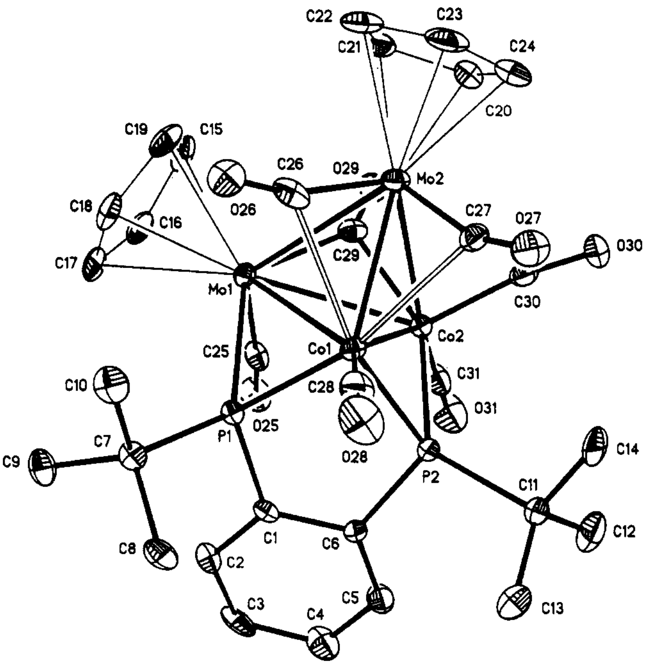

Figure 2. Structure diagram of 7. To facilitate comparison with Figure 1, the molecule shown is an inversion relative of the one whose coordinates appear in the supplementary tables. Selected bond distances (Å): Co1–Mo1, 2.871 (2); Co2–Mo1, 2.802 (2); Co1–Co2, 2.535 (2); Co2–Mo2, 2.776 (2); Co1–Mo2, 2.579 (2); Mo1–Mo2, 3.0570 (13); P1–Co1, 2.145 (3); P1–Mo1, 2.426 (3); P2–Co1, 2.137 (3); P2–Co2, 2.214 (3); Mo2–C26 1.927 (510); Mo2–C27, 1.976 (511); Co1···C26, 2.432 (11); Co1···C27, 2.454 (410). Selected bond angles (deg): Co1–Co2–Mo1, 64.87 (5); Co1–Mo1–Co2, 53.07 (4); Co1–Mo2–Co2, 56.35 (5); Co1–Mo2–Mo1, 60.54 (4); Co2–Co1–Mo1, 62.07 (5); Co2–Mo2–Mo1, 57.17 (4); Co2–Co1–Mo2, 65.75 (5); Co2–Mo1–Mo2, 56.37 (4); Co1–Mo1–Mo2, 51.47 (4); Co1–Co2–Mo2, 57.90 (5); Mo1–Co1–Mo2, 67.99 (5); Mo1–Co2–Mo2, 66.46 (4); Co1–P1–Mo1, 77.55 (9); Co2–P2–Co1, 71.25 (10); O26–C26–Mo2, 163.7 (9); O27–C27–Mo2, 162.5 (9).

associated with the chelated cobalt instead of the molybdenum center. As a result of this deep-seated rearrangement, the metallic tetrahedron is much less symmetrical in terms of bond lengths of the metallic tetrahedron (see metal–metal bond lengths in the figure captions).

It is reasonable that the bis(μ-phosphido) ligand system in 7 leads to a more stable complex, since the better σ-donor ligands now chelate the more electronegative cobalt carbonyl site. Our attempts to establish an equilibrium between 3 and 7 starting from 7 led to no detectable amounts of the former. Since this attempted equilibration was carried out 13 °C higher and for 14 h longer than when 3 was converted into 7, it can be estimated that 7 is at least 3.4 kcal/mol more stable than 3. Since carbonyl ligands are quite mobile on cluster frameworks,[13] presumably it is the barrier to migration of the bis(μ-phosphido) ligand which confers the kinetic stability upon cluster 3. This property gives us a clue to the mechanism of formation 3, since no 7 is formed in the process. Apparently, 3 is assembled via a pathway which does not allow access to the more stable isomer. We are continuing to investigate this aspect.

Preliminary work on the chemistry of cluster 3 indicates that it is reactive toward electrophilic reagents such as Brønsted acids and nitrosonium ion (to give a novel μ^2,η^4-NO cluster complex[14]) and that the bis(μ-phosphido) ligand enforces cluster integrity in such reactions.

Acknowledgment. Financial support from the Robert A. Welch Foundation (Grant No. F573 to E.P.K. and Grant No. F233 to R.E.D.), Alcon Laboratories (E.P.K.), and the National Science Foundation (E.P.K., Grant CHE84-19282) is gratefully acknowledged.

Supplementary Material Available: Tables of fractional coordinates and isotropic or equivalent thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles, and torsional angles (non-hydrogens) for 3 and 7 (25 pages); listings of observed and calculated structure factor amplitudes for 3 and 7 (75 pages). Ordering information is given on any current masthead page.

First Example of a Neutral Homoleptic Uranium Alkyl. Synthesis, Properties, and Structure of $U[CH(SiMe_3)_2]_3$

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Summary: The reaction of $U(O\text{-}2,6\text{-}Bu^t_2C_6H_3)_3$ with 3 equiv of $LiCH(SiMe_3)_2$ in hexane at ambient temperature provides royal blue $U[CH(SiMe_3)_2]_3$ (**1**) in ca. 40% isolated yield. In the solid state, **1** is pyramidal with crystallographically imposed C_3 symmetry, a U(1)–C(4) (i.e., U–C_α) bond length of 2.48 (2) Å, and a C(4)–U(1)–C(4′) bond angle of 107.7 (4)°. The molecular structure also features a γ-agostic interaction with three symmetry-related silyl methyl groups [U(1)–C(7) = 3.09 (2) Å]. **1** is thermally stable as a solid at room temperature but decomposes with loss of $H_2C(SiMe_3)_2$ at ca. 60 °C. Solutions of **1** in hexane or THF slowly decompose over the course of several hours. Reaction of $UCl_3(THF)_x$ with 3 equiv of $LiCH(SiMe_3)_2$ in THF does not produce $U[CH(SiMe_3)_2]_3$ but rather a green ionic complex of formula $[Li(THF)_3][UCl\{CH(SiMe_3)_2\}_3]$.

The synthesis of isolable binary σ-alkyl complexes of uranium has been a goal of organometallic chemists for almost half a century. Prior to World War II, Gilman and co-workers attempted the preparation of simple uranium(IV) organometallics such as UMe_4. They concluded that homoleptic uranium alkyls, if they existed at all, were highly unstable and that their isolation offered little chance of success.[1] Subsequent attempts to prepare UR_4 complexes were likewise unsuccessful,[2-4] and the course of the complicated reactions between UCl_4 and alkyllithium reagents in alkane and ether solvents has been contro-

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versial.[5-8] In 1981, Andersen and co-workers discovered that uranium(IV) alkyls could be stabilized by 1,2-bis(dimethylphosphino)ethane (dmpe).[9] Thus, treatment of $UCl_4(dmpe)_2$ with methyllithium in diethyl ether affords crystalline $UMe_4(dmpe)_2$. Several years earlier, Sigurdson and Wilkinson[5] isolated the thermally stable ionic uranium(V) derivatives, $[Li(dioxane)]_3UR_8$ (R = Me, CH_2Bu^t, CH_2SiMe_3), by treating $U_2(OEt)_{10}$ with RLi in hexane/ether followed by the addition of dioxane. The reason that $UMe_4(dmpe)_2$ and $[Li(dioxane)]_3UR_8$ are isolable, while their neutral homoleptic counterparts, UMe_4 and UR_5, are not, is a consequence of their high coordination numbers, i.e., kinetic stabilization.[10] This also explains why $(C_5Me_5)_2UR_2$ (formally eight-coordinate) and especially $(C_5H_5)_3UR$ (ten-coordinate) compounds are quite stable.[11,12] One other way to achieve kinetic stabilization of binary metal alkyls is to employ bulky alkyl ligands. This approach has been very useful in transition-metal chemistry[13,14] (e.g., in the preparation of MoR_4 complexes[15]) and in lanthanide chemistry, where Lappert and co-workers have used the sterically demanding $[CH(SiMe_3)_2]^-$ ligand to prepare LnR_3 (Ln = Sm, La) complexes.[16] Here we describe its successful application in uranium(III) chemistry.

The reaction of $U(O\text{-}2,6\text{-}Bu^t_2C_6H_3)_3$[17] with 3 equiv of $LiCH(SiMe_3)_2$[18] in hexane at ambient temperature (eq 1)

$$U(O\text{-}2,6\text{-}Bu^t_2C_6H_3)_3 + 3LiCH(SiMe_3)_2 \xrightarrow[2\ h]{C_6H_{14}} \underset{\mathbf{1}}{U[CH(SiMe_3)_2]_3} + 3LiO\text{-}2,6\text{-}Bu^t_2C_6H_3 \quad (1)$$

produces, after 2 h of stirring, a blue-purple solution and a white precipitate of LiOAr. Filtration, solvent removal, and recrystallization of the residue from hexane at −40 °C provides bright royal blue needles of **1** in ca. 40% yield. Compound **1** is exceedingly air- and moisture-sensitive and very soluble in hydrocarbons and ethers. Only one type of $SiMe_3$ resonance is observed in the ^1H NMR spectrum (benzene-d_6) of **1** at δ −5.8; we were unable to locate the α-proton resonance.[19] Elemental analysis of vacuum-dried samples of **1** were consistent with the formula $U[CH(SiMe_3)_2]_3$.[20] Attempts to obtain an electron-impact mass spectrum were unsuccessful; the only gas phase species observed were $H_2C(SiMe_3)_2$ and $HSiMe_3$ (trace). Compound **1** follows Curie–Weiss behavior between 100 and 270 K with $\mu_{eff} = 3.0\ \mu_B$.[21] The latter is considerably lower than the spin-only value of 3.87 μ_B (U^{3+} has a $5f^3$ ground-state configuration) but comparable to that observed in several other monomeric uranium(III) complexes containing strong field ligands, including Andersen's $U[N(SiMe_3)_2]_3$.[22,23]

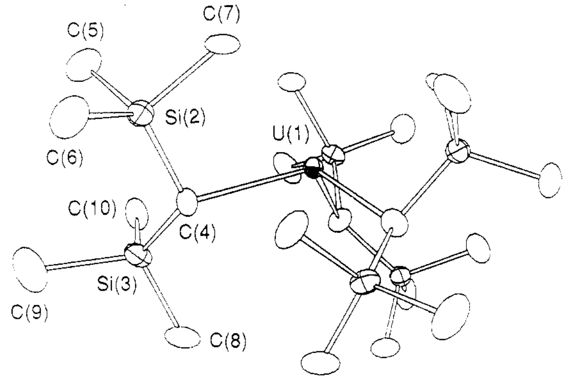

Figure 1. An ORTEP view of **1**. Selected distances and angles: U(1)–C(4) = 2.48 (2) Å; U(1)–C(7) = 3.09 (2) Å; C(4)–Si(2) = 1.83 (2) Å; C(4)–Si(3) = 1.86 (2) Å; U(1)–C(4)–Si(2) = 101.8 (8)°, U(1)–C(4)–Si(3) = 122 (1)°, Si(2)–C(4)–Si(3) = 120 (1)°.

In benzene-d_6 solution, **1** slowly decomposes over the course of ca. 12 h to form $H_2C(SiMe_3)_2$ plus as yet uncharacterized, uranium-containing products. Addition of 3 equiv of $HO\text{-}2,6\text{-}Bu^t_2C_6H_3$ to a hexane solution of **1** slowly produces $U(O\text{-}2,6\text{-}Bu^t_2C_6H_3)_3$ and $CH_2(SiMe_3)_2$.[24] As a solid, **1** shows no evidence of decomposition at 25 °C in a sealed evacuated ampule. At temperatures greater than ca. 60 °C, **1** decomposes under high vacuum to give $H_2C(SiMe_3)_2$ (NMR, GC–MS) and a brown hydrocarbon-insoluble residue. The formation of alkane is consistent with either α- or γ-hydrogen abstraction. In view of the agostic U···CH_3–Si interactions observed in the solid state (vide infra), γ-hydrogen abstraction is the more likely decomposition pathway, but labeling studies will be required to confirm this.

Attempts to prepare **1** directly from $UCl_3(THF)_x$[25] (generated in situ from UCl_4 and sodium amalgam) and ≥3 equiv of $LiCH(SiMe_3)_2$ in THF were not successful. This reaction affords a green crystalline complex **2** (eq 2),

$$UCl_3(THF)_x + 3LiCH(SiMe_3)_2 \xrightarrow{THF} \underset{\mathbf{2}}{[Li(THF)_3][UCl\{CH(SiMe_3)_2\}_3]} + 2LiCl \quad (2)$$

which is sparingly soluble in hexane but appreciably soluble in THF. Elemental analyses and ^1H NMR data are consistent with the formula $[Li(THF)_3][UCl\{CH(SiMe_3)_2\}_3]$.[26] Atwood, Lappert, and co-workers have

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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) Å^3, $Z = 2$, 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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