

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 molvbdenum 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 $bis(\mu$ -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 $bis(\mu$ -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 complex¹⁴) and that the bis(μ -phosphido) ligand enforces cluster integrity in such reactions.

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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(SIMe₃)₂]₃

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Summary: The reaction of $U(O-2,6-Bu_2^tC_6H_3)_3$ 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 C₃ 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 silvl 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 H2C(SiMe3)2 at ca. 60 °C. Solutions of 1 in hexane or THF slowly decompose over the course of several hours. Reaction of UCI₃(THF), with 3 equiv of LiCH(SiMe₃)₂ in THF does not produce U[CH- $(SiMe_3)_2]_3$ but rather a green ionic complex of formula $[\text{Li}(\text{THF})_3]$ $[\text{UCI}(\text{CH}(\text{SiMe}_3)_2)_3].$

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 UMe₄. 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 UR₄ complexes were likewise unsuccessful,²⁻⁴ and the course of the complicated reactions between UCl₄ and alkyllithium reagents in alkane and ether solvents has been contro-

⁽¹³⁾ Johnson, B. F. G.; Benfield, R. E. In *Transition Metal Clusters*;
Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 7.
(14) Kyba, E. P.; Kerby, M. C.; Kashyap, R. P.; Davis, R. E., manu-

script in preparation.

^{(1) (}a) Gilman, H. Adv. Organomet. Chem. 1968, 7, 33. (b) Gilman, H.; Jones, R. G.; Bindschadler, E.; Blume, D.; Karmas, G.; Martin, G. A., Jr.; Nobis, J. F.; Thirtle, J. R.; Yale, H. L.; Yoeman, F. A. J. Am. Chem. Soc. 1956, 78, 2790.

⁽²⁾ Yagupski, G.; Mowat, W.; Shortland, A.; Wilkinson, G. J. Chem. Soc., Chem. Commun. 1970, 1369.

⁽³⁾ Cotton, S. A.; Hart, F. A., unpublished results cited by: Cotton, S. A. In Organometallic Chemistry Library 3; Seyferth, D., Ed.; Elsevier: Amsterdam, 1977; p 197.
 (4) Marks, T. J.; Seyam, A. M. J. Organomet. Chem. 1974, 67, 61.

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 UMe₄(dmpe)₂. Several years earlier, Sigurdson and Wilkinson⁵ isolated the thermally stable ionic uranium(V) derivatives, $[Li(dioxane)]_3UR_8$ (R = Me, CH₂Bu^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, UMe₄ and UR₅, 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 MoR₄ complexes¹⁵) 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 $U(O-2,6-Bu_2^tC_6H_3)_3^{17}$ with 3 equiv of $LiCH(SiMe_3)_2^{18}$ in hexane at ambient temperature (eq 1)

$$U(O-2,6-Bu^{t}_{2}C_{6}H_{3})_{3} + 3LiCH(SiMe_{3})_{2} \xrightarrow{C_{6}H_{14}} U[CH(SiMe_{3})_{2}]_{3} + 3LiO-2,6-Bu^{t}_{2}C_{6}H_{3} (1)$$

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 SiMe₃ 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

- (10) (a) Uranium(IV)-hydrocarbyl bond disruption enthalpies^{10b} [D-(U-R) = 60-85 kcal/mol] are comparable to mean early transition metal-carbon σ bond D values. (b) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Mark, T. J. J. Am. Chem. Soc. 1986, 108, 7275 and references therein.
- (11) Marks, T. J. In The Chemistry of the Actinide Elements; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York,
- 1986; Vol. 2, Chapter 23 and references therein. (12) Marks, T. J.; Ernst, R. D. In Comprehensive Organometallic Chemistry; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 21 and references therein.
 - (13) Schrock, R. R.; Parshall, G. W. Chem. Rev. 1976, 76, 243.
- (14) Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 4th ed.; Wiley: New York, 1980; pp 1119-1140. (15) (a) Seidel, W.; Burger, L. J. Organomet. Chem. 1979, 171, C45.
- (b) Kolodziej, R. M.; Schrock, R. R.; Davis, W. M. Inorg. Chem. 1988, 27, 3253
- (16) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G.; Bartlett, R. A.; Power, P. P. J. Chem. Soc., Chem. Commun. 1988, 1007. (17) Van Der Sluys, W. G.; Burns, C. J.; Huffman, J. C.; Sattelberger,
- A. P. J. Am. Chem. Soc. 1988, 110, 5924.
- (18) (a) Cowley, A. H.; Kemp, R. A. Synth. React. Inorg. Met.-Org.
 Chem. 1981, 11, 591. (b) Davidson, P. J.; Harris, D. H.; Lappert, M. F. J. Chem. Soc., Dalton Trans. 1976, 2268. (c) Barton, T. J.; Hoekman S. K. J. Am. Chem. Soc. 1980, 102, 1584.
- (19) The α -proton resonance of $(C_5Me_b)_2 U^{III}$ [CH(SiMe_3)₂] was also not observed. See: Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. Organometallics **1982**, 1, 170.



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)°, $U(1)-C(4)-Si(3) = 122 (1)^{\circ}, Si(2)-C(4)-Si(3) = 120 (1)^{\circ}.$

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 H₂C(SiMe₃)₂ and HSiMe₃ (trace). Compound 1 follows Curie–Weiss behavior between 100 and 270 K with $\mu_{\text{eff}} = 3.0 \ \mu_{\text{B}}^{21}$ The latter is considerably lower than the spin-only value of 3.87 μ_{B} (U³⁺ has a 5f³ 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}

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-2,6- $Bu_2^tC_6H_3$ to a hexane solution of 1 slowly produces $U(O-2,6-But_2C_6H_3)_3$ 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 -(SiMe₃)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…CH₃-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 UCl₃(THF)_x²⁵ (generated in situ from UCl₄ and sodium amalgam) and \geq 3 equiv of LiCH(SiMe₃)₂ in THF were not successful. This reaction affords a green crystalline complex 2 (eq 2),

$$\frac{\text{UCl}_{3}(\text{THF})_{x} + 3\text{LiCH}(\text{SiMe}_{3})_{2}}{[\text{Li}(\text{THF})_{3}][\text{UCl}(\text{CH}(\text{SiMe}_{3})_{2})_{3}] + 2\text{LiCl} (2)}{2}$$

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which is sparingly soluble in hexane but appreciably soluble in THF. Elemental analyses and ¹H NMR data are consistent with the formula $[{\rm Li}({\rm THF})_3][UCl\{{\rm CH-}$ $(SiMe_3)_{2}$].²⁶ Atwood, Lappert, and co-workers have

(25) Moody, D. C.; Odom, J. D. J. Inorg. Nucl. Chem. 1979, 41, 533.

⁽⁵⁾ Sigurdson, E. R.; Wilkinson, G. J. Chem. Soc., Dalton Trans. 1977, 812

 ⁽⁶⁾ Marks, T. J. Prog. Inorg. Chem. 1979, 25, 224.
 (7) Evans, W. J.; Wink, D. J.; Stanley, D. R. Inorg. Chem. 1982, 21, 2565.

⁽⁸⁾ Seyam, A. M. Inorg. Chim. Acta 1983, 77, L123.

⁽⁹⁾ Edwards, P. G.; Andersen, R. A.; Zalkin, A. J. Am. Chem. Soc. 1981, 103, 7792. See also: Edwards, P. G.; Andersen, R. A.; Zalkin, A. Organometallics 1984, 3, 293.

⁽²⁰⁾ The analytical sample was dried in vacuo (10^{-5} Torr, 25 °C) for 12 h. Anal. Calcd for USi₆C₂₁H₅₇: C, 35.2; H, 8.0; Li, 0.0. Found: C, 34.5: H. 7.7: Li. <0.1.

⁽²¹⁾ A discussion of the optical and magnetic properties of monomeric (21) A discussion of the optical and magnetic properties of monomeric UX₃ complexes (X = N(SiMe₃)₂, O-2,6-Bu¹₂C₆H₃, CH(SiMe₃)₂ will be presented elsewhere: Dyer, R. B.; McElfresh, M.; Burns, C. J.; Van Der Sluys, W. G.; Dewey, H. J.; Sattelberger, A. P., in preparation. (22) Cymbaluk, T. H.; Liu, J.-Z.; Ernst, R. D. J. Organomet. Chem.

^{1983, 255, 311} and references therein.

⁽²³⁾ Andersen, R. A. Inorg. Chem. 1979, 18, 1507.

⁽²⁴⁾ This reaction is not quantitative. Some UR₃ decomposes before the methathesis is complete.

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 $1 \cdot C_6 H_{14}$ 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 UR₃ 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 UR₃ 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 $Cp_3U(n-C_4H_9)^{29}$ 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 silvl methyl groups [U(1)-C(7) =3.09 (2) Å; all other U–C contacts \geq 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.

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, mixedring complex $(C_8H_8)(C_5Me_5)$ ThCl $(THF)_x$ (2.THF $(x \le 1)$). Treatment of 2.THF with Me₃CCH₂MgCl in THF/Et₂O gives the ten-coordinate Grignard addition product $(C_8H_8)(C_5Me_5)Th(\mu-Cl)_2Mg(CH_2CMe_3)(THF)$ (3). The adduct 2.THF loses THF quantitatively at 100 °C under high vacuum, providing the base-free dimer [(C₈H₈)(C₅Me₅)-ThCl₂ (2). Metathesis of the chloride ligand in 2 with LiCH(SiMe₃)₂ gives the monomeric alkyl complex $(C_8H_8)(C_5Me_5)Th[CH(SiMe_3)_2]$ (4). The analogous amido complex (C₈H₈)(C₅Me₅)Th[N(SiMe₃)₂] (5) was prepared from 2 and NaN(SiMe₃)₂ in toluene at 100 °C. Alkyl complex 4 reacts slowly with H₂ 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

^{(26) &}lt;sup>1</sup>H NMR in benzene- d_6 (22 °C): δ -3.8 (s, Si(CH₃)₃), δ -1.6 (s, THF), -0.7 (s, THF). Anal. Calcd for UO₃LiClSi₆C₃₃H₈₁: 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. (27) (a) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. J. Chem. Soc., Chem. Commun. 1978, 140. (b) Atwood, J. L.; Lappert, M. F.; Smith, R. G.; Zhang, H. J. Chem. Soc. Chem. Commun. 1978, 140. (c) Harden Commun. 1988 H. J. Chem. Soc., Chem. Commun. 1988, 1308.

^{(28) 1-}C₆H₁₄ crystallizes in the trigonal space group P31c 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 2 θ angle of 45° on an Enraf-Nonius CAD4 automated diffractometer using Mo K α 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 UR3 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 $I \ge 2\sigma(I)$ were $R_F = 0.041$ and $R_{wF} =$ 0.049

⁽²⁹⁾ Perego, G.; Cesari, M.; Farina, F.; Lugli, G. Acta Crystallogr., Sect. B 1976, 32, 3034

⁽³⁰⁾ Andersen, R. A.; Stewart, J. L., personal communication.
(31) (a) Tilley, T. D.; Andersen, R. A.; Zalkin, A. J. Am. Chem. Soc.
1982, 104, 3725. (b) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. Organometallics 1986, 5, 1726. (c) Mauermann, H.; Swepston, P. N.; Marks, T. J. Organometallics 1986, 6, 1987. 1985, 4, 200. (d) Tilley, T. D.; Andersen, R. A.; Zalkin, A. Inorg. Chem. 1984, 23, 2271. (e) Gilbert, T. M.; Ryan, R. R.; Sattelberger, A. P. Organometallics 1988, 7, 2514.

⁽¹⁾ For recent reviews, see: (a) Marks, T. J.; Day, V. W. In Fundamental and Technological Aspects of Organo-f-Element Chemistry; Marks, T. J., Fragala, I. L., Eds.; D. Reidel: Dordrecht, Holland, 1985; p 115. (b) Streitwieser, A.; Kinsley, S. A. Ibid; p 77. (c) Marks, T. J.; Ernst, R. D. In Comprehensive Organometallic Chemistry; Wilkinson, G. W., Stone, F. G. A., Abel, E. A., Eds.; Pergamon Press: Oxford, 1982; Chapter 21. (d) Marks, T. J.; Streitwieser, A., Jr. In *The Chemistry of the Actinide Elements*; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1986, Vol. 2, Chapter 22. (e) Marks, T. J. Ibid. Chapter 23.

⁽²⁾ Transition-metal^{2a-c} and lanthanide^{2d} mixed COT-Cp complexes have been reported. (a) Highcock, W. J.; Mills, R. M.; Spencer, J. L.; Woodward, P. J. Chem. Soc., Dalton Trans. 1986, 821. (b) Segal, J. A.; Green, M. L. H.; Daran, J.-C.; Prout, K. J. Chem. Soc., Chem. Commun. 1976, 766. (c) Kroon, P. A.; Helmholdt, R. B. J. Organomet. Chem. 1970, 25, 451. (d) Jamerson, J. D.; Masino, A. P.; Takats, J. J. Organomet. Chem. 1974, 65, C33.

^{(3) (}a) Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. J. Am. Chem. Soc. 1984, 106, 3484. (b) Rosetto, G.; Paolucci, G.; Zanella, P.; Fischer, R. D. Proc. IUPAC Symp. Organomet. Chem., 2nd, Dijon Aug, 1983.