Synthesis and Properties of a New Class of Highly Reactive Trivalent Actinide Organometallic Compounds. Derivatives of Bis(pentamethylcyclopentadienyl)uranium(III)

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Hydrogenolysis of the uranium(IV) alkyl complexes $U[\eta^5\text{-}(CH_3)_5C_5]_2(R)Cl$ results in clean reduction to the uranium(III) complex $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$, which has been structurally characterized by single-crystal X-ray diffraction. This molecule crystallizes in the monoclinic space group $C2/c$—$C_{2h}{}^6$ (No. 15) with four molecules in a unit cell of dimensions $a = 21.886$ (7) Å, $b = 14.236$ (5) Å, $c = 24.517$ (7) Å, and $\beta = 128.65$ (2)°. Least-squares refinement led to a value for the conventional R index (on F) of 0.042 for 6813 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 65.2°$ and $I > 3\sigma(I)$. The molecular structure consists of approximately D_{3h} trimers with pseudotetrahedral $U[\eta^5\text{-}(CH_3)_5C_5]_2$ units connected by bridging chloride ligands. The average U–C distance is 2.768 (11) Å, and the average U–Cl, 2.900 (2) Å. The average Cl–U–Cl angle is 83.8 (1)°. The trimer reacts with Lewis bases to form adducts $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\cdot L$, where L = THF, pyridine, $P(CH_3)_3$, and $(C_2H_5)_2O$. Stable, monomeric uranium(III) alkyl and amide complexes, $U[\eta^5\text{-}(CH_3)_5C_5]_2CH[Si(CH_3)_3]_2$ and $U[\eta^5\text{-}(CH_3)_5C_5]_2N[Si(CH_3)_3]_2$ can be prepared by the reaction of the chloride trimer with $LiCH[Si(CH_3)_3]_2$ and $NaN[Si(CH_3)_3]_2$, respectively. Reaction of unsaturated organic molecules with $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ results in an interesting "disproportionation" reaction in which the trimer formally donates 1.5 equiv each of $U[\eta^5\text{-}(CH_3)_5C_5]_2$ and $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$. In particular, the reaction of diphenylacetylene, tetraphenylcyclopentadienone, and 9,10-phenanthrenequinone produces, respectively, $[\mu^5\text{-}(CH_3)_5C_5]_2\overline{UC(C_6H_5){=}C(C_6H_5)C(C_6H_5){=}C}(C_6H_5)$, $U[\eta^5\text{-}(CH_3)_5C_5]_2[\eta^2\text{-}COC_4(C_6H_5)_4]$, and $\{U[\eta^5\text{-}(CH_3)_5C_5]_2[\text{9,10-phenanthrenequinonate}]\}_x$ with an equivalent amount of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ formed in each case. The reduction of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ has been accomplished with sodium amalgam and, after workup, yields the complex $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2Na\cdot(THF)_x$. Sodium amalgam reduction of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ in the presence of diphenylacetylene produces the uranotetraphenylcyclopentadiene complex in good yield. Overall, the organometallic chemistry of U(III) has distinct similarities to that of Ti(III), as well as to that of lanthanides in the +3 oxidation state.

The widespread tendency of transition-metal ions to exist in a multiplicity of formal oxidation states and to pass readily among them is a pivotal feature of stoichiometric and catalytic organometallic chemistry.[3] In contrast, the great majority of thorium and uranium organometallic compounds contain the actinide ion in the +4 oxidation state, with little known about lower oxidation states or the facility of oxidation state shuttling.[4] The well-characterized trivalent complexes consist largely of marginally soluble tris(cyclopentadienyls), $M(\eta^5\text{-}C_5H_5)_3$, and the Lewis base adducts thereof, $M(\eta^5\text{-}C_5H_5)_3\cdot L$.[4–6] Far less is known about the properties of indenyls,[7] $M(\eta^5\text{-}C_5H_5)_2X$ complexes (X = CN, Cl, etc.),[8] and the insoluble, unstable arene $U(\eta^6\text{-}C_6H_6)(AlCl_4)_3$.[9]

Barriers to progress in trivalent uranium chemistry have included the intractability of uranium trichloride prepared by conventional routes[10] and the lack of suitable ligands. We have recently demonstrated that the pentamethylcyclopentadienyl ligand stabilizes highly reactive tetravalent thorium and uranium organometallics of the stoichiometry $M[\eta^5\text{-}(CH_3)_5C_5]_2R_2$[11] and $M[\eta^5\text{-}(CH_3)_5C_5]R_3$.[12] Among the interesting properties of the former compounds is the marked tendency for hydrogenolysis to produce *trivalent* bis(pentamethylcyclopentadienyl)uranium compounds.[11,13] This synthetic entry has allowed the first extensive investigation of U(III) organometallic chemistry.

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In the present contribution we relate in detail the synthesis and a number of the chemical/physicochemical characteristics of this new class of organoactinides. Included in this discussion is an analysis, by single-crystal X-ray diffraction, of the molecular structure of the precursor for much of this chemistry, the trimeric bis(pentamethylcyclopentadienyl)uranium monochloride, $\{U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\}_3$.

Experimental Section

Physical and Analytical Measurements. ^1H NMR (60 MHz) spectra were recorded on a Perkin-Elmer R-20B spectrometer. Chemical shifts are reported relative to internal $Si(CH_3)_4$. Samples were prepared either in a glovebox or on a high vacuum line. Deuterated aromatic solvents were dried over Na/K alloy and were degassed by freeze–thaw cycles on a vacuum line.

Infrared spectra were recorded on a Perkin-Elmer 267 or Perkin-Elmer 283 spectrometer and were calibrated with polystyrene film. Samples were prepared in a glovebox as mulls using previously dried and degassed Nujol. Mulls were sandwiched between polished KBr plates contained in an airtight holder.

Elemental analyses were performed by Dornis and Kolbe Mikroanalytiches Laboratorium, West Germany.

Cryoscopic molecular weights were measured by using an apparatus described elsewhere.[11]

Materials and Methods. All procedures were performed in Schlenk-type glassware using normal benchtop Schlenk techniques, in Schlenk-type glassware interfaced to a high vacuum (10^{-4}–10^{-5} torr) line, or in a nitrogen (or argon) filled glovebox.[11] Argon (Matheson, prepurified), nitrogen (Matheson, prepurified), and hydrogen (Linde) were purified further by passage thrugh a supported MnO oxygen removal column[14] and a Davison 4-Å molecular sieve column. Reactions with gases were performed in an enclosed volume on the vacuum line. Gas uptake, when observable, was monitored with a mercury manometer. Toluene, diethyl ether, benzene, tetrahydrofuran, and pentane (previously distilled from Na/K/benzophenone) were condensed and stored in vacuo in bulbs on the vacuum line.

Pyridine (distilled from BaO), chlorobenzene, and trimethylphosphine (Strem) were degassed by freeze–thaw cycles on a high vacuum line and were dried by condensing in vacuo onto freshly activated 4-Å molecular sieves. Diphenylacetylene (Aldrich), tetraphenylcyclopentadienone (Aldrich), and 9,10-phenanthrenequinone (Aldrich, free of anthraquinone) were purified by sublimation in vacuo before use. The complexes $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$, $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$, $U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$, $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)_2$, and $\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2$ were prepared according to our procedures.[11] The reagents $LiCH[Si(CH_3)_3]_2$[15] and $NaN[Si(CH_3)_3]_2$[16] were prepared by literature procedures.

$\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$. A 50-mL round-bottom flask was charged with 3.04 g (4.82 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$. Toluene (20 mL) was condensed into the flask in vacuo, and the solution was then filtered into a 50-mL receiving flask. An atmosphere of hydrogen (740mmHg) was introduced, and the solution was stirred for 15 h at room temperature. After this time, a green microcrystalline precipitate was observed. This solid was then isolated by filtration and was washed several times with 2-mL portions of toluene which were condensed in vacuo from the filtrate onto the solid. The green product was then dried in vacuo; yield, 85%.

IR (Nujol mull): 1019 m, 799 cm^{-1}. Anal. Calcd for $C_{60}H_{90}Cl_3U_3$: C, 44.16; H, 5.56; Cl, 6.52. Found: C, 44.09; H, 5.59; Cl, 6.60.

This complex can also be prepared from $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$ by a hydrogenolysis procedure similar to that described above.

In a separate experiment, a 25-mL round-bottom flask was charged with 0.30 g (0.52 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 0.26 g (0.25 mmol) of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2$. Toluene (15 mL) was condensed into the flask, and the mixture was stirred at room temperature. A green precipitate was observed, and this solid was isolated by filtration, was washed with toluene several times, and was dried in vacuo. The infrared spectrum and chemical properties of this product were identical with those of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$.

Reduction of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ with Sodium Amalgam. A 50-mL round-bottom flask with a stopcock/side arm was charged with 0.60 g (1.1 mmol) of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$. Toluene (15 mL) was condensed in vacuo into the flask. Sodium amalgam (3 mL, 0.9 wt % Na) was syringed into the flask under a flush of argon, and the mixture was stirred vigorously at 25 °C. After 10 min, a green precipitate was evident. The reaction mixture was stirred for another 20 min. Because separation of the green solid from the reaction mixture was not possible, extraction of the uranium-containing product with tetrahydrofuran was carried out. Tetrahydrofuran (2 mL) was condensed into the flask in vacuo. An emerald green solution resulted, and this toluene/THF solution was filtered. The filtrate was then concentrated in vacuo to ca. 0.5 mL. A green crystalline solid was observed, and pentane (3–4 mL) was condensed into the flask. The product was isolated by filtration, was washed twice with 1-mL portions of pentane, and was dried in vacuo; yield, 74%. This complex was recrystallized in a manner similar to the isolation procedure.

IR (Nujol mull): 1049 (m), 1031 (m, sh), 1020 (m), 860 (m), 800 (w) cm^{-1}. Anal. Calcd for $C_{28}H_{46}Cl_2O_2NaU$: C, 45.05; H, 6.21; Cl, 9.50. Found (average of two analyses): C, 45.19; H, 6.16; Cl, 10.44.

$U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\cdot THF$. A 25-mL round-bottom flask was charged with 0.50 g of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$. Pentane (10 mL) and tetrahydrofuran (0.4 mL) were condensed into the flask in vacuo. The solution became emerald green, and a green crystalline material was observed after stirring at room temperature for 4 min. The reaction mixture was stirred for another 30 min. Pentane and excess THF were then removed in vacuo, and toluene (10 mL) was condensed into the flask. The green solution was filtered, and the upper portion of the filtration apparatus was washed several times by condensation of toluene from the filtrate. The washings were combined with the filtrate which was subsequently concentrated to ca. 1 mL. Pentane (10 mL) was condensed into the flask which was then cooled to −78 °C. The green crystalline precipitate was isolated by cold filtration and was dried in vacuo; yield, 85%.

IR (Nujol mull): 1032 (s), 1020 (m), 916 (m), 799 (w), 898 (m) cm^{-1}. Anal. Calcd for $C_{24}H_{38}OClU$: C, 46.79; H, 6.22; Cl, 5.75. Found: C, 46.71; H, 6.18; Cl, 5.75.

$U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\cdot NC_5H_5$. A 25-mL round-bottom flask was charged with 0.50 g (0.31 mmol) of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$. Pentane (10 mL) and pyridine (0.5 mL) were condensed into the flask in vacuo. A blue-gray crystalline precipitate was observed almost immediately. Pentane and excess pyridine were then removed in vacuo. Toluene (10 mL) was next condensed into the flask, and the dark blue solution was filtered. The remaining solid was washed down by condensing toluene from the filtrate into the upper portion of the filtration apparatus. The washings were combined with the filtrate which was then concentrated to 2 mL. Pentane (10 mL) was condensed into the flask, and the blue-black crystalline solid was isolated by filtration, was washed once with 1 mL of pentane, and was dried in vacuo; yield, 86%.

IR (Nujol mull): 1591 (m), 1438 (s), 1210 (m), 1060 (m), 1037 (m), 1019 (m), 1001 (m), 800 (w), 750 (s), 700 (s), 621 (m) cm^{-1}. Anal. Calcd for $C_{25}H_{35}NClU$: C, 48.20; H, 5.66; N, 2.25; Cl, 5.69. Found: C, 48.16; H, 5.70; N, 2.31; Cl, 5.63.

$U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\cdot(OC_4H_{10})_x$ and $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\cdot[P(CH_3)_3]_x$. The green crystalline adducts, $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\cdot(OC_4H_{10})_x$ and $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\cdot[P(CH_3)_3]_x$ are formed in cold (−78 °C) pentane when excess diethyl ether or trimethylphosphine are condensed in vacuo into a flask containing $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$. These adducts lose diethyl ether or trimethylphosphine, respectively, when dried in vacuo at room temperature. The trimethylphosphine is lost almost immediately, while the diethyl ether is lost over a period of several hours. The $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ was recovered unchanged.

$U[\eta^5\text{-}(CH_3)_5C_5]_2N[Si(CH_3)_3]_2$. A 50-mL round-bottom flask was charged with 0.52 g (0.32 mmol) of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$

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and 0.20 g (1.1 mmol) of $NaN[Si(CH_3)_3]_2$. Diethyl ether (15 mL) was condensed into the flask in vacuo, and the reaction mixture was then stirred for 5 h at 25 °C. During this time, a blue-black crystalline material was observed along with a white precipitate (NaCl). Diethyl ether was removed in vacuo, and the reaction residue was dried under vacuum for 12 h. Toluene (15 mL) was then condensed into the flask, and the resulting blue-black solution was filtered. The residual solids were washed several times by condensing toluene from the filtrate into the upper portion of the filtration apparatus. The washings were combined with the filtrate, and the toluene was then removed in vacuo.

Pentane (10 mL) was condensed into the flask. The blue-black crystalline solid was isolated by filtration, was washed with 2-mL portions of pentane, and was dried in vacuo; yield, 69%. Recrystallization of this complex was accomplished in a manner similar to the isolation procedure.

IR (Nujol mull): 1255 (m), 1242 (s), 1025 (s), 862 (s), 833 (s), 820 (s), 760 (m), 590 (m) cm^{-1}. Anal. Calcd for $C_{26}H_{48}NSi_2U$: C, 46.69; H, 7.23; N, 2.09; mol wt, 669 g/mol. Found: C, 46.77; H, 7.19; N, 2.27; mol wt (cryoscopic in benzene), 676 ± 10% g/mol.

$U[\eta^5-(CH_3)_5C_5]_2CH[Si(CH_3)_3]_2$. A 50-mL round-bottom flask with a side arm/stopcock was charged with 1.00 g (0.613 mmol) of $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$. Diethyl ether (20 mL) was condensed into the flask in vacuo. Under a flush of argon, 2.8 mL of a diethyl ether solution of $LiCH[Si(CH_3)_3]_2$ (0.65 M, 1.8 mmol) was added via syringe. The reaction mixture was next stirred at room temperature for 15 h. The diethyl ether was then removed in vacuo, and the solid residue was dried under high vacuum for 12 h. Pentane (20 mL) was then condensed into the flask, and the black-brown solution was filtered. The residual solids were washed by condensing pentane from the filtrate into the upper portion of the filtration apparatus. The washings were combined with the filtrate which was then cooled to -78 °C. The black crystalline product was isolated by cold filtration and was dried in vacuo; yield, 41%. Recrystallization of this complex was accomplished from cold (-78 °C) pentane.

IR (Nujol mull): 1250 (s), 1239 (s), 1019 (m), 858 (s), 829 (s), 756 (m), 574 (m) cm^{-1}. Anal. Calcd for $C_{27}H_{49}Si_2U$: C, 48.56; H, 7.39, mol wt, 668 g/mol. Found: C, 48.44; H, 7.31, mol wt (cryscopic in benzene), 623 ± 10% g/mol.

Reaction of $U[\eta^5-(CH_3)_5C_5]_2CH[Si(CH_3)_3]_2$ with Hydrogen. A $C_6D_5CD_3$ solution of $U[\eta^5-(CH_3)_5C_5]_2CH[Si(CH_3)_3]_2$ was sealed in an NMR tube under an atmosphere of hydrogen, and the ^1H NMR spectrum was recorded as rapidly as possible. The reaction was complete in less than 10 min, and analysis of the spectrum was in accord with the production of 1 equiv of $[(CH_3)_3Si]_2CH_2/U$ (verified by comparison with a ^1H NMR spectrum of authentic $[(CH_3)_3Si]_2CH_2$) along with the complexes $\{U[\eta^5-(CH_3)_5C_5]_2H_2\}_2$ and $\{U[\eta^5-(CH_3)_5C_5]_2H\}_x$ in the ratio of 5:1, respectively.

Reaction of Diphenylacetylene and Tetraphenylcyclopentadienone with $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$ and $U[\eta^5-(CH_3)_5C_5]_2Cl_2\cdot Na(THF)_x$. An NMR tube was charged with a small amount of $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$. An excess of diphenylacetylene was then added followed by C_6D_6. The tube was shaken until all of the $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$ dissolved (ca. 2–4 min), forming a homogeneous red-brown solution. The ^1H NMR spectrum was obtained, and analysis of the spectrum indicated the formation of a 1:1 mixture of $U[\eta^5-(CH_3)_5C_5]_2Cl_2/[\eta^5-(CH_3)_5C_5]_2\overline{UC(C_6H_5)=C(C_6H_5)C(C_6H_5)=C}(C_6H_5)$.[11] The same reaction occurred if the complex $U[\eta^5-(CH_3)_5C_5]_2Cl_2Na(THF)_x$ was used, but in addition, 1 equivalent of THF was evident in the ^1H NMR spectrum.

A similar experiment was performed by using tetraphenylcyclopentadienone and *excess* $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$. After the solution was shaken, it became dark red-brown. The excess solid $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl\}_3$ was centrifuged to the top of the NMR tube, and a ^1H NMR spectrum of the solution was recorded. Analysis of the spectrum indicated the formation of a 1:1 mixture of $U[\eta^5-(CH_3)_5C_5]_2Cl_2/U[\eta^5-(CH_3)_5C_5]_2[\eta^2-COC_4(C_6H_5)_4]$.[11b]

Preparation of $[\eta^5-(CH_3)_5C_5]_2\overline{UC(C_6H_5)=C(C_6H_5)C(C_6H_5)=C}(C_6H_5)$ by Sodium Amalgam Reduction of $U[\eta^5-(CH_3)_5C_5]_2Cl_2$ in the Presence of Diphenylacetylene. A 100-mL round-bottom flask with a stopcock/side arm was charged with 0.50 g (0.86 mmol) of $U[\eta^5-(CH_3)_5C_5]_2Cl_2$ and 0.55 g (3.1 mmol) of diphenylacetylene. Toluene (20 mL) was condensed into the flask in vacuo. Under a flush of argon, sodium amalgam (0.5 mL, 0.9% wt of Na) was syringed into the flask, and the reaction mixture was stirred vigorously for 1 h during which time the solution color changed from red to dark brown-yellow. Stirring was then halted, and the solution was allowed to stand for 10–15 min. The solution was next filtered. The toluene was removed in vacuo, and pentane (10 mL) was condensed into the flask. The red-brown crystalline product was then isolated by filtration, was washed several times with pentane, an was dried in vacuo; yield, 62%. A ^1H NMR spectrum of the product was identical with the spectrum of the complex prepared from $U[\eta^5-(CH_3)_5C_5]_2Cl_2$ and $Li_2C_4(C_6H_5)_4$.[11]

Reaction of $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$ with 9,10-Phenanthrenequinone. A 25-mL round-bottom flask with a stopcock/side arm was charged with 0.60 g (0.37 mmol) of $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$ and 0.11 g (0.53 mmol) of 9,10-phenanthrenequinone. Toluene (15 mL) was condensed into the flask in vacuo. Argon (1 atm) was then admitted, and the reaction mixture was heated at 50 °C with an oil bath for 20 min. The $U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$ dissolved and the solution became red. The solution was then allowed to cool. Under a flush of argon, 1.5 mL of sodium amalgam (0.9% wt of Na) was syringed into the flask, and the mixture was stirred vigorously for 1.5 h. This reduced the $U[\eta^5-(CH_3)_5C_5]_2Cl_2$ produced in the above reaction to the insoluble complex $U[\eta^5-(CH_3)_5C_5]_2Cl_2^-Na^+$. The solution was then filtered, and the filtrate was concentrated in vacuo until *ca.* 0.2 mL of toluene remained. Pentane (10 mL) was then condensed into the flask. The solution was cooled to -78 °C, and the brown precipitate was isolated by cold filtration and was dried in vacuo; yield 66% (based on 9,10-phenanthrenequinone). The crude product was recrystallized by the following procedure. The crude product was dissolved partially in 15 mL of toluene, and the solution was filtered. Any remaining product was combined with the filtrate by Soxhlet extraction, condensing toluene into the upper portion of the filtration apparatus. The filtrate was then concentrated until the product was just wet with toluene. Pentane (10 mL) was next condensed into the flask. The brown microcrystalline product was isolated by filtration, was washed twice with 1-mL portions of pentane, and was dried in vacuo.

IR (Nujol mull): 3060 (w), 1601 (w), 1570 (m), 1513 (w), 1482 (m), 1411 (m), 1363 (s), 1337 (s), 1278 (w), 1247 (w), 1221 (w), 1161 (w), 1108 (m), 1092 (w), 1050 (s), 1026, 918 (m), 800 (w), 788 (s), 753 (s), 724 (s), 720 (s), 683 (s), 657 (m), 550 (s) cm^{-1}. Anal. Calcd for $C_{34}H_{38}O_2U$: C, 56.98; H, 5.34. Found: C, 56.79; H, 5.28.

Reaction of $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$ with Chloromethane and Chlorobenzene. A 25-mL flask was charged with 0.30 g (0.18 mmol) of $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$. Toluene (10 mL) was condensed into the flask in vacuo. The flask was cooled to -78 °C, and an excess of CH_3Cl was admitted to the toluene slurry of the complex.

The reaction mixture was allowed to warm slowly to room temperature. The $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$ dissolved, and the solution became red. Solvents were then removed in vacuo. An analysis of the ^1H NMR spectrum of the residual solids indicated the product was a 6.4:1 mixture of $U[\eta^5-(CH_3)_5C_5]_2Cl_2/U[\eta^5-(CH_3)_5C_5]_2(CH_3)Cl$.[11]

An analogous experiment was performed by using C_6H_5Cl. In this case, the uranium-containing product was exclusively $U[\eta^5-(CH_3)_5C_5]_2Cl_2$ as determined by ^1H NMR analysis.

X-ray Crystallographic Study[17] of $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$ (2). Single crystals of 2 were obtained by allowing a toluene solution of $U[(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$ to stand under 1 atm of hydrogen. The crystals were collected and sealed under nitrogen in thin-walled glass capillaries. They are, at 20 ± 1 °C, monoclinic with $a = 21.886$ (7) Å, $b = 14.236$ (5) Å, $c = 24.517$ (7) Å, $\beta = 128.65$ (2)°, $V = 5965.7$ Å^3, and $Z = 4$ trimeric units (μ_a(Mo $K\bar{\alpha}$)[18a] = 7.87 mm^{-1}; $d_{calcd} = 1.82$ g cm^{-3}). The systematically absent reflections in the diffraction pattern were consistent with the centrosymmetric space group $C2/c$—C^6_{2h} (No. 15)[19a] or the non-

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(17) See paragraph at end of paper regarding supplementary material.

(18) (a) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 55–66. (b) *Ibid.*, pp 99–101. (c) *Ibid.*, pp 149–150.

(19) (a) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 101. (b) *Ibid.*, p 89.

centrosymmetric space group Cc—C_s^4 (No. 9);[19b] the choice of the centrosymmetric space group $C2/c$ was fully supported by the various statistical indicators employing normalized structure factors and by all stages of the subsequent structure determination and refinement.

Intensity measurements were made on a Nicolet P$\bar{1}$ autodiffractometer using 1.0° wide ω scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation for a wedge-shaped crystal with dimensions of 0.40 × 0.40 × 0.80 mm. A total of 10 891 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 65.2°$ (the equivalent of 1.6 limiting Cu K$\bar{\alpha}$ spheres) were measured in five concentric shells of increasing 2θ. Three different scanning speeds were used during data collection: 3°/min for reflections with $3° < 2\theta < 43.0°$, 2°/min for $43.0° < 2\theta < 55.0°$, and 1°/min for $55.0 < 2\theta < 65.2°$. Each of these 1.0° wide scans were divided into 19 equal (time) intervals, and those 13 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for half the total time used for the net scan (13/19 of the total scan time), were measured at ω settings 1° above and below the calculated K$\bar{\alpha}$ doublet value for each reflection. The structure was solved by using the "heavy-atom" technique without correcting the intensity data for absorption effects. The results of preliminary full-matrix least-squares refinement cycles which used anisotropic thermal parameters for all nonhydrogen atoms and those 2922 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$ have been reported.[13]

The entire intensity data set was subsequently corrected empirically for absorption using ψ scans for six reflections having 2θ values between 10° and 32°; the appropriate Lorentz and polarization corrections were then reapplied. Unit-weighted full-matrix least-squares refinement which used this absorption-corrected data and anisotropic thermal parameters for all nonhydrogen atoms gave R_1 (unweighted, based on F)[20] = 0.033 and R_2 (weighted, based on F)[20] = 0.037 for 2866 independent reflections having $(\sin\theta)/\lambda < 0.515$ and $I > 3\sigma(I)$; similar refinement cycles with the more complete ($2\theta_{\mathrm{MoK}\bar{\alpha}} < 65.2°$) data set gave $R_1 = 0.042$ and $R_2 = 0.045$ for 6813 independent absorption-corrected reflections having $I > 3\sigma(I)$. These and all subsequent structure factor calculations employed recent tabulations of atomic form factors[18b] and anomalous dispersion corrections[18c] to the scattering factors of the U and Cl atoms. The final cycles[17] of empirically weighted[21] full-matrix least-squares refinement which utilized anisotropic thermal parameters for all nonhydrogen atoms gave $R_1 = 0.042$ and $R_2 = 0.051$ for 6813 reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 65.2°$ and $I > 3\sigma(I)$. Since a careful examination of the final F_0 and F_c values[17] indicated the absence of extinction effects, extinction corrections were not made.

All calculations with the absorption-corrected intensity data were performed on a Data General Eclipse S-200 computer with 64K of 16-bit words, a floating-point processor for 32- and 64-bit arithmetic and versions of the Nicolet E-XTL interactive crystallographic software package as modified at Crystalytics Co.

Results and Discussion

Synthesis of $\{U[(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ (2). We have previously shown that the chlorohydrocarbyl thorium complexes, $Th[(CH_3)_5C_5]_2(R)Cl$, undergo clean hydrogenolysis to yield the chlorohydride dimer 1 (eq 1).[11] In

$$2Th[(CH_3)_5C_5]_2(R)Cl + 2H_2 \rightarrow \underset{\mathbf{1}}{\{Th[(CH_3)_5C_5]_2(\mu\text{-}H)Cl\}_2} + 2RH \quad (1)$$

striking contrast, hydrogenolysis of the corresponding uranium chlorohydrocarbyls proceeds according to eq 2

$$xU[\eta^5\text{-}(CH_3)_5C_5]_2(R)Cl + (x/2)H_2\ (1\ \mathrm{atm}) \xrightarrow[25\ °C,\ 12\ h]{toluene} \underset{\mathbf{2}}{\{U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\}_x} + xRH \quad (2)$$

$$R = CH_3,\ CH_2Si(CH_3)_3$$

with clean reduction of the uranium(IV) hydrocarbyl to a uranium(III) complex of composition $\{U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\}_x$ (2). The infrared spectrum of this compound exhibits bands at 1019 and 799 cm^{-1}, which are characteristic of a η^5-bound pentamethylcyclopentadienyl ligand.[11] There is no indication of a hydride complex in any of the spectroscopic data for 2 or in the chemical reactions it undergoes (vide infra). No other unambiguous structural information could be obtained from the spectroscopic data.

Complex 2 can also be prepared by the metathesis reaction of eq 3. Recalling that the analogous reaction in

$$(1/2)\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2 + U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 \xrightarrow[toluene]{-H_2} (2/3)\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_x \quad (3)$$

the case of thorium yields $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)Cl\}_2$ (eq 1), it is tempting to speculate that eq 3 involves the intermediacy of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)Cl\}_2$. However, rather than direct loss of H_2 from the dimeric uranium chlorohydride, it is also possible that the formation of 2 is coupled to the marked tendency of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2$ to lose hydrogen.[11] Thus an alternative sequence for the formation of 2, such as that illustrated in eq 4–6, cannot be dismissed.

$$\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}H)Cl\}_2 \rightleftharpoons (1/2)\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2 + U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 \quad (4)$$

$$\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2 \overset{-H_2}{\rightleftharpoons} 2U[\eta^5\text{-}(CH_3)_5C_5]_2H \quad (5)$$

$$\begin{array}{l} U[\eta^5\text{-}(CH_3)_5C_5]_2H + U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 \rightarrow \\ \qquad U[\eta^5\text{-}(CH_3)_5C_5]_2Cl + U[\eta^5\text{-}(CH_3)_5C_5]_2(H)Cl \quad (6) \\ \qquad\qquad \downarrow \\ \qquad (1/3)\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3\downarrow \end{array}$$

Molecular Structure of $\{U[(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ (2). Single crystals of 2 suitable for X-ray diffraction could be obtained by diffusing hydrogen gas into solutions of $U[\eta^5\text{-}(CH_3)_5C_5]_2(R)Cl$ compounds in toluene. Final atomic coordinates and anisotropic thermal parameters for nonhydrogen atoms of 2 which resulted from the X-ray crystallographic study are given with estimated standard deviations in Tables I and II,[17] respectively. Relevant structural parameters for the coordination groups of 2 are presented with estimated standard deviations in Table III; bond lengths and angles involving nonhydrogen ligand atoms are given in Table IV.

The structural analysis shows that crystals of 2 are composed of discrete trinuclear $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ molecules; perspective views of the nonhydrogen atoms in 2 are shown in Figures 1 and 2. The numbering scheme used to designate atoms of 2 is as follows. Crystallographically independent U and Cl atoms are distinguished from one another by a numerical subscript to their atomic symbol. Methyl carbon atoms all have a subscripted m. Atoms of different pentamethylcyclopentadienyl ligands are differentiated by a subscripted a, b, or c, and within each ligand, ring and methyl carbon atoms are distinguished from one another by a numerical subscript.

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(20) The R values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, where w is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where K is the scale factor.

(21) Empirical weights were calculated from the equation $\sigma = \sum_0^3 a_n|F_o|^n = 6.86 - (3.82 \times 10^{-2})|F_o| + (1.74 \times 10^{-4})|F_o|^2 - (1.38 \times 10^{-7})|F_o|^3$, the a_n being coefficients derived from the least-squares fitting of the curve $||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$, where F_c values were calculated from the fully refined model using unit weighting and an $I > 3\sigma(I)$ rejection criterion.

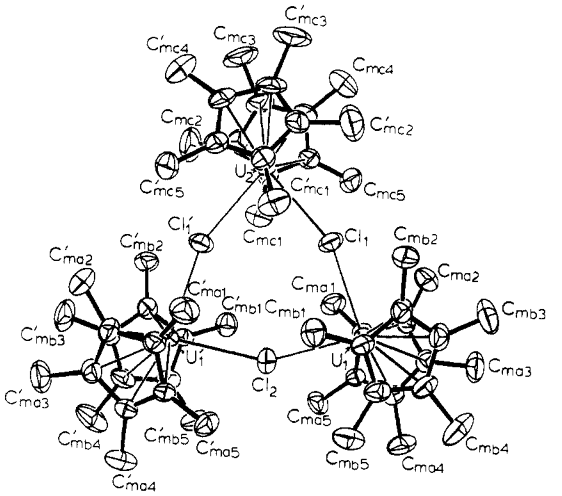

Figure 1. ORTEP drawing of the nonhydrogen atoms for the solid-state structure of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ (2) viewed along the *pseudo*-C_3 axis which is perpendicular to the (–U–Cl–)$_3$ ring. All atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Atoms labeled with a prime (′) are related to those labeled without a prime by the crystallographic C_2 axis which passes through U_2 and Cl_2. The labeling scheme is described in the text.

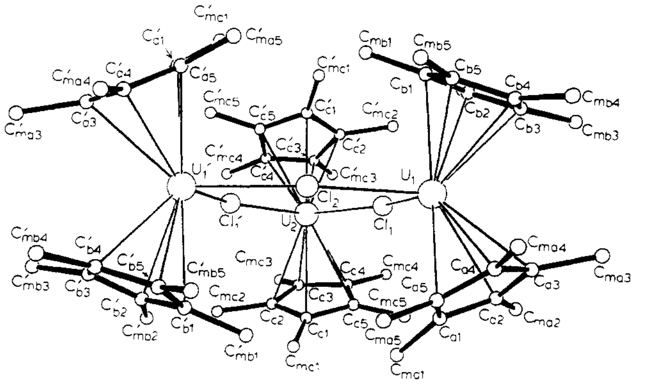

Figure 2. Perspective drawing of the nonhydrogen atoms of 2 viewed nearly along the crystallographic C_2 axis which passes through U_2 and Cl_2. All atoms are represented by arbitrarily sized spheres for purposes of clarity.

Although the $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ molecule approximates idealized D_{3h} symmetry, it exhibits only crystallographic C_2 symmetry. The idealized C_3 axis of a D_{3h} description for 2 would be oriented perpendicular to the (nearly) planar[22a] (to within 0.015 Å) (–U–Cl–)$_3$ ring and pass through its center; the vector through each U atom and the Cl opposite it in this six-membered ring would represent an idealized C_2 axis. Of these axes, the $U_2 \rightarrow Cl_2$ vector is the only rigorous C_2 axis; it is collinear with the crystallographic C_2 axis at (0, *y*, $^1/_4$) in the unit cell and relates the atoms labeled with primes (′) to those labeled without primes.

Each U(III) ion adopts the familar pseudotetrahedral "bent sandwich" $M(C_5H_5)_2X_2$ configuration[23] with the X groups being doubly bridging Cl^- ligands. Each of the five-membered rings for the three crystallographically independent $\eta^5\text{-}(CH_3)_5C_5^-$ ligands is coplanar to within 0.018 Å[22b-d] and makes dihedral angles of 20.2–28.3° with the plane of the six-membered (–U–Cl–)$_3$ ring.[22a] Methyl groups for each of these $(CH_3)_5C_5^-$ ligands are displaced from the 5-carbon ring mean plane by 0.018–0.343 Å in a direction away from the metal ion; in each ligand, the methyl group having the largest such displacement (>0.33 Å) is one of those closest to the "equatorial girdle" defined by the Cl–U–Cl grouping.[22e,f] The two independent (ring-center-of-gravity)–U–(ring-center-of-gravity) groupings (C_{ga}–U_1–C_{gb}[22g] and C_{gc}–U_2–C'_{gc},[22h] respectively) make dihedral angles of 82.0° and 86.4° with the mean plane of the six-membered (–U–Cl–)$_3$ ring.[22a]

As in other bis(pentamethylcyclopentadienyl)actinide species,[24] the (ring-center-of-gravity)–M–(ring-center-of-gravity) angles and the orientation of the $(CH_3)_5C_5^-$ ligands about their respective local fivefold axes in 2 appear to be dictated largely by nonbonded methyl···methyl interactions. The observed relative orientations of these (C-

Table I. Atomic Coordinates in Crystalline $[U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)]_3$ [a]

atom type [b]	10^4x	10^4y	10^4z
U_1	198.0 (2)	2076.5 (2)	1465.7 (1)
U_2	0 (...)[c]	–1380.9 (2)	2500 (...)[c]
Cl_1	121 (1)	157 (1)	1793 (1)
Cl_2	0 (–)[c]	2568 (2)	2500 (...)[c]
C_{a1}	1810 (4)	2077 (5)	2414 (4)
C_{a2}	1619 (5)	1853 (6)	1757 (5)
C_{a3}	1317 (5)	2660 (6)	1335 (4)
C_{a4}	1291 (5)	3391 (5)	1718 (4)
C_{a5}	1596 (4)	3039 (5)	2375 (4)
C_{b1}	–1382 (4)	2152 (5)	535 (4)
C_{b2}	–1191 (5)	1516 (6)	207 (4)
C_{b3}	–825 (5)	2034 (7)	–9 (4)
C_{b4}	–807 (5)	2994 (6)	166 (4)
C_{b5}	–1125 (5)	3060 (5)	521 (4)
C_{c1}	1607 (5)	–1393 (6)	3501 (5)
C_{c2}	1325 (6)	–2110 (6)	3709 (5)
C_{c3}	1035 (6)	–2872 (6)	3235 (6)
C_{c4}	1116 (6)	–2627 (6)	2715 (6)
C_{c5}	1470 (5)	–1721 (6)	2885 (5)
C_{ma1}	2236 (6)	1465 (7)	3044 (6)
C_{ma2}	1781 (8)	925 (8)	1573 (7)
C_{ma3}	1228 (7)	2777 (9)	673 (6)
C_{ma4}	1109 (6)	4418 (6)	1523 (6)
C_{ma5}	1780 (6)	3621 (7)	2974 (5)
C_{mb1}	–1797 (5)	1899 (7)	827 (5)
C_{mb2}	–1424 (6)	500 (6)	29 (5)
C_{mb3}	–636 (8)	1645 (10)	–456 (6)
C_{mb4}	–641 (8)	3835 (9)	–116 (6)
C_{mb5}	–1243 (6)	3949 (7)	781 (6)
C_{mc1}	2016 (7)	–520 (8)	3885 (6)
C_{mc2}	1369 (9)	–2060 (11)	4352 (7)
C_{mc3}	878 (10)	–3843 (7)	3374 (9)
C_{mc4}	985 (9)	–3242 (9)	2152 (8)
C_{mc5}	1726 (6)	–1262 (7)	2502 (6)

[a] Figures in parentheses are the estimated standard deviation for the last significant digit. [b] Atoms are labeled in accord with Figure 1. [c] This is a symmetry-required value and is therefore listed without a standard deviation.

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(22) The least-squares mean planes for the following groups of atoms or points in **2** are defined by the equation $aX + bY + cZ = d$, where *X*, *Y*, and *Z* are orthogonal coordinates measured in angstroms along $\vec{a}$, $\vec{b}$, and $\vec{c}^*$, respectively, of the crystal system: (a) U_1, U_2, U'_1, Cl_1, Cl_2, and Cl'_1 (coplanar to within 0.015 Å), $a = 0.703$, $b = 0.000$, $c = 0.711$, $d = 0.712$; (b) C_{a1}, C_{a2}, C_{a3}, C_{a4}, and C_{a5} (coplanar to within 0.011 Å), $a = 0.890$, $b = 0.282$, $c = 0.358$, $d = 2.717$; (c) C_{b1}, C_{b2}, C_{b3}, C_{b4}, and C_{b5} (coplanar to within 0.018 Å), $a = -0.443$, $b = 0.164$, $c = -0.881$, $d = 1.299$; (d) C_{c1}, C_{c2}, C_{c3}, C_{c4}, and C_{c5} (coplanar to within 0.007 Å), $a = 0.713$, $b = -0.422$, $c = 0.560$, $d = 3.275$; (e) Cl_1, U_1, and Cl_2, $a = 0.699$, $b = -0.007$, $c = 0.715$, $d = 0.718$; (f) Cl_1, U_2, and Cl'_1, $a = 0.709$, $b = 0.000$, $c = 0.705$, $d = 0.663$; (g) C_{ga}–U_1–C_{gb}, $a = -0.416$, $b = 0.850$, $c = 0.323$, $d = 4.172$; (h) C_{gc}–U_2–C_{gc}', $a = -0.606$, $b = 0.000$, $c = 0.796$, $d = 6.128$.

(23) (a) Petersen, J. L.; Lichtenberger, C. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433–6441 and references therein. (b) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. F.; Denton, B.; Rees, R. V. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2290–2304 and references therein.

(24) (a) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1978**, *100*, 7112–7114. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *Ibid.* **1980**, *102*, 5396–5398. (c) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *Ibid.* **1981**, *103*, 2206–2220.

Table III. Bond Lengths, Ligand-Ligand Contacts, and Bond Angles Subtended at U(III) Atoms in Crystalline $\{\mathrm{U}[\eta^5\text{-}(\mathrm{CH_3})_5]_2(\mu\text{-Cl})\}_3$[a]

type[b]	value	type[b]	value
	Distances, Å		
$\mathrm{U_1-Cl_1}$	2.883 (2)	$\mathrm{U_1-C_{a1}}$	2.758 (10)
$\mathrm{U_1-Cl_2}$	2.912 (1)	$\mathrm{U_1-C_{a2}}$	2.741 (13)
$\mathrm{U_2-Cl_1}$	2.904 (2)	$\mathrm{U_1-C_{a3}}$	2.787 (13)
av[c]	2.900 (2, 11, 17, 3)	$\mathrm{U_1-C_{a4}}$	2.784 (11)
$\mathrm{U_1-C_{ga}}$[d]	2.492 (...)	$\mathrm{U_1-C_{a5}}$	2.772 (9)
$\mathrm{U_1-C_{gb}}$[d]	2.488 (...)	$\mathrm{U_1-C_{b1}}$	2.706 (10)
$\mathrm{U_2-C_{gc}}$[d]	2.491 (...)	$\mathrm{U_1-C_{b2}}$	2.772 (8)
av[c]	2.490 (..., 2, 2, 3)	$\mathrm{U_1-C_{b3}}$	2.823 (8)
$\mathrm{U_1\cdots U_2}$	5.676 (1)	$\mathrm{U_1-C_{b4}}$	2.819 (8)
$\mathrm{U_1\cdots U_1}$	5.653 (1)	$\mathrm{U_1-C_{b5}}$	2.708 (10)
av[c]	5.665 (1, 12, 12, 2)	$\mathrm{U_2-C_{c1}}$	2.758 (12)
$\mathrm{Cl_1\cdots Cl_1'}$	3.818 (4)	$\mathrm{U_2-C_{c2}}$	2.745 (11)
$\mathrm{Cl_1\cdots Cl_2}$	3.928 (4)	$\mathrm{U_2-C_{c3}}$	2.791 (11)
av[c]	3.873 (4, 55, 55, 2)	$\mathrm{U_2-C_{c4}}$	2.789 (13)
		$\mathrm{U_2-C_{c5}}$	2.772 (13)
		av[c]	2.768 (11, 26, 62, 15)
	Angles, Deg		
$\mathrm{Cl_1U_1Cl_2}$	85.3 (1)	$\mathrm{C_{ga}U_1Cl_1}$[d]	114.6 (...)
$\mathrm{Cl_1U_2Cl_1'}$	82.2 (1)	$\mathrm{C_{ga}U_1Cl_2}$[d]	107.8 (...)
av[c]	83.8 (1, 16, 16, 2)	$\mathrm{C_{gb}U_1Cl_1}$[d]	104.9 (...)
$\mathrm{U_1Cl_2U_1'}$	152.2 (1)	$\mathrm{C_{gb}U_1Cl_2}$[d]	108.3 (...)
$\mathrm{U_1Cl_1U_2}$	157.5 (1)	$\mathrm{C_{gc}U_2Cl_1}$[d]	104.5 (...)
av[c]	154.9 (1, 27, 27, 2)	$\mathrm{C_{gc}U_2Cl_1}$	114.0[d] (...)
$\mathrm{C_{ga}U_1C_{gb}}$[d]	127.7 (...)	av[c]	109.0 (..., 35, 56, 6)
$\mathrm{C_{gc}U_2C'_{gc}}$[d]	128.2 (...)	$\mathrm{C_{a1}U_1C_{a3}}$	49.0 (3)
av[c]	128.0 (..., 3, 3, 2)	$\mathrm{C_{a1}U_1C_{a4}}$	49.0 (3)
$\mathrm{C_{a1}U_1C_{a2}}$	30.0 (3)	$\mathrm{C_{a2}U_1C_{a4}}$	48.9 (3)
$\mathrm{C_{a2}U_1C_{a3}}$	29.4 (3)	$\mathrm{C_{a2}U_1C_{a5}}$	49.1 (3)
$\mathrm{C_{a3}U_1C_{a4}}$	29.7 (3)	$\mathrm{C_{a3}U_1C_{a5}}$	48.5 (3)
$\mathrm{C_{a4}U_1C_{a5}}$	29.1 (3)	$\mathrm{C_{b1}U_1C_{b3}}$	49.3 (3)
$\mathrm{C_{a5}U_1C_{a1}}$	30.0 (3)	$\mathrm{C_{b1}U_1C_{b4}}$	49.0 (3)
$\mathrm{C_{b1}U_1C_{b2}}$	30.3 (3)	$\mathrm{C_{b2}U_1C_{b4}}$	48.4 (3)
$\mathrm{C_{b2}U_1C_{b3}}$	29.2 (3)	$\mathrm{C_{b2}U_1C_{b5}}$	49.7 (3)
$\mathrm{C_{b3}U_1C_{b4}}$	29.3 (3)	$\mathrm{C_{b3}U_1C_{b5}}$	49.2 (3)
$\mathrm{C_{b4}U_1C_{b5}}$	29.6 (3)	$\mathrm{C_{c1}U_2C_{c3}}$	49.6 (3)
$\mathrm{C_{b5}U_1C_{b1}}$	30.4 (3)	$\mathrm{C_{c1}U_2C_{c4}}$	49.4 (3)
$\mathrm{C_{c1}U_2C_{c2}}$	30.4 (3)	$\mathrm{C_{c2}U_2C_{c4}}$	49.1 (3)
$\mathrm{C_{c2}U_2C_{c3}}$	29.6 (4)	$\mathrm{C_{c2}U_2C_{c5}}$	49.2 (3)
$\mathrm{C_{c3}U_2C_{c4}}$	29.8 (4)	$\mathrm{C_{c3}U_2C_{c5}}$	49.2 (3)
$\mathrm{C_{c4}U_2C_{c5}}$	29.8 (3)	av[c]	49.1 (3, 2, 7, 15)
$\mathrm{C_{c5}U_2C_{c1}}$	29.8 (3)		
av[c]	29.8 (3, 3, 7, 15)		

[a] The number in parentheses following an individual entry is the estimated standard deviation in the last significant digit. [b] Atoms are labeled in agreement with Figures 1 and 2 and Tables I and II. [c] See ref 29. [d] $\mathrm{C_{ga}}$, $\mathrm{C_{gb}}$, and $\mathrm{C_{gc}}$ refer to the centers of gravity for the 5-carbon rings of pentamethylcyclopentadienyl ligands a, b, and c, respectively.

Table IV. Ligand Bond Lengths and Angles Involving Nonhydrogen Atoms in Crystalline $\{\mathrm{U}[\eta^5\text{-}(\mathrm{CH_3})_5\mathrm{C_5}]_2(\mu\text{-Cl})\}_3$[a]

type[b]	value	type[b]	value
	Bond Lengths, Å		
$\mathrm{C_{a1}-C_{a2}}$	1.425 (13)	$\mathrm{C_{a1}-C_{ma1}}$	1.488 (13)
$\mathrm{C_{a1}-C_{a5}}$	1.432 (11)	$\mathrm{C_{a2}-C_{ma2}}$	1.507 (16)
$\mathrm{C_{a2}-C_{a3}}$	1.406 (12)	$\mathrm{C_{a3}-C_{ma3}}$	1.519 (17)
$\mathrm{C_{a3}-C_{a4}}$	1.427 (13)	$\mathrm{C_{a4}-C_{ma4}}$	1.513 (12)
$\mathrm{C_{a4}-C_{a5}}$	1.395 (12)	$\mathrm{C_{a5}-C_{ma5}}$	1.506 (13)
$\mathrm{C_{b1}-C_{b2}}$	1.435 (13)	$\mathrm{C_{b1}-C_{mb1}}$	1.507 (17)
$\mathrm{C_{b1}-C_{b5}}$	1.419 (12)	$\mathrm{C_{b2}-C_{mb2}}$	1.505 (13)
$\mathrm{C_{b2}-C_{b3}}$	1.413 (16)	$\mathrm{C_{b3}-C_{mb3}}$	1.501 (20)
$\mathrm{C_{b3}-C_{b4}}$	1.425 (13)	$\mathrm{C_{b4}-C_{mb4}}$	1.536 (17)
$\mathrm{C_{b4}-C_{b5}}$	1.418 (17)	$\mathrm{C_{b5}-C_{mb5}}$	1.510 (14)
$\mathrm{C_{c1}-C_{c2}}$	1.441 (17)	$\mathrm{C_{c1}-C_{mc1}}$	1.476 (15)
$\mathrm{C_{c1}-C_{c5}}$	1.422 (15)	$\mathrm{C_{c2}-C_{mc2}}$	1.521 (21)
$\mathrm{C_{c2}-C_{c3}}$	1.416 (14)	$\mathrm{C_{c3}-C_{mc3}}$	1.513 (17)
$\mathrm{C_{c3}-C_{c4}}$	1.436 (19)	$\mathrm{C_{c4}-C_{mc4}}$	1.505 (19)
$\mathrm{C_{c4}-C_{c5}}$	1.428 (14)	$\mathrm{C_{c5}-C_{mc5}}$	1.509 (19)
av[c]	1.423 (14, 9, 28, 15)	av[c]	1.508 (16, 9, 32, 15)
	Bond Angles, Deg		
$\mathrm{C_{a5}C_{a1}C_{a2}}$	106.6 (8)	$\mathrm{C_{ma1}C_{a1}C_{a5}}$	126.6 (9)
$\mathrm{C_{a1}C_{a2}C_{a3}}$	108.6 (9)	$\mathrm{C_{ma1}C_{a1}C_{a2}}$	126.4 (9)
$\mathrm{C_{a2}C_{a3}C_{a4}}$	107.8 (9)	$\mathrm{C_{ma2}C_{a2}C_{a1}}$	125.2 (10)
$\mathrm{C_{a3}C_{a4}C_{a5}}$	108.2 (9)	$\mathrm{C_{ma2}C_{a2}C_{a3}}$	125.9 (10)
$\mathrm{C_{a4}C_{a5}C_{a1}}$	108.7 (8)	$\mathrm{C_{ma3}C_{a3}C_{a2}}$	124.3 (10)
$\mathrm{C_{b5}C_{b1}C_{b2}}$	107.6 (8)	$\mathrm{C_{ma3}C_{a3}C_{a4}}$	126.4 (10)
$\mathrm{C_{b1}C_{b2}C_{b3}}$	108.3 (8)	$\mathrm{C_{ma4}C_{a4}C_{a3}}$	127.3 (9)
$\mathrm{C_{b2}C_{b3}C_{b4}}$	107.7 (9)	$\mathrm{C_{ma4}C_{a4}C_{a5}}$	123.7 (9)
$\mathrm{C_{b3}C_{b4}C_{b5}}$	108.4 (9)	$\mathrm{C_{ma5}C_{a5}C_{a4}}$	124.9 (9)
$\mathrm{C_{b4}C_{b5}C_{b1}}$	108.0 (8)	$\mathrm{C_{ma5}C_{a5}C_{a1}}$	125.8 (8)
$\mathrm{C_{c5}C_{c1}C_{c2}}$	106.8 (10)	$\mathrm{C_{mb1}C_{b1}C_{b5}}$	126.5 (8)
$\mathrm{C_{c1}C_{c2}C_{c3}}$	109.0 (10)	$\mathrm{C_{mb1}C_{b1}C_{b2}}$	126.0 (8)
$\mathrm{C_{c2}C_{c3}C_{c4}}$	107.5 (11)	$\mathrm{C_{mb2}C_{b2}C_{b1}}$	127.2 (9)
$\mathrm{C_{c3}C_{c4}C_{c5}}$	107.8 (10)	$\mathrm{C_{mb2}C_{b2}C_{b3}}$	124.1 (9)
$\mathrm{C_{c4}C_{c5}C_{c1}}$	108.8 (10)	$\mathrm{C_{mb3}C_{b3}C_{b2}}$	124.2 (10)
av[c]	108.0 (9, 5, 14, 15)	$\mathrm{C_{mb3}C_{b3}C_{b4}}$	127.2 (10)
		$\mathrm{C_{mb4}C_{b4}C_{b3}}$	125.6 (10)
		$\mathrm{C_{mb4}C_{b4}C_{b5}}$	124.8 (10)
		$\mathrm{C_{mb5}C_{b5}C_{b4}}$	126.4 (9)
		$\mathrm{C_{mb5}C_{b5}C_{b1}}$	125.4 (9)
		$\mathrm{C_{mc1}C_{c1}C_{c5}}$	126.5 (10)
		$\mathrm{C_{mc1}C_{c1}C_{c2}}$	126.5 (11)
		$\mathrm{C_{mc2}C_{c2}C_{c1}}$	124.7 (11)
		$\mathrm{C_{mc2}C_{c2}C_{c3}}$	126.3 (12)
		$\mathrm{C_{mc3}C_{c3}C_{c2}}$	124.3 (12)
		$\mathrm{C_{mc3}C_{c3}C_{c4}}$	126.4 (12)
		$\mathrm{C_{mc4}C_{c4}C_{c3}}$	128.0 (12)
		$\mathrm{C_{mc4}C_{c4}C_{c5}}$	123.4 (11)
		$\mathrm{C_{mc5}C_{c5}C_{c4}}$	123.7 (10)
		$\mathrm{C_{mc5}C_{c5}C_{c1}}$	127.2 (10)
		av[c]	125.7 (10, 10, 23, 30)

[a] Numbers in parentheses following individual entries are are the estimated standard deviations in the last significant digit. [b] Atoms labeled in agreement with Figure 1 and Tables I and II. [c] See ref 29.

$\mathrm{H_3)_5C_5^-}$ ligands in 2 produce several intramolecular nonbonded methyl···methyl contacts which are only slightly longer than the 3.40-Å van der Waals diameter[25] of carbon and 0.40–0.50 Å less than the 4.00-Å van der Waals diameter[25] of a methyl group: $\mathrm{C_{ma3}\cdots C_{mb3}}$, 3.58 (2) Å; $\mathrm{C_{ma3}\cdots C_{mb4}}$, 3.59 (2) Å; $\mathrm{C_{ma4}\cdots C_{mb4}}$, 3.50 (2) Å; $\mathrm{C_{mc3}\cdots C'_{mc3}}$, 3.54 (3) Å; $\mathrm{C_{mc3}\cdots C'_{mc4}}$, 3.53 (3) Å. These short methyl···methyl contacts are also undoubtedly responsible for the large (>0.33 Å) displacements of $\mathrm{C_{ma3}}$, $\mathrm{C_{mb4}}$, and $\mathrm{C_{mc3}}$ from their respective 5-carbon ring mean planes and the slight elongation of the U–C bond for the ring carbon atom to which they are bonded. Similar steric effects have been observed in other bis(pentamethylcyclopentadienyl)actinide complexes.[24,26]

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Intramolecular nonbonded methyl···methyl interactions above and below the $(-U-Cl-)_3$ ring between $(CH_3)_5C_5^-$ ligands on different metal atoms also seem to be responsible for bis(pentamethylcyclopentadienyl)uranium monochloride adopting a trimeric structure similar to that observed for $[Zr(\eta^5\text{-}C_5H_5)_2(\mu\text{-}O)]_3$[27] rather than a dimeric structure such as $[Bk(\eta^5\text{-}C_5H_5)_2(\mu\text{-}Cl)]_2$.[28] The methyl substituent on each $(CH_3)_5C_5^-$ ligand nearest the pseudo-C_3 axis of the molecule (C_{m1}) is involved in two short (3.51–3.70 Å) methyl···methyl contacts with the threefold-related methyls on the other two metals. Clearly, a dimer with the same metrical parameters about the U(III) would produce unacceptably short $C_{m1}\cdots C_{m1}$ contacts. These same nonbonded $C_{m1}\cdots C_{m1}$ contacts are also probably responsible for the somewhat compressed (by ~10°) Cg–U–Cg angles (average 128.0 (..., 3, 3, 2)°[29]) in 2 relative to those in mononuclear bis(pentamethylcyclopentadienyl)actinides.

Whereas the gross solid-state structural features of 2 and $[Zr(\eta^5\text{-}C_5H_5)_2(\mu\text{-}O)]_3$ are quite similar, there are (not unexpectedly) significant differences in the metal ion coordination parameters. For $[Zr(\eta^5\text{-}C_5H_5)_2(\mu\text{-}O)]_3$, the average M–X distance is 0.942 Å shorter, the average Cg–M–Cg and Cg–M–X angles are 4.3° and 0.9° smaller, respectively, and the average X–M–X angle is 11.7° larger than in 2. Interestingly, even with this enormous difference in M–X bond lengths and the 11.7° difference in X–M–X angles, the X···X contact on each metal ion coordination sphere in $[Zr(\eta^5\text{-}C_5H_5)_2(\mu\text{-}O)]_3$ and in 2 is, on the average, only slightly larger (0.14 and 0.27 Å, respectively) than the corresponding van der Waals diameter. The 2.900 (2, 11, 17, 3) Å average U–Cl bond length in 2 is quite similar to the values determined for bridging U–Cl bonds in $U(\eta^6\text{-}C_6H_6)(AlCl_4)_3\cdot C_6H_6$[9] and $LiU_2Cl_5[CH_2(C_5H_4)_2]_2(OC_4H_8)_2$:[30] 2.878 (7, 24, 40, 6) and 2.83 (1, 1, 1, 3) Å, respectively. The 2.768 (11, 26, 62, 15)-Å average $(CH_3)_5C_5$ U(III)–C bond length in 2 can be compared with average metal–carbon bond lengths in several tetravalent bis(pentamethylcyclopentadienyl)actinide complexes: 2.776 (9, 20, 56, 10) Å in $U[\eta^5\text{-}(CH_3)_5C_5]_2[\eta^2\text{-}CO(N(CH_3)_2)]_2$,[24c,26] 2.79 (2, 2, 3, 10) Å in $Th[\eta^5\text{-}(CH_3)_5C_5]_2[\eta^2\text{-}CO(N(C_2H_5)_2)]Cl$,[24c,26] 2.80 (2, 2, 3, 10) Å in $Th[\eta^5\text{-}(CH_3)_5C_5]_2[\eta^2\text{-}COCH_2C(CH_3)_3]Cl$,[24b,26] 2.82 (2, 3, 5, 20) Å in $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2[\mu\text{-}CO(CH_2C(CH_3)_3)_2CO]Cl\}_2$,[24b,26] and 2.845 (13, 28, 66, 10) Å in $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}O_2C_2(CH_3)_2)\}_2$.[24a,26]

The metrical data now available for bis(pentamethylcyclopentadienyl)actinide complexes provide a useful means of testing the generality of a recently proposed, commendable formalism[31] for understanding the metal-ligand bond lengths in f element organometallics. This formalism utilizes Pauling's radius ratio[32] but, in its original form,[31b,c] did not specifically incorporate the effects of ligand size and intramolecular ligand–ligand contacts (fundamental considerations in the original Pauling treatment[32]). The importance of such considerations in analyzing higher coordination polyhedra has been discussed[33] and also expressed in terms of a simplified graphic representation of Pauling's minimum radius ratios.[33e] In regard to organoactinides, we noted earlier[34] that the metrical parameters in $U(\eta^5\text{-}CH_3C_5H_4)Cl_3(THF)_2$ do not conform to the original formalism. In the most recent version,[31a] the formalism restricts comparisons to structures within a given "structural type" (e.g., $M(\eta^5\text{-}C_5H_5)_3$, $M(\eta^5\text{-}C_5H_5)_3X$, $M(\eta^8\text{-}C_8H_8)_2$). Since the actinide complexes $M[\eta^5\text{-}(CH_3)_5C_5]_2X_2$ reasonably constitute a "structural type", it is of interest to examine the applicability of the refined formalism.[31a] For this analysis, we employ, as does the aforementioned formalism, the electronically based (as opposed to sterically based) definition[31] of coordination number; i.e., the number of electron pairs donated by the ligands. Since the metal centers in 2 are formally eight-coordinate, we employ eight-coordinate ionic radii of 1.00 Å (U(IV)), 1.05 Å (Th(IV)), and 1.12 Å (U(III)).[35a,b] Although comparisons could be made between the metrical parameters in 2 and all of the above structures, discussion will be restricted to those of highest precision and having comparable formal coordination numbers.

Comparing eight-coordinate U(III) in 2 to eight-coordinate Th(IV) in $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2[\mu\text{-}O_2C_2(CH_3)_2]\}_2$, the formalism predicts that the U–C(cyclopentadienyl)distance in 2 will be ≥0.07 Å longer. In fact, it is 0.077 Å shorter. Reasonably, these are compounds of the same structural type[31a] with similar types of ligands; also the $\eta^5\text{-}(CH_3)_5C_5$ functionality occupies a majority[31a] (75%) of the coordination sites. The metrical parameters for 2 can also be compared to those for U(IV) in $U[\eta^5\text{-}(CH_3)_5C_5]_2[\eta^2\text{-}CON(CH_3)_2]_2$. There is some ambiguity here as to whether the carbamoyl ligands contribute two or four units to the formal coordination number. Valency and steric arguments[24c] suggest that eight is the appropriate formal coordination number for uranium; however, ten will be considered as well. The formalism predicts that the U–C(cyclopentadienyl) distance in 2 will be ≥0.12 Å longer if the U(IV) is eight-coordinate and ≥0.03 Å longer if the U(IV) is ten-coordinate.[35c] In reality the U–C distance in 2 is identical with that in the uranium(IV) bis(carbamoyl). These comparisons underscore the not unexpected difficulties in applying radius ratio arguments to organometallic systems with sterically demanding ligands. Not only are comparisons between metal ions with the same formal coordination numbers and greatly different ligand arrays sometimes tenuous,[34] but also the present actinide $M[\eta^5\text{-}(CH_3)_5C_5]_2X_2$ results indicate that significant deviations can arise even in systems with similar ligand arrays.

Reduction of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ with Sodium Amalgam. Reduction of the uranium(IV) complex $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ can also be effected with sodium amal-

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(29) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

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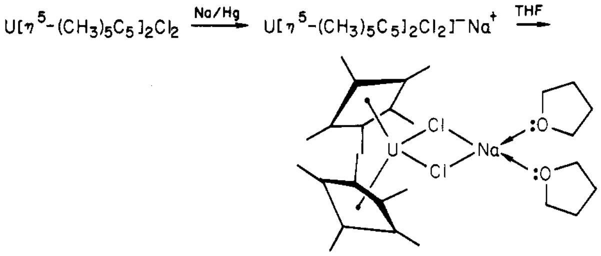
(35) (a) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767. (b) The eight-coordinate U(III) radius of 1.12 Å was obtained via eq 4 of ref 31a and is likely a conservative estimate. Trends in lanthanide(III) and U(IV) radii[35a] suggest that it may be as large as 1.15 Å. (c) If the uranium bis(carbamoyl) is formally ten-coordinate, then the formalism predicts that the U–C distance will be 0.03 Å longer than the Th–C distance in $\{Th[\eta^5\text{-}(CH_3)_5C_5]_2[\mu\text{-}O_2C_2(CH_3)_2]\}_2$. Experimentally, it is found to be 0.07 Å shorter. (d) Professor R. G. Finke has informed us of similar findings.

Table V. ^{1}H NMR Spectral Data for Bis(pentamethylcyclopentadienyl)uranium(III) Complexes^{a,b}

complex	η^5-$(CH_3)_5C_5$	other
$U[\eta^5-(CH_3)_5C_5]_2Cl_2Na(THF)_x$ (3)	−5.07 (30 H, s, lw = 100 Hz)	*c*
$U[\eta^5-(CH_3)_5C_5]_2Cl\cdot$pyridine (4)	−4.95 (30 H, s, lw = 40 Hz)	−9.19 (2 H, lw = 14 Hz), 56.6 (2 H, lw = 75 Hz), 7.02 (1 H, lw = 8 Hz)
$U[\eta^5-(CH_3)_5C_5]_2Cl\cdot THF$ (5)	−4.86 (30 H, s, lw = 100 Hz)	−14.3 (4 H, lw = 120 Hz), −47.6 (4 H, lw = 180 Hz)
$U[\eta^5-(CH_3)_5C_5]_2CH[Si(CH_3)_3]_2$ (8)	−5.56 (30 H, s, lw = 19 Hz)	−22.8 (18 H, s, lw = 20 Hz)
$U[\eta^5-(CH_3)_5C_5]_2N[Si(CH_3)_3]_2$ (9)	−5.43 (30 H, s, lw = 7 Hz)	−24.9 (18 H, s, lw = 20 Hz)
$U[\eta^5-(CH_3)_5C_5]_2$(9,10-phenanthrenequinonate) (12)	3.65 (30 H, s)	−24.3 (2 H, m, H's at positions 1 and 8), −1.25 (2 H, m, H's at positions 2 and 7), 2.23 (2 H, M, H's at positions 3 and 6), 3.07 (2 H, m, H's at positions 4 and 5)

^{a} Recorded in C_6D_6 at 35 °C. Chemical shifts are reported in ppm from Me_4Si; lw = line width at half-maximum. ^{b} s = singlet; d = doublet; t = triplet, q = quartet; m = multiplet. ^{c} Resonances of the THF ligands vary depending on the exact amount of THF in the sample.

gam in toluene solution. The product of this reaction is an insoluble green precipitate. Extraction with THF and workup yields a green, crystalline product (**3**). Although the spectral data for this compound (IR and ^{1}H NMR (Table V)) are rather similar to those for $U[\eta^5-(CH_3)_5C_5]_2Cl\cdot THF$ (vide infra), the elemental analyses were consistently to high in Cl for this formulation. Rather, the analyses and spectral data best fit the formulation $U[\eta^5-(CH_3)_5C_5]_2Cl_2Na(THF)_x$, where x = 1.5–2.[35d] Thus, the probable course of this reaction is shown in eq 7. Anionic lanthanide complexes of this type have recently been prepared by Watson[36a] and Wayda and Evans.[36b] As will be shown below, the redox reactions of this complex are very similar to those of $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$.



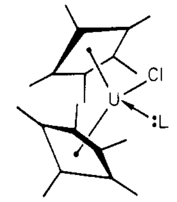
(7)

Reaction of $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$ with Lewis Bases. Although $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$ is insoluble in hydrocarbon solvents, it readily dissolves in the presence of Lewis bases to form the corresponding crystalline adducts **4**–**7** (eq 8). The pyridine and THF adducts are

$$(1/3)\{U[\eta^5-C_5(CH_3)_5]_2(\mu-Cl)\}_3 + L \rightleftharpoons [\eta^5-C_5(CH_3)_5]_2UCl\cdot L \quad (8)$$

4, L = pyridine (dark blue-black crystals)
5, L = tetrahydrofuran (green crystals)
6, L = diethyl ether (green crystals)
7, L = $P(CH_3)_3$ (green crystals)

sufficiently stable to allow isolation, drying in vacuo, and complete characterization. The diethyl ether complex is somewhat less stable, and the trimethylphoshine adduct, which would be the first organouranium phosphine complex, loses $P(CH_3)_3$ rapidly in vacuo. We report elsewhere the molecular structure of another, more stable uranium(III) phosphine complex, $U[(CH_3)_5C_5]_2[(CH_3)_2PCH_2CH_2P(CH_3)_2]H$.[37] The $U[\eta^5-(CH_3)_5C_5]_2Cl\cdot L$ complexes are modestly soluble in toluene but are only slightly soluble in pentane. The ^{1}H NMR spectra of the new U(III) complexes display large isotropic shifts; however, line widths are significantly greater than those for U(IV) complexes.[11] Thus, the η^5-$(CH_3)_5C_5$ resonances of the above THF and pyridine adducts appear as broad singlets in the ^{1}H NMR spectrum at δ −4.86 (lw = 100 Hz) and δ −4.95 (lw = 40 Hz), respectively. The Lewis base resonances are also shifted isotropically and broadened. Incremental addition of THF or pyridine to C_6D_6 solutions of the respective adducts produces a single set of base resonances which progressively shift toward the diamagnetic region. The η^5-$(CH_3)_5C_5$ line widths remain unchanged. This result indicates that exchange is occurring between free base and coordinated base which is rapid on the NMR time scale. ^{1}H NMR data are compiled in Table V. The infrared spectra of the THF and pyridine $U[(CH_3)_5C_5]_2Cl\cdot L$ adducts exhibit transitions characteristic of the particular coordinated bases.[38,39] On the basis of the chemical and spectroscopic data, structure A is proposed for these complexes; it is analogous to that for lanthanide $M(\eta^5-C_5H_5)_2X\cdot L$[36,38c,40] and $Ti(\eta^5-C_5H_5)_2Cl\cdot$pyridine[41] complexes.



A

Synthesis and Properties of the Uranium(III) Alkyl and Amide Complexes, $U[\eta^5-(CH_3)_5C_5]_2CH[Si(CH_3)_3]_2$ and $U[\eta^5-(CH_3)_5C_5]_2N[Si(CH_3)_3]_2$. Alkylation of $\{U[\eta^5-(CH_3)_5C_5]_2(\mu-Cl)\}_3$ with the sterically bulky lithium reagent $LiCH[Si(CH_3)]_2$ can be accomplished according to eq 9. This particular alkyl functionality was selected

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(36) (a) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652–653. (b) Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1980**, *19*, 2190–2192. (c) Analogous chloride effects may be involved in some syntheses of **2** using lithium reagents as the reductants.[13] This is presently under investigation.

(37) Duttera, M. R.; Fagan, P. J.; Marks, T. J.; Day, V. W., submitted for publication.

(38) (a) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978. (b) Bellamy, L. M. "The Infrared Spectra of Complex Molecules", 3rd ed.; Chapman and Hall: London, 1975. (c) Marks, T. J.; Grynkewich, G. W. *Inorg. Chem.* **1976**, *15*, 1302–1307.

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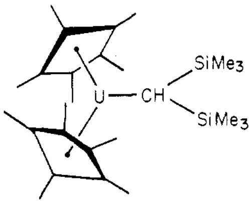
$$(1/3)\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3 + LiCH[Si(CH_3)_3]_2 \xrightarrow[25\ ^\circ C]{\text{ether}} \underset{8}{U[\eta^5\text{-}(CH_3)_5C_5]_2CH[Si(CH_3)_3]_2} + LiCl \quad (9)$$

because we[11] and others[15,42] have noted that it frequently forms low-valent metal hydrocarbyls with high thermal stability and low degrees of association. Carrying out eq 9 with less sterically demanding alkyl reagents results in far less soluble and thermally stable products.[11,43] Compound 8 can be obtained as black needles from cold (−78 °C) pentane solution and was characterized by elemental analysis, ^{1}H NMR and IR spectroscopy, and a cryoscopic molecular weight measurement. The ^{1}H NMR spectrum exhibits two isotropically shifted, somewhat broadened resonances at δ −5.56 and −22.8 assigned to the η^5-$(CH_3)_5C_5$ and $Si(CH_3)_3$ group resonances, respectively. The methine resonance was too broad to be located. The cryoscopic molecular weight measurement indicates that this complex is monomeric in benzene solution. On the basis of the above data, structure 8 is proposed for this complex, the first uranium(III) alkyl compound.

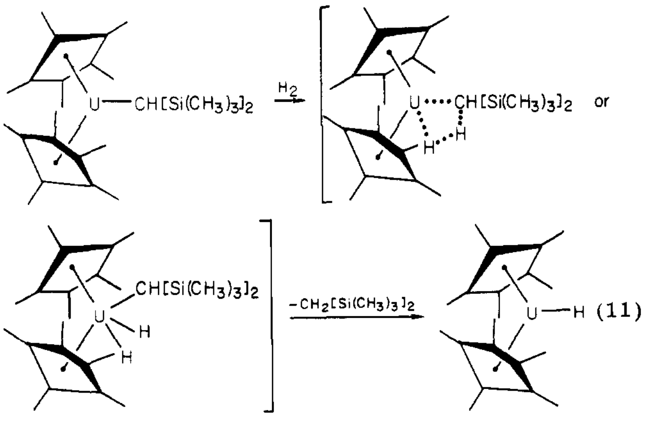


8

The reaction of complex 8 with hydrogen was also investigated. This reaction proceeds according to eq 10 as

$$U[\eta^5\text{-}(CH_3)_5C_5]_2CH[Si(CH_3)_3]_2 \xrightarrow[\text{toluene, <10 min}]{H_2\ (1\ atm)} 0.4\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2 + (0.2/x)\{U[\eta^5\text{-}(CH_3)_5C_5]_2H\}_x + CH_2[Si(CH_3)_3]_2 \quad (10)$$

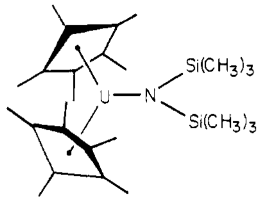
shown by quantitative ^{1}H NMR studies. Hydrogenolysis of uranium(III)–carbon carbon bond occurs much more rapidly than the corresponding hydrogenolysis of a uranium(IV)–carbon bond.[11c] A priori, either a four-center or an oxidative addition (U(III) → U(V)) mechanism (eq 11) is a plausible monometallic pathway for the hydrogenolysis process. Considering the paucity of U(V) organometallic compounds[4] and the many parallels between uranium and thorium (where the +5 oxidation state is inaccessible) organometallic chemistry, the U(III) → U(V) pathway seems far less likely. In either case the trivalent uranium hydride $\{U[\eta^5\text{-}(CH_3)_5C_5]_2H\}_x$,[11c] is expected to be the primary product. However, the excess hydrogen present under the reaction conditions should convert much of this hydride to the tetravalent $\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2$ complex,[11c] as observed.



It has also proven possible to synthesize a uranium(III) amide complex according to eq 12.

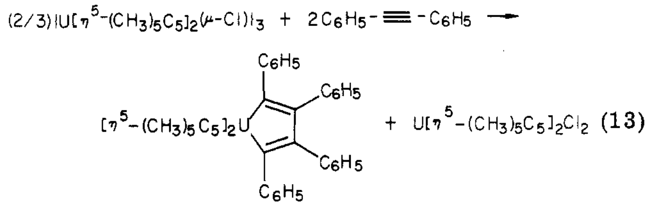
$$(1/3)\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3 + NaN[Si(CH_3)_3]_2 \xrightarrow[25\ ^\circ C]{\text{ether}} \underset{9}{[\eta^5\text{-}C_5(CH_3)_5]_2UN[Si(CH_3)_3]_2} + NaCl \quad (12)$$

The ^{1}H NMR spectrum of this complex (Table V) exhibits two singlets δ −5.43 and −24.9 assigned to η^5-$(CH_3)_5C_5$ and $Si(CH_3)_3$ group resonances, respectively. The infrared spectrum contains bands which are characteristic of a σ-bound $-N[Si(CH_3)_3]_2$ moiety.[10b] A cryoscopic molecular weight measurement indicates this complex is monomeric in benzene solution. Thus, structure 9 is proposed. There is only one other uranium(III) amide complex known, $U\{N[Si(CH_3)_3]_2\}_3$.[10b]

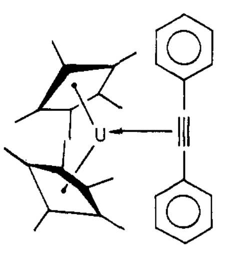


9

Trivalent Uranium in Reductive Coupling and Oxidative Addition Reactions. Reaction of excess diphenylacetylene with a slurry of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ in C_6D_6 proceeds quantitatively according to eq 13. Thus, a 1:1 mixture of the known[11] uranium(IV) complexes $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and $U[\eta^5\text{-}(CH_3)_5C_5]_2C_4(C_6H_5)_4$ is produced. The complex $[\eta^5\text{-}C_5(CH_3)_5]_2UCl_2Na\cdot(THF)_x$ will similarly reductively couple diphenylacetylene, the reaction proceeding instantaneously upon mixing the reactants. Such metallacycle-forming reductive-coupling processes are well-documented in low-valent transition-metal chemistry.[44] In the present case, an acetylene complex such as B is a plausible precursor to the metallacyclopentadiene.



10



B

We provide evidence elsewhere[11c] for the existence of an analogous transitory uranium benzyne complex. Formally, then, the uranium(III) trimer $\{U[(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ can be thought of as a source of 1.5 equiv of U(II) and 1.5 equiv of U(IV) (eq 14).

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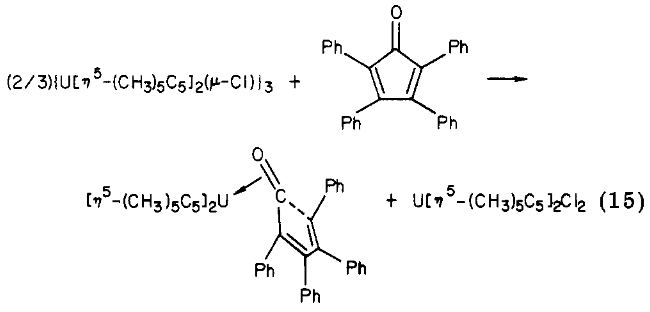
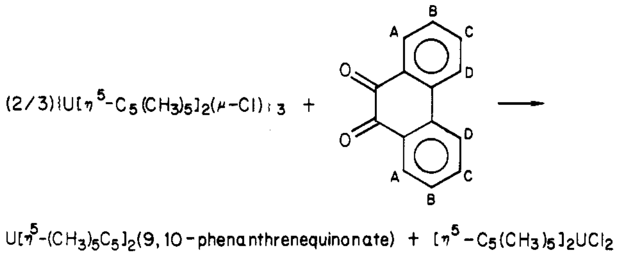
$$\{U[(CH_3)_5C_5]_2(\mu\text{-Cl})\}_3 \rightarrow 1.5U[(CH_3)_5C_5]_2Cl_2 + 1.5\text{``}U[(CH_3)_5C_5]_2\text{''} \quad (14)$$

The scope of $\{U[(CH_3)_5C_5]_2(\mu\text{-Cl})\}_3$ oxidative addition processes was also probed with bulky ketones unlikely to undergo coupling reactions and with high potential quinones. Reaction with tetraphenylcyclopentadienone proceeds smoothly according to eq 15 to yield the known[11,45]

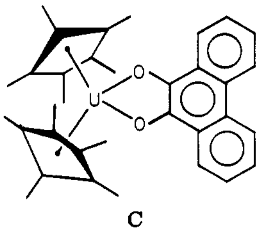


11

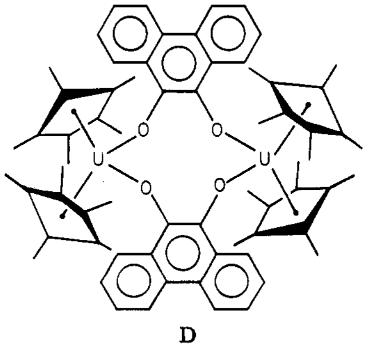
η^2-tetraphenylcyclopentadienone complex 11. The reaction of $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-Cl})\}_3$ with 9,10-phenanthrenequinone in toluene proceeds similarly with the production of 1.5 equiv of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ and 1.5 equiv of the new complex, 12 (eq 16). The quinonate complex was characterized by ^1H NMR, infrared spectroscopy, and elemental analysis; it was insufficiently soluble for accurate cryoscopic molecular weight determinations. The ^1H NMR spectrum of 12 exhibits a singlet as δ 3.65 assigned to $\eta^5\text{-}(CH_3)_5C_5$ and four other isotropically shifted multiplets at δ −24.3 (2 H), −1.25 (2 H), 2.23 (2 H), and 3.07 (2 H) assigned to the protons at H_A, H_B, H_C, and H_D, respectively. These results and the infrared spectra are in accord with either a monomeric (C) or dimeric (D) molecular structure. The analogous reaction of $Ti(\eta^5\text{-}C_5H_5)_2(CO)_2$ with 9,10-phenanthrenequinone yields a monomeric bis(cyclopentadienyl)titanium complex of structure similar to C.[46]



12 (16)

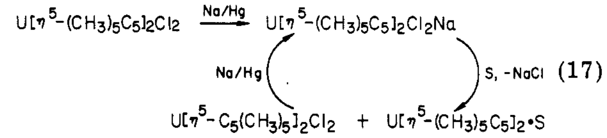


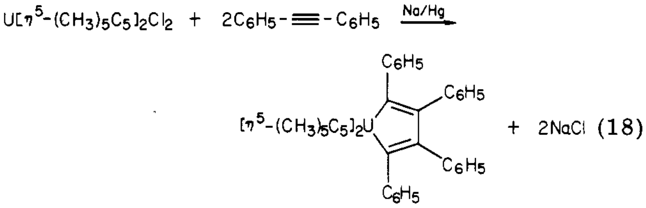
C



D

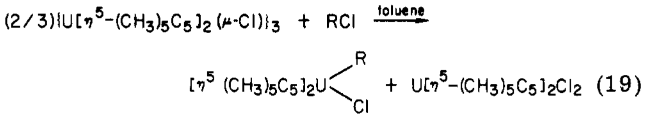
Since $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ is readily reduced with sodium amalgam, a cycle such as that shown in eq 17 appeared feasible. This has been verified in the case where the substrate S is diphenylacetylene as shown in eq 18, to



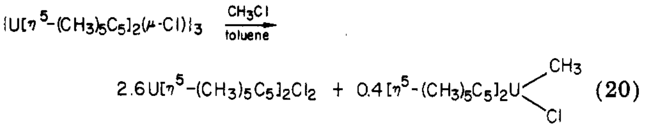


produce the uranium metallacyclopentadiene in good yield. The reduction of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ and $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$ with sodium naphthalide followed by addition of diphenylacetylene is reported[47] to yield the analogous titanium and zirconium metallacyclopentadiene complexes.

It was also of interest to investigate whether alkyl halides would oxidatively add to the uranium(III) chloride complex according to eq 19. Reaction of methyl chloride with



$\{U[\eta^5\text{-}(CH_3)_5C_5](\mu\text{-Cl})\}_3$ proceeds, however, as shown in eq 20, with the production of a 6.4:1 mixture of $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2/U[\eta^5(CH_3)_5C_5]_2(CH_3)Cl$. If a similar reaction is carried out with chlorobenzene, the uranium-containing product is exclusively $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$ (eq 21). Such



$$(1/3)\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-Cl})\}_3(s) + C_6H_5Cl \xrightarrow{\text{toluene}} U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2 \quad (21)$$

results are highly suggestive of halogen atom abstraction to produce free radicals (R·),[48] and Finke has recently shown that monomeric $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl$ is an exceedingly potent halogen atom abstractor.[49] Low-valent group 4B complexes display similar reaction patterns.[50]

Conclusions

This work demonstrates that actinide-to-carbon σ-bond hydrogenolysis represents an attractive synthetic entry into trivalent organouranium chemistry. Precursors such as $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-Cl})\}_3$ are versatile reagents for a wealth of new U(III) organometallics. This work also demonstrates that overall one-electron oxidation state shuttling processes are feasible for uranium organometallics, and U(III) ⇌ U(IV) reductive elimination, oxidative addition, and unsaturated molecule reductive coupling reactions are identified. One of the most intriguing aspects of this work is the observation that $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-Cl})\}_3$ can formally act as a source of "$U[\eta^5\text{-}(CH_3)_5C_5]_2$". These observations

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[45] Fagan, P. J.; Maatta, E. A.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W., submitted for publication.

[46] Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 2297–2302.

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[48] Reference 3d, Chapter 7.

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[50] (a) Williams, G. M.; Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3660–3662. (b) Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, *244*–246. (c) Dormand, A.; Kolavudh, T.; Tirouflet, J. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1976**, *282*, 551–553. (d) Floriani, C.; Fachinetti, G. *J. Chem. Soc., Chem. Commun.* **1972**, 790–791.

and results we report elsewhere[11] suggest that species which may formally involve the +2 uranium oxidation state such as B and 11 are mechanistically plausible entities. This question is presently under further investigation.

To place these results in perspective, it is also important to note that the properties of the bis(pentamethylcyclopentadienyl)uranium(III) complexes are similar to those of bis(cyclopentadienyl)titanium(III) complexes,[41] both in terms of redox behavior and coordination chemistry. The structural and stoichiometric similarities to the coordination chemistry of bis(cyclopentadienyl)lanthanide(III) complexes should also be noted.[4a,36,40]

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Registry No. 2, 71794-95-1; **3**, 79448-93-4; **4**, 71763-75-2; **5**, 71763-76-3; **6**, 79448-94-5; **7**, 79448-95-6; **8**, 71763-77-4; **9**, 71762-98-6; **10**, 71763-62-7; **11**, 79448-96-7; **12**, 79448-97-8; $U[\eta^5\text{-}(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$, 68963-88-2; $U[\eta^5\text{-}(CH_3)_5C_5]_2(CH_3)Cl$, 67506-91-6; $U[\eta^5\text{-}(CH_3)_5C_5]_2Cl_2$, 67506-89-2; $\{U[\eta^5\text{-}(CH_3)_5C_5]_2H_2\}_2$, 67588-76-5.

Supplementary Material Available: Crystal structure analysis report, a table of anisotropic thermal parameters for nonhydrogen atoms (Table II), and a listing of observed and calculated structure factors from the final cycle of least-squares refinement for $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ (37 pages). Ordering information is given on any current masthead page.

Piano-Stool Complexes of the $CpML_4$ Type

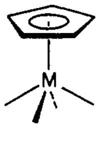
Pavel Kubáček,† Roald Hoffmann,* and Zdeněk Havlas†

Department of Chemistry, Cornell University, Ithaca, New York 14853

Received August 14, 1981

$CpML_4$ complexes apparently occur only in the four-legged piano-stool geometry. The electronic structure of this class of compounds is explored, with emphasis on geometrical distortions, the orientational preferences of single-faced π-donor and -acceptor ligands. An analysis of the electronic structure of a sterically encumbered alternative geometry, a Cp-capped trigonal bipyramid or 3:3:1 structure, leads to some criteria for stabilizing this type. Axial substituents which are good σ and π donors, yet small in size, are required. An explanation of the cis specificity of photochemical substitution in $CpML_4$ complexes is provided in terms of the geometry of the $CpML_3$ intermediates and the directionality of the vacant orbitals thereof.

The cyclopentadienyl ligand is the emblem of modern organometallic chemistry. In one structural type we often see two, and more rarely three or four Cp's surrounding a metal atom. In another common materialization the Cp ring binds to it a metal and an associated set of from zero to five ligands. These are the ubiquitous $CpML_n$ complexes, and one of them, $CpML_4$, 1, is the subject of this work.



1

A "four-legged piano-stool" geometry is the paradigm for $CpML_4$ complexes of group 5B and 6B transition metals.[1] Several dozen X-ray structures give a good picture of this class. All $CpML_4$ complexes whose solid-state structures are known are conveniently described as square pyramids,[2-5] with the Cp at the apex. Pseudo-five-coordination evokes immediately an entire complex of ideas on the nonrigidity of the five-coordinate type. At the same time it is clear that the Cp^- ligand is the electronic equivalent of three simple Lewis bases. So $CpML_4$ complexes are electronically in the seven-coordinate manifold. Indeed nearly all known to date are d^4, adhering to the 18-electron rule.[6] The tension generated by the seemingly conflicting perspectives of steric pseudo-five-coordination and electronic seven-coordination is part of what makes these complexes interesting.

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† P.K.: Department of Theoretical and Physical Chemistry, University of J. E. Purkyne, Brno, Czechoslovakia. Z.H.: Institute of Organic Chemistry and Biochemistry of the Czechoslovak Academy of Sciences, Prague, Czechoslovakia.

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