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Synthesis and Structure of the Bis(tetramethylcyclopentadienyl)uranium Metallocenes $(C_5Me_4H)_2UMe_2$, $(C_5Me_4H)_2UMeCl$, $[(C_5Me_4H)_2U][(\mu\text{-}\eta^6{:}\eta^1\text{-Ph})(\mu\text{-}\eta^1{:}\eta^1\text{-Ph})BPh_2]$, and $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$

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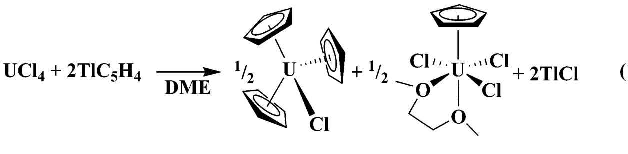
Although bis(pentamethylcyclopentadienyl)uranium metallocene chemistry has been extensively explored, relatively little is known about the reactivity of the bis(tetramethylcyclopentadienyl) analogues. To provide the essential $(C_5Me_4H)_2U$-containing complexes for comparison with $(C_5Me_5)_2U$-containing species, a series of bis(tetramethylcyclopentadienyl)uranium complexes has been prepared. The recently isolated $(C_5Me_4H)_2UCl_2$ (**1**) reacts with MeLi to form the methyl complexes $(C_5Me_4H)_2UMe_2$ (**2**) and $(C_5Me_4H)_2UMeCl$ (**3**), both of which were characterized by X-ray crystallography. Complex **3** can also be synthesized by ligand redistribution between **1** and **2**. Complex **2** is easily reduced with potassium to form $(C_5Me_4H)_2UMe_2K$ (**4**), which provides entry into unsolvated bis(tetramethylcyclopentadienyl) U(III) chemistry. Complex **4** reacts with 2 equiv of Et_3NHBPh_4 to form the trivalent cationic complex $[(C_5Me_4H)_2U][(\mu\text{-Ph})_2BPh_2]$ (**5**), which has a structure differing from that of $[(C_5Me_5)_2U][(\mu\text{-Ph})_2BPh_2]$ in that one arene ring in **5** approaches the uranium ion in an η^6 mode and the other in an η^1 orientation. Attempts to make unsolvated bis(tetramethylcyclopentadienyl) U(III) complexes with the tethered olefin ligand $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$ by reacting $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]K$ with $UI_3(THF)_4$ led to the formation of $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ (**6**). Although solvated, **6** readily loses THF and is the first example of an actinide complex that contains a tethered olefin functionality.

Cyclopentadienyl ligands have been central to the development of organometallic uranium chemistry since its inception.[1−4] Hence, the first well-characterized organouranium complex to be isolated was the cyclopentadienyl compound $(C_5H_5)_3UCl$.[5] However, this was a tris- rather than a bis(cyclopentadienyl) species. Apparently the large size of the uranium ion rendered bis(cyclopentadienyl)uranium metallocenes more difficult to synthesize than the tris complexes due to redistribution reactions. In fact, attempts to make the bis(cyclopentadienyl) metallocene "$(C_5H_5)_2UCl_2$" were unsuccessful[6−12] and resulted in isolation of a mixture of tris- and mono(cyclopentadienyl) complexes: e.g., eq 1.[9]



(1)

A major breakthrough in uranium metallocene chemistry occurred in 1978,[13,14] when Marks and co-workers showed that the $(C_5Me_5)^-$ ligand could be used to isolate a bis(cyclopentadienyl)uranium complex, $(C_5Me_5)_2UCl_2$, that was stable to ligand redistribution. The discovery of this complex led to an extensive development of bis(pentamethylcyclopentadienyl)uranium chemistry that continues today.[1−4,13−26]

The uranium chemistry of $(C_5Me_4H)^-$ has received much less attention than that of $(C_5H_5)^-$ and $(C_5Me_5)^-$.

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Until recently, the focus was entirely on tris(tetramethylcyclopentadienyl) species of the general formulas $(C_5Me_4H)_3U$,[27,28] $(C_5Me_4H)_3UL$ (L = neutral ligand),[27−29] and $(C_5Me_4H)_3UX$ (X = anion).[27,28,30,31] Although the $(C_5Me_4H)^-$ ligand has delivered interesting chemistry in tris(cyclopentadienyl)uranium systems,[27−31] its bis(cyclopentadienyl)uranium chemistry has not been extensively developed.

Recently, as part of a study to evaluate the chemistry of the sterically crowded complexes $(C_5Me_5)_3U$,[32] $(C_5Me_5)_3UX$ (X = halide[33] and methyl[34]), and $(C_5Me_5)_3UL$ (L = CO,[35] N_2[29]), we have become interested in comparative studies with the slightly less crowded $(C_5Me_4H)^-$ analogues. These efforts led to the first synthesis of the bis(tetramethylcyclopentadienyl)uranium complex $(C_5Me_4H)_2UCl_2$ (**1**).[31] As an analogue of $(C_5Me_5)_2UCl_2$,[13,14] **1** should also have an extensive chemistry. If this is analogous to the $(C_5Me_5)^-$ chemistry, its primary use will be in furnishing complexes for comparison. However, since $(C_5Me_4H)^-$ complexes are typically less soluble than $(C_5Me_5)^-$ complexes, they may prove to be more useful when full characterization by X-ray crystallography is desired. In addition, in light of the recent results observed for $(C_5Me_4H)_2ZrCl_2$[36,37] vs $(C_5Me_5)_2ZrCl_2$,[38,39] it is possible that bis(tetramethylcyclopentadienyl)uranium complexes could display their own unique chemistry.

We report here the synthesis and characterization of some basic classes of bis(tetramethylcyclopentadienyl)uranium complexes. This includes a dialkyl, a mixed alkyl halide, and a synthetically important tetraphenylborate complex that displays an unusual structure. In addition, we report the first uranium metallocene containing a tethered olefin, a uranium complex of the tetramethylcyclopentadienyl ligand, $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$.

Experimental Section

General Experimental Considerations. The syntheses and manipulations of the extremely air- and moisture-sensitive compounds described below were conducted under nitrogen or argon with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. Except where noted, all glovebox manipulations were carried out in an argon-filled glovebox that was free of coordinating solvents. THF, diethyl ether, benzene, toluene, and hexanes were saturated with Ar and passed through a GlassContour column.[40] Benzene-d_6 and THF-d_8 (Cambridge Isotope Laboratories) were distilled over NaK alloy and benzophenone and degassed by three freeze−pump−thaw cycles. $(C_5Me_4H)_2UCl_2$[31] was prepared as previously described from UCl_4 and $(C_5Me_4H)MgCl$. $UI_3(THF)_4$,[31,41] $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]K$,[42] and Et_3NHBPh_4[43] were prepared as previously described. Et_3NHBPh_4 was washed (3×) with diethyl ether and dried overnight under vacuum before use (10^{-5} Torr). MeLi was obtained as a 2 M solution in diethyl ether (Aldrich), transferred by cannulation into a Schlenk flask, and isolated as a white powder upon removal of solvent under vacuum. NMR experiments were conducted with Bruker 400 and 500 MHz spectrometers. IR samples were analyzed as thin films from benzene using an ASI ReactIR1000 instrument.[44] Elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany. Samples were prepared for melting point determination by charging a capillary tube with a small amount of compound and then closing off approximately three-fourths of the capillary with Dow Corning silicone grease. Samples were analyzed with a Uni-melt capillary melting point apparatus.

$(C_5Me_4H)_2UMe_2$ (2) from $(C_5Me_4H)_2UCl_2$. A red solution of $(C_5Me_4H)_2UCl_2$ (581 mg, 1.05 mmol) in toluene (10 mL) was added to a flask containing a suspension of MeLi (77 mg, 3.51 mmol) in toluene (5 mL). After 10 h, the color of the mixture slowly had changed to dark red and black insoluble solids were removed by centrifugation. The solids were washed with toluene (3×), the extracts were combined, and the solids were discarded. Upon removal of the solvent, **2** (393 mg, 73%) was isolated as rust-colored microcrystals. ^1H NMR (C_6D_6): δ 11.3 (s, 12H, $\Delta\nu_{1/2} = 7$ Hz, C_5Me_4H), −2.9 (s, 12H, $\Delta\nu_{1/2} = 7$ Hz, C_5Me_4H), −38.2 (s, 2H, $\Delta\nu_{1/2} = 38$ Hz, C_5Me_4H), −73.5 (s, 6H, $\Delta\nu_{1/2} = 20$ Hz, U−*Me*) ppm. IR: 2961 s, 2910 s, 2860 s, 2725 w, 1644 w, 1536 m, 1478 m, 1444 s, 1382 s, 1328 m, 1262 m, 1146 w, 1104 m, 1077 m, 1023 m, 972 w, 787 s, 679 s cm^{-1}. Anal. Calcd for $C_{20}H_{32}U$: C, 47.05; H, 6.27; U, 46.63. Found: C, 47.15; H, 6.27; U, 46.92. X-ray-quality crystals of **2** were grown at −35 °C from saturated solutions of toluene. In contrast to $(C_5Me_4H)_2UCl_2$, which was found to melt at 227 °C, **2** was observed to melt at 119 °C.

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$(C_5Me_4H)_2UMeCl$ (3) from $(C_5Me_4H)_2UMe_2$ and $(C_5Me_4H)_2UCl_2$. A red solution of $(C_5Me_4H)_2UCl_2$ (**1**; 441 mg, 0.800 mmol) in toluene (5 mL) was added to a flask containing a red-orange solution of $(C_5Me_4H)_2UMe_2$ (**2**; 408 mg, 0.800 mmol) in toluene (5 mL). The solution was stirred for 12 h, and the solution darkened. The solution was concentrated under vacuum to approximately 7 mL and cooled to −35 °C. After 12 h crystals suitable for X-ray analysis formed and the red solution was removed by decanting. The crystals were dried under vacuum, and **3** was isolated (602 mg, 71% crystalline yield). ^{1}H NMR (C_6D_6, 298 K): δ 31.9 (s, 6H, $\Delta\nu_{1/2}$ = 8 Hz, $C_5\mathit{Me}_4H$), 25.8 (s, 6H, $\Delta\nu_{1/2}$ = 8 Hz, $C_5\mathit{Me}_4H$), −7.6 (s, 6H, $\Delta\nu_{1/2}$ = 9 Hz, $C_5\mathit{Me}_4H$), −13.0 (s, 6H, $\Delta\nu_{1/2}$ = 9 Hz, $C_5\mathit{Me}_4H$,), −44.2 (s, 2H, $\Delta\nu_{1/2}$ = 17 Hz, $C_5Me_4\mathit{H}$), −108.9 (s, 3H, $\Delta\nu_{1/2}$ = 37 Hz, U−*Me*) ppm. IR: 2964 s, 2907 s, 2860 s, 1444 m, 1382 s, 1332 w, 1262 w, 1146 w, 1108 w, 1023 m, 977 w, 842 m, 815 s, 753 s, 703 s, 690 m cm^{-1}. Anal. Calcd for $C_{19}H_{29}ClU$: C, 42.98; H, 5.50; Cl, 6.68; U, 44.84. Found: C, 42.84; H, 5.46; Cl, 6.57; U, 44.63. Attempts to determine the melting point of **3** resulted in decomposition at 137 °C evident by a distinct color change, from red to black, and the evolution of a gas.

$(C_5Me_4H)_2UMe_2$ (2) from $(C_5Me_4H)_2UMeCl$ (3). A red solution of $(C_5Me_4H)_2UMeCl$ (525 mg, 0.99 mmol) in toluene (10 mL) was added to a flask containing a suspension of MeLi (45 mg, 2.05 mmol) in toluene (5 mL). After 10 h, the mixture slowly changed to dark red and black insoluble solids were removed by centrifugation. The solids were washed with toluene (3×), the extracts were combined, and the solids were discarded. Upon removal of the solvent, **2** (459 mg, 90%) was isolated as rust-colored microcrystals (see above).

$(C_5Me_4H)_2UMe_2K$ (4). Toluene (15 mL) was added to a flask that contained freshly scraped potassium (22 mg, 0.563 mmol). The flask was heated as the mixture was vigorously stirred. When the potassium melted, a solution of $(C_5Me_4H)_2UMe_2$ (**2**; 290 mg, 0.568 mmol) in toluene (5 mL) was slowly added dropwise and the reaction mixture was cooled to room temperature. After 24 h, the reaction turned olive green, and after 3 days insoluble solids were removed from a light red solution. The solids were washed with toluene (3×), and the washings were discarded. The solids were dried by rotary evaporation, and **4** (302 mg, 99%, with respect to potassium) was isolated as an olive green solid. Anal. Calcd for $C_{20}H_{32}UK$: C, 43.73; H, 5.83; U, 43.33; K 7.11. Found: C, 43.53; H, 5.69; U, 43.40; K, 7.29.

$[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ (5). Benzene (20 mL) was added to a flask that contained an intimate mixture of olive green $(C_5Me_4H)_2UMe_2K$ (**5**; 302 mg, 0.550 mmol) and white Et_3NHBPh_4 (463 mg, 1.100 mmol), both of which are arene insoluble. Gas evolution was immediately observed upon addition of solvent, and the mixture turned brown within 30 min. After the reaction mixture was stirred for 12 h, gray insoluble solids were separated from the brown solution by centrifugation. The solids were washed with toluene (3×), the extracts were combined, and the solids were discarded. Upon removal of the solvent by rotary evaporation, **5** (384 mg, 87%) was isolated as a brown powder. X-ray-quality crystals of **5**·(toluene) formed from saturated solutions of boiling toluene cooled to −35 °C over 5 days. The ^{1}H NMR spectrum of $[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ recrystallized from toluene indicates that one molecule of toluene is retained. ^{1}H NMR (C_6H_6): δ 21.2 (s, 12H, $\Delta\nu_{1/2}$ = 37 Hz, $C_5\mathit{Me}_4H$), −12.3 (s, 2H, $\Delta\nu_{1/2}$ = 34 Hz, $C_5\mathit{Me}_4H$), −35.1 (s, 2H, $\Delta\nu_{1/2}$ = 25 Hz, $C_5Me_4\mathit{H}$) ppm. The tetraphenylborate resonances could not be definitively identified. Variable-temperature studies down to 193 K did not provide additional information. ^{11}B NMR (referenced to $BF_3 \cdot Et_2O$): δ −33.0 ppm. IR: 2964 s, 2910 s, 2860 s, 2729 w, 1590 m, 1563 m, 1478 s, 1432 s, 1382 s, 1316 m, 1262 s, 1243 s, 1185 m, 1150 m, 1092 s, 1069 s, 1031 s, 973 w, 926 w, 884 w, 849 m, 803 s, 776 s, 745 s, 733 s, 703 s, 679 s cm^{-1}. Anal. Calcd for **5**·(toluene): C, 66.02; H, 6.06. Found: C, 66.21; H, 6.17. Mp: 194 °C.

$[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ (6). In a nitrogen-filled glovebox, a blue mixture of $UI_3(THF)_4$ (336 mg, 0.370 mmol) in THF (5 mL) was added slowly to $K(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)$ (191 mg, 0.742 mmol) in THF (5 mL). The mixture immediately turned green, and after 6 h white solids had precipitated from the solution. The solution was separated from white solids by centrifugation, and the solvent was removed by rotary evaporation, leaving a green solid. Hexane (2 mL) was added, and the green solution was separated from white hexane-insoluble solids by centrifugation. Upon removal of the solvent, the green solids turned brown within 3 h under vacuum (10^{-3} Torr). The resulting brown powder was insoluble in alkane or arene solvents, but upon addition of THF, the brown solids readily dissolved, re-forming the green solution. The THF was removed by rotary evaporation to afford **6** as a green solid (312 mg, 96%). X-ray-quality crystals of **6** formed from a saturated solution of hexanes at −35 °C within 24 h. ^{1}H NMR (THF-d_8, 268 K): δ 34.2 (s, 6H, $\Delta\nu_{1/2}$ = 470 Hz, $C_5\mathit{Me}_4R$), 10 (s, 6H, $C_5\mathit{Me}_4R$), −3.0 (s, 6H, $\Delta\nu_{1/2}$ = 400 Hz, $C_5\mathit{Me}_4R$), −5.6 (s, 6H, $\Delta\nu_{1/2}$ = 370 Hz, $C_5\mathit{Me}_4R$), −30.3 (s, 12H, $\Delta\nu_{1/2}$ = 450 Hz, $Si\mathit{Me}_3$) ppm. ^{1}H NMR (THF-d_8, 238 K): δ 47.8 (s, $\Delta\nu_{1/2}$ = 230 Hz, 6H, $C_5\mathit{Me}_4R$), 5.0 (s, 6H, Hz, $C_5\mathit{Me}_4R$), −1.3 (s, 6H, $\Delta\nu_{1/2}$ = 160 Hz, $C_5\mathit{Me}_4R$), −7.5 (s, 6H, $\Delta\nu_{1/2}$ = 75 Hz, $C_5\mathit{Me}_4H$), 41.9 (s, 6H, $\Delta\nu_{1/2}$ = 180 Hz, $Si\mathit{Me}_3$), −42.8 (s, 6H, $\Delta\nu_{1/2}$ = 140 Hz, $Si\mathit{Me}_3$) ppm. ^{1}H NMR (THF-d_8, 208 K): δ 61.5 (s, 6H, $\Delta\nu_{1/2}$ = 370 Hz, $C_5\mathit{Me}_4R$), 7.2 (s, 6H, $C_5\mathit{Me}_4R$), −0.8 (s, 6H, $\Delta\nu_{1/2}$ = 260 Hz, $C_5\mathit{Me}_4R$), −9.9 (s, 6H, $\Delta\nu_{1/2}$ = 110 Hz, $C_5\mathit{Me}_4R$), −53.4 (s, 6H, $\Delta\nu_{1/2}$ = 250 Hz, $Si\mathit{Me}_3$), −55.3 (s, 6H, $\Delta\nu_{1/2}$ = 185 Hz, $Si\mathit{Me}_3$) ppm. Resonances attributable to the tethered olefin could not be identified. IR: 2961 s, 2922 s, 2860 s, 2737 w, 1629 m, 1444 m, 1420 m, 1390 m, 1251 s, 1220 m, 1193 w, 1154 s, 1123 m, 1112 m, 1042 s, 1023 s, 984 s, 953 m, 930 m, 891 s, 834 s, 752 m, 699 s, 649 s cm^{-1}. Anal. Calcd for the desolvated complex $C_{38}H_{46}Si_2IU$: C, 41.83; H, 5.77; Si, 7.24; I, 16.04; U, 29.61. Found: C, 41.79; H, 5.84; Si, 7.10; I, 15.52; U, 29.28.

X-ray Data Collection, Structure Solution, and Refinement. $(C_5Me_4H)_2UMe_2$ (2). A red crystal of approximate dimensions 0.24 × 0.26 × 0.33 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[45] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[46] and SADABS[47] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[48] program. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the monoclinic space groups *Cc and C*2/*c*. It was later determined that the centrosymmetric space group *C*2/*c* was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Analytical scattering factors[49] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on a 2-fold rotation axis. At convergence, wR2 = 0.0350 and GOF = 1.129 for 101 variables refined against 2350 data. As a comparison for refinement on *F*, R1 = 0.0143 for those 2224 data with $I > 2.0\sigma(I)$.

$(C_5Me_4H)_2UMeCl$ (**3**), $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ (**5**), and $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ (**6**) were handled simi-

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Table 1. Crystal Data and Structure Refinement Details for $(C_5Me_4H)_2UMe_2$ (2), $(C_5Me_4H)_3UMeCl$ (3), $[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ (5), and $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ (6)

	2	**3**	**5**	**6**
empirical formula	$C_{20}H_{32}U$	$C_{19}H_{29}ClU$	$C_{42}H_{46}BU\cdot C_7H_8$	$C_{32}H_{54}IOSi_2U$
formula wt	510.49	530.90	891.76	875.86
space group	*C*2/*c*	*Cmcm*	*P*2$_1$/*c*	*P*2$_1$/*n*
a (Å)	20.538(2)	17.7970(19)	9.9966(13)	8.9828(4)
b (Å)	6.9493(8)	6.8129(7)	16.700(2)	28.1474(11)
c (Å)	16.1938(19)	15.6369(17)	23.666(3)	14.0992(6)
α (deg)	90	90	90	90
β (deg)	123.680(2)	90	99.917(2)	104.4150(10)
γ (deg)	90	90	90	90
V (Å^3)	1923.3(4)	1896.0(3)	3891.9(9)	3452.6(3)
Z	4	4	4	4
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
calcd density (Mg/m^3)	1.763	1.860	1.522	1.685
abs coeff (mm^{-1})	8.433	8.695	4.204	5.687
goodness of fit on F^2	1.129	1.251	1.082	1.108
R^a ($I > 2\sigma(I)$): R1	0.0143	0.0123	0.0257	0.0228
R^b (all data): wR2	0.0350	0.0288	0.0683	0.0495

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

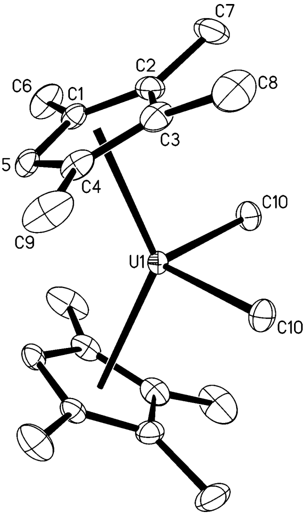
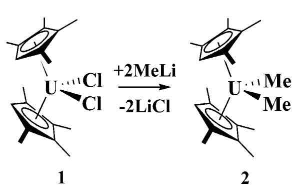


Figure 1. Thermal ellipsoid plot of $(C_5Me_4H)_2UMe_2$ (**2**), drawn at the 30% level.

larly. The details are given in Table 1 and in the Supporting Information.

Results

Synthesis of Bis(tetramethylcyclopentadienyl)uranium Methyl Complexes. $(C_5Me_4H)_2UCl_2$ (**1**) reacts with 2 equiv of MeLi to form $(C_5Me_4H)_2UMe_2$ (**2**) (eq 2). Complex **2** was characterized by analytical and spectroscopic methods and identified by X-ray crystallography (Figure 1). Typically, excess MeLi, ~3 equiv total, was used to ensure that the room-temperature reaction proceeds to completion within 24 h. Otherwise, small amounts of $(C_5Me_4H)_2UMeCl$ (**3**; see below) can be present.



(2)

$(C_5Me_4H)_2UMeCl$ (**3**) was identified by independent synthesis in diethyl ether from **1** and 1 equiv of MeLi. Complex **3** was also synthesized by ligand redistribution from the reaction between $(C_5Me_4H)_2UMe_2$ and $(C_5Me_4H)_2UCl_2$ (eq 3). The room-temperature ^{1}H NMR spectrum of **3** is distinct from those of **1** and **2** and indicates that a mixture of **1** and **2** favors formation of $(C_5Me_4H)_2UMeCl$ in >90% yield. Complex **3** was isolated in 70% crystalline yield and identified by X-ray crystallographic analysis (Figure 2). Since, as described below, complexes **1**−**3** are similar in structure, the preference to form the mixed alkyl halide seems to be electronic in origin. As expected, **3** reacts with an additional 1 equiv of MeLi to generate **2**.

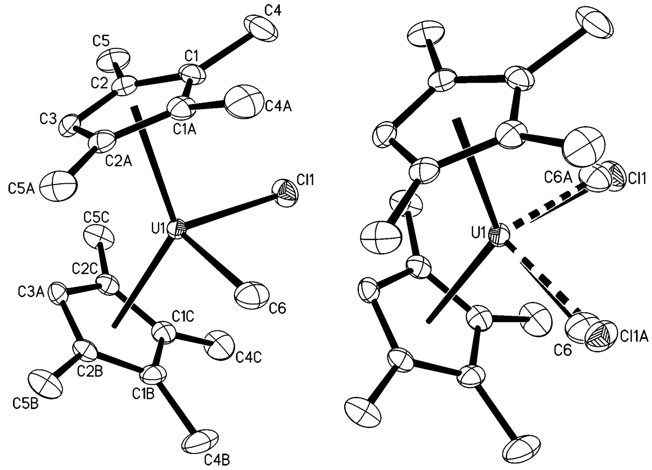
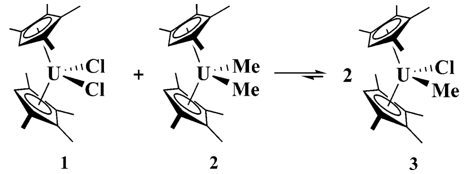


Figure 2. Thermal ellipsoid plots of $(C_5Me_4H)_2UMeCl$ (**3**), drawn at the 50% level: (left) disordered methyl and chloride ligands omitted; (right) disordered methyl and chloride ligands shown. The chloride and methyl ligands are disordered over two positions.



(3)

Structures of Bis(tetramethylcyclopentadienyl)uranium Methyl Complexes. Both $(C_5Me_4H)_2UMe_2$ (**2**) and $(C_5Me_4H)_2UMeCl$ (**3**) readily crystallize from toluene and have structures similar to that of $(C_5Me_4H)_2UCl_2$[31] (Figure 3). In **3**, the chloride and

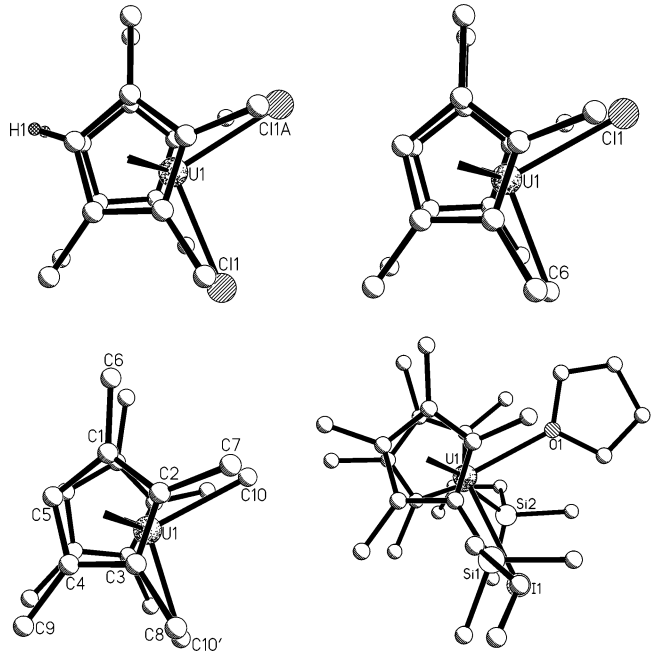


Figure 3. Ball and stick representations of $(C_5Me_4H)_2UCl_2$ (**1**; top left), $(C_5Me_4H)_2UMeCl$ (**3**; top right), $(C_5Me_4H)_2UMe_2$ (**2**; bottom left), and $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ (**6**; bottom right).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Tetravalent $(C_5Me_4H)_2UMe_2$ (2) and $(C_5Me_4H)_3UMeCl$ (3)

2		**3**	
U(1)−C(1)	2.701(2)	U(1)−C(1)	2.653(6)
U(1)−C(2)	2.765(2)	U(1)−C(2)	2.6962(17)
U(1)−C(3)	2.768(3)	U(1)−C(3)	2.655(2)
U(1)−C(4)	2.716(2)	Cl(1)−U(1)−C(6)	98.4(6)
U(1)−C(5)	2.668(2)	C(6a)−U(1)−Cl(1a)	3.1(9)
U(1)−Cnt	2.444	U(1)−Cnt	2.429
U(1)−C(10)	2.426(2)	U(1)−Cl(1)	2.653(6)
Cnt−U(1)−C(10)	104.5	U(1)−C(6)	2.38(2)
Cnt−U−Cnt	134.3	Cnt−U−Cnt	133.6
C(10)−U(1)−C(10a)	100.76(13)	C(6a)−U(1)−C(6)	101.5(15)

methyl groups are disordered, but an adequate model resulted from refining the X-ray data with half-occupancy at each position (Figure 2). A similar disorder in a $(C_5Me_4H)^-$ complex has been modeled in the past: i.e., $(C_5Me_4H)_3U(CN)_{0.6}(Cl)_{0.4}$.[28]

As observed for **1**,[31] the $(C_5Me_4H)^-$ ligands in complex **3** are eclipsed and have a 0° C(3)−ring centroid(1)−ring centroid(2)−C(3a) torsion angle (Figure 3). Complex **2** is similar, although not rigorously eclipsed: the analogous torsion angle is 8.4°. All three complexes are similar in that the cyclopentadienyl rings are oriented in such a way that the ring hydrogen atoms are located in the most congested position opposite of the metallocene wedge and the ring methyl substituents eclipse the two X ligands (Figure 3).

The structural data for **2** and **3** are given in Table 2. Structural comparisons with other $(C_5R_5)_2UX_2$ methyl and chloride complexes are provided in Table 3.[25,31,50−54] In general, all of these complexes have distorted-tetrahedral geometries with (ring centroid)−U−(ring centroid) angles that span a wide range from 123 to 140.5°. The $(C_5Me_4H)_2UX_2$ complexes **1**−**3** have regular (ring centroid)−U−(ring centroid) angles of 133.1, 134.3, and 133.6°, respectively. The X−U−X angles in **1**−**3** are similar, 99.79(3), 100.76(13), and 101.5(15)°, respectively, although analogous angles in other $(C_5R_5)_2UX_2$ complexes can range from 91.0(2) to 101.1(15)°. The $U-C(C_5R_5)$ distances in all of the $(C_5R_5)_2UX_2$ complexes are similar, with 2.42−2.49 Å U−(ring centroid) distances.

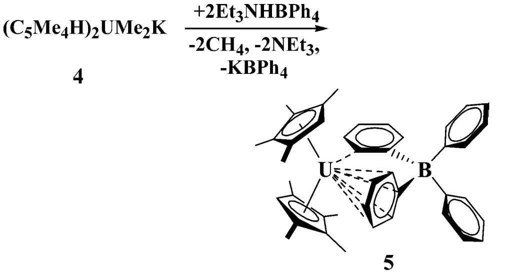
The 2.426(2) Å U−C(10) distance in $(C_5Me_4H)_2UMe_2$ (**2**) is indistinguishable from analogous U−C(Me) distances in $(C_5Me_5)_2UMe_2$,[50,25] $[(3,5\text{-}C_6H_3Me_2)(^tBu)N]_3UMe$,[55] and $[C_5H_3(SiMe_3)_2]UMe_2$,[51] which are 2.424(7), 2.446(7), and 2.42(2) Å, respectively. The 2.38(2) Å U−C(6) distance in $(C_5Me_4H)_2UMeCl$ (**3**) is not as precisely defined, but it is similar within the statistical limit to the other uranium−alkyl distances provided in Table 3.

Synthesis of $[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ (5). Another tetramethylcyclopentadienyl compound that was of interest was the unsolvated trivalent tetraphenylborate complex $[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ (**5**). The analogous $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2)]$ compound has proven to be a critical precursor in the synthesis of $(C_5Me_5)_3U$[22] and serves as a convenient starting material to other $(C_5Me_5)_2U(\text{ligand})_x$ complexes such as $[(C_5Me_5)_2U]_2(C_6H_6)$,[56] as well as some unusual azide nitride complexes.[57]

$[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ can be synthesized by the same route used for the pentamethyl analogue.[22] $(C_5Me_4H)_2UMe_2$ (**2**) reacts with potassium to give a green arene-insoluble solid that analyzes for $(C_5Me_4H)_2UMe_2K$ (**4**) (eq 4). Though **4** is insoluble in arenes and

$$\underset{\mathbf{2}}{(C_5Me_4H)_2UMe_2} + K \xrightarrow[\text{toluene}]{} \underset{\mathbf{4}}{(C_5Me_4H)_2UMe_2K} \qquad (4)$$

alkanes, it does react with Et_3NHBPh_4 in benzene to give $[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ (**5**) (eq 5 and Figure 4).



(5)

5

5 can be prepared in three steps in 63% overall yield from $(C_5Me_4H)_2UCl_2$ (**1**). In comparison, $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$[22] can be prepared from $(C_5Me_5)_2UCl_2$[14] in 55% yield.

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Table 3. Comparison of U−X (X = Cl, Me) Bond Distances (Å) and Angles (deg) in $(C_5R_5)_2UX_2$ Complexes

compd	U−X	U−Cnt	X−U−X	Cnt−U−Cnt	ref
$(C_5Me_5)_2UMe_2$	2.424(7), 2.414(7)	2.456	94.5(3)	140.5	25, 50
$[1,3\text{-}(Me_3Si)_2C_5H_3]_2UMe_2$	2.42(2)	2.44	105.0(7)	130.8	51
$(C_5Me_4H)_2UMe_2$ (**2**)	2.426(2)	2.444	100.76(13)	134.3	this work
$(C_5Me_4H)_2UMeCl$ (**3**)	2.653(6) (U(1)−Cl(1)) 2.38(2) (U(1)−C(6))	2.429	101.5(15)	133.6	this work
$(C_5Me_4H)_2UCl_2$ (**1**)	2.5909(7)	2.42	99.79(3)	133.1	31
$(C_5Me_5)_2UCl_2$	2.583(6)	2.47	97.9(4)	132	52
$[1,3\text{-}(Me_3Si)_2C_5H_3]_2UCl_2$	2.579(2)	2.44	95.3(1)	124.7	51, 53
$[1,3\text{-}{}^tBu_2C_5H_3]_2UCl_2$	2.577(4)	2.49	91.0(2)	128.1	51
$[1,2\text{-}{}^tBu_2C_5H_3]_2UCl_2$	2.591(4), 2.576(4)	2.43	97.66(14)	123	54

Table 4. Selected Bond Distances (Å) and Angles (deg) for Trivalent $[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ (5) and $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ (6)

5				6	
U−C(1)	2.747(4)	U−C(10)	2.790(4)	U(1)−C(1)	2.746(3)
U−C(2)	2.932(4)	U−C(11)	2.811(4)	U(1)−C(2)	2.808(3)
U−C(3)	2.935(4)	U−C(12)	2.817(4)	U(1)−C(3)	2.827(3)
U−C(4)	2.811(4)	U−C(13)	2.807(4)	U(1)−C(4)	2.810(3)
U−C(5)	2.690(4)	U−C(14)	2.743(4)	U(1)−C(5)	2.758(3)
U−Cnt1(Cp)	2.554	U−Cnt2(Cp)	2.521	U(1)−Cnt	2.513
U−C(19)	2.957(4)	U−C(23)	3.066(4)	U(1)−I(1)	3.0852(2)
U−C(20)	2.868(4)	U−C(24)	3.016(4)	U(1)−O(1)	2.501(2)
U−C(21)	2.902(4)	U−C(26)	3.050(4)	O(1)−U(1)−I(1)	92.06(5)
U−C(22)	2.993(4)	Cnt1−U−Cnt2	121.8	Cnt−U−Cnt	132.6
U−Cnt(Ph)	2.618				

Structure of $[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ (5). The structure of **5** (Figure 4 and Table 4) differs from that of its analogue $[(C_5Me_5)_2U](\mu\text{-}Ph)_2BPh_2]$ (**7**)[22] in several respects. For example, the $U-C(C_5Me_4H)$ distances in **5** span a wide range, 2.690(4)−2.935(4) Å, compared to the more regular 2.745(8)−2.830(8) Å $U-C(C_5Me_5)$ distances in **7**. However, the 2.521 and 2.554 Å $U-(C_5Me_4H$ ring centroid) distances in **5** are similar to those in **7**: 2.490 and 2.516 Å. The 2.81(8) Å average $U-C(C_5Me_4H)$ bond distance in **5** is large and approaches the mean 2.84(4) Å $U-(C_5Me_5)$ distance in the sterically crowded $(C_5Me_5)_3U$. However, the shortest bonds in **5** are approximately 0.2 Å shorter than those in $(C_5Me_5)_3U$.[32]

Complexes **5** and **7** also differ in how the $[BPh_4]^-$ counteranions approach the uranium center. In **7**, each bridging phenyl group has two carbon atoms oriented toward the uranium atom at long distances. These are 2.857(7) and 3.138(8) Å in one phenyl ring and 2.880(7) and 3.166(8) Å in the other. In **5**, one phenyl ring has one 3.050(4) Å U−C(arene) distance (U−C(26)) and all the other U−C(arene) distances of that ring range from 3.55 to 4.79 Å. The other phenyl ring in **5** has one 2.868(4) Å U−C(arene) distance, and the rest are between 2.902(4) and 3.066(4) Å, all of which are shorter than the 3.138(8) and 3.166(8) Å distances in **7**. Although it is not clear how to assign these long connections in terms of hapticity, if **7** is viewed as a $[(\mu\text{-}\eta^2\text{: }\eta^1\text{-}Ph)_2BPh_2]^-$ complex, then **5** would be designated a $[(\mu\text{-}\eta^6\text{: }\eta^1\text{-}Ph)(\mu\text{-}\eta^1\text{: }\eta^1\text{-}Ph)BPh_2]^-$ system.

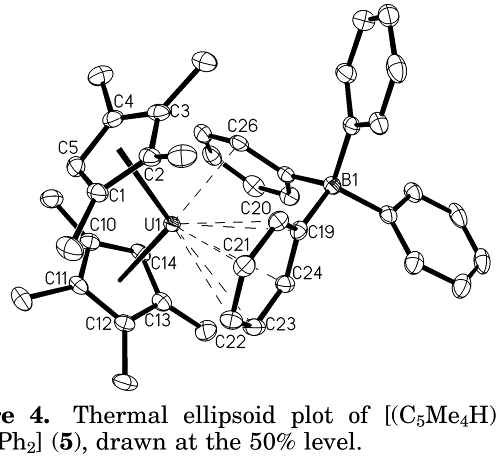

Figure 4. Thermal ellipsoid plot of $[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ (**5**), drawn at the 50% level.

The 2.98(7) Å U−C(arene) average distance in the η^6-arene ring of **5** can be compared with the analogous averages in previously characterized arene coordination complexes. Tetravalent $(C_6H_6)U(AlCl_4)_4$,[58] tetravalent $(C_6Me_6)U(BH_4)_4$,[59] and trivalent $[U(OC_6H_3{}^iPr_2\text{-}2,6)_3]_2$[60] have 2.94(1), 2.93(2), and 2.92(2) Å averages, respectively. All of these distances are much longer than the U−C(arene) distances in $\{[(Ad)(C_6H_3Me_2)N]_2U\}_2(C_6H_5Me)$,[61] $\{[(Me_3Si)_2N](C_5Me_5)U\}_2(C_6H_6)$,[56] and $[(C_5Me_5)_2U]_2(C_6H_6)$,[56] which are 2.593(9), 2.59(3), and 2.62(9) Å, respectively, and much shorter than the 3.731, 3.798, and 3.864 Å U−C(alkane) distances in $[(C_6H_3{}^tBu_2O)_3tacn]U\cdot(alkane)$ (alkane = cyclohexane, methylcyclohexane, and neohexane/cyclohexane), respectively.[62] Although lanthanide complexes have been isolated that contain η^6-arene bridged borate anions, including an η^6:η^1 coordination in $\{[(Me_3Si)_2N]Yb\}[(\mu\text{-}Ph)_2BPh_2]$,[63,64] complex **5** provides the first example of this kind of borate binding in actinide chemistry to our knowledge.

^{1}H NMR Spectra of 1−3 and 5. Although complexes **1**−**3** and **5** differ in formal uranium oxidation state and

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Table 5. ^{1}H NMR Resonances (δ, ppm; C_6D_6) for the $(C_5Me_4H)^-$ Ligands in $[(C_5Me_4H)_2U]^{n+}$ Complexes Isolated to Date

compd	C_5Me_4H	C_5Me_4H	$C_5Me_4\mathit{H}$
$(C_5Me_4H)_2UCl_2$ (**1**)	47.0	−16.4	−55.1
$(C_5Me_4H)_2UMe_2$ (**2**)	11.3	−2.9	−38.2
$(C_5Me_4H)_2UMeCl$ (**3**)	31.9, 25.8	−7.6, −13.0	−44.2
$[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ (**5**)	21.2	−12.3	−35.1

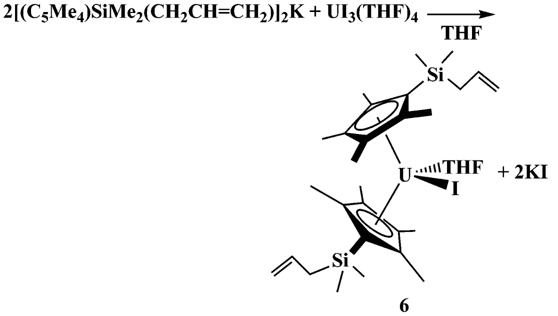
in the identity of their non-cyclopentadienyl ligands, the $(C_5Me_4H)^-$ chemical shifts in their paramagnetic ^{1}H NMR spectra are similar (Table 5). The alkyl resonances for complexes **2** and **3** are shifted far upfield at −73.5 and −108.9 ppm, respectively. The chemical shifts for the methyl ligands are less negative than those for $(C_5Me_5)_2UMeCl$[14] and $(C_5Me_5)_2UMe_2$,[14] which are −124 and −154 ppm, respectively. The methyl resonances in **2** and **3** are more negative than the methyl resonances for $[1,3\text{-}(Me_3Si)_2C_5H_3]_2UMe_2$,[51] $(1,3\text{-}{}^tBu_2C_5H_3)_2UMe_2$,[51] $[1,3\text{-}(Me_3Si)_2C_5H_3]_2UMeCl$,[51] and $(1,3\text{-}{}^tBu_2C_5H_3)_2UMeCl$[51] which are −21.0, −35.4, −49.9, and −52.4 ppm, respectively. In all cases, the methyl resonance for the methyl chloride metallocene is shifted to more negative values than in the corresponding dimethyl metallocene.

$[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2)]$ (**5**) was also studied by ^{11}B NMR spectroscopy, a technique that has previously been quite useful in characterizing uranium borate complexes.[34] Complex **5** displays a single resonance in the room-temperature ^{11}B NMR spectrum at −33.0 ppm, referenced to $BF_3{\cdot}OEt_2$. This is similar to the ^{11}B NMR spectrum of $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$, which has a single resonance at −43 ppm, and $[(C_5Me_5)_2UMe][MeBPh_3]$, which is only observed at low temperatures and displays a single resonance at −46 ppm (268 K).[34]

Synthesis of $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ (6). The tetraphenylborate complexes $[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ and $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ are convenient precursors to trivalent uranium metallocene compounds that have the advantage of being unsolvated. Another way to access trivalent uranium chemistry is from the conveniently available $UI_3(THF)_4$.[41] However, $UI_3(THF)_4$ typically forms THF-solvated products,[65] and removal of THF can be difficult. Desolvation can often require heating and high vacuum,[66] repeated extraction with nonpolar solvents,[67] or addition of Lewis acids such as $B(C_6F_5)_3$ to completely remove the THF.[68]

Another facile route to unsolvated f element and related complexes involves cyclopentadienyl ligands containing tethered olefins.[69−71] Use of the $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$ ligand can provide unsolvated products directly from THF-solvated metal chloride precursors, as shown in eq 6.[71] To determine if the $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$ ligand would also provide facile access to unsolvated metallocenes of U(III), $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]K$ was reacted with $UI_3(THF)_4$. Though the product isolated from this reaction was a THF adduct, $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ (**6**) (eq 7 and Figure 5), the THF could be removed under modest vacuum (10^{-3} Torr) at room temperature in less than 3 h. This desolvation involves a dramatic color change from the emerald green **6** to the brown color of $\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI\}_x$ (**8**). Since **8**, like unsolvated $[(C_5Me_5)_2UCl]_3$,[14] is insoluble in arene and alkane solvents, it could only be characterized by elemental analysis. Complex **8** does readily dissolve in THF to re-form **6** quantitatively, and **6** is soluble in alkane and arene solvents.

$$\mathrm{YCl_3(THF)_{3.5}} \xrightarrow[-2\mathrm{KCl}]{+2[(\mathrm{C_5Me_4})\mathrm{SiMe_2}(\mathrm{CH_2CH{=}CH_2})]\mathrm{K}} [(\mathrm{C_5Me_4})\mathrm{SiMe_2}(\mathrm{CH_2CH{=}CH_2})]_2\mathrm{YCl} \quad (6)$$



(7)

6

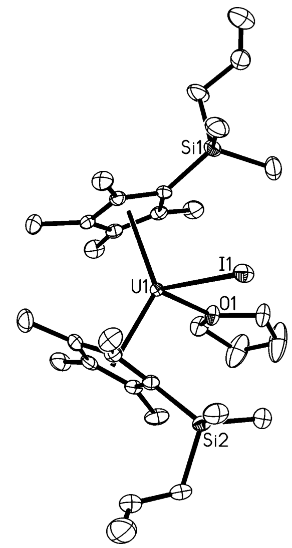


Figure 5. Thermal ellipsoid plot of $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ (**6**), drawn at the 50% level.

The ^{1}H NMR spectrum of **6** in either benzene-d_6 or THF-d_8 at room temperature shows only resonances for the residual protons of the deuterated solvent. However, in THF-d_8 as the temperature is lowered, resonances grow in attributable to **6**. Resonances attributable to the tethered olefins could not be definitively identified.

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Structure of $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ (6). Complex **6** represents the first example of a structurally characterized uranium complex containing an olefin-functionalized cyclopentadienyl ligand (Figure 5). In **6**, the olefin groups are not oriented toward the metal ion, as observed in $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Ln$ (Ln = Eu, Yb, Sm) and $\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Sm\}[BPh_4]$,[70] and are pointed away from the uranium coordination sphere, as observed in $\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y\}_2[(\mu\text{-}Me_2)AlMe_2]_2$.[71] This may in part be due to the molecule of THF that remains coordinated to **1** under the conditions of crystallization.

The 18.8° C(16)−ring centroid(1)−ring centroid(2)−C(2) torsional angle indicates that the $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$ ligands are more staggered than observed for **1**−**3** (Figure 3). The $-SiMe_2(CH_2CH{=}CH_2)$ substituents are on the same side of the metallocene and eclipse the iodide ligand. The 2.501(2) Å U(1)−O(1) distance (Table 4) is similar to the trivalent U−O(THF) bond distances in $[(Me_3Si)_3C_5H_2]UCl_2(THF)(\mu\text{-}Cl)_2Li(THF)_2$,[72] $(C_9H_7)UCl_3(THF)_2$,[73] and $(C_5H_4Me)UCl_3(THF)_2$[9] which are 2.449(9), 2.444(6), and 2.449(8) Å, respectively. The 3.0852(2) Å U(1)−I(I) distance is similar to the 3.161(1) and 3.103(2) Å distances in $(C_5Me_5)UI_2(THF)_3$[65] and $UI_3(THF_4)$,[41] but to the best of our knowledge, there does not exist another structurally characterized trivalent bis(cyclopentadienyl)uranium iodide complex with which to compare.

Discussion

The results reported here show that the $(C_5Me_4H)^-$ ligand displays chemistry in bis(cyclopentadienyl)uranium complexes that is similar to that for $(C_5Me_5)^-$ complexes. $(C_5Me_4H)_2UCl_2$ (**1**),[31] $(C_5Me_4H)_2UMe_2$ (**2**), and $(C_5Me_4H)_2UMeCl$ (**3**) can all be synthesized by reactions analogous to those used to make their pentamethyl analogues.[14] The trivalent complex $[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ (**5**) is prepared in a similar way from $(C_5Me_4H)_2UMe_2K$, but its structure differs from that of the pentamethyl analogue in that the bridging phenyl groups display different hapticities. Hence, the absence of two methyl groups allows one phenyl group to approach the U(III) center an η^6 fashion rather than in an η^1 or η^2 manner. The fact that unsolvated **5** can also be synthesized from **1** in three high-yielding steps provides a convenient synthetic route into unsolvated metallocene chemistry that bypasses additional desolvation steps[66−68] as well as solid-state syntheses of unsolvated trivalent starting materials such as UI_3.[31,74−76]

The isolation of the tetramethylcyclopentadienyl tethered olefin uranium metallocene $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ (**6**) shows that, in this uranium system, the tethered olefins do not facilitate loss of THF as readily as observed in eq 6 with yttrium.[71] However, **6** is easily desolvated and should be a good precursor to unsolvated, bis(pentasubstituted cyclopentadienyl)uranium chemistry.

Conclusion

$(C_5Me_4H)_2UCl_2$, $(C_5Me_4H)_2UMe_2$, $(C_5Me_4H)_2UMeCl$, $(C_5Me_4H)_2UMe_2K$, and $[(C_5Me_4H)_2U][(\mu\text{-}Ph)_2BPh_2]$ are all now available for comparative studies of $(C_5Me_4H)^-$ vs $(C_5Me_5)^-$ chemistry in the bis(cyclopentadienyl)uranium metallocene series. The tethered olefin complex $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2UI(THF)$ provides an alternative in bis(cyclopentadienyl)uranium metallocene chemistry with the added option of examining incorporation of a nearby olefin.

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Supporting Information Available: X-ray diffraction data, including atomic coordinates, thermal parameters, and complete bond distances and angles, for compounds **2**, **3**, **5**, and **6** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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