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Mono(pentamethylcyclopentadienyl)uranium(III) Complexes: Synthesis, Properties, and X-ray Structures of (η-C_5Me_5)$UI_2(THF)_3$, (η-C_5Me_5)$UI_2(py)_3$, and (η-C_5Me_5)U[$N(SiMe_3)_2$]$_2$

Larry R. Avens,[1a] Carol J. Burns,*[,1b] Raymond J. Butcher,[1c] David L. Clark,*[,1d]
John C. Gordon,[1b] Ann R. Schake,[1a] Brian L. Scott,[1b] John G. Watkin,[1b] and
Bill D. Zwick[1a]

Nuclear Materials Technology (NMT) Division and Chemical Science and Technology (CST)
Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, and
Department of Chemistry, Howard University, Washington D.C., 20059

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The uranium(III) iodide complex $UI_3(THF)_4$ reacts cleanly at ambient temperature with 1 equiv of sodium and potassium pentamethylcyclopentadienide salts in tetrahydrofuran to form the mono-ring uranium(III) complex (η-C_5Me_5)$UI_2(THF)_3$ (**1**). Additionally, reaction of $UI_3(THF)_4$ with 2 equiv or more of $K(C_5Me_5)$ in THF solution leads to the formation of the bis-ring adduct (η-C_5Me_5)$_2$UI(THF) (**2**) in high yield. In the solid state **1** exhibits a pseudo-octahedral *mer,trans* ligand geometry with the C_5Me_5 ligand occupying one axial position. U−I bond lengths range from 3.161(1) to 3.179(1) Å, while U−O distances to the THF ligands lie in the range 2.496(8)−2.594(10) Å. **1** also provides a convenient entry into a variety of other mono-ring complexes of uranium(III). In the presence of excess pyridine, the coordinated THF ligands of **1** are readily displaced to form the tris(pyridine) adduct (η-C_5Me_5)$UI_2(py)_3$ (**3**), which exhibits a *mer,trans* ligand geometry in the solid state similar to that of **1**. Metathesis of the iodide ligands in **1** with 2 equiv of $KN(SiMe_3)_2$ affords the bis(amido) complex (η-C_5Me_5)U[$N(SiMe_3)_2$]$_2$ (**4**). An X-ray diffraction study of this molecule reveals that methyl groups from both amido ligands are involved in agostic interactions with the uranium(III) center.

Introduction

Examination of ligand affinities of actinide complexes in nonaqueous media has often revealed that lower valent species, and in particular those of trivalent uranium, display the greatest evidence for metal orbital involvement in π back-donation to ligands.[2] Indeed, uranium in the +3 oxidation state has demonstrated several unique examples of reactivity among the actinide elements, including the formation of molecular complexes containing carbon monoxide and dinitrogen ligands.[2c,3,4] Recently, Clark and co-workers reported the preparation of a series of organic solvent soluble Lewis base adducts of uranium triiodide that have proven to be useful precursors to new trivalent uranium compounds[5]—the most commonly employed of these being $UI_3(THF)_4$.

Monocyclopentadienyl complexes of the tri- and tetravalent early transition metals and lanthanides have been the subject of extensive study.[6] Interest in this class of compounds is generated by the reduced steric constraints which exist at the metal center (in comparison to complexes containing two cyclopentadienyl ligands) and the presence of two or three additional sites for functionalization and potential substrate addition. Structurally characterized examples of actinide complexes employing mono-ring frameworks are restricted largely to tetravalent complexes of uranium and thorium. Mono(cyclopentadienyl) complexes of uranium of the general formula $CpMX_3L_2$ (X = Cl, Br; L = oxygen or nitrogen donor ligand) were first prepared in the 1970s.[7]

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[1] (a) NMT Division, Los Alamos National Laboratory. (b) CST Division, Los Alamos National Laboratory. (c) Howard University. (d) G. T. Seaborg Institute, Los Alamos National Laboratory.

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Since then, structurally characterized members of this series have included both those employing variants on the cyclopentadienyl ligand[8] and those where the halide ligands have been replaced by such groups as benzyl or allyl,[9] pyrazolylborate,[10] amide,[11] borohydride,[12] and other carbocyclic ligands.[13] The sole structurally characterized example of a U(III) mono-ring moiety exists within the unusual charge-transfer complex $[Na(THF)_6]$-$[(\eta\text{-}C_5Me_5)U(BH_4)_3]_2$, produced adventitiously during the reaction of $U(BH_4)_3 \cdot n THF$ with $(\eta\text{-}C_5Me_5)_2Th(PPh_2)_2$.[14] To generate a more general class of U(III) mono-ring compounds, it is desirable to identify neutral trivalent precursors for further synthetic studies. In the course of investigating the preparation and behavior of tris(cyclopentadienyl)uranium complexes, we have determined that metathesis reactions of $UI_3(THF)_4$ are also successful in producing stable mono- and bis(cyclopentadienyl) complexes, which are themselves useful precursors for a range of trivalent uranium chemistry. We describe here the preparation of the complexes $(\eta\text{-}C_5Me_5)UI_2(THF)_3$ and $(\eta\text{-}C_5Me_5)_2UI(THF)$, as well as the molecular structures of the mono-ring compounds $(\eta\text{-}C_5Me_5)UI_2(py)_3$ and $(\eta\text{-}C_5Me_5)U[N(SiMe_3)_2]_2$.

Experimental Section

General Procedures and Techniques. All manipulations were carried out under an inert atmosphere of argon using standard Schlenk line techniques or under an atmosphere of helium in a Vacuum Atmospheres drybox. Toluene, hexane, tetrahydrofuran, and diethyl ether were distilled from Na/K alloy under nitrogen. Toluene-d_8 and benzene-d_6 were degassed, dried, and stored over Na/K alloy. Pyridine was distilled from CaH_2 under nitrogen. Potassium hydride was purchased from Aldrich as a 60% dispersion in mineral oil and vacuum-filtered on a coarse-porosity frit. The resulting solid was washed with hexane and dried in vacuo to yield a white powder. Pentamethylcyclopentadiene was obtained from Aldrich and used as received. Potassium pentamethylcyclopentadienide was prepared by refluxing a slight excess of pentamethylcyclopentadiene with potassium hydride in toluene. $UI_3(THF)_4$ was prepared as previously reported.[5]

NMR spectra were recorded at 22 °C on Bruker AF 250 or Varian Unity 300 MHz spectrometers. All ^1H NMR chemical shifts are reported in ppm (δ) relative to the ^1H impurity in toluene-d_8 set at 2.09 ppm or in benzene-d_6 set at 7.15 ppm. Infrared spectra were recorded on a Bio-Rad Digilab FTS 40 spectrophotometer as Nujol mulls between KBr plates. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer utilizing sealed tin capsules for sample delivery. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 9 UV−vis−near-IR spectrophotometer, and extinction coefficients were measured from the baseline.

$(\eta\text{-}C_5Me_5)UI_2(THF)_3$ (1). To a solution of $UI_3(THF)_4$ (3.00 g, 3.31 mmol) in THF (50 mL) was added $K(C_5Me_5)$ (0.58 g, 3.33 mmol) as a solid over ca. 3 min. The resulting blue-green reaction mixture was stirred at room temperature for 24 h, at which point a white precipitate was observed in the blue-green solution. The reaction mixture was filtered through Celite, and then THF was removed from the filtrate in vacuo. The resulting blue-green powder was extracted with toluene (50 mL) and stirred for 3 h. The reaction mixture was again filtered through Celite and the toluene removed from the filtrate in vacuo. The green powder was taken up in THF (50 mL) and filtered once more through Celite, and the volume of the filtrate was taken down to ca. 30 mL. Upon addition of diethyl ether and storage at −40 °C for 48 h, blue crystals of **1** were isolated by filtration in 70−80% yield. Anal. Calcd for $C_{22}H_{39}O_3I_2U$: C, 31.33; H, 4.66; I, 30.09. Found: C, 31.17; H, 4.40; I, 29.89. Electronic spectrum (THF; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 285 sh (1860), 343 sh (1140), 401 (760), 502 (225), 595 (320), 738 (420), 792 (275), 835 (140), 856 (120), 913 (80), 932 (70), 1020 (40), 1069 (35), 1090 sh (30), 1105 sh (25), 1185 (80), 1191 (70), 1214 sh (40), 1239 (40). IR (Nujol, cm^{-1}): 1312 (w), 1294 (w), 1244 (m), 1174 (m), 1070 (m), 1010 (s), 922 (m), 912 (m), 854 (d), 832 (m), 666 (m). ^1H NMR (22 °C, C_6D_6): δ −6.00 (br s, 8 H, THF), 1.09 (br s, 8 H, THF), 1.86 (s, 15 H, C_5Me_5), 8.16 (br s, 4 H, THF), 21.20 (br s, 4 H, THF). ^1H NMR (22 °C, d_8-toluene): δ −5.99 (br s, 8 H, THF), 1.09 (br s, 4 H, THF), 1.79 (s, 15 H, C_5Me_5), 2.60 (br s, 8 H, THF), 8.03 (br s, 4H, THF). ^1H NMR (−88 °C, d_8-toluene): δ −20.64 (br s, 8 H, THF), −17.76 (br s, 8 H, THF), −10.60 (br s, 4 H, THF), 5.81 (s, 15 H, C_5Me_5), 14.94 (br s, 4 H, THF).

$(\eta\text{-}C_5Me_5)_2UI(THF)$ (2). To a solution of $UI_3(THF)_4$ (3.00 g, 3.31 mmol) in THF (50 mL) was added KC_5Me_5 (1.73 g, 9.93 mmol) as a slurry in THF. The resulting green suspension was stirred for 48 h, and then the reaction mixture was filtered through Celite. The THF was removed from the filtrate in vacuo, the resulting green powder was extracted with toluene, and the extracts were stirred for 48 h. The resulting brown solution was filtered through Celite and the toluene removed in vacuo, forming a brown powder. The powder was dissolved in THF and the solution layered with Et_2O. After storage at −40 °C for 48 h, green crystals of **2** were isolated by filtration in 90% yield. Anal. Calcd for $C_{24}H_{38}IOU$: C, 40.74; H, 5.41. Found: C, 41.07; H, 5.85. ^1H NMR (22 °C, C_6D_6): δ −56.10 (s, 4 H, THF), −17.91 (s, 4 H, THF), −1.09 (s, 30 H, C_5Me_5).

$(\eta\text{-}C_5Me_5)UI_2(py)_3$ (3). To a solution of $(\eta\text{-}C_5Me_5)UI_2(THF)_3$ (**1**; 1.26 g, 1.49 mmol) in toluene (50 mL) was added ca. 1.0 mL of pyridine. The color of the solution changed from green to purple as the pyridine was added. The solution was stirred for 1 h at room temperature, and then the volume was reduced to ca. 25 mL in vacuo. After storage at −40 °C for 24 h, a purple microcrystalline solid had been deposited. The mother liquor was decanted away and the solid pumped dry. A second crop was obtained by further concentration of the mother liquor and storage at −40 °C. Total yield: 0.995 g (77%). Anal. Calcd for $C_{25}H_{30}I_2N_3U(C_7H_8)_{0.6}$: C, 38.14; H, 3.81; N, 4.57. Found: C, 38.32; H, 3.81; N, 4.46. ^1H NMR (22 °C, C_6D_6): δ 21.04, 13.65 (v br), 10.62, 5.67 (s, C_5Me_5), −2.26, −5.02, −29.77.

$(\eta\text{-}C_5Me_5)U[N(SiMe_3)_2]_2$ (4). To a solution of $(\eta\text{-}C_5Me_5)UI_2(THF)_3$ (0.505 g, 0.60 mmol) in THF (30 mL) was added a solution of $KN(SiMe_3)_2$ (0.239 g, 1.20 mmol) in THF (10 mL). The color changed immediately from blue-green to dark brown. After 30 min of stirring, the solution was filtered through Celite and the filtrate pumped to dryness. Hexane (30 mL) was added and the extract filtered through Celite to give a clear deep brown solution. The volume of the filtrate was reduced to ca. 5 mL in vacuo, and the solution was placed in a freezer at −40 °C. Overnight, large brown crystals were deposited. The mother liquor was decanted away, and the

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Table 1. Crystallographic Data

	1[a]	**3**[a]	**4**[a]
empirical formula	$C_{22}H_{39}O_3I_2U$	$C_{25}H_{30}I_2N_3U$	$C_{22}H_{51}N_2Si_4U$
space group	$P2_1/n$	$P3_12_1$	$P2_1/c$
temp (K)	203	183	213
a (Å)	17.698(4)	11.205(2)	19.148(4)
b (Å)	16.997(3)	11.205(2)	13.401(3)
c (Å)	18.813(4)	23.324(3)	12.061(2)
β (deg)	107.74(3)		90.18(3)
V, Å^3	5930(2)	2536.0(7)	3094.9(11)
Z (molecules/ unit cell)	8	3	4
D_{calcd}, g/cm^3	2.077	1.698	1.490
λ(Mo Kα)	0.71073	0.71073	0.71073
fw	842.9	864.35	694.04
abs coeff (mm^{-1})	8.00	6.639	5.411
$R(F_o)^b$	0.0392	0.0625	0.0632
$R_w(F_o^2)^b$	0.0445	0.1416	0.1665

[a] **1** = (η-C_5Me_5)$UI_2(THF)_3$; **3** = (η-C_5Me_5)$UI_2(py)_3$; **4** = (η-C_5Me_5)U[N(SiMe$_3$)$_2$]$_2$. [b] $R(F_o) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w(F_o^2) = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

crystals were pumped dry. Total yield: 0.155 g (57%). Anal. Calcd for $C_{22}H_{51}N_2Si_4U$: C, 38.07; H, 7.41; N, 4.04. Found: C, 36.96; H, 6.73; N, 3.38. ^{1}H NMR (22 °C, C_6D_6): δ −9.27 (s, 15 H, C_5Me_5), −17.12 (s, 36 H, −N(SiMe$_3$)$_2$).

Crystallographic Studies. (η-C$_5$Me$_5$)UI$_2$(THF)$_3$ (1). Single crystals of (η-C_5Me_5)$UI_2(THF)_3$ were grown by layering a saturated THF solution with diethyl ether and slowly cooling to −40 °C. The crystals appeared to lose solvent from the lattice at room temperature in the X-ray beam, necessitating low-temperature data collection. A single crystal measuring 0.20 × 0.25 × 0.25 mm was mounted on a glass fiber and transferred directly to the cold stream of an Enraf-Nonius CAD4 automated diffractometer operating at −70 °C. Cell constants and the orientation matrix were determined from the setting angles of 25 reflections. The data were collected utilizing Mo Kα radiation (λ = 0.710 73 Å). Examination of the systematic absences uniquely identified the space group as $P2_1/n$. A semiempirical absorption correction was applied to the data on the basis of the average relative intensity curve of azimuthal scans. The structure was solved by a combination of Patterson and difference Fourier methods.[15] The structure was found to contain two independent molecules per asymmetric unit. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with fixed thermal parameters and not refined. The final residuals for the full-matrix least-squares refinement were R = 3.92% and R_w = 4.45%[16] and GOF = 1.59 based on 505 refined parameters. Crystallographic parameters are provided in Table 1.

(η-C$_5$Me$_5$)UI$_2$(py)$_3$ (3). Single crystals of (η-C_5Me_5)$UI_2(py)_3$ were grown by slow evaporation of a toluene solution in the drybox. A black, irregular-shaped crystal measuring 0.10 × 0.21 × 0.37 mm was attached to a thin glass fiber using silicone grease and placed into the nitrogen cold stream on a Siemens P4/PC diffractometer set at −90 °C. The radiation used was graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections of high Bragg angle. The data were collected using ω scans with a 0.90° scan range. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination, data collection, and data reduction including Lorentz and polarization corrections were carried out using XSCANS Version 2.10b software.[17a] Due to an error in this software, only one-third of the data were collected ($2\theta = 45°$). This lack of data completeness was not discovered until several months later during the final stages of refinement. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL 5.1 software.[17b] The data were corrected for absorption using the XEMP facility in SHELXTL PC. Data collection and refinement parameters are presented in Table 1.

The structure refinement was initiated in space group $P3_12_1$ using the coordinates from the previously solved neodymium analogue.[18] The refinement of the pyridine and C_5Me_5 ligands was problematic due to the partial data set, and so these were refined as “variable metric” rigid bodies. The lack of data resulted in several large temperature factors for the ligand atoms. However, the bond distances and angles of the uranium coordination sphere were reasonable when compared to those of the isostructural neodymium analogue. The final refinement included anisotropic temperature factors on the uranium and iodine atoms only. Hydrogen atoms were not included in the refinement. The final refinement[19] converged to R1 = 0.0625 and wR2 = 0.1416.

(η-C$_5$Me$_5$)U[N(SiMe$_3$)$_2$]$_2$ (4). Single crystals of **4** were grown by slow evaporation of a hexane solution in the drybox. A single crystal measuring 0.08 × 0.20 × 0.28 mm was mounted on a glass fiber and transferred directly to the cold stream of an Enraf-Nonius CAD4 automated diffractometer operating at −60 °C. The data were collected using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), with the scan width defined by the equation 0.80 + 0.35 tan θ. Data were reduced using the program XCAD4.[20] Absorption corrections were applied using the XEMP/ellipsoidal program within SHELXTL PC.[21] These absorption corrections were of rather low quality since ψ-scan data were collected on only one reflection. The structure was solved in space group $P2_1/c$. This solution yielded the uranium, the silicon, and the majority of all non-hydrogen atom positions. However, the refinement was problematic, with disorder of all ligands and anomalous bond distances and angles. Because of the small β angle of 90.18(1)°, a pseudo-orthorhombic refinement was pursued. Two twin components, related by the matrix [100] [0,−1,0] [0,0,−1], were refined with a final batch scale factor of 0.439(4). The hydrogen atom positions were fixed using the HFIX command in SHELXTL PC (C−H = 0.96 Å). The hydrogen atoms were refined using a riding model, with their isotropic temperature factors set to 1.5 times the equivalent isotropic U value of the carbon atom to which they were bound. Hydrogen atoms were not placed on the methyl groups having agostic interactions with the uranium atom. Because of the absorption problem (vide supra), the refinement of many anisotropic temperature factors was restrained using ISOR. The final refinement[22] included anisotropic temperature factors on all non-hydrogen atoms and converged to R1 = 0.0632 and wR2 = 0.1665. Structure solution and graphics were performed using SHELXTL PC. SHELX-93 was used for structure refinement and creation of publication tables.[23]

Results and Discussion

Initial NMR-scale reactions between Cp$_3$U(THF)[24] and $UI_3(THF)_4$ in THF-d_8 revealed three C_5H_5 reso-

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[15] All calculations were performed on a MicroVax local area network utilizing SHELXTL PLUS software and all physical constants tabulated therein.

[16] $w^{-1} = \sigma^2(F) + 0.0002(F^2)$.

[17] (a) XSCANS Version 2.10b; Siemens Analytical X-ray Inc., Madison, WI 53719, 1994. (b) SHELXTL Version 5.1; Siemens Analytical X-ray Inc., Madison, WI 53719, 1997

[18] Clark, D. L.; Gordon, J. C.; Scott, B. L.; Watkin, J. G. *Polyhedron* **1999**, *18*, 1389.

[19] R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.0854P)^2]$.

[20] Harms, K.; Wocadlo, S. XCAD4; University of Marburg, Marburg, Germany, 1996.

[21] SHELXTL PC Version 4.2/360; Bruker Analytical X-ray Instruments, Inc., Madison, WI 53719, 1994.

[22] R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.1331P)^2]$.

[23] Sheldrick, G. SHELX-93; University of Göttingen, Göttingen, Germany, 1993.

nances consistent with ligand redistribution to give tris-, bis-, and mono-C_5H_5-substituted uranium(III) complexes, as shown in eq 1. As has been demonstrated

$$UI_3(THF)_4 + (\eta\text{-}C_5H_5)_3U(THF) \xrightleftharpoons[25\ °C]{THF\text{-}d_8} (\eta\text{-}C_5H_5)UI_2(THF)_x + (\eta\text{-}C_5H_5)_2UI(THF)_y \quad (1)$$

previously in actinide chemistry, increasing the steric requirement of the cyclopentadienyl ligand inhibits ligand redistribution reactions, and it was found that the use of pentamethylcyclopentadienyl ligands allowed the isolation of mono-ring complexes directly. As shown in eq 2, $UI_3(THF)_4$ reacts readily with $M(C_5Me_5)$ (M =

$$UI_3(THF)_4 + K(C_5Me_5) \xrightarrow[25\ °C]{THF} (\eta\text{-}C_5Me_5)UI_2(THF)_3 + KI \quad (2)$$

Na, K) in THF solution. Extraction with toluene and recrystallization from a cooled (−40 °C) THF/diethyl ether solution provides blue crystals of $(\eta\text{-}C_5Me_5)UI_2(THF)_3$ (**1**) in 70−80% yield.

The highly air- and moisture-sensitive crystals are readily soluble in THF and toluene but less soluble in diethyl ether and hexane. Once formed, redistribution of the C_5Me_5 ligand has not been observed. The room-temperature ^1H NMR spectrum of **1** displays very broad resonances due to the paramagnetic uranium(III) metal. However, a 2:1 pattern of THF ligand resonances can be observed, indicating that two different sites are occupied by the ligands and that there is no exchange between these sites on the NMR time scale. This observation is rather unusual for an f-element complex, in which rapid intramolecular ligand site exchange is commonplace, but the NMR data alone did not distinguish between a *cis* or *trans* arrangement of iodide ligands. To confirm the stoichiometry and determine the geometry of the complex, a crystallographic determination was sought and is described below.

Using a synthetic strategy analogous to that described above, it was found that the stoichiometric addition of 2 equiv or more of $K(C_5Me_5)$ to $UI_3(THF)_4$ in THF solution, followed by recrystallization from a cooled toluene solution, gives green crystals of the bis(pentamethylcyclopentadienyl) derivative $(\eta\text{-}C_5Me_5)_2UI(THF)$ (**2**) in 90% yield, according to eq 3. Attempts to prepare

$$UI_3(THF)_4 + 2K(C_5Me_5) \xrightarrow[25\ °C]{THF} (\eta\text{-}C_5Me_5)_2UI(THF) + 2KI \quad (3)$$

the tris-η-C_5Me_5 complex $(\eta\text{-}C_5Me_5)_3U$[25] by direct metathesis have not been successful. However, as mentioned above and suggested by eq 1, the tris-η-C_5H_5 complex $Cp_3U(THF)$, having the unsubstituted Cp ligand, can be prepared by a metathesis reaction with $UI_3(THF)_4$ in THF.

Treatment of a toluene solution of **1** with an excess of pyridine results in displacement of all three THF ligands and substitution by pyridine, to provide the tris(pyridine) adduct $(\eta\text{-}C_5Me_5)UI_2(py)_3$ (**3**). ^1H NMR spectra of **3** in C_6D_6 solution show a broad singlet resonance at δ 5.67 assigned to the C_5Me_5 ligand, plus additional broadened and shifted resonances arising from the coordinated pyridine ligands. Since NMR data alone did not allow for an unambiguous determination of molecular structure, a single-crystal X-ray analysis was undertaken, the results of which are described below. The X-ray analysis revealed the presence of a toluene solvent molecule within the lattice, and it was found that this lattice solvent molecule was readily lost whenever crystals of **3** were exposed to the drybox atmosphere. Thus, ^1H NMR spectra reveal resonances consistent with the presence of varying amounts of free toluene in samples of **3**, and microanalytical data were consistent with the formulation **3**·0.6(toluene).

The mono-ring complex $(\eta\text{-}C_5Me_5)UI_2(THF)_3$ (**1**) has been shown to be a useful precursor to several other uranium(III) complexes. We have previously reported that reaction of **1** with 1 equiv of K_2COT (COT = cyclooctatetraenide) produces the mixed-ring complex $(COT)(\eta\text{-}C_5Me_5)U(THF)$[26] in 75% yield (eq 4). Several

$$(\eta\text{-}C_5Me_5)UI_2(THF)_3 + K_2(COT) \xrightarrow[25\ °C]{THF} (\eta\text{-}COT)(\eta\text{-}C_5Me_5)U(THF) + 2KI \quad (4)$$

Lewis-base adducts of this mixed-ring complex have been prepared and described, including the molecular structure of the 4,4′-dimethyl-2,2′-dipyridyl (Me_2bpy) adduct $(\eta\text{-}C_8H_8)(\eta\text{-}C_5Me_5)U(Me_2bpy)$.[26]

Treatment of a THF solution of $(\eta\text{-}C_5Me_5)UI_2(THF)_3$ (**1**) with 2 equiv of $KN(SiMe_3)_2$ leads to formation of the bis(amido) complex $(\eta\text{-}C_5Me_5)U[N(SiMe_3)_2]_2$ (**4**), which may be isolated from hexane in moderate yield (eq 5).

$$(\eta\text{-}C_5Me_5)UI_2(THF)_3 + 2KN(SiMe_3)_2 \xrightarrow[25\ °C]{THF} (\eta\text{-}C_5Me_5)[N(SiMe_3)_2]_2 + 2KI \quad (5)$$

Ambient-temperature ^1H NMR spectra of **4** reveal two resonances in the expected 15:36 ratio at δ −9.27 and −17.12, assigned respectively to the C_5Me_5 and $-N(SiMe_3)_2$ ligands. However, even when single crystals of **4** are dissolved in C_6D_6 at ambient temperature, the free amine $HN(SiMe_3)_2$ is always observed together with several additional resonances which are suggestive of a second species in solution. The integrals of the additional resonances indicate that the second species contains a C_5Me_5 ligand and a cyclometalated silylamido ligand of the type $U[N(SiMe_3)SiMe_2CH_2]$. Integrals of the cyclometalated ligand are in the ratio 9:3:3:1:1, which implies a diastereotopic ligand environment and strongly suggests that an additional ligand is present on the uranium center besides the C_5Me_5. Additionally, the line widths of the second set of resonances are relatively small, which is usually associated with the presence of a uranium(IV) rather than a uranium(III) metal center. We postulate that the second species in solution may be the uranium(IV) hydrido species $(\eta\text{-}C_5Me_5)UH[N(SiMe_3)SiMe_2CH_2]$, in which the hydride resonance is too broadened to be observed. Similar metallacycle formation has been observed previously for the hydrido complexes $HAn[N(SiMe_3)_2]_3$ (An = Th, U),

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which are converted under mild thermolytic conditions to the complexes An[N(SiMe$_3$)SiMe$_2$CH$_2$][N(SiMe$_3$)$_2$]$_2$,[27] as well as in a number of other actinide complexes.[28,29,30] The solid-state structure of **4**, featuring two close U···H−C interactions with trimethylsilyl groups, gives strong indication that the molecule is geometrically predisposed to undergo relatively facile metallacycle formation.

The solution behavior of **4** was investigated further. An NMR tube was loaded with ca. 20 mg of (η-C$_5$Me$_5$)UI$_2$(THF)$_3$ (**1**) together with 2 equiv of solid KN(SiMe$_3$)$_2$. Toluene-d_8 was then trap-to-trap-distilled into the tube, which was held at liquid-nitrogen temperature until it was placed into a precooled NMR probe at −80 °C. As the sample was warmed through −20 °C, a clean reaction occurred to give **4** plus THF which had been displaced from the starting material. Judging by the broadness of the THF resonances and their chemical shifts (1.35 and 3.20 ppm), the THF ligands coordinate to the paramagnetic uranium(III) metal center in the form of a complex of the type (η-C$_5$Me$_5$)U[N(SiMe$_3$)$_2$]$_2$(THF)$_x$. We note that the coordinated THF ligands must be relatively labile, since they are lost from the coordination sphere of **4** following workup and isolation of preparative-scale reactions (vide supra). Most interestingly, further warming of the NMR sample to 60 °C did not cause any additional resonances to appear in the NMR spectrum, indicating that the presence of THF in the NMR sample was inhibiting the facile cyclometalation pathway referred to above. We speculate that THF ligands may coordinate weakly to the metal center and displace the agostic U···H−C interactions, resulting in a structure which is much less favorably disposed to undergo metallacycle formation. During further investigations, reaction mixtures containing **1** and 2 equiv of KN(SiMe$_3$)$_2$ were heated for several hours in an attempt to prepare a pure sample of the metallacyclic species. These efforts proved to be unsuccessful.

We note that the neodymium analogue of **4**, namely (η-C$_5$Me$_5$)Nd[N(SiMe$_3$)$_2$]$_2$, has been previously isolated by Andersen and co-workers.[31] However, no mention was made of any observation of cyclometalation reactions, and this may be due to the inaccessibility of higher oxidation states for neodymium.

Solid-State and Molecular Structures. (η-C$_5$Me$_5$)UI$_2$(THF)$_3$ (1). Crystals of **1** were found to readily desolvate. However, after several attempts a crystal was successfully mounted and the structure obtained. **1** crystallizes in the monoclinic space group $P2_1/n$ with two independent molecules in the asymmetric unit. The solid-state structure of one of these molecules is shown in Figure 1. Selected bond distances and angles are given in Table 2. The uranium metal center is coordinated to one η^5-bonded pentamethylcyclopentadienyl group, three THF oxygen atoms, and two iodide ions. The uranium atom would have a formal coordination number of 8 if the η-C$_5$Me$_5$ ring is considered to occupy three coordination sites. However, the geometry about the uranium is best described as pseudo-octahedral, with the Cp ligand occupying one coordination site. Within this pseudo-octahedral geometry, the complex may be described as the *mer,trans* isomer, with the THF ligands occupying meridional sites and iodide ligands in a *trans* arrangement.

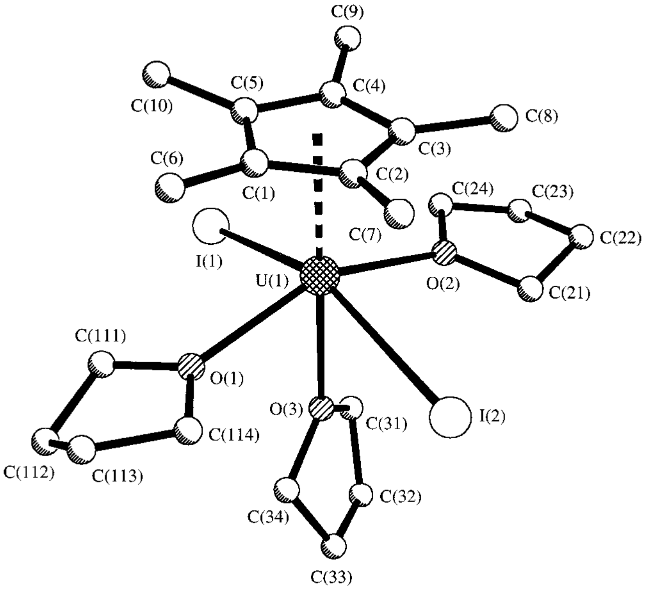

Figure 1. Ball-and-stick drawing of one of the two crystallographically independent molecules of (η-C$_5$Me$_5$)UI$_2$(THF)$_3$ (**1**), giving the labeling scheme used in the tables.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for (η-C$_5$Me$_5$)UI$_2$(THF)$_3$ (1)

U(1)−I(1)	3.161(1)	U(1)−I(2)	3.179(1)
U(2)−I(3)	3.162(1)	U(2)−I(4)	3.168(1)
U(1)−O(1)	2.496(8)	U(1)−O(2)	2.546(9)
U(1)−O(3)	2.594(10)	U(2)−O(4)	2.507(8)
U(2)−O(5)	2.533(8)	U(2)−O(6)	2.569(11)
U(1)−C$_{avg}$	2.80(1)	U(2)−C$_{avg}$	2.77(1)
I(1)−U(1)−I(2)	151.7(1)	I(1)−U(1)−O(1)	89.4(2)
I(1)−U(1)−O(2)	85.9(2)	I(1)−U(1)−O(3)	76.3(3)
I(2)−U(1)−O(2)	85.8(2)	I(2)−U(1)−O(1)	85.8(2)
O(1)−U(1)−O(2)	152.8(3)	I(2)−U(1)−O(3)	75.5(3)
O(1)−U(1)−O(3)	76.7(3)	O(2)−U(1)−O(3)	76.1(3)
I(3)−U(2)−I(4)	154.7(1)	I(3)−U(2)−O(4)	88.5(2)
I(3)−U(2)−O(5)	88.8(2)	I(3)−U(2)−O(6)	76.8(2)
I(4)−U(2)−O(5)	86.2(2)	I(4)−U(2)−O(4)	84.3(2)
I(4)−U(2)−O(6)	77.9(2)	O(4)−U(2)−O(5)	151.7(3)
O(4)−U(2)−O(6)	78.7(3)	O(5)−U(2)−O(6)	73.2(3)

The metrical parameters associated with **1** reveal that a number of interligand repulsions produce distortions from ideal geometries in the structure. A steric interaction between the methyl groups on the cyclopentadienyl ring and the equatorial ligands is apparent from the bending of the methyl substituents out of the ring plane (the mean displacement from the plane is 0.18 Å). This steric interaction also induces a bending of the adjacent *trans* equatorial groups away from 180°. As shown in Table 2, the O(1)−U(1)−O(2) angle is 152.8(3)° (in the second independent molecule O(4)−U(2)−O(5) = 151.7(3)°) and the I(1)−U(1)−I(2) angle is 151.7(1)° (I(3)−U(2)−I(4) = 154.7(1)°). Although there are no compa-

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Table 3. Comparative Bond Angles (deg) for Related Mono(cyclopentadienyl) Complexes

complex	O(eq)−M−O(eq)	X−M−X	ref
(η-C_5Me_5)$UI_2(THF)_3$	152.8(3)	151.7(1)	*a*
(η-C_5Me_5)$CeI_2(THF)_3$	152.9(3)	152.18(3)	32
(η-C_5H_5)$YbBr_2(THF)_3$	155.7(3)	155.31(5)	42
(η-C_5H_5)$ErCl_2(THF)_3$	155.18(1)	154.85(4)	43
(η-C_5H_5)$YbCl_2(THF)_3$	155.1	154.8	44

[a] This work.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for (η-C_5Me_5)$UI_2(py)_3$ (3)

U(1)−I(1)	3.182(4)	U(1)−N(1)	2.67(3)
U(1)−N(2)	2.76(8)		
N(1)−U(1)−N(1)#1	153.0(1)	N(1)−U(1)−N(2)	76.5(6)
N(1)−U(1)−I(1)#1	89.1(5)	N(1)−U(1)−I(1)	84.5(5)
N(2)−U(1)−I(1)	76.37(8)	I(1)−U(1)−I(1)#1	152.75(17)

[a] Symmetry transformations used to generate equivalent atoms: (#1) *y*, *x*, −*z* + 2.

rable trivalent mono-ring actinide complexes with which to compare these values, there are several mono-ring lanthanide complexes (Table 3) having the same pseudo-octahedral *mer,trans* geometry that contain comparable steric environments. The most closely related complex is *mer,trans*-(η-C_5Me_5)$CeI_2(THF)_3$.[32] In this complex a similar distortion is seen away from idealized octahedral geometry—the O(eq)−Ce−O(eq) angle is 152.9(3)°, and the I(eq)−Ce−I(eq) angle is 152.18(3)°.

U−I and $U-O_{thf}$ bond distances of **1** are found to be directly comparable to those of the trivalent iodide complex $UI_3(THF)_4$. In **1** the U−I distances in the two independent molecules range from 3.161(1) to 3.179(1) Å, while those in $UI_3(THF)_4$ fall between 3.103(2) and 3.167(2) Å.[5] The U−O distances in $UI_3(THF)_4$ lie between 2.48(1) and 2.56(1) Å, while those in **1** range from 2.496(8) to 2.594(10) Å. The $U-C_{Cp}$ distances in (η-C_5Me_5)$UI_2(THF)_3$ are also comparable to those previously determined for other cyclopentadienyl complexes of uranium(III). In particular, the $U-C_{Cp}$ distances in **1** ($U-C_{avg}$ = 2.78(1) Å) are well within the range of U−C distances observed in bis-[33] and tris(cyclopentadienyl)[2a,3e,34] complexes of uranium(III) (2.76−2.79 and 2.67−2.89 Å, respectively).

(η-C_5Me_5)$UI_2(py)_3$ (3). To ascertain whether **3** possessed a solid-state structure analogous to that of **1**, a single-crystal X-ray analysis was undertaken on crystals obtained by slow cooling of a concentrated toluene solution. Selected bond distances and angles for **3** are presented in Table 4. **3** crystallizes in the trigonal space group $P3_221$ with no unusual intermolecular contacts. The molecular structure of **3** is shown in Figure 2. It can be seen that (η-C_5Me_5)$UI_2(py)_3$ adopts a *mer,trans* pseudo-octahedral geometry very similar to that found for **1**. The U−I distance of 3.182(4) Å is comparable to those found in **1**, while the U−N distances are of two types—2.67(3) Å to the pyridine ligands *cis* to the Cp* and 2.76(8) Å to the *trans* pyridine ligand. Very few other examples of pyridine coordinated to a uranium(III) metal center have been structurally characterized. The only direct comparisons available for the U−N distance in **3** are those of 2.662(13) and 2.627(12) Å for the $U-N_{py}$ distances in (η-C_5H_4Me)$_3$U(4-$NMe_2C_5H_4N$).[35] I−U−I and N−U−N angles between *trans* ligands also follow the trend discussed above, in which the iodide and pyridine ligands distort somewhat away from the bulky C_5Me_5 ligand, resulting in an I−U−I angle of 152.75(17)° and a N−U−N angle of 153.0(1)°.

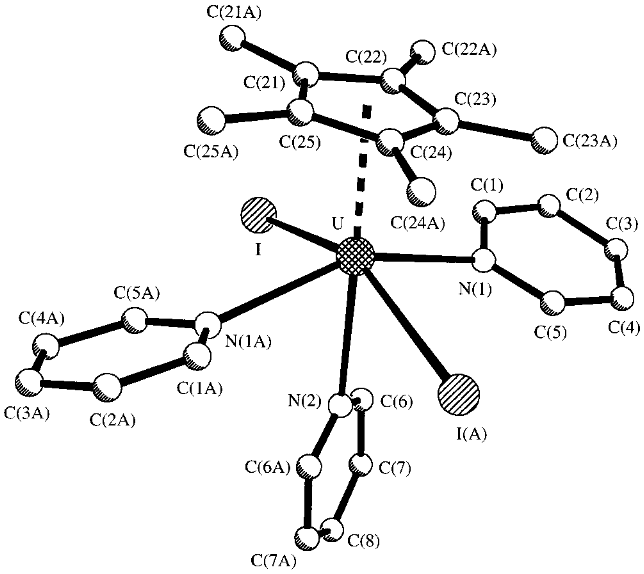

Figure 2. Ball-and-stick drawing of the molecular structure of (η-C_5Me_5)$UI_2(py)_3$ (**3**), giving the labeling scheme used in the tables.

(η-C_5Me_5)U[N(SiMe_3)$_2$]$_2$ (4). Single crystals of **4** suitable for an X-ray diffraction study were grown from a concentrated hexane solution at −40 °C. A ball-and-stick figure of the solid-state structure is shown in Figure 3, and selected bond lengths and angles appear in Table 5. **4** crystallizes in the monoclinic space group $P2_1/c$. The overall molecular structure of **4** comprises a trigonal arrangement of the C_5Me_5 and two amido ligands, if the ring centroid is considered as a single ligand site. The average U−C(ring) distance of 2.777 Å is consistent with those observed in **1** and **3** (vide supra). The U−N distances of 2.23(3) and 2.358(19) Å in **4** are very similar to those of 2.320(4) and 2.339(3) Å observed in the uranium(III) complexes U[N(SiMe_3)$_2$]$_3$[36] and [$(Me_3Si)_2N$]$_4U_2$[μ-N(H)(mesityl)]$_2$,[37] respectively. These distances are, as expected, somewhat longer than those of 2.284(11) Å (average) and 2.237(9) Å found in the uranium(IV) species U(O-2,6-*t*-$Bu_2C_6H_3$)[N(SiMe_3)$_2$]$_3$[38] and HU[N(SiMe_3)$_2$]$_3$,[39] respectively. The most notable feature of the structure is the presence of two very short U−C contacts with two of the methyl groups within the bis(trimethylsilyl)amido ligands. Specifically, the U(1)−C(4) and U(1)−C(7) contacts are 2.86(2) and 2.80(2) Å, respectively. Such short contacts have been observed

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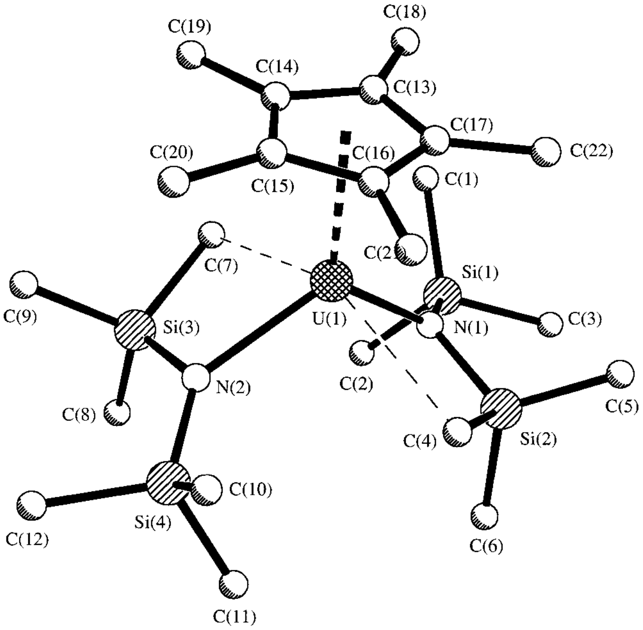

Figure 3. Ball-and-stick drawing of the molecular structure of (η-C_5Me_5)U[N($SiMe_3$)$_2$]$_2$ (**4**), giving the labeling scheme used in the tables.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for (η-C_5Me_5)U[N($SiMe_3$)$_2$]$_2$ (4)

U(1)−N(1)	2.23(3)	U(1)−N(2)	2.358(19)
U(1)−C(4)	2.86(2)	U(1)−C(7)	2.80(2)
U(1)−C(13)	2.770(10)	U(1)−C(14)	2.803(9)
U(1)−C(15)	2.800(11)	U(1)−C(16)	2.764(11)
U(1)−C(17)	2.746(10)		
N(1)−U(1)−N(2)	113.6(6)	Si(2)−N(1)−Si(1)	119.5(15)
Si(2)−N(1)−U(1)	106.3(11)	Si(1)−N(1)−U(1)	134.2(12)
Si(4)−N(2)−Si(3)	125.2(12)	Si(4)−N(2)−U(1)	132.4(12)
Si(3)−N(2)−U(1)	101.5(9)		

previously in actinide chemistry[3i,40] and have been interpreted as an indication of the presence of agostic U···H−C interactions. These interactions also manifest themselves in the very significant differences in U−N−Si angles within each silylamido ligand. Thus, the U(1)−N(1)−Si(2) angle is only 106.3(11)°, whereas the U(1)−N(1)−Si(1) angle is 134.2(12)°. Similarly, the U(1)−N(2)−Si(3) angle is 101.5(9)°, whereas the U(1)−N(2)−Si(4) angle is 132.4(12)°. Analogous short metal−carbon contacts have also been observed for the bis(trimethylsilyl)methyl ligands in the lanthanide complexes (η-C_5Me_5)La[CH($SiMe_3$)$_2$]$_2$[41a−c] and (η-C_5Me_5)Y(O-2,6-*t*-$Bu_2C_6H_3$)[CH($SiMe_3$)$_2$]$_2$.[41d] Following detailed neutron diffraction and theoretical studies, these contacts have recently been interpreted as β-SiC rather than γ-CH interactions, and significant lengthening of the silicon−carbon bond was observed.[41e] In the case of **4**, however, the relatively large esd's on the Si−C distances (typically 0.03 Å) do not allow a meaningful comparison to be made.

Concluding Remarks

Reaction of $UI_3(THF)_4$ with 1 equiv of K(C_5Me_5) provides a convenient entry into mono(pentamethylcyclopentadienyl) complexes of uranium(III), while avoiding problematic ring redistribution reactions. The Lewis base adducts (η-C_5Me_5)UI_2(THF)$_3$ (**1**) and (η-C_5Me_5)UI_2(py)$_3$ (**3**) have been isolated and subjected to single-crystal X-ray diffraction studies. Both **1** and **3** have been shown to display *mer,trans* pseudo-octahedral geometries in the solid state. Reaction of $UI_3(THF)_4$ with 2 (or 3) equiv of K(C_5Me_5) produces the bis(pentamethylcyclopentadienyl)uranium(III) complex (C_5Me_5)$_2$UI(THF) (**2**). The utility of **1** as a precursor to additional uranium(III) moieties is demonstrated by the reaction with 2 equiv of KN($SiMe_3$)$_2$ to produce the bis(amido) derivative (η-C_5Me_5)U[N($SiMe_3$)$_2$]$_2$ (**4**). In the solid state **4** exhibits two short U−C contacts with methyl groups of the bis(trimethylsilyl)amido ligands, which are indicative of agostic U···H−C interactions. Samples of **4** in toluene solution undergo a facile cyclometalation reaction, which appears to be inhibited by the presence of stoichiometric quantities of THF.

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Supporting Information Available: Complete sets of positional and equivalent isotropic thermal parameters of the non-hydrogen atoms, bond lengths and angles, hydrogen coordinates and isotropic thermal parameters, and anisotropic thermal parameters for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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