Multiple Syntheses of (C₅Me₅)₃U

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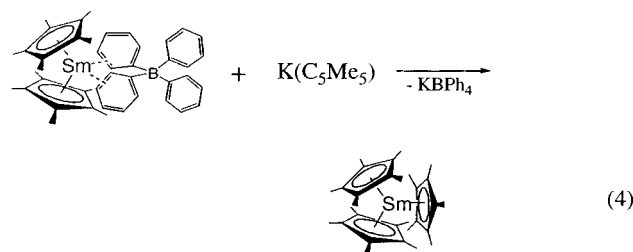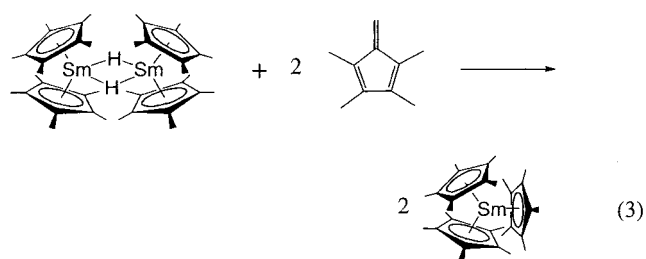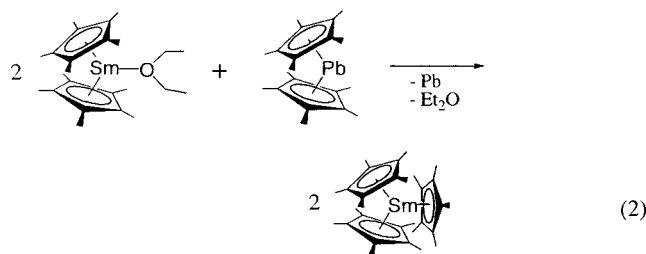*Department of Chemistry, University of California, Irvine, Irvine, California 92697-2025*
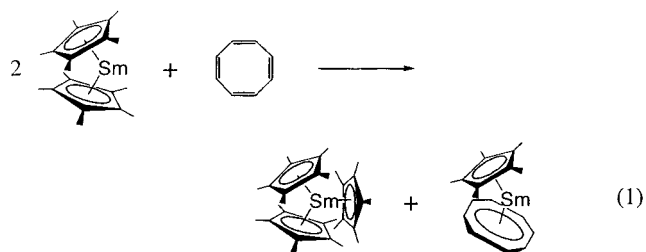
Several new synthetic routes to the sterically crowded $(C_5Me_5)_3U$ complex have been developed. $(C_5Me_5)_3U$ can be prepared by (a) reaction of $[(C_5Me_5)_2UH_2]_2$ with tetramethylfulvene, (b) reduction of $(C_5Me_5)_2Pb$ with $(C_5Me_5)_2UH(DMPE)$, (c) reaction of $[(C_5Me_5)_2U-(L)]^+$ (L = THF, DMPE) with $K(18\text{-crown-}6)(C_5Me_5)$, and (d) reaction of $[(C_5Me_5)_2U][BPh_4]$ with KC_5Me_5. Reaction of $(C_5Me_5)_2UH(DMPE)$ with C_8H_8 forms the product of the $(C_5Me_5)_3U/C_8H_8$ reaction, $[(C_8H_8)(C_5Me_5)U]_2(C_8H_8)$. The X-ray crystal structures of the $(C_5Me_5)_2U-[N(SiMe_3)_2]$ and $[(C_5Me_5)_2U][BPh_4]$ precursors used in this study are reported, as well as the convenient synthesis of a new trivalent uranium precursor, $(C_5Me_5)_2UMe_2K$.

Introduction

One of the recent advances in the organometallic chemistry of the pentamethylcyclopentadienyl ligand has been the synthesis of $(C_5Me_5)_3M$ complexes containing three of these large moieties. Previously, it was thought that such a molecule was too sterically crowded to exist, since the cone angle of $(C_5Me_5)^-$ was thought to be much larger than the 120° necessary for a $(C_5-Me_5)_3M$ complex.[1] However, syntheses of $(C_5Me_5)_3Sm$,[2] $(C_5Me_5)_3Nd$,[3] $(C_5Me_5)_3U$,[4] $(C_5Me_5)_3UX$ (X = Cl, F),[5] and $(C_5Me_4R)_3La$[6] (R = Me, Et, ^iPr, SiMe₃) have shown that this class of compounds is accessible. Interestingly, once the existence of $(C_5Me_5)_3Sm$ was established by one synthetic method[2a] (eq 1), several other syntheses were subsequently found (eqs 2−4).[2b,3,4] Similarly, formation of $(C_5Me_5)_3UCl$ via eq 5 led to four other synthetic routes[5] from either $(C_5Me_5)_3U$[4] or $[(C_5Me_5)_2UCl]_3$.[10]

The only reported synthetic route to $(C_5Me_5)_3U$ is the reaction of the 1,2-bis(dimethylphosphinoethane) adduct of a trivalent uranium hydride, $(C_5Me_5)_2UH(DMPE)$,[7] with tetramethylfulvene[8] (eq 6),[4] which is an analogue of eq 3. Although this route provides $(C_5Me_5)_3U$ in reasonable yield, the tetramethylfulvene precursor requires several steps to prepare and slowly decomposes over time.[8] Since the multiple electron reduction reactivity discovered so far for $(C_5Me_5)_3U$[5,9] indicates that this molecule deserves further study, it was desirable to develop better synthetic routes.

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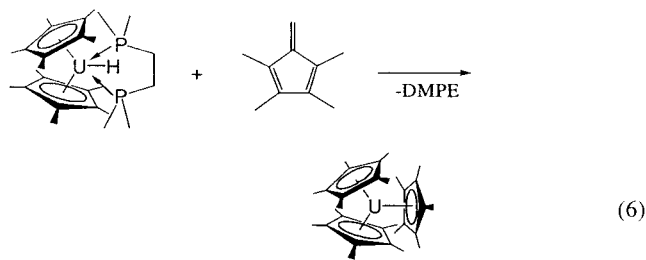(5) Evans, W. J.; Nyce, G. W.; Johnston, M. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2000,** *122,* 12019.
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Since multiple synthetic routes to $(C_5Me_5)_3Sm$ and $(C_5Me_5)_3UCl$ had been found, other routes to $(C_5Me_5)_3U$

$$(6)$$

were sought. We report here four new syntheses of (C₅Me₅)₃U, as well as new synthetic and structural data on three precursors: $[(C_5Me_5)_2U[N(SiMe_3)_2]]$,[10] the unsolvated metallocene cation complex $[(C_5Me_5)_2U][BPh_4]$, and a new U(III) organometallic precursor, $(C_5Me_5)_2$-UMe₂K.

Experimental Section

The complexes described below are extremely air and moisture sensitive. Syntheses and manipulations of these compounds were conducted under nitrogen or argon with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. The argon glovebox used in these experiments was free of coordinating solvents. Silylated glassware was prepared using Silaclad (Gelest). $(C_5Me_5)_2$-UMe₂,[11] $(C_5Me_5)_2UCl_2K$,[10] $(C_5Me_5)_2UH[dmpe]$,[7] $[(C_5Me_5)_2UH_2]_2$,[11] and $Na[N(SiMe_3)_2]$[12] were prepared according to literature procedures. 1,2-Bis(dimethylphosphino)ethane (DMPE) was dried over sieves and degassed before use. Although all of the uranium complexes discussed here are paramagnetic, ¹H NMR spectra were recorded on Bruker DRX 400 and GN 500 spectrometers at 25 °C. Infrared spectra were recorded as thin films on an AST ReactIR 1000 instrument. The extremely air sensitive organouranium complexes were sent to Analytische Laboratorien, Lindlar, Germany, for elemental analysis.

(C₅Me₅)₃U from $[(C_5Me_5)_2UH_2]_2$ and Tetramethylfulvene. In an argon-filled glovebox, $[(C_5Me_5)_2UH_2]_2$ (213 mg, 0.418 mmol) was dissolved in 5 mL of toluene in a glass vial equipped with a stirbar. Tetramethylfulvene (112 mg, 0.840 mmol) was dissolved in toluene and was slowly added to the stirred $[(C_5Me_5)_2UH_2]_2$ solution. The solution immediately turned dark brown, and the reaction mixture was stirred for 5 min. The solvent was removed by rotary evaporation to yield a dark brown powder. Recrystallization of the powder yielded (C₅Me₅)₃U (135 mg, 50%), identified by ¹H NMR spectroscopy.[4]

(C₅Me₅)₃U from (C₅Me₅)₂UH(DMPE) and (C₅Me₅)₂Pb. In an argon-filled glovebox, (C₅Me₅)₂UH(DMPE) (50 mg, 0.076 mmol) and (C₅Me₅)₂Pb (18 mg, 0.038 mmol) were combined in a glass vial equipped with a stirbar. The vial was then wrapped with aluminum foil. Hexanes (5 mL) were added to the vial, and the reaction mixture was stirred for 24 h. The solvent was removed by rotary evaporation, and the reaction mixture was redissolved in toluene. Centrifugation of the reaction mixture removed Pb (7.6 mg), and the solvent was removed by rotary evaporation to yield (C₅Me₅)₃U (45 mg, 92%), identified by ¹H NMR spectroscopy.[4]

$[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$ from (C₅Me₅)₂UH(DMPE) and C₈H₈. Addition of C₈H₈ (24 mg, 0.23 mmol) in an argon-filled glovebox to a stirred benzene (5 mL) solution of (C₅Me₅)₂UH-[DMPE] (38 mg, 0.057 mmol) caused an immediate color change from black to brown. After 3 h, the solvent was removed by rotary evaporation to yield a tacky brown solid. The product was washed with hexanes and dried under

vacuum to yield $[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$ (24 mg, 88%), identified by ¹H NMR spectroscopy.[9]

(C₅Me₅)₂U[N(SiMe₃)₂] (1).[13] In an argon-filled glovebox, a toluene solution of $Na[N(SiMe_3)_2]$ (27 mg, 0.147 mmol) was added to a slurry of $(C_5Me_5)_2UCl_2K$ (100 mg, 0.147 mmol) in ca. 5 mL of toluene. After 1 h, the reaction mixture had turned from green to black. This mixture was then stirred for an additional 6 h. A white precipitate was removed from the reaction mixture by centrifugation to yield a black solution. Toluene was removed by rotary evaporation to yield **1** as a blue-black solid (74 mg, 75%). ¹H NMR (C₆D₆): δ −5.7 (s, C₅Me₅); −25.5 (br s, N(SiMe₃)₂, $\Delta\nu_{1/2}$ = 920 Hz). Crystals suitable for X-ray diffraction were grown by slowly cooling a saturated hexane solution of **2** to −30 °C.

(C₅Me₅)₂UMe₂K (2). In an argon-filled glovebox, potassium metal (29 mg, 0.742 mmol) was added to a stirred toluene solution of (C₅Me₅)₂UMe₂ (400 mg, 0.742 mmol). After 8 h, a green precipitate was observed. The reaction mixture was stirred for an additional 48 h and then filtered to leave **2** as a pale green powder (407 mg, 95%). ¹H NMR (THF-d_8): δ −11.9 (s, C₅Me₅, $\Delta\nu_{1/2}$ = 15 Hz). Only the ring methyl resonances were located in the ¹H NMR spectrum. $[(C_5Me_5)_2UMe_2K$-$(THF)_x]$: IR (cm⁻¹) 2957 s, 2903 vs, 2853 vs, 2721 w, 1444 s, 1374 m, 1258 m, 1239 m, 1058 vs, 1031 s, 942 m, 903 s, 826 m, 803 m, 664 s. Anal. Calcd for C₂₂H₃₆UK: C, 45.74; H, 6.28; U, 41.21; K, 6.77. Found: C, 44.56; H, 6.00; U, 42.55, K, 7.05.

$[(C_5Me_5)_2U(THF)_2][BPh_4]$ (3).[14] In the glovebox, [Et₃NH]-[BPh₄] (219 mg, 0.52 mmol) was dissolved in THF and slowly added to a dark brown stirred solution of **2** (150 mg, 0.26 mmol). Upon addition, gas evolution was immediately observed and the solution turned emerald green with formation of a white precipitate. After the mixture was stirred for an additional 30 min, the white precipitate was removed by centrifugation. The solvent was removed by rotary evaporation to yield **3** as an emerald green powder (240 mg, 95%). Characterization was consistent with literature values.[14]

(C₅Me₅)₃U from 3 and K(18-crown-6)(C₅Me₅). In an argon-filled glovebox, a green suspension of **3** (104 mg, 0.107 mmol) in 5 mL of benzene was added to a yellow solution of KC₅Me₅ (18 mg, 0.106 mmol) and 18-crown-6 (28 mg, 0.106 mmol) in 5 mL of benzene. Upon addition, the solution immediately turned brown. The reaction mixture was stirred for 12 h. Centrifugation removed a white precipitate, and the solvent was removed by rotary evaporation to yield (C₅Me₅)₃U (35 mg, 50%), identified by ¹H NMR spectroscopy.[4]

$[(C_5Me_5)_2U(DMPE)][BPh_4]$ (4).[14] In an argon-filled glovebox, (C₅Me₅)₂UH(DMPE) (95 mg, 0.144 mmol) was partially dissolved in 5 mL of toluene to form a black solution. Upon addition of [Et₃NH][BPh₄] (60 mg, 0.144 mmol) to the reaction mixture, immediate gas evolution was observed. The reaction mixture was stirred for an additional 2 h. A green precipitate was isolated by centrifugation and dried under vacuum to yield **4** (130 mg, 93%) as a light green powder. Characterization was consistent with literature values.[14]

(C₅Me₅)₃U from 4 and K(18-crown-6)(C₅Me₅). In an argon-filled glovebox, a green suspension of **4** (143 mg, 0.146 mmol) in 5 mL of benzene was added to a yellow solution of KC₅Me₅ (24 mg, 0.14 mmol) and 18-crown-6 (37 mg, 0.14 mmol) in 5 mL of benzene. Upon addition, the solution immediately turned brown. The reaction mixture was stirred for 12 h. Centrifugation removed a white precipitate, and the solvent was removed by rotary evaporation to yield (C₅Me₅)₃U (63 mg, 70%), identified by ¹H NMR spectroscopy.[4]

$[(C_5Me_5)_2U][BPh_4]$ (5). In an argon-filled glovebox, [Et₃NH][BPh₄] (357 mg, 0.848 mmol) was added to a slurry of **2** (245 mg, 0.424 mmol) in ca. 10 mL of benzene. The reaction

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(13) This is a modification of an existing procedure.[10]

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mixture immediately began to turn brown, and gas evolution was observed. The mixture was stirred for 6 h. A white precipitate was removed by centrifugation, and the solvent was removed by rotary evaporation to yield **5** as a brown powder (291 mg, 83%). ^1H NMR (C_6D_6): δ 4.7 (s, C_5Me_5, $\Delta\nu_{1/2}$ = 55 Hz). Only the ring methyl resonances were located in the ^1H NMR spectrum. IR (cm^{-1}): 3057 s, 3038 s, 2961 s, 2910 vs, 2856 s, 1961 w, 1903 w, 1884 w, 1818 w, 1590 s, 1478 s, 1432 s, 1378 s, 1378 s, 1316 m, 1262 vs, 1239 vs, 1185 s, 1154 s, 1092 s, 1069 s, 1031 s, 1019 s, 883 m, 841 m, 803 m, 745 m, 702 vs, 679 vs. Anal. Calcd for $C_{44}H_{50}UB$: C, 63.85; H, 6.09; U, 28.76. Found: C, 63.15; H, 5.77; U, 29.60.

(C_5Me_5)$_3$U from [(C_5Me_5)$_2$U][BPh_4] (5). In an argon-filled glovebox, **5** (150 mg, 0.18 mmol) was combined with 10 mL of benzene, in a silylated glass vial equipped with a stir bar, to form a dark brown solution. KC_5Me_5 (35 mg, 0.19 mmol) was added to the stirred solution. The reaction mixture was stirred for 9 h at room temperature. A white precipitate was removed by centrifugation, and the solvent was removed by rotary evaporation to yield (C_5Me_5)$_3$U (98 mg, 85%), identified by ^1H NMR spectroscopy.

X-ray Data Collection, Structure Determination, and Refinement for (C_5Me_5)$_2$U[N(SiMe_3)$_2$] (1). A black crystal of approximate dimensions 0.16 × 0.17 × 0.23 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[15] program package was used to determine the unit cell parameters and for data collection (30 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[16] and SADABS[17] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[18] program. The systematic absences were consistent with the rhombohedral space groups $R3$ and $R\bar{3}$. It was later determined that the centrosymmetric space group $R\bar{3}$ was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0541 and GOF = 1.052 for 271 variables refined against 7061 data (as comparison for refinement on F, R1 = 0.0220 for those 6278 data with I > 2.0$\sigma(I)$). Experimental parameters for data collection and structure refinement for **1** are given in Table 1. Selected bond distances and angles for **1** are given in Table 2.

X-ray Data Collection, Structure Determination, and Refinement for [(C_5Me_5)$_2$U][BPh_4]·C_6H_6. A brown crystal of approximate dimensions 0.03 × 0.07 × 0.23 mm was handled as described for **1**. The diffraction symmetry was 2/m, and systematic absences were consistent with the centrosymmetric space group $P2_1/c$, which was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. There was one molecule of benzene solvent per formula unit. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0887 and GOF = 1.045 for 469 variables refined against 6980 unique data (as comparison for refinement on F, R1 = 0.0426 for those 4862 data with I > 2.0$\sigma(I)$). The data were very weak. The final least-squares refinement was limited to data with 0.85 Å resolution. Experimental parameters for data collection and

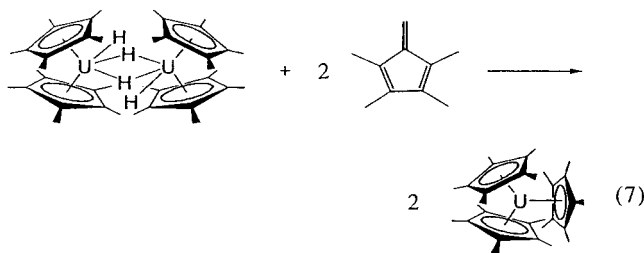(15) *SMART Software Users Guide, Version 5.0*; Bruker Analytical X-ray Systems: Madison, WI, 1999.
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Table 1. Data Collection Parameters[a] for (C_5Me_5)$_2$U[N(SiMe_3)$_2$] (1) and [(C_5Me_5)$_2$U][BPh_4]·C_6H_6 (5·C_6H_6)

	1	**5·C_6H_6**
formula	$C_{26}H_{48}NSi_2U$	$C_{44}H_{50}BU·C_6H_6$
fw	668.86	905.79
temp (K)	163(2)	163(2)
cryst syst	rhombohedral	monoclinic
space group	$R\bar{3}$	$P2_1/c$
a (Å)	17.7735(4)	10.9677(5)
b (Å)	17.7735(4)	27.9202(13)
c (Å)	47.2029(13)	13.5321(7)
α (deg)	90	90
β (deg)	90	98.0130(10)
γ (deg)	120	90
V (Å^3)	12913.5(5)	4103.3(3)
Z	18	4
ρ_{calcd} (Mg/m^3)	1.548	1.466
μ (mm^{-1})	5.752	3.989
R1	0.0220	0.0426
wR2 (I > 2$\sigma(I)$)	0.0519	0.0887

[a] Radiation: Mo Kα (μ = 0.710 73 Å). Monochromator: highly oriented graphite. R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_c|$; wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (C_5Me_5)$_2$U[N(SiMe_3)$_2$] (1)

U–Cnt1[a]	2.532	N–Si(1)	1.696(3)
U–Cnt2[b]	2.523	N–Si(2)	1.699(3)
U–N(1)	2.352(2)	Si(1)–C(21)	1.871(4)
U–C(1)	2.826(3)	Si(1)–C(22)	1.874(4)
U–C(2)	2.816(3)	Si(1)–C(23)	1.892(4)
U–C(3)	2.800(3)	Si(2)–C(24)	1.868(4)
U–C(4)	2.788(3)	Si(2)–C(25)	1.869(4)
U–C(5)	2.783(3)	Si(2)–C(26)	1.891(4)
U–C(11)	2.791(3)	U–C(14)	2.806(3)
U–C(12)	2.781(3)	U–C(15)	2.787(3)
U–C(13)	2.808(3)	U–C(23)	3.197(4)
U–C(26)	3.222(4)		
Cnt1–U–N	113.1	Cnt2–U–N	114.6
Cnt1–U–Cnt2	132.4	Si(1)–N–Si(2)	131.36(16)
Si(1)–N–U	114.12(13)	Si(2)–N–U	114.48(13)
N–Si(1)–C(23)	105.8(1)	N–Si(2)–C(26)	106.1(1)

[a] Cnt1 is the centroid of the C(1)–C(5) ring. [b] Cnt2 is the centroid of the C(11)–C(15) ring.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [(C_5Me_5)$_2$U][BPh_4] (5)

U–Cnt1[a]	2.490	U–C(11)	2.808(7)
U–Cnt2[b]	2.516	U–C(12)	2.755(8)
U–C(1)	2.787(7)	U–C(13)	2.755(7)
U–C(2)	2.746(7)	U–C(14)	2.790(7)
U–C(3)	2.753(7)	U–C(15)	2.830(8)
U–C(4)	2.745(8)	U–C(22)	2.857(7)
U–C(5)	2.796(8)	U–C(28)	2.880(7)
U–C(23)	3.138(8)	U–C(29)	3.166(8)
B–C(21)	1.637(11)	B–C(33)	1.619(11)
B–C(27)	1.637(11)	B–C(39)	1.650(11)
Cnt1–U–Cnt2	132.7	C22–U–C23	65.5(2)
Cnt1–U–C22	101.9	Cnt2–U–C22	116.3
Cnt2–U–C23	98.1	Cnt2–U–C23	103.7

[a] Cnt1 is the centroid of the C(1)–C(5) ring. [b] Cnt2 is the centroid of the C(11)–C(15) ring.

structure refinement for **5** are given in Table 1. Selected bond distances and angles for **5** are given in Table 3.

Results

New Syntheses: Tetramethylfulvene Routes. Reaction of (C_5Me_5)$_2$UH(DMPE) with tetramethylfulvene (TMF) (eq 6) was the first successful synthesis of (C_5-

Me$_5$)$_3$U. This route was originally examined in analogy to the [(C$_5$Me$_5$)$_2$SmH]$_2$-based synthesis of (C$_5$Me$_5$)$_3$Sm (eq 3). It has now been found that this tetramethylfulvene route can also provide (C$_5$Me$_5$)$_3$U, starting from the U(IV) hydride [(C$_5$Me$_5$)$_2$UH$_2$]$_2$,[11] in 50% yield (eq 7).


The mechanism of this reaction is unknown, but the insertion of TMF into one of the U^{IV}−H bonds to form a (C$_5$Me$_5$)$^-$ ring may lead to the reductive elimination of hydrogen to generate the U(III) product, (C$_5$Me$_5$)$_3$U. Reductive elimination of hydrogen from U(IV) hydride complexes to yield U(III) products has been observed in other systems.[11,20−22]

(C$_5$Me$_5$)$_2$Pb As a Reagent. To mimic the reductive route used in the (C$_5$Me$_5$)$_2$Sm/(C$_5$Me$_5$)$_2$Pb reaction (eq 2), the reduction of (C$_5$Me$_5$)$_2$Pb with (C$_5$Me$_5$)$_2$UH-(DMPE) was studied. The U(III) reduction of (C$_5$Me$_5$)$_2$-Pb could form (C$_5$Me$_5$)$_3$UH, in direct analogy to eq 2, or it could generate hydrogen and (C$_5$Me$_5$)$_3$U directly. No evidence for the formation of (C$_5$Me$_5$)$_3$UH was observed, but the (C$_5$Me$_5$)$_2$UH(DMPE)/(C$_5$Me$_5$)$_2$Pb reaction does produce (C$_5$Me$_5$)$_3$U in 90% yield (eq 8). This constitutes a third synthetic route to (C$_5$Me$_5$)$_3$U.
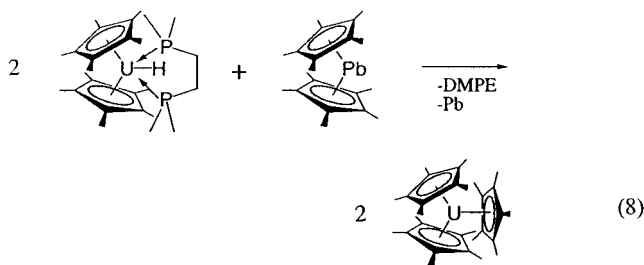
Cyclooctatetraene as a Reagent. The original synthesis of (C$_5$Me$_5$)$_3$Sm involved Sm(II) reduction of 1,3,5,7-cyclooctatetraene (eq 1). The analogous reduction using (C$_5$Me$_5$)$_2$UH(DMPE) did not form (C$_5$Me$_5$)$_3$U but instead gave [(C$_8$H$_8$)(C$_5$Me$_5$)U]$_2$(C$_8$H$_8$) (eq 9), the product
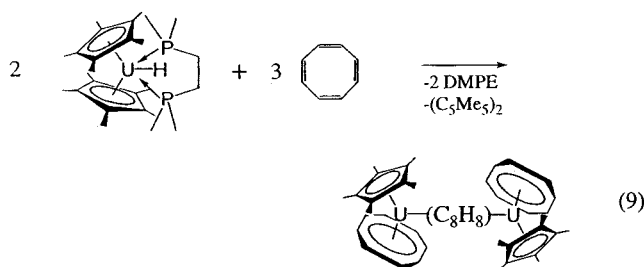
obtained by reacting (C$_5$Me$_5$)$_3$U with cyclooctatetraene.[23] Although eq 9 is not a new route to (C$_5$Me$_5$)$_3$U, it is an

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improved synthesis of [(C$_8$H$_8$)(C$_5$Me$_5$)U]$_2$(C$_8$H$_8$), since reaction times are shorter and the synthesis does not require the preparation of (C$_5$Me$_5$)$_3$U.

Reactions Based on Cationic Precursors. After successfully mimicking the Sm-based reactions described above, attention was turned to developing a route analogous to eq 4, involving the reaction of a (C$_5$Me$_5$)$^-$ salt with a [(C$_5$Me$_5$)$_2$M]$^+$ cation. This cationic route was used to make (C$_5$Me$_5$)$_3$Nd[3] as well as the (C$_5$-Me$_4$R)$_3$La[6] complexes (R = Me, Et, ^{i}Pr, SiMe$_3$) and appears to be the best route if an analogue of divalent (C$_5$Me$_5$)$_2$Sm is unavailable. In the Sm and Nd cases, it was essential that the cationic precursor, [(C$_5$Me$_5$)$_2$Ln]-[BPh$_4$], be THF-free, since (C$_5$Me$_5$)$_3$Ln complexes ring-open THF to form (C$_5$Me$_5$)$_2$Ln[O(CH$_2$)$_4$C$_5$Me$_5$][24,25] and KC$_5$Me$_5$ reacts with [(C$_5$Me$_5$)$_2$Ln(THF)$_2$]$^+$ to make the same ring-opened product. However, (C$_5$Me$_5$)$_3$U does not ring-open THF as readily as (C$_5$Me$_5$)$_3$Sm. Thus, solvated and unsolvated cations were examined.

One route to an appropriate solvated cationic precursor involves the protonation of (C$_5$Me$_5$)$_2$U[N(SiMe$_3$)$_2$] (**1**) with [NH$_4$][BPh$_4$] to make [(C$_5$Me$_5$)$_2$U(THF)$_2$][BPh$_4$][14] (**3**). Since high yields of this cation were not readily obtainable in our hands, we questioned the purity of the (C$_5$Me$_5$)$_2$U[N(SiMe$_3$)$_2$] precursor that we had prepared. To definitively confirm the identity of the (C$_5$Me$_5$)$_2$U-[N(SiMe$_3$)$_2$] precursor, the crystal structure of this complex was determined and is described below. Concomitantly, we developed an alternative synthesis of **3** involving the new trivalent precursor (C$_5$Me$_5$)$_2$UMe$_2$K (**2**). This complex has not been reported in the literature, to our knowledge, and can be synthesized in high yield by reacting (C$_5$Me$_5$)$_2$UMe$_2$ [11] with potassium in toluene or benzene (eq 10). Although this compound was not

$$(C_5Me_5)_2UMe_2 + K \rightarrow (C_5Me_5)_2UMe_2K \quad (10)$$
$$\mathbf{2}$$
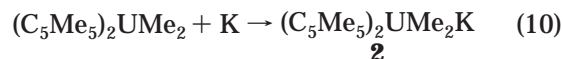
characterized by X-ray crystallography, its analytical data and reactivity are consistent with the formula (C$_5$-Me$_5$)$_2$UMe$_2$K. Unlike (C$_5$Me$_5$)$_2$UMe$_2$, **2** is insoluble in arenes and can be easily isolated by filtration or centrifugation. Protonation of **2** with [Et$_3$NH][BPh$_4$] in THF afforded **3** in excellent yield.

The reaction of **3** with KC$_5$Me$_5$ in arene solvents does not yield (C$_5$Me$_5$)$_3$U, perhaps because both reactants are insoluble. However, addition of 18-crown-6 partially solubilizes KC$_5$Me$_5$ in arene solvents[26] and allows (C$_5$-Me$_5$)$_3$U to be made by this route in 50% yield (eq 11).
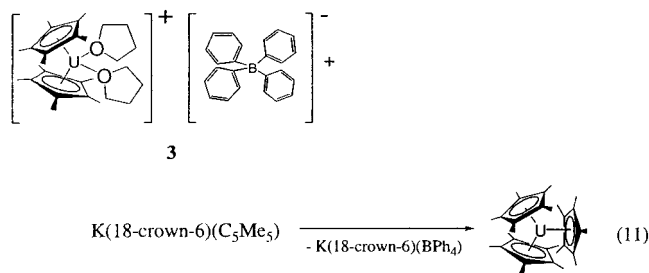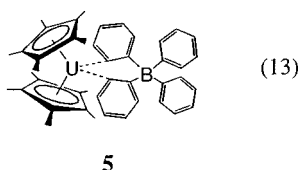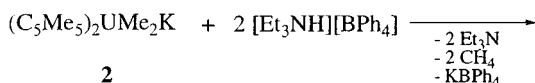

Interestingly, small amounts of THF do not prevent the isolation of (C$_5$Me$_5$)$_3$U.

An alternative solvated cation approach involved the cation formed by the reaction of (C$_5$Me$_5$)$_2$UH(DMPE)

with $[Et_3NH][BPh_4]$ to form $[(C_5Me_5)_2U(DMPE)][BPh_4]$[14] (**4**). Complex **4** also reacts with $K(18\text{-crown-}6)(C_5Me_5)$, in toluene, to produce $(C_5Me_5)_3U$ in 70% yield (eq 12).

$$[(C_5Me_5)_2U(DMPE)][BPh_4] +$$
$$K(18\text{-crown-}6)(C_5Me_5) \xrightarrow[-DMPE]{-K(18\text{-crown-}6)(BPh_4),}$$
$$(C_5Me_5)_3U \quad (12)$$
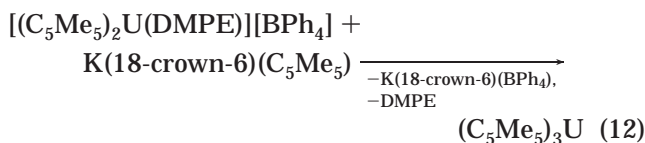
The synthesis of $(C_5Me_5)_3U$ from an unsolvated cation required that a synthetic route to the unsolvated cationic precursor, $[(C_5Me_5)_2U][BPh_4]$, be developed. Although **2** and $[Et_3NH][BPh_4]$ are both insoluble in arene solvents, they react cleanly to form $[(C_5Me_5)_2U][BPh_4]$ (**5**) and $KBPh_4$ (eq 13). **5** is soluble in benzene and can

$$(C_5Me_5)_2UMe_2K \quad + \quad 2\,[Et_3NH][BPh_4] \xrightarrow[\substack{-\,2\,Et_3N \\ -\,2\,CH_4 \\ -\,KBPh_4}]{}$$

2

(13)

5

be separated from the insoluble $KBPh_4$ byproduct. As described below, the X-ray structure of the unsolvated cation **5** was also determined to see how the anion approached the metallocene cation.

The cationic complex **5** reacts with KC_5Me_5 in benzene to form $(C_5Me_5)_3U$, but the yield was <20%. Recently, in investigations of cationic routes to $(C_5Me_4R)_3La$ complexes,[6] we have found that, for some $(C_5Me_4R)_3La$ complexes,[6] it was beneficial to conduct the reaction in silylated glassware. When silylated glassware was used, the $(C_5Me_5)_3U$ yield was improved to 85% (eq 14).

5

$+ \; K(C_5Me_5) \xrightarrow[-KBPh_4]{}$

(14)
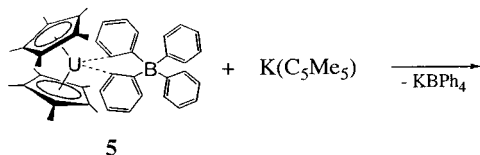
Structural Studies. $(C_5Me_5)_2U[N(SiMe_3)_2]$ (**1**; Figure 1) was found to be isomorphous with $(C_5Me_5)_2Sm[N(SiMe_3)_2]$[27] (**6**), which is similar to but not isomorphous with $(C_5Me_5)_2Y[N(SiMe_3)_2]$.[28] All of the distances in **1** are about 0.05 Å longer than those in **6**, which is close to the 0.067 Å difference between six-coordinate

Figure 1. Plot of $(C_5Me_5)_2U[N(SiMe_3)_2]$ (**1**), with thermal ellipsoids drawn at the 50% probability level.

U(III) and Sm(III), the only M(III) comparison possible for these elements in the table of Shannon radii.[29] Hence, **1** has $U-(C_5Me_5)$ ring centroid distances of 2.523 and 2.532 Å compared to 2.470 and 2.479 Å in **6** and the M–N distances are 2.352(2) and 2.301(3) Å, respectively. Like **6**, **1** contains small N–Si–C angles which are often associated with agostic $M-H-CH_2-Si$ or M–C–Si interactions in $N(SiMe_3)_2$ complexes.[30–33] The 105.78(14)° N–Si(1)–C(23) and 106.09(15)° N–Si(2)–C(26) angles are both smaller than the other N–Si–C angles in **1**, which range from 113.16(17) to 115.1(2)°. However, the U–C(23) and U–C(26) distances, 3.197(4) and 3.222(4) Å, respectively, are not close to the very short 2.80(2) and 2.86(2) Å U–C distances noted for two of the silylmethyl carbon atoms in $(C_5Me_5)U[N(SiMe_3)_2]_2$.[34] Hence, the situation is like that in **6**, in which small angles do not correlate with close Sm–C contacts.

$[(C_5Me_5)_2U][BPh_4]$ (**5**; Figure 2) cocrystallized with C_6H_6 as $[(C_5Me_5)_2U][BPh_4]\cdot C_6H_6$ and hence is not isomorphous with the Sm analogue $[(C_5Me_5)_2Sm][BPh_4]$ (**7**).[35] However, the two structures are similar. The

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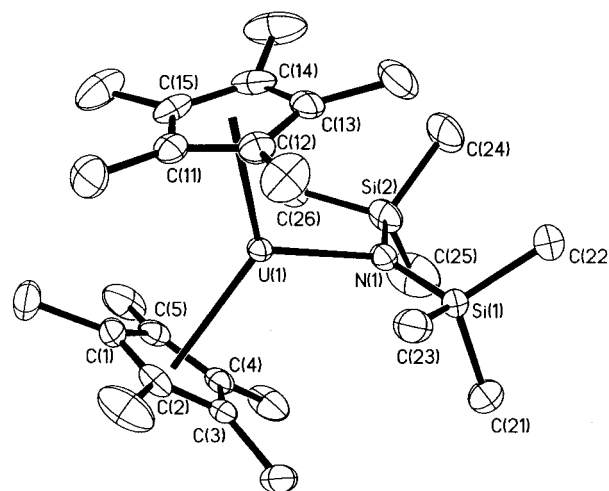
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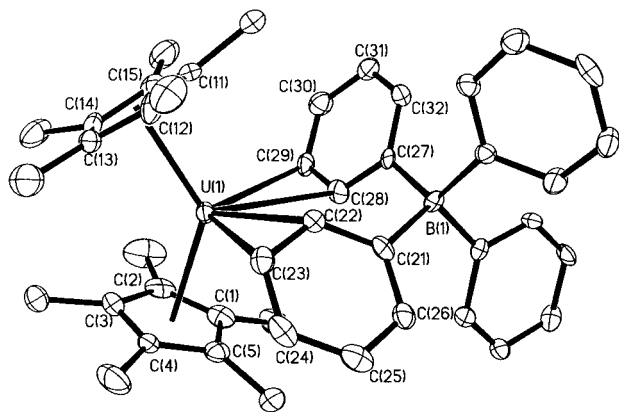
Figure 2. Plot of $[(C_5Me_5)_2U][BPh_4]$ (**5**), with thermal ellipsoids drawn at the 50% probability level.

2.77(3) Å U$-$C(C$_5$Me$_5$) average distance is as expected compared to the 2.70(2) Å Sm analogue, when the differences in ionic radii are taken into account. The 132.7° (C$_5$Me$_5$)$-$U$-$(C$_5$Me$_5$) ring centroid angle is also similar to the 134.4° value in **7**.

In each of these complexes, the [BPh$_4$]$^-$ approaches the cation through two ortho carbon positions, C(22) and C(28). For **5**, these 2.857(7) and 2.880(7) Å distances are intermediate between the 2.825(3) and 2.917(3) Å distances in **7**. The next closest U$-$C(BPh$_4$) distances, 3.138(8) and 3.166(8) Å, for U$-$C(23) and U$-$C(29) are also intermediate between the analogous distances in **7**, 3.059(3) and 3.175(3) Å. The 69.3(2)° C(22)$-$U-C(28) angle is similar to the 67.8(3)° C(22)$-$Sm$-$C(28) angle. The dihedral angles between the planes defined by U, C22, C23 and C22, C23, and the C21$-$C26 arene ring centroid (128°) and U, C28, C29, and C28, C29, and the C27$-$C32 arene ring centroid (122°) show that the arene rings do not approach the uranium directly via the edge or face of the ring.

The six C$-$B$-$C angles around boron in **5** span a wider range, 102.2(6)$-$115.4(6)°, than the 107.5(2)$-$110.9(2)° angles in **7**. The B$-$C distances of the interacting rings, B$-$C(21) and B$-$C(27), have lengths which happen to be equivalent, 1.637(11) Å, and are intermediate between those of the other rings: B$-$C(33) = 1.619(11) Å, and B$-$C(39) = 1.650(10) Å. Hence, no effect on the local geometry around the boron is observed by coordination of the anion to the cation.

Discussion

Like (C$_5$Me$_5$)$_3$Sm and (C$_5$Me$_5$)$_3$UCl, (C$_5$Me$_5$)$_3$U can also be made by several different routes. Syntheses similar or analogous to three of the four routes to (C$_5$Me$_5$)$_3$Sm (eqs 2$-$4) are available for (C$_5$Me$_5$)$_3$U, even though Sm(II)/Sm(III) chemistry and U(III)/U(IV) chemistry have significant differences. These results suggest that there may be more connections between samarium and uranium chemistry, if the appropriate modifications in procedures and starting materials are made.

The first synthesis of (C$_5$Me$_5$)$_3$U from a U(III) hydride and tetramethylfulvene (eq 6) was exactly analogous.

Direct analogues of the reductive reactions used to make (C$_5$Me$_5$)$_3$Sm from the Sm(II) precursors (eqs 1 and 2) were not possible, since U(II) precursors are unavailable. However, reductive approaches using U(III) reducing agents are successful because of the tendency of U(IV) hydrides to form U(III) complexes. Hence, the U(III) product, (C$_5$Me$_5$)$_3$U, can be obtained using the U(III) hydride precursor (C$_5$Me$_5$)$_2$UH(DMPE) to reduce (C$_5$Me$_5$)$_2$Pb (eq 8) in a reaction with similarities to the (C$_5$Me$_5$)$_2$Sm(OEt$_2$) reduction in eq 2. The U(IV) hydride to U(III) conversion can also be used to make trivalent (C$_5$Me$_5$)$_3$U from the U(IV) hydride [(C$_5$Me$_5$)$_2$UH$_2$]$_2$ and tetramethylfulvene (eq 7).

The remaining new syntheses are based on the trivalent cationic precursors [(C$_5$Me$_5$)$_2$U]$^+$, which are formally similar to the samarium and neodymium systems.[3] Subtle differences arise, since (C$_5$Me$_5$)$_3$U is more THF tolerant than (C$_5$Me$_5$)$_3$Sm; thus, a THF-solvated uranium cation is a suitable precursor to the synthesis of (C$_5$Me$_5$)$_3$U (eq 11). Solubility problems of the solvated uranium cations can be overcome by using the 18-crown-6 solubilized K(C$_5$Me$_5$) (eqs 11 and 12). The reaction of the unsolvated [(C$_5$Me$_5$)$_2$U][BPh$_4$] with K(C$_5$Me$_5$) (eq 14) is analogous to the samarium case, except that silylated glassware was needed to obtain high yields.

The synthesis of [(C$_5$Me$_5$)$_2$U][BPh$_4$] required the development of a new trivalent uranium compound, (C$_5$Me$_5$)$_2$UMe$_2$K. Since (C$_5$Me$_5$)$_2$UMe$_2$K and [(C$_5$Me$_5$)$_2$U][BPh$_4$] are readily synthesized and easily isolated, these compounds are the most convenient precursors for the synthesis of (C$_5$Me$_5$)$_3$U. Hence, eq 14 is the preferred synthesis of all those discovered so far.

Conclusion

Several synthetic routes to (C$_5$Me$_5$)$_3$U are now available, just as several have been developed for (C$_5$Me$_5$)$_3$Sm and (C$_5$Me$_5$)$_3$UCl. In addition to the new syntheses, the multiple synthetic connections between uranium and samarium syntheses shown in this study suggest that, with the appropriate modifications, analogous chemistry can be developed between U(III) and Sm(III). The structural studies on (C$_5$Me$_5$)$_2$U[N(SiMe$_3$)$_2$] and [(C$_5$Me$_5$)$_2$U][BPh$_4$] also show that similarities exists between trivalent uranium and trivalent samarium coordination chemistry.

There are now 13 different reactions that are known to form (C$_5$Me$_5$)$_3$M complexes, a class of compounds originally thought to be too crowded to exist. In retrospect, most of the routes are quite reasonable, but they were not attempted most probably due to the expectation that the products would not be isolable.

Supporting Information Available: Tables of crystallographic data and figures giving additional views of compounds **1** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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