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Facile Triphenylborane-Based Syntheses of the Sterically Crowded Tris(pentamethylcyclopentadienyl) Complexes $(C_5Me_5)_3UMe$ and $(C_5Me_5)_3UCl$

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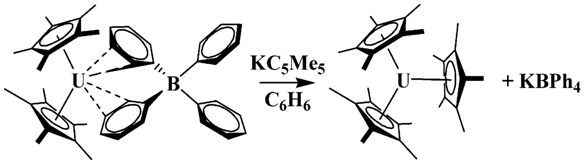
An atom- and time-efficient synthetic route to sterically crowded organoactinide $(C_5Me_5)_3UX$ complexes involving the in situ formation of borate salts is reported. Addition of BPh_3 to $(C_5Me_5)_2UMeCl$ followed by KC_5Me_5 provides a much improved synthesis of $(C_5Me_5)_3UCl$ that presumably proceeds through a $[(C_5Me_5)_2UCl][MeBPh_3]$ intermediate borate salt. Attempts to make $(C_5Me_5)_3UMe$, the first tris(pentamethylcyclopentadienyl) metal alkyl complex, by reaction of BPh_3 with $(C_5Me_5)_2UMe_2$ followed by KC_5Me_5 were also successful, and the product was characterized by X-ray crystallography. In this reaction system, the formation of the borate intermediate, $[(C_5Me_5)_2UMe][MeBPh_3]$, was confirmed by variable-temperature NMR spectroscopy and by X-ray crystallography of the THF adduct.

Introduction

Recent synthetic advances in f element organometallic chemistry have shown that an entire family of tris(pentamethylcyclopentadienyl) metal complexes can be isolated in which all of the metal ligand bonds are longer than normal.[1] This was unexpected since metal−ligand distances in f element complexes are generally quite regular from one complex to another.[2−6] Prior to the isolation of $(C_5Me_5)_3Sm$,[7] it also seemed sterically impossible to put three $(C_5Me_5)^-$ groups around one metal center. The subsequent isolation of $(C_5Me_5)_3UCl$[8] demonstrated that, in addition to three $(C_5Me_5)^-$ groups, a metal could also accommodate a fourth ligand. In each of the subsequently isolated $(C_5Me_5)_3MX$ (X = H,[9] F,[8] Cl[8]) and $(C_5Me_5)_3ML$ (L = CO,[10] N_2[11]) complexes, the fourth ligand is either a single atom or a small, cylindrical molecule that could fit into the space along the C_3 axis perpendicular to the plane defined by the metal and the three ring centroids, Figure 1.

These long bond organometallic complexes are highly reactive since unusual $(C_5Me_5)^-$ reactivity accompanies the unconventional bond distances.[1] This includes an η^1-C_5Me_5 alkyl-like reactivity, $(C_5Me_5)^-$-based reduction called sterically induced reduction (SIR),[12] and unexpectedly facile $(C_5Me_5)^-$ displacement.[13] In contrast, the $(C_5Me_5)^-$ ligands in complexes displaying "normal" M−C bond distances are generally inert ancillary ligands.

Devising synthetic routes to these highly reactive, sterically disfavored, $(C_5Me_5)_3M$ and $(C_5Me_5)_3MX$ complexes is challenging since less crowded alternative products prefer to form if any pathway is available. Currently the highly reactive $(C_5Me_5)_3M$ species are prepared in reactions that produce stable byproducts and leave the three $(C_5Me_5)^-$ ligands as well as the trivalent metal with no alternative but to form the sterically crowded complexes.[9,14−16] One of the most general syntheses involves addition of KC_5Me_5 to a $(BPh_4)^-$ salt, which eliminates $KBPh_4$ and adds a $(C_5Me_5)^-$ ligand, eq 1.



(1)

The $[(C_5Me_5)_2M][(\mu\text{-Ph})_2BPh_2]$ starting materials for these syntheses contain loosely ligated $(BPh_4)^-$ anions that stabilize the cationic metallocenes, but interact only through long M−C(arene) distances.[15,16]

We report here that this borate route for $(C_5Me_5)_3M$ synthesis can also be applied to the synthesis of

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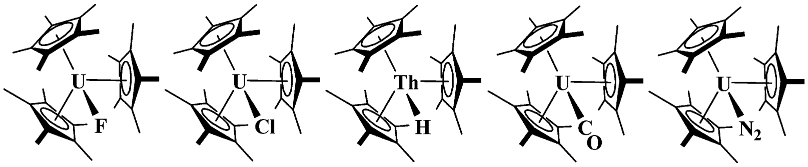

Figure 1. Crystallographically characterized $(C_5Me_5)_3MX$ and $(C_5Me_5)_3UL$ complexes.

$(C_5Me_5)_3UX$ (X = Cl, Me) complexes. In this case, the borate salts are generated in situ by addition of BPh_3 to the appropriate conventional bis(pentamethylcyclopentadienyl) uranium(IV) alkyl complexes. The basis for this approach has actually been in the literature since Fischer and co-workers analyzed the addition of BPh_3 to $(C_5H_5)_3UMe$ in 1988.[17] We describe below the first example of this type of reaction applied to the synthesis of long bond organometallic species. The results demonstrate that $(MeBPh_3)^-$ salts, formed in situ, react analogously to the $(BPh_4)^-$ salts as precursors to sterically crowded complexes.

This approach was initially tested as a route to the previously characterized $(C_5Me_5)_3UCl$[8] and was subsequently used to make the first $(C_5Me_5)_3UX$ complex with a polyatomic X, namely, $(C_5Me_5)_3UMe$. Since alkyl abstraction from metallocenes by Lewis acids to form borate and aluminate salts is extensively studied in polymerization chemistry,[18,19] many variations of the approach demonstrated here can be envisaged based on the cationic complexes available in the literature.

Experimental Section

General Experimental Procedures. The synthesis and manipulations of these extremely air- and moisture-sensitive compounds were conducted with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. Unless otherwise specified, the compounds were handled under argon with rigorous exclusion of coordinating solvents. Glassware was treated with Siliclad (Gelest) to avoid formation of oxide decomposition products. Toluene, benzene, and THF were saturated with Ar and passed through a GlassContour column.[20] Benzene-d_6 and toluene-d_8 (Cambridge Isotope Laboratories) were distilled over NaK alloy and benzophenone and were degassed by three freeze−pump−thaw cycles. BPh_3 (Aldrich) was sublimed (65 °C at 6×10^{-6} Torr) before use. $(C_5Me_5)_2UCl_2$,[21] $(C_5Me_5)_2UMe_2$,[21] and C_5Me_5K[13] were prepared as previously described. NMR experiments were conducted with Bruker 400 or 500 MHz spectrometers, and ^{11}B NMR data were referenced to an external standard of $BF_3{\cdot}OEt_2$. Electronic absorption measurements were made in benzene and conducted using a Perkin-Elmer Lambda 900 UV/vis/NIR spectrophotometer in Teflon sealable 1 cm quartz cells. IR samples were analyzed as thin films from benzene using an ASI ReactIR1000.[22] Elemental analyses were provided by Analytische Laboratorien, Lindlar, Germany.

$(C_5Me_5)_3UCl$, 1. A solution of $(C_5Me_5)_2UMe_2$ (39 mg, 0.072 mmol) in benzene (5 mL) was added to a stirred solution of $(C_5Me_5)_2UCl_2$ (42 mg, 0.072) in benzene (5 mL) to generate $(C_5Me_5)_2UMeCl$.[21] After 5 min, a solution of BPh_3 (35 mg, 0.144 mmol) in benzene (5 mL) was added to the reaction vessel. After the mixture was stirred for 3 h, it was transferred to a silylated flask that had been charged with KC_5Me_5 (36 mg, 0.207 mmol). After the mixture was stirred for an additional 20 h, a white precipitate was removed by centrifugation. The solvent was removed by rotary evaporation, and the previously characterized $(C_5Me_5)_3UCl$[8] was isolated as a red powder (96 mg, 97%) and identified by ^1H NMR spectroscopy.

$[(C_5Me_5)_2UMe][MeBPh_3]$, 2. A red solution of $(C_5Me_5)_2UMe_2$ (202.4 mg, 0.376 mmol) in toluene (7 mL) was added to BPh_3 (91 mg, 0.376 mmol) in toluene (7 mL). After the mixture was stirred for 12 h, the mixture was centrifuged and $[(C_5Me_5)_2UMe][MeBPh_4]$ (291 mg, 99%) was isolated as a red solid upon removal of the solvent by rotary evaporation. ^1H NMR (C_6D_6, 298 K): 7.6 (m, br B*Ph*$_3$), 7.2 (m, br $\Delta\nu_{1/2}$ = 90 Hz, B*Ph*$_3$), 5.2 (s, 30H, $\Delta\nu_{1/2}$ = 90 Hz, C_5Me_5), −133.2 (s, 6H, $\Delta\nu_{1/2}$ = 190 Hz, *Me*) ppm. ^{11}B NMR (C_6D_6): δ 67.3 ppm. IR: 2961s, 2907s, 2860s, 2725w, 1594s, 1567w, 1494m, 1432s, 1378m, 1355w, 1320s, 1282s, 1239s, 1185m, 1158w, 1096m, 1069m, 1027s, 999m, 884s, 803m, 776m, 745s, 699s, 645s cm^{-1}. Anal. Calcd for $C_{40}H_{54}BU$: C, 61.57; H, 6.54; B, 1.38; U, 30.51. Found: C, 61.38; H, 6.48; B, 1.30; U 30.75. X-ray quality crystals of the THF adduct of **2**, $[(C_5Me_5)_2UMe(THF)][MeBPh_3]$, **2**·THF, formed from a saturated solution of **2** in THF at −35 °C in a nitrogen-filled glovebox.

$(C_5Me_5)_3UMe$, 3, from $(C_5Me_5)_2UMe_2$. Following the procedure for **1**, BPh_3 (142 mg, 0.587 mmol) in benzene (7 mL), $(C_5Me_5)_2UMe_2$ (322 mg, 0.598 mmol) in benzene (7 mL), and KC_5Me_5 (125 mg, 0.718 mmol) were combined to produce $(C_5Me_5)_3UMe$, which was isolated as a red powder (261 mg, 66%). Hexagonal crystals of **3** suitable for crystallographic analysis were grown from benzene solutions at room temperature in an NMR tube by slow evaporation. The synthesis can also be carried out in toluene. ^1H NMR (C_6D_6): δ 9.2 (s, 45H, C_5Me_5, $\Delta\nu_{1/2}$ = 10 Hz); −204 (s, 3H, CH_3, $\Delta\nu_{1/2}$ = 70 Hz) ppm. ^{13}C NMR (C_6D_6): δ −30.5 (s, C_5Me_5), 260.4 (s, C_5Me_5) ppm, assignments confirmed by HMQC. IR (thin film): 2964s, 2910s, 2856s, 2725vw, 1436m, 1378m, 1262s, 1069s, 1019s, 949w, 864w, 799s, 698w, 671m cm^{-1}. Anal. Calcd for $C_{31}H_{48}U$: C, 56.52; H, 7.29. Found: C, 57.65; H, 6.88.

$(C_5Me_5)_3UMe$, 3, from 2. A solution of $[(C_5Me_5)_2UMe][MeBPh_3]$ (298 mg, 0.382 mmol) in benzene (10 mL) was added to silylated flask containing KC_5Me_5 (86 mg, 0.494 mmol). The mixture darkened in color as it stirred for 12 h. A white solid was separated from the red solution by centrifugation. Upon removal of solvent by rotary evaporation, as described above, $(C_5Me_5)_3UMe$, **3**, was isolated as a red powder (154 mg, 61%).

X-ray Data Collection, Structure Solution, and Refinement $[(C_5Me_5)_2UMe(THF)][MeBPh_3]$, 2·THF. A red crystal of approximate dimensions 0.08 × 0.10 × 0.12 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[23] 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[24] and

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Table 1. Crystal Data and Structure Refinement for $[(C_5Me_5)_2UMe(THF)][MeBPh_3]$, 2·THF, and $(C_5Me_5)_3UMe$, 3

	2·THF	**3**
empirical formula	$C_{44}H_{59}BOU$	$C_{31}H_{48}U$
fw	852.75	658.72
space group	$P\bar{1}$	$P6_3/m$
a (Å)	9.299(2)	10.0075(12)
b (Å)	13.881(4)	10.0075(12)
c (Å)	16.137(4)	15.452(4)
α (deg)	69.988(5)	90
β (deg)	83.060(5)	90
γ (deg)	74.169(5)	120
volume (Å^3)	1882.0(8)	1340.2(4)
Z	2	2
λ (Å)	0.71073	0.71073
density$_{calc}$ (Mg/m^3)	1.505	1.632
abs coeff (mm^{-1})	4.344	6.072
goodness-of-fit on F^2	1.045	1.263
R^a [$I > 2\sigma(I)$]: R1	0.0657	0.0294
R^b (all data): wR2	0.1834	0.0719

SADABS[25] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[26] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and 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[27] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The uranium atom was refined anisotropically. All remaining atoms were included using isotropic thermal parameters. At convergence, wR2 = 0.1834 and GOF = 1.045 for 194 variables refined against 6363 data (0.85 Å). As a comparison for refinement on F, R1 = 0.0657 for those 4980 data with $I > 2.0\sigma(I)$, Table 1.

$(C_5Me_5)_3UMe$, 3. A red crystal of approximate dimensions 0.07 × 0.13 × 0.14 mm was handled as described above for **2**·THF. The systematic absences were consistent with the hexagonal space group $P6_3/m$, 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 molecule was located on a site of $\bar{6}$ symmetry. Carbon atom C(7) was disordered and was included with a site-occupancy factor of 1/6. At convergence, wR2 = 0.0719 and GOF = 1.263 for 57 variables refined against 1156 data. As a comparison for refinement on F, R1 = 0.0294 for those 971 data with $I > 2.0\sigma(I)$, Table 1.

Results

Synthesis of $(C_5Me_5)_3UCl$. The most convenient previously reported synthesis of $(C_5Me_5)_3UCl$ proceeds from $(C_5Me_5)_2UMe_2$ in four steps in 62% overall yield via the sequence shown in Scheme 1.[8] Although each step in Scheme 1 proceeds in high yield, the preparation typically required 7 or 8 days.

To shorten this procedure, an attempt was made to synthesize $(C_5Me_5)_3UCl$ in analogy with the KC_5Me_5/$[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ synthesis of $(C_5Me_5)_3U$ in eq 1 by reacting KC_5Me_5 with $[(C_5Me_5)_2UCl][MeBPh_3]$, generated in situ. The precursor to the necessary borate salt, $(C_5Me_5)_2UMeCl$,[21] was conveniently prepared by mixing $(C_5Me_5)_2UMe_2$ and its precursor $(C_5Me_5)_2UCl_2$ with a slight modification of the previously described procedure.[21]

Scheme 1

$$(C_5Me_5)_2UMe_2 + K \longrightarrow (C_5Me_5)_2UMe_2K$$

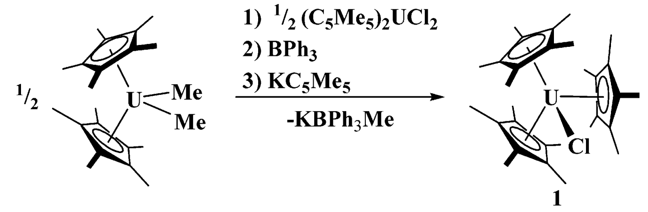
$$(C_5Me_5)_2UMe_2K + 2[HNEt_3][BPh_4] \longrightarrow [(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2] + 2NEt_3 + 2CH_4 + KBPh_4$$

$$[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2] + KC_5Me_5 \longrightarrow (C_5Me_5)_3U + KBPh_4$$

$$(C_5Me_5)_3U + PhCl \longrightarrow (C_5Me_5)_3UCl + {}^1/_2\, Ph_2$$

Addition of 1 equiv of BPh_3 to a silylated vessel charged with $(C_5Me_5)_2UMeCl$ generated a solution that had a ^1H NMR spectrum similar to the starting material, but contained broadened resonances. After 3 h, addition of KC_5Me_5 resulted in precipitation of a white solid, presumably $KMeBPh_4$, which was removed by centrifugation from the red solution. $(C_5Me_5)_3UCl$,[8] **1**, was isolated from the solution as a red powder in >90% yield, Scheme 2.

Scheme 2



Synthesis of $[(C_5Me_5)_2UMe][MeBPh_4]$ and $(C_5Me_5)_3UMe$. The synthesis of $(C_5Me_5)_3UMe$, via the method of Scheme 2, was subsequently attempted to determine if it would provide the first $(C_5Me_5)_3MX$ or $(C_5Me_5)_3ML$ complex in which the fourth ligand is more than a single

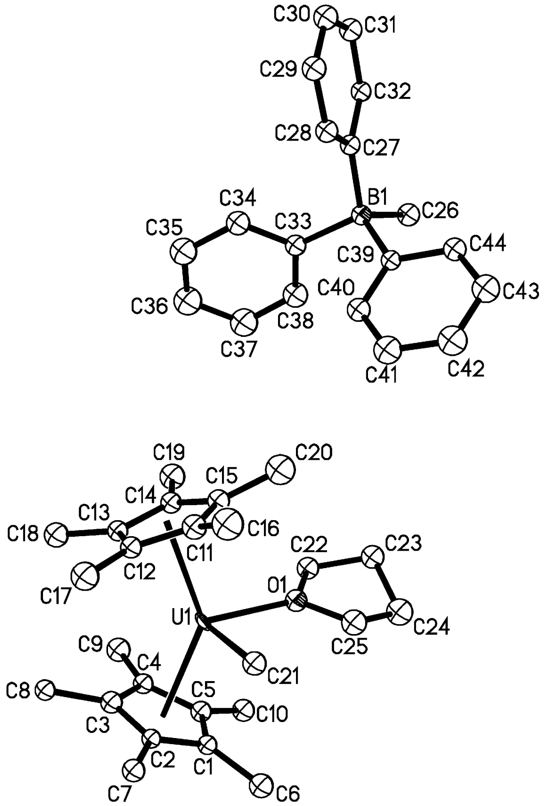


Figure 2. Thermal ellipsoid plot of $[(C_5Me_5)_2UMe(THF)][MeBPh_3]$, **2**·THF, drawn at the 50% probability level.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2UMe(THF)][MeBPh_3]$, 2·THF, and $(C_5Me_5)_3UMe$, 3

2·THF				**3**	
U(1)−O(1)	2.419(8)	U(1)−C(21)	2.393(12)	U(1)−C(7)	2.66(2)
U(1)−C(1)	2.739(11)	U(1)−C(11)	2.751(12)	U(1)−C(1)	2.904(6)
U(1)−C(2)	2.733(11)	U(1)−C(12)	2.733(11)	U(1)−C(2)	2.832(4)
U(1)−C(3)	2.717(12)	U(1)−C(13)	2.704(11)	U(1)−C(3)	2.802(4)
U(1)−C(4)	2.670(12)	U(1)−C(14)	2.687(12)		
U(1)−C(5)	2.703(11)	U(1)−C(15)	2.702(12)		
U(1)−Cnt(1)	2.428	U(1)−Cnt(2)	2.435	U(1)−Cnt	2.418
Cnt(1)−U(1)−O(1)	106.5	Cnt(2)−U(1)−O(1)	106.6		
C(21)−U(1)−Cnt(1)	100.0	C(21)−U(1)−Cnt(2)	98.8	C(7)−U(1)−Cnt	90
O(1)−U(1)−C(21)	94.9(3)	Cnt−U(1)−Cnt	140.0	Cnt−U(1)−Cnt	120

atom (X = H,[9] Cl,[8] and F[8]) or a cylindrical diatomic (L = CO[8] or N_2[8]). In this case, the intermediate borate salt was isolated and fully characterized.

Addition of BPh_3 to $(C_5Me_5)_2UMe_2$ to make the putative borate $[(C_5Me_5)_2UMe][MeBPh_3]$ in situ caused substantial broadening of ^1H NMR resonances without a significant change in chemical shift, as observed in the $(C_5Me_5)_2UMeCl$ reaction in Scheme 2. The room-temperature ^{11}B NMR spectrum of this mixture contained a single broad resonance at 67 ppm consistent with a BPh_3 standard. Variable-temperature NMR experiments in toluene-d_8 suggested that a reversible equilibrium exists between $(C_5Me_5)_2UMe_2$ and BPh_3 and the methyl abstraction product, $[(C_5Me_5)_2UMe][MeBPh_3]$, eq 2. At 268 K the dominant peak in the ^{11}B NMR

$$(C_5Me_5)_2UMe_2 + BPh_3 \rightleftharpoons \underset{\mathbf{2}}{[(C_5Me_5)_2UMe][MeBPh_4]} \tag{2}$$

spectrum is still that of the free BPh_3. However, a resonance at −46 ppm that is similar to the −43 ppm shift of $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ is also observed. In the ^1H NMR spectrum at this temperature, the most intense resonances are those of $(C_5Me_5)_2UMe_2$ and BPh_3, but a small peak at 14.1 ppm is also observed that is attributable to the $(C_5Me_5)^-$ ligands of $[(C_5Me_5)_2UMe][MeBPh_3]$. As the sample is cooled, the resonances of $(C_5Me_5)_2UMe_2$ and BPh_3 in the ^1H and ^{11}B NMR spectra decrease in intensity and the resonances assigned to $[(C_5Me_5)_2UMe][MeBPh_3]$ increase in intensity until at 238 K only the resonances associated with $[(C_5Me_5)_2UMe][MeBPh_3]$ are observed.

Removal of solvent from this equilibrium mixture and crystallization from THF gave crystals of $[(C_5Me_5)_2UMe(THF)][MeBPh_3]$, **2**·THF, suitable for X-ray diffraction, Figure 2 and Table 1. The trapping of "$[(C_5Me_5)_2UMe][MeBPh_4]$" by THF is similar to the addition of THF to $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$,[16] which generates the solvated complex $[(C_5Me_5)_2U(THF)_2](BPh_4)$.[28] Mono- and di-solvated thorium analogues of **2** are also known: $[(C_5Me_5)_2Th(Me)(THF)]\{{}^tBuCH_2CH[B(C_6F_5)_2]_2H\}$[29] and $[(C_5Me_5)_2Th(Me)(THF)_2][B(C_6F_5)_4]$.[30]

Complex **2**·THF displays conventional bond distances for an eight-coordinate U(IV) metallocene, Table 2. The 2.71(3) Å U−C(C_5Me_5) average bond distance is similar to the analogous 2.72(2)−2.739(6) Å distances in $(C_5Me_5)_2UCl_2$[31] and $(C_5Me_5)_2UMe_2$.[32] The 2.393(12) Å U−C(21) distance in **2**·THF is similar to other tetravalent U−C(alkyl) distances, which are typically 2.4 Å in length.[33] The 2.419(8) Å U−O(THF) distance is also comparable to other eight-coordinate U(IV)−O(THF) distances, i.e., 2.449(9), 2.444(6), and 2.449(8) Å in $[(Me_3Si)_3C_5H_2]UCl_2(THF)(\mu\text{-}Cl)_2Li(THF)_2$,[41] $(C_9H_7)UCl_3(THF)_2$,[42] and $(C_5MeH_4)UCl_3(THF)_2$,[43] respectively. This length is approximately 0.1 Å shorter than analogous distances in U(III) complexes, e.g., 2.511(8), 2.55(2), and 2.55(1) Å in $[(C_5Me_5)_2U(THF)_2](BPh_4)$,[28] $(C_5Me_5)U(NMe_2)_3(THF)$,[44] and $(C_5H_5)_3U(THF)$,[45] respectively. The $(MeBPh_3)^-$ anion is structurally similar to that in the previously characterized pyridinium triphenylmethylborate.[46]

Addition of KC_5Me_5 instead of THF to the in situ generated $[(C_5Me_5)_2UMe][MeBPh_3]$ salt at room temperature in benzene precipitated white solids and left a red solution from which $(C_5Me_5)_3UMe$, **3**, was isolated in 66% yield, Scheme 3. The identity of **3** as the first $(C_5Me_4R)_3UMe$ complex was established by X-ray crystallography, Figure 3 and Table 1.

The ^1H NMR spectrum of $(C_5Me_5)_3UMe$ has a $(C_5Me_5)^-$ resonance at 9.2 ppm which displays $^{13}C{-}^1H$ satellites

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(33) $(C_5H_5)_3U(C_4H_9)$,[34] 2.426(23) Å; $(C_5H_5)_3U(\eta^1\text{-}2\text{-methylallyl})$,[35] 2.48(3) Å; $(C_5H_5)_3U(p\text{-}MeC_6H_4CH_2)$, 2.541(15) Å;[35] $(PhCH_2)_3UMe(DMPE)$,[36] 2.41(1) Å; $Li({}^tBu_2CHO)_4UMe$,[37] 2.465(7) Å; $[C_5H_3(SiMe_3)_2]_2UMe_2$,[38] 2.42(2) Å; $[(3,5\text{-}C_6H_3Me_2)({}^tBu)N]_3UMe$,[39] 2.446(7) Å; $(C_5Me_5)U(CH_2C_6H_5)_3$,[40] 2.477(18) to 2.53(2) Å; $(C_5Me_5)_2UMe_2$ 2.424(7) Å.[32]

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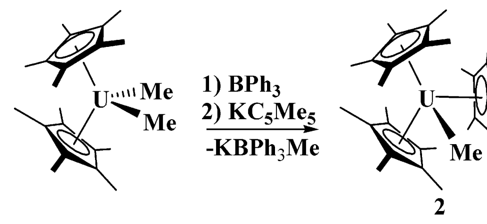
Scheme 3



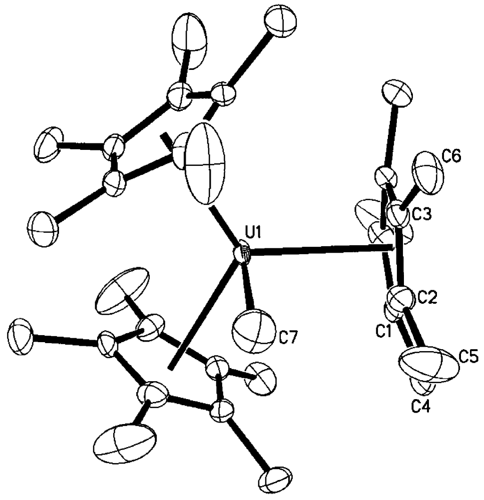


Figure 3. Thermal ellipsoid plot of $(C_5Me_5)_3UMe$, **3**, drawn at the 50% probability level. The disordered portion of the C7 methyl carbon atom has been omitted.

(J = 125 Hz) despite the paramagnetism of the complex. The spectrum also contains a resonance at −204 ppm consistent with a U(IV) methyl complex. For example, the U(IV) methyl complexes $(C_5H_5)_3UMe$,[47] $(C_5Me_5)\{O[SiMe_2(^tBuN)]_2\}UMe$,[48] and $(C_5Me_5)_2UMe_2$[21] have resonances at δ −202, −146, and −124 ppm, respectively.

The near-IR spectrum of **3** in the 16,700 to 6300 cm^{-1} region, Figure 4, contains absorptions consistent with a $5f^2$ uranium complex.[49–55] The intensities of these absorptions ($\epsilon \approx 30$ to 130 M^{-1} cm^{-1}) are greater than those observed for $(C_5Me_5)_2UMe_2$, $(C_5Me_5)_2UCl_2$, and $(C_5Me_5)_2UMeCl$ ($\epsilon \approx 10$ to 80 M^{-1} cm^{-1}), but are less than those observed in pentamethylcyclopentadienyl uranium complexes containing imido and ketimido ligands ($\epsilon \approx 40$ to 400 M^{-1} cm^{-1}). The absorption intensities displayed by **3** are most similar to metallocenes that contain two hydrazonato ligands ($\epsilon \approx 30$ to 120 M^{-1} cm^{-1}). This makes $(C_5Me_5)_3UMe$ most similar to the second class of organouranium complexes identified by Morris and co-workers.[55]

The solid state structure of **3** is shown in Figure 3. The complex crystallizes in the same $P6_3/m$ space group, as do all the other related complexes, $(C_5Me_5)_3U$,[56] $(C_5Me_5)_3MX$ (M = U; X = Cl,[8] F;[8] M = Th, Z = H[9]), and $(C_5Me_5)_3UL$ (L = CO,[10] N_2[11]), Table 1. Complex **3** has similar unit cell constants to these other sterically crowded complexes despite the presence of the larger methyl ligand (van der Waals radii of F, Cl, and Me are 1.35, 1.8, and 2.0 Å, respectively[57]). $(C_5Me_5)_3UMe$ is also like these complexes in that its bond distances and angles are unusual, Table 2. The (C_5Me_5 ring centroid)−U−(C_5Me_5 ring centroid) angles in **3** are rigorously 120°, as in $(C_5Me_5)_3U$, despite the presence of the methyl group and in contrast to the 140° (C_5Me_5 ring centroid)−U−(C_5Me_5 ring centroid) angle in **2**·THF. The (C_5Me_5 ring centroid)−U−C(7) angles in **3** are rigorously 90°, as are the (C_5Me_5 ring centroid)−M−fourth ligand angles in the $(C_5Me_5)_3MX$ and $(C_5Me_5)_3UL$ complexes. The 2.802(4)−2.904(6) Å U−C(C_5Me_5) distances and 2.569 Å U−centroid length are longer than those in conventional uranium cyclopentadienyl complexes. For example, the U(IV)−C(C_5Me_4H) distances in $(C_5Me_4H)_3UCl$[58] range from 2.658(11) to 2.911(10) Å and the U−centroid is 2.52 Å. Analogous distances in $[C_5H_3(SiMe_3)_2]_3UCl$ are 2.718(8)−2.81(1) and 2.49 Å, respectively.[59]

Despite the high quality of the crystallographic data on **3**, the refinement yielded an elongated anisotropic thermal ellipsoid for the uranium atom along the U−C(7) axis. In light of this, it is difficult to compare the 2.66(2) Å U−C(7) distance with other tetravalent U−C(alkyl) distances, which typically are around 2.4 Å.[33] Long uranium to fourth ligand distances have been observed with all the other $(C_5Me_5)_3UX$ and $(C_5Me_5)_3UL$ complexes characterized to date, but elongated ellipsoids were identified only in complexes containing anionic ligands. Refinements in lower space groups were examined as well as models in which the uranium was disordered on either side of the trigonal plane. These did not give any additional definitive information on this issue.

Discussion

The in situ borate route to $(C_5Me_5)_3UCl$, **1**, Scheme 2, is a much improved route to this compound compared to the previously reported synthesis, Scheme 1. Both routes start with $(C_5Me_5)_2UMe_2$, but Scheme 1 avoids the reduction, protonolysis, and PhCl re-oxidation steps. The Scheme 2 synthesis occurs without change in metal oxidation state and with intermediates that do not need to be isolated for successful synthesis.

The value of this in situ borate approach for preparing $(C_5Me_5)_3UX$ compounds was further demonstrated by making $(C_5Me_5)_3UMe$, **3**. The synthesis of this com-

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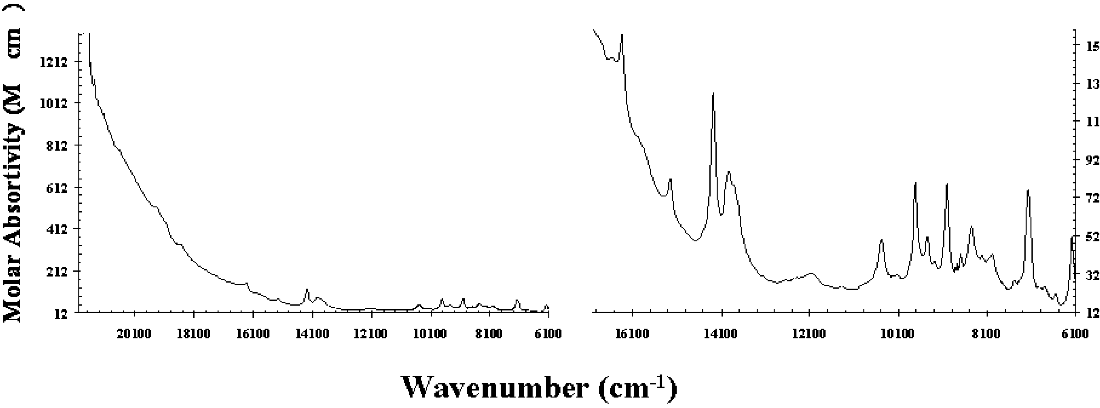

Figure 4. UV−vis−NIR electronic absorption spectrum of a 3.15 mM solution of $(C_5Me_5)_3UMe$, **3**, in benzene. Left: The entire spectrum. Right: The near-infrared region.

pound was challenging since even $(C_5Me_5)_3UBr$[8] has yet to be crystallographically confirmed due to its instability and Me has a larger van der Waals radius (2.0 Å) than Br (1.85 Å).[57] Hence, it was uncertain if **3** would form for steric reasons. In addition, all previous $(C_5Me_5)_3MX$ and $(C_5Me_5)_3ML$ complexes had X and L ligands that could remove electron density from the metal center. The electronic difficulties in making $(C_5Me_4R)_3MX$ complexes with electron-donating X ligands such as H and Me have previously been discussed and can also be substantial.[58,60,61] The successful isolation of **3** showed that neither steric nor electronic constraints prevent its formation.

Conclusion

The facile syntheses of **1** and **3** described here provide the necessary synthetic methodology to readily prepare sufficient quantities of $(C_5Me_5)_3UCl$ and $(C_5Me_5)_3UMe$ for reactivity studies. The isolation of $(C_5Me_5)_3UMe$ demonstrates that the steric limits of tris(pentamethylcyclopentadienyl) complexes are still expanding and that $(C_5Me_5)_3MX$ and $(C_5Me_5)_3ML$ complexes can be obtained with X or L ligands that are electron donating and are more than monatomic ions or cylindrical diatomics. These syntheses also demonstrate that in addition to the $(BPh_4)^-$ displacements done in the past, displacement by $(C_5Me_5)^-$ of $(BPh_3Me)^-$ borates generated in situ can be accomplished. The breadth of this approach to uranium alkyls remains to be determined, but it is likely that it could apply to complexes with conventional bond distances as well as these long bond organometallics.

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Supporting Information Available: ^1H NMR spectrum of **3**. X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles; listing of observed and calculated structure factor amplitudes for compounds **2**·THF and **3** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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