

Structure, Reactivity, and Density Functional Theory Analysis of the Six-Electron Reductant, $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, Synthesized via a New Mode of $(C_5Me_5)_3M$ Reactivity

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Abstract: The sterically crowded $(C_5Me_5)_3U$ complex reacts with KC_8 or $K/(18\text{-crown-6})$ in benzene to form $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1**, and KC_5Me_5 . These reactions suggested that $(C_5Me_5)_3U$ could be susceptible to $(C_5Me_5)^{1-}$ substitution by benzene anions via ionic salt metathesis. To test this idea in the synthesis of a more conventional product, $(C_5Me_5)_3U$ was treated with $KN(SiMe_3)_2$ to form $(C_5Me_5)_2U[N(SiMe_3)_2]$ and KC_5Me_5 . **1** has long U–C(C_5Me_5) bond distances comparable to $(C_5Me_5)_3U$, and it too is susceptible to $(C_5Me_5)^{1-}$ substitution via ionic metathesis: **1** reacts with $KN(SiMe_3)_2$ to make its amide-substituted analogue $\{[(Me_3Si)_2N](C_5Me_5)U\}_2(\mu-\eta^6:\eta^6-C_6H_6)$, **2**. Complexes **1** and **2** have nonplanar C_6H_6 -derived ligands sandwiched between the two uranium ions. **1** and **2** were examined by reactivity studies, electronic absorption spectroscopy, and density functional theory calculations. $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$ functions as a six-electron reductant in its reaction with 3 equiv of cyclooctatetraene to form $[(C_5Me_5)(C_8H_8)U]_2(\mu-\eta^3:\eta^3-C_8H_8)$, $(C_5Me_5)_2$, and benzene. This multielectron transformation can be formally attributed to three different sources: two electrons from two U(III) centers, two electrons from sterically induced reduction by two $(C_5Me_5)^{1-}$ ligands, and two electrons from a bridging $(C_6H_6)^{2-}$ moiety.

Introduction

The synthesis of the sterically crowded tris(pentamethylcyclopentadienyl) metal complexes, $(C_5Me_5)_3M$ ($M = \text{lanthanide and uranium}$),^{1,2} not only demonstrated that new classes of organometallic molecules could be isolated in which every metal–ligand bond was longer than normal, but it also revealed that steric crowding can be accompanied by the transformation of normally inert ancillary ligands into reactive action ligands.³ Hence, in these $(C_5Me_5)_3M$ “long bond organometallics,” the $(C_5Me_5)^{1-}$ ligands are no longer spectator ligands, a result which is presumably due to the steric crowding.⁴ For example, with some substrates, the $(C_5Me_5)^{1-}$ groups can function as bulky alkyl groups that participate in CO insertion chemistry^{5,6} and olefin polymerization chemistry.⁷ With other substrates, $(C_5Me_5)^{1-}$ redox chemistry is activated via a $(C_5Me_5)^{1-}/C_5Me_5$ redox couple.²

Since this reductive reactivity is not observed in $(C_5Me_5)^{1-}$ complexes with conventional bond lengths,⁸ it has been termed sterically induced reduction (SIR).⁹ This SIR provides a means to accomplish reductions with metal complexes containing redox inactive metals.^{3,4} SIR can also enhance the redox chemistry of redox active metal complexes by combining with conventional redox couples to generate multielectron reduction systems.^{9,10}

The only other type of reaction observed for $(C_5Me_5)_3M$ complexes has been simple adduct formation which generates $(C_5Me_5)_3UL$ species.^{6,11} This in itself is unusual: because the $(C_5Me_5)_3M$ complexes are already crowded, formation of more highly ligated products was not expected. These reactions were further surprising in that they could be accomplished with $L = CO^6$ and N_2 ,¹¹ substrates that are not conventional ligands for the f element metal ions which prefer ligation by hard σ donors.

In this report, we describe a new type of reaction for $(C_5Me_5)_3M$ complexes, a $(C_5Me_5)^{1-}$ substitution reaction. Although removal of $(C_5Me_5)^{1-}$ is very reasonable due to the steric crowding in these long bond organometallics and the loss of $(C_5Me_5)^{1-}$ anions from $(C_5Me_5)_3M$ complexes by η^1 alkyl or SIR pathways is well known,² the removal of $(C_5Me_5)^{1-}$ rings

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from f element complexes by ionic metathesis is not a common reaction. Overall, there are few examples of $(C_5Me_5)^{-}$ displacement reactions.^{12–16} Generally, other more reactive ligands are displaced in preference to the normally inert, polydentate, $(C_5Me_5)^{-}$ anions.

This $(C_5Me_5)_3M$ reaction was discovered in efforts to understand the formation of the bimetallic arene derivative, $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1**, which is readily generated from $(C_5Me_5)_3U$ and potassium reagents in benzene. Complex **1** is of interest because it shows structural features similar to $(C_5Me_5)_3U$ indicative of steric crowding, and it functions as a six-electron reductant by formally combining three types of redox processes. The reductive chemistry of **1** also represents the first well-defined example of SIR in a bis(pentamethylcyclopentadienyl) $(C_5Me_5)_2ML$ complex rather than a tris(pentamethylcyclopentadienyl) $(C_5Me_5)_3M$ species.

In addition to **1**, the synthesis and isolation of the amide analogue, $\{[(Me_3Si)_2N](C_5Me_5)U\}_2(\mu-\eta^6:\eta^6-C_6H_6)$, **2**, is described here. These molecules add to the unusual class of uranium arene sandwich complexes originally exemplified by the crystallographically characterized $[(AdArN)_2U]_2(\mu-C_6H_5Me)$, **3**,¹⁷ and $[K(Ar^tBuCN)_3U]_2(C_{10}H_8)$, **4**,¹⁸ complexes (Ad = adamantyl; Ar = $C_6H_4Me_{2-3,5}$). Compounds **1–4** are unusual in that assignment of formal charge to the metals and ligands involves either unconventional charged forms of the bridging arenes or unconventional uranium oxidation states. Possible formal valence assignments include U(II) complexes of neutral arenes, U(III) complexes of arene dianions, and U(IV) complexes of arene tetraanions. The structural and spectroscopic properties of **1** and **2** are presented along with substitution, hydrolytic, and arene exchange reactivity as well as a density functional theory evaluation of their electronic structure.

Experimental Section

The complexes described here are extremely air and moisture sensitive. Except where noted, the synthesis and manipulations of these compounds were conducted in an argon-filled glovebox that was free of coordinating solvents with rigorous exclusion of air and water. THF, toluene, benzene, and *n*-hexane were saturated with Ar and passed through a GlassContour column.¹⁹ Benzene-*d*₆ and *para*-xylene were distilled over NaK alloy and benzophenone and degassed by three freeze–pump–thaw cycles. KN(SiMe₃)₂, C₈H₈, and 18-crown-6 were purchased from Aldrich. KN(SiMe₃)₂ was recrystallized from toluene before use. C₈H₈ was distilled, dried over Type 4 activated molecular sieves, and degassed by three freeze–pump–thaw cycles. 18-crown-6 was dried by exposure to vacuum (10^{-3} Torr) for 12 h. KC₈ was freshly made in a glovebox before each experiment by heating a 1.1:1 mixture of K and graphite (C₈, Aldrich, 235 mesh, 99.999) in a vial on a hot plate similarly to published syntheses.²⁰ C₅Me₅H was obtained from Strem, dried over Type 4 activated molecular sieves, and degassed by three freeze–pump–thaw cycles. KC₅Me₅ was synthesized by slowly

adding a solution of KN(SiMe₃)₂ (2.302 g, 0.0115 mol) in toluene (ca. 20 mL) to a solution of C₅Me₅H (1.309 g, 0.0096 mol) in toluene (ca. 20 mL). After 12 h, the insoluble KC₅Me₅ was isolated by centrifugation and repeatedly washed with toluene. The white KC₅Me₅ (1.379 g, 82%) was dried in vacuo. $[HNEt_3][BPh_4]$,²¹ $(C_5Me_5)_3U$,²² and $(C_5Me_5)_2U-[(\mu-Ph_2)BPh_2]$ ²² were prepared as previously described. NMR experiments were conducted with a Bruker 400 MHz spectrometer or a Bruker 500 MHz spectrometer. IR samples were analyzed as thin films using an ASI ReactIR1000. Electronic absorption measurements were conducted in hexane (UV–vis) or in benzene (near-IR) solutions, on a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrophotometer using Teflon sealable 1 cm quartz cells. Room-temperature magnetic data were obtained by Evans Method.^{23,24} GC-MS data were obtained on a Waters (Micromass) Autospec and a Therus (Finnigan) Trace MS. The fused silica GC columns used were a 30 m × 0.32 mm i.d. DB-5 for C₅Me₅H and related products and a 60 m × 0.25 mm i.d. RTX-VMS for C₆ separations. Elemental analyses were provided by Analytische Laboratorien, Lindlar Germany.

$(C_5Me_5)_2U[N(SiMe_3)_2]$ from $(C_5Me_5)_3U$. A solution of $(C_5Me_5)_3U$ (16 mg, 0.025 mmol) in C₆D₆ was added to an NMR tube containing a sealed capillary tube filled with (Me₃Si)₂O, and the ¹H NMR spectrum was obtained. The NMR tube was taken into a glovebox, and the $(C_5Me_5)_3U/C_6D_6$ solution was added to a vial containing KN(SiMe₃)₂ (5 mg, 0.025 mmol). A white precipitate immediately formed and was removed by centrifugation. The solution was transferred back to the NMR tube containing the (Me₃Si)₂O standard. Analysis by ¹H NMR showed complete consumption of $(C_5Me_5)_3U$ and formation of $(C_5Me_5)_2U[N(SiMe_3)_2]$ ^{22,25,26} as the only product in 95% yield. ¹H NMR (C₆D₆, 298 K): δ –5.7 (s, 30H, C₅Me₅, ¹J_{C,H} 125 Hz, $\Delta v_{1/2}$ 10 Hz), δ –25.7 (s, 18H, SiMe₃ $\Delta v_{1/2}$ = 680 Hz).

$(C_5Me_5)_2U[N(SiMe_3)_2]$ from $[(C_5Me_5)_2U][(\mu-Ph_2)BPh_2]$. A solution of KN(SiMe₃)₂ (8 mg, 0.040 mmol) in C₆H₅Me was added to a stirred solution of $(C_5Me_5)_2U[(\mu-Ph_2)BPh_2]$ (33 mg, 0.040 mmol) in C₆H₅Me. After 12 h, a white precipitate was removed by centrifugation. Removal of solvent by rotary evaporation afforded $(C_5Me_5)_2U[N(SiMe_3)_2]$ ^{22,25,26} (26 mg, 97%) as a brown powder (see above).

$(C_5Me_5)_2U[(\mu-\eta^6:\eta^6-C_6H_6)]$, **1, from $(C_5Me_5)_3U$.** A solution of $(C_5Me_5)_3U$ (123 mg, 0.191 mmol) in C₆H₆ was added dropwise to a stirred suspension of KC₈ (29 mg, 0.215 mmol) in C₆H₆. After 3 h, black and white solids were separated from the solution by centrifugation. The solvent was removed by rotary evaporation, affording $[(C_5Me_5)_2U]_2-(\mu-\eta^6:\eta^6-C_6H_6)$ (94 mg, 90%) as a brown solid. ¹H NMR (C₆D₆, 298 K): δ 3.06 (s, 60H, C₅Me₅, ¹J_{C,H} 124 Hz, $\Delta v_{1/2}$ 15 Hz), –99.4 (s, 6H, C₆H₆, $\Delta v_{1/2}$ 30 Hz). (C₇D₈, δ 2.09, 298 K): δ 2.97 (s, 60H, C₅Me₅, ¹J_{C,H} 125 Hz, $\Delta v_{1/2}$, 5 Hz), –98.9 (s, 6H, C₆H₆, $\Delta v_{1/2}$ 28 Hz). ¹³C NMR (C₆D₆, 298 K): δ –25.7 (s–sp³ C–C₅Me₅), 281.7 (sp² C–C₅Me₅), 455 (s, C–C₆H₆), assignments confirmed by HMQC. FT-IR: 2961(s), 2910(s), 2856(s), 2725(w), 1494(m), 1440(s), 1378(s), 1324(m), 1262(s), 1089(b), 1069(s), 1023(s), 949(w), 911(w), 802(s), 663(s), 586(w). Magnetic susceptibility, 298 K: $\chi_m = 186.2 \times 10^{-6} \mu_{\text{eff}} = 2.1 \mu_B$. Anal. Calcd for U₂C₄₆H₆₆: U, 43.49. Found: U, 43.75. The hydrolysis and deuteration of the black and white arene insoluble solids formed C₅Me₅H and C₅Me₅D, which were identified by GC-MS.

$(C_5Me_5)_2U[(\mu-\eta^6:\eta^6-C_6H_6)]$, **1, from $[(C_5Me_5)_2U][(\mu-Ph_2)BPh_2]$.** A solution of 18-crown-6 (18 mg, 0.068 mmol) in C₆H₆ was added to a vial charged with freshly scraped potassium (3 mg, 0.077 mmol). The mixture was stirred for 30 min, and the color changed to dark green. A solution of $[(C_5Me_5)_2U][(\mu-Ph_2)BPh_2]$ (59 mg, 0.071 mmol)

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in C₆H₆ was added dropwise. The mixture was stirred for an additional 3 h, and white precipitates were removed by centrifugation. The solvent was removed by rotary evaporation, and [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆) was isolated (32 mg, 82%) (see above).

{[(Me₃Si)₂N][(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆), **2**. A solution of freshly recrystallized KN(SiMe₃)₂ (92 mg, 0.463 mmol) in C₆H₆ was added dropwise over a period of 20 min to a solution of [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆) (260 mg, 0.238 mmol) in C₆H₆. A white precipitate immediately forms. After the reaction was stirred for 13 h, the white precipitate was separated from the brown solution by centrifugation. Upon removal of the solvent by rotary evaporation, {[(Me₃Si)₂N][(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆) (235 mg, 89%; based on KN(SiMe₃)₂) was isolated as a brown solid. ¹H NMR (C₆D₆, 298 K): δ 0.56 (s, 30H, C₅Me₅, ¹J_{C,H} 125 Hz, Δ*v*_{1/2} 6 Hz), -7.9 (s, 36H, SiMe₃, Δ*v*_{1/2} 24 Hz), -84 (s, 6H, C₆H₆, Δ*v*_{1/2} 36 Hz). ¹³C NMR (C₆D₆, 298 K): δ -25.5 (s, sp³ C-C₅Me₅), -3.11 (s, C-SiMe₃), 212.9 (s, sp² C-C₅Me₅), 422.3 (s, C-C₆H₆) assignments confirmed by HMQC. FT-IR (thin film from C₆H₆, cm⁻¹): 3655(s), 2961(s), 2922(s), 2856(s), 2725(w), 1444(w), 1378(w), 1262(s), 1092(s), 1019(s), 864(m), 799(s), 656(m). Magnetic susceptibility, 298 K: χ_m = 131.0 × 10⁻⁶ μ_{eff} = 1.8 μ_B. Anal. Calcd for C₃₈H₇₂Si₄N₂U₂: C, 39.86; H, 6.29; Si, 9.81; N, 2.45; U, 41.58. Found: C, 40.75; H, 6.06; Si, 9.65; N, 2.56; U, 40.50.

[(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆D₆), **1-d₆**, from **1**. A solution of [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆) (10 g, 0.009 mmol) in C₆D₆ in an NMR tube sealed under vacuum was heated at 65 °C and monitored daily by ¹H NMR spectroscopy. After 7 days, quantitative conversion from **1** to **1-d₆** had occurred. ¹H NMR (C₆D₆, 298 K): δ 3.02 (s, H-C₅Me₅, ¹J_{C,H} 125 Hz, Δ*v*_{1/2} 6 Hz). ²H NMR (C₆H₅Me, 2.09): -98.3 (s, D-C₆D₆, Δ*v*_{1/2} 29 Hz).

[(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆D₆), **1-d₆**, from (C₅Me₅)₃U in C₆D₆. A solution of (C₅Me₅)₃U (43 mg, 0.067 mmol) in C₆D₆ was added dropwise to a stirring suspension of KC₈ (10 mg, 0.074 mmol) in C₆D₆. The mixture was stirred for 3 h, at which point white and black solids were removed by centrifugation. The ¹H and ²H NMR spectra are consistent with clean formation of **1-d₆** (see above).

[(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆D₆), **1-d₆**, from (C₅Me₅)₃U in *para*-Xylene. A solution of (C₅Me₅)₃U (29 mg, 0.045 mmol) in *para*-xylene was added dropwise to a suspension of KC₈ (6 mg, 0.045 mmol) in *para*-xylene (10 mL). After 3 h, both black and white solids were separated from the solution by centrifugation. The solvent was removed by rotary evaporation, affording a brown solid consistent with [(C₅Me₅)₂U]₂(1,4-C₆Me₂H₄) (22 mg, 87%) by ¹H NMR spectroscopy. ¹H NMR (C₆D₆, 298 K): δ -5.6 (s, 6H, 1,4-C₆Me₂H₄), -7.9 (s, 60H, C₅Me₅). Immediately upon isolation, the brown solid was dissolved in C₆D₆ and transferred to an NMR tube. The tube was sealed under vacuum and heated to 65 °C. The reaction was monitored by ¹H NMR spectroscopy, and quantitative conversion to **1-d₆** occurred within 12 h (see above).

[(C₅Me₅)₂U][μ-Ph₂BPh₂], from **1**. A solution of [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆) (8 mg, 0.007) in C₆D₆ was added to an NMR tube charged with [HNEt₃][BPh₄] (6 mg, 0.014). Gas evolution was immediately observed. The reaction was analyzed by ¹H NMR spectroscopy, and resonances consistent with NEt₃ and [(C₅Me₅)₂U][μ-Ph₂BPh₂]²² were observed. The volatile contents of the NMR tube were transferred under vacuum to a round-bottom flask and were analyzed by GC-MS and ¹H NMR spectroscopy. No evidence for the formation of cyclohexadienes or cyclohexene was found. To confirm the identity of the evolved gas, the reaction was repeated by adding, via syringe, [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆) in C₆H₆ to a 5 mL flask equipped with a septum that had been charged with [HNEt₃][BPh₄]. EI analysis of the gas in the flask showed an ion at *m/z* = 2, consistent with the formation of H₂.

[(C₅Me₅)(C₈H₈)U]₂(μ-η³:η³-C₈H₈) from **1**. (Me₃Si)₂O (5 μL) was added as an internal standard to an NMR tube that contained a solution of [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆) (9.5 mg, 0.0087 mmol) in C₆D₁₂. The ¹H NMR spectrum was obtained, and the tube was brought into a nitrogen-filled glovebox that contained coordinating solvents. A

Table 1. X-ray Data Collection Parameters for [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆), **1**, and {[(Me₃Si)₂N][(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆), **2**

	1	2
empirical formula	C ₄₆ H ₆₆ U ₂ ^{1/2} (C ₆ H ₁₄)	C ₃₈ H ₇₂ N ₂ Si ₄ U ₂ ·C ₆ H ₁₄
formula weight	1138.13	1231.57
crystal system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	17.3074(16)	8.6030(16)
<i>b</i> (Å)	10.7815(10)	11.624(2)
<i>c</i> (Å)	23.129(2)	13.269(3)
α (deg)	90	107.460(3)
β (deg)	94.617(2)	99.515(3)
γ (deg)	90	90.328(3)
volume (Å ³)	4301.9(7)	1246.2(4)
<i>Z</i>	4	1
λ (Å)	0.71073	0.71073
ρ _{calc} (Mg/m ³)	1.732	1.641
absorption coeff	7.551	6.615
GOF on <i>F</i> ²	1.088	1.174
<i>R</i> ^a [<i>I</i> > 2σ(<i>I</i>): <i>R</i> ₁	0.0646	0.0168
<i>R</i> ^b (all data): w <i>R</i> ₂	0.1910	0.0520

microliter syringe was used to add C₈H₈ (2.9 μL, 0.026 mmol) to the tube, and the reaction was monitored by ¹H NMR spectroscopy. After 12 h, NMR analysis showed quantitative formation of the previously characterized [(C₅Me₅)(C₈H₈)U]₂(μ-η³:η³-C₈H₈) complex⁹ accompanied by the formation of 1 equiv of C₆H₆ and (C₅Me₅)₂. ¹H NMR (C₆D₁₂, 298 K): [(C₅Me₅)(C₈H₈)U]₂(μ-η³:η³-C₈H₈): δ 4.9 (s, 30H, C₅Me₅ ¹J_{C,H} 125 Hz, Δ*v*_{1/2} 6 Hz), -38.7 (s, 8H, C₈H₈, Δ*v*_{1/2} 21 Hz), -41.7 (s, 16H, C₈H₈, Δ*v*_{1/2} 13 Hz). (C₅Me₅)₂: δ 1.61 [s, 24H, (C₅Me₅)₂], 1.05 [s, 6H, (C₅Me₅)₂]. C₆H₆: δ 7.21 (s, 6H, C₆H₆).

X-ray Data Collection, Structure Determination, and Refinement

for [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆D₆), **1**. A dark purple crystal of approximate dimensions 0.04 × 0.14 × 0.30 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART²⁷ 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 SAINT²⁸ and SADABS²⁹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL³⁰ program. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the centrosymmetric monoclinic space group *P*2₁/*n*, 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 factors³¹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There was one-half molecule of hexane solvent (located about an inversion center) present per formula unit. During refinement, several carbon atoms became nonpositive-definite. Only the uranium atoms were refined with anisotropic thermal parameters. The final least-squares analysis yielded w*R*₂ = 0.1910 and GOF = 1.088 for 216 variables refined against 7328 data (0.85 Å resolution). As a comparison for refinement on *F*, *R*₁ = 0.0646 for those 5483 data with *I* > 2.0σ(*I*). Details are given in Table 1.

X-ray Data Collection, Structure Determination, and Refinement

for [(Me₃Si)₂N][(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆), **2**. A purple crystal of approximate dimensions 0.12 × 0.33 × 0.33 mm was handled as described for **1**. There were no systematic absences or any diffraction

(27) SMART Software Users Guide, Version 5.1; Bruker Analytical X-ray Systems, Inc.; Madison, WI, 1999.

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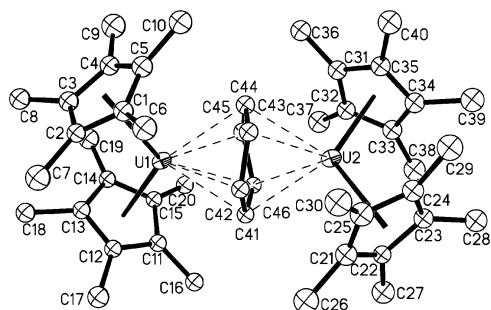


Figure 1. Thermal ellipsoid plot of $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1**, drawn at the 50% probability level. All carbon atoms were refined isotropically.

symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. Hydrogen atoms were located from a difference Fourier map and refined (x, y, z and U_{iso}). The molecule was located about an inversion center. There was one molecule of hexane present per formula unit, which was also located on an inversion center. At convergence, $wR2 = 0.0520$ and $GOF = 1.174$ for 407 variables refined against 5736 data. As a comparison for refinement on F , $R1 = 0.0168$ for those 5511 data with $I > 2.0\sigma(I)$. Details are given in Table 1.

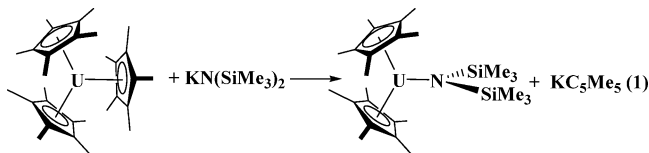
Computational Details. All calculations were performed with the Amsterdam Density Functional (ADF) program suite, version 2003.01.^{32–36} Scalar relativistic corrections³⁷ were included via the ZORA to the Dirac equation.^{38,39} The uranium basis set was taken from the ADF ZORA/TZ2P directory and may be characterized as containing uncontracted, Slater-type functions of primarily triple- ζ quality. For C and H, the basis sets were taken from the ADF ZORA/DZP directory, double- ζ plus polarization. The frozen core approximation was used for C (1s) and U (5d). The local density parametrization of Vosko, Wilk, and Nusair⁴⁰ was employed in conjunction with the PBE⁴¹ gradient corrections. Mulliken population analyses were performed. Molecular orbital plots were generated using the program MOLDEN, written by G. Schaftenaar of the CAOS/CAMM Centre, Nijmegen, The Netherlands.⁴²

Results

$(C_5Me_5)^{1-}$ Ligand Displacement from $(C_5Me_5)_3U$. The title complex, $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1**, Figure 1, whose synthesis, structure, and properties are described below, was originally isolated in an attempt to identify a byproduct in the synthesis of $(C_5Me_5)_3U$ ²² prepared in benzene from $[(C_5Me_5)_2U]-[(\mu-Ph_2)BPh_2]$ ²² and a sample of KC_5Me_5 made from KH and C_5Me_5H . This synthesis is generally a reliable route to $(C_5Me_5)_3U$, but, in this case, **1** was isolated instead. The examination of various routes to **1** (see below) raised the possibility that $(C_5Me_5)_3U$ could participate in ionic metathesis reactions with alkali metal anions. To test this concept in the synthesis of a more conventional product, $(C_5Me_5)_3U$ was treated with

$KN(SiMe_3)_2$, and a new type of reaction for $(C_5Me_5)_3U$ complexes was identified.

Addition of $KN(SiMe_3)_2$ to a brown solution of $(C_5Me_5)_3U$ in C_6D_6 resulted in the rapid formation of a white precipitate. NMR spectroscopy identified the product in solution as the previously reported $(C_5Me_5)_2U[N(SiMe_3)_2]$.^{22,25,26} The white precipitate was identified as KC_5Me_5 because hydrolysis and deuteriolysis formed C_5Me_5H and C_5Me_5D , respectively. The overall reaction is shown in eq 1. A 1H NMR spectroscopic

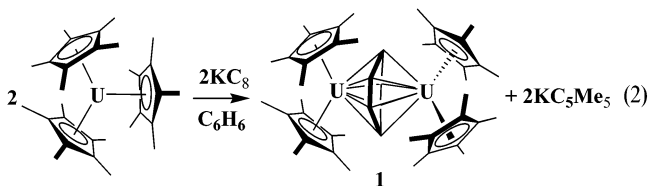


study with $(Me_3Si)_2O$ as an internal standard indicated that $(C_5Me_5)_2U[N(SiMe_3)_2]$ formed in 95% yield within 15 min.

$(C_5Me_5)_2U[N(SiMe_3)_2]$ has been previously synthesized by addition of $M[N(SiMe_3)_2]$ ($M = Na, K$) to $[(C_5Me_5)_2UCl]_3$,^{25,26} or $(C_5Me_5)_2UMe_2K$.²² It can also be obtained from $KN(SiMe_3)_2$ and $[(C_5Me_5)_2U][(\mu-Ph_2)BPh_2]$, a complex which is an excellent reagent for ionic metathesis reactions because it contains the $[(C_5Me_5)_2U]^+$ cation loosely ligated by bridging η^2 -arenes of the $(BPh_4)^{1-}$ anion.^{22,43}

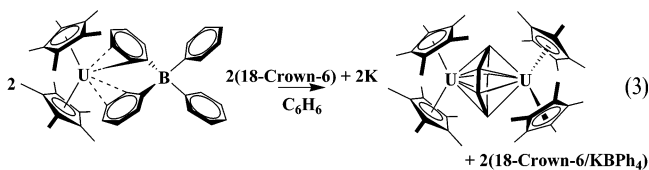
The ionic metathesis reaction between $(C_5Me_5)_3U$ and $KN(SiMe_3)_2$ to form $(C_5Me_5)_2U[N(SiMe_3)_2]$ represents a rare example of a complex undergoing $(C_5Me_5)^{1-}$ substitution.^{12–16} In general, displacement of the anionic polydentate $(C_5Me_5)^{1-}$ is not favored as compared to removal of other less tightly bound ligands. The $(C_5Me_5)^{1-}$ reactivity is quite reasonable for the sterically crowded $(C_5Me_5)_3U$, because a less crowded uranium metallocene is generated.

Synthesis of $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1.** An ionic metathesis reaction similar to that in eq 1 appears to be an effective synthetic route to **1** using the anions generated from benzene solutions containing potassium and crown ethers.^{44–47} Hence, the addition of $(C_5Me_5)_3U$ to a benzene solution containing potassium and 18-crown-6 or KC_8 provides **1** in quantitative yield after 3 h, eq 2. Complex **1** was characterized



by spectroscopic and chemical means and was identified by X-ray crystallography as described below.

Complex **1** can also be made from $[(C_5Me_5)_2U][(\mu-Ph_2)BPh_2]$, the precursor to $(C_5Me_5)_3U$. The synthesis from a K/18-crown-6/benzene combination is shown in eq 3.



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Table 2. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1**, and $\{[(Me_3Si)_2N](C_5Me_5)U\}_2(\mu-\eta^6:\eta^6-C_6H_6)$, **2**

complex 1		complex 2	
U(1)···U(2)	4.396	U(1)···U(2)	4.291
U(1)–Cnt(Cp1)	2.567	U(1)–Cnt(Cp)	2.506
U(1)–Cnt(Cp2)	2.583	U(1)–N(1)	2.306(2)
U(1)–C(1)	2.812(14)	U(1)–C(1)	2.788(3)
U(1)–C(2)	2.795(14)	U(1)–C(2)	2.783(3)
U(1)–C(3)	2.866(14)	U(1)–C(3)	2.773(3)
U(1)–C(4)	2.823(14)	U(1)–C(4)	2.766(3)
U(1)–C(5)	2.878(14)	U(1)–C(5)	2.795(3)
U(1)–Cnt(Bz)	2.194	U(1)–Cnt(Bz)	2.146
U(1)–C(45)	2.509(14)	U(1)–C(11)	2.564(3)
U(1)–C(42)	2.547(13)	U(1)–C(11#)	2.612(3)
U(1)–C(46)	2.730(13)	U(1)–C(12)	2.631(3)
U(1)–C(43)	2.733(14)	U(1)–C(12#)	2.559(3)
U(1)–C(44)	2.617(14)	U(1)–C(13)	2.569(3)
U(1)–C(41)	2.591(13)	U(1)–C(13#)	2.603(3)
Cnt(Cp)–U(1)–Cnt(Cp)	121.1	C(11)–C(12)	1.449(4)
Cnt(Cp)–U(1)–Cnt(Bz)	118.9	C(12)–C(13)	1.458(4)
Cnt(Cp)–U(2)–Cnt(Bz)	119.2	C(13)–C(11A)	1.453(4)
Cnt(Cp)–U(2)–Cnt(Cp)	121.7	C(11)–C(13A)	1.453(4)
		C(41)–C(42)	1.441(19)
		C(41)–C(46)	1.448(19)
		C(42)–C(43)	1.447(18)
		C(43)–C(44)	1.42(2)
		C(44)–C(45)	1.44(2)
		C(45)–C(46)	1.462(18)

In the absence of benzene, $(C_5Me_5)_3U$ in methylcyclohexane is stable to suspensions of KC_8 or $K/(18\text{-crown-6})$ for at least 24 h. In addition, **1** is not detected in the reaction of $[(C_5Me_5)_2U]-[(\mu-Ph_2)BPh_2]$ with KC_5Me_5 , when the latter reagent is prepared from $KN(SiMe_3)_2$ and C_5Me_5H . The reaction of $[(C_5Me_5)_2U]-[(\mu-Ph_2)BPh_2]$ with KH in benzene also does not form **1**. However, **1** can be identified in the 1H NMR spectrum of the products of the reaction between $(C_5Me_5)_3U$ and excess KH in benzene, which demonstrates that multiple combinations of potassium reagents, benzene, and $(C_5Me_5)_3U$ can be used to generate **1** by displacement of $(C_5Me_5)^{1-}$.

Structure of $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1.** As shown in Figure 1, complex **1** crystallizes as a bimetallic species in which an arene ring is sandwiched between two $[(C_5Me_5)_2U]$ moieties. In this regard, **1** is similar to the uranium amide toluene complex $[(R_4ArN)_2U]_2(C_6H_5Me)$, **3**¹⁷ ($R = \text{adamantyl}$; $Ar = C_6H_4Me_{2-3,5}$), with which it will be compared later. The $U(1)\cdots U(2)$ distance in **1** is 4.396 Å, and the $(C_5Me_5)^{1-}$ rings in **1** have a tetrahedral arrangement around the $U-C_6H_6-U$ core, Table 2. The $(C_5Me_5 \text{ ring centroid})-U-(C_5Me_5 \text{ ring centroid})$ angles within each metallocene unit are 121.1° and 121.7°. These angles are more similar to the 120° angles in the sterically crowded $(C_5Me_5)_3U^7$ than to the angles in typical uranium metallocenes which are generally 127°–142°. ^{22,23,48,49} The $(C_5Me_5 \text{ ring centroid})-U-(C_6H_6 \text{ ring centroid})$ angles are similarly small and range from 118.9° to 119.8°.

In addition to the small $(C_5Me_5 \text{ ring centroid})-U-(C_5Me_5 \text{ ring centroid})$ angles, another similarity between **1** and $(C_5Me_5)_3U$ is that the $U-C(C_5Me_5)$ bond lengths are unusually long. They range from 2.794(16) to 2.89(1) Å and average 2.84(3) Å for U1 and 2.83(2) Å for U(2) (2.564–2.583 Å

U -centroid distances). In fact, the $U-C(C_5Me_5)$ lengths in **1** are indistinguishable from those in sterically crowded $(C_5Me_5)_3U^7$ [2.813(3)–2.920(4) Å; average 2.84(4) Å] and $(C_5Me_5)_3UCl^{10}$ [2.780(6)–2.899(9) Å; average 2.83(9) Å]. Few nine-coordinate trivalent uranium metallocenes are available for comparison, but in the structures that are known, the $U-C(C_5Me_5)$ average bond distances are typically in the 2.75–2.82 Å range. $U-C(C_5Me_5)$ averages for specific examples follow: $(C_5Me_5)_2UH(\text{DMPE})$ [2.79(5) Å],⁵⁰ $(C_5Me_4H)_3U$ [2.82(5) Å],⁵¹ $(C_5Me_5)(C_8H_8)U([NC_5H_3Me]_2)$ [2.75(2) Å],⁵² and $[(C_5Me_5)_2U(NMe_2)(NCCMe_3)_2][BPh_4]$ [2.77(2) Å].⁵³

Within the bridging C_6H_6 unit, the 1.42(2)–1.462(18) Å $C-C$ bond distances and 117.5(12)°–121.4(12)° $C-C-C$ angles are unfortunately indistinguishable within the error limits from those in free benzene, 1.39 Å and 120°. ⁵⁴ However, the bridging ligand is not planar. As shown in Figure 2, C(42), C(43), C(45), and C(46) all deviate from the average plane of the ring by 0.10–0.14 Å to give the ligand a shallow boat conformation. The dihedral angles between the average plane of C(41), C(45), C(42), and C(44) and the plane defined by either C(45), C(46), and C(41), or C(42), C(44), and C(43), are 18° and 12.5°, respectively. Consistent with this nonplanarity, C(45) and C(42) have the shortest $U(1)-C(C_6H_6)$ distances, 2.51(1) and 2.55(1) Å, and the longest $U(2)-C(C_6H_6)$ distances, 2.72(1) and 2.73(1) Å. Conversely, C(46) and C(43) have the longest $U(1)-C(C_6H_6)$ distances, 2.73(1) Å, and the shortest $U(2)-C(C_6H_6)$ distances, 2.51(1) and 2.54(1) Å. The $U-C(44)$ and $U-C(41)$ distances are not so disparate: 2.59(1)–2.66(1) Å.

Nonplanar ligands derived from arenes have been observed in complexes such as $(18\text{-crown-6})K(C_6H_6)Ln[C_5H_5(SiMe_3)_2]_2$,^{55,56}

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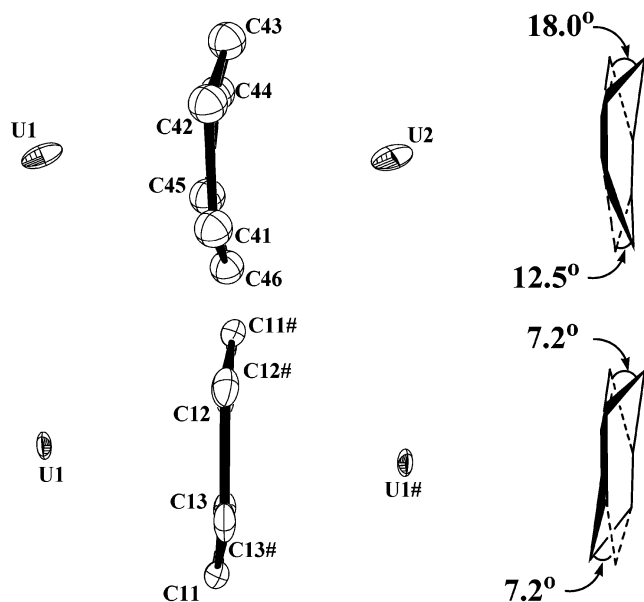
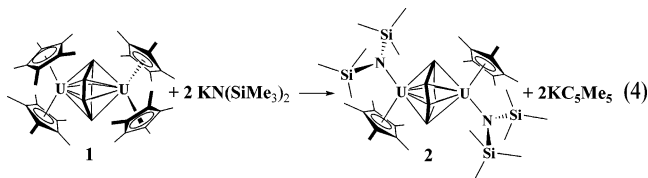


Figure 2. Thermal ellipsoid plot of the U–C₆H₆–U core of [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆), **1**, above, and {(Me₃Si)₂N}(C₅Me₅)U}₂(μ-η⁶:η⁶-C₆H₆), **2**, below, drawn at the 50% probability level as well as depiction of the dihedral angles of the (C₆H₆)²⁻ ligands.

[Li(DME)₂]₂[C₆H₂(SiMe₃)₄-1,2,4,5],⁴⁵ {Na(diglyme)}⁺{Na(diglyme)₂}⁺(1,2,3-triphenylbenzene)²⁻,⁵⁷ Hf₂I₄(PMe₂Ph)₄(μ-arene) (arene = C₆H₆ or C₆H₅Me),⁵⁸ and [(R₂ArN)₂U]₂(C₆H₅Me), **3**.¹⁷ The nonplanar toluene bridge in complex **3** can be viewed as a shallow asymmetric boat with the ipso carbon, C(6), and para carbon, C(3), above the plane of the other four carbons. The dihedral angle between the average plane generated from C(1), C(2), C(4), and C(5) and each of the planes defined by C(5), C(6), and C(1) and by C(2), C(3), and C(4) are 2.4° and 13.4°, respectively.

(C₅Me₅)¹⁻ Ligand Displacement from [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆), **1.** Because the structure of **1** revealed steric crowding equivalent to that in (C₅Me₅)₃U, this provided a good test case for the (C₅Me₅)¹⁻ displacement reaction for long bond organometallics. Indeed, the bimetallic [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆) complex immediately reacts with 2 equiv of KN(SiMe₃)₂ to lose two (C₅Me₅)¹⁻ ligands and form {(Me₃Si)₂N}(C₅Me₅)U}₂(μ-η⁶:η⁶-C₆H₆), **2**, eq 4. Complex **2** was identified by crystal-



lographic and spectroscopic methods, and the byproduct KC₅Me₅ was identified by analyzing the hydrolysis and deuteroiolysis products of the insoluble white powder that formed.

Structure of {(Me₃Si)₂N}(C₅Me₅)U}₂(μ-η⁶:η⁶-C₆H₆), **2.** As shown in Figure 3, complex **2** has a structure similar to that of **1** except that one (C₅Me₅)¹⁻ ring on each uranium has been

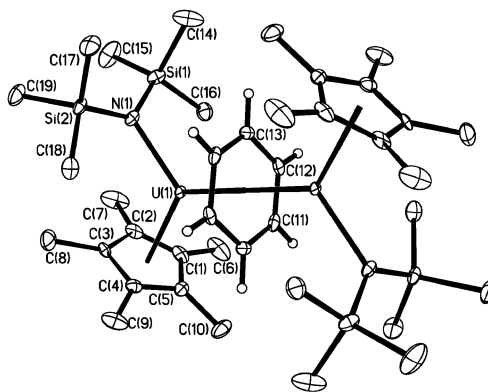


Figure 3. Thermal ellipsoid plot of {(Me₃Si)₂N}(C₅Me₅)U}₂(μ-η⁶:η⁶-C₆H₆), **2**, drawn at the 50% probability level.

replaced by a bis(trimethylsilyl)amide ligand. This substitution changes several structural features in comparison to **1** and appears to relieve the steric crowding. The U–C(C₅Me₅) bond distances are shorter than those in **1** with a narrow range, 2.766(3)–2.795(3) Å, and an average of 2.78(1) Å (2.506 Å U–ring centroid distance). These distances are more normal for trivalent uranium metallocenes (see examples above).^{22,25,26,48–53,59} Another feature which suggests less steric crowding is that the 130.9° (C₅Me₅ ring centroid)–U–(C₆H₆ ring centroid) angle in **2** is 10° larger than the corresponding angles in **1**, Table 2. In **2**, the two (C₅Me₅)¹⁻ ring centroids and the two nitrogen donor atoms describe a square plane rather than the sterically more compact tetrahedral arrangement of the four (C₅Me₅)¹⁻ rings in **1**.

The crystallographic data on **2** provided a more detailed description of the metrical parameters of the arene ligand derived from benzene. The three independent C–C distances, 1.449(4) Å and two values of 1.453(4) Å, are clearly longer than those in free C₆H₆ and do not exhibit the alternating long (1.558(10) Å)–short (1.392(11) Å) behavior found in [Li(DME)₂]₂[C₆H₂(SiMe₃)₄-1,2,4,5].⁴⁵ The X-ray data were also refined to show one hydrogen atom on each of the carbon atoms, which is consistent with the peak areas in the ¹H NMR spectrum. Like complex **1**, the C₆H₆ unit is slightly nonplanar, Figure 2, but in this case the arene adopts a chair conformation that puts the C(11) and C(11#) atoms 0.092 Å above and below the average plane defined by C(13), C(12), C(13#), and C(12#). The dihedral angle between the average plane of C(13), C(12), C(13#), and C(12#) and the plane defined by C(13), C(11), and C(13#) is 7.2°. The three unique C–C–C angles are 119.0(2)°, 120.1(2)°, and 120.3(2)°.

The U–(C₆H₆) distances in **2** vary due to the nonplanarity of the ring, but the range is smaller than that in **1**. For each of the three crystallographically unique carbons in the arene ring, the two U–C distances are 2.564(3) and 2.612(3) Å for U–C(11) and U–C(11#), 2.631(3) and 2.559(3) Å for U–C(12) and U–C(12#), and 2.569(3) and 2.603(3) Å for U–C(13) and U–C(13#), respectively.

The 2.306(2) Å U–N(N(SiMe₃)₂) distance is in the range of analogous U–N distances observed in trivalent uranium amides: 2.352(2) Å in (C₅Me₅)₂U[N(SiMe₃)₂],²² 2.358(19) and 2.23(3) Å in (C₅Me₅)U[N(SiMe₃)₂]₂,⁶⁰ and 2.330(4) Å in

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Table 3. A Comparison of U–C(arene) Average Bond Distances (Å)

compound	U–C(arene) average	ref
$\{[(Me_3Si)_2N](C_5Me_5)U\}_2(\mu-\eta^6:\eta^6-C_6H_6)$, 2	2.59(3)	this work
$[(AdArN)_2U]_2(C_6H_5Me)$, 3	2.593(9)	17
$[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, 1	2.62(9)	this work
$[K(Ar^tBuCN)_3U]_2(C_{10}H_8)$, 4	2.65(6)	18
$(C_6H_6)U(AlCl_4)_3$	2.91(1)	61
$\{[U(C_6Me_6)Cl_2]_2(\mu-Cl)_3\}[AlCl_4]$	2.92(4)	62
$U(C_6Me_6)Cl_2(\mu-Cl)_3UCl_2(\mu-Cl)_3UCl_2(C_6Me_6)$	2.94(3)	63
$[U_3(\mu_3-Cl)_2(\mu_2-Cl)_3(\mu-\eta^2-AlCl_4)(\eta^6-C_6Me_6)]$	2.92(4)	64
$(C_6Me_6)U(AlCl_4)_4$	2.94(1)	65
$[U(O-2,6-Pr^iC_6H_3)_3]_2$	2.92(2)	66
$(C_6Me_6)U(BH_4)_3$	2.93(2)	67
$(C_6H_5Me)U(AlCl_4)_3$	2.94(5)	68

$U[N(SiMe_3)_2]_3$.⁶¹ In comparison, tetravalent $HU[N(SiMe_3)_2]_3$ has a 2.237(9) Å U–N distance.⁶²

Structural Comparisons. The two structurally characterized uranium complexes in the literature which are most closely related to **1** and **2** are $[(AdArN)_2U]_2(C_6H_5Me)$, **3**,¹⁷ and $[K(Ar^tBuCN)_3U]_2(C_{10}H_8)$, **4**,¹⁸ (Ad = adamantyl; Ar = C_6H_4 -Me₂-3,5). Complexes **1–4** all have nonplanar arene-derived ligands sandwiched between two uranium ions, each of which is bound to additional ligands which have an overall formal charge of –2, that is, two $(C_5Me_5)^{1-}$ ligands, a $(C_5Me_5)^{1-}$ and a $(NR_2)^{1-}$ ligand, two $(NR_2)^{1-}$ ligands, or three $(R_2C=N)^{1-}$ ligands and K^{1+} , respectively. Table 3 compares the structural data of these complexes. The 2.504(8)–2.660(8) Å U–C(C_6H_5 -Me) bond lengths in **3** are quite similar to those of **2**, which are shorter than those of sterically crowded **1**. The 2.565(11)–2.749–(10) Å U–C($C_{10}H_8$) distances in **4** span a wider range more similar to those in **1**. The 2.334(6) Å U–N(NAdAr) distance in **3** is very similar to the U–N[N(SiMe₃)₂] distance in **2**.

The U–C(arene) distances in **1–4** are all substantially shorter (by ca. 0.4 Å) than those in previously reported trivalent and tetravalent uranium complexes of neutral arenes as shown in Table 3.^{63–72} These neutral arene complexes include species such as $(C_6H_6)U(AlCl_4)_3$,⁶³ $\{[(C_6Me_6)UCl_2]_2(\mu-Cl)_3\}[AlCl_4]$,⁶⁴ $(C_6Me_6)U(BH_4)_3$,⁶⁹ and $[U(O-2,6,Pr^iC_6H_3)_3]_2$,⁶⁸ which involves intramolecular arene interactions. The shorter U–C(C_6H_6) distances in **1** and **2** are consistent with reduction of the arenes, which would increase the electrostatic interactions between the anionic arene ligand and the cationic metal center leading to shorter bond lengths. This is a common feature in f element

chemistry. For example, the typical 2.5 Å U–O(THF) distance^{73–75} of a neutral THF coordinated to trivalent uranium is about 0.4 Å longer than the typical 2.1 Å U–O(OR) distances of anionic alkoxide ligands in comparable compounds.^{68,76,77}

If the arene ligands in **1** and **2** are reduced, the uranium centers could be formally assigned either as U(III) or as U(IV). The U–C(C_5Me_5) bond distances in **1** are ambiguous on this point because they are unusually long and comparable to sterically crowded distances in U(III), U(IV), and Th(IV) complexes, that is, $(C_5Me_5)_3U$,⁷ $(C_5Me_5)_3UL$ (L = CO,⁶ N₂¹¹), $(C_5Me_5)_3UX$ (X = Cl, F),¹⁰ and $(C_5Me_5)_3ThH$.⁷⁸ The U–C(C_5 -Me₅) and the U–N[N(SiMe₃)₂] bond distances in **2**, however, are clearly in the U(III) range. The nonplanarity of the C_6H_6 units as well as the longer C–C distances within the bridging C_6H_6 unit of **2** are also consistent with the bridging ligand being anionic.

Magnetic and Optical Properties of 1 and 2. The structural features of **1** and **2** as well as formation of **1** via $(C_5Me_5)^{1-}$ displacement from trivalent $(C_5Me_5)_3U$ and $[BPh_4]^{1-}$ displacement from trivalent $[(C_5Me_5)_2U][(\mu-Ph_2)BPh_2]$ are consistent with formulation of **1** as a sterically crowded U(III) complex containing a $(C_6H_6)^{2-}$ moiety. However, magnetic data are ambiguous on this point. The room-temperature magnetic moments of **1**, $\mu_{eff} = 2.2 \mu_B$, and **2**, $\mu_{eff} = 1.8 \mu_B$, are in the range for U(III) complexes. However, these values are also similar to magnetic moments found for U(IV)^{10,79} as well as $5f^4$ compounds which would be isoelectronic with U(II).^{80,81} Similarly, the ¹H NMR spectra of **1** and **2** contain $(C_5Me_5)^{1-}$ resonances with 14.6 and 6.1 Hz half-height line widths, respectively. Resonances with $\Delta\nu_{1/2}$ in this range are similar to those of previously reported U(III) and U(IV) compounds.^{9,82}

The electronic absorption spectra of **1** and **2** are compared to that of $(C_5Me_5)_3U$ in Figure 4. The spectrum of $(C_5Me_5)_3U$ contains transitions between 600 and 1600 nm (16 700 to 6300 cm^{-1}) in the near-IR that are characteristic of Laporte-forbidden $f \rightarrow f$ transitions of the U(III) ion. It has been shown that these transitions can serve as an “electronic” fingerprint for trivalent uranium.⁸³ The spectrum of $(C_5Me_5)_3U$ is similar to those of other trivalent complexes, that is, $(C_5H_5)_3U(THF)$,^{84,85} $\{[K(THF)_2]_2U(NH-2,6-i-Pr_2C_6H_3)_3\} \cdot THF$,⁸⁶ $[Zr(O^iPr)_9]U_2(THF)$,⁸⁷ and $U_3(THF)_4$.⁸⁸ The near-IR region of the absorption spectrum of **1** does not provide definitive evidence on oxidation state because the absorptions in this region are not well resolved.

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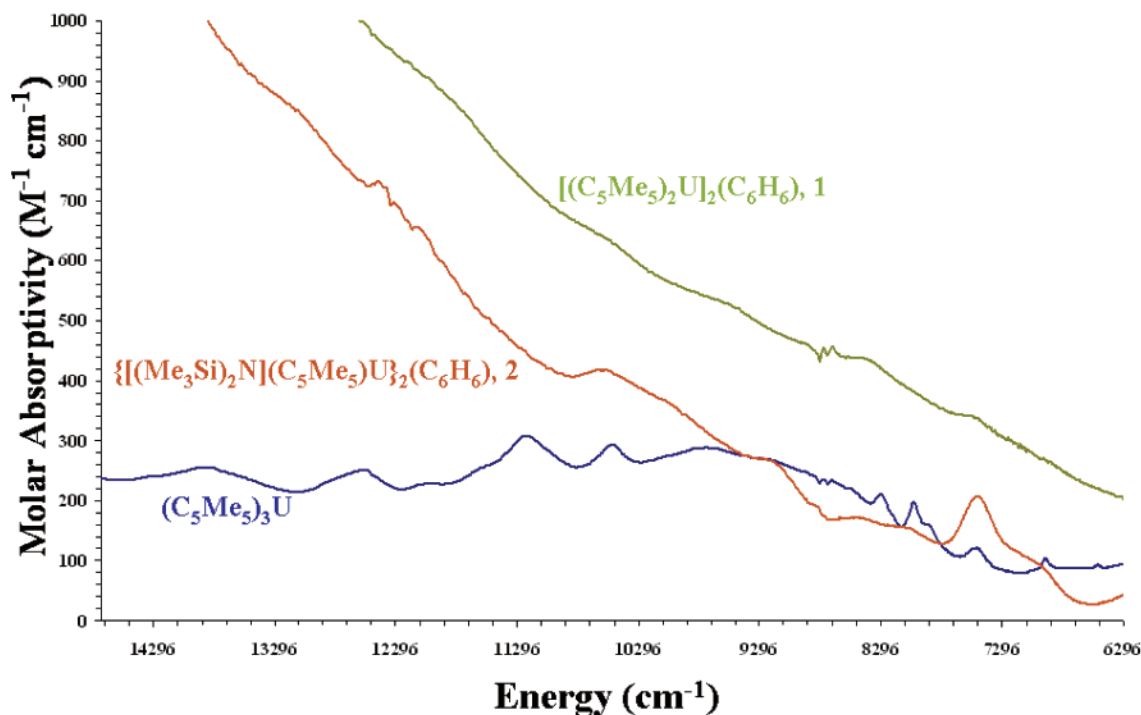
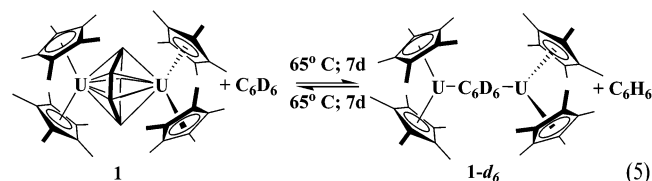


Figure 4. Electronic absorbance spectrum of a 2.8 mM solution of $(C_5Me_5)_3U$, 1.4 mM solution of $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1**, and a 1.9 mM solution of $\{[(Me_3Si)_2N](C_5Me_5)U\}_2(\mu-\eta^6:\eta^6-C_6H_6)$, **2**, in C_6H_6 .

However, the spectrum of **2**, which has one less $(C_5Me_5)^{1-}$ ligand per metal center, is more informative. Although the near-IR absorptions of **2** are not as sharp as those of $(C_5Me_5)_3U$, the similarities between the spectra are consistent with the presence of U(III) in **2**. The ultraviolet spectra of $(C_5Me_5)_3U$, **1**, and **2** are all similar and contain a maximum at 212 nm ($47\,200\text{ cm}^{-1}$) that is distinct from both benzene and the benzene radical anion.^{89–91}

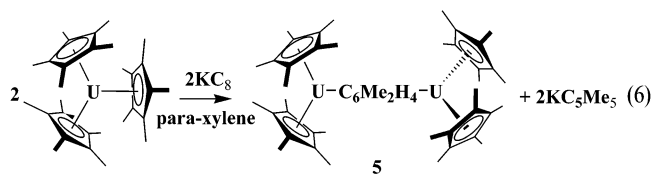
C_6H_6/C_6D_6 Exchange Reactions. To obtain further information on the nature of bonding in **1**, exchange reactions with other arenes were examined. Complex **1** is stable to arene exchange at room temperature. In fact, **1** crystallizes from saturated solutions of toluene. **1** is also stable at room temperature in C_6D_6 , but after 7 days at 65 °C, a new complex formulated as $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6D_6)$, **1-d₆**, is obtained. The deuterated complex, **1-d₆**, can be independently synthesized from $(C_5Me_5)_3U$, KC_8 , and C_6D_6 . The C_6H_6/C_6D_6 reaction is reversible: **1-d₆** in C_6H_6 forms **1** after 7 days at 65 °C, eq 5.



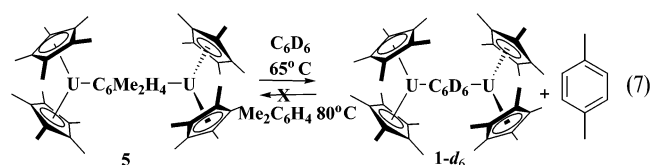
No evidence of $C_6H_{6-x}D_x$ was observed by NMR analysis during the reaction. Furthermore, NMR analysis of **1** in a 1:1

mixture of C_6H_6 and C_6D_6 at 65 °C for 7 d results in a 1:1 mixture of **1:1-d₆**. GC-MS analysis of the volatile organics from this reaction showed no evidence of $C_6H_{6-x}D_x$,⁹² only C_6H_6 and C_6D_6 were observed. The gradual conversion of **1** to **1-d₆** can be analyzed by 1H and 2H NMR spectroscopy. Figure 5 shows that this reversible reaction can be monitored by following the subtle changes that occur for the methyl resonances of the $(C_5Me_5)^{1-}$ ligands.

Complex **1-d₆** can also be made by adding C_6D_6 to product **5**, which formed from the reaction between $(C_5Me_5)_3U$, KC_8 , and *para*-xylene, eq 6. The formation of **1-d₆** from **5** and C_6D_6



occurs much faster than the analogous reaction between **1** and C_6D_6 : quantitative formation of **1-d₆** from the **5** and C_6D_6 is complete in 1 d at 65 °C versus 7 d at 65 °C for the **1**/ C_6D_6 reaction. In contrast to the **1**/ C_6D_6 reaction, the **5**/ C_6D_6 reaction is not reversible, eq 7, and neither **1** nor **1-d₆** reacts with *para*-xylene to form **5**.



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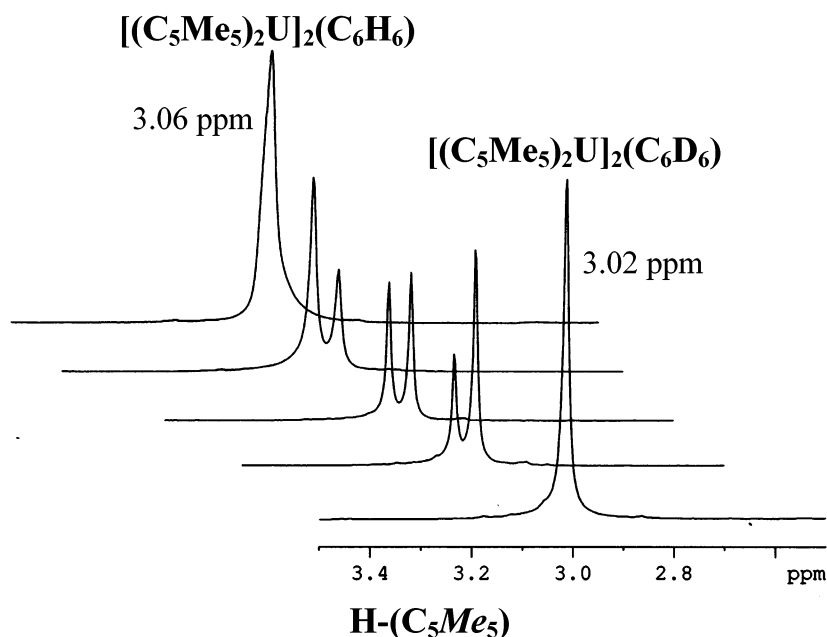


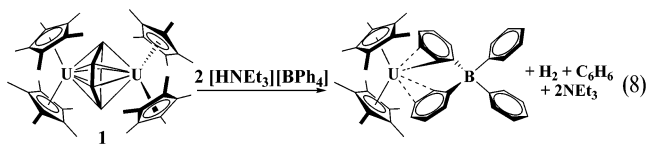
Figure 5. 1H NMR spectra of the methyl $(C_5Me_5)^{1-}$ region depicting conversion of $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1**, to $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6D_6)$, **1-d₆**. Top spectrum, pure **1**; bottom spectrum, pure **1-d₆** obtained after 7 d at 65 °C.

In a competition experiment for comparison with neutral f element arene reactions in the literature (see below),⁹³ $(C_5Me_5)_3U$ was treated with KC_8 in a 1:1 mixture of C_6H_6 and *para*-xylene. $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$ and $[(C_5Me_5)_2U]_2(C_6H_4Me_2-1,4)$ were observed by 1H NMR spectroscopy in a 3:1 mixture. The synthesis of a C_6Me_6 analogue was not achieved via the routes that were successful for **1** and **5**.

Attempts to replace the arene ligand in **1** with THF were unsuccessful. Complex **1** is stable in neat THF at room temperature.

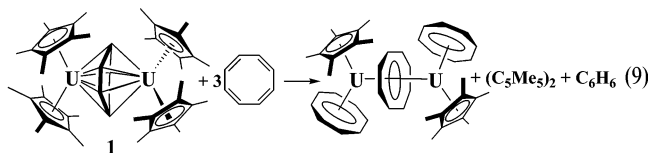
Reactivity of 1 with Protic Reagents. Hydrolysis and deuteriolysis of **1** were conducted to further probe the nature of the metal and arene ligand. The mass spectral data on these reactions were complicated, and more products were observed than would be expected from simple protonation or reduction reactions.⁹⁴

The reactivity of **1** with stoichiometric amounts of $[HNEt_3][BPh_4]$ was also examined. Reduction rather than protonation is observed with the formation of the trivalent precursor to **1**, $[(C_5Me_5)_2U][(\mu-Ph_2)BPh_2]$, along with NEt_3 , C_6H_6 , and hydrogen, eq 8. No cyclohexadienes were detected.



Multielectron Reductive Reactivity of 1. Since the structure of $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$ reveals steric crowding equivalent to that in $(C_5Me_5)_3U$, complex **1** has the potential to react via sterically induced reduction like the $(C_5Me_5)_3M$ complexes.² Examination of the reaction between **1** and 1,3,5,7- C_8H_8 shows that it reacts with 3 equiv of substrate to quantitatively generate

the previously characterized $[(C_5Me_5)(C_8H_8)U]_2(\mu-\eta^3:\eta^3-C_8H_8)$ ⁹ along with C_6H_6 and $(C_5Me_5)_2$, eq 9.



In the conversion of three C_8H_8 substrates to three $C_8H_8^{2-}$ ligands, **1** functions as a six-electron reductant. Two of the electrons can come from two sterically induced reductions involving the $(C_5Me_5)^{1-}/C_5Me_5$ redox couple, and the $[U_2(C_6H_6)]^{4+}$ moiety would provide the remaining four electrons through formation of neutral benzene and the two U^{4+} ions. Hence, sterically induced reduction is coupled with other reductive processes to generate a multielectron reduction system.

Density Functional Theory Calculations. Molecular Geometry of 1. The geometry of **1** was fully optimized subject to the constraint of C_{2v} symmetry. This process was by no means straightforward, however. It is often the case that the presence of unpaired 5f electrons makes even self-consistent field (SCF) convergence problematic, and this was certainly found to be so in the present calculations. The procedure adopted was as

(94) Hydrolysis of **1** gave a mixture of products including benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, cyclohexene, H_2 , C_5Me_5H , and $(C_5Me_5)_2$. The presence of hydrogen is consistent with reduction of water by low valent uranium (II or III) or by an arene anion (with formation of benzene). The presence of the reduced arenes is consistent with protonation of arene anions. Deuteriolysis of **1** gave a more complicated mixture of products, which included benzene, cyclohexadiene- d_2 , cyclohexene- d_4 , H_2 , HD, D_2 , and C_5Me_5D . The presence of H_2 and HD is difficult to rationalize by primary processes. In the converse reaction, hydrolysis of **1-d₆**, products included C_5Me_5H , approximately equal amounts of C_6D_6 , C_6D_5H , 1,3-cyclohexadiene- d_6 , 1,4-cyclohexadiene- d_6 , and cyclohexene- d_6 , as well as H_2 and DH. DH is an unusual product in this case because the only source of deuterium is the C_6D_6 ligand. Interestingly, C_6D_5H is also a reaction product. Deuteriolysis products of **1-d₆** included C_6D_6 , H_2 , C_6D_5H , $C_6D_4H_2$, $C_6D_{10-1}H_3$, H_2 , HD, D_2 , and C_5Me_5D . Hence, all of the combinations of **1** or **1-d₆** with H_2O or D_2O resulted in complicated product mixtures.

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Table 4. Calculated Bond Lengths (Å) for [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆), **1**, and {[(Me₃Si)₂N](C₅Me₅)₂U}₂(μ-η⁶:η⁶-C₆H₆), **2**

	quintet, unrestricted	singlet, unrestricted
Compound 1		
U1–C(C ₆ H ₆)	2.719 × 2, 2.591 × 4 average = 2.634	2.723 × 2, 2.607 × 4 average = 2.646
U2–C(C ₆ H ₆)	2.532 × 2, 2.674 × 4 average = 2.627	2.553 × 2, 2.683 × 4 average = 2.640
U1–C(C ₅ Me ₅)	2.841 × 2, 2.849 × 2, 2.906 average = 2.857	2.839 × 2, 2.845 × 2, 2.907 average = 2.855
U2–C(C ₅ Me ₅)	2.817 × 2, 2.847 × 2, 2.872 average = 2.840	2.819 × 2, 2.839 × 2, 2.877 average = 2.839
U1–U2	4.406	4.438
C–C(C ₆ H ₆)	1.444 × 2, 1.442 × 2 average = 1.443	1.440 × 6
Compound 2		
U–C(C ₆ H ₆)	2.585, 2.622, 2.586, 2.632, 2.585, 2.639 average = 2.608	
U–C(C ₅ Me ₅)	2.727, 2.722, 2.726, 2.731, 2.754 average = 2.732	
U–N	2.321	
N–Si	1.740, 1.748	
U1–U2	4.339	
C–C(C ₆ H ₆)	1.453 × 3, 1.445 × 2, 1.446 average = 1.449	

follows. Initially, the atoms were placed at a plausible geometry on the basis of the crystallographic data, and the symmetry was idealized to *C*_{2v}. A singlet, spin-restricted calculation (i.e., one in which there is no excess α over β spin density and the α spin electron in a given MO is constrained to have the same spatial wave function as its β spin counterpart) was then performed using a very large (0.5 hartree) value of the ADF “smear” parameter to aid SCF convergence by spreading the least stable electrons over a wide range of MOs, that is, allowing nonintegral MO occupancy. The extensively nonintegral MO occupations thus obtained have questionable physical significance, but without the electron smearing approach the SCF oscillated wildly and convergence proved impossible. Once a converged, nonintegral but aufbau electronic structure was obtained, the calculation was restarted using that electronic structure as an initial guess but with a smaller value of the smearing parameter. This process was repeated with progressively smaller values of the smearing parameter (finishing at 0.001 hartree) until a converged, aufbau electronic structure was obtained with only the highest few MOs having nonintegral occupation. These MOs were found to be almost entirely U 5f in character and were very close to one another energetically.

At this point, a geometry optimization was performed, taking the converged singlet electronic structure as an initial guess and retaining the small smear parameter. The calculation proceeded smoothly to a converged geometry.

Analysis of the electronic structure at this optimized geometry suggested the presence of four U 5f-localized electrons in the bimetallic molecule. It was therefore decided to run another geometry optimization with a more realistic arrangement of the electrons, that is, a quintet system at the spin-unrestricted level with an excess of four up-spin over down-spin electrons in the molecule as a whole. This calculation also proceeded smoothly to an optimized geometry, with the four least stable electrons all being U 5f-localized and of α spin. The two least stable electrons were distributed nonintegrally in four MOs of very similar energy. As the population of each of the MOs was close to 0.5, a further geometry optimization was performed constraining the occupation of the four highest occupied MOs to

be 0.5. This constraint had very little effect on the molecular geometry, and the resulting structure was found to be 111 kJ mol⁻¹ more stable than the spin-restricted singlet discussed above.

The *C*_{2v}-optimized, spin-unrestricted quintet geometry of **1** compares extremely favorably with the experimental structure; key bond lengths are given in Table 4. As with experiment, the calculation shows that the U–C(C₅Me₅) bond distances are long, the average being 2.86 Å for one U and 2.84 Å for the other (there are no symmetry operations which interchange the U atoms in *C*_{2v}-optimized **1**, and hence the two U atoms are symmetry-unique), in comparison with 2.84(3) and 2.83(2) Å from experiment. The range is also comparable. Furthermore, the experimental U–U distance is reproduced computationally to within 0.01 Å.

Similarly good agreement is found in the U–C(C₆H₆) distances. As with experiment, calculation finds that the bridging ligand is significantly nonplanar, with a >0.1 Å range of U–C(C₆H₆) distances. The average computed C–C distance within the C₆H₆ ring is exactly the same as found experimentally (1.44 Å). Whereas the experimental errors are such that it is not possible to say if this represents a lengthening with respect to free benzene, we can be more confident in drawing this conclusion on the basis of the computational data. A calculation on C₆H₆, using the same method as employed for **1**, yielded a C–C distance of 1.394 Å, and thus we find a 0.05 Å lengthening on going from free to complexed benzene. The importance of this will be discussed later.

Electronic Structure of 1. The energies, compositions, and characters of the highest occupied MOs of **1** are given in Table 5, and atomic population data for U are collected in Table 6. As noted above, the population of each of the four highest occupied MOs (36b₁ α , 36b₂ α , 44a₁ α , and 43a₁ α , the most stable of the four) has been constrained to 0.5. Below these MOs are two further orbitals (35b₁ α and 35b₂ α) which contain one electron each and which have essentially the same character as the 36b₁ α through 43a₁ α ; that is, they are almost entirely U-localized. The calculation therefore suggests that the four least stable electrons of **1** occupy 6 U-based one-electron spin–

Table 5. Calculated Energy and Composition Data for the Highest Occupied Molecular Orbitals of Quintet $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1**

MO (irrep and spin)	energy (eV)	occupation	composition (%)	character
36b ₁ α (HOMO)	-2.576	0.5	93.5 U2 f, 1.82 U1 f	U f nonbonding
36b ₂ α	-2.598	0.5	89.2 U1 f, 3.9 U2 f	U f nonbonding
44a ₁ α	-2.663	0.5	89.3 U1 f, 6.1 U2 f	U f nonbonding
43a ₁ α	-2.702	0.5	87.8 U2 f, 5.1 U1 f	U f nonbonding
35b ₁ α	-2.707	1.0	82.2 U1 f, 6.9 U1 d, 1.4 U2 f	U f/d nonbonding
35b ₂ α	-2.763	1.0	78.6 U2 f, 6.5 U2 d, 4.5 U1 f	U f/d nonbonding
27a ₂ β	-3.389	1.0	19.9 U1 f, 4.2 U1 d, 12.9 U2 f, 2.6 U2 d, 45.9 C(C ₆ H ₆) p	U f/d → C ₆ H ₆ e _{2u} δ back-bonding
42a ₁ β	-3.496	1.0	13.0 U2 f, 9.7 U2 d, 7.1 U1 f, 7.1 U1 d, 41.3 C(C ₆ H ₆) p	U f/d → C ₆ H ₆ e _{2u} δ back-bonding
42a ₁ α	-3.637	1.0	19.5 U2 f, 8.6 U2 d, 10.5 U1 f, 2.0 U1 d, 35.1 C(C ₆ H ₆) p	U f/d → C ₆ H ₆ e _{2u} δ back-bonding
27a ₂ α	-3.717	1.0	8.9 U1 f, 1.9 U1 d, 19.4 U2 f, 2.1 U2 d, 34.7 C(C ₆ H ₆) p	U f/d → C ₆ H ₆ e _{2u} δ back-bonding
34b ₂ β	-4.535	1.0	8.9 U1 f, 1.9 U1 d, 66.7 C(C ₅ Me ₅ , bonded to U1) p	mainly C ₅ Me ₅ e ₁

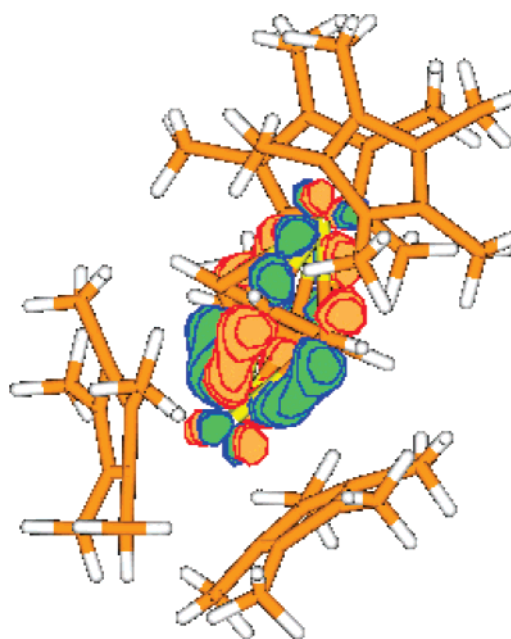
Table 6. Calculated U Atomic Population Data for $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1**, and $\{[(Me_3Si)_2N](C_5Me_5)_2U\}_2(\mu-\eta^6:\eta^6-C_6H_6)$, **2**

	charge	spin	s (6s + 7s)	p (6p + 7p)	6d	5f
1						
U1	+2.730	α	1.013	2.578	0.641	2.499
		β	1.003	2.560	0.503	0.473
U2	+2.793	α	1.009	2.554	0.646	2.471
		β	1.001	2.537	0.516	0.474
2						
U	+2.553	α	1.036	2.595	0.690	2.467
		β	1.022	2.577	0.565	0.494

orbitals of the same spin. Interestingly, each of these MOs is localized on only one of the U atoms, and it may therefore be appropriate to describe the U atoms as each possessing two 5f electrons, which are ferromagnetically coupled to two similar electrons on the other U.

The next four electrons occupy the 27a₂ β, 42a₁ β, 42a₁ α, and 27a₂ α one-electron MOs and are more than 0.5 eV more stable than the U-localized electrons discussed above. These four electrons are in orbitals that are not metal-localized, but have significant contributions from both metals and the carbon atoms of the bridging ligand. These orbitals are δ back-bonding between the U and the C₆H₆ ring. As an example, a three-dimensional representation of the 27a₂ α electron is shown in Figure 6. The MOs of free benzene that participate in the 27a₂ β through 27a₂ α MOs of **1** are the e_{2u} levels (those ring pπ orbitals with two vertical nodes) that are unoccupied in neutral benzene. The partial population of these levels in **1**, as a result of the δ back-bonding, is consistent with the 0.05 Å lengthening of the C–C distances in the complexed ring, as the e_{2u} levels have significant C–C antibonding character. Consistent with the transfer of electron density from U → arene are the calculated charges on the ring C and H atoms, averaging -0.43 and +0.07, respectively (an overall arene ring charge of -2.21). The U atomic population data (Table 6) suggest that this transfer involves mainly the two 7s electrons and a single 6p electron of the free atom. Hence, the U atoms in the complex are calculated to have an approximately 5f³6d¹ configuration, that is, retaining the free atom f and d values. The 6p “hole” in U complexes (i.e., the partial involvement of the semi-core U 6p electrons in bonding and the concomitant atomic population reduction from 6.0) is well known.⁹⁵

The depletion of electrons from the U atoms leaves them with a computed charge of between +2.7 and +2.8. The relation between such calculated charges and formal oxidation states is

**Figure 6.** Three-dimensional representation of the 27a₂ α orbital calculated for $[(C_5Me_5)_2U]_2(C_6H_6)$, **1**.

cloudy, especially given the sensitivity of Mulliken charges to the choice of basis set. Nevertheless, the calculated U charges can be nicely related to the chemistry of **1**, as is discussed below.

That the four least stable electrons of **1** all have the same spin and are localized on either one U or the other suggests that an alternative antiferromagnetic coupling may be possible. Using the ADF keyword “modifystartpotential” and following the same computational procedure as before, it did indeed prove possible to obtain an optimized geometry and converged electronic structure of **1** in which the two U 5f-based electrons on one U atom are of α spin and the two on the other are of β spin. Interestingly, this low-spin singlet arrangement is calculated to be 9.6 kJ mol⁻¹ more stable than the high-spin quintet discussed above. The geometries of the two systems are very similar to one another, as are the non-U 5f-based MOs.

A more complete approach would of course be to include spin-orbit coupling. Single-point spin-orbit coupled calculations were attempted using the geometries and electronic structures of singlet and quintet **1** as input, but SCF convergence proved impossible in both cases. From the scalar calculations, we can conclude that at least two arrangements of the f-based electrons lie very close in energy, but we cannot definitely say which is the ground state as the singlet–quintet energy difference is so small. Both the high-spin and the low-spin

(95) Kaltsoyannis, N. *Chem. Soc. Rev.* **2003**, 32, 9.

Table 7. Calculated Energy and Composition Data for the Highest Occupied Molecular Orbitals of Quintet $\{[(\text{C}_5\text{Me}_5)_2\text{N}](\text{C}_5\text{Me}_5)_2\text{U}\}_2(\mu-\eta^6-\eta^6-\text{C}_6\text{H}_6)$, **2**

MO (irrep and spin)	energy (eV)	occupation	composition (%)	character
71a _u α (HOMO)	-2.821	1.0	90.4 U f, 1.7 U d	U f nonbonding
70a _g α	-2.864	1.0	87.0 U f, 1.6 U d	U f nonbonding
70a _u α	-2.875	1.0	88.4 U f, 1.8 U d	U f nonbonding
69a _g α	-2.935	1.0	86.0 U f, 2.8 U d	U f nonbonding
69a _u β	-3.751	1.0	26.3 U f, 14.7 U d, 49.4 C(C ₆ H ₆) p	U f/d → C ₆ H ₆ e _{2u} δ back-bonding
68a _u β	-3.833	1.0	24.8 U f, 14.1 U d, 50.4 C(C ₆ H ₆) p	U f/d → C ₆ H ₆ e _{2u} δ back-bonding
69a _u α	-3.934	1.0	35.6 U f, 14.4 U d, 41.1 C(C ₆ H ₆) p	U f/d → C ₆ H ₆ e _{2u} δ back-bonding
68a _u α	-4.062	1.0	36.6 U f, 12.6 U d, 42.4 C(C ₆ H ₆) p	U f/d → C ₆ H ₆ e _{2u} δ back-bonding
67a _u β	-5.020	1.0	4.6 U f, 3.3 U d, 10.3 N p, 59.2 C(C ₅ Me ₅) p	mainly C ₅ Me ₅ e ₁

arrangements, however, yield essentially the same picture of the valence electronic structure and bonding of **1**.

Molecular Geometry and Electronic Structure of 2. A process similar to that followed for **1** was adopted for **2**. A series of single-point calculations at a guess geometry based on the crystal structure were performed with increasingly small values of the smear parameter. Given the results for **1**, it was assumed from the start that **2** would have four unpaired electrons, and the spin-unrestricted approach was adopted. Unlike **1**, the final result of the single-point calculations was an aufbau and fully integral electronic structure. The four least stable electrons in **2** all have the same spin and occupy four U 5f-based orbitals, in contrast to **1** in which the four α spin U 5f-based electrons are spread over six one-electron MOs (an unavoidable consequence of the very small energy gaps between the f orbitals). This electronic structure for **2** was then used as a starting guess for a full geometry optimization subject to the constraint of *C*₂ symmetry.

Key bond lengths from the calculated geometry of **2** are given in Table 4. As with **1**, there is generally excellent agreement between the calculated and experimental geometries of **2**. The U–C(C₅Me₅) bond distance reduction found experimentally on going from **1** to **2** is reproduced computationally; indeed, it is overestimated by ca. 0.05 Å in the calculation. The reduction in the U–U distance from **1** to **2** is also found computationally, and the U–N and N–Si distances are reproduced very satisfactorily. As was found experimentally, the range of U–C distances to the bridging ligand is smaller in **2** than in **1**. The average U–C(C₆H₆) distance is calculated to be 2.61 Å, in excellent agreement with the 2.59(3) Å value found experimentally. The significant lengthening of the free arene C–C distances found in **1** is also present in **2**, with experiment and calculation once again being in excellent agreement [1.45(2) (av., expt) vs 1.449 Å].

The energies, compositions, and characters of the highest occupied MOs of **2** are given in Table 7, and the U atomic populations are given in Table 6. Comparison of Tables 5 and 7 suggests that the valence electronic structures of **1** and **2** are similar. The four least stable electrons in **2** are U 5f-based (now with equal contributions from the two U atoms due to the inversion symmetry imposed on the calculation), and there are then four electrons in the 69a_u β, 68a_u β, 69a_u α, and 68a_u α MOs which are U → arene δ back-bonding. The transfer of electrons from U to arene seen in **1** is once again found in **2**, with a charge of +2.55 on the U and an overall -2.39 charge on the C₆H₆ ring. Once again, it is the 7s and 6p atomic orbitals of U that have significantly smaller populations than in the free atom.

Despite extensive attempts using several weeks of CPU time, it proved impossible to converge the geometry of an unrestricted singlet form of **2** (i.e., the antiferromagnetically coupled arrangement of the four 5f-based electrons). This may well be due to running with no symmetry constraints, as it is necessary to remove all symmetry operations connecting the metal atoms when doing such a “broken symmetry” calculation.

Discussion

(C₅Me₅)¹⁻ Substitution Reactions in Long Bond Organometallics. The rapid reaction of (C₅Me₅)₃U with KN(SiMe₃)₂ to form (C₅Me₅)₂U[N(SiMe₃)₂] in high yield indicates that (C₅Me₅)¹⁻ displacement is highly favored for this sterically crowded complex. In comparison, no (C₅Me₅)¹⁻ substitution is observed in reactions of KN(SiMe₃)₂ with conventional trivalent U(III) (C₅Me₅)¹⁻ complexes, that is, [(C₅Me₅)₂UCl]₃,^{25,26} (C₅Me₅)₂U Me₂K,²² or [(C₅Me₅)₂U][μ-Ph₂BPh₂], which have normal metal ligand bond distances. The only product isolated from these reactions is the bis(pentamethylcyclopentadienyl) complex, (C₅Me₅)₂U[N(SiMe₃)₂], which retains the two (C₅Me₅)¹⁻ ligands of the starting material.

The reaction of **1**, another complex with unusually long U–C(C₅Me₅) bond lengths, with KN(SiMe₃)₂ to form **2** suggests that (C₅Me₅)¹⁻ displacement by ionic metathesis may be a general reaction for long bond organometallic complexes. The fact that an additional equivalent of KN(SiMe₃)₂ does not displace additional (C₅Me₅)¹⁻ ligands from **2** or from (C₅Me₅)₂U[N(SiMe₃)₂], compounds which have normal bond distances, is consistent with the generalization that this (C₅Me₅)¹⁻ displacement reaction is more favorable with sterically crowded complexes.

Although the formation of (C₅Me₅)₂U[N(SiMe₃)₂] from (C₅Me₅)₃U by the (C₅Me₅)¹⁻ ionic metathesis route is not synthetically useful, because (C₅Me₅)₂U[N(SiMe₃)₂] can be made in fewer steps by other routes, the reaction does offer synthetic utility in other cases. For example, it is not so clear how to form **2** by other routes. Complex **2** is a rare example of an f element complex that has three different ligands per metal center. In general, it is difficult to synthesize heteroleptic complexes containing more than one type of ancillary ligand. It is also more difficult to synthesize mono- versus bis-cyclopentadienyl complexes.^{60,96,97} Indeed, the predominance of the (C₅Me₅)¹⁻ ligand with early transition metals, lanthanides, and actinides is generally associated with the bis(pentamethylcyclopentadienyl) (C₅Me₅)₂M metallocene unit. Hence, (C₅Me₅)¹⁻

(96) Heeres, H. J.; Teuben, J. H. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 226.
 (97) Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Organometallics* **2002**, *21*, 5978.

displacement reactions may provide a convenient route to form heteroleptic mono- $(C_5Me_5)^{1-}$ complexes that currently are synthetically inaccessible. Extension of the $(C_5Me_5)^{1-}$ displacement reaction to less crowded species may also be possible if the appropriate conditions can be identified.

Synthesis of 1. Since **1** can be formed in the presence of benzene from several combinations of trivalent uranium complexes and potassium reductants, for example, $(C_5Me_5)_3U$ or $[(C_5Me_5)_2U][(\mu-Ph_2)BPh_2]$ with K/18-crown-6 or K/C₈ and $(C_5Me_5)_3U/KH$, there may be several synthetic pathways available to this complex. The $[(C_5Me_5)_2U][(\mu-Ph_2)BPh_2]$ reaction, eq 3, is the most conventional in terms of ionic metathesis because the $[(\mu-Ph_2)BPh_2]^{1-}$ anion, attached to uranium only by two η^2 -arene interactions, is easily displaced.^{22,43} However, the $(C_5Me_5)_3U$ reactions show that the $(C_5Me_5)^{1-}$ ligands in these sterically crowded complexes can be just as easily displaced as the weakly held $[(\mu-Ph_2)BPh_2]^{1-}$ anion.

The formation of **1** as one of the products from reactions of $(C_5Me_5)_3U$ and KH in benzene is less clear unless the KH had residual K that generated the necessary arene anions for a displacement reaction. The original synthesis of **1** from a KC_5Me_5 sample prepared from KH and C_5Me_5H most likely was contaminated with either KH or K. These results suggest that caution must be exercised when using potassium reagents in arene solvents. Unexpected formation of arene anions could interfere with yields of the desired product particularly in reactions involving sterically crowded complexes. To better control synthetic conditions, we have employed $KN(SiMe_3)_2$ in place of KH in the synthesis of KC_5Me_5 and other insoluble KZ salts. This $KN(SiMe_3)_2$ -based synthesis of KC_5Me_5 is additionally preferred because it can be done in toluene in the absence of coordinating solvents and provides THF-free KC_5Me_5 in one step. This synthetic procedure bypasses additional desolvation steps that must be taken in the synthesis of KC_5Me_5 from KH and C_5Me_5H , which is typically done in coordinating solvents.

Structure and Chemical Reactivity of 1 and 2. Complexes **1** and **2** could be formulated in several ways depending on how the oxidation state of the metal and the charge on the bridging arene-derived ligands are formally assigned. None of the integral assignments involve conventional oxidation levels for both the metal and the arene. The most common oxidation states for uranium in organometallic complexes are U(III) and U(IV). If **1** and **2** involved U(IV), this would imply the presence of highly reduced bridging ligands, $(C_6H_6)^{4-}$ tetraanions. U(III) complexes would require only $(C_6H_6)^{2-}$ dianions. Crystallographically characterized examples of arene dianions exist in some alkali metal complexes, but being anti-aromatic, they are not common. If the bridging ligand is a neutral arene, a type of ligand that has previously been shown to complex U(IV) and U(III) in complexes such as $(C_6H_6)U(AlCl_4)_3$,⁶³ $(C_6Me_6)U(AlCl_4)_3$,⁶⁷ and those in Table 3, this would require an unconventional U(II) oxidation state for the metal in **1** and **2**.⁹⁸ Consideration of oxidation states lower than 2 for uranium would require cationic arene bridges, and this seems unlikely in view of the relative electronegativities of the elements involved.

Several of the conventional methods used to assign oxidation states are not definitive for **1** and **2**. The magnetic moments of U(IV) and U(III) are similar to and within the experimental error

of the moment expected of a $5f^4$ U(II) species on the basis of data on isoelectronic $5f^4$ systems.^{78–81} Hydrolytic and deuterolytic reactions are also ambiguous, because mixtures of many types of products are obtained.⁹⁴ Since anionic arene ligands either could be protonated by water to cyclohexadiene or cyclohexene or could reduce water to hydrogen leaving the neutral arene as a byproduct, these data are not definitive. The often definitive optical absorptions characteristic of U(III) are not evident in the NIR spectrum of **1**, but the NIR spectrum of **2** is similar to that of $(C_5Me_5)_3U$ and appears to contain $f \rightarrow f$ transitions typical of trivalent uranium.

Density functional theory calculations on **1** and **2** suggest that both molecules have similar valence electronic structures, which lie intermediate between the U(II) and U(IV) extremes. Both molecules possess two U 5f nonbonding electrons per U, which occupy the highest occupied molecular orbitals in each case. This indicates that the oxidation state of the uranium atoms is at most U(IV).

The localization properties of the next four electrons in these molecules are crucial to the assignment of oxidation state. These electrons are in $U \rightarrow$ arene δ back-bonding molecular orbitals. If these electrons are arene-localized, **1** and **2** are best formulated as containing U(IV) and $(C_6H_6)^{4-}$. If the electrons are uranium-based, U(II) and a neutral arene would be appropriate. The composition analysis of the MOs ($27a_2 \beta$, $42a_1 \beta$, $42a_1 \alpha$, and $27a_2 \alpha$ in **1** and $69a_u \beta$, $68a_u \beta$, $69a_u \alpha$, and $68a_u \alpha$ in **2**) occupied by these electrons suggests that the electrons are very much of mixed U/arene character, and hence the best description is intermediate between U(IV) and U(II). This fits nicely with the computed charges on the U (+2.7 to +2.8 in **1** and +2.6 in **2**) and the arene (−2.2 in **1** and −2.4 in **2**), but it should be noted that computed charges can be quite unreliable because they are often very sensitive to the computational method. In summary, the calculations reveal the presence of orbitals of suitable energy and symmetry for significant uranium arene covalent interactions, and the formal oxidation state of the metal depends on the amount of back-bonding in the system. This is a common situation in many transition metal complexes of unsaturated hydrocarbon ligands. Of the three possibilities (i.e., U(II)–U(IV)), there is little doubt that the calculations suggest that U(III) is the most appropriate description of both **1** and **2**.

Interestingly, the calculations on **1** and **2** give an orbital picture very similar to that found previously for **3** and **4**.^{17,18} It would therefore appear that the nature of the anionic ligands on the outside of the $[U-(C_6H_5R)-U]^{4+}$ unit ($R = H, Me$) does not affect the orbital picture within the molecular core to any significant extent.

Several other lines of evidence suggest that the model which contributes most to the structure of complexes **1** and **2** is the one involving U(III) complexes of benzene dianions. Synthetic, structural, and reactivity support for this model is described in the following paragraphs.

The formation of **1** from $(C_5Me_5)_3U$ and $[(C_5Me_5)_2U][(\mu-Ph_2)BPh_2]$ can be readily explained by ionic metathesis reactions with trivalent precursors in which no change in oxidation state is necessary. There would be no basis to expect oxidation of the metal to U(IV) in these reactions. A U(IV) product would require that the U(III) centers formally reduced $(C_6H_6)^{2-}$ dianions to $(C_6H_6)^{4-}$ tetraanions. This seems unlikely.

(98) Clark, D. L.; Hobart, D. E.; Neu, M. P. *Chem. Rev.* **1995**, *95*, 25.

Both experiment and theory find that **1** and **2** have nonplanar C₆H₆ ligands, a structural feature that would be unlikely for a neutral C₆H₆ ligand in a U(II) complex. Since the well-defined C–C bond distances in **2** are longer than those in benzene, this also seems inconsistent with the presence of a neutral arene. This is reinforced by the calculations, which find a calculated 0.05 Å C–C lengthening from free to complexed arene in both **1** and **2**. This is consistent with the partial population of the free benzene e_{2u} C–C π* MOs due to transfer of electron density from U to arene.

In many cases, U–C(C₅Me₅) distances are indicative of the metal oxidation state. However, the discovery of the long bond organometallics such as trivalent (C₅Me₅)₃U⁷ and tetravalent (C₅Me₅)₃UCl,¹⁰ complexes of different oxidation states that have similarly long U–C(C₅Me₅) lengths, complicates this analysis.⁹⁹ The bond distances in **2** are more straightforward. The U–C(C₅Me₅) lengths in **2** are not unusually long and are similar to less sterically crowded trivalent uranium complexes. This suggests that **2** is not a U(II) complex. Similarly, the U–N[N(SiMe₃)₂] distance in **2** matches U(III)–N distances in the literature.^{17,22,60,61}

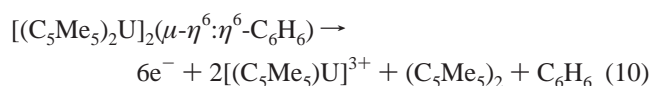
Further evidence for a U(III)/(C₆H₆)²⁻ dianion description of **1** and **2** comes from the arene exchange chemistry. If the arene bridge is neutral, one would expect that arene exchange would be facile and that the more substituted arenes would displace the less substituted species, according to the basicity of the arene. This is the type of chemistry that is observed in neutral arene uranium and lanthanide coordination complexes already in the literature. Hence, in the presence of toluene, hexamethylbenzene displaces the mesitylene in (C₆Me₃H₃)U(BH₄)₃ to make (C₆Me₆)U(BH₄)₃.^{69,106} Tetramethylbenzene will also preferentially replace toluene and benzene in complexes such as (η⁶-C₆R₆)Ln(AlCl₄)₃.⁹³

The chemistry of **1** is the opposite of that of established coordinated arene complexes. For example, **1** crystallizes from toluene without displacement of the C₆H₆ ligand. Complex **1** is also formed preferentially over the more highly substituted *para*-xylene analogue in a competitive reaction involving a 1:1 solution of benzene and *para*-xylene. The *para*-xylene analogue, **5**, made by the reaction of (C₅Me₅)₃U with KC₈ in *para*-xylene, reacts with C₆D₆ to make [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆D₆), **1-d₆**. This is consistent with the presence of a (1,4-C₆Me₂H₄)²⁻ dianion in **5**, which would have the capacity to reduce benzene to form **1**. Complex **1** does not react with *para*-xylene to make

5 because a (C₆H₆)²⁻ dianion in **1** should not be able to reduce *para*-xylene to (1,4-C₆Me₂H₄)²⁻. The fact that a C₆Me₆ analogue of **1** has not been prepared would be consistent with the difficulty of reducing this more electron-rich arene, but other factors, such as steric crowding, might also account for this observation. In contrast, in the neutral arene complexes of f element tetrahaloaluminates and tetrahydroborates, C₆Me₆ generally provides the most stable complexes.^{67,93,106}

Further support for the presence of a (C₆H₆)²⁻ bridge in **1** is that THF does not displace this ligand. Neutral arene f element complexes readily decompose in coordinating solvents such as THF and pyridine.^{63–70,93,106} They are said to be obtainable only in the absence of a coordinating solvent.

Multielectron Reduction Chemistry of 1. Regardless of the formal oxidation state in **1**, its reaction with 3 equiv of cyclooctatetraene demonstrates that it can function as a six-electron reductant. The half reaction is shown in eq 10.



To the extent that the six electrons arise from two (C₅Me₅)¹⁻/C₅Me₅ processes, two U(III)/U(IV) reactions, and a (C₆H₆)²⁻/C₆H₆ process, the overall reaction involves three different sources of electrons: SIR ligand processes, conventional metal-based redox chemistry, and arene anion reduction, respectively.

The reductions of cyclooctatetraene by **1** could also be explained via U(II)–U(IV) processes instead of U(III) and (C₆H₆)²⁻ reactions, but we are reluctant to claim the formation of a U(II) complex in the absence of more definitive data.

Conclusion

These results show that a fourth type of reaction is available to sterically crowded (C₅Me₅)₃M complexes, displacement of a (C₅Me₅)¹⁻ ligand by ionic metathesis. Successful execution of this reaction with sterically crowded [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆), **1**, to form {[(Me₃Si)₂N](C₅Me₅)U}₂(μ-η⁶:η⁶-C₆H₆), **2**, suggests that this reaction may be available to other organometallic complexes with unusually long bonds. As demonstrated in the transformation of **1** to **2**, these (C₅Me₅)¹⁻ ligand displacement reactions provide new options for the synthesis of the relatively rare classes of complexes with two different types of ancillary ligands.

The synthesis of **1** demonstrates that anion displacement reactions involving arene anions are powerful routes to unusual f element sandwich complexes involving arene-derived bridging ligands. The facility by which **1** is formed via different pathways suggests that this type of reaction may be more accessible than previously expected.

Chemical, structural, and density functional theory analysis of **1** and **2** suggests that the best integral valence model for describing these complexes is one containing U(III) metal centers complexed to arene dianions. Of the six valence electrons of elemental uranium, two are given up to the two (C₅Me₅)¹⁻ ligands on each metal, two remain as essentially U 5f nonbonding electrons, and the final two are employed in a U → arene δ back-bond. This picture of the electronic structure arises from DFT calculations with both high-spin and low-spin models.

The six-electron reduction reactivity of [(C₅Me₅)₂U]₂(μ-η⁶:η⁶-C₆H₆) shows another way in which sterically induced

(99) Since the U–C(C₅Me₅) lengths in **1** are long, they could arise because it is a long bond organometallic U(III) or U(IV) complex. Since **1** has the reactivity of a long bond organometallic, that is, SIR and (C₅Me₅)¹⁻ displacement, and a very small (C₅Me₅ ring centroid)–U–(C₅Me₅ ring centroid) angle characteristic of long bond organometallic (C₅Me₅)¹⁻ complexes, this is reasonable. However, a U(II) complex could also have U–C(C₅Me₅) distances longer than conventional U(III) complexes. Divalent lanthanide complexes typically have M–C distances 0.1 Å longer than trivalent analogues.^{100–103} However, in the zerovalent arene complexes of Cloke, the M–C distances are much shorter than those expected by extrapolating from Ln(III) and Ln(II).^{104,105}

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reduction can be combined with traditional redox couples to make multielectron reductants. The SIR reactivity of $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$ also shows that this type of reduction can be done with complexes beyond the $(C_5Me_5)_3M$ class.

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

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