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Synthesis of Heteroleptic Uranium $(\mu-\eta^6:\eta^6\text{-}C_6H_6)^{2-}$ Sandwich Complexes via Facile Displacement of $(\eta^5\text{-}C_5Me_5)^{1-}$ by Ligands of Lower Hapticity and Their Conversion to Heteroleptic Bis(imido) Compounds

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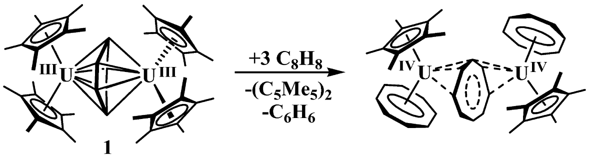
Abstract: Reactivity studies on the sterically crowded $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6\text{-}C_6H_6)$, **1**, have revealed that η^1-ligands can displace one of the normally inert $(\eta^5\text{-}C_5Me_5)^{1-}$ ligands in each metallocene unit to form a series of heteroleptic bimetallic sandwich complexes of nonplanar $(C_6H_6)^{2-}$, namely, $[(C_5Me_5)(X)U]_2(\mu-\eta^6:\eta^6\text{-}C_6H_6)$, where X = $N(SiMe_3)_2$, $OC_6H_2(CMe_3)_2$-2,6-Me-4, and $CH(SiMe_3)_2$. Displacement by an amidinate is also possible, that is, X = ^{i}PrNC(Me)N^{i}Pr. This allows the multielectron reactivity of the $(\mu-\eta^6:\eta^6\text{-}C_6H_6)^{2-}$ sandwich complexes to be studied as a function of ancillary ligands. Specifically, the reaction of **1** with $K[N(SiMe_3)_2]$, previously found to form $\{(C_5Me_5)[(Me_3Si)_2N]U\}_2(C_6H_6)$, **2**, also occurs with $K[OC_6H_2(CMe_3)_2$-2,6-Me-4], $Li[CH(SiMe_3)_2]$, and Li[^{i}PrNC(Me)N^{i}Pr] to form $\{(C_5Me_5)[4\text{-Me-2,6-}(Me_3C)_2C_6H_2O]U\}_2(C_6H_6)$, **3**, $\{(C_5Me_5)[(Me_3Si)_2CH]U\}_2(C_6H_6)$, **4**, and $\{(C_5Me_5)[^iPrNC(Me)N^iPr]U\}_2(C_6H_6)$, **5**, respectively. The reactivity of **2**−**5** vis-à-vis **1** has been compared with the substrates 1,3,5,7-cyclooctatetraene (C_8H_8) and 1-azidoadamantane (AdN_3). Complex **1** acts as a six electron reductant to convert three equiv of C_8H_8 to $[(C_5Me_5)(C_8H_8)U]_2(\mu-\eta^3\text{-}\eta^3\text{-}C_8H_8)$, whereas the sterically less crowded **2**−**5** provide only four electrons to reduce two equiv of C_8H_8 generating U^{4+} products of formula $(C_5Me_5)(X)U(C_8H_8)$. With AdN_3, complexes **1**, **2**, and **5** react similarly to form bis(imido) U^{6+} complexes, $(C_5Me_5)(X)U({=}NAd)_2$. Complexes **2** and **5** also form the ligand redistribution product, $(C_5Me_5)_2U({=}NAd)_2$. The reaction of **4** with AdN_3 generates at least three imido complexes: $(C_5Me_5)_2U({=}NAd)_2$ from reduction and ligand redistribution, $(C_5Me_5)[AdN_3CH(SiMe_3)_2\text{-}\kappa^2N^{1,2}]U({=}NAd)_2$, from reduction and insertion, and $(C_5Me_5)(\eta^5{:}\kappa N\text{-}C_5Me_4CH_2NAd)U({=}NAd)$, from reduction, ligand redistribution, metalation, and insertion.

Introduction

Recent studies of the sterically crowded tris(pentamethylcyclopentadienyl) uranium complex, $(C_5Me_5)_3U$,[1] led to the isolation of a bis(pentamethylcyclopentadienyl) complex with similarly extreme metrical parameters, $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6\text{-}C_6H_6)$, **1**.[2] Structural, reactivity, and density functional studies on **1** suggest that it can be considered to be a U^{3+} complex of a slightly nonplanar benzene dianion.[2] In addition to the U^{3+} and $(C_6H_6)^{2-}$ reactive components, complex **1** is sufficiently sterically crowded to effect the unusual reactions found for $(C_5Me_5)^{1-}$ rings in $(C_5Me_5)_3M$ complexes (M = U, lanthanides) such as sterically induced reduction (SIR).[2] Indeed, complex **1** functions as a six electron reductant when reacted with C_8H_8, formally deriving two electrons from the two U^{3+} centers, two from the $(C_6H_6)^{2-}$ ion, and two from loss of one $(C_5Me_5)^{1-}$ ligand per uranium via SIR, eq 1. Complex **1** has also been shown to deliver 2, 4, and 8 electrons in reactions with $[HNEt_3][BPh_4]$,[2] diphenylacetylene,[3] and azobenzene,[3] respectively, Scheme 1.



$$3\,C_8H_8 \;+\; 6\,e^- \longrightarrow 3\,(C_8H_8)^{2-} \qquad (1)$$

In addition to this reductive reactivity, **1** also revealed the first $(C_5Me_5)^{1-}$ displacement reaction for a sterically crowded complex,[2] eq 2. It was unexpected that the normally inert pentahapto $(C_5Me_5)^{1-}$ ligand could be displaced by a formally monohapto amide and that this $(C_5Me_5)^{1-}$ displacement would be favored over that of the highly reactive $(C_6H_6)^{2-}$ unit.

We report here that eq 2 is general and can be expanded to include aryloxide, alkyl, and amidinate ligands. These reactions have generated a series of heteroleptic uranium $(C_6H_6)^{2-}$ sandwich complexes, $[(C_5Me_5)(X)U]_2(C_6H_6)$ where X = $OC_6H_2(CMe_3)_2$-2,6-(Me)-4, $CH(SiMe_3)_2$, and ^{i}PrNC(Me)N^{i}Pr. The reactivity of these $(C_6H_6)^{2-}$ complexes as a function of the ancillary ligand set has been studied with 1,3,5,7-cyclooctatetraene and 1-azidoadamantane. With the latter reagent, new heteroleptic bis(imido) U^{6+} complexes, $(C_5Me_5)(X)U({=}NAd)_2$, difficult to generate by conventional syntheses, have been obtained. These $[U({=}NR)_2]^{2+}$ complexes are of great interest

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(1) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *Angew. Chem., Int. Ed.* **1997**, *36*, 774–776.

(2) Evans, W. J.; Kozimor, S. A.; Ziller, J. W.; Kaltsoyannis, N. *J. Am. Chem. Soc.* **2004**, *126*, 14533–14547.

(3) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Chem. Commun.* **2005**, 4681–4683.

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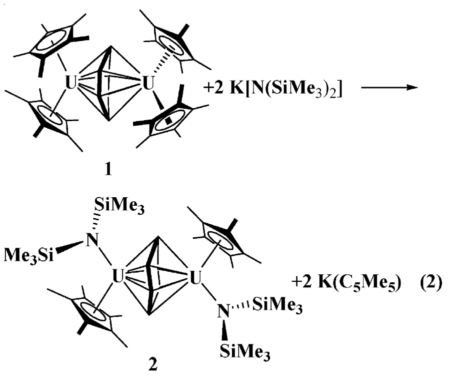


for evaluating uranium-element multiple bonding and for making comparisons with the common uranyl ion $(UO_2)^{2+}$.[4]

Experimental Section

The manipulations described below were performed under argon with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. All syntheses were conducted in an argon-filled glovebox, unless otherwise noted. Solvents were dried over Q-5 and molecular sieves and saturated with argon using GlassContour columns. Benzene-d_6 was dried over NaK alloy, degassed by three freeze−pump−thaw cycles, and vacuum transferred before use. NMR spectra were recorded using a Bruker DRX500 spectrometer and infrared spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 CHNS elemental analyzer. $[(C_5Me_5)_2U]_2(C_6H_6)$, **1**, and $\{(C_5Me_5)[(Me_3Si)_2N]U\}_2(C_6H_6)$, **2**, were prepared according to the literature.[2] 1,3,5,7-Cyclooctatetraene (Aldrich) was distilled over 4A sieves and degassed. Potassium bis(trimethylsilyl)amide (Aldrich) was dissolved in toluene and centrifuged to remove insoluble contaminants prior to use. 1-Azidoadamantane, AdN_3, (Aldrich) was stored under vacuum (10^{-3} torr) for 12 h prior to use. Lithium *N,N′*-diisopropylmethylamidinate was synthesized by stirring excess diisopropylcarbodiimide (Aldrich) with methyllithium in hexane for 12 h. The resulting white powder was collected by centrifugation and dried in vacuo. Potassium 2,6-bis(*tert*-butyl)-4-methylphenoxide (KOAr) was synthesized by reacting an excess of the phenol with KH in tetrahydrofuran. The solvent was removed and resulting powder was washed with toluene and dried in vacuo. Lithium bis(trimethylsilyl)methane was synthesized as previously reported.[5]

$\{(C_5Me_5)[2,6\text{-}(Me_3C)_2\text{-}4\text{-}Me\text{-}C_6H_2O]U\}_2(C_6H_6)$, 3. In a glovebox, solutions of **1** (0.051 g, 0.047 mmol) in 3 mL of toluene and KOAr (0.024 g, 0.093 mmol) in 3 mL of dimethoxyethane were chilled to −35 °C. The KOAr solution was added slowly to a stirred solution of **1** in three portions over 15 min. After the reaction was stirred 13 h at ambient temperature, solvent was removed under vacuum. The solids were extracted with toluene and the solvent was evaporated to give **3** as a brown powder (0.045 g, 76%). Crystals of **3** were grown from a saturated hexane solution at −35 °C. ^1H NMR (C_6D_6, 298 K) δ 18.53 (s, 4H, $C_6H_2Me(CMe_3)_2$), 8.89 (s, 6H, $C_6H_2Me(CMe_3)_2$), −1.04 (s, 36H, $C_6H_2Me(CMe_3)_2$), −2.05 (s, 30H, C_5Me_5), −89.27 (s, 6H, C_6H_6). ^{13}C NMR (C_6D_6, 298 K) δ 420 (C_6H_6), 142.8 (meta $C_6H_2Me(CMe_3)_2$), 25.8 ($C_6H_2Me(CMe_3)_2$), 20.4 ($C_6H_2Me(CMe_3)_2$), −37.8 (C_5Me_5). IR: 2956s, 2916s, 2859s, 1416s, 1384 m, 1360w, 1275 m, 1228s, 1182 m, 1023w, 914w, 858w, 830 m, 796 m, 742 m cm^{-1}. Anal. calcd for $C_{56}H_{82}O_2U_2$: C, 53.24; H, 6.54. Found: C, 53.69; H, 6.79.

$\{(C_5Me_5)[(Me_3Si)_2CH]U\}_2(C_6H_6)$, 4. Toluene solutions of **1** (0.250 g, 0.23 mmol, in 8 mL) and $Li[CH(SiMe_3)_2]$ (0.076 g, 0.46 mmol, in 8 mL) were chilled to −35 °C. The $Li[CH(SiMe_3)_2]$ solution was added slowly to the stirred solution of **1** in three portions over 15 min. After the reaction was stirred for 16 h at ambient temperature, solvent was removed under vacuum. The solids were extracted with hexane and the solvent was removed under vacuum to give **4** as a brown powder (0.190 g, 73%). Crystals suitable for X-ray diffraction were grown from a concentrated hexane solution at −35 °C. ^1H NMR (C_6D_6, 298 K) δ 1.57 (s, 30H, C_5Me_5), −6.11 (s, 36H, $-CH(SiMe_3)_2$), −79.19 (s, 6H, C_6H_6). ^{13}C NMR (C_6D_6, 298 K) δ 454 (C_6H_6), 236.8 (C_5Me_5), 9.4 ($CH(SiMe_3)_2$), −20.7 (C_5Me_5). IR: 2923s, 2908s, 2857s, 1444 m, 1381w, 1252 m, 1238 m, 1055w, 1017 m, 912w, 848s, 827s, 760w, 733 m cm^{-1}. Anal. calcd for $C_{40}H_{74}Si_4U_2$: C, 42.00; H, 6.20. Found: C, 41.32; H, 6.58.

$\{[C_5Me_5][^iPrNC(Me)N^iPr]U\}_2(C_6H_6)$, 5. $Li[^iPrNC(Me)N^iPr]$ (0.027 g, 0.18 mmol) was added to a chilled solution (−35 °C) of **1** (0.100 g, 0.091 mmol) in 12 mL of toluene over a 20 min period. The reaction mixture was allowed to warm to ambient temperature and was stirred for 18 h. The solvent was then removed under vacuum, the solids were extracted with hexane, and the mixture was centrifuged. The supernatant was collected and the solvent removed to give **5** as a brown powder (0.087 g, 86%). ^1H NMR (C_6D_6, 298 K) δ 18.55 (s, 4H, N-CHMe$_2$), 15.47 (s, 6H, N−C(Me)-N), 0.07 (s, 30H, C_5Me_5), −4.40 (d, J = 5 Hz, 12H, N−CHMe_2), −4.52 (d, J = 5 Hz,12H, N−CHMe_2), −83.98 (s, 6H, C_6H_6). ^{13}C NMR (C_6D_6, 298 K) δ 403 (C_6H_6), 53.7 (N-CHMe$_2$), 38.4 (NC(Me)N), −32.2 (C_5Me_5). IR: 2962s, 2911s, 2860s, 1649 m, 1468s, 1415s, 1374s, 1358s, 1323 m, 1307 m, 1264w, 1199s, 1169w, 1115w, 1046w, 1016w, 908 m, 808 m, 716 m, 649 m cm^{-1}. Anal. calcd for $C_{42}H_{70}N_4U_2$: C, 45.57; H, 6.03; N, 5.06. Found: C, 45.87; H, 6.22; N, 4.70.

Reaction of 2 with C_8H_8. Complex **2** (0.025 g, 0.022 mmol) and C_8H_8 (0.019 g, 0.18 mmol) were stirred in 3 mL of toluene for 91 h at ambient temperature, after which resonances corresponding

Scheme 1. Reduction Reactions in Which **1** Delivers 2, 4, and 8 Electrons

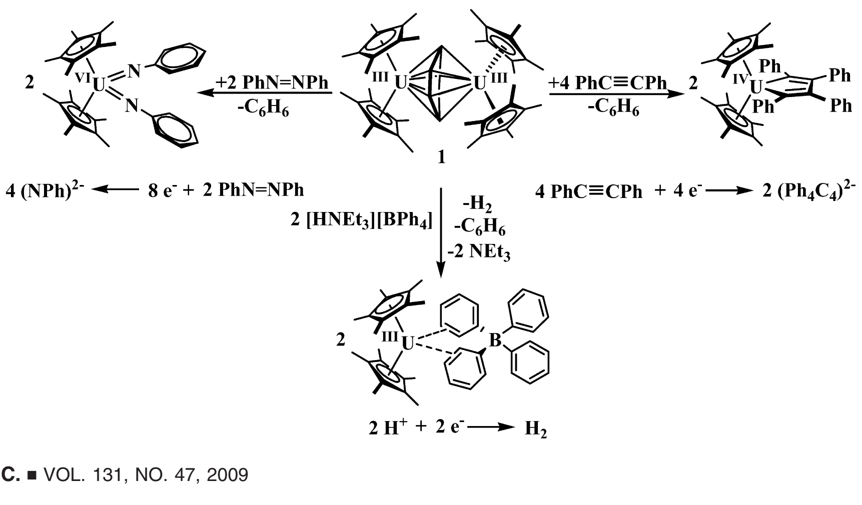


Table 1. X-Ray Data Collection Parameters for $\{(C_5Me_5)[2,6\text{-}(Me_3C)_2\text{-}4\text{-}Me\text{-}C_6H_2O]U\}_2(C_6H_6)$, **3**, $\{(C_5Me_5)[(Me_3Si)_2CH]U\}_2(C_6H_6)$, **4**, $(C_5Me_5)[{}^iPrNC(Me)N^iPr]U({=}NAd)_2$, **11**, $(C_5Me_5)[AdN_3CH(SiMe_3)_2\text{-}\kappa^2N^{1,2}]U({=}NAd)_2$, **13**, and $(C_5Me_5)(\eta^5{:}\kappa N\text{-}C_5Me_4CH_2NAd)U({=}NAd)$, **14**[a]

	3	**4**	**11**	**13**	**14**
empirical formula	$C_{56}H_{82}O_2U_2$	$C_{40}H_{74}Si_4U_2$	$C_{38}H_{62}N_4U \bullet 1/2(C_6H_{14})$	$C_{47}H_{79}N_5Si_2U$	$C_{40}H_{59}N_2U$
formula weight	1263.28	1143.41	856.03	1008.36	805.92
crystal system	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	11.0169(17)	8.6310(3)	9.9380(7)	13.5148(7)	9.9011(6)
b (Å)	17.007(3)	11.2450(3)	10.8469(8)	18.2529(9)	13.3585(8)
c (Å)	13.543(2)	12.1742(4)	20.2681(19)	19.2967(10)	15.3247(9)
α (deg)	90	99.8602(3)	92.8200(10)	90	84.6455(7)
β (deg)	90.3839(19)	104.2888(3)	91.4350(10)	90.0839(7)	80.7060(7)
γ (deg)	90	99.0500(3)	116.5340(10)	90	80.4456(7)
Volume (Å^3)	2537.3(7)	1103.19(6)	1949.6(3)	4760.2(4)	1967.9(20)
Z	2	1	2	4	2
ρ_{calc} (Mg/m^3)	1.653	1.721	1.458	1.407	1.360
absorption coeff	6.413	7.464	4.195	3.496	4.150
GOF on F^2	1.220	1.045	1.044	1.042	1.125
R^b $[I > 2\sigma(I)]$: R_1	0.0552	0.0132	0.0159	0.0452	0.0261
R^c(all data): $wR2$	0.1450	0.0329	0.0393	0.1128	0.0767

[a] $\lambda = 0.71073$ Å. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\,]^{1/2}$.

to **2** were no longer visible in the ^1H NMR spectrum. This mixture was centrifuged, the supernatant was collected, and the solvent was removed under vacuum, leaving a red solid (0.014 g, 50%) that was identified by ^1H NMR spectroscopy as the previously reported $(C_5Me_5)[(Me_3Si)_2N]U(C_8H_8)$,[6] **6**.

Reaction of 4 with C_8H_8. Complex **4** (0.020 g, 0.018 mmol) and C_8H_8 (0.021 g, 0.20 mmol) were stirred in 3 mL of toluene for 21 h at ambient temperature after which resonances corresponding to **4** were no longer visible in the ^1H NMR spectrum. The reaction mixture was centrifuged, the supernatant was collected, and the solvent was removed under vacuum, giving a red solid (0.019 g, 85%) that was identified by ^1H NMR spectroscopy to be the previously reported $(C_5Me_5)[(Me_3Si)_2CH]U(C_8H_8)$,[7] **7**.

Reaction of 5 with C_8H_8. Complex **5** (0.035 g, 0.032 mmol) and C_8H_8 (0.033 g, 0.34 mmol) were stirred in 3 mL of toluene for 68 h at ambient temperature after which resonances corresponding to **5** were no longer visible in the ^1H NMR spectrum. This mixture was centrifuged, the supernatant was collected, and the solvent was removed under vacuum, leaving a red powder (0.031 g, 79%) that was identified by ^1H NMR spectroscopy to be the known compound, $(C_5Me_5)[{}^iPrNC(Me)N^iPr]U(C_8H_8)$,[7] **8**.

Reaction of 1 with 1-Azidoadamantane. A solution of **1** in 8 mL of toluene (0.100 g, 0.091 mmol) was added to AdN_3 (0.065 g, 0.37 mmol) and the reaction mixture was stirred for 12 h at ambient temperature. Removal of solvent gave a black powder (0.141 g, 95%), which was identified by ^1H NMR spectroscopy to be the previously reported $(C_5Me_5)_2U({=}NAd)_2$,[8] **9**.

Reaction of 2 with 1-Azidoadamantane. A solution of **2** (0.030 g, 0.026 mmol) in 4 mL of toluene was added to AdN_3 (0.019 g, 0.11 mmol), and the reaction mixture was stirred for 5.5 h at ambient temperature. The solvent was removed, and the remaining oil was dissolved in hexane and centrifuged. The supernatant was collected, and the solvent was removed to give a black oil (0.041 g). The ^1H NMR spectrum showed peaks corresponding to $(C_5Me_5)[(Me_3Si)_2N]U({=}NAd)_2$, **10**, as the major product, with $(C_5Me_5)_2U({=}NAd)_2$,[8] **9**, identified as the minor product (<10%). ^1H NMR (**10**, C_6D_6, 298 K) δ 4.66 (s, 15H, $C_5\mathit{Me}_5$), 3.29 (m, 6H, adamantyl), 1.42 (d, $J = 11$ Hz, 6H, adamantyl), 1.30 (d, $J = 11$ Hz, 6H, adamantyl), 1.09 (s, 12H, adamantyl), 0.63 (s, 18H, $N(Si\mathit{Me}_3)_2$). ^{13}C NMR (**10**, C_6D_6, 298 K) δ 85.5 (adamantyl), 36.7 (adamantyl), 34.5 (adamantyl), 9.3 ($C_5\mathit{Me}_5$), 6.3 ($N(Si\mathit{Me}_3)$). ^1H NMR (**9**, C_6D_6, 298 K) δ 4.08 (s, 30H, $C_5\mathit{Me}_5$), 3.18 (s, 6H, adamantyl), 1.46 (d, $J = 11$ Hz, 6H, adamantyl), 1.36 (d, $J = 11$ Hz, 6H, adamantyl), 1.16 (s, 12H, adamantyl).

Reaction of 5 with 1-Azidoadamantane. A solution of **5** (0.025 g, 0.023 mmol) in 3 mL of methylcyclohexane was added to AdN_3 (0.016 g, 0.090 mmol) and the reaction mixture was stirred for 5.5 h at ambient temperature. The solvent was then removed and the remaining oil dissolved in hexane and centrifuged. The supernatant was collected and the solvent was removed to give a black oil (0.032 g). Dark brown crystals of $(C_5Me_5)[{}^iPrNC(Me)N^iPr]U({=}NAd)_2$,**11**, were grown from a concentrated hexane/toluene solution at −35 °C (0.010 g, 27% recrystallized yield). ^1H NMR (C_6D_6, 298 K) δ 5.96 (m (7), $J = 6.5$ Hz, 2H, NCN-$C\mathit{H}Me_2$), 4.10 (s, 15H, $C_5\mathit{Me}_5$), 3.06 (s, 6H, adamantyl), 2.39 (s, 3H, $NC(\mathit{Me})NCHMe_2$), 1.53 (d, $J = 11$ Hz, 6H, adamantyl), 1.48 (d, $J = 6.5$ Hz, 12H, $NC(Me)NCH\mathit{Me}_2$), 1.44 (d, $J = 2$ Hz, 12H, adamantyl), 1.39 (d, $J = 11$ Hz, 6H, adamantyl). ^{13}C NMR (C_6D_6, 298 K) δ 78.2 (adamantyl), 49.5 ($NC(Me)NC\mathit{H}Me_2$), 37.04 (adamantyl), 34.19 (adamantyl), 28.0 ($NC(Me)NCH\mathit{Me}_2$), 14.7 (${}^iPrNC(\mathit{Me})N^iPr$), 11.2 ($C_5\mathit{Me}_5$). IR: 2959s, 2903s, 2848s, 1490s, 1456 m, 1373 m, 1350 m, 1335 m, 1308 m, 1199 m, 1156s, 1096 m, 1025w, 802w cm^{-1}. Anal. calcd for $C_{38}H_{62}N_4U$: C, 56.14; H, 7.69; N, 6.89. Found: C, 56.62; H, 8.08; N, 6.44.

Reaction of 4 with 1-Azidoadamantane. A solution of **4** (0.050 g, 0.044 mmol) in 4 mL of methylcyclohexane was added to AdN_3 (0.031 g, 0.18 mmol) and the reaction mixture was stirred for 5.5 h at ambient temperature. The solvent was then removed, and the remaining oil was dissolved in hexane and centrifuged. The supernatant was collected, and the solvent was removed to give a black oil (0.074 g). The ^1H NMR spectrum of the oil showed the presence of multiple products. Resonances for $(C_5Me_5)_2U({=}NAd)_2$, **9**, were present as well as resonances at 4.89 ppm (15H) and 0.63 ppm (18H), assignable to an analog of **9**−**11**, namely $(C_5Me_5)[(Me_3Si)_2CH]U({=}NAd)_2$, **12**. However, this complex could not be separated in pure form. Crystallization of the black oil in saturated hexane solution at −35 °C gave several crystals of $(C_5Me_5)[AdN_3CH(SiMe_3)_2\text{-}\kappa^2N^{1,2}]U({=}NAd)_2$, **13**. (Not all ^1H NMR resonances were located.) ^1H NMR (C_6D_6, 298 K) δ 4.39 (s, 15H, $C_5\mathit{Me}_5$), 3.07 (s, 6H), 2.16 (s, 9H), 1.74 (m, 6H), 1.42 (d, $J = 11$ Hz, 6H), 1.30 (d, $J = 11$ Hz, 6H, adamantyl), 1.11 (d, $J = 11$ Hz, 3H), 1.07 (d, $J = 11$ Hz, 3H), 0.51 (s, 18H, $CH(Si\mathit{Me}_3)_2$). IR: 2905s, 2848s, 1491w, 1450 m, 1299w, 1280w, 1247 m, 1142w, 1094w, 1049w, 1022w, 928w, 845s.

A different crystalline product was isolated when an analogous reaction of **4** (0.050 g, 0.044 mmol) in 4 mL of methylcyclohexane and AdN_3 (0.031 g, 0.18 mmol) was stirred for 18.5 h at ambient temperature, followed by solvent removal under vacuum. The remaining oil was dissolved in hexane and centrifuged, and the supernatant was collected. The solvent was removed to give a black oil (0.086 g). The ^1H NMR spectrum again contained resonances for **9**, **12**, and **13**, as well as other

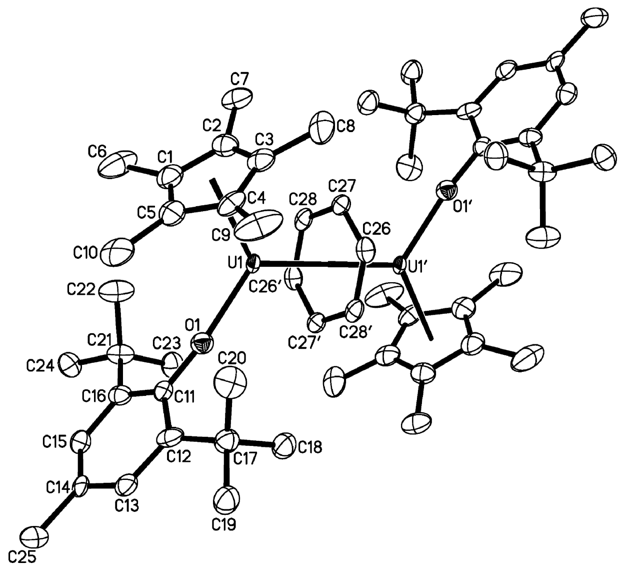


Figure 1. Thermal ellipsoid plot of $[(C_5Me_5)(ArO)U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **3**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected ^{1}H NMR Data in ppm for $[(C_5Me_5)_2U]_2(C_6H_6)$,[2] **1**, $\{(C_5Me_5)[(Me_3Si)_2N]U\}_2(C_6H_6)$,[2] **2**, $\{(C_5Me_5)[2,6-(Me_3C)_2-4-Me-C_6H_2O]U\}_2(C_6H_6)$, **3**, $\{(C_5Me_5)[(Me_3Si)_2CH]U\}_2(C_6H_6)$, **4**, and $\{(C_5Me_5)[^iPrNC(Me)N^iPr]U\}_2(C_6H_6)$, **5**

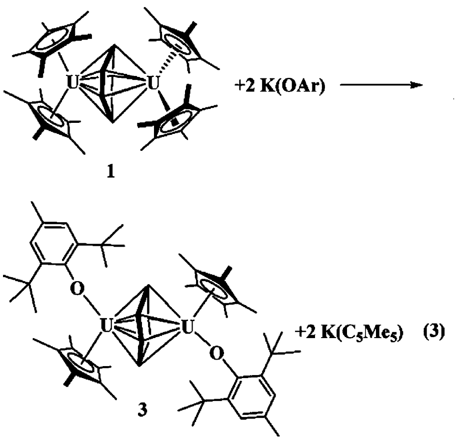
	1	2	3	4	5
$(C_5Me_5)^{1-}$	3.06	0.56	−2.05	1.57	−4.39
$(C_6H_6)^{2-}$	−99.4	−84	−89.27	−79.19	−83.98

unidentified products. Crystals of $(C_5Me_5)(\eta^5:\kappa N-C_5Me_4CH_2-NAd)U(=NAd)$, **14**, were grown from a saturated hexane solution at −35 °C. (Not all ^{1}H NMR resonances were located.) ^{1}H NMR (C_6D_6, 298 K) δ 18.20 (bs, 6H), 13.40 (s, 3H), 9.30 (s, 3H), 7.42 (s, 3H), 1.85 (s, 3H), 1.69 (s, 3H), 0.47 (bs, 15H), −1.58 (s, 3H), −2.48 (s, 3H), −3.56 (s, 3H), −7.90 (s, 3H), −12.32 (s, 3H), −20.51 (bs, 3H). IR: 2905s, 2848s, 1585bw, 1451 m, 1376w, 1344w, 1308w, 1263w, 1190w, 1136 m, 1095 m, 1033bw, 926w, 904w, 811w, 788w, 750w, 667bm.

X-Ray Crystallographic Data. Information on X-ray data collection, structure determination, and refinement for **3**, **4**, **11**, **13**, and **14** are given in Table 1. Details are given in the Supporting Information.

Results

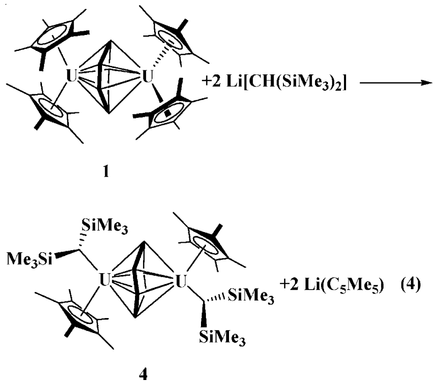
Ligand Substitution of $(\eta^5-C_5Me_5)^{1-}$ in $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, 1, by $[\eta^1-OC_6H_2(CMe_3)_2-2,6-Me-4]^{1-}$. To investigate the generality of the $(\eta^5-C_5Me_5)^{1-}$ substitution reaction in eq 2 and to capitalize on the oxophilicity of uranium through the formation of strong U−O bonds, cyclopentadienyl displacement with a bulky aryloxide ligand was examined. Two equivalents of potassium 2,6-bis(*tert*-butyl)-4-methylphenolate (KOAr) react with **1** to make a new aryloxide-substituted $(C_6H_6)^{2-}$ sandwich complex, $[(C_5Me_5)(ArO)U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **3**, in which one $(\eta^5-C_5Me_5)^{1-}$ ligand per uranium was replaced by $[\eta^1-OC_6H_2(CMe_3)_2-2,6-Me-4]^{1-}$, eq 3. Complex **3** was characterized by NMR and IR spectroscopy and elemental analysis and the structure of **3** was established by single-crystal X-ray crystallography, Figure 1.



As shown in Table 2, the ^{1}H NMR spectrum of **3** was similar to that of **1** and **2** and the other new $(C_6H_6)^{2-}$ complexes reported below in that it contained a large, broad signal corresponding to the $(C_5Me_5)^{1-}$ group in the 5 to −5 ppm region (−2.05) and a smaller upfield resonance assignable to $(C_6H_6)^{2-}$ in the −79 to −100 ppm region (−89.3). The protons of the aryloxide group appear as singlets at −1.04 ppm (*tert*-butyl), 8.89 ppm (methyl), and 18.53 ppm (aryl-H), similar to shifts reported for $U[OC_6H_3(CMe_3)_2-2,6]_3$.[9]

Although the quality of the crystals of **3** did not provide X-ray data sufficient for detailed metrical analysis, atomic connectivity was established. The structure of **3** is similar to those of **1** and **2** in that the $(C_6H_6)^{2-}$ unit is sandwiched between two uranium centers each attached to two terminal ligands. Like **2**, the $(C_5Me_5)^{1-}$ ligands are oriented in a trans configuration and the bridging $(C_6H_6)^{2-}$ moiety adopts a flattened chair conformation similar to **2**, rather than the flattened boat shape seen in **1**.

$(\eta^5-C_5Me_5)^{1-}$ Substitution by $[CH(SiMe_3)_2]^{1-}$. Given the success of $(\eta^5-C_5Me_5)^{1-}$ displacement with η^1-nitrogen- and oxygen-donor ligands, eqs 2 and 3, the more challenging substitution with an η^1-carbon-donor ligand was attempted. $LiCH(SiMe_3)_2$ was chosen as a reagent since it would deliver a ligand similar in size to the $[N(SiMe_3)_2]^{1-}$ ligand successfully used in eq 2. $LiCH(SiMe_3)_2$ reacts with **1** to form $\{(C_5Me_5)[(Me_3Si)_2CH]U\}_2(\mu-\eta^6:\eta^6-C_6H_6)$, **4**, eq 4, in a reaction analogous to eqs 2 and 3.



The ^{1}H NMR spectrum of **4** was similar to that of **1**−**3** (Table 2) with a broad resonance assignable to the $(C_5Me_5)^{1-}$ ligand (1.57 ppm) and an upfield signal (−79 ppm) assignable to $(C_6H_6)^{2-}$, in addition to the resonance for the trimethylsilyl protons at −6.11 ppm. The resonance for the methine proton attached to the uranium-bound carbon of the $[CH(SiMe_3)_2]^{1-}$ ligand could not be located in this paramagnetic system.

The identity of **4** was established by X-ray crystallography, Figure 2, and metrical comparisons with the structures of **1** and **2** are shown in Table 3. The structure of **4** is very similar

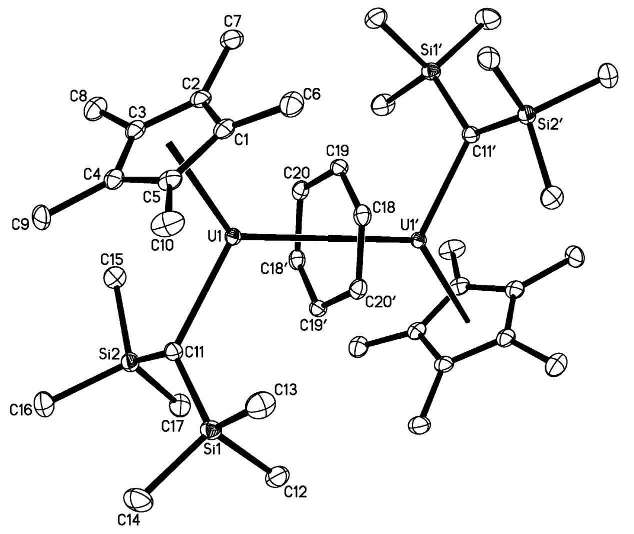


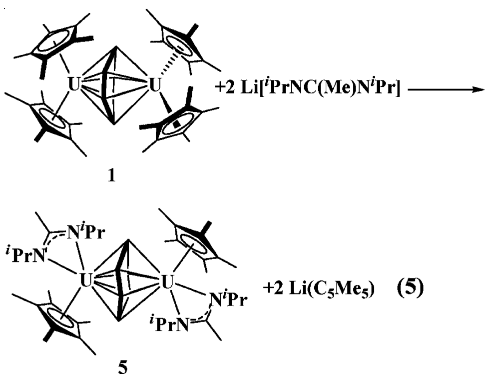
Figure 2. Thermal ellipsoid plot of $\{(C_5Me_5)[(Me_3Si)_2CH]U\}_2(\mu-\eta^6:\eta^6-C_6H_6)$, **4**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

to **2** and **3** in that the substituted ligands adopt a trans arrangement and the $(C_6H_6)^{2-}$ unit bridges the metal centers in a flattened chair conformation. The 2.486 Å U−(C_5Me_5 ring centroid) distance in **4** is close to that of **2** (2.506 Å) and shorter than the comparable distances in sterically crowded **1**, which range from 2.564−2.583 Å.[10] The average U−C(C_5Me_5) bond lengths are also similar to those of **2** and shorter than those of **1**. The U−(C_6H_6 ring centroid) distances follow the same trend.

Thus, while complex **1** is sterically crowded on the basis of its U−C(C_5Me_5) bond lengths, complexes **2** and **4** are not. Consistent with this, the (C_5Me_5 ring centroid)−uranium−(C_6H_6 ring centroid) angle is significantly larger for **2** (130.9°) and **4** (132.9°) than for **1** (118.9°, 119.2°). Another measure of steric crowding in $(C_5Me_5)^{1-}$ complexes is the displacement of the methyl groups from the cyclopentadienyl ring plane.[10] Sterically crowded complexes with unusual $(C_5Me_5)^{1-}$ reactivity have one methyl per ring at least 0.48 Å from the plane of the ring, as per **1** (0.48 Å).[10] The maximum methyl displacement for **4**, 0.21 Å, is not in that sterically crowded range as was also found for **2** (0.26 Å).[2]

The bridging $(C_6H_6)^{2-}$ unit for **4** is twisted into a chair conformation, similar to **2**, though the angle between the two three carbon planes, C18/C18′/C20 and C18/C19/C20, is greater than for **2**, 12.1° vs 7.2°, respectively. The 2.508(2) Å U−C[$CH(SiMe_3)_2$] bond distance in **4** is slightly longer than the analogous distances of 2.48(2) Å in the U^{3+} complex, $U[CH(SiMe_3)_2]_3$,[11] and 2.469(3) Å in the U^{4+} compound, $(C_5Me_5)(C_8H_8)U[CH(SiMe_3)_2]$.[7] This U1−C11 distance is significantly longer than the analogous 2.306(2) Å U−N distance in **2**,[2] as is typical for $[CH(SiMe_3)_2]^{1-}$ vs $[N(SiMe_3)_2]^{1-}$.[12]

$(C_5Me_5)^{1-}$ Substitution by $[^iPrNC(Me)N^iPr]^{1-}$. Complex **1** was also treated with lithium *N,N′*-diisopropylmethylamidinate, $Li[^iPrNC(Me)N^iPr]$, since this ligand has recently been shown to generate unusual chemistry with organoactinides.[13] This reaction produces $\{(C_5Me_5)[^iPrNC(Me)N^iPr]U\}_2(\mu-\eta^6:\eta^6-C_6H_6)$, **5**, eq 5, which was characterized by spectroscopic and analytical methods and subsequent reactivity. The ^{1}H NMR spectrum of **5** is similar to those of **1**−**4**, as resonances at 0.07 and −84 ppm, assignable to $(C_5Me_5)^{1-}$ and $(C_6H_6)^{2-}$, respectively, are present. Amidinate ligand resonances are observed at 18.55 and 15.47 ppm for the isopropyl methine protons and the methyl group attached to the central carbon, respectively; the methyl hydrogens from the isopropyl groups are diasteriotopic and therefore display separate resonances at −4.40, and −4.52 ppm. However, no solid-state structural details could be obtained, as crystals suitable for X-ray crystallography proved to be elusive.



Reductive Reactivity of 2−5 with C_8H_8. The syntheses of **2**−**5** provided a series of heteroleptic diuranium $(\mu-\eta^6:\eta^6-C_6H_6)^{2-}$ sandwich compounds which, along with **1**, allowed a comparison of the effects of ancillary ligands on reactivity. Reductive reactivity could be anticipated from the formally U^{3+} centers and the dianionic $(C_6H_6)^{2-}$ bridging ligand, but given the normal bond distances for the $(C_5Me_5)^{1-}$ ligands in each $[(C_5Me_5)(X)U]_2(C_6H_6)$ complex, sterically induced reduction (SIR) would not be expected.[14] As a consequence, 2 or 4 electron reduction could occur, but the six electron reduction by **1** in eq 1 would not be anticipated.

To test this idea, **2**−**5** were treated with C_8H_8 for comparison with eq 1. As shown in eq 6, reactions of **2**, **4**, and **5** cleanly generated monometallic U^{4+} complexes of the general formula, $(C_5Me_5)(X)U(C_8H_8)$, that is, $(C_5Me_5)[(Me_3Si)_2N]U(C_8H_8)$,[6] **6**, $(C_5Me_5)[(Me_3Si)_2CH]U(C_8H_8)$,[7] **7**, and $(C_5Me_5)[^iPrNC(Me)N^iPr]U(C_8H_8)$,[7] **8**. Since each of these complexes has been previously reported, they were easily identified by ^{1}H NMR

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(4) (a) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. J. *Science* **2005**, *310*, 1941. (b) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R. *J. Am. Chem. Soc.* **2006**, *128*, 12622, and references therein.

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(12) Den Haan, K. H.; De Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726–1733.

(13) Evans, W. J.; Walensky, J. R.; Ziller, J. W.; Rheingold, A. L. *Organometallics* **2009**, *28*, 3350–3357.

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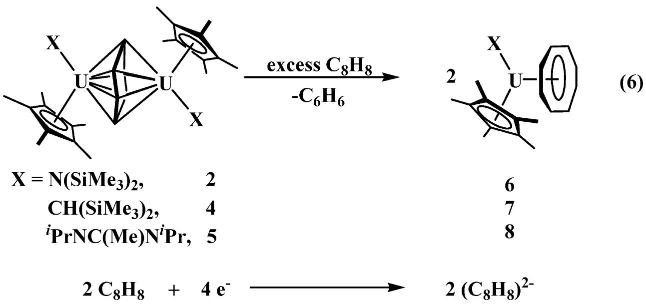
Table 3. Comparison of Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2U]_2(C_6H_6)$, **1**,[2] $\{(C_5Me_5)[(Me_3Si)_2N]U\}_2(C_6H_6)$, **2**,[2] and$\{(C_5Me_5)[(Me_3Si)_2CH]U\}_2(C_6H_6)$, **4**

	1	2	4
U−(C_5Me_5 ring centroid)	2.564−2.583 Å	2.506 Å	2.486 Å
U−C(C_5Me_5) range	2.794(16)−2.89(1) Å	2.766(3)−2.795(3) Å	2.7353(18)−2.7837(18) Å
U−C(C_5Me_5) avg	2.84(3), 2.83(2) Å	2.78(1) Å	2.76(2) Å
U−(C_6H_6 ring centroid)	2.194, 2.203 Å	2.146 Å	2.139 Å
(C_5Me_5 ring centroid)−U−(C_6H_6 ring centroid)	118.9°, 119.2°	130.9°	132.9°
C_6H_6 out of plane angle	12.5, 18°	7.2°	12.1°
C_5Me_5 Me-displacement	0.04−0.48	0.08−0.26	0.09−0.21

Table 4. Selected ^1H NMR Data in ppm for $(C_5Me_5)[(Me_3Si)_2N]U(C_8H_8)$,[6] **6**, $(C_5Me_5)[(Me_3Si)_2CH]U(C_8H_8)$,[7] **7**, and $(C_5Me_5)[^iPrNC(Me)N^iPr]U(C_8H_8)$,[7] **8**

	6	7	8
$(C_5Me_5)^{1-}$	2.81	3.13	2.05
$(C_8H_8)^{2-}$	−35.14	−35.37	−30.33

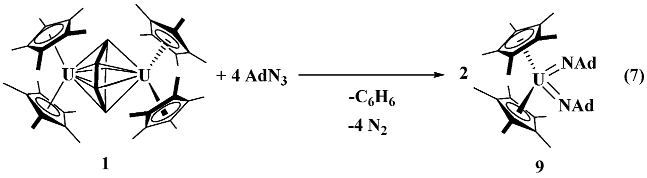
spectroscopy. Equation 6 shows that in each case, two equiv of C_8H_8 were reduced per bimetallic complex, that is, each complex acted as a four electron reductant.

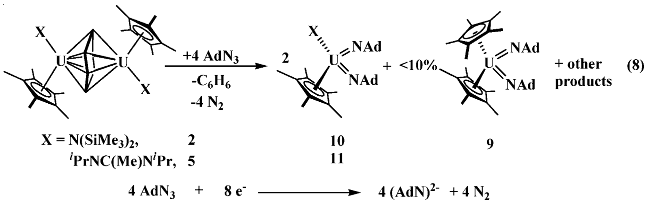


The reaction of **3** with C_8H_8 was different in that multiple products were observed by ^1H NMR spectroscopy. Although a single product could not be isolated from the reaction with **3**, resonances consistent with the analogous $(C_5Me_5)(ArO)U(C_8H_8)$ product were found. As shown in Table 4, complexes **6**−**8** have similar ^1H NMR shifts near −30 ppm for their common $(C_8H_8)^{2-}$ units. This is similar to the uniformity in NMR shifts for **1**−**5** shown in Table 2 and other series of uranium complexes.[15] Among the resonances in the reaction mixture obtained from **3** and C_8H_8 were signals at −2.10 and −36.32 ppm with a 15:8 intensity ratio along with a resonance at −1.84 ppm which integrated to 18 protons (OAr *tert*-butyl) that are consistent with a $(C_5Me_5)(ArO)U(C_8H_8)$ product.

Reductive Reactivity with 1-Azidoadamantane (AdN_3). The reactivity of **1**, **2**, **4**, and **5** with AdN_3 was studied to investigate a new reaction for the $(\mu-\eta^6:\eta^6-C_6H_6)^{2-}$ sandwich complexes and to determine if the heteroleptic $[(C_5Me_5)(X)U]_2(C_6H_6)$ complexes would be capable of 8-electron reductive reactivity. Reduction of organic azides, RN_3, by $(C_5Me_5)_2UCl(NaCl)$ in the presence of Na/Hg has previously been observed to form bis(imido) U^{6+} complexes, $(C_5Me_5)_2U({=}NR)_2$.[8] $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6-C_6H_6)$, **1**, has been shown to form a complex of this type, $(C_5Me_5)_2U({=}NPh)_2$, from azobenzene, Scheme 1, but it is also conceivable that bis(imido) U^{6+} complexes could be made from RN_3 precursors. Analogous reactions with **2**−**5** would then provide heteroleptic bis(imido) compounds that could not be easily accessed by currently known synthetic methods.

As shown in eq 7, complex **1** reacts with AdN_3 to generate the previously reported bis(imido) complex, $(C_5Me_5)_2U({=}NAd)_2$, **9**.[8] Complexes **2** and **5** also react with AdN_3, but the initially isolated products are oils. ^1H NMR analysis of the oils show resonances appropriate for the new products, $(C_5Me_5)[(Me_3Si)_2N]U({=}NAd)_2$, **10**, and $(C_5Me_5)[^iPrNC(Me)N^iPr]U({=}NAd)_2$, **11**, but resonances with shifts identical to those of $(C_5Me_5)_2U({=}NAd)_2$, **9**, are also present. Complex **9** could form in these reactions by ligand redistribution, which is not uncommon with heteroleptic compounds containing $(C_5Me_5)^{1-}$ ligands.[16] The amount of **9** present in the oil is less than 10% in each case, but it has complicated the analysis of **10** and **11**. Crystals of **11** were obtained that allowed spectroscopic and analytical characterization of a pure sample as well as the determination of its crystal structure by X-ray diffraction, Figure 3. The ^1H NMR spectrum of the crystals contained a resonance at 4.10 ppm assignable to $(C_5Me_5)^{1-}$ based on its similarity to the 4.07 ppm resonance for **9**; the analogous resonance for **10** is at 4.66 ppm.





The structure of **11** is compared to that of $(C_5Me_5)_2U({=}NAd)_2$, **9**, in Table 5. The 1.952(2) Å U1−N1 and 1.953(2) Å U1−N2 bond distances in **11** are similar to the 1.94(2) and 1.96(2) Å analogues in **9** and are typical for U^{6+} bis(imido) compounds.[8,17] These bond lengths are significantly shorter than typical uranium-amide distances as exemplified by the 2.277(6) and 2.296(4) Å U−N distances in the U^{6+} carbene complex, $[\kappa N{:}\ \eta^1\text{-}Me_3CNCH_2CH_2\text{-}(NHC)\text{-}R]_2UO_2$, where *NHC* = N-heterocyclic carbene and R = mesityl, *tert*-butyl.[18] Another similarity between **11** and **9** is the near linearity of the U−N−C(adamantyl) bond angles with values of 170.25(13)° (N1) and 167.40(14)° (N2) for **11** and 172(2)° and 177(2)° for **9**.[8] These are comparable to those observed for other uranium imido complexes.[8,17] The 96.59(7)° N−U−N angle between the adamantyl(imido) moieties in **7** matches the 96.6(8)° value observed for $(C_5Me_5)_2U({=}NAd)_2$[8] and the (C_5Me_5 ring centroid)−uranium−N(NAd) bond angles are similar for both complexes.

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(15) Evans, W. J.; Takase, M. K.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. *Organometallics* **2009**, *28*, 236–243.

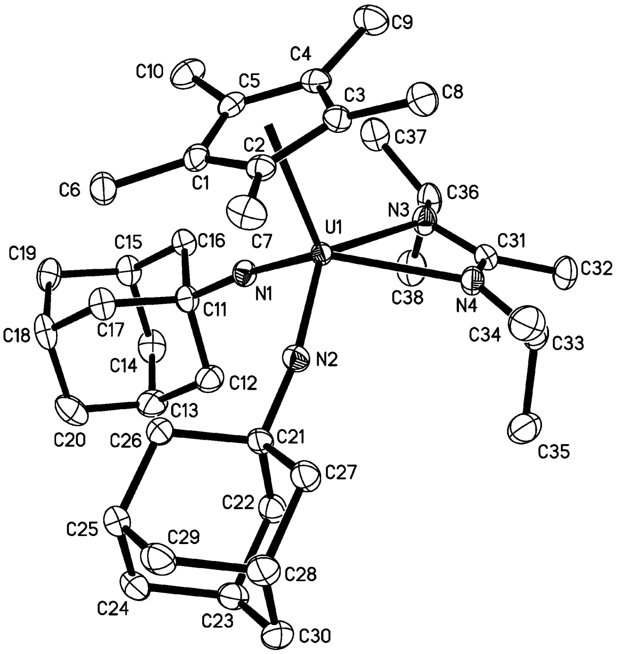


Figure 3. Thermal ellipsoid plot of $(C_5Me_5)[{}^iPrNC(Me)N{}^iPr]U(=NAd)_2$, **11**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2U(=NAd)_2$,[8] **9**, and $((C_5Me_5)[{}^iPrNC(Me)N{}^iPr]U(=NAd)_2$, **11**

	9	11
$U-Cnt(C_5Me_5)$	2.584 Å, 2.615 Å	2.497 Å
U−N(Ad)	1.94(2) Å, 1.96(2) Å	1.9522(16) Å, 1.9531(16) Å
U−N−C(Ad)	177(2)°, 172(2)°	170.25(13)°, 167.40(14)°
N−U−N	96.6(8)°	96.59(7)°
$Cnt(C_5Me_5)-U-N(Ad)$	106.4°, 106.5°, 107.2°, 109.6°	107.8°, 108.2°

In contrast to the similar numbers above, the 2.497 Å $U-(C_5Me_5$ ring centroid) distance in **11** is shorter than the 2.584 and 2.615 Å distances in **9**. This difference provides a calibration of the relative steric demands of the $[{}^iPrNC(Me)N{}^iPr]^{1-}$ amidinate ligand compared to $(C_5Me_5)^{1-}$, since **9** and **11** constitute the first pair of directly analogous and crystallographically characterized $(C_5Me_5)_2U$(other ligand)$_2$ and $(C_5Me_5)[{}^iPrNC(Me)N{}^iPr]U$(other ligand)$_2$ complexes.

The reaction of $\{(C_5Me_5)[(Me_3Si)_2CH]U\}_2(C_6H_6)$, **4**, with AdN_3 is more complex than those of **1**, **2**, and **5** in eq 7 and 8. Eight electron reduction of the organic azide to form imido ligands occurs as shown in eq 9 and is accompanied by ligand redistribution to form $(C_5Me_5)_2U(=NAd)_2$, **9**. ^1H NMR resonances attributable to an analogue of **9**−**11**, namely $(C_5Me_5)[(Me_3Si)_2CH]U(=NAd)_2$, **12**, were observed, but **12** could not be isolated in pure form. Other signals were also present in the ^1H NMR spectrum and the ratios of their intensities changed over time. Although the sequence of these reactions and their detailed mechanistic description are not easily discernible in this multiproduct reaction and is beyond the scope of this study, X-ray data on the two compounds derived from this reaction are included to show the reaction possibilities that may be available from the heteroleptic imido complexes.

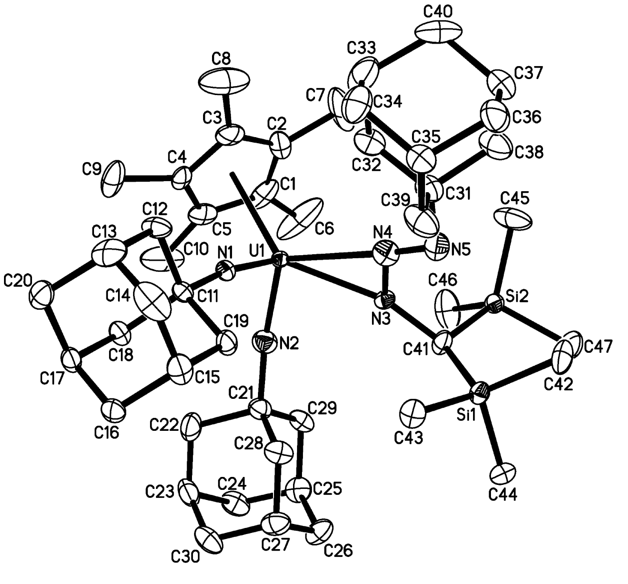
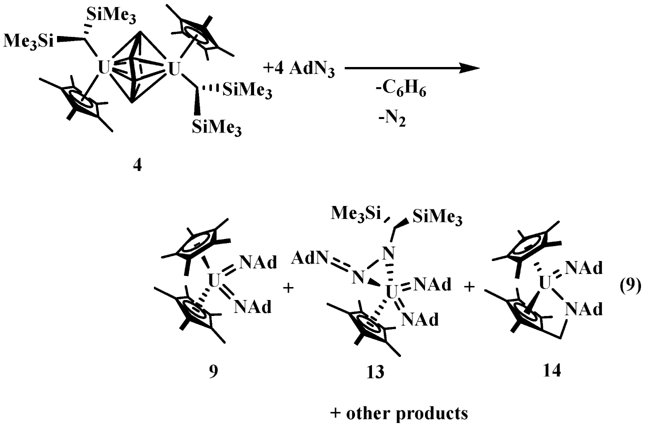


Figure 4. Thermal ellipsoid plot of $(C_5Me_5)[AdN_3CH(SiMe_3)_2\text{-}\kappa^2N^{1,2}]U(=NAd)_2$, **13**, drawn at the 30% probability level. The minor component, U1B, and hydrogen atoms have been omitted for clarity.

Crystallization of a mixture from a 5.5 h reaction of **4** and AdN_3 allowed the isolation of the triazenido bis(imido) complex, $(C_5Me_5)[AdN_3CH(SiMe_3)_2\text{-}\kappa^2N^{1,2}]U(=NAd)_2$, **13**, Figure 4, eq 9. This complex is similar to **9**−**11** in that it contains two adamantyl-imido ligands. However, it appears that a third equiv of azidoadamantane has reacted with **4** by insertion into the U−C bond to form a triazenido ligand, $[AdN_3CH(SiMe_3)_2\text{-}\kappa^2\text{-}N^{1,2}]^{1-}$.[13,19] This demonstrates the enhanced reactivity available from heteroleptic bis(imido) complexes. The ^1H NMR spectrum of **13** is similar to those of bis(imido) complexes **9**−**11** in that the $(C_5Me_5)^{1-}$ signal is observed at 4.39 ppm and the adamantyl protons appear at 1−3.5 ppm. However, the quality of the diffraction data did not allow detailed analysis of the metrical parameters.



Crystallization of the reaction mixture from an 18.5 h reaction between **4** and AdN_3 gave another type of product, $(C_5Me_5)(\eta^5{:}\kappa N\text{-}C_5Me_4CH_2NAd)U(=NAd)$, **14**, Figure 5. This product could result from (a) reduction of adamantylazide to form imido ligands, $(NAd)^{2-}$, (b) metalation of a $(C_5Me_5)^{1-}$ ligand (presumably by a $[CH(SiMe_3)_2]^{1-}$ ligand in the system) to form $(C_5Me_4CH_2)^{2-}$ accompanied by insertion of an NAd moiety to make an $(\eta^5{:}\kappa N\text{-}C_5Me_4CH_2NAd)^{2-}$ ligand, followed by ligand redistribution to provide **14** with two C_5 rings.

The $(\eta^5{:}\kappa N\text{-}C_5Me_4CH_2NAd)^{2-}$ ligand in **14** has previously been observed to form by intramolecular C−H activation upon heating $(C_5Me_5)_2U(=NAd)_2$, **9**, in benzene which generates the

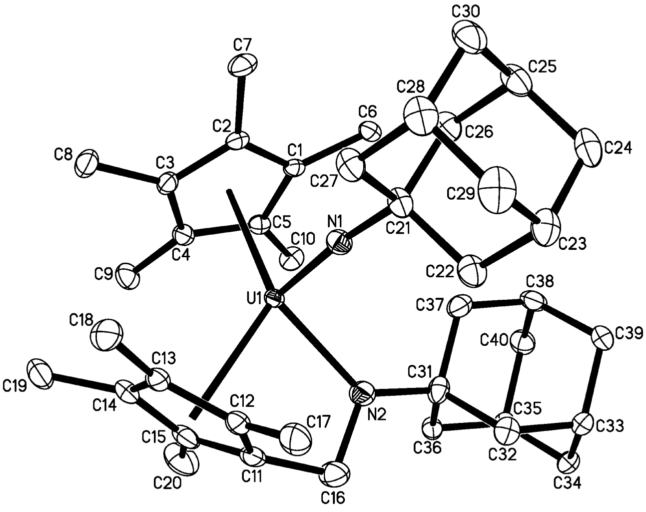


Figure 5. Thermal ellipsoid plot of $(C_5Me_5)(\eta^5{:}\kappa N\text{-}C_5Me_4CH_2NAd)U(=NAd)$, **14**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)(\eta^5{:}\kappa N\text{-}C_5Me_4CH_2NAd)U(=NAd)$, **14**, and $(C_5Me_5)(\eta^5{:}\kappa N\text{-}C_5Me_4CH_2NAd)U(NHAd)$,[20] **15**

	14	**15**
U−(C_5Me_5 ring centroid)	2.536 Å	2.55 Å
U−($C_5Me_4CH_2NAd$ ring centroid)	2.471 Å	2.48 Å
U−N1	1.955(3) Å	2.155(7) Å
U−N2 ($C_5Me_4CH_2NAd$)	2.251(3) Å	2.231(6) Å
U−N1−C21	173.5(3)°	161.0(6)°
U−N2−C31	133.6(3)°	135.3(5)°

bis(*amido*) U^{4+} complex $(C_5Me_5)(\eta^5{:}\kappa N\text{-}C_5Me_4CH_2NAd)U(NHAd)$, **15.**[20] Complex **14** is similar to **15**, except that it contains an $(NAd)^{2-}$ *imido* ligand rather than a $(NHAd)^{1-}$ *amido* unit and **14** is a U^{5+} complex.

The structures of **14** and **15**, which are not isomorphous, are compared in Table 6. The differences between the $(NAd)^{2-}$ and $(NHAd)^{1-}$ amido ligands are clear from the bond distances and angles. The 1.955(3) Å U1−N1 distance in **14** is in the range appropriate for imido bonds and is much shorter than the 2.155(7) Å U−N(NHAd) distance in **15**. The 173.5(3)° U1−N1−C21 angle is also consistent with imido complexes and more linear than the 161.0(6)° analog in **15**.

Discussion

The bimetallic uranium $(C_6H_6)^{2-}$ complex, $[(C_5Me_5)_2U]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$, **1**, has been shown to be capable of undergoing $(C_5Me_5)^{1-}$ substitution reactions to form complexes of the form, $[(C_5Me_5)(X)U]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$, where X = $N(SiMe_3)_2$,[2] $OC_6H_2(CMe_3)_2$-2,6-Me-4, $CH(SiMe_3)_2$, and ${}^iPrNC(Me)N{}^iPr$, eqs 2−5. These reactions are unusual for the normally stable $(\eta^5\text{-}C_5Me_5)^{1-}$ ligands since the penta-hapto groups are being displaced by ligands of lower hapticity. This reactivity presumably arises because of the steric crowding in **1**, but it is unusual that this would be relieved by loss of $(\eta^5\text{-}C_5Me_5)^{1-}$ rather than the reactive $(C_6H_6)^{2-}$ group. It is possible that the dianion is not substituted due to its higher charge and bridging position. The substitution of $(\eta^5\text{-}C_5Me_5)^{1-}$ by $[N(SiMe_3)_2]^{1-}$ and $(OAr)^{1-}$ makes new bonds to donor atoms with an affinity for electropositive metals. However, the formation of $\{(C_5Me_5)[(Me_3Si)_2CH]U\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$, **4**, is most unusual in that a single carbon donor atom ligand, $[CH(SiMe_3)_2]^{1-}$, is replacing a five carbon donor atom group.

Overall, eqs 2−5 show the generality of the $(\eta^5\text{-}C_5Me_5)^{1-}$ displacement reaction. This appears to be a broadly useful method to make heteroleptic organouranium complexes that are often difficult to isolate due to ligand redistribution reactivity. As other sterically crowded bis(pentamethylcyclopentadienyl) complexes like **1** are discovered, these reactions could provide an immediate route to heteroleptic derivatives. Furthermore, since this reaction is applicable to an alkyl reagent, a new route to U^{3+} alkyl complexes has been discovered, thus providing opportunity to access a class of compounds that currently has few members.[11,21] Additionally, formation of **2**−**5** shows that the unusual $(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)^{2-}$ ligand can exist in a variety of actinide environments beyond the $(C_5Me_5)_2U$- and $(ArNR)_2U$-ligated examples previously identified.[2,22]

Structural comparisons of **1** to **2** and **4** indicate that the latter heteroleptic $[(C_5Me_5)(X)U]_2(C_6H_6)$ complexes do not have the extreme metrical parameters of **1** and therefore would not be expected to participate in the unusual $(C_5Me_5)^{1-}$ displacement reactivity that led to their formation. Indeed, the fact that just one $(C_5Me_5)^{1-}$ ligand is substituted per uranium is consistent with the generalization that $(C_5Me_5)^{1-}$ rings are generally not displaced from organo-f-element complexes with normal metal ring bonding parameters.[2]

The differences in reductive reactivity of **2**−**5** versus **1** are also consistent with this view. Hence, sterically induced reduction in which $(C_5Me_5)^{1-}$ acts as a reductant is not observed with the sterically "normal" **2**−**5**. The four electron cyclooctatetraene reductions in eq 6 arise from the reducing capacity of the $(C_6H_6)^{2-}$ ligand and the two U^{3+} metal centers. In the case of the eight electron reductions in eqs 7 and 8, reduction by $(C_6H_6)^{2-}$ is accompanied by two U^{3+} to U^{6+} transformations.

The reductive results in eq 6−8 do not reveal any particular effect of the $[(C_5Me_5)(X)]^{2-}$ vs $[(C_5Me_5)_2]^{2-}$ ligation on the reduction reaction itself. Reductions of these substrates are sufficiently favorable with $(C_6H_6)^{2-}$ and U^{3+} as reducing agents, that the specific ancillary ligands on the metal did not alter the reaction pathway. However, differences were observed in the facility of isolating the products. The more complicated nature of the reaction of **3** with C_8H_8 and AdN_3 demonstrates the importance of selecting the appropriate ligand set for

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controlling the reaction chemistry. Historically, the $[(C_5Me_5)_2]^{2-}$ ligand set has been excellent for identifying many types of new chemistry. However, extensive efforts to develop "post-metallocene" complexes[23] with ligand sets alternative to $(C_5Me_5)^{1-}$ indicate the strong expectation that other reactions will be available when different ancillary ligands are present.

The bis(imido) U^{6+} chemistry represents a good example of the value of developing heteroleptic ligand sets. An enormous amount of new chemistry has been developed via $[U(=NR)_2]^{2+}$ complexes[4,8,16,24] but the chance to vary the ancillary ligand set is minimal.[25] Sterically crowded bis(pentamethylcyclopentadienyl) complexes such as **1** may provide a general route to heteroleptic species by $(C_5Me_5)^{1-}$ displacement. If the sterically crowded complex has components of high reactivity as found with the U^{3+} and $(C_6H_6)^{2-}$ contained in **1**, this could provide reactivity pathways to heteroleptic species inaccessible by current synthetic methods.

Conclusion

Steric crowding in the bis(pentamethylcyclopentadienyl) complex, $[(C_5Me_5)_2U]_2(\mu-\eta^6:\eta^6\text{-}C_6H_6)$, provides a route for unusual $(C_5Me_5)^{1-}$ displacement reactions in which amide, aryloxide, alkyl, and amidinate (X) ligands of lower hapticity can be attached to the metal. These heteroleptic $[(C_5Me_5)(X)U]_2(\mu-\eta^6:\eta^6\text{-}C_6H_6)$ complexes are highly reactive reductants due to their U^{3+} and $(C_6H_6)^{2-}$ components and they can function as 4 electron reductants to reduce two equiv of C_8H_8 to make heteroleptic cyclooctatetraenyl complexes, $(C_5Me_5)(X)U(C_8H_8)$, and as 8 electron reductants with organic azides to make bis(imido) U^{6+} products, $(C_5Me_5)(X)U(=NR)_2$. In the 8 electron reduction that forms U^{6+} bis(imido) complexes with $\{(C_5Me_5)[(Me_3Si)_2CH]U\}_2(\mu-\eta^6:\eta^6\text{-}C_6H_6)$, further reaction sequences become possible involving insertion and metalation to expand the chemistry beyond that which is possible with the homoleptic $[(C_5Me_5)_2]^{2-}$ ancillary ligand set.

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Supporting Information Available: X-ray data collection, structure solution, and refinement (PDF) and X-ray diffraction details of compounds **3**, **4**, **11**, **13**, and **14** (CIF, CCDC No. 742781−742785). This material is available free of charge via the Internet at http://pubs.acs.org.

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