

Synthesis of $(C_5Me_5)_2(C_5Me_4H)UMe$, $(C_5Me_5)_2(C_5H_5)UMe$, and $(C_5Me_5)_2UMe[CH(SiMe_3)_2]$ from Cationic Metallocenes for the Evaluation of Sterically Induced Reduction

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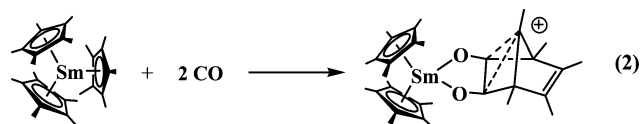
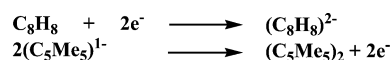
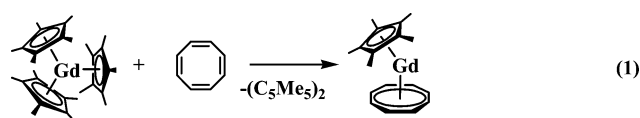
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To probe the correlation of unusual $(C_5Me_5)^{1-}$ reactivity with steric crowding in complexes such as $(C_5Me_5)_3UMe$ and $(C_5Me_5)_3UCl$, slightly less crowded $(C_5Me_5)_2(C_5Me_4H)UX$ analogues ($X = Me, Cl$) were synthesized and their reactivity was evaluated. The utility of the cationic precursors $[(C_5Me_5)_2UMe]^{1+}$, **1**, and $[(C_5Me_5)_2UCl]^{1+}$, **2**, in the synthesis of $(C_5Me_5)_2(C_5Me_4H)UMe$, **3**, and $(C_5Me_5)_2(C_5Me_4H)UCl$, **4**, was also explored. Since the use of precursor $[(C_5Me_5)_2UMe][MeBPh_3]$, **1a**, is complicated by the equilibrium between **1a** and $(C_5Me_5)_2UMe_2/BPh_3$, the reactivity of $[(C_5Me_5)_2UMe(OTf)]_2$, **1b**, ($OTf = O_3SCF_3$) prepared from $(C_5Me_5)_2UMe_2$ and $AgOTf$, was also studied. Both **1a** and **1b** react with KC_5Me_4H to form **3**. Complex **4** readily forms by addition of KC_5Me_4H to $[(C_5Me_5)_2UCl][MeBPh_3]$, generated *in situ* from $(C_5Me_5)_2UMeCl$ and BPh_3 . Complex **1b** was preferred to **1a** for the synthesis of $(C_5Me_5)_2(C_5H_5)UMe$, **5**, and $(C_5Me_5)_2UMe[CH(SiMe_3)_2]$, **6**, from KC_5H_5 and $LiCH(SiMe_3)_2$, respectively. Complex **6** is the first example of a mixed alkyl uranium metallocene complex. Sterically induced reduction (SIR) reactivity was not observed with **3–6** although the methyl displacements from the $(C_5Me_5)^{1-}$ ring plane for **3** are the closest observed to date to those of SIR-active complexes. The 1H NMR spectra of **3** and **4** are unusual in that all of the $(C_5Me_4H)^{1-}$ methyl groups are inequivalent. This structural rigidity is consistent with density-functional theory calculations.

Introduction

Recent studies of sterically crowded tris(pentamethylcyclopentadienyl) lanthanide and actinide complexes, $(C_5Me_5)_3M$, have shown that extreme steric crowding can activate reactivity in the normally inert ancillary $(C_5Me_5)^{1-}$ ligand.¹ For example, this ligand can function as a one-electron reductant and confer redox activity on complexes containing redox inactive metals, eq 1,^{1b} in a process called sterically induced reduction (SIR). The $(C_5Me_5)^{1-}$ ligand can also react like an η^1 -alkyl moiety as shown in eq 2.²

A detailed metrical analysis of the steric crowding in these $(C_5Me_5)_3M$ complexes indicated that the reactivity shown



in eqs 1 and 2 was associated with structures in which one methyl group per $(C_5Me_5)^{1-}$ ligand was displaced by 0.48–0.54 Å from the cyclopentadienyl ring plane.³ Some 33 examples³ of $(C_5Me_5)^{1-}$ complexes with maximum methyl displacements of 0.12–0.42 Å showed no unusual $(C_5Me_5)^{1-}$

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(1) (a) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119. (b) Evans, W. J.; Davis, B. L.; Champagne, T. M.; Ziller, J. W. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 12678.

(2) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 12635.

(3) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Inorg. Chem.* **2005**, *44*, 7960.

reactivity, whereas 17 examples³ with the 0.48–0.54 Å displacements did have special $(C_5Me_5)^{1-}$ reactivity. This correlation is complicated by the fact that these ranges are very close and their difference starts to approach the limit of uncertainty in the measurement. Moreover, each $(C_5Me_5)_3M$ complex has two methyl displacements per ring that are in the “normal” range in addition to the one large methyl displacement per ring.³

To further probe the boundary between reactive, sterically crowded complexes and their slightly less crowded, presumably less reactive analogues, the synthesis of $(C_5Me_5)_2(C_5Me_4H)UMe$ and $(C_5Me_5)_2(C_5Me_4H)UCl$ was pursued for comparison with $(C_5Me_5)_3UMe$ ⁴ and $(C_5Me_5)_3UCl$.⁵ These efforts have provided a complex for evaluation that has the second largest methyl displacement observed to date, as well as insight into the utility of cations such as $[(C_5Me_5)_2UMe]^{1+}$, **1**, and $[(C_5Me_5)_2UCl]^{1+}$, **2**, in producing the first mixed-alkyl U(IV) complex, $(C_5Me_5)_2UMe[CH(SiMe_3)_2]$, **6**.

Experimental Section

The syntheses and manipulations described were conducted with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. The glovebox contained an argon atmosphere free from coordinating solvents. Solvents were sparged with UHP argon and dried over columns containing Q-5 and molecular sieves. Benzene-*d*₆ and toluene-*d*₈ (Cambridge Isotope Laboratories) were dried over NaK alloy and benzophenone, degassed by three freeze–pump–thaw cycles, and vacuum transferred before use. $[(C_5Me_5)_2UMe][MeBPh_3]$, **1a**,⁴ $(C_5Me_5)_2UMe_2$,⁶ $(C_5Me_5)_2UMeCl$,⁶ KC_5H_5 ,⁷ KC_5Me_4H ,⁸ and $Li[CH(SiMe_3)_2]^9$ were prepared as previously described. Triphenylborane was purchased from Aldrich and sublimed prior to use. Silver trifluoromethanesulfonate (triflate) was purchased from Strem and used as received. NMR experiments were conducted with Bruker DRX 400 or Omega 500 MHz spectrometers. ¹³C NMR spectra were collected with sweep widths of 300 Hz for 25 k scans. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany) or with a Perkin-Elmer 2400 CHNS elemental analyzer.

$[(C_5Me_5)_2UMe(OTf)]_2$, **1b**. AgOTf (167 mg, 0.650 mmol) was added to a stirred solution of $(C_5Me_5)_2UMe_2$ (350 mg, 0.650 mmol) in benzene (12 mL). After 12 h, silver metal was removed by centrifugation, and the solvent was removed under vacuum to yield **1b** as a red microcrystalline powder (385 mg, 94%). Complex **1b** was identified by X-ray crystallography as the previously characterized $[(C_5Me_5)_2UMe(OTf)]_2$.¹⁰ ¹H NMR (*C*₆D₆, 298 K): 9.8 (s, *C*₅Me₅) ppm. The methyl group could not be observed. Methane was observed in the ¹H NMR spectrum at 0.15 ppm.

$(C_5Me_5)_2(C_5Me_4H)UMe$, **3**. KC_5Me_4H (125 mg, 0.781 mmol) was added to a solution of **1a** (534 mg, 0.777 mmol) in benzene (10 mL). After 6 h, a white precipitate was removed by centrifugation. The solvent was removed under vacuum to yield **3** as a red powder (475 mg, 87%). Crystals appropriate for X-ray crystallography were obtained from a saturated toluene solution at –35 °C. ¹H NMR (*C*₆D₆, 298 K): 46.4 (s, 1H, *C*₅Me₄H), 14.1 (s, 3H, *C*₅Me₄H), 10.9 (s, 3H, *C*₅Me₄H), 10.7 (s, 15H, *C*₅Me₅), 6.9 (s, 15H, *C*₅Me₅), 3.7 (s, 3H, *C*₅Me₄H), –29.6 (s, 3H, *C*₅Me₄H), –207 (s, 3H, Me) ppm. ¹³C NMR (tol-*d*₈, 298 K): –1.1 (*C*₅Me₄H), –17.4 (*C*₅Me₄H), –26.6 (*C*₅Me₅), –29.7 (*C*₅Me₄H), –32.2 (*C*₅Me₅), –105.3 (*C*₅Me₄H) ppm. Anal. Calcd for C₃₀H₄₆U: C, 55.89; H, 7.19; U, 36.92. Found: C, 55.58; H, 7.15; U, 37.10. IR: 2901s, 2860s, 2720m, 1486m, 1435s, 1379s, 1332w, 1101m, 1016m, 793m, 702w, 608w, 593w cm^{–1}.

3 from 1b and KC₅Me₄H. KC_5Me_4H (18 mg, 0.087 mmol) was added to a solution of **1b** (54 mg, 0.086 mmol) in benzene (5 mL). After 16 h, a white precipitate was removed by centrifugation, and the solvent removed under vacuum to yield **3** as a red powder (45 mg, 81%). The ¹H NMR spectrum matched that above for **3**.

$(C_5Me_5)_2(C_5Me_4H)UCl$, **4**. BPh₃ (126 mg, 0.520 mmol) was added to a solution of $(C_5Me_5)_2UMeCl$ (290 mg, 0.519 mmol) in toluene (10 mL). After 4 h, KC_5Me_4H (83 mg, 0.518 mmol) was added, and the resulting solution was allowed to stir for an additional 16 h. A white precipitate was removed by centrifugation, and the solvent was removed under vacuum to yield **4** as a dark red microcrystalline powder (300 mg, 87%). ¹H NMR (*C*₆D₆, 298 K): 41.7 (s, 1H, *C*₅Me₄H), 24.2 (s, 3H, *C*₅Me₄H), 16.9 (s, 3H, *C*₅Me₄H), 13.9 (s, 15H, *C*₅Me₅), 9.0 (s, 15H, *C*₅Me₅), 3.2 (s, 3H, *C*₅Me₄H), –34.8 (s, 3H, *C*₅Me₄H) ppm. ¹³C NMR (*C*₆D₆, 298 K): –5.2 (*C*₅Me₄H), –22.4 (*C*₅Me₅), –28.3 (*C*₅Me₅), –35.8 (*C*₅Me₄H), –38.3 (*C*₅Me₄H), –99.7 (*C*₅Me₄H). Anal. Calcd for C₂₉H₄₃UCl: C, 52.37; H, 6.52. Found: C, 51.87; H, 5.99. IR: 2952s, 2907s, 2858s, 2727w, 1593w, 1434s, 1379s, 1275m, 1256m, 1239m, 1185w, 1120w, 1067w, 1021m, 886w, 788m, 750m, 700s, 602w cm^{–1}.

$(C_5Me_5)_2(C_5H_5)UMe$, **5**. KC_5H_5 (29 mg, 0.28 mmol) was added to a solution of **1a** (190 mg, 0.243 mmol) in benzene (10 mL). After 16 h, a white precipitate was removed by centrifugation. The solvent was removed under vacuum to yield **5** as a red-orange powder (135 mg, 76%). Crystals appropriate for X-ray crystallography were obtained from a saturated toluene solution at –35 °C. ¹H NMR (*C*₆D₆, 298 K): 9.3 (s, 30H, *C*₅Me₅), –19.3 (s, 5H, *C*₅H₅), –207 (s, 3H, Me) ppm. ¹³C NMR (*C*₆D₆, 298 K): 146.8 (*C*₅H₅), 218.5 (*C*₅Me₅) ppm. Anal. Calcd for C₂₆H₃₈U: C, 53.06; H, 6.51; U, 40.44. Found: C, 52.83; H, 6.62; U, 40.10. IR: 2913s, 2861s, 2720m, 1489m, 1436s, 1377s, 1320m, 1104m, 1014s, 776s, 701m, 606m, 536w cm^{–1}.

$(C_5Me_5)_2UMe[CH(SiMe_3)_2]$, **6**. $LiCH(SiMe_3)_2$ (83 mg, 0.50 mmol) was added to a solution of **1b** (310 mg, 0.494 mmol) in toluene (10 mL). After 2 h, a white precipitate was removed by centrifugation, and the solvent was removed under vacuum to yield **6** as a red microcrystalline powder (315 mg, 93%). Crystals appropriate for X-ray crystallography were obtained from slow cooling of a saturated hot toluene solution at –35 °C. ¹H NMR (*C*₆D₆, 298 K): 8.99 (s, 15H, *C*₅Me₅), 7.90 (s, 15H, *C*₅Me₅), –4.71 (s, 18H, SiMe₃), –7.35 (s, 1H, CHSiMe₃) –114 (s, 3H, Me) ppm. ¹³C NMR (*C*₆D₆, 298 K): 16.4 (SiMe₃), –28.5 (*C*₅Me₅), –28.7 (*C*₅Me₅) ppm. Anal. Calcd for C₂₈H₅₂Si₂U: C, 49.24; H, 7.68; Si, 8.02; U, 34.86. Found: C, 49.45; H, 7.78; Si, 7.50; U, 35.39. IR: 2948s, 2899s, 2724w, 1489w, 1434m, 1377m, 1241s, 1018w, 988w, 834s, 769s, 660s, 596s cm^{–1}.

- (4) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 3407.
- (5) Evans, W. J.; Nyce, G. W.; Johnston, M. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 12019.
- (6) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.
- (7) Panda, T. K.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2003**, *22*, 877.
- (8) Evans, W. J.; Lee, D. S.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 6393.
- (9) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.
- (10) Kiplinger, J. L.; John, K. D.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Organometallics* **2002**, *21*, 4306.

Reactivity of 3. Phenazine (40 mg, 0.22 mmol) was added to **3** (146 mg, 0.226 mmol) in benzene (8 mL). After 12 h, no color change was seen, and no reaction was observed by ^1H NMR spectroscopy. The mixture was redissolved in toluene and heated to 100 °C for 6 h. The solvent was removed under vacuum, and no reaction was observed by ^1H NMR spectroscopy. Diphenylditeluride (14 mg, 0.034 mmol) was added to **3** (20 mg, 0.031 mmol) in toluene- d_8 . No reaction was observed by ^1H NMR spectroscopy even after heating at 100 °C for 6 h.

Computational Details. The structures of **3**, **4**, and **5** were optimized using the Tao, Perdew, Staroverov, and Scuseria meta-GGA functional (TPSS)¹¹ and polarized triple- ζ valence basis sets (def2-TZVP).¹² In recent benchmark studies,¹³ TPSS was found to perform exceptionally well for structures of transition metal π complexes. The multipole-accelerated resolution of the identity (MARI-J) approximation for the Coulomb energy was used throughout.¹⁴ Quadrature grids were of size m4;¹⁵ default convergence criteria were used otherwise. Optimized structures were confirmed to be minima by harmonic vibrational frequency calculations using split valence basis sets with polarization functions on non-hydrogen atoms (def2-SV(P)).¹² All calculations were carried out using the TURBOMOLE program package.¹⁶

X-ray Data Collection, Structure Solution, and Refinement. **(C₅Me₅)₂(C₅Me₄H)UMe, 3.** A red plate 0.06 × 0.03 × 0.02 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 208(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 20 s per frame using a scan width of 0.3°. Data collection was 97.3% complete to 25.00° in θ . A total of 8177 reflections were collected covering the indices, $-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-20 \leq l \leq 21$. A total of 8177 reflections were found to be symmetry independent, with an R_{int} of 0.1210. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be $P\bar{1}$ (No. 2). Details are given in Table 1. The data were integrated using the Bruker SAINT software program and scaled using the TWINABS software program. Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

(C₅Me₅)₂(C₅H₅)UMe, 5. A red plate 0.05 × 0.03 × 0.02 mm in size was handled as described for **3**. Data were collected at 100(2) K. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be $P2(1)/n$ (No. 14).

[(C₅Me₅)(C₅Me₄H)(OTf)U]₂(μ -O), 7. A red crystal of approximate dimensions 0.14 × 0.23 × 0.38 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹⁷ program package was used to

Table 1. X-ray Data Collection Parameters for (C₅Me₅)₂(C₅Me₄H)UMe, **3**, (C₅Me₅)₂(C₅H₅)UMe, **5**, and [(C₅Me₅)(C₅Me₄H)(OTf)U]₂(μ -O), **7**

	3	5	7
empirical formula	C ₃₀ H ₄₆ U	C ₂₆ H ₃₈ U	C ₄₀ H ₅₆ F ₆ O ₇ S ₂ U ₂ ·C ₇ H ₈
formula weight (g/mol)	644.70	588.59	1395.16
temperature (K)	208(2)	100(2)	173(2)
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
<i>a</i> (Å)	8.695(4)	8.443(2)	12.1011(13)
<i>b</i> (Å)	9.660(4)	32.730(9)	33.777(4)
<i>c</i> (Å)	16.242(7)	9.048(3)	12.1939(13)
α (deg)	92.102(7)	90	90
β (deg)	93.323(7)	114.787(3)	93.448(2)
γ (deg)	105.441(7)	90	90
volume (Å ³)	1310.8(10)	2270.1(11)	4975.1(9)
<i>Z</i>	2	4	4
ρ_{calcd} (Mg/m ³)	1.633	1.722	1.863
μ (mm ⁻¹)	6.206	7.158	6.656
R1 [$I > 2.0\sigma(I)$] ^a	0.0860	0.0305	0.0402
wR2 (all data) ^a	0.2315	0.0592	0.0826

^a Definitions: $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT¹⁸ and SADABS¹⁹ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL²⁰ program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ that 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 factors²¹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There was one molecule of toluene solvent present per formula unit. The solvent molecule was disordered and included using multiple components, partial site-occupancy-factors, and isotropic thermal parameters.

Results

Synthesis. (C₅Me₅)₂(C₅Me₄H)UMe, 3. The initial synthetic target of this study was (C₅Me₅)₂(C₅Me₄H)UMe, **3**. A direct route to this complex involving ionic metathesis between (C₅Me₅)₂UMeCl and KC₅Me₄H was unsuccessful: these compounds do not react under ambient conditions. This was not unexpected based on previous attempts to make sterically crowded f element complexes from cyclopentadienyl metal halides.²² In addition, no reaction occurs between (C₅Me₅)₂UMe₂ and C₅Me₄H.

In light of the success found in reactions of cationic f element metallocenes²³ and specifically the reaction of [(C₅Me₅)₂UMe]-[MeBPh₃] with KC₅Me₅,⁴ eq 3, the reactions of [(C₅Me₅)₂UMe]⁺ cations with KC₅Me₄H were examined. Addition of

- (11) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.
- (12) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *18*, 3297.
- (13) (a) Furche, F.; Perdew, J. P. *J. Chem. Phys.* **2006**, *124*, 44103. (b) Bühl, M.; Kabrede, H. *J. Chem. Theory Comput.* **2006**, *2*, 1282.
- (14) (a) Eichkorn, K. et al. *Chem. Phys. Lett.* **1995**, *242*, 283. (b) Sierka, M.; Hogeckamp, A.; Ahlrichs, R. *J. Chem. Phys.* **2003**, *118*, 9136. (c) Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *9*, 1057.
- (15) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346.
- (16) (a) Ahlrichs, R. *Chem. Phys. Lett.* **1989**, *162*, 165. (b) <http://www.turbomole.com/>.
- (17) *SMART Software Users Guide*, Version 5.1; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999.

- (18) *SAINTE Software Users Guide*, Version 6.0; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999.
- (19) Sheldrick, G. M. *SADABS*, Version 2.10; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2002.
- (20) Sheldrick, G. M. *SHELXTL*, Version 6.12; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2001.
- (21) *International Tables for X-Ray Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.
- (22) See, for example, Schumann, H.; Glanz, M.; Gorlitz, F. H.; Hemling, H. *J. Organomet. Chem.* **1993**, *462*, 155.
- (23) (a) Berthet, J.-C.; Ephritikhine, M. *Coord. Chem. Rev.* **1998**, *83*, 178–180. (b) Evans, W. J.; Seibel, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 6745.

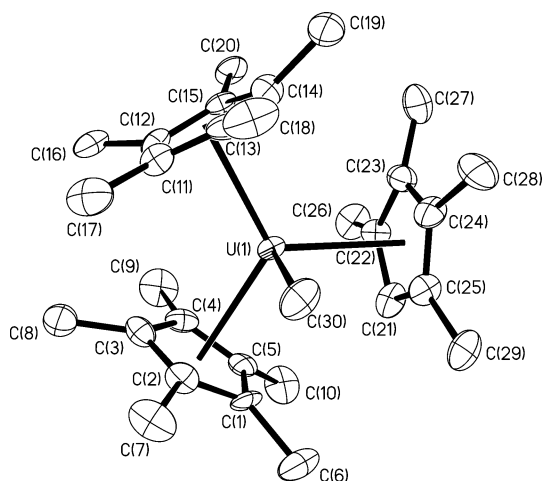
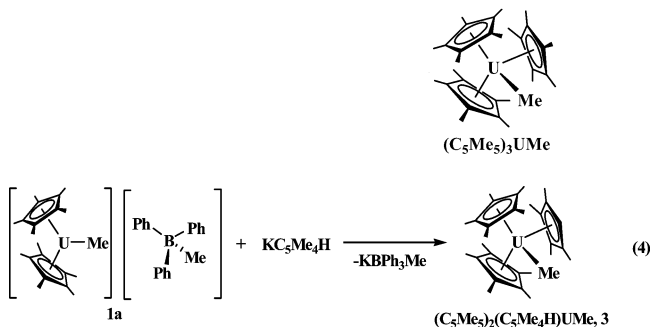
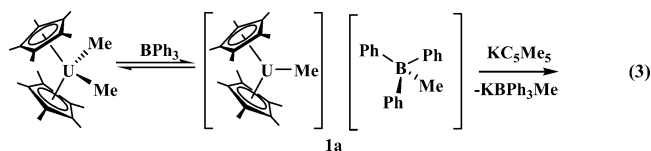


Figure 1. Thermal ellipsoid plot of $(C_5Me_5)_2(C_5Me_4H)UMe$, **3**, drawn at the 50% probability level. The hydrogens have been omitted for clarity.

KC_5Me_4H to the equilibrium mixture of $[(C_5Me_5)_2UMe]-[MeBPh_3]$, **1a**, and $(C_5Me_5)_2UMe_2$ and BPh_3 ,⁴ shown in eq 3, generated the desired complex, $(C_5Me_5)_2(C_5Me_4H)UMe$ **3**, eq 4.



Complex **3** was characterized by spectroscopic and analytical methods and definitively identified by X-ray crystallography, Figure 1. The 1H NMR spectrum of **3** is unusual in that two $(C_5Me_5)^{1-}$ resonances are observed at

10.7 and 6.9 ppm, and four methyl resonances are found for the methyl groups of $(C_5Me_4H)^{1-}$ at 14.1, 10.9, 3.7, and -29.6 ppm. The $(C_5Me_4H)^{1-}$ proton resonance is found at 46.4 ppm. These multiple resonances are indicative of a structure with restricted rotation in solution at room temperature. Upon heating **3** to $80^\circ C$ in toluene, these resonances broadened, but did not coalesce.

Complex **3** has a tris(cyclopentadienyl) uranium methyl composition analogous to that of $(C_5Me_5)_3UMe$, but the structures differ as shown in Figure 2. In $(C_5Me_5)_3UMe$, the uranium is in the plane of the three $(C_5Me_5)^{1-}$ ring centroids and each $(C_5Me_5)^{1-}$ ring centroid–U–Me vector is 90° . In **3**, the uranium is 0.264 \AA out of the plane of the three ring centroids and the Me–U– $(C_5Me_5)^{1-}$ ring centroid angles vary from 94.9 to 96.7° , that is, the complex has moved slightly toward the more normal tetrahedral arrangement of the four ligands around uranium. Figure 2 also shows how the hydrogen substituent in the $(C_5Me_4H)^{1-}$ ring is located close to the plane of the three ring centroids and uranium. This puts the smallest ring substituent in the most crowded location. In $(C_5Me_5)_3UMe$, C(13) has the longest M–C(C_5Me_5) distance and its methyl group is displaced the furthest from the ring plane. The hydrogen substituent in **3** on C(21) is in a position analogous to C(13) in $(C_5Me_5)_3UMe$. The 1H NMR spectrum suggests that this location preference may persist in solution.

The $2.415(14) \text{ \AA}$ U–C(methyl) bond distance in **3**, Table 2, is typical of tetravalent U–C(alkyl) complexes. For example, the U–C(methyl) distance in $(C_5Me_5)_2UMe_2$ is $2.414(7) \text{ \AA}$.²⁴ This distance in **3** is much shorter than the $2.66(2) \text{ \AA}$ U–C(methyl) distance in $(C_5Me_5)_3UMe$ and suggests that the steric strain has been considerably reduced in **3**. However, the $2.815(13)$ – $2.886(12) \text{ \AA}$ U–C(C_5Me_5) distances and the 2.574 and 2.567 \AA U–(C_5Me_5) ring centroid distances in **3** have larger values than the corresponding $2.670(12)$ – $2.739(11) \text{ \AA}$ and 2.418 – 2.435 \AA distances observed for $(C_5Me_5)_3UMe$.⁴ The U–(C_5Me_4H) ring centroid distance of 2.547 \AA is also longer than the 2.448 and 2.437 \AA analogues in $(C_5Me_4H)_2U(SPh)_2$,²⁵ but similar to the 2.520 \AA distance in $(C_5Me_4H)_3UCl$.²⁶

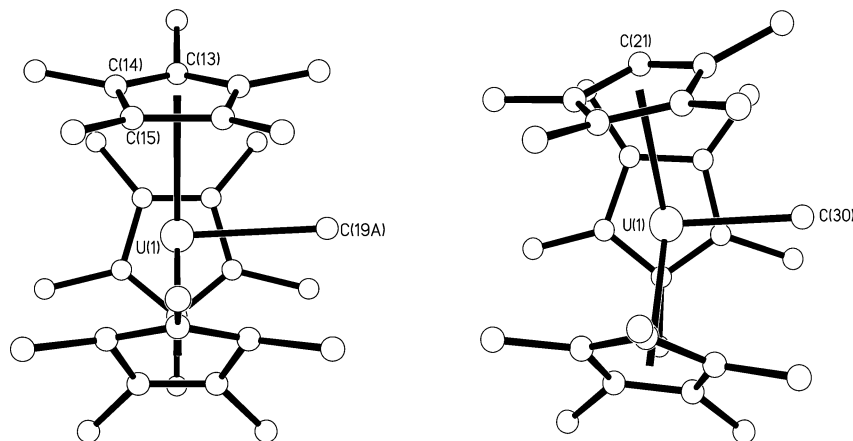


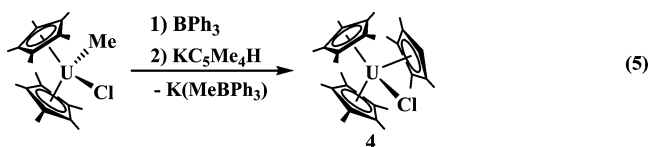
Figure 2. Side-on views of $(C_5Me_5)_3UMe$ (left) and $(C_5Me_5)_2(C_5Me_4H)UMe$, **3**, (right).

Table 2. Selected Observed and Calculated Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2(C_5Me_4H)UMe$, **3**

bond distance/angle	3	calculated
U(1)–C(30)	2.415(14)	2.436
U(1)–Cnt(C_5Me_5)	2.574	2.590
U(1)–Cnt(C_5Me_5)	2.567	2.565
U(1)–Cnt(C_5Me_4H)	2.547	2.574
Cnt(1)–U(1)–C(30)	96.7	95.5
Cnt(C_5Me_5)–U(1)–Cnt(C_5Me_5)	122.0	121.9
Cnt(C_5Me_5)–U(1)–Cnt(C_5Me_4H)	116.1	116.1
Cnt(C_5Me_5)–U(1)–Cnt(C_5Me_4H)	118.7	119.2
U(1)–C(1)	2.843(13)	2.834
U(1)–C(2)	2.815(13)	2.865
U(1)–C(3)	2.886(12)	2.903
U(1)–C(4)	2.815(12)	2.854
U(1)–C(5)	2.857(12)	2.845
U(1)–C(11)	2.806(13)	2.835
U(1)–C(12)	2.834(13)	2.827
U(1)–C(13)	2.869(13)	2.843
U(1)–C(14)	2.867(15)	2.865
U(1)–C(15)	2.805(12)	2.819
U(1)–C(21)	2.709(13)	2.728
U(1)–C(22)	2.718(12)	2.786
U(1)–C(23)	2.893(13)	2.933
U(1)–C(24)	2.907(14)	2.935
U(1)–C(25)	2.843(14)	2.835

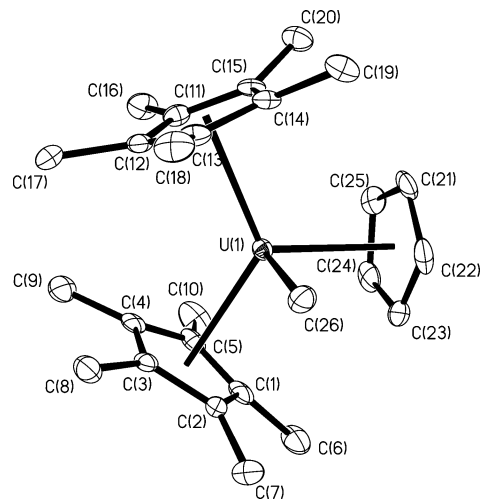
The structure of **3** proved to be special in that the maximum methyl displacements in the $(C_5Me_5)^{1-}$ rings in **3** are 0.539 Å and 0.467 Å for C(8) and C(19), respectively. These values fall in and just below the range of SIR-active complexes, 0.48–0.54 Å. Hence, complex **3** provided an opportunity to examine the methyl displacement/SIR reactivity correlation further as described in the reductive reactivity section below.

$(C_5Me_5)_2(C_5Me_4H)UCl$, **4**. The synthesis of **4** was carried out in a similar manner to that which produced $(C_5Me_5)_3UCl$.⁴ In the case of **4**, $(C_5Me_5)_2UMeCl$ and BPh_3 were stirred for 4 h presumably to form $[(C_5Me_5)_2UCl][MeBPh_3]$ *in situ*. Then KC_5Me_4H was added to displace $(BPh_3Me)^{1-}$, eq 5. As described above for **3**, reaction of KC_5Me_4H with the neutral chloride precursor, in this case, $(C_5Me_5)_2UCl_2$, does not form **4**.



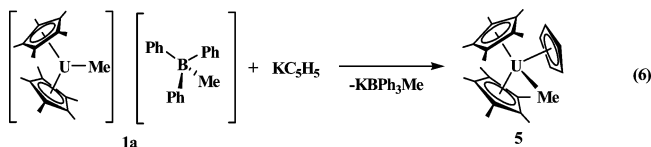
Complex **4** was characterized by spectroscopic and analytical methods. However, the small crystals that were repeatedly isolated upon recrystallization were not suitable for X-ray diffraction. The 1H NMR spectrum of **4** was similar to that of **3** in that two resonances were observed for the $(C_5Me_5)^{1-}$ ligands at 13.9 and 9.0 ppm and four resonances for the methyl groups of the $(C_5Me_4H)^{1-}$ ligand at 24.2, 16.9, 3.2, and –34.8 ppm. Likewise, heating **4** to 80 °C in toluene- d_8 only led to broadening of the resonances without coalescence. The 1H NMR spectrum of $(C_5Me_4H)_3UCl$ similarly showed four separate methyl resonances regardless of the temperature.²⁶

$(C_5Me_5)_2(C_5H_5)UMe$, **5**. To further explore the reactivity of **1**, the reaction with KC_5H_5 was examined. Complex **1a** reacts with KC_5H_5 to produce $(C_5Me_5)_2(C_5H_5)UMe$, **5**, which was identified by X-ray crystallography, Figure 3, eq 6. In

**Figure 3.** Thermal ellipsoid plot of $(C_5Me_5)_2(C_5H_5)UMe$, **5**, drawn at the 50% probability level. The hydrogens have been omitted for clarity.**Table 3.** Selected Observed and Calculated Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2(C_5H_5)UMe_2$, **5**

bond distance/angle	5	calculated
U(1)–C(26)	2.457(4)	2.452
U(1)–Cnt(C_5Me_5)	2.522	2.545
U(1)–Cnt(C_5Me_5)	2.533	2.557
U(1)–Cnt(C_5H_5)	2.488	2.472
Cnt(1)–U(1)–C(26)	97.1	97.2
Cnt(C_5Me_5)–U(1)–Cnt(C_5Me_5)	125.8	126.1
Cnt(C_5Me_5)–U(1)–Cnt(C_5H_5)	115.7	114.7
Cnt(C_5Me_5)–U(1)–Cnt(C_5H_5)	114.9	115.0
U(1)–C(1)	2.838(5)	2.861
U(1)–C(2)	2.804(4)	2.839
U(1)–C(3)	2.772(4)	2.806
U(1)–C(4)	2.786(5)	2.798
U(1)–C(5)	2.778(5)	2.793
U(1)–C(11)	2.791(5)	2.838
U(1)–C(12)	2.833(5)	2.864
U(1)–C(13)	2.821(5)	2.824
U(1)–C(14)	2.786(4)	2.805
U(1)–C(15)	2.790(4)	2.820
U(1)–C(21)	2.776(5)	2.764
U(1)–C(22)	2.757(5)	2.768
U(1)–C(23)	2.735(5)	2.739
U(1)–C(24)	2.751(5)	2.735
U(1)–C(25)	2.771(4)	2.743

contrast to **3** and **4**, the 1H NMR spectrum of complex **5** contains only one $(C_5Me_5)^{1-}$ resonance, and the $(C_5H_5)^{1-}$ signal is a single peak.

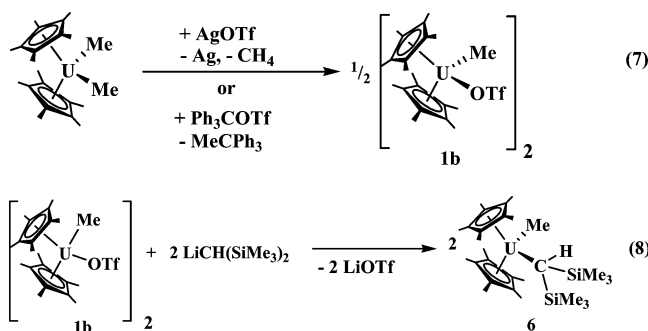


The structure of **5** shows no unusual bond distances or angles, Table 3. The four ligands are arranged in a distorted tetrahedral geometry with a 125.8° $(C_5Me_5$ ring centroid)–U– $(C_5Me_5$ ring centroid) angle. This is larger than the 120° found in $(C_5Me_5)_3UMe$,⁴ but much less than 140.5° found in $(C_5Me_5)_2UMe_2$.²⁵ The 2.522 Å U– $(C_5Me_5$ ring centroid) distance is similar to the 2.456 Å analogue in $(C_5Me_5)_2UMe_2$.²⁴ The 2.735(5)–2.776(5) Å U–C(C_5H_5) distances are similar to those of $(\eta^5-C_5H_5)_4U$, namely 2.785(22)–2.833(17)

Å.²⁷ Complex **5** has maximum methyl displacements of 0.388 and 0.390 Å for C(9) and C(17), respectively, which fall in the range of complexes that do not undergo SIR.

$(C_5Me_5)_2UMe[CH(SiMe_3)_2]$, **6**. The reaction of $[(C_5Me_5)_2UMe][MeBPh_3]$ and $LiCH(SiMe_3)_2$ generated a mixture of products by 1H NMR spectroscopy with $(C_5Me_5)_2UMe_2$ as the major product. This product would be formed if the $[CH(SiMe_3)_2]^{1-}$ anion reacted with the BPh_3 in the equilibrium in eq 3 instead of with **1a**. A similar 1H NMR spectrum was obtained from the reaction of **1a** and $KN(SiMe_3)_2$, that is, $(C_5Me_5)_2UMe_2$ was again the main product. These reactions indicated that the equilibrium in eq 3 could be problematic with these reagents, and a precursor alternative to **1a** was sought.

An alternative that proved viable was the triflate salt, $[(C_5Me_5)_2UMe(OTf)]_2$, **1b**. This salt was originally prepared by Kiplinger et al. from $(C_5Me_5)_2UMe_2$ and Ph_3COTf ,¹⁰ but it can also be made from $(C_5Me_5)_2UMe_2$ and $AgOTf$, eq 7. Using $[(C_5Me_5)_2UMe(OTf)]_2$ as a precursor, $(C_5Me_5)_2UMe[CH(SiMe_3)_2]$, **6**, was obtained cleanly from $LiCH(SiMe_3)_2$, eq 8. The triflate complex, **1b**, also reacts with KC_5Me_4H and KC_5H_5 to form **3** and **5**, respectively. Complex **6** was



crystallized from hot toluene and identified by X-ray crystallography, Figure 4, however, the quality of the crystal data was not sufficient to allow for a detailed discussion of bond angles and lengths. Two $(C_5Me_5)^{1-}$ resonances are observed in the 1H NMR spectrum of **6**, but this is common in f element metallocene complexes containing $[CH(SiMe_3)_2]^{1-}$ ligands.²⁸ For example, $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$ ($Ln = La, Nd, Sm, Lu$) have all been reported to have two resonances for the $(C_5Me_5)^{1-}$ methyl groups.²⁸ To our knowledge, **6** is the first uranium metallocene complex to have two different alkyl groups.

Reductive Reactivity. Since complex **3** had a maximum methyl displacement in the range of SIR-active compounds, its reactivity with reducible substrates was examined. Complex **3** reacts with $AgOTf$ to form silver metal and $(C_5Me_5)_2$, the two products expected from sterically induced reduction.

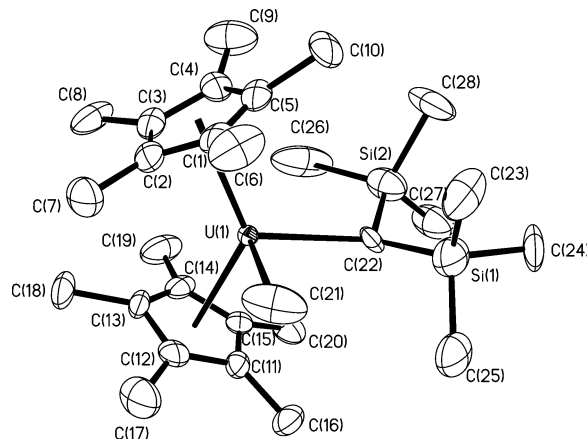


Figure 4. Thermal ellipsoid plot of $(C_5Me_5)_2UMe[CH(SiMe_3)_2]$, **6**, drawn at the 50% probability level. The hydrogens have been omitted for clarity.

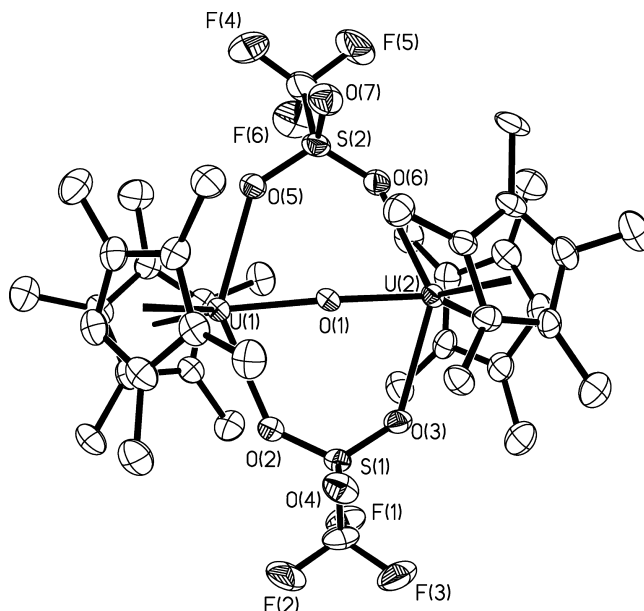
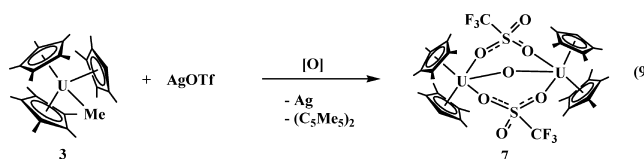


Figure 5. Thermal ellipsoid plot of $[(C_5Me_5)(C_5Me_4H)(OTf)U]_2(\mu-O)$, **7**, drawn at the 50% probability level. The hydrogens and solvent (toluene) molecule have been omitted for clarity.

However, those products would also be formed from the abstraction of a $(C_5Me_5)^{1-}$ ligand and decomposition of AgC_5Me_5 .²⁹ Attempts to characterize the uranium-containing product of the reaction of **3** with $AgOTf$ led to the isolation of a product derived from an adventitious source of oxygen, $[(C_5Me_5)(C_5Me_4H)(OTf)U]_2(\mu-O)$, **7**, eq 9, a rare example of a heteroleptic uranium complex, Figure 5.



The $158.7(2)^\circ$ U–O–U angle in **7** is the second smallest observed to date in U^{4+} oxide complexes, Table 4.^{30–40} Selected bond distances and angles for complex **7** are given in Table 5.

Since the reaction leading to **7** involved loss of both $(C_5Me_5)^{1-}$ and $(Me)^{1-}$ ligands, it offered little information

(24) Jantunen, K. C.; Burns, C. J.; Castro-Rodríguez, I.; Da Re, R. E.; Golden, J. T.; Morris, D. E.; Scott, B. L.; Taw, F. L.; Kiplinger, J. L. *Organometallics* **2004**, *23*, 4682.

(25) Evans, W. J.; Miller, K. A.; Hillman, W. R.; Ziller, J. W. *J. Organomet. Chem.* **2007**, *692*, 3649.

(26) Cloke, F. G. N.; Hawkes, S. A.; Hitchcock, P. B.; Scott, P. *Organometallics* **1994**, *13*, 2895.

(27) Burns, J. H. *J. Organomet. Chem.* **1974**, *69*, 225.

(28) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

Table 4. U–O Bond Distances (Å) and U–O–U Bond Angles (deg) in Bimetallic Tetravalent Uranium Oxo Complexes

compound	U–O distance (Å)	U–O–U bond angle (deg)	reference
$[(C_9H_7UBr(CH_3CN)_4)_2O]^{2+}[UBr_6]^{2-}$	2.057(2)	180	30
$[(Me_3SiC_5H_4)_3U]_2(\mu-O)$	2.1053(2)	180	31
$[(C_5H_5)_3U]_2(\mu-O)$	2.0881(4)	180	32
$\{[(ArO)_3tacn]U\}_2(\mu-O)$	2.1095(4)	180	33
$\{UCl_2[HB(3,5-Me_2Pz)_3]\}_2(\mu-O)^a$	2.075(1)	178.3(5)	34
$[U_2(BH_4)_6O(18-crown-6)]$	1.979(5) and 2.187(5)	173.8(3)	35
$\{[(-CH_2)_5]_4-calix[4]tetrapyrrole\}-UK(THF)_2(\mu_2-O)$	2.0861(5)	171.3(2)	36
$\{UI(terpy)_2(\mu-O)\}_2\{UI_2(terpy)\}_2^{4+}$	2.022(7)	169.3(3)	37
$[Tp^*UI(dmpz)]_2(\mu-O)^{b,c}$	2.098(1)	166.7(5)	38
$\{[U(OTf)_2(py)_3]_2(\mu-O)(\mu-OTf)_2\}$	2.0987(17)	159.2(5)	39
$[(C_5Me_5)(C_5Me_4H)(OTf)U]_2(\mu-O)$	2.116(4)	158.7(2)	this work
$\{(C_5Me_5)U[\mu-(CH_2)PPh_2(CH_2)]_2Mg-[CH_2PMePh_2]_2(\mu_3-O)(\mu_2-O)(\mu_2-Cl)_2\}$	2.13(2)	108(1)	40

^a 3,5-Me₂Pz = 3,5-Dimethylpyrazolylborate. ^b Tp* = hydridotris(3,5-dimethylpyrazolylborate). ^c dmpz = 3,5-dimethylpyrazolide.

Table 5. Selected Observed Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)C_5Me_4H](OTf)U]_2(\mu-O)$, **7**

bond distance/angle	7
U(1)–Cnt(C ₅ Me ₄ H)	2.514
U(1)–Cnt(C ₅ Me ₅)	2.489
U(1)–O(1)	2.116(4)
U(1)–O(2)	2.500(4)
U(1)–O(5)	2.529(4)
Cnt(1)–U(1)–Cnt(2)	115.7
Cnt(1)–U(1)–O(1)	130.0
Cnt(1)–U(1)–O(2)	96.1
U(1)–O(1)–U(2)	158.7(2)
S(1)–O(2)	1.456(4)
S(1)–O(3)	1.450(4)
S(1)–O(4)	1.423(5)
S(1)–C(39)	1.838(7)

about the details of the AgOTf reaction. To obtain more insight about the reactivity of AgOTf with these organouranium complexes and to compare the reactivity of a complex that was in the sterically normal range, the reaction of AgOTf with $(C_5Me_5)_2UMe_2$ was examined. This produced the previously known $[(C_5Me_5)_2UMe(OTf)]_2$, **1b**, eq 7, which had been synthesized from $(C_5Me_5)_2UMe_2$ and Ph₃COTf.¹⁰ The abstraction of a methyl group by silver followed by the subsequent reduction of Ag¹⁺ to Ag metal and liberation of methane has been previously reported with group 4 metals.⁴¹ The production of methane was confirmed by ¹H NMR spectroscopy. It is interesting to note that in eq 7 a methyl group was removed by the Ag¹⁺ reagent rather than a

$(C_5Me_5)^{1-}$ group as in the formation of **7**. However, the abstraction of Ag¹⁺ salts can be unpredictable.^{23a}

The reactions of **3** with phenazine and diphenyl ditelluride were subsequently examined since they are readily reduced by $(C_5Me_5)_3Ln$ complexes (Ln = La, Sm) by sterically induced reduction.⁴² Complex **3** did not react with these compounds that have reduction potentials of –0.364 V versus SCE⁴³ and –1.06 V versus SCE,⁴⁴ respectively, even upon heating to 100 °C in toluene. From these reactions it does not appear that **3** is sterically crowded enough to display SIR reactivity with its $(C_5Me_5)^{1-}$ ligands. Neither **5** nor **6** reacted with phenazine and diphenyl ditelluride as expected for complexes with normal $(C_5Me_5)^{1-}$ ring methyl displacements.

Density Functional Theory. To explore further the basis of the unusual NMR spectra observed for **3** and **4**, density functional theory calculations were carried out on these molecules as well as **5** for comparison. Since the crystal structure of **4** could not be obtained, the calculated converged structure was generated and looks very similar to that of **3** (see Supporting Information).

All three U⁴⁺ complexes, **3**–**5**, feature triplet ground states with 5f² electron configurations. The calculations indicate that the bonding of the $(C_5Me_5)^{1-}$ and $(C_5Me_4H)^{1-}$ ligands is predominantly ionic as evidenced by computed harmonic vibrational frequencies below 50 cm^{–1} for rotations of these ligands. This suggests that **3** and **4** differ from **5** mainly because of steric factors. The calculations revealed a plethora of low-lying rotamers that differ marginally (<1 kcal) in their energies. While a complete characterization of the potential energy surface is beyond our scope, the computed structures we discuss here are reasonable representatives of low-lying conformers. In view of these complications, packing effects in the X-ray structures, and inaccuracies inherent in our theoretical and experimental methods, the agreement between the computed and experimental structures is good. Tables 2 and 3 show that with few exceptions, the differences in computed and measured bond lengths and angles for **3** and **5** are 1% or less.

The calculations of **3** and **4** converged to structures in which the $(C_5Me_4H)^{1-}$ ligand is locked in an asymmetric position relative to the methyl and chloride groups, respectively, bound to uranium. Consequently, the methyl groups on the $(C_5Me_4H)^{1-}$

(29) Zybilla, C.; Muller, G. *Organometallics* **1987**, *6*, 2489.

(30) Beckman, W.; Goffart, J.; Rebizant, J.; Spirlet, M. R. *J. Organomet. Chem.* **1986**, *307*, 23.

(31) Berthet, J.-C.; Le Marechal, J.-F.; Nierlich, M.; Lance, M.; Vigner, J.; Ephritikhine, M. *J. Organomet. Chem.* **1991**, *408*, 335.

(32) Spirlet, M.-R.; Rebizant, J.; Apostolidis, C.; Dornberger, E.; Kanelakopoulos, B.; Powietzka, B. *Polyhedron* **1996**, *15*, 1503.

(33) Castro-Rodriguez, I.; Olsen, K.; Gantzel, P.; Meyer, K. *Chem. Commun.* **2002**, 2764.

(34) Domingos, A.; Marques, N.; Pires De Matos, A.; Santos, I.; Silva, M. *Polyhedron* **1992**, *11*, 2021.

(35) Villier, C.; Thuery, P.; Ephritikhine, M. *Acta Crystallogr.* **2006**, *C62*, m243.

(36) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2001**, *20*, 2552.

(37) Berthet, J.-C.; Nierlich, M.; Miquel, Y.; Madic, C.; Ephritikhine, M. *Dalton Trans.* **2005**, 369.

(38) Enriquez, A. E.; Scott, B. L.; Neu, M. P. *Inorg. Chem.* **2005**, *44*, 7403.

(39) Natrajan, L.; Mazzanti, M.; Bezombes, J.-P.; Pecaut, J. *Inorg. Chem.* **2005**, *44*, 6115.

(40) Cramer, R. E.; Bruck, M. A.; Gilje, J. W. *Organometallics* **1988**, *7*, 1465.

(41) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E. *Organometallics* **1987**, *6*, 1041.

(42) Evans, W. J.; Perotti, J. M.; Kozimor, S. A.; Champagne, T. M.; Davis, B. L.; Nyce, G. W.; Fujimoto, C. H.; Clark, R. D.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 3916.

(43) Nechaeva, O. N.; Pushkareva, Z. V. *Zh. Obshch. Khim.* **1958**, *28*, 2693.

(44) Liftman, V.; Albeck, M. *Electrochim. Acta* **1984**, *29*, 95.

Table 6. Selected Calculated Bond Distances (Å) and Angles (deg) for (C₅Me₅)₂(C₅Me₄H)UCl, **4**

bond distance/angle	calculated
U(1)—Cl(1)	2.610
U(1)—Cnt(C ₅ Me ₅)	2.587
U(1)—Cnt(C ₅ Me ₅)	2.566
U(1)—Cnt(C ₅ Me ₄ H)	2.563
Cnt(1)—U(1)—Cl(1)	97.5
Cnt(C ₅ Me ₅)—U(1)—Cnt(C ₅ Me ₅)	121.6
Cnt(C ₅ Me ₅)—U(1)—Cnt(C ₅ Me ₄ H)	115.4
Cnt(C ₅ Me ₅)—U(1)—Cnt(C ₅ Me ₄ H)	118.4
U(1)—C(1)	2.822
U(1)—C(2)	2.858
U(1)—C(3)	2.903
U(1)—C(4)	2.860
U(1)—C(5)	2.842
U(1)—C(11)	2.813
U(1)—C(12)	2.814
U(1)—C(13)	2.847
U(1)—C(14)	2.886
U(1)—C(15)	2.832
U(1)—C(21)	2.738
U(1)—C(22)	2.788
U(1)—C(23)	2.916
U(1)—C(24)	2.902
U(1)—C(25)	2.827

ring are inequivalent. The gap caused by the hydrogen atom perturbs the adjacent (C₅Me₅)¹⁻ ligands. As a result, the structural parameters of the two (C₅Me₅)¹⁻ rings in **3** and **4** given in Tables 2 and 6 differ considerably. This sterically induced perturbation may explain why the two (C₅Me₅)¹⁻ rings in **3** and **4** are inequivalent in the NMR spectra. In **5**, the perturbation is absent, and the two (C₅Me₅)¹⁻ ligands in **5** are nearly identical in their structural parameters, see Table 3. Further, we may compare the computed harmonic frequencies of the lowest vibrational modes in **3** and **5** inducing a rotation of the (C₅Me₄H)¹⁻ and (C₅H₅)¹⁻ ligands, respectively. In **5**, the (C₅H₅)¹⁻ rotation comes at about 29 cm⁻¹ and is thus considerably softer than the (C₅Me₄H)¹⁻ rotation in **3** at about 45 cm⁻¹.

Discussion

The slightly less crowded analogues of (C₅Me₅)₃UMe and (C₅Me₅)₃UCl, namely, (C₅Me₅)₂(C₅Me₄H)UMe, **3**, and (C₅Me₅)₂(C₅Me₄H)UCl, **4**, were readily synthesized from the metallocene cations, [(C₅Me₅)₂UMe]¹⁺, **1**, and [(C₅Me₅)₂UCl]¹⁺, **2**, according to eqs 4 and 5, respectively. The less crowded variants, (C₅Me₅)₂(C₅H₅)UMe, **5**, and (C₅Me₅)₂UMe[CH-(SiMe₃)₂], **6**, could also be obtained from **1**, but in the case of **6**, the nature of the precursor anion was crucial. The formation of **6** demonstrates a viable route to mixed alkyl uranium metallocenes. The use of [(C₅Me₅)₂UMe][MeBPh₃] as a precursor is complicated by its equilibrium with (C₅Me₅)₂UMe₂/BPh₃ and this factor will have to be considered in reactions with any anions that could form adducts with BPh₃. The triflate salt, [(C₅Me₅)₂UMe(OTf)]₂,¹⁰ **1b**, provides a good alternative and this suggests that triflates in general should be more broadly evaluated as precursors in reactions of this type.⁴⁵ For example, in the lanthanide area, triflate analogues of the popular (C₅Me₅)₂Ln(μ-Ph₂BPh₂)

should be studied more extensively than they have so far. Complex **1b** is most likely a good precursor because of the loose coordinating nature of the triflate anion.

The isolation of **3**, with its 0.539 Å and 0.467 Å methyl displacements for C(8) and C(19), respectively, provided another test for the correlation between unusual (C₅Me₅)¹⁻ reactivity and maximum methyl displacement. The 0.539 Å displacement suggests that this complex should exhibit sterically induced reduction reactivity. However, complex **3** showed no reactivity of this type. This indicates that the 0.48–0.54 Å range of methyl displacements alone is not sufficient to predict SIR or other types of unusual ligand reactivity. Indeed, when the correlation was discovered, there was a question if this was fortuitous or meaningful. Time will tell how many more exceptions will be found.

A significant difference between **3** and the 17 complexes that have large methyl displacements and SIR is that the reactive examples have three (C₅Me₅)¹⁻ ligands with large methyl displacements, whereas **3** has only one ring with a large displacement and one ring with a 0.46 Å displacement at the edge of the range of reactive species. It is possible that in the (C₅Me₅)₃UX complexes, it is important that all three rings are equally crowded and there is no option in any direction to relieve steric crowding. Certainly in **3**, the (C₅Me₄H)¹⁻ ligand provides relief from crowding. The small hydrogen substituent goes to the site of greatest congestion and locks the structure as shown by X-ray crystallography, NMR spectroscopy, and density-functional theory calculations. The option to place a much smaller substituent in a location to relieve crowding probably leads to the striking differences in the structures of (C₅Me₅)₃UMe and (C₅Me₅)₂(C₅Me₄H)UMe, **3**. Hence, **3** has more typical (ring centroid)—U—(ring centroid) angles and a normal U—Me bond distance. Complex **3** does not have an overall structure as unusual as (C₅Me₅)₃UMe, and consistent with that, it does not display unusual reactivity.

Conclusion

Cationic precursors such as [(C₅Me₅)₂UMe][MeBPh₃], [(C₅Me₅)₂UMe(OTf)]₂, and [(C₅Me₅)₂UCl][MeBPh₃] have provided synthetic routes to organouranium metallocenes that allow subtle variation in steric crowding. This has allowed refinement of the correlation between unusual (C₅Me₅)¹⁻ ligand reactivity and displacements of methyl groups attached to the cyclopentadienyl rings. The results of this study emphasize the importance of having three identical large ligands to observe unusual ligand reactivity in crowded complexes.

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Supporting Information Available: X-ray diffraction details (CIF) and X-ray data collection, structure, solution, and refinement of compounds **3**, **5**, and **7** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(45) (a) Maynadie, J.; Berthet, J.-C.; Thuery, P.; Ephritikhine, M. *Organometallics* **2007**, *26*, 2623. (b) Berthet, J.-C.; Lance, M.; Nierlich, M.; Ephritikhine, M. *Chem. Commun.* **1998**, 1373.