

How Much Steric Crowding Is Possible in Tris(η^5 -pentamethylcyclopentadienyl) Complexes? Synthesis and Structure of $(C_5Me_5)_3UCl$ and $(C_5Me_5)_3UF^1$

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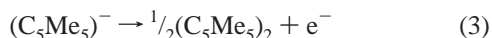
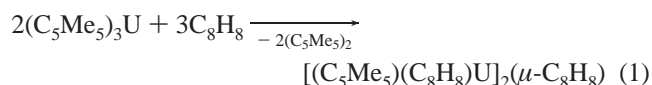
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Received July 10, 2000

During several decades of investigation of organometallic pentamethylcyclopentadienyl chemistry, no examples of tris-(ligand) complexes, $(C_5Me_5)_3M$, were reported.² Such complexes were assumed to be too sterically crowded to exist since the C_5Me_5 cone angle was estimated to be much greater than 120° .³ The discovery of $(C_5Me_5)_3Sm^4$ not only showed that this class of complexes could exist, but it also revealed new opportunities in organometallic reaction chemistry.^{5–7} Most surprising was the fact that this trivalent complex could accomplish one-electron reduction chemistry.^{5c} This has led to the development of “sterically induced reduction” chemistry in which sterically crowded complexes of redox inactive metals act as reductants.^{6,7}

Although three new synthetic routes in addition to the original synthesis of $(C_5Me_5)_3Sm$ have been discovered,^{5a,8} only two other crystallographically characterized $(C_5Me_5)_3M$ complexes have been reported in the literature, $(C_5Me_5)_3Nd^{8a}$ and $(C_5Me_5)_3U$.^{5a} It is clear that formation and isolation of $(C_5Me_5)_3M$ complexes is not easy and requires conditions where more sterically favorable options are not accessible. Although it is expected that metals larger than Sm(III) should form these complexes (e.g., La(III)–Pr(III)), it is uncertain if complexes of smaller metals would be isolable. We now report that the reaction chemistry of $(C_5Me_5)_3U$ has led to the isolation of significantly more crowded $(C_5Me_5)_3M$ systems in which a fourth ligand is present.

Previous studies of $(C_5Me_5)_3U$ showed that the sterically induced reduction chemistry of this crowded molecule could be coupled with a U(III)/U(IV) reduction to make this a multielectron reductant.⁷ Hence, $(C_5Me_5)_3U$ reacts with 1,3,5,7- C_8H_8 , as a three-electron reductant, eq 1. One electron arises from U(III), eq 2, and two result from two $C_5Me_5^-/C_5Me_5$ half reactions, eq 3,



presumably via sterically induced reduction. To gain insight into

(1) Reported in part at Contemporary Inorganic Chemistry II, College Station, Texas, March, 2000.

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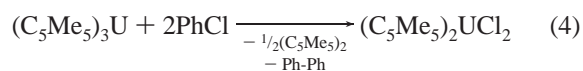
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the sequence of the multielectron reduction of $(C_5Me_5)_3U$, we sought a system in which $(C_5Me_5)_3U$ would reduce a substrate stepwise, the intermediate(s) could be identified, and it could be determined which of the two half reactions, eq 2 or 3, occurred first. Phenyl halides, which had previously been useful in organouranium chemistry,^{9,10} proved suitable for this purpose.

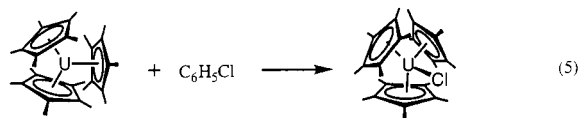
$(C_5Me_5)_3U$ reacts instantly at room temperature with one equiv of PhCl to form a dark red complex, **1**, as the primary product. Upon addition of another equiv of PhCl, **1** is transformed over several days to $(C_5Me_5)_2UCl_2$, **2**. The latter complex can be made in good yield using 2 equiv of PhCl as shown in eq 4 in which $(C_5Me_5)_3U$ is functioning as a two-electron reductant.



As is typical in reactions of organic halides with f element reductants,⁹ other metal-containing complexes are produced in this reaction and, in this case, $(C_5Me_5)_2UCl(Ph)$ was also observed.

If the first equiv of PhCl was reduced by sterically induced reduction according to eq 3, complex **1** would be the known compound, $[(C_5Me_5)_2UCl]_3$.¹⁰ On the other hand, if the first electron transfer was a result of a U(III)/U(IV) redox process, eq 2, the composition of the product would be $(C_5Me_5)_3UCl$. Such a product would be most surprising, since it would be much more crowded than $(C_5Me_5)_3U$, due to the extra ligand, and since U(IV) is 0.135 Å smaller than U(III).¹¹

The ¹H NMR spectrum, the solubility in arene solvents, and the red color of **1** were not consistent with the formation of $[(C_5Me_5)_2UCl]_3$.¹⁰ Since the NMR spectra were not definitive, an X-ray diffraction study¹² was conducted which established that **1** was in fact $(\eta^5-C_5Me_5)_3UCl$ (Figure 1), eq 5.¹³



This is the most crowded $(C_5Me_5)_3M$ complex isolated to date, and like $(C_5Me_5)_3Sm$, it was not expected to be isolable.^{14,15} Once

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(12) **1** crystallizes from toluene in the hexagonal space group $P6_3/m$ with $a = 9.9903(3)$ Å, $b = 9.9903(3)$ Å, $c = 15.3902(6)$ Å, $V = 1330.25(8)$ Å³, $D_{calc} = 1.696$ mg/m³ for $Z = 2$. At convergence, $wR2 = 0.1247$ and $GOF = 1.398$ for 54 parameters refined against 1137 unique reflections.

(13) In a THF-free glovebox, PhCl (0.18 mL, 0.18 mmol) was added via a microsyringe to a dark brown solution of $(C_5Me_5)_3U$ (1.16 g, 0.18 mmol) in 50 mL of toluene. The solution immediately became dark red. The reaction was stirred for 1 h after which the solvent was removed under reduced pressure. The solid was washed with hexamethyldisiloxane to yield $(C_5Me_5)_3UCl$ as a rose colored powder (850 mg, 70%): ¹H NMR (295 K, C_6D_6) C_5Me_5 , 12.1 (s, 45H, $\Delta\nu_{1/2} = 15$ Hz). IR 2964 s, 2910 s, 2856 s, 1490 w, 1440 m, 1378 m, 1262 w, 1123 w, 1065 s, 1023 s, 1004 s, 984 s, 950 s, 803 m, 675 s cm^{-1} . Magnetic susceptibility: $\chi_m = 2.2 \times 10^{-3}$, $\mu_{eff} = 2.3 \mu_B$. Anal. Calcd for $C_{30}H_{45}UCl$: C, 53.05; H, 6.68. Found: C, 52.90; H, 6.97. $(C_5Me_5)_2UCl(Ph)$ ¹⁴ is a byproduct in this reaction which can be separated from the product by recrystallization.

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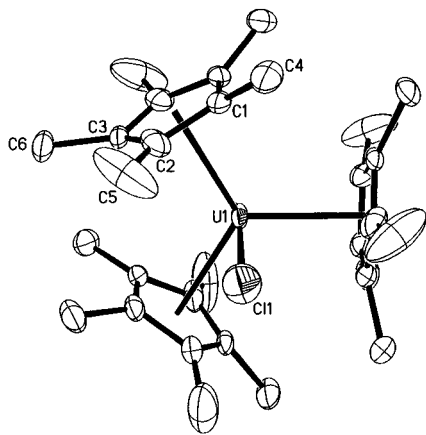
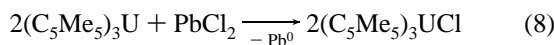
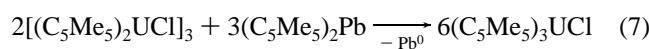
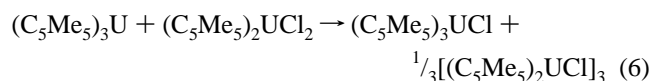


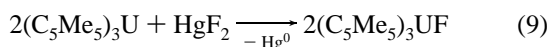
Figure 1. Structure of $(C_5Me_5)_3UCl$ with thermal ellipsoids drawn to 50% probability; (ring centroid)–U–(ring centroid), 120° , (ring centroid)–U–Cl, 90° .

the existence of $(C_5Me_5)_3UCl$ was established, several alternative syntheses were examined and found to be successful as shown in eq 6–8.



1 crystallizes in the same $P6_3/m$ space group as $(C_5Me_5)_3U$,^{5a} and both have similar unit cell constants. A molecular mirror plane bisects the three symmetry-equivalent C_5Me_5 rings, and the chloride ligand is disordered on either side.¹⁶ The U–C(C_5Me_5) distances (2.780(6)–2.899(9) Å range; 2.833(9) Å average) are equivalent within experimental error to those of $(C_5Me_5)_3U$ (2.857–(4) Å)^{5a} and $(C_5Me_5H)_3UCl$ (2.791(12) Å).¹⁷ In fact, the positions and orientations of the rings around U in **1** are indistinguishable, within experimental error, from those of the $(C_5Me_5)_3M$ complexes which have been reported to date: M = Sm,⁴ U,^{5a} Nd.^{8a} Thus, the chloride ligand in **1** does not appear to perturb the U–C(C_5Me_5) parameters, but instead an exceptionally long U–Cl bond of 2.90(1) Å is found relative to the U–Cl bond lengths in $(C_5Me_5)_3UCl$ ¹⁷ (2.637 Å) and in $(C_4Me_4P)_3UCl$ ^{15a} (2.67(1) Å).

Once $(C_5Me_5)_3UCl$ was isolated, it seemed clear that the fluoride analogue should be isolable.¹⁸ $(C_5Me_5)_3UF$, **2**, can be readily made from HgF_2 , eq 9,



and has been completely characterized by X-ray crystallography.¹⁹ As in **1**, the U–X bond in **2** is much longer than those in the

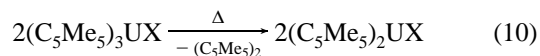
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(16) The disorder is similar to that found in the $P6_3/m$ structure of $(C_5H_5)_3ZrH$. Edelbach, B. L.; Fazlur Rahman, A. K.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 3170–3177.

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literature: 2.43(2) Å versus 2.073 and 2.086 Å in $\{[1,3-(Me_3Si)_2C_5H_3]_2UF_2\}_2$ and $[1,3-(Me_3C)_2C_5H_3]_2UF_2$, respectively.²⁰

Although reactions of $(C_5Me_5)_3U$ with PhBr and PhI have not yet yielded crystallographically characterizable $(C_5Me_5)_3UX$ analogues, the reactions provide further information on sterically induced reduction. $(C_5Me_5)_3U$ reacts with 1 equiv of PhBr to make a red intermediate which analyses for $(C_5Me_5)_3UBr^{21}$ and reacts further with an additional equiv of PhBr to make $(C_5Me_5)_2UBr_2$, in direct analogy with the $(C_5Me_5)_3U/PhCl$ system, eq 4. However, the red intermediate can be thermally transformed within 2 min at 60 °C to $(C_5Me_5)_2$ and a pale green powder with properties consistent with $[(C_5Me_5)_2UBr]_n$.²² This suggests that $(C_5Me_5)_3-UBr$ can undergo sterically induced reduction chemistry without an external substrate at 60 °C, eq 10.



The $(C_5Me_5)_3U/PhI$ reaction product decomposes in the same manner as that of the bromide analogue, but in just 3 h at room temperature. By comparison, $(C_5Me_5)_3UCl$ shows no sign of decomposition at 60 °C over a period of 3 days.

The isolation of $(C_5Me_5)_3UCl$ shows that significantly more steric crowding is possible in tris(pentamethylcyclopentadienyl) complexes than has previously been observed. The $(C_5Me_5)_3U/PhCl$ reaction demonstrates that in this combination of a traditional redox couple (U(III)/U(IV)) with sterically induced reduction, U(III) does reduction first. The $(C_5Me_5)_3U/PhX$ reactions show that the balance between U(III) redox chemistry and sterically induced reduction can be manipulated by slight changes in the components of the complex.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters; listing of observed and calculated structure factor amplitudes (PDF). X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18) In a THF-free glovebox, $(C_5Me_5)_3U$ (98 mg, 0.152 mmol) and HgF_2 (18 mg, 0.075 mmol) were combined in toluene (10 mL) and stirred for 12 h. The mixture was centrifuged to remove Hg. The solvent was removed under reduced pressure to afford a red solid (90 mg, 90%): ¹H NMR (298 K, C_6D_6) C_5Me_5 , 7.25 (s, 45H, $\Delta\nu_{1/2} = 17$ Hz). IR 2961 s, 2910 s, 2856 s, 1440 m, 1378 m, 1262 m, 1100 m, 1065 m, 1023 m, 803 w, 702 w, 675 w. Magnetic susceptibility: $\chi_m = 2.4 \times 10^{-3}$, $\mu_{eff} = 2.4 \mu_B$. Anal. Calcd. for $(C_5Me_5)_3UF$: C, 54.37; H, 6.84. Found: C, 54.34; H, 6.37.

(19) **2** crystallizes from toluene in the hexagonal space group $P6_3/m$ with $a = 9.9804(5)$ Å, $b = 9.9804(5)$ Å, $c = 15.4529(11)$ Å, $V = 1333.02(13)$ Å³, $D_{calc} = 1.651$ mg/m³ for $Z = 2$. At convergence, $wR2 = 0.1025$ and $GOF = 1.176$ for 55 parameters refined against 1146 unique reflections.

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(21) $(C_5Me_5)_3UBr$ was synthesized following the procedure in footnote 13. $(C_5Me_5)_3UBr$ was isolated as light rose powder (73 mg, 65%): ¹H NMR (295 K, C_6D_6) C_5Me_5 , 13.3 (s, 45H, $\Delta\nu_{1/2} = 9$ Hz). IR 2961 s, 2910 s, 2856 s, 1490 w, 1440 m, 1378 m, 1262 m, 1204 w, 1185 w, 1089 s, 1061 s, 1019 s, 803 s, 698 w, 679 w cm^{-1} . Magnetic susceptibility: $\chi_m = 2.2 \times 10^{-3}$, $\mu_{eff} = 2.3 \mu_B$. Anal. Calcd. for $(C_5Me_5)_3UBr$: C, 49.80; H, 6.27; Br, 11.04. Found: C, 49.42; H, 6.51; Br, 10.78.

(22) The green powder reacts cleanly with PhBr to make $(C_5Me_5)_2UBr_2$. Addition of THF to the green powder forms $(C_5Me_5)_2UBr(THF)$: ¹H NMR (C_6D_6 , 25 °C) δ –2.8 (s, 30 H, C_5Me_5 , $\Delta\nu_{1/2} = 120$ Hz), –16.9 (br s, 4H, THF), –51.84 (br s, 4H, THF). These shifts are between those of $(C_5Me_5)_2-UCI(THF)$ (Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170–180) and $(C_5Me_5)_2UI(THF)$ (Avens, L. R.; Burns, C. J.; Butcher, R. J.; Clark, D. L.; Gordon, J. C.; Schake, A. R.; Scott, B. L.; Watkin, J. G.; Zwick, B. D. *Organometallics* **2000**, *19*, 451–457).