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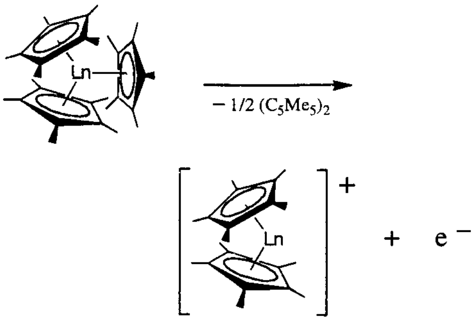
Formal Three-Electron Reduction by an f-Element Complex: Formation of $[\{(C_5Me_5)(C_8H_8)U\}_2(C_8H_8)]$ from Cyclooctatetraene and $[(C_5Me_5)_3U]$**

William J. Evans,* Gregory W. Nyce, and
Joseph W. Ziller

Reduction reactions involving more than two electrons are not common for metal complexes containing just one metal.[1] In f-element chemistry, multielectron reductions from monometallic species are particularly rare[2] since the common low-valent ions Th^{III}, U^{III}, Eu^{II}, Yb^{II}, Sm^{II}, and Tm^{II} typically react as one-electron An^{IV}/An^{III} or Ln^{III}/Ln^{II} redox couples.[3–5] Recently however, we have shown that there is a new way of accomplishing reductive chemistry with f-element complexes by steric crowding[6, 7] and we report here how this method can be coupled with a traditional one-electron redox couple to accomplish multielectron reduction with a monometallic uranium complex.

It has recently been discovered that the sterically crowded $[(C_5Me_5)_3Ln]$ complexes (Ln = Sm,[6] Nd[7]) can act as one-electron reductants as shown in Equation (1). The reductive reactivity of the $[(C_5Me_5)_3Ln]$ complexes can be rationalized by the fact that the $C_5Me_5^-$ ions are not well-stabilized electrostatically in these compounds due to the long Ln–C(C_5Me_5) distances caused by steric congestion. If the redox reaction in Equation (1) is coupled to a one-electron metal-based reduction, for example, the U^{IV}/U^{III} couple[8] of uranium, then a complex such as $[(C_5Me_5)_3U]$[9] could be a two-electron reducing agent. This concept was tested by reacting $[(C_5Me_5)_3U]$ with 1,3,5,7-cyclooctatetraene (C_8H_8). It had been shown that U^{III} complexes would act as one-electron reductants with cyclooctatetraene.[10] Our efforts to couple that reactivity with sterically induced reduction are reported here.



(1)

Reaction of $[(C_5Me_5)_3U]$ with C_8H_8 in a 1:1 stoichiometry formed $(C_5Me_5)_2$ and a new product, **1**, but residual $[(C_5Me_5)_3U]$ remained at the end of the reaction. Subsequently, it was determined that a 2:3 $[(C_5Me_5)_3U]$:C_8H_8

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[*] Prof. W. J. Evans, G. W. Nyce, Dr. J. W. Ziller
Department of Chemistry, University of California
Irvine, CA 92697 (USA)
Fax: (+1) 949-824-2210
E-mail: wevans@uci.edu

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stoichiometry was optimal for the production of **1** in good yield. The ^1H NMR spectrum of **1** at 25 °C contains a resonance attributable to $C_5Me_5^-$ at $\delta = 5.5$ and two resonances attributable to $C_8H_8^{2-}$ at $\delta = -41.7$ and -42.2 in a 2:1 ratio, respectively. The $C_8H_8^{2-}$ chemical shifts and line widths of **1** are similar to those of other $U^{IV}/C_8H_8^{2-}$ compounds.[11] Since neither the NMR, the IR, nor the analytical data were structurally definitive, the complex was examined by X-ray crystallography[12] and found to be $[\{(C_5Me_5)(C_8H_8)U\}_2(C_8H_8)]$ (**1**) (Figures 1 and 2). The net reaction is shown in Equation (2).

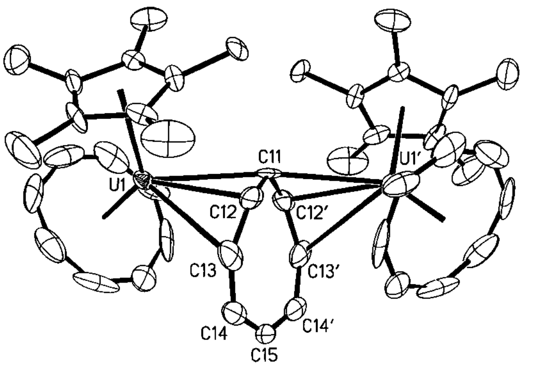


Figure 1. Molecular structure of $[\{(C_5Me_5)(C_8H_8)U\}_2(C_8H_8)]$ (**1**) with thermal ellipsoids drawn at the 50 % probability level.

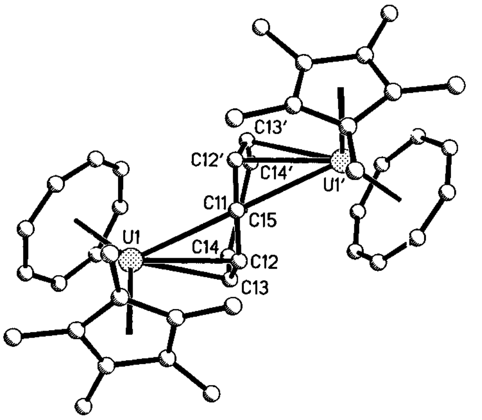
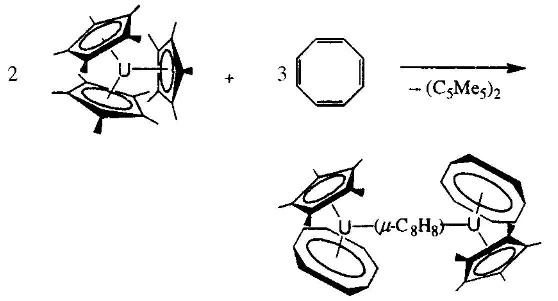


Figure 2. Side view of **1** showing the nonplanarity of the bridging ring. C12 is 0.19 Å out of the average plane of the bridging ring carbon atoms.



1

(2)

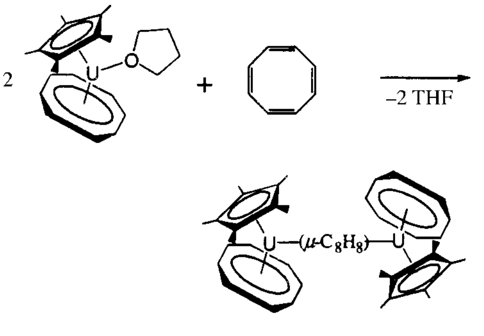
Complex **1** contains two mixed ligand bent metallocene units, $[(C_5Me_5)(C_8H_8)U]^+$, coordinated to a bridging $C_8H_8^{2-}$ moiety. The bridging $C_8H_8^{2-}$ moiety is nonplanar as shown in Figure 2 and is bound in an unusual $\eta^3{:}\eta^3$ fashion in which one atom is common to both pseudo-allyl moieties. The three unique U–C distances in this bridge have disparate values, U–C12 2.687(17), U–C11 2.878(2), and U–C13 3.00(2) Å, but the difference between the longest and shortest distances is not outside the range observed in allyl f-element complexes,[13] and the shortest of these distances matches the U–C(terminal C_8H_8) average, 2.68(2) Å. The η^3-C_8H_8 bonding in **1** has similarities to that found in one part of **2**[14] although

$[(\eta^8\text{-}C_8H_8)Nd(\mu\text{-}\eta^8,\eta^3\text{-}C_8H_8)Nd(thf)_2(\eta^8\text{-}C_8H_8)]$ (**2**)

in **2** the bridging $C_8H_8^{2-}$ ring is planar. The η^3–C_8H_8 distances in **2** (2.70(2), 2.90(2), and 3.06(2) Å) are also quite similar to those in **1**. Nonplanar $C_8H_8^{2-}$ rings have previously been observed in $[(C_8H_8)_3Ti_2]$[15] and $[(C_8H_8)_3Cr_2]$.[16] Apparently, the $\eta^3{:}\eta^3$ mode of attachment in **1** is an acceptable way to fit a bridging $C_8H_8^{2-}$ ring between two $[(C_5Me_5)(C_8H_8)U]^+$ units. Space-filling models suggest that **1** is sterically crowded.

The U–C(terminal C_8H_8) 2.68(2) Å and U–C(C_5Me_5) 2.80(2) Å average bond lengths are numerically reasonable for a sterically crowded U^{IV} complex,[17] but comparison with literature values is limited due to the large error limits of the data. For example, the average distance of U–C(terminal C_8H_8) 2.68(2) Å can be compared with the 2.647(4) Å average distance in [K(diglyme)][$U(MeC_8H_7)_2$] with trivalent uranium (diglyme = diethylene glycol dimethyl ether).[18]

Complex **1** is remarkable in several respects. It contains the components of the very stable uranocene molecule $[U(C_8H_8)_2]$[19] yet it does not adopt the uranocene structure. Moreover, complex **1** is the preferred product regardless of the $[(C_5Me_5)_3U]{:}C_8H_8$ stoichiometry between 1:1 and 1:100. Complex **1** is stable for at least two weeks at room temperature in C_6D_6. It decomposes slowly at 80 °C, but it does not decompose to $[U(C_8H_8)_2]$.[19] Complex **1** is also stable in THF, which raised the possibility that it could be generated from the known U^{III} complex $[(C_5Me_5)(C_8H_8)U(thf)]$[20] and C_8H_8. This reaction does occur to make **1** in quantitative yield as shown in Equation (3).



1

(3)

Examination of the optimal stoichiometry in Equation (2) shows that $[(C_5Me_5)_3U]$ is not a two-electron reductant as originally hypothesized, but rather a three-electron reductant! The net reaction is accomplished through one U^{IV}/U^{III} and two $(C_5Me_5)/(C_5Me_5)^-$ couples as shown in Equation (4). Hence this study shows that the one-electron reduction chemistry of sterically crowded $[(C_5Me_5)_3Ln]$ lanthanide

$$(C_5Me_5)_3U^{III} \longrightarrow [(C_5Me_5)U^{IV}]^{3+} + (C_5Me_5)_2 + 3e^- \qquad (4)$$

complexes can be generalized to U^{III} and can be coupled to the U^{III} redox chemistry to do multielectron reductions. This also shows that the $C_8H_8^{2-}/U^{IV}$ components of uranocene can exist in forms other than the very stable parallel ring structure of $[U(C_8H_8)_2]$. This reaction suggests a rich reductive chemistry can be accessed by coupling steric crowding and lower f-element oxidation states.

Experimental Section

All manipulations were performed under an N_2 or Ar atmosphere by glove box or Schlenk techniques.

1: In a THF-free glovebox, 1,3,5,7-C_8H_8 (24 mg, 0.23 mmol) was added to a brown solution of $[(C_5Me_5)_3U]$ (100 mg, 0.155 mmol) in toluene (10 mL). After the brown solution was stirred at room temperature for 4 d, the solvent was removed by rotary evaporation. The gummy brown solid was washed with hexanes and dried under reduced pressure to afford **1** as a dark brown powder (70 mg, 85%). IR (KBr): $\tilde{\nu}$ 3022 m, 2903 s, 2851 m, 1435 w, 1373 w, 1020 w, 902 w, 797 w, 729 sh, 673 sh, 568 w cm^{-1}; Elemental analysis ($U_2C_{44}H_{54}$): calcd: C 49.91, H 5.14; found: C 49.64, H 4.92; ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): $\delta = 5.5$ (s, C_5Me_5; $\Delta\nu_{1/2} = 10$ Hz, 30 H), -41.7 (s, C_8H_8; $\Delta\nu_{1/2} = 14$ Hz,16 H), -42.2 (s, C_8H_8; $\Delta\nu_{1/2} = 20$ Hz, 8 H); ^{1}H NMR (400 MHz, [D$_8$]toluene, -100 °C): $\delta = 14.5$ (s, C_5Me_5), -80.8 (s, C_8H_8, 16 H), -87.5 (s, C_8H_8, 8 H); ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): $\delta = 395$, 280, 279, -26.

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[12] X-ray quality crystals were grown by slowly cooling a hot toluene solution of **1**. A brown crystal of approximate dimensions 0.03 × 0.20 × 0.30 mm in Paratone oil was mounted on a glass fiber and transferred to a Siemens CCD diffractometer. Crystal data for **1** at 158 K: $C_{44}H_{54}U_2$, monoclinic, space group $C2$, $a = 15.2722(9)$, $b = 9.9717(6)$, $c = 13.8865(8)$ Å, $\beta = 103.7740(10)°$, $V = 2054.0(2)$ Å^3, $Z = 2$. At convergence, $wR2 = 0.1978$ and GOF $= 1.070$ for 210 parameters refined against 4136 unique reflections [as a comparison for refinement against F, $R1 = 0.0725$ for those 3950 reflections with $I > 2.0\sigma(I)$]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-129637. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Application of Reductive Samariation to the Synthesis of Small Unnatural Peptides[**]

Marina Ricci, Leire Madariaga, and Troels Skrydstrup*

Dedicated to Professor Anders Kjær
on the occasion of his 80th birthday

The selective introduction of side chains to a specific glycine residue in a peptide strand represents a challenging task for the preparation of unnatural peptides. Instead of a stepwise approach where commercially available or synthetic amino acids are incorporated by a traditional peptide synthesis, application of a direct peptide modification step is justified by the numerous analogues which may be quickly synthesized from a single and intact peptide. As reactive intermediates, glycine enolates[1–4] and radicals[5–7] as well as

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[*] Prof. Dr. T. Skrydstrup, Dr. M. Ricci, L. Madariaga
Department of Chemistry
University of Aarhus
Langelandsgade 140, 8000 Aarhus C (Denmark)
Fax: (+45) 86196199
E-mail: ts@kemi.aau.dk

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