$[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ as a four electron reductant†

William J. Evans,* Stosh A. Kozimor and Joseph W. Ziller

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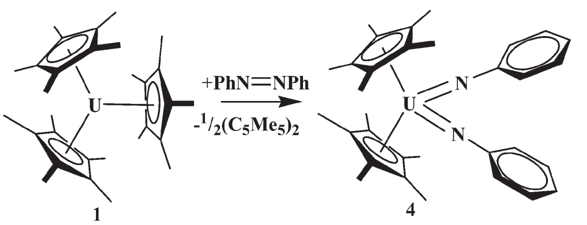
Examination of the reactivity of $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ as a "blank" for comparison with the four- and eight-electron reductive chemistry of the sterically crowded $(C_5Me_5)_3U$ and $[(C_5Me_5)_2U]_2(C_6H_6)$ complexes revealed that the tetraphenylborate complex surprisingly functions as a four-electron reductant by combining $[BPh_4]^{1-}$ and U(III) reduction; all three complexes cleave the N=N bond in PhN=NPh to form the bis(organoimido) U(VI) complex, $(C_5Me_5)_2U(NPh)_2$, and they also reduce PhC≡CPh to form $(C_5Me_5)_2U(C_4Ph_4)$.

Recent studies of the sterically crowded organouranium complexes $(C_5Me_5)_3U$, **1**,[1] and $[(C_5Me_5)_2U]_2(C_6H_6)$, **2**,[2] have shown that they can function as three and six electron reductants, respectively, by combining a traditional U(III)/U(IV) reduction with formal ligand-based reductions involving the $(C_5Me_5)^{1-}$ and $(C_6H_6)^{2-}$ anions.[2,3] We report here that both **1** and **2** can combine ligand-based electron transfer with a U(III)/U(*VI*) process to achieve the four electron reductive cleavage of the N=N bond in azobenzene to form $(C_5Me_5)_2U(NPh)_2$,[4] a U(VI) bis(imido) complex. Surprisingly, when the azobenzene reaction was examined with the sterically normal complex $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$,[5] **3**, to make a comparison with a U(III) compound that did not have a redox active ligand, four electron reduction was also found. This represents the first example, to our knowledge, in which the reductive reactivity of $(BPh_4)^{1-}$ has been combined with metal-based reductants to effect multi-electron reduction. Since tetraphenylborate is widely used as a counteranion, this raises interesting possibilities for alternative reaction pathways for complexes of this anion containing redox active metals.

The unusual reductive reactivity of **1–3** was initially defined by analyzing the reduction of PhN=NPh, a topic that has been approached in many ways.[6] Reaction of azobenzene with f element complexes in a 1 : 1 or 1 : 2 stoichiometry typically results in the formation of the one and two electron reduction products $(PhNNPh)^{1-}$ and $(PhNNPh)^{2-}$, respectively.[7] Complete cleavage to $(NPh)^{2-}$ imido ligands has been achieved in the past, but generally requires either a metal ion capable of transferring four electrons, *e.g.* W(II),[8] or addition of multiple equivalents of the reducing species.[4c,6,7b,d,e] For example, two equivalents of $(C_5Me_5)_2UCl_2Na$ reduces azobenzene to make a mixture of $(C_5Me_5)_2UCl_2$ and $(C_5Me_5)_2U(NPh)_2$.[4c]

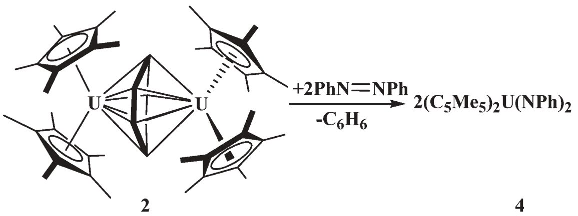
In contrast, a *single* equiv. of $(C_5Me_5)_3U$ reacts with one equiv. of PhN=NPh to form $(C_5Me_5)_2$ and $(C_5Me_5)_2U(NPh)_2$, **4**,[4a] in 80% yield, eqn (1).‡ Complex **4** was identified by comparison of its ^1H and ^{13}C NMR spectra with those in the literature[4a] as well as GC-MS analysis of its hydrolysis products which contain $PhNH_2$ and no PhNHNHPh, the product expected if $(PhNNPh)^{2-}$ had formed.



1 **4** (1)

In eqn (1), one equiv. of $(C_5Me_5)_3U$ functions as a four electron reductant by formally combining a three electron U(III)/U(VI) redox process with a $(C_5Me_5)^{1-}/(C_5Me_5)$ redox couple termed sterically induced reduction (SIR).[9]

Encouraged by eqn (1), the reaction of PhN=NPh with another sterically crowded complex, $[(C_5Me_5)_2U]_2(C_6H_6)$, **2**,[2] was examined. A *single* equiv. of **2** reacts with *two* equivalents of PhN=NPh to form **4** and free C_6H_6 in 95% yield, eqn (2).‡



2 **4** (2)

Based on previous studies, we describe this reaction as formally involving two U(III)/U(VI) redox processes and a two electron $(C_6H_6)^{2-}/(C_6H_6)$ process such that **2** acts as an eight electron reductant as depicted in the formal half reaction in eqn (3).

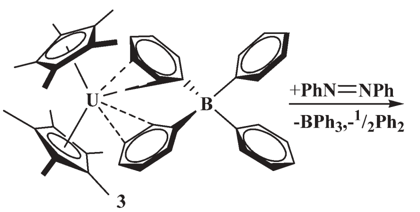
$$[(C_5Me_5)_2U]_2(C_6H_6) \rightarrow 8e^{1-} + C_6H_6 + 2[(C_5Me_5)_2U]^{4+} \quad (3)$$

Previously it was found that the reaction of $\{[(^tBu)(Ar)N]_2U\}_2(C_6H_5Me)$, a less crowded analogue of **2**, with one equiv. of PhN=NPh did not form an analogue of **4**, but rather an $(NPh)^{2-}$ bridged U(IV) dimer, $\{[(^tBu)(Ar)N]_2U\}_2(\mu\text{-}NPh)_2$.[7d] Eqns (1) and (2) are unusual since reductions by trivalent uranium complexes typically involve the U(III)/U(IV) redox couple.[4a,10] To our knowledge, no previous example of an f element complex that is an eight electron reductant has been reported.

In the course of examining these azobenzene reductions, the reactivity of trivalent $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$, **3**,[5] was studied to see how a U(III) metallocene would react with azobenzene in the absence of a redox-active ligand. This reaction was in essence a "blank" reaction. Surprisingly, **3** also reductively cleaves azobenzene to form **4** in 85% yield, eqn (4).‡

Department of Chemistry, University of California, Irvine, CA 92697-2025, USA. E-mail: wevans@uci.edu; Fax: +1-949-824-2210

† Electronic Supplementary Information (ESI) available: X-ray diffraction data for **5**. See http://dx.doi.org/10.1039/b508612d



(4)

3 **4**

The ^{1}H, ^{13}C, and ^{11}B NMR spectra were consistent with the formation of **4**[4a] with Ph_2 and BPh_3 as byproducts. Since we were skeptical that this reaction actually produced the monomeric hexavalent $(C_5Me_5)_2U(NPh)_2$ complex, single crystals of the product were grown and X-ray diffraction studies were carried out to confirm the product's identity as **4**.[4a] The N···N distance, which was greater than 3 Å, was consistent with two terminal $(NPh)^{2-}$ ligands rather than a $(PhNNPh)^{2-}$ complex of U(IV). GC-MS of the hydrolysis products of **4** also supported this assignment.

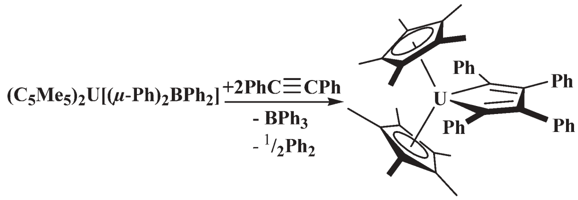
In eqn (4), the $(BPh_4)^{1-}$ anion formally acts as a one electron reductant according to eqn (5).

$$(BPh_4)^{1-} \rightarrow e^{1-} + BPh_3 + \tfrac{1}{2}Ph_2 \tag{5}$$

Although thermochemical, photochemical, and electrochemical oxidations of $(BPh_4)^{1-}$ have been extensively studied,[11] combining this type of reactivity with a metal-based reductant, such as U(III), to effect multi-electron reductions has never been reported to our knowledge.

This result raises questions about the reasons why $(BPh_4)^{1-}$ is typically avoided as the counteranion in olefin polymerization reactions involving cationic metal alkyl complexes. It is generally presumed that $(BPh_4)^{1-}$ can block the incoming olefin substrates by weakly coordinating the metal.[11f,12] It can also interfere with catalysis by being metalated.[13] However, if eqn (5) occurs in these polymerization reactions, this would be another reason that catalyst performance is diminished with $(BPh_4)^{1-}$.

To demonstrate the generality of the metal/$(BPh_4)^{1-}$ reduction combination, the reductive coupling of PhC≡CPh to $(C_4Ph_4)^{2-}$ by **3** was examined. **3** functions as a two electron reductant with PhC≡CPh to form BPh_3, Ph_2, and $(C_5Me_5)_2U(C_4Ph_4)$,[14] **5**, in 50% yield, eqn (6).§



(6)

3 **5**

For comparison, the reactions of **1** and **2** with PhC≡CPh were also examined and they also form **5** quantitatively by NMR spectroscopy, eqns (7) and (8).§ With both PhN=NPh and PhC≡CPh, **2** reacts fastest and **3** reacts slowest.

$$\underset{\mathbf{1}}{(C_5Me_5)_3U} \xrightarrow[-\frac{1}{2}(C_5Me_5)_2]{+2PhC\equiv CPh} \underset{\mathbf{5}}{(C_5Me_5)_2U(C_4Ph_4)} \tag{7}$$

$$[(C_5Me_5)_2\underset{\mathbf{2}}{U}]_2(C_6H_6) \xrightarrow[-C_6H_6]{+4PhC\equiv CPh} 2\underset{\mathbf{5}}{(C_5Me_5)_2U(C_4Ph_4)} \tag{8}$$

In order to confirm the unusual nature of eqn (5) and since only analytical and spectroscopic data were available on **5**,[14] the reaction product was analyzed by X-ray crystallography, Fig. 1.¶ The 2.731(3) to 2.774(3) Å U–C(C_5Me_5) distances in **5** are similar to those in **3**[5] and are ~0.1 Å shorter than those in **1**[1] and **2**.[2] The 2.395(2) Å U–C(12) distance is similar to other U–C(alkyl) distances.[15] The 1.365(3) Å C(12)–C(11) distance is shorter than the 1.509(4) Å C(11)–C(11′) distance and consistent with a localized metallacyclopentadiene structure as originally proposed.[14]

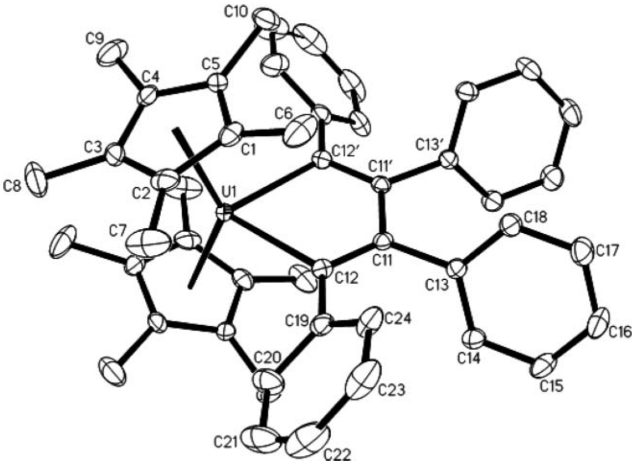


Fig. 1 A thermal ellipsoid plot of $(C_5Me_5)_2U(C_4Ph_4)$, **5**, drawn at the 50% probability level.

In summary, as shown in the half reactions in Scheme 1, ligand-based reductions with $(C_5Me_5)^{1-}$, $(C_6H_6)^{2-}$, and $(BPh_4)^{1-}$ can be combined with *U(III)/U(VI)* redox processes to effect four electron reductions by monometallic **1** and **3** and eight electron reduction by bimetallic **2**. Complexes **1** and **3** can also act as two electron reductants and complex **2** as a bimetallic four electron reductant with substrates such as PhC≡CPh. Future studies will examine the generality of $(BPh_4)^{1-}$ as a reductant in other f element and transition metal complexes, but eqns (4) and (6) indicate that eqn (5) should be considered as an alternative pathway in any system that contains tetraphenylborate counteranions.

$$\tfrac{1}{2}(C_5Me_5)_2 + [(C_5Me_5)_2U]^{2+} + 2e^{1-} \longleftarrow \underset{\mathbf{1}}{(C_5Me_5)_3U} \longrightarrow 4e^{1-} + [(C_5Me_5)_2U]^{4+} + \tfrac{1}{2}(C_5Me_5)_2$$

$$\tfrac{1}{2}Ph_2 + BPh_3 + [(C_5Me_5)_2U]^{2+} + 2e^{1-} \longleftarrow \underset{\mathbf{3}}{(C_5Me_5)_2U[(\mu\text{-}Ph)_2BPh_2]} \longrightarrow 4e^{1-} + [(C_5Me_5)_2U]^{4+} + \tfrac{1}{2}Ph_2 + BPh_3$$

$$C_6H_6 + 2[(C_5Me_5)_2U]^{2+} + 4e^{1-} \longleftarrow \underset{\mathbf{2}}{[(C_5Me_5)_2U]_2(C_6H_6)} \longrightarrow 8e^{1-} + 2[(C_5Me_5)_2U]^{4+} + C_6H_6$$

Scheme 1

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Notes and references

‡ *Syntheses:* **4 from 1.** A solution of $(C_5Me_5)_3U$[5] (58 mg, 0.09 mmol) in C_6H_6 was added to a flask that had been covered with electrical tape to exclude light and charged with PhN=NPh (16 mg, 0.088 mmol) in C_6H_6. After the solution had been stirred for 12 h, the solvent was removed by rotary evaporation and the resulting tacky brown solid was washed with $(Me_3Si)_2O$ to remove $(C_5Me_5)_2$. The extract was separated by centrifugation and $(C_5Me_5)_2$ was identified by ^1H NMR spectroscopy and GC-MS. The $(Me_3Si)_2O$ insoluble brown solid was dried under vacuum affording **4**[4a] (50 mg, 80%) as a powder. ^1H and ^{13}C NMR (C_6D_6) spectra were consistent with the literature values.[4a] The hydrolysis products of **4** contain a compound that by GC-MS has a mass spectrum, fragmentation pattern, and retention time consistent with a H_2NPh standard. No PhNHNHPh was observed. Deuterolysis forms products consistent with D_2NPh. **4 from 2.** In a procedure similar to that described above, $[(C_5Me_5)_2U]_2(C_6H_6)$[2] (17 mg, 0.016 mmol) reacted with PhN=NPh (6 mg, 0.032 mmol) in C_6D_6 (1 mL) to form **4**[4a] (21 mg, 95%) as a brown powder that was identified by NMR spectroscopy.[4a] **4 from 3.** In a similar procedure, $[(C_5Me_5)_2U][BPh_4]$[5] (47 mg, 0.056 mmol) reacted with PhN=NPh (10 mg, 0.054 mmol) in benzene (5 mL) to form $(C_5Me_5)_2U(NPh)_2$[4a] (30 mg, 85%). The crude reaction mixture was analyzed by ^1H, ^{11}B, and ^{13}C NMR spectroscopy as well as GC-MS to confirm the formation of **4**,[4a] BPh_3, and Ph_2. Crystals suitable for X-ray analysis were grown as previously described.[4a]

§ *Syntheses:* **5 from 1.** A brown solution of $(C_5Me_5)_3U$[5] (25 mg, 0.039 mmol) in C_6D_6 was combined with a solution of $PhC{\equiv}CPh$ (14 mg, 0.079 mmol) in C_6D_6 in an NMR tube. Within 3 h, the color of the solution changed to red and ^1H NMR analysis indicated approximately 85% consumption of **1** and formation of **5**.[14] Within 24 h, red crystalline needles of **5** formed in the NMR tube and the red solution was decanted away from the crystals (13 mg, crystalline yield 39%). Red crystals of **5** suitable for X-ray analysis were grown from a saturated solution in diethyl ether at -35 °C. **5 from 2.** As described above, $[(C_5Me_5)_2U]_2(C_6H_6)$[2] (15 mg, 0.014 mmol) was reacted with $PhC{\equiv}CPh$ (9 mg, 0.051 mmol) in C_6D_{12}. Within 30 min, NMR spectroscopy indicated quantitative conversion to **5**[14] and C_6H_6. **5 from 3.** In the dark, a solution of $[(C_5Me_5)_2U][BPh_4]$[5] (17 mg, 0.021 mmol) in C_6D_6 was combined with $PhC{\equiv}CPh$ (7 mg, 0.039 mmol) in C_6D_6 in an NMR tube that had been wrapped in aluminium foil. After 24 h, the ^1H, ^{13}C, ^{11}B NMR spectra indicated 50% consumption of **3** and formation of **5**,[14] BPh_3, and Ph_2.

¶ *Crystal data for* **5**: $C_{48}H_{50}U$, $M = 864.91$, Monoclinic, $a = 13.4841(14)$ Å, $b = 16.8939(17)$ Å, $c = 17.3869(18)$ Å, $\alpha = 90°$, $\beta = 103.794(2)°$, $\gamma = 90°$, $V = 3846.5(7)$ Å^3, $T = 163(2)$ K, space group $C2/c$, $Z = 4$, μ(Mo–Kα) = 4.251 mm^{-1}, $\rho_{calcd} = 1.494$ Mg m^{-3}, 19 006 reflections were measured on a Bruker CCD platform diffractometer, 4188 unique ($R_{int} = 0.0279$) which were used in all calculations. The final $R1$ was 0.0211 [$I > 2\sigma(I)$], and $wR2 = 0.0566$, GOF = 1.102. The SMART program package was used to determine the unit-cell parameters and for data collection (25 s per frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. The molecule was located about a two-fold rotation axis. Hydrogen atoms were included using a riding model. CCDC reference number 262985. See http://dx.doi.org/10.1039/b508612d for crystallographic data in CIF or other electronic format.

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