The Catalytic Reduction of Azides and Hydrazines Using High-Valent Organouranium Complexes

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Uranium compounds act as catalysts for many reactions including the oxidation of organics,[1] alkyne hydroamination,[2] olefin hydrogenation,[3] and olefin polymerization.[4] In these processes, U(IV) metallocene compounds often show reactivity similar to lanthanide and group IV transition metal metallocenes in such steps as olefin insertion and ligand protonation. In contrast to the lanthanides and group IV metals, however, uranium can also access the +6 oxidation state, giving rise to the possibility of 2-electron (+4/+6) redox processes. We have recently reported the synthesis of U(VI) complexes of the type $(C_5Me_5)_2U(=NR)_2$ (R = Ph, **1**, R = Ad = 1-adamantyl, **2**);[5,6] it has been postulated that 5f orbitals play a significant role in stabilizing metal−ligand bonding in these species. Any catalytic process requiring the intermediacy of these higher valent complexes would also, therefore, rely upon the involvement of f orbitals in mediating chemical transformations.

We have previously reported that $(C_5Me_5)_2UCl_2Na$,[7] produced by treatment of $(C_5Me_5)_2UCl_2$ with sodium amalgam, reacts with organic oxidants such as azobenzene and adamantyl azide to produce U(VI) bis(imido) complexes **1** and **2** (eq 1).[5b]


$$R = Ph\ (\mathbf{1}),\ Ad\ (\mathbf{2})$$
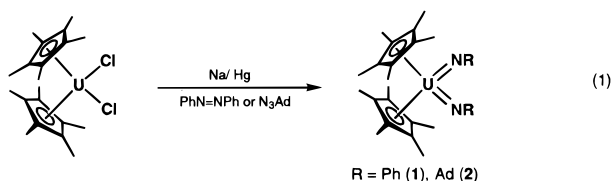
These bis(imido) species are easily reduced to their corresponding U(IV) bis(amide) analogues under an atmosphere of hydrogen.[5] By combination of these discrete steps, it is possible to generate the first examples of well-defined catalytic two-electron redox processes mediated by an f element.

When $(C_5Me_5)_2U(=NPh)_2$ and $(C_5Me_5)_2U(=NAd)_2$ are exposed to an atmosphere of hydrogen, they are reduced to the corresponding bis(amide) complexes $(C_5Me_5)_2U(NHR)_2$ (R = Ph, **3**,[8]

Ad, **4**[9]) (eq 2). The reactions proceed cleanly to completion as evidenced by ^{1}H NMR and comparison with independently prepared samples of **3** and **4**.[10] The rate of hydrogenation of **2** is faster than that of **1** ($t_{1/2}$ for **2** = 4 h, $t_{1/2}$ for **1** = 21 h).

$$R = Ph\ (\mathbf{3}),\ Ad\ (\mathbf{4})$$
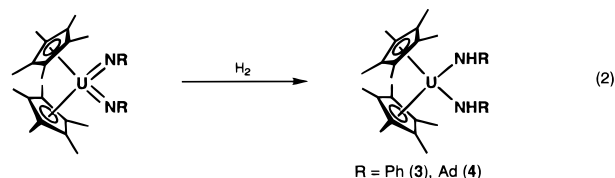
When AdN_3 is added to a solution of the bis(amide) **4** and benzene, the bis(imido) **2** and $AdNH_2$ are generated cleanly (eq 3).[11] With evidence supporting the oxidation of **4** to **2** by AdN_3,
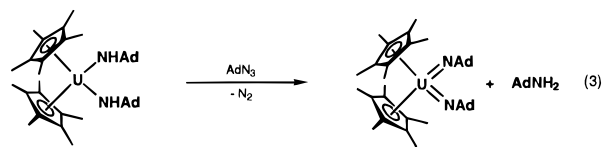
and the subsequent reduction of **2** to **4** under an atmosphere of H_2, it may be anticipated that treatment of either **2** or **4** with H_2 and AdN_3 would result in the catalytic hydrogenation of adamantyl azide to adamantylamine. When **4** is heated to 55 °C in a Schlenk tube with THF and AdN_3 under an atmosphere of hydrogen, catalytic hydrogenation of AdN_3 to $AdNH_2$ is observed (eq 4).[12]
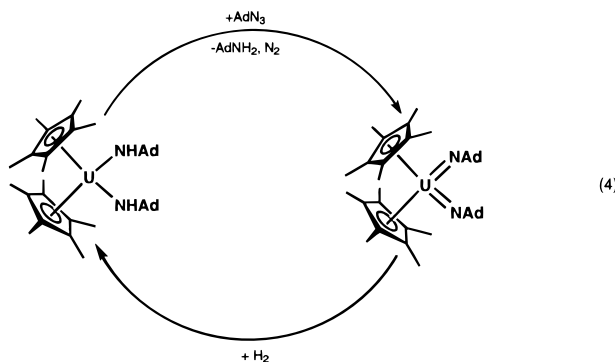
The use of *N,N'*-diphenylhydrazine as a potential oxidant was also examined. Prior results have shown that *N,N'*-diphenylhydrazine effectively oxidizes U(IV) to U(VI), converting $(C_5Me_5)_2$-UMe_2 to **1**.[8] This reaction occurs formally by the protonation of the methyl groups, liberating methane. Unlike transition metal

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(1) Hutchings, G. J.; Heneghan, C. S.; Hudson, I. D.; Taylor, S. H. *Nature* (*London*) **1996,** *384,* 341−343.

(2) Haskel, A.; Straub, T.; Eisen, M. S. *Organometallics* **1996,** *15,* 3773.

(3) Fagan, P. J.; Bowman, R. G.; Nakamura, R.; Burwell, R. L.; Marks, T. J. *J. Chem. Soc., Chem Commun.* **1981,** *6,* 257.

(4) Campbell, R. E. J. *Pentaalkylcyclopentadienyl Actinide Olefin Polymerization Catalysts*; Dow Chemical Co.: Midland, MI, 1985.

(5) (a) Arney, D. S. J.; Burns, C. J.; Smith, D. C. *J. Am. Chem. Soc.* **1992,** *114,* 10068. (b) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem., Int. Ed. Engl.* **1997,** *37,* 9959.

(6) There are several reports of transition metal and actinide imido complexes. (a) Wigley, D. E.; *Prog. Inorg. Chem.* **1994,** *42,* 239. (b) Lockwood, M. A.; Fanwick, P. E.; Eisenstein, O.; Rothwell, I. P. *J. Am. Chem. Soc.* **1996,** *118,* 2762. (c) Aubart, M. A.; Bergman, R. G. *Organometallics* **1999,** 18, 811. (d) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985,** *107,* 514.

(7) $(C_5Me_5)_2U(Cl)(NaCl)$ was prepared according to an established literature procedure: Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982,** *1,* 170.

(8) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995,** *117,* 9448.

(9) The hydrogenation of **2** was performed by charging a degassed solution of **2** (0.020 g, 0.025 mmol) in 0.5 mL of benzene-d_6 with H_2. The reaction was complete after 24 h.

(10) Compounds **3** and **4** can both be synthesized from primary amines and $(\eta^5\text{-}C_5Me_5)_2UMe_2$. Compound **3** has already been reported.[8] Compound **4** was synthesized from $(\eta^5\text{-}C_5Me_5)_2UMe_2$ and $AdNH_2$. A vial in a helium-filled drybox was charged with $(\eta^5\text{-}C_5Me_5)_2UMe_2$ (0.258 g, 0.48 mmol), $AdNH_2$ (0.145 g, 0.96 mmol), and pentane (5 mL). The solution was stirred for 24 h, during which time vigorous bubbling occurred and a tan precipitate developed. The pentane was removed in vacuo, to yield **4** (0.366 g, 0.45 mmol, 94%) as a tan powder. **4**: ^{1}H NMR (250 MHz, C_6D_6) δ 2.53 (s, 30 H), 1.20 (s, 6 H), −0.02 (d, *J* = 11.6 Hz, 6 H), −0.58 (d, *J* = 11.8 Hz, 6 H), −5.29 (s, 12 H), −80.32 (s, 2 H). ^{13}C NMR (62.5 MHz, C_6D_6) δ 193.02, 79.13, 33.50, 32.81, 2.39, −38.44. IR (KBr, cm⁻¹) 3651, 2905, 2847, 1451, 1438, 1356, 1346, 1311, 1302, 1261, 1119, 1094, 1020, 986, 943, 931, 902, 829, 803, 780, 725, 645, 627. Anal. Calcd for $C_{40}H_{62}N_2U$: C, 59.39; H, 7.73; N, 3.46. Found: C, 59.08; H, 7.48; N, 3.40.

(11) An NMR tube in a helium-filled drybox was charged with **4** (0.016 g, 0.020 mmol), AdN_3 (0.004 g, 0.022 mmol), mesitylene (0.003 g, 0.020 mmol) as an internal standard, and C_6D_6 (0.7 mL). The reaction was monitored by NMR and found to be complete and quantitative after 3 h.

group VI analogues which form stable tetravalent η^2-hydrazide complexes,[13] the corresponding uranium (IV) hydrazido complex is not isolated; the metal center is further oxidized to produce the U(VI) bis(imido) complex **1**.

When $(C_5Me_5)_2U(=NPh)_2$ is treated with an excess of N,N'-diphenylhydrazine in the absence of hydrogen, the substrate is entirely consumed, and aniline and azobenzene are observed to form in a 2:1 ratio (eq 5).[14] This disproportionation was
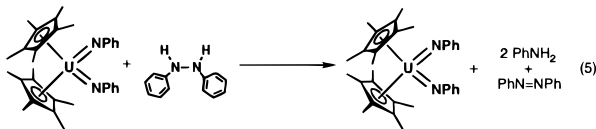
unexpected and indicated that the N,N'-diphenylhydrazine acted upon the uranium complexes as both oxidant and reductant. The formation of aniline during this reaction suggests that the U(IV) bis(amide) **3** should be present to reduce the hydrazine. The only observed uranium species in solution throughout the reaction, however, was $(C_5Me_5)_2U(=NPh)_2$; no buildup of the expected reduction product $(C_5Me_5)_2U(NHPh)_2$ **3** was detected by ^{1}H NMR. If this reaction proceeds through a U(VI/IV) redox couple, the absence of any detectable amount of U(IV) in solution during the course of the reaction qualitatively indicates that the oxidation from U(IV) to U(VI) is faster than the subsequent reduction.[15]

Thermodynamic considerations suggest this reaction is favored both enthalpically and entropically. The calculated ΔH_f of converting two molecules of N,N'-diphenylhydrazine to two molecules of aniline and one molecule of azobenzene is -14.6 kcal/mol.[16] Entropy considerations also qualitatively favor product formation; two molecules of starting material are converted to three molecules of product.

As an initial step to probe the mechanism of this transformation, the catalytic activity of $(C_5Me_5)_2U(=NAd)_2$ **2** was also examined.[17] If the mechanism of catalysis proceeds via protonation of the U(IV) bis(amide) by N,N'-diphenylhydrazine in a manner similar to the reaction of N,N'-diphenylhydrazine with $(C_5Me_5)_2$-UMe_2,[8] initial product formation would include adamantylamine and azobenzene, with concomitant formation of $(C_5Me_5)_2U$-$(=NPh)_2$. However, the only organic products are aniline and azobenzene, and the only uranium species observed throughout this reaction is the catalyst **2**. This indicates that the imido ligands may serve as the sites for mediating H-atom transfer. To rule out the possibility that compound **1** is formed and undergoes subsequent rapid reaction with 1-adamantanamine to regenerate **2**, the stoichiometric reaction of **1** with 1-adamantanamine was examined. No reaction was observed at room temperature, supporting the hypothesis that there is no rupture of the U−N bond during catalysis.

These processes demonstrate a novel type of reactivity for f-element complexes: catalytic transformations of substrates by two-electron processes. The involvement of U(VI) species suggests the requirement for f-orbital participation in metallocene-mediated substrate cleavage reactions of this type.[18] Future work will focus upon elucidating mechanistic details and will include an examination of other substrates that may serve as oxidants or reductants.

(12) A Schlenk tube was charged in a helium-filled drybox with **4** (0.162 g, 0.2 mmol), AdN_3 (0.177 g, 1.00 mmol), and THF (10 mL). The solution was degassed, placed under an atmosphere of H_2, and stirred at 55 °C for 16 h. Ethanol (2 mL) was added, and the volatiles were removed in vacuo. The $AdNH_2$ (0.160 g, 1.06 mmol, 76%) was purified by flash chromatography.

(13) Nakamura, A.; Aotake, M.; Otsuka, S. *J. Am. Chem. Soc.* **1974**, *96*, 3456.

(14) An NMR tube in an argon-filled drybox was charged with **1** (0.020 g, 0.029 mmol), N,N'-diphenylhydrazine (0.045 g, 0.244 mmol), and C_6D_6 (0.6 mL). After 18 h, the reaction was complete and quantitative formation of azobenzene and aniline observed. A vial in an argon-filled drybox was charged with **1** (0.132 g, 0.191 mmol), N,N'-diphenylhydrazine (0.470 g, 2.55 mmol), and hexane (15 mL). After 96 h, the reaction was complete by TLC. The volatiles were removed in vacuo and the residue extracted and chromatographed with 19:1 hexane:Et_2O to yield azobenzene (0.235 g, 1.29 mmol, quantitative).

(15) Both stoichiometric oxidation and reduction steps were examined. While the reaction of **3** plus hydrazine can be observed directly and results in the formation of aniline and **1**, formation of **3** by reduction of **1** with N,N'-diphenylhydrazine cannot be directly observed; only **1** is present in detectable quantities throughout the course of the reaction, suggesting that the oxidation of **3** to **1** is faster than the reduction of **1** to **3**.

(16) Cole, L. G.; Gilbert, E. C. *J. Am. Chem. Soc.* **1951**, *73*, 5423.

(17) An NMR tube in an argon-filled drybox was charged with **2** (0.018 g, 0.022 mmol), N,N'-diphenylhydrazine (0.041 g, 0.21 mmol), and C_6D_6 (0.6 mL). After 42 h at room temperature, all of the N,N'-diphenylhydrazine starting material had been consumed. The only organic products observed by NMR were aniline and azobenzene in a 2:1 ratio. Compound **2** was the only uranium-containing compound observed in solution.

(18) An explanation of f orbitals and their role in the bonding and reactivity of U(VI) complexes is provided in ref 5b.