A Simple Preparative Route to Bis(imido)uranium(VI) Complexes by the Direct Reductions of Diazenes and Azides**

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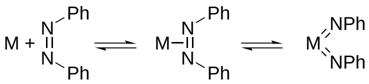
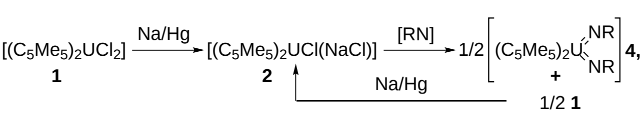
The four-electron reductive cleavage of a double bond is rarely observed on a single metal center (Scheme 1).[1] It has been suggested that this reaction is symmetry-forbidden for most metal d-electron counts in the absence of strongly π-accepting ligands.[2] Metallocene complexes are not expected to effect this reaction, as they possess only three metal-based valence orbitals available to accommodate the four metal–ligand bonds formed. These orbital constraints do not exist for actinide metallocenes, however, if f orbitals are capable of participating in the metal–nitrogen bonding. This is illustrated by our previous report of the two-electron cleavage of hydrazines by uranium(IV) to yield stable uranium(VI) bis(organoimido) complexes.[3]



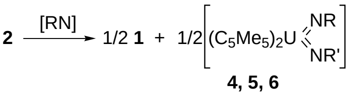
Scheme 1. Reaction of azobenzene to form bis(phenylimido) complexes.

We are investigating high valent uranium compounds to elucidate the role of f orbitals in chemical bonding. This requires the development of simple synthetic routes to a broad spectrum of organouranium(VI) imido compounds. Previously reported preparations of these compounds involved multistep syntheses starting from **1**.[3] We now report two one-pot procedures for this transformation.

The uranium(III) complex **2** is known to act as a uranium(II) synthetic equivalent.[4] We report here that compound **2** also reacts with either organic azo or azido compounds to yield bis(imido)uranium(VI) compounds in high yields in a one-pot procedure (Scheme 2). Compound **2** is generated in situ by the Na/Hg reduction of **1**. The organic oxidant is then added, and the additional **1** that is produced in the course of the reaction is reduced by the second equivalent of Na present, so that all of the uranium is converted into the desired product (Scheme 2). These reactions have also been carried out with independently prepared **2**[5] in the absence of added Na, demonstrating that **2** is able to perform the four-electron reduction of the azo or azido functional groups, with the formation of one half equivalent of **1** (Scheme 3).

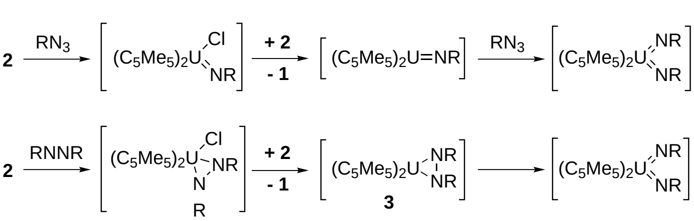


Scheme 2. One-pot synthesis of [$(C_5Me_5)_2U(NR)_2$] (**4** and **5**) from **1**. **4** (R = Ph): [RN] = PhNNPh, 92%; [RN] = PhN_3, 84%; **5** (R = 1-Ad): [RN] = 1-AdN_3, 71%.



Scheme 3. Synthesis of [$(C_5Me_5)_2U(NR)_2$] (**4**–**6**) from **2**. **4** (R = R′ = Ph): [RN] = PhNNPh, 94%; **5** (R = R′ = 1-Ad): [RN] = 1-AdN_3, 95%; **6** (R = Ph; R′ = $SiMe_3$): [RN] = $PhNNSiMe_3$,[16] 70%.

Although **2** acts as a uranium(II) synthetic equivalent,[4] there is no evidence that any uranium(II) species is ever produced.[6] By analogy to known reactions, it may be suggested that this reaction occurs as depicted in Scheme 4.



Scheme 4. Proposed mechanisms.

Compound **2** can react with an azide to generate a chloroimidouranium(V) species.[7] This species can comproportionate with a second equivalent of **2** to generate **1** and a imidouranium(IV) compound[8] which is known to react with azides to form bis(imido)uranium(VI) complexes.[3] Azo compounds can react similarly via the intermediacy of a chlorohydrazineuranium(V)[9] complex and an azouranium complex (**3**).

These reactions provide a source of high-valent organoimido complexes with a wider range of N-substitution, including saturated alkylimido analogues. The reaction of **2** with two equivalents of adamantylazide generates the bis(adamantylimido) complex **5** in high yield (Figure 1[10]). As in other organoimidouranium complexes,[11] the complex displays short uranium–nitrogen bonds (U–N(1):1.94(2) Å, U–N(2):1.96(2) Å), and nearly linear U-N-C angles (U-N(1)-C(1): 177(2)°, U-N(2)-C(11): 172(2)°), indicative of metal–ligand multiple bonding.[12] The N-U-N angle (96.6(8)°) is similar to that observed in **4**.[3a]

The oxidation of **2** with diazenes illustrates some differences between the transition metals and the f-block elements and suggests the possible involvement of the f orbitals in metal–ligand multiple bonding. As stated earlier, the four-electron reduction of unsaturated ligands does not often occur on a single transition metal center.[1] In contrast to proposed intermediate **3**, the analogous η^2-azobenzene- (or η^2-hydrazido-) molybdocene complex is stable.[13] There are both thermodynamic and kinetic factors that might explain these differences in reactivity. The analogous Group 6 bis(imido) metallocene complexes would be unstable as 20-electron species (assuming metal–nitrogen double bonds and η^5-Cp ligands). Further, the concerted cleavage of an E–E bond at a

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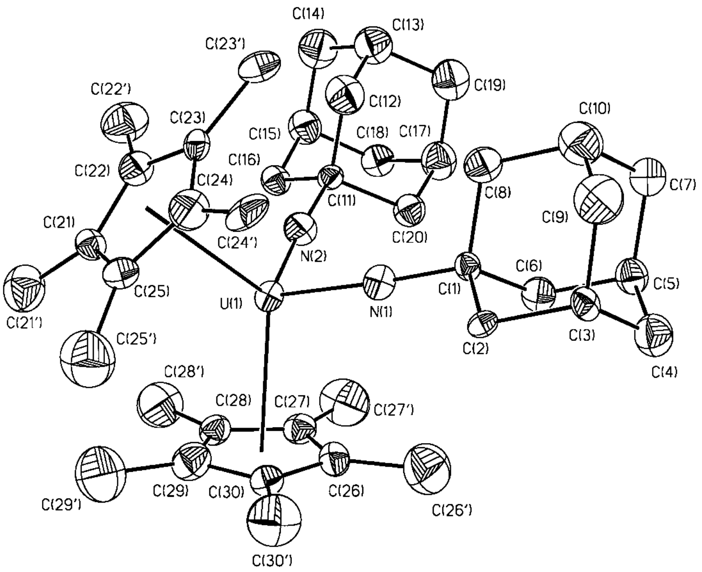

Figure 1. ORTEP depiction of **5**.

single metal center is generally symmetry-forbidden, based on a forbidden level crossing involving stabilization of the high-lying b_2-symmetric $E-E$ σ^* orbital.[2b] In contrast to the d^2 Cp_2Mo fragment, the d^2f^2 uranium center in **3** has low-lying f orbitals of the appropriate symmetry[14b] to assist both in making the cleavage symmetry allowed and in stabilizing the resulting organoimido ligands.

In conclusion, we have developed new one-pot syntheses of bis(imido)uranium(VI) compounds, based on the four-electron reduction of an azo or two azido functionalities. This azo–imido conversion is rare in the transition metals and has not been previously observed in either an actinide complex or a metallocene. That these reactions readily occur in our simple system illustrates one role of f-orbital participation in reactions of uranium. This synthetic methodology permits the preparation of a wide variety of organoimidouranium(VI) complexes. Preliminary experiments indicate that the alkylimido complexes display enhanced reactivity with respect to their arylimido analogues; we are currently investigating this reactivity.

Experimental Section

All operations were conducted in a He-filled drybox.

4: A vial was charged with **1**[15] (0.290 g, 0.5 mmol), Na (0.023 g, 1.0 mmol), THF (5 mL), and Hg (1 mL) and stirred for 1 h. Azobenzene (0.091 g, 0.5 mmol) was then added and the solution was stirred 16 h. The THF was removed in vacuo, and the residue was extracted with toluene (15 mL), filtered, and dried in vacuo to leave **4** (0.320 g, 0.46 mmol, 92 %).

5: A vial was charged with **1** (1.74 g, 3.0 mmol), Na (0.138 g, 6.0 mmol), THF (25 mL), and Hg (1 mL). The solution was stirred for 1 h, then 1-azidoadamantane (1.063 g, 6.0 mmol) was added, and the solution was stirred 16 h. The THF was removed in vacuo, and the residue was extracted with toluene (15 mL), filtered, and crystallized at $-30\,^{\circ}C$ to yield **5** (1.720 g, 2.13 mmol, 71 %) as black crystals. ^1H NMR (300 MHz, C_6D_6) $\delta = 4.07$ (s, 30H), 3.18 (s, 6H), 1.46 (d, $J = 11$ Hz, 6H), 1.36 (d, $J = 11$ Hz, 6H), 1.16 (s, 12H); ^{13}C NMR (75 MHz, C_6D_6) $\delta = 137.2$, 84.4, 60.6, 36.6, 34.4, 10.6; IR (Kbr): $\tilde{\nu} = 748$ (w), 787 (w), 1095 (w), 1132 (m), 1298 (m), 1341 (w), 1376 (m), 1437 (w), 1449 (m), 2847 (s), 2900 (s), 2977 (w). Analysis calcd. for $C_{40}H_{60}N_2U$: C 59.54, H 7.49, N 3.47; found: C 59.26, H 7.48, N 3.40.

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