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Multi-Electron Reduction from Alkyl/Hydride Ligand Combinations in U^{4+} Complexes

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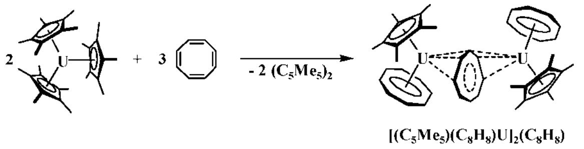
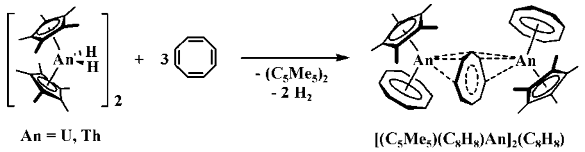
Multielectron reduction chemistry has been recently expanded in the organoactinide area by the realization that traditional metal-based redox couples can be combined with a growing list of ligand-based redox processes.[1−7] For example, in sterically crowded complexes such as $(C_5Me_5)_3U$,[8] the $(C_5Me_5)^{1-}$ ligand becomes activated for reduction and 2 equiv of this U^{3+} complex can effect a six-electron reduction of 3 equiv of C_8H_8 to form the U^{4+} product $[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$, eq 1.[1] Multielectron reduction can also be achieved with ligands such as $(BPh_4)^{1-}$ and H^{1-}.[2,5] For example, in eq 2 $[(C_5Me_5)_2UH_2]_2$[9] and $[(C_5Me_5)_2ThH_2]_2$[9] act as six-electron reductants with C_8H_8 by using the hydride ligands as reductants in combination with $(C_5Me_5)^{1-}$ reduction.[5]

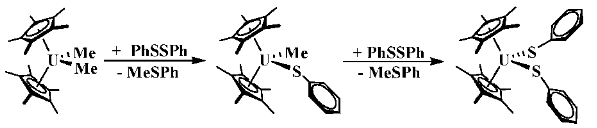


(1)



(2)

In contrast to these tetravalent actinide hydrides, the U^{4+} methyl complex, $(C_5Me_5)_2UMe_2$,[9] does not act as an analogous reductant. With PhSSPh, a reagent more easily reduced than C_8H_8, the alkyl ligands reacted via σ bond metathesis, a reaction more precedented for f element hydride and alkyl complexes, eq 3.[10−15]

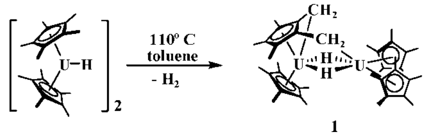


(3)

We now report that the *combination* of one alkyl and one hydride ligand in U^{4+} complexes can effectively function as a two-electron reductant to make U^{4+} products. The redox couple in eq 4 shows only the net reaction and does not have any mechanistic implications. This alkyl hydride reduction chemistry is formally related to reductive elimination reactions in transition metal chemistry in which two ligands eliminate and the metal oxidation state is reduced by two.[16] The reactions reported here were unexpected since two anions are eliminated and the electrons are passed directly onto a substrate instead of forming a reduced metal complex. This type of reaction has not been observed before in f element chemistry. The reaction in the literature that is closest to the results reported here is the reversible interconversion between the U^{4+} and U^{3+} hydrides, $[(C_5Me_5)_2UH_2]_2$ and $[(C_5Me_5)_2UH]_2$, which formally involves a bimetallic reductive elimination and oxidative addition of dihydrogen.[9]

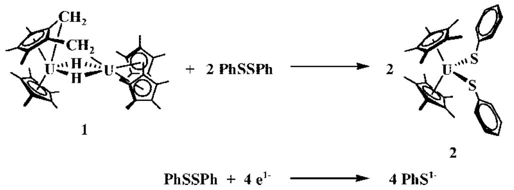
$$(\mathrm{RCH_2})^{1-} + \mathrm{H}^{1-} \rightarrow \mathrm{RCH_3} + 2\mathrm{e}^{1-} \tag{4}$$

The alkyl hydride reductive reactivity was observed in the course of characterizing the product of heating $[(C_5Me_5)_2UH]_2$ shown in eq 5. This complex, $(C_5Me_5)U[\mu\text{-}\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_3(CH_2)_2](\mu\text{-}H)_2U(C_5Me_5)_2$, **1**,[17] has a $[C_5Me_3(CH_2)_2]^{3-}$ ligand that has one methylene group ”tucked-in” to bind to the uranium of its ring and one ”tucked-over” to the uranium of another metallocene unit. Since **1** is a U^{4+} hydride, like $[(C_5Me_5)_2UH_2]_2$ in eq 2, it could have hydride reduction chemistry that would generate new tuck-in and tuck-over derivatives beyond **1**, the sole example in the literature. Accordingly, the reductive chemistry of **1** was examined.



(5)

Scheme 1



As shown in Scheme 1, complex **1** quantitatively reduces 2 equiv of PhSSPh in benzene in a four electron reduction process, but the product $(C_5Me_5)_2U(SPh)_2$,[11,18] **2**, contains neither tuck-in nor tuck-over ligands. In fact, the cyclopentadienide ligands in the product contain no metalated methylene groups. Since the starting material and product both contain U^{4+} and there are only two hydride ligands, two additional electrons in the four electron reduction must come from some other source. Since the methylene groups in **1** have regained hydrogen to become methyl groups and there is no other obvious source of hydrogen in the reaction other than the hydride ligands, the four electron reduction can be explained by the formal half-reaction shown in eq 6. This is a variation of eq 4 involving two hydrides and R = “$(C_5Me_3CH_2)^{2-}$”. Reactions in toluene-d_8 give the fully protonated $(C_5Me_5)_2U(SPh)_2$. Mechanistic studies with a deuterium analog of **1** were not possible due to deuterium exchange with the $(C_5Me_5)^{1-}$ ring in **1** and the precursors.[17]

$$[\mathrm{C_5Me_3(CH_2)_2}]^{3-} + 2\mathrm{H}^{1-} \rightarrow (\mathrm{C_5Me_5})^{1-} + 4\mathrm{e}^{1-} \tag{6}$$

Complex **1** can also function as a six-electron reductant in the reduction of C_8H_8 to $[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$, **3**,[1] in benzene,

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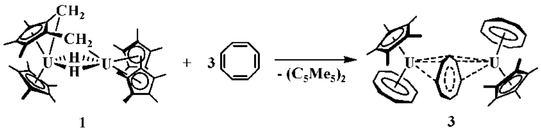
Scheme 2. Again, in this case, there is no obvious source of hydrogen for the intact $(C_5Me_5)^{1-}$ ligands in the product except the hydride ligands in **1**. The quantitative six electron reduction formally can be accounted for by two two-electron alkyl hydride reductions and two one-electron $(C_5Me_5)^{1-}$-based reductions which give the $(C_5Me_5)_2$ byproduct observed.

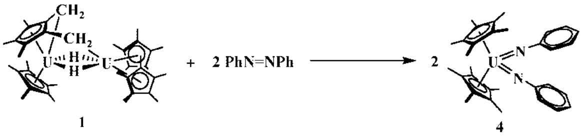
Scheme 2



$$3\,C_8H_8 + 6\,e^{1} \longrightarrow 3\,(C_8H_8)^{2}$$
$$[C_5Me_3(CH_2)_2]^{3-} + 2\,H^{1-} \longrightarrow (C_5Me_5)^{1-} + 4\,e^{1-}$$
$$2\,(C_5Me_5)^{1-} \longrightarrow (C_5Me_5)_2 + 2\,e^{1-}$$

Complex **1** can also quantitatively reduce 2 equiv of PhN=NPh in benzene to form the previously characterized U^{6+} imido complex $(C_5Me_5)_2U(=NPh)_2$, **4**,[19] Scheme 3. In this case, an eight-electron reduction occurs involving two two-electron alkyl hydride reductions and two two-electron U^{4+} to U^{6+} processes.

Scheme 3



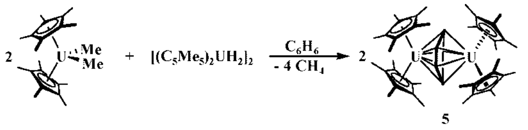
$$2\,PhN{=}NPh + 8\,e^{1-} \longrightarrow 4\,(PhN)^{2-}$$
$$[C_5Me_3(CH_2)_2]^{3-} + 2\,H^{1-} \longrightarrow (C_5Me_5)^{1-} + 4\,e^{1-}$$
$$2\,[(C_5Me_5)_2U]^{2+} \longrightarrow 2\,[(C_5Me_5)_2U]^{4+} + 4\,e^{1-}$$

While the reduction of PhSSPh can be rationalized by a series of σ bond metathesis transformations, such an explanation is not obvious for the C_8H_8 and PhN=NPh reactions. An alternative mechanistic pathway that can be envisaged for Schemes 1−3 is the reductive elimination of two pairs of U−H and U-CH_2 units to reform the CH_3 groups of the $(C_5Me_5)^{1-}$ ligands. Reductive elimination of both pairs leaves 2 equiv of an intermediate of formal composition "$(C_5Me_5)_2U$." However, since U^{2+} organometallic complexes have only been inferred and not yet isolated,[4,9,20−25] it is more likely that these reactions occur stepwise via U^{3+} intermediates.

To determine if the alkyl hydride reductive chemistry was specific to the unusual tuck-in tuck-over complex, **1**, reactions of combinations of U^{4+} hydride and methyl complexes were examined. Combinations of $(C_5Me_5)_2UMe_2$ and $[(C_5Me_5)_2UH_2]_2$ could not be examined with C_8H_8 and PhNNPh, since the hydride complex alone reduces these substrates.[5] However, the combination of $(C_5Me_5)_2UMe_2$ and $[(C_5Me_5)_2UH_2]_2$ achieves an even more surprising reduction. As shown in Scheme 4, the combination of U^{4+} hydrides and methyls reduces benzene to make the formally trivalent complex of $(C_6H_6)^{2-}$, that is, the previously characterized $[(C_5Me_5)_2U]_2(C_6H_6)$,[3] **5**. Methane is observed as a byproduct and again the formal half-reaction is as shown in eq 4.

In summary, it appears that multielectron reductive chemistry can be unexpectedly obtained from combinations of alkyl and hydride ligands in organoactinide complexes. These reactions are formally analogous to bimetallic reductive elimination reactions in transition metal chemistry, but in this case, the electrons reduce substrates directly rather than providing metal complexes in lower oxidation states. Neither reductive elimination of two anions nor regeneration of a $(C_5Me_5)^{1-}$ ring from a $(C_5Me_4CH_2)^{2-}$ and a hydride involve reaction pathways seen before with organoactinides. The general applicability of this approach to accessing multielectron reduction from mixed ligand complexes is under investigation.

Scheme 4



$$2\,C_6H_6 + 4\,e^{1-} \longrightarrow 2\,(C_6H_6)^{2-}$$
$$4\,[(C_5Me_5)_2U]^{2+} + 4\,e^{1-} \longrightarrow 4\,[(C_5Me_5)_2U]^{1+}$$
$$4\,CH_3^{\,1-} + 4\,H^{1-} \longrightarrow 4\,CH_4 + 8\,e^{1-}$$

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Supporting Information Available: Synthetic and spectroscopic details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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