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Reduction of Pentavalent Uranyl to U(IV) Facilitated by Oxo Functionalization

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The reduction of uranyl (UO_2^{2+}) to U(IV) has relevance to speciation of uranium in the environment and geological storage of spent nuclear fuel.[1−3] This transformation is thought to proceed stepwise through UO_2^+,[4,5] a moiety that has received increased attention in recent years.[6,7] While reduction of UO_2^{2+} to UO_2^+ is now well-established, the reduction of UO_2^+ to U(IV) is still poorly understood, in part because reduction to U(IV) is not possible without substantial rearrangement of the uranyl moiety or cleavage of the U−O(oxo) bond.[8] For example, reduction of $UO_2(OTf)_2$ with $U(OTf)_3$ yields a uranium(IV) oxo cluster, $U_6(\mu_3\text{-}O)_8(\mu\text{-}OTf)_8(py)_8$, in which the uranyl moiety is not conserved.[9] Nonetheless, this is a key mechanistic step in uranyl reduction, and its exploration would help validate the proposed mechanisms for U(IV) formation.[4,5] Herein we report that *reversible* reduction of pentavalent uranyl to U(IV) can be achieved by functionalization of the two oxo ligands of the uranyl moiety.

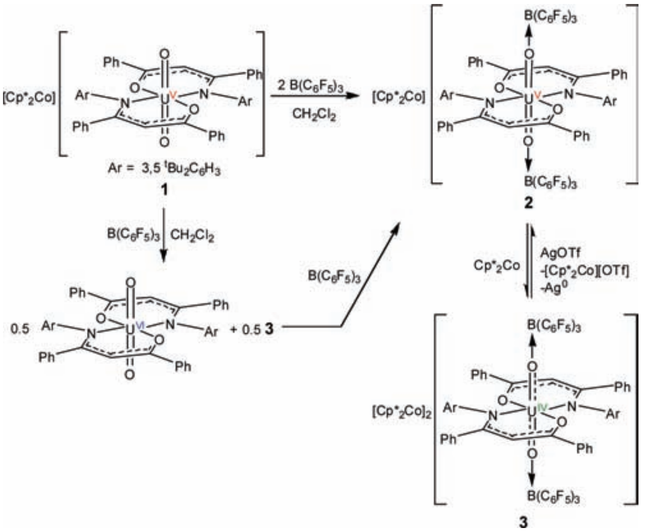
Addition of 2 equiv of $B(C_6F_5)_3$ to $[Cp^*_2Co][U^VO_2(^{Ar}acnac)_2]$ (**1**)[10] [^{Ar}acnac = Ar*N*C(Ph)CHC(Ph)*O*; Ar = 3,5-$^tBu_2C_6H_3$] results in the functionalization of both uranyl oxo ligands to afford $[Cp^*_2Co][U^V\{OB(C_6F_5)_3\}_2(^{Ar}acnac)_2]$ (**2**) in good yield (Scheme 1). Complex **2** exhibits two peaks in its $^{19}F\{^1H\}$ NMR spectrum at −98.1 and −101.0 ppm in a 1:2 ratio, corresponding to the para and meta fluorine atoms, respectively, indicating the incorporation of $B(C_6F_5)_3$ into the complex.[11] No signal was observed for the ortho fluorine atoms, most likely because of their proximity to the paramagnetic uranium center. Its ^1H NMR spectrum and elemental analysis are also consistent with the proposed formulation, while its NIR spectrum is similar to those exhibited by other U(V) compounds,[12,13] supporting the presence of a $5f^1$ ion. Unlike complex **1**, which exhibits limited thermal stability, **2** is stable in CD_2Cl_2 for up to 40 h.

The ability to functionalize both oxo ligands in **1** contrasts with the reactivity of the U(VI) parent complex, $UO_2(^{Ar}acnac)_2$, which forms only the monofunctionalized product $U^{VI}O\{OB(C_6F_5)_3\}(^{Ar}acnac)_2$ upon reaction with excess $B(C_6F_5)_3$.[10] This difference in reactivity is likely a result of the increased electron density at the metal center in **2**, which renders the oxo ligands more nucleophilic.

The solution redox properties of complex **2** were investigated by cyclic voltammmetry. Its cyclic voltammogram in CH_2Cl_2 reveals a quasi-reversible reduction feature at $E_{1/2} = -1.21$ V (vs Fc/Fc^+), which we attribute to the UO_2^+/U(IV) redox couple (see the Supporting Information). Also observed was a reversible redox couple for $[Cp^*_2Co]^+$ (−1.81 V vs Fc/Fc^+, which is comparable to the literature value for this species[14]). Notably, a U(V)/U(IV) reduction feature was not observed in the cyclic voltammogram of the parent complex $U^{VI}O_2(^{Ar}acnac)_2$,[10] suggesting that coordination of $B(C_6F_5)_3$ to **1** moves this redox couple to a chemically accessible value.

In line with the cyclic voltammetry results, reduction of **2** with Cp^*_2Co provides the unprecedented U(IV) complex $[Cp^*_2Co]_2[U^{IV}\{OB(C_6F_5)_3\}_2(^{Ar}acnac)_2]$ (**3**), which can be isolated as a green crystalline solid in good yield (Scheme 1). This process is chemically reversible, as shown by the reaction of **3** with AgOTf, which cleanly regenerates complex **2**, as determined by ^1H and ^{19}F NMR spectroscopies.[11]

Scheme 1



The ^1H NMR spectrum of **3** exhibits large chemical shifts, which supports its formulation as a U(IV) ion. For instance, the γ-CH resonance of the ^{Ar}acnac ligand appears as a singlet at −36.62 ppm, while one set of *o*-CH resonances appears at −29.08 ppm. Its $^{19}F\{^1H\}$ NMR spectrum exhibits two extremely broad peaks at −97.4 ppm (fwhm = 340 Hz) and −98.5 ppm (fwhm = 140 Hz) that are assignable to **3**. Also present are resonances at −93.2, −103.1, and −104.5 ppm due to an unidentified minor product (see Figure S12 in the Supporting Information). Its NIR spectrum and magnetic susceptibility (2.37μ_B at 290 K) are both consistent with the presence of a $5f^2$ ion,[15−17] while its elemental analysis also fits the proposed formulation.

The reduction of **2** to **3** is facilitated by the use of the strongly electron-withdrawing $B(C_6F_5)_3$, which lowers the redox potential of the UO_2^+ moiety upon coordination. It also converts the two oxo groups of the uranyl ion into ligands that are better described as $B(C_6F_5)_3$-substituted alkoxides. As a result, cleavage of the U−O bond is not required to access the 4+ oxidation state.

Interestingly, addition of only 1 equiv of $B(C_6F_5)_3$ to **1** does not produce the monofunctionalized U(V) complex. Instead, the products of disproportionation, namely, **3** and $U^{VI}O_2(^{Ar}acnac)_2$, are observed in a 1:1 ratio, as determined by ^1H NMR spectroscopy (Scheme 1). This transformation mirrors the proposed reaction scheme for the disproportionation of UO_2^+ in aqueous solution[4] and the reduction of uranyl by *Geobacter sulfurreducens*.[5] In both cases, protonation of an oxo ligand in UO_2^+ is thought to trigger disproportionation. Addition of a second equivalent of $B(C_6F_5)_3$ to this reaction mixture results in the formation of complex **2** via conproportionation of **3** and $U^{VI}O_2(^{Ar}acnac)_2$. However, a small amount of $U^{VI}O_2(^{Ar}acnac)_2$ remains in the reaction mixture after

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$B(C_6F_5)_3$ addition. This is attributable to a competing reaction pathway whereby $B(C_6F_5)_3$ acts solely as a one-electron oxidant[18] that converts **3** to **2** and leaves some $UO_2(^{Ar}acnac)_2$ unreacted (see the Supporting Information).

While we were unable to grow X-ray-quality crystals of **3**, we determined the structure of a similar oxo-functionalized complex, namely, $[Cp^*_2Co][U^{IV}\{OB(C_6F_5)_3\}_2(^{Ar}acnac)(OEt_2)]$ (Ar = 2,4,6-$Me_3C_6H_2$) (**5**). This complex was formed in low yield by reaction of 2 equiv of $B(C_6F_5)_3$ with $[Cp^*_2Co][U^{V}O_2(^{Ar}acnac)_2]$ (Ar = 2,4,6-$Me_3C_6H_2$) (**4**),[10] the mesityl-substituted analogue of complex **1**.

The solid-state molecular structure of **5** reveals a distorted pentagonal bipyramidal geometry about uranium in which ^{Ar}acnac, Et_2O, and two *o*-F dative interactions occupy the equatorial plane (Figure 1). The two U−O(oxo) bond lengths, 2.029(6) and 2.025(6) Å, are much longer than those observed in previously reported uranyl−$B(C_6F_5)_3$ adducts[10,19] but similar to that observed in the $SiMe_3$-functionalized uranyl(V) complex [1.993(4) Å] reported by Arnold.[20,21] In addition, the O−U−O angle [153.3(2)°] deviates significantly from linearity. This distortion likely stems from the *o*-F interactions with the U(IV) center, which pull the oxygen atoms out of the axial positions. Overall, these metrical parameters demonstrate that **5** is no longer a uranyl complex and that its U−O bond lengths are better compared to those of a uranium alkoxide.[22]

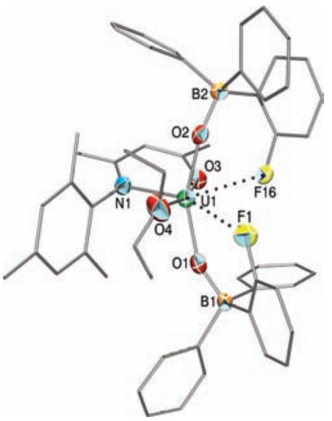
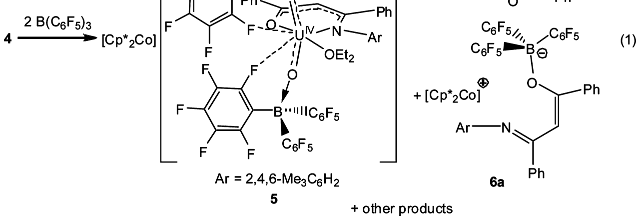


Figure 1. Molecular structure of $[Cp^*_2Co][U\{OB(C_6F_5)_3\}_2(^{Ar}acnac)(OEt_2)]$ (Ar = 2,4,6-$Me_3C_6H_2$) ($\mathbf{5}\cdot CH_2Cl_2\cdot 1.5C_6H_{14}$) showing 50% probability ellipsoids. Nonessential atoms have been removed for clarity. Selected bond lengths (Å) and angles (deg): U1−O1, 2.029(6); U1−O2, 2.025(6); U1−O3, 2.256(6); U1−O4, 2.566(7); U1−N1, 2.474(8); U1−F1, 2.762(6); U1−F16, 2.789(5); O1−B1, 1.473(13); O2−B2, 1.453(12); O1−U1−O2, 153.3(2).

Also formed during the reaction of **4** with $B(C_6F_5)_3$ is $[Cp^*_2Co][(2,4,6\text{-}Me_3C_6H_2)NC(Ph)CHC(Ph)OB(C_6F_5)_3]$ (**6a**), the result of $[^{Ar}acnac]^-$ abstraction by $B(C_6F_5)_3$ (eq 1):



Crystals of **6a** were isolated from the crude reaction mixture in low yield, allowing for structure determination by X-ray crystallography (Figure S2). Its spectral properties were corroborated by the synthesis of $[NEt_4][(2,4,6\text{-}Me_3C_6H_2)NC(Ph)CHC(Ph)OB(C_6F_5)_3]$ (**6b**), which was independently generated by reaction of $Na(^{Ar}acnac)$ with 1 equiv of $B(C_6F_5)_3$ and 1 equiv of $[NEt_4][Cl]$.[11]

The isolation of **5** and **6a** from the reaction mixture suggests that addition of $B(C_6F_5)_3$ to **4** also results in disproportionation. Consistent with this, monitoring the reaction by ^1H and $^{19}F\{^1H\}$ NMR spectroscopies revealed the formation of $U^{VI}O_2(^{Ar}acnac)_2$ along with **6a** (eq 1). However, we could not definitively assign any resonances in these spectra to complex **5**, possibly because it is NMR-silent, and its full characterization remains to be completed.

In summary, the formation of complex **3** demonstrates that functionalization of UO_2^+ with $B(C_6F_5)_3$ allows for reduction to U(IV) without cleavage of the U−O bond. The reduction is facilitated by the coordination of the electron-withdrawing $B(C_6F_5)_3$ groups to the uranyl oxo ligands, which lowers the redox potential of the pentavalent precursor, and represents a new strategy for effecting reduction of UO_2^{2+} to U(IV). Future studies will focus on developing new methods for uranyl oxo functionalization and selective cleavage of the U−O bond.

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Supporting Information Available: Experimental procedures, crystallographic details (CIF), and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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