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Borane-Mediated Silylation of a Metal−Oxo Ligand

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S Supporting Information

ABSTRACT: The addition of 1 equiv of $HSiPh_3$ to $UO_2(^{Ar}acnac)_2$ ($^{Ar}acnac$ = Ar*N*C(Ph)CHC(Ph)*O*; Ar = 3,5-$^tBu_2C_6H_3$), in the presence of 1 equiv of $B(C_6F_5)_3$, results in the formation of $U(OSiPh_3)(OB\{C_6F_5\}_3)(^{Ar}acnac)_2$ (**1**), via silylation of an oxo ligand and reduction of the uranium center. The addition of 1 equiv of Cp_2Co to **1** results in a reduction to uranium(IV) and the formation of $[Cp_2Co][U(OSiPh_3)(OB\{C_6F_5\}_3)(^{Ar}acnac)_2]$ (**2**) in 78% yield. Complexes **1** and **2** have been characterized by X-ray crystallography, while the solution-phase redox properties of **1** have been measured with cyclic voltammetry.

$B(C_6F_5)_3$-mediated hydrosilylation reactions are known for a variety of organic substrates including ketones,[1−3] aldehydes,[4] imines,[5] alkenes,[6] and even CO_2.[7] These transformations proceed by the initial formation of a weak borane−silane adduct, $[R_3SiH\cdots B(C_6F_5)_3]$, which is thought to activate the silicon center toward nucleophilic attack.[2,3,8] The rapid development of this methodology over the last 10 years suggests that many further applications are possible. In this regard, we have discovered a unique $B(C_6F_5)_3$-mediated silylation of an inorganic functional group, namely, the recalcitrant uranyl moiety (UO_2^{2+}).[9]

The controlled functionalization and/or substitution of the uranyl oxo ligands has proven to be a difficult endeavor,[9,10] and only a few examples are known. For instance, the formation of a uranyl-derived uranium(V) silyloxide, $[UO(OSiMe_3)(THF)Fe_2I_2L]$, was achieved by deprotonation of $UO_2(THF)(H_2L)$ (L = "Pacman" = polypyrrolic macrocycle).[11−14] During the reaction, $UO_2(THF)(K_2L)$ is formed as an intermediate species, which is then reduced and silylated by $HN(SiMe_3)_2$ to generate the final product. Additionally, oxo ligand metalation, concomitant with uranyl reduction, can be achieved by the reaction of $UO_2(THF)(H_2L)$ with a variety of lithium reagents[15] or rare-earth silylamides.[16] In a similar transformation, we observed the reductive silylation of $UO_2(^Racnac)_2$ (^Racnac = R*N*C(Ph)CHC(Ph)*O*; R = 3,5-$^tBu_2C_6H_3$, ^tBu) by reaction with excess Me_3SiI.[17,18] Interestingly, the addition of silanes, such as $HSiPh_3$, to $UO_2(^Racnac)_2$ under the same experimental conditions results in no reaction. This was surprising, considering that R_3SiH is anticipated to be a substantially better reducing agent than Me_3SiI. Given this, we turned our attention to the $B(C_6F_5)_3$-mediated hydrosilylation methodology.

The addition of 1 equiv of $HSiPh_3$ to $UO_2(^{Ar}acnac)_2$ (Ar = 3,5-$^tBu_2C_6H_3$),[19] in the presence of 1 equiv of $B(C_6F_5)_3$, leads to the formation of a deep-red solution, from which $U(OSiPh_3)(OB\{C_6F_5\}_3)(^{Ar}acnac)_2$ (**1**) can be isolated as a red-brown solid in 78% yield (Scheme 1). Complex **1** crystallizes in the monoclinic space group $P2_1/n$ as the toluene solvate $\mathbf{1}\cdot 4.5C_7H_8$, and its solid-state molecular structure is shown in Figure 1. Complex **1** exhibits an octahedral geometry similar to that of the parent uranium(VI) complex. However, one uranyl oxo ligand has been converted into a triphenylsilyloxide group, while the other oxo ligand has been coordinated by a molecule of $B(C_6F_5)_3$. The U−O(silyloxide) bond length [U1−O2 = 2.034(9) Å] is substantially longer than the U═O bond in uranyl (1.76 Å) but is comparable to the previously reported U^V-silyloxide distances.[11,17] The U−O(borane) bond length in **1** [U1−O1 = 1.941(8) Å] is slightly shorter than the U−O($SiPh_3$) bond but is somewhat longer than the U−O bonds reported for the uranyl(VI)-$B(C_6F_5)_3$ adducts $UO(OB\{C_6F_5\}_3)(^{Ar}acnac)_2$ [1.890(4) Å] and $UO(OB\{C_6F_5\}_3)(NCN)_2$ [NCN = $(Me_3SiN)CPh(NSiMe_3)$] [1.898(3) Å].[19,20] Interestingly, the U−O(acnac) bond lengths in **1** [2.188(8) and 2.140(8) Å] are shorter than those of the starting material [2.255(5) Å for $UO_2(^{Ar}acnac)_2$].[21] This is somewhat unexpected, given the larger size of the U^{5+} ion.

Silane addition across an M = E (E = O, S, NR) linkage, while rare, has been observed previously.[22−26] For example, Toste and co-workers observed the hydrosilylation of $ReO_2I(PPh_3)_2$ by the addition of a Si−H bond across a Re═O group.[27−30] In this example, the Re═O bond exhibits a bond order of 2.5,[30] a factor that may contribute to its relatively facile silylation. In contrast, the U═O bond in uranyl exhibits a bond order of 3 and an extremely strong U−O interaction (604 kJ/mol),[10] which may explain why addition of $B(C_6F_5)_3$ is required to observe oxo silylation.

The ^1H NMR spectrum of **1** in CD_2Cl_2 is characterized by the presence of two ^tBu resonances at −0.24 and −0.48 ppm, assignable to the 3,5-$^tBu_2C_6H_3$ aryl substituent. The observation of two resonances likely arises from hindered rotation about the N−C_{ipso} bond, which results in the generation of two distinct chemical environments. This hindered rotation is probably due to the bulky functional groups attached to each functionalized oxo ligand. The $^{19}F\{^1H\}$ NMR spectrum consists of three resonances at −73.65, −96.73, and −100.45 ppm in a 2:1:2 ratio, corresponding to the *o*-, *p*-, and *m*-fluorine atoms of the C_6F_5 groups, respectively. Interestingly, a second, less-intense, set of resonances is also observed in the ^1H NMR spectrum of **1**, which we have assigned to a minor isomer. The two isomers are observed in a 5.5:1 ratio. The minor isomer is characterized by four inequivalent ^tBu resonances, at −0.54, −0.85, −1.00, and −1.24 ppm, in a 1:1:1:1 ratio, respectively. Given the observation of four ^tBu resonances for the minor isomer, we tentatively suggest that this isomer is characterized by a cis configuration of the silyloxide and borate ligands because this

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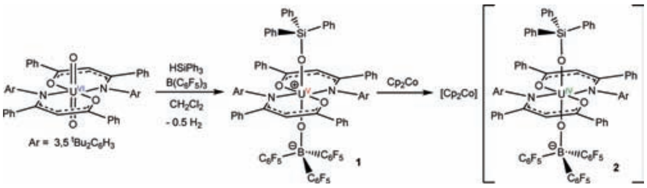
Scheme 1. Synthesis of 1 and 2



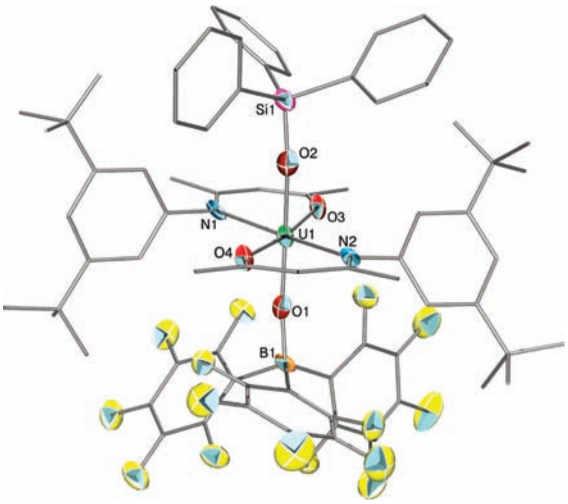


Figure 1. Solid-state structure of $1\cdot4.5C_7H_8$ with 50% probability ellipsoids. The phenyl rings on the ^{Ar}acnac backbone have been removed for clarity. Bond lengths and angles are listed in Table S2 in the Supporting Information.

arrangement most easily explains the observation of four unique ^{t}Bu environments. Finally, the near-IR spectrum for **1** is similar to those of other uranium(V) complexes,[17,31−33] supporting the presence of a $5f^1$ ion.

We have examined the solution-phase redox properties of **1** using cyclic voltammetry. Its cyclic voltammogram reveals a reversible reduction feature at $E_{1/2} = -0.72$ V (vs Fc/Fc^+), which we attribute to the U^V/U^{IV} redox couple (Figure 2). This feature is 0.63 V higher than that observed for $[Cp^*_2Co][U(OB\{C_6F_5\}_3)_2({}^{Ar}acnac)_2]$, which exhibits a U^V/U^{IV} redox potential at $E_{1/2} = -1.21$ V (vs Fc/Fc^+).[33] We attribute the less negative reduction potential in **1** to the replacement of a neutral $B(C_6F_5)_3$ substituent with the cationic Ph_3Si^+ fragment. In addition, complex **1** exhibits an irreversible oxidation feature at 0.96 V (vs Fc/Fc^+, 200 mV/s). The irreversibility of this feature, coupled with its relatively high potential, suggests that conversion of **1** back to uranyl by Si−O and B−O bond cleavage will not be easily achievable. Consistent with this hypothesis, the attempted oxidation of complex **1** with I_2 results in no reaction, while oxidation with AgOTf results in partial decomposition, but no evidence for the formation of $UO_2({}^{Ar}acnac)_2$ is observed.

In agreement with the cyclic voltammetry data, the addition of 1 equiv of Cp_2Co to an Et_2O suspension of **1** results in reduction and formation of a brown powder. Recrystallization of this solid from a mixture of CH_2Cl_2 and hexane affords the uranium(IV) complex $[Cp_2Co][U(OSiPh_3)(OB\{C_6F_5\}_3)({}^{Ar}acnac)_2]$ (**2**) as a brown-red solid in 78% yield (Scheme 1). Complex **2** crystallizes in the monoclinic space group $P2_1/n$ as the hexane solvate $2\cdot2C_6H_{14}$ (Figure S1 in the Supporting Information). In the solid state, **2** exists as a discrete cation/anion pair. The ligand arrangement around the uranium center is similar to that exhibited by complex **1**; i.e., two ^{Ar}acnac ligands define the equatorial plane, and the two oxo-derived ligands occupy the axial positions, resulting in an overall octahedral geometry. The O1−U1−O2 bond angle is 175.3(3)°, and the U−O(borane) and U−O(silyloxide) bond lengths are U1−O1 = 2.056(8) Å and U1−O2 = 2.173(8) Å, respectively (Table S2 in the Supporting Information). These distances are slightly longer than those observed in **1**, consistent with the presence of the larger U^{4+} ion.

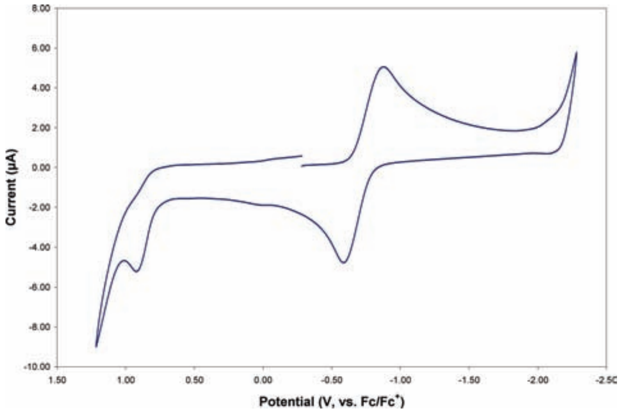


Figure 2. Room temperature cyclic voltammogram for **1** in CH_2Cl_2 (0.1 M $[NBu_4][PF_6]$ as the supporting electrolyte). Scan rate: 200 mV/s.

As was observed for **1**, the ${}^1H$ and ${}^{19}F$ NMR spectra of **2** are also consistent with the presence of major and minor isomers in solution, in a 3:1 ratio. Upon cooling to −60 °C, the ratio of major and minor isomers changes to 9:1, respectively. In CD_2Cl_2 at −60 °C, the major isomer is characterized by two broad resonances at −3.18 and −11.44 ppm, assignable to two unique ^{t}Bu environments, while the minor isomer is characterized by four broad resonances at 0.45, −2.16, −2.33, and −2.75 ppm, assignable to four inequivalent ^{t}Bu environments. Also observed is a sharp singlet at 6.64 ppm, revealing the incorporation of $[Cp_2Co]^+$. The room temperature ${}^{19}F$ NMR spectrum of **2** is also consistent with the presence of both the major and minor isomers in solution.

As anticipated, the near-IR spectrum for **2** is indicative of the presence of a $5f^2$ ion.[34,35] We have also examined the chemical reversibility of the reduction from **1** to **2**. Thus, the addition of 1 equiv of AgOTf to **2** in CD_2Cl_2 cleanly regenerates **1**, as determined by ${}^1H$ and ${}^{19}F$ NMR spectroscopies (Figures S20−S22 in the Supporting Information).

To gain further insight into the formation of **1**, we monitored the reaction of $UO_2({}^{Ar}acnac)_2$, $HSiPh_3$, and $B(C_6F_5)_3$ in C_6D_6 by ${}^1H$ NMR spectroscopy. The ${}^1H$ NMR spectrum of the reaction mixture reveals the clean formation of complex **1** along with the presence of H_2, as evidenced by a sharp singlet at 4.46 ppm (Figures S28−S30 in the Supporting Information).[36] To confirm the origin of H_2, we followed the reaction between $UO_2({}^{Ar}acnac)_2$, $DSiPh_3$,[37,38] and $B(C_6F_5)_3$ in C_6H_6 by ${}^2H$ NMR spectroscopy. In agreement with the protio experiment, the ${}^2H$ NMR spectrum of the reaction mixture reveals a sharp resonance at 4.45 ppm, consistent with the formation of D_2 (Figures S25−S27 in the Supporting Information) and demonstrating that silane is the source of the H_2. However, there are also two minor resonances present in the spectrum, at 12.10 and 0.76 ppm, revealing that some scrambling of the ^2H label is occurring over the course of the reaction. Additionally, we can rule out reduction of the ^{Ar}acnac ligand by hydrogen addition. A comparison of the metrical parameters of both **1** and **2** with $UO_2(^{Ar}acnac)_2$ and $[Cp^*_2Co][UO_2(^{Ar}acnac)_2]$[19] reveals little change in the N−C, C−C, and C−O bond lengths of the ^{Ar}acnac backbone (Figure S35 in the Supporting Information).

Given the importance of uranyl redox chemistry in the environmental behavior of uranium, the mechanism of silylation is of considerable interest. In our system, we believe that the initial formation of a borane−silane adduct, $[Ph_3SiH\cdots B(C_6F_5)_3]$, promotes a nucleophilic attack of the silyl cation by the uranyl oxo ligand. Several lines of evidence support this hypothesis. First, no reaction is observed between $UO_2(^{Ar}acnac)_2$ and Ph_3SiH alone, demonstrating the need for $B(C_6F_5)_3$ in the reduction. Second, the reaction of HSi^iPr_3 with $UO_2(^{Ar}acnac)_2$ in the presence of $B(C_6F_5)_3$ results in the formation of the previously characterized adduct $UO(OB\{C_6F_5\}_3)(^{Ar}acnac)_2$[19] as the only uranium-containing product (Figures S31−S32 in the Supporting Information). This is consistent with our proposed mechanism, as Piers et al. have demonstrated that $B(C_6F_5)_3$ cannot activate HSi^iPr_3 because of the bulky isopropyl substituents.[2] Future work will focus on further elucidation of the mechanism by which silylation occurs and on expansion of its scope to other silanes.

In summary, we have demonstrated that facile silylation of the uranyl oxo ligands, concomitant with reduction to uranium(V), can be achieved via borane-mediated silylation of $UO_2(^{Ar}acnac)_2$. This uranium(V) complex can be further reduced with Cp_2Co to uranium(IV). However, oxidation back to UO_2^{2+} with common oxidants, such as AgOTf or I_2, was not observed, likely owing to the strong Si−O and B−O bonds in **1**. While borane-mediated silylation has been extensively used in organic synthesis, it has not, to our knowledge, been previously applied to the reduction of a metal−oxo complex. This opens up new avenues for borane-mediated silylation beyond organic chemistry, as this transformation should be applicable to the reduction of a variety of unreactive metal−ligand multiple bonds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, NMR spectroscopy, and X-ray crystallography details. This material is available free of charge via the Internet at http://pubs.acs.org.

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This paper was published on May 9, 2011. One sentence was deleted and the corrected version was reposted on May 13, 2011.