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Reductive Silylation of the Uranyl Ion with Ph_3SiOTf

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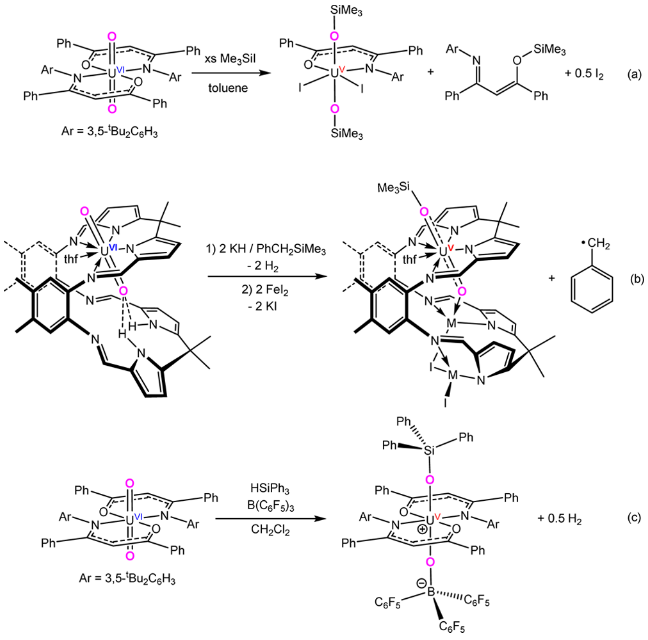
Supporting Information

ABSTRACT: The reaction of 2 equiv of Ph_3SiOTf with $UO_2(dbm)_2(THF)$ (dbm = *O*C(Ph)CHC(Ph)*O*) and $UO_2(^{Ar}acnac)_2$ (^{Ar}acnac = Ar*N*C(Ph)CHC(Ph)*O*; Ar = 3,5-$^tBu_2C_6H_3$) results in the formation of $U(OSiPh_3)_2(dbm)_2(OTf)$ (**1**) and $[U(OSiPh_3)_2(^{Ar}acnac)_2][OTf]$ (**2**), respectively, in good yield.

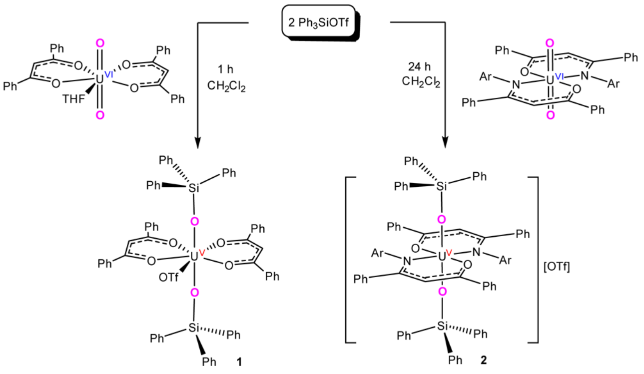
Reductive silylation of uranyl (UO_2^{2+}), defined as the one-electron ($1e^-$) reduction of U^{6+} to U^{5+} concomitant with silylation of one or both of the uranyl oxo ligands,[1−5] has become a promising means of chemically modifying the recalcitrant uranyl ion.[6,7] The reductive silylation reaction is compatible with a variety of coligand types, including a polypyrrolic "Pacman" macrocycle,[2,5,7−11] *β*-diketonate and *β*-ketoiminates,[3,4,12−14] and even halides.[1] In contrast, however, the scope of silylating reagents that are able to effect reductive silylation is not as well established. In particular, it is not clear what roles the leaving group or the incoming silyl group play in promoting Si−O bond formation and U^{6+} reduction. The identity of both is potentially important, a fact that is illustrated by several examples. For instance, reductive silylation of $UO_2(^{Ar}acnac)_2$ (^{Ar}acnac = Ar*N*C(Ph)CHC(Ph)*O*; Ar = 3,5-$^tBu_2C_6H_3$) with Me_3SiI is enabled by virtue of the accessible I_2/I^- redox potential (Scheme 1a),[3] which allows I^- to function as the reductant in the transformation. Similarly, reductive silylation of $UO_2(THF)(H_2L)$ (THF = tetrahydrofuran; L = polypyrrolic macrocycle) with $PhCH_2SiMe_3$ is no doubt enabled by the relative stability of the benzyl radical (Scheme 1b).[2] In another example, we demonstrated that reductive silylation of $UO_2(^{Ar}acnac)_2$ with R_3SiH (R = Et, Ph) only proceeded in the presence of a Lewis acid activator, namely, $B(C_6F_5)_3$, which was required to increase the electrophilicity of the Si center by abstraction of the hydride ligand (Scheme 1c).[12,13]

In this contribution, we explore the ability of Ph_3SiOTf to effect reductive silylation of a uranyl *β*-diketonate complex, $UO_2(dbm)_2(THF)$ (dbm = *O*C(Ph)CHC(Ph)*O*), and a uranyl *β*-ketoiminate complex, $UO_2(^{Ar}acnac)_2$. We rationalized that Ph_3SiOTf would be an excellent reagent for this purpose, in part, because of its use as a silylating reagent in organic and main-group synthesis.[15−17] In addition, the enhanced electrophilicity of the Si center in Ph_3SiOTf, relative to that of R_3SiH (R = Et, Ph), suggests that it should not require the addition of a Lewis acid activator.[12−14]

Scheme 1



Scheme 2



The addition of 2 equiv of Ph_3SiOTf to $UO_2(dbm)_2(THF)$, in CH_2Cl_2, results in the formation of a dark-red solution over the course of 1.5 h. From this solution, the uranium(V) bis(silyloxide) $U(OSiPh_3)_2(dbm)_2(OTf)$ (**1**) can be isolated as a red crystalline material in 61% yield (Scheme 2). Similarly, the addition of 2 equiv of Ph_3SiOTf to $UO_2(^{Ar}acnac)_2$, in CH_2Cl_2, results in the formation of a dark-red-brown solution, from which $[U(OSiPh_3)_2(^{Ar}acnac)_2][OTf]$ (**2**) can be isolated as a dark-red crystalline solid in 57% yield (Scheme 2). Complexes **1** and **2** are derived from $1e^-$ reduction of the U center, concomitant with silylation of both oxo ligands. Importantly, the formation of complexes **1** and **2** proceeds in higher yields if 2 equiv of

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Ph_3SiOTf is added to the reaction mixtures. The addition of 1 equiv of Ph_3SiOTf to $UO_2(dbm)_2(THF)$ results in the formation of complex **1** in only 33% yield.

Complex **1** crystallizes in the monoclinic space group $P2_1/c$, while complex **2** crystallizes in the triclinic space group $P\overline{1}$ as a THF solvate, **2**·THF. Their solid-state molecular structures are shown in Figure 1. Complex **1** exhibits a pentagonal-bipyramidal geometry about the U center, wherein two oxo-derived triphenylsilyl alkoxide ligands occupy the axial coordination sites, while two dbm ligands and one triflate ligand occupy the five equatorial coordination sites. In contrast, the cation in complex **2** features an octahedral coordination geometry about the U center, wherein two oxo-derived triphenylsilyl alkoxide ligands occupy the axial coordination sites while two ^{Ar}acnac ligands occupy the four equatorial sites. The monocationic charge of this fragment is balanced by the presence of an outer-sphere triflate anion. The $U{-}O_{Si}$ bond lengths in **1** are 2.005(2) and 2.018(2) Å, while for **2**, the $U{-}O_{Si}$ bond length is 2.044(2) Å (Table 1). These values are consistent with a significant reduction in the U−O bond order upon silylation and are comparable to other recently reported uranium(V) silyloxide U−O bond distances.[2,3,12−14] For example, $U(OB\{C_6F_5\}_3)(OSiPh_3)(dbm)_2(THF)$ features a U−O bond length of 2.024(2) Å,[14] and $[U(OSiEt_3)_2(^{Ar}acnac)_2][HB(C_6F_5)_3]$ features a U−O bond length of 2.011(4) Å.[13] The $U{-}O_{dbm}$ bond lengths in **1** (av. U−O = 2.25 Å) are slightly shorter than those observed for uranyl dibenzoylmethanate complexes,[14,18−21] which is consistent with the absence of uranyl character in the molecule. However, the $U{-}O_{triflate}$ distance in **1** [2.349(2) Å] is similar to those exhibited by uranyl triflate complexes.[3,22,23] Finally, the U−N and $U{-}O_{acnac}$ bond lengths in **2** are 2.380(2) and 2.153(2) Å, respectively, and are comparable to those observed for related U(V) silyloxide complexes.[12]

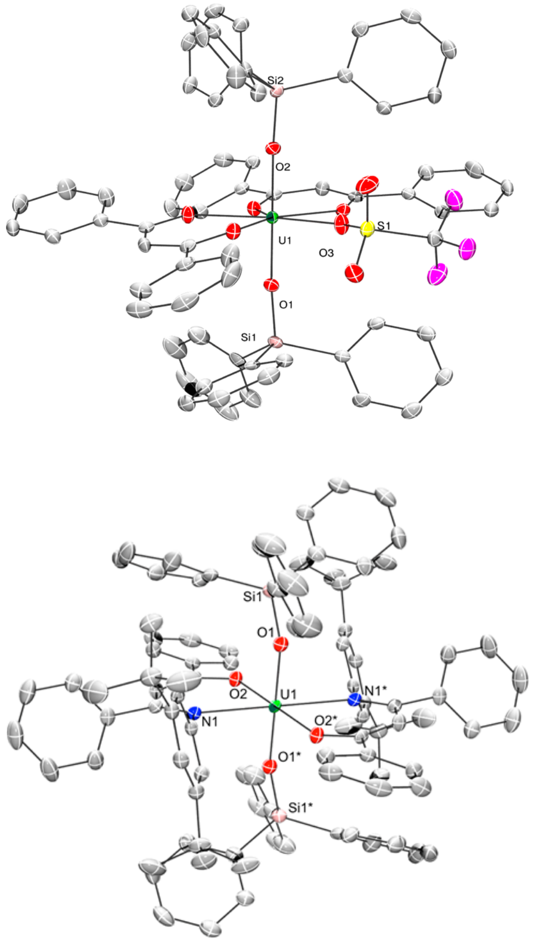

Figure 1. Solid-state structures of **1** (top) and **2**·THF (bottom) with 50% probability ellipsoids. For **1**, all H atoms have been removed for clarity. For **2**, all H atoms, one THF molecule, and the $[OTf]^-$ counterion have been removed for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1 and 2

	1	2
$U{-}O_{Si1}$	2.005(2)	2.044(2)
$U{-}O_{Si2}$	2.018(2)	
$U{-}O_{eq}$	2.246(2)	2.153(2)
	2.259(3)	
	2.261(2)	
	2.267(2)	
$U{-}O_{triflate}$	2.349(2)	
U−N		2.380(2)
O−Si1	1.669(2)	1.664(2)
O−Si2	1.668(2)	
O−U−O	178.81(8)	180.0
U−O−Si1	169.0(1)	164.8(1)
U−O−Si2	176.1(1)	

The ^1H NMR spectrum of **1** in CD_2Cl_2 features two broad resonances at 11.09 and 7.57 ppm, which are present in a 12:18 ratio, respectively, and which correspond to the three proton environments of the Ph_3Si groups (Figure S1 in the Supporting Information, SI). The ^1H NMR spectrum of **2** in CD_2Cl_2 features three broad resonances, at 9.78, −0.43, and −0.98 ppm, which correspond to the three proton environments of the Ph_3Si groups (Figure S10 in the SI). In addition, the presence of the ^{Ar}acnac ligand is confirmed by the observation of a broad singlet at −0.53 ppm, which is assignable to the ^{t}Bu groups of the ^{Ar}acnac moiety. The $^{19}F\{^1H\}$ NMR spectra of **1** and **2** each consist of a single resonance at −81.28 and −78.99 ppm, respectively, corresponding to the F atoms of the $[OTf]^-$ group (Figures S2 and S11 in the SI). The $^{29}Si\{^1H\}$ NMR spectrum of **1** consists of a broad resonance at 102.2 ppm (Figure S3 in the SI), which is similar to the chemical shifts reported for related uranium(V) silyloxides.[24] The ^{29}Si resonance for complex **2** was not observed. Finally, the near-IR spectra for **1** and **2** are similar to those of other uranium(V) complexes,[3,12−14,25−27] supporting the presence of a $5f^1$ ion in each complex (Figures S14 and S15 in the SI). Interestingly, the extinction coefficients for the f−f transitions of **2** are much weaker than those observed for **1**, consistent with the presence of an inversion center in the former.[28,29]

Both complexes **1** and **2** require 2 equiv of Ph_3SiOTf for their formation, but only 1 equiv of OTf is incorporated into the final product. Moreover, the identity of the reducing agent involved in the transformation is not immediately apparent. To probe these questions, we monitored the formation of **1** by ^1H NMR spectroscopy in toluene-d_8. The ^1H NMR spectrum of the reaction mixture reveals the formation of complex **1** and unreacted Ph_3SiOTf, along with small amounts of H(dbm) and unidentified products characterized by resonances at 8.22, 7.90, 6.93, and 6.85 ppm (Figures S7 and S8 in the SI).[30] These data suggest that, perhaps, the dbm ligand is sacrificially oxidized to generate the U^V center observed in the final product. The resulting dbm radical then undergoes further reactivity, such as abstracting a H atom from the solvent. To test this hypothesis, we recorded a ^{2}H NMR spectrum of the reaction mixture in CH_2Cl_2 (Figure S9 in the SI). However, this spectrum does not reveal ^{2}H incorporation in complex **1**, H(dbm), or the unidentified products. We also followed the formation of **1** by $^{19}F\{^1H\}$ NMR spectroscopy in CD_2Cl_2. The $^{19}F\{^1H\}$ NMR spectrum of this reaction mixture also reveals the formation of complex **1**, as indicated by a broad singlet at −81.16 ppm, along with the presence of unreacted Ph_3SiOTf, as indicated by a sharp singlet at −76.97 ppm. Three other triflate environments are also observed at −76.48, −77.02, and −77.65 ppm, but we have been unable to determine their identities (Figure S6 in the SI). Attempts to intercept a transiently formed dbm radical by performing the reaction in the presence of an easily oxidizable substrate, such as 1,4-cyclohexadiene,[31] or with a radical trap, such as 5,5-dimethyl-1-pyrroline-*N*-oxide,[32] have also been unsuccessful.

In summary, the reaction of $UO_2(dbm)_2(THF)$ and $UO_2(^{Ar}acnac)_2$ with 2 equiv of Ph_3SiOTf results in isolation of the reductive silylation products, **1** and **2**, respectively. Most notably, Ph_3SiOTf, unlike Ph_3SiH, is capable of effecting reductive silylation of uranyl without the addition of an exogenous Lewis acid activator. This observation can be rationalized by the increased electrophilicity of the Si center in Ph_3SiOTf versus Ph_3SiH, as evidenced by the ^{29}Si NMR resonance of Ph_3SiOTf (3.6 ppm),[33] which is downfield of that observed for Ph_3SiH (−21.1 ppm),[34] consistent with its greater silylium character.[35] Also of note, we previously reported that the reaction of $UO_2(^{Ar}acnac)_2$ with Me_3SiOTf did not result in reductive silylation. Instead, this reaction only resulted in formation of the product of ligand protonation, namely, $UO_2(OTf)_2(H\{^{Ar}acnac\})_2$.[3] This result is significant because it reveals the importance of the R_3Si- group in determining the outcome of the reductive silylation reaction.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, crystallographic details (in CIF format), and spectral data for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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