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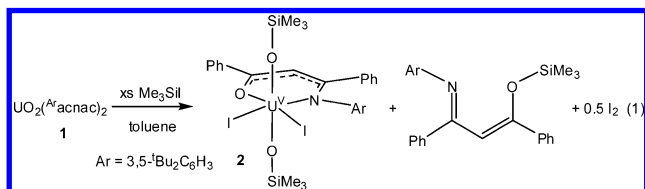
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The microbial reduction of the uranyl ion (UO_2^{2+}) to U(IV) is a vital component of the environmental remediation of legacy waste sites.^{1,2} This process requires the functionalization and/or substitution of the normally inert uranyl oxo ligands. However, there is little evidence available for the mechanism of reduction,^{3,4} and model systems are scarce.^{5,6} In one recent example, oxo ligand silylation in uranyl was achieved by deprotonation of $\text{UO}_2(\text{THF})(\text{H}_2\text{L})$ (L = "Pacmac" polypyrrolic macrocycle), ultimately resulting in the formation of a U(V) silyloxide complex $[\text{UO}(\text{OSiMe}_3)(\text{THF})\text{Fe}_2\text{I}_2\text{L}]$.⁷ During the reaction, an intermediate species, $\text{UO}_2(\text{THF})(\text{K}_2\text{L})$, is both reduced and silylated by $\text{HN}(\text{SiMe}_3)_2$ to generate the final product.^{8,9} The ability of $\text{HN}(\text{SiMe}_3)_2$ to act as a reducing agent in this system is surprising, given the relatively small oxidation potential of the uranyl ion (-0.35 V for $\text{UO}_2^{2+}(\text{aq})$ vs Fc/Fc^+).¹⁰ Herein we report the synthesis and characterization of a novel uranyl(V) *bis*-silyloxide complex, namely $\text{U}(\text{OSiMe}_3)_2\text{I}_2(\text{Aracnac})$, derived from the uranyl ion and Me_3SiI , and provide a redox-based rationale for why oxo ligand silylation occurs concomitant with uranyl reduction. Me_3SiX reagents have long been employed for oxo ligand substitution in transition metal synthesis,¹¹ but only one example is previously known for uranyl.¹²

Addition of excess Me_3SiI to $\text{UO}_2(\text{Aracnac})_2$ (**1**) (Aracnac = $\text{ArNC}(\text{Ph})\text{CHC}(\text{Ph})\text{O}$, Ar = $3,5\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3$) results in the formation of $\text{U}(\text{OSiMe}_3)_2\text{I}_2(\text{Aracnac})$ (**2**), which can be isolated from hexanes as a black crystalline solid in 42% yield (eq 1). Complex **2** is formed by concurrent reduction of the uranium center and silylation of *both* oxo ligands. Additionally, one of the Aracnac ligands is replaced by two iodide ligands. The ^1H NMR spectrum of **2** in $\text{tol-}d_8$ exhibits broad singlets at 0.63 ppm and 4.68 ppm, in a 1:1 ratio, assignable to the ^tBu and Me_3Si protons, respectively. Its NIR spectrum (see the Supporting Information) is similar to those observed for other U(V) compounds,^{13,14} supporting the presence of a $5f^1$ ion, while elemental analysis is also consistent with the proposed formulation. The reaction also proceeds in CH_2Cl_2 , but the isolated yields are lower.



The solid-state molecular structure of **2** is shown in Figure 1. Complex **2** exhibits a distorted octahedral geometry with a *trans* arrangement of the oxo-derived silyloxide ligands. Its U–O(SiMe_3) bond lengths (U1–O1 = 1.996(5) Å and U1–O2 = 1.986(5) Å) are significantly longer than a typical uranyl U–O(oxo) bond (ca. 1.76 Å) but are comparable to the U–O(SiMe_3) bond length observed in $[\text{UO}(\text{OSiMe}_3)(\text{THF})\text{Fe}_2\text{I}_2\text{L}]$ (1.993(4) Å).⁷ In addition, the O–Si bond lengths in **2** (O1–Si1 = 1.687(6) Å, O2–Si2 = 1.682(6) Å) are consistent with other oxo-derived silyloxides.^{15,16}

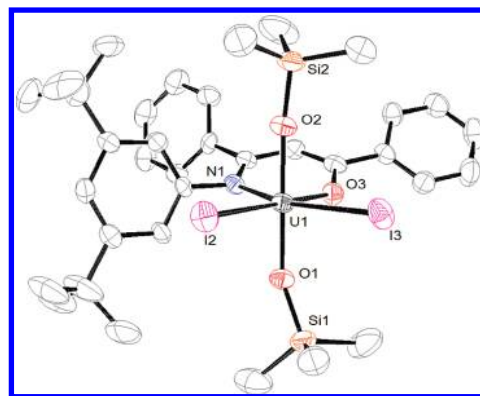


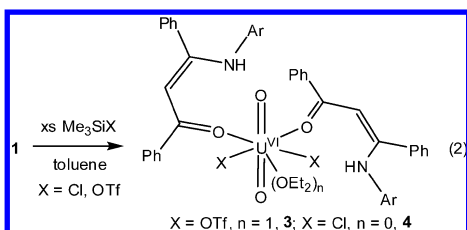
Figure 1. Molecular structure of $\text{U}(\text{OSiMe}_3)_2\text{I}_2(\text{Aracnac})$ (**2**) with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): U1–O1 = 1.996(5), U1–O2 = 1.986(5), U1–O3 = 2.154(5), U1–N1 = 2.379(7), U1–I2 = 2.9902(7), U1–I3 = 2.9863(7), O1–Si1 = 1.687(6), O2–Si2 = 1.682(6), O1–U1–O2 = 179.1(2).

To confirm the fate of the missing β -ketoiminate ligand in **2**, the reaction between **1** and Me_3SiI was followed by ^1H NMR spectroscopy. This revealed the generation of $\text{ArNC}(\text{Ph})\text{CHC}(\text{Ph})\text{OSiMe}_3$, the product of $[\text{Aracnac}]^-$ abstraction by Me_3Si^+ , during the formation of **2**. The spectral properties of $\text{ArNC}(\text{Ph})\text{CHC}(\text{Ph})\text{OSiMe}_3$ were corroborated by comparison with material prepared independently, via reaction of $\text{Na}(\text{Aracnac})$ with 1 equiv of Me_3SiCl (see the Supporting Information).

We have also endeavored to determine the identity of the reducing agent involved in the transformation. Previously, we had shown that coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ to an oxo ligand in **1** forms $\text{UO}(\text{OB}(\text{C}_6\text{F}_5)_3)(\text{Aracnac})_2$ and dramatically changes the uranyl reduction potential from -1.35 to -0.78 V (vs Fc/Fc^+).¹⁷ A similar effect may also be operative during formation of **2**; i.e., coordination of the strongly Lewis acidic Me_3Si^+ to the oxo ligands of **1** results in an increase of the $\text{U}^{6+}/\text{U}^{5+}$ oxidation potential. However, because of the inclusion of two Me_3Si^+ groups, the affect would be greater than that in the $\text{B}(\text{C}_6\text{F}_5)_3$ example. As a result, the $\text{U}^{6+}/\text{U}^{5+}$ redox potential may rise above that of I^-/I_2 , resulting in the oxidation of I^- and formation of iodine. To assess this hypothesis we performed the reaction of **1** with Me_3SiI in the presence of Ph_3P . The latter forms a phosphonium salt, Ph_3PI_2 , with I_2 ,¹⁸ which can be easily separated from the reaction mixture. Gratifyingly, the reaction of a mixture of **1** and Me_3SiI with Ph_3P leads to the rapid deposition of a yellow solid. This material was collected and identified as Ph_3PI_2 by comparison of its ^{31}P NMR and UV–vis spectra with the independently prepared material.¹⁸

To further probe the oxo ligand silylation of uranyl we investigated the reaction of **1** with other Me_3Si^+ sources. Addition of excess Me_3SiX (X = OTf, Cl) to **1** in toluene leads to the isolation of $\text{UO}_2(\text{OTf})_2(\text{AracnacH})_2(\text{Et}_2\text{O})$ (**3**) and $\text{UO}_2\text{Cl}_2(\text{AracnacH})_2$ (**4**), respectively, in moderate yields (eq 2). No evidence for the formation of an oxo functionalized complex was observed in any

of these transformations. Complexes **3** and **4** can also be prepared by reaction of **1** with triflic anhydride or SOCl_2 , respectively. Alternately, **3** and **4** can be synthesized simply by addition of 2 equiv of ($^{\text{Ar}}$ acnac)H to $\text{UO}_2(\text{OTf})_2$ or $\text{UO}_2\text{Cl}_2(\text{THF})_3$ (see the Supporting Information). The ^1H NMR spectra of **3** and **4** contain broad singlets at 13.02 ppm and 13.28 ppm, respectively, assignable to the amine proton of the ($^{\text{Ar}}$ acnac)H ligand. The solid-state molecular structure of **3** was determined by X-ray crystallography, demonstrating a pentagonal bipyramidal geometry about the uranium center and an η^1 binding mode for the two ($^{\text{Ar}}$ acnac)H ligands (see the Supporting Information). Also coordinated to the uranyl equatorial plane are two OTf^- anions and a molecule of diethyl ether.

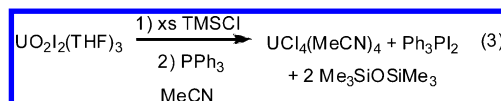


The NH protons in complexes **3** and **4** are probably derived from solvent decomposition, which may occur via Friedel–Crafts silylation.¹⁹ This subsequently generates the required equivalent of HX. This unwanted reaction pathway is probably also occurring during the formation of **2**, as at longer reaction times a broad singlet at 13.14 ppm is observed in the ^1H NMR spectrum of the crude reaction mixture. This resonance is assignable to the amine proton of the ($^{\text{Ar}}$ acnac)H ligand in $\text{UO}_2\text{I}_2(\text{Ar}^{\text{acnac}}\text{H})_2$ (**5**). However, this is only a minor pathway, and **5** is not formed in significant amounts. Complex **5** can also be made by addition of 2 equiv of $\text{H}(\text{Ar}^{\text{acnac}})$ to $\text{UO}_2\text{I}_2(\text{THF})_3$, facilitating its complete characterization.

The difference in reaction outcomes between Me_3SiI and Me_3SiX ($\text{X} = \text{OTf}, \text{Cl}$) probably derives from the reducing ability of the anion, which is greatest for I^- . However, the relative strengths of the Si–X bonds may also play a role. In particular, the bond dissociation energies (BDEs) of the Si–Cl bond (113 kcal/mol in Me_3SiCl) or the Si–O bond (e.g., 123 kcal/mol in Me_3SiOMe) are much larger than the Si–I BDEs in Me_3SiI (77 kcal/mol).^{20,21} The formation of a strong Si–O bond is also a factor in driving the formation of **2**, as no reaction is observed between **1** and MeI ($\text{C–I} = 55$ kcal/mol).²² To further explore the importance of BDEs we also reacted complex **1** with $\text{Me}_3\text{SiSiMe}_3$ ($\text{Si–Si} = 81$ kcal/mol), $\text{Ph}_3\text{Si–H}$ (Si–H , 89 kcal/mol), and $\text{Et}_3\text{Si–H}$ (Si–H , 92 kcal/mol).²⁰ However, according to ^1H NMR spectroscopy, no reaction occurred with these substrates, which is unexpected given that R_3SiH is anticipated to be a better reducing agent than Me_3SiI .

Finally, we have revisited the preparation of $\text{UX}_4(\text{MeCN})_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) via addition of Me_3SiX to $\text{UO}_2\text{I}_2(\text{THF})_3$ (eq 3), which was first reported by Ephritikhine and co-workers.¹² We hypothesized that this transformation proceeded in a manner analogous to the formation of **2** and that iodine was generated as a byproduct. To test for I_2 formation, Ph_3P was added to the supernatant produced by the reaction of Me_3SiCl with $\text{UO}_2\text{I}_2(\text{THF})_3$. This led to the isolation of a yellow powder, which was identified as Ph_3PI_2 by ^{31}P NMR spectroscopy (eq 3), confirming the generation of I_2 during the formation of UCl_4 . Thus it seems likely that $\text{UCl}_4(\text{MeCN})_4$ is

formed via a silyloxide intermediate similar to **2**. The fate of the uranyl oxo ligands was not determined, but they are probably converted into $\text{Me}_3\text{SiOSiMe}_3$.²³



In conclusion, we report that oxo functionalization of a uranyl(VI) complex with Me_3SiI is concomitant with oxidation of I^- and formation of a U^{5+} center. It appears that coordination of Me_3Si^+ to the uranyl oxo ligand decreases the uranium reduction potential, making the U^{6+} a better oxidant. The modulation of the $\text{U}^{6+}/\text{U}^{5+}$ redox potential by oxo functionalization may explain previous uranyl silylation chemistry, in particular the results of Arnold and co-workers who invoke a K^+ -functionalized uranyl complex during the reductive silylation of $\text{UO}_2(\text{THF})(\text{H}_2\text{L})$.⁷ Most importantly, reductive silylation appears to be a general phenomenon for the uranyl ion, and further study of this transformation could lead to novel treatment strategies for uranium-contaminated soil and groundwater.

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Supporting Information Available: X-ray crystallographic details (CIF) of **2** and **3**; IR spectra for **2–5**; UV/vis spectra of **2** and Ph_3PI_2 ; NMR spectra for complexes **2–5**, complete refs 1 and 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Wu, W.-M. *Environ. Sci. Technol.* **2006**, *40*, 3978–3985.
- (2) Wu, W.-M. *Environ. Sci. Technol.* **2006**, *40*, 3986–3995.
- (3) Renshaw, J. C.; Butchins, L. J. C.; Livens, F. R.; May, I.; Charnock, J. M.; Lloyd, J. R. *Environ. Sci. Technol.* **2005**, *39*, 5657–5660.
- (4) Sundararajan, M.; Campbell, A. J.; Hillier, I. H. *J. Phys. Chem. A* **2008**, *112*, 4451–4457.
- (5) Fortier, S.; Hayton, T. W. *Coord. Chem. Rev.* **2010**, *254*, 197–214.
- (6) Schnaars, D. D.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2009**, *131*, 17532–17533.
- (7) Arnold, P. L.; Patel, D.; Wilson, C.; Love, J. B. *Nature* **2008**, *451*, 315–317.
- (8) Arnold, P. L.; Love, J. B.; Patel, D. *Coord. Chem. Rev.* **2009**, 1973–1978.
- (9) Yahia, A.; Arnold, P. L.; Love, J. B.; Maron, L. *Chem. Commun.* **2009**, 2402–2404.
- (10) Morss, L. R.; Edelstein, N. M.; Fuger, J.; Katz, J. J., Eds. *The Chemistry of the Actinide and Transactinide Elements*; Springer: 2006.
- (11) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1989.
- (12) Berthet, J.-C.; Siffredi, G.; Thuery, P.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2007**, 4017–4020.
- (13) Graves, C. R.; Vaughn, A. E.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Morris, D. E.; Kiplinger, J. L. *Inorg. Chem.* **2008**, *47*, 11879–11891.
- (14) Ryan, J. L. *J. Inorg. Nucl. Chem.* **1971**, *33*, 153–177.
- (15) Money, J. K.; Folting, K.; Huffman, J. C.; Collison, D.; Temperley, J.; Mabbs, F. E.; Christou, G. *Inorg. Chem.* **1986**, *25*, 4583–4589.
- (16) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1831–1838.
- (17) Hayton, T. W.; Wu, G. *Inorg. Chem.* **2009**, *48*, 3065–3072.
- (18) Bricklebank, N.; Godfrey, S. M.; Mackie, A. G.; McAuliffe, C. A.; Pritchard, R. G.; Kobryn, P. J. *J. Chem. Soc., Dalton Trans.* **1993**, 101–103.
- (19) Olah, G. A.; Bach, T.; Prakash, G. K. S. *J. Org. Chem.* **1989**, *54*, 3770–3771.
- (20) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246–252.
- (21) Becerra, R.; Walsh, R. Thermochemistry. In *The chemistry of organic silicon compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, U.K., 1998; Vol. 2, pp 153–180.
- (22) deB Darwent, B. *Nat. Stand. Ref. Data Ser.* **1970**, *31*, 1–48.
- (23) Gibson, V. C.; Kee, T. P.; Shaw, A. *Polyhedron* **1988**, *7*, 579–580.

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