J|A|C|S COMMUNICATIONS

Oxo Ligand Silylation in a Uranyl β-Ketoiminate Complex

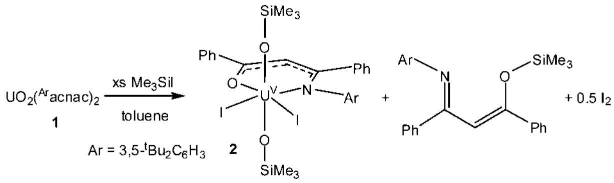
Jessie L. Brown, Guang Wu, and Trevor W. Hayton*

Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106

Received February 16, 2010; E-mail: hayton@chem.ucsb.edu

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 $UO_2(THF)(H_2L)$ (L = "Pacmac" polypyrrolic macrocycle), ultimately resulting in the formation of a U(V) silyloxide complex $[UO(OSiMe_3)(THF)Fe_2I_2L]$.[7] During the reaction, an intermediate species, $UO_2(THF)(K_2L)$, is both reduced and silylated by $HN\{SiMe_3\}_2$ to generate the final product.[8,9] The ability of $HN\{SiMe_3\}_2$ 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 UO_2^{2+}(aq) vs Fc/Fc^+).[10] Herein we report the synthesis and characterization of a novel uranyl(V) *bis*-silyloxide complex, namely $U(OSiMe_3)_2I_2(^{Ar}acnac)$, 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 $UO_2(^{Ar}acnac)_2$ (**1**) ($^{Ar}acnac$ = Ar*N*C(Ph)CHC(Ph)*O*, Ar = 3,5-$^tBu_2C_6H_3$) results in the formation of $U(OSiMe_3)_2I_2(^{Ar}acnac)$ (**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 $^{Ar}acnac$ ligands is replaced by two iodide ligands. The ^1H NMR spectrum of **2** in 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.



(1)

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 $[UO(OSiMe_3)(THF)Fe_2I_2L]$ (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]

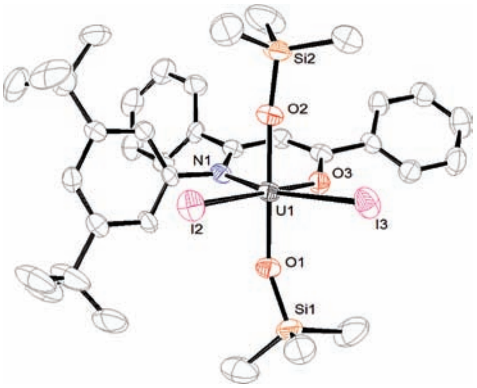


Figure 1. Molecular structure of $U(OSiMe_3)_2I_2(^{Ar}acnac)$ (**2**) with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): U1−O1 = 1.996(5), U1−O2 = 1.986(5), U1−O3 = 2.154(5), U1−N1 = 2.379(7), U1−I2 = 2.9902(7), U1−I3 = 2.9863(7), O1−Si1 = 1.687(6), O2−Si2 = 1.682(6), O1−U1−O2 = 179.1(2).

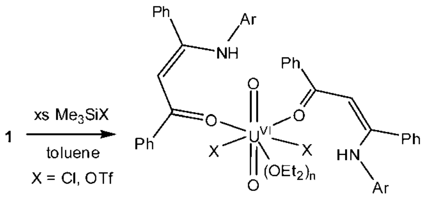
To confirm the fate of the missing β-ketoiminate ligand in **2**, the reaction between **1** and Me_3SiI was followed by ^1H NMR spectroscopy. This revealed the generation of ArNC(Ph)CHC(Ph)$OSiMe_3$, the product of $[^{Ar}acnac]^-$ abstraction by Me_3Si^+, during the formation of **2**. The spectral properties of ArNC(Ph)CHC(Ph)$OSiMe_3$ were corroborated by comparison with material prepared independently, via reaction of $Na(^{Ar}acnac)$ 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 $B(C_6F_5)_3$ to an oxo ligand in **1** forms $UO(OB\{C_6F_5\}_3)(^{Ar}acnac)_2$ 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 U^{6+}/U^{5+} oxidation potential. However, because of the inclusion of two Me_3Si^+ groups, the affect would be greater than that in the $B(C_6F_5)_3$ example. As a result, the U^{6+}/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 $UO_2(OTf)_2(^{Ar}acnacH)_2(Et_2O)$ (**3**) and $UO_2Cl_2(^{Ar}acnacH)_2$ (**4**), respectively, in moderate yields (eq 2). No evidence for the formation of an oxo functionalized complex was observed in any

10.1021/ja1013739

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 $(^{Ar}acnac)H$ to $UO_2(OTf)_2$ or $UO_2Cl_2(THF)_3$ (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 $(^{Ar}acnac)H$ 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 $(^{Ar}acnac)H$ ligands (see the Supporting Information). Also coordinated to the uranyl equatorial plane are two OTf^- anions and a molecule of diethyl ether.



(2)

X = OTf, n = 1, **3**; X = Cl, n = 0, **4**

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 $(^{Ar}acnac)H$ ligand in $UO_2I_2(^{Ar}acnacH)_2$ (**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 $H(^{Ar}acnac)$ to $UO_2I_2(THF)_3$, facilitating its complete characterization.

The difference in reaction outcomes between Me_3SiI and Me_3SiX (X = OTf, 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 (C–I = 55 kcal/mol).[22] To further explore the importance of BDEs we also reacted complex **1** with $Me_3SiSiMe_3$ (Si–Si = 81 kcal/mol), $Ph_3Si{-}H$ (Si–H, 89 kcal/mol), and $Et_3Si{-}H$ (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 $UX_4(MeCN)_4$ (X = Cl, Br, I) via addition of Me_3SiX to $UO_2I_2(THF)_3$ (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 $UO_2I_2(THF)_3$. 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 $UCl_4(MeCN)_4$ 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 $Me_3SiOSiMe_3$.[23]

$$UO_2I_2(THF)_3 \xrightarrow[\text{2) }PPh_3\text{, MeCN}]{\text{1) xs TMSCl}} UCl_4(MeCN)_4 + Ph_3PI_2 + 2\,Me_3SiOSiMe_3 \qquad (3)$$

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+} ion a better oxidant. The modulation of the U^{6+}/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 $UO_2(THF)(H_2L)$.[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.

Acknowledgment. We thank the University of California, Santa Barbara and the Department of Energy (BES Heavy Element Program) for financial support of this work.

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.

JA1013739