Inorganic Chemistry
Communication
pubs.acs.org/IC

# Tetrakis(bis(trimethylsilyl)amido)uranium(IV): Synthesis and Reactivity

Andrew J. Lewis, Ursula J. Williams, Patrick J. Carroll, and Eric J. Schelter*

P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104, United States

Supporting Information

**ABSTRACT:** The synthesis of the sterically saturated uranium(IV) complex U[N(SiMe$_3$)$_2$]$_4$ (**1**) is demonstrated from the one-electron oxidation of U[N(SiMe$_3$)$_2$]$_3$ with a variety of oxidants in THF. A high yielding synthesis of **1** directly from UI$_3$(THF)$_4$ is provided.

Directing structure and reactivity in synthetic uranium complexes has relied heavily on the stabilization provided by steric protection.[1] In fact, much of the development in low valent uranium chemistry can be attributed to the facile synthesis of sterically saturated U[N(SiMe$_3$)$_2$]$_3$,[2] a ubiquitous starting material that has led to numerous recent discoveries in coordination and reduction chemistry.[3] Herein, we report the synthesis of U[N(SiMe$_3$)$_2$]$_4$, a stable complex that we have observed as a recurring product in the redox chemistry of U[N(SiMe$_3$)$_2$]$_3$. The title compound is a rare example of a complex comprising four bis(trimethylsilyl)amide ligands. We expect that the identification of U[N(SiMe$_3$)$_2$]$_4$ will be useful to the investigation of redox chemistry for this important ligand framework.

In the course of investigating the one-electron oxidation chemistry of U[N(SiMe$_3$)$_2$]$_3$,[3m] we noted a persistent side product by $^1$H NMR at −3.2 ppm in $d_6$-benzene, particularly when these reactions were carried out in THF. Furthermore, attempts to generate a cationic uranium(IV) complex in THF repeatedly led to the rapid catalytic polymerization of the solvent, in which the $^1$H NMR spectrum displayed *poly*-THF and the resonance at −3.2 ppm as the sole products. Extraction of this mixture with a 1:4 mixture of Et$_2$O/hexanes and crystallization at −21 °C allowed for an initial isolation of U[N(SiMe$_3$)$_2$]$_4$ (**1**) in low yield (Figure 1).

The crystal structure of **1** revealed a pseudotetrahedral coordination environment. Within each uranium-amide linkage, the two U−N−Si angles differ by ~12°. Comparison of the average U−N bond lengths in **1** of 2.297(2) Å with the reported structure of [K(THF)$_6$][U[N(SiMe$_3$)$_2$]$_4$] (**1-K**) of 2.432(7)[4] shows a difference of 0.135 Å. This difference is the same as the difference in ionic radii of six-coordinate uranium(III) and uranium(IV) ions.[5] Similar data are not available for a coordination number of four, but the difference is expected to be comparable. Also, the U−N bond lengths in **1** are only slightly longer than the average U−N bond lengths in U[N(SiMe$_2$H)$_2$]$_4$ of 2.281(5).[6] Therefore, the steric crowding enforced by the four amide ligands is not so substantial that it restricts U−N bonding.

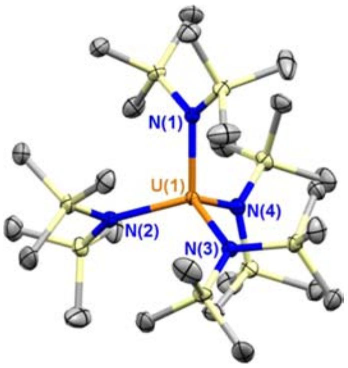
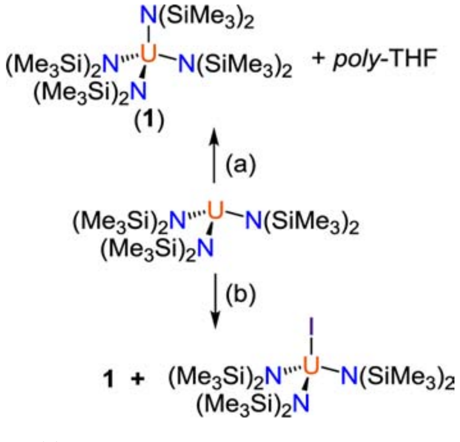


**Figure 1.** Thermal ellipsoid plot of **1** at 30% probability. Hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (deg): U(1)−N(1), 2.2941(17); U(1)−N(2), 2.2958(17); U(1)−N(3), 2.2977(17); U(1)−N(4), 2.3013(17); N(1)−U(1)−N(2), 111.12(6); N(1)−U(1)−N(3), 106.18(6); N(1)−U(1)−N(4), 111.72(6).

U[N(SiMe$_3$)$_2$]$_3$ reacted with AgBF$_4$, [TEMPO][BF$_4$], AgPF$_6$, FcPF$_6$, or [Ph$_3$C][PF$_6$] in THF to produce **1** in low yields (Scheme 1). Oxidants containing the noncoordinating anions BF$_4^-$ and PF$_6^-$ produced **1** almost immediately and

**Scheme 1. Oxidation Reactions of U[N(SiMe$_3$)$_2$]$_3$ to Form 1 That Proceeded in Low Yields**[a]



[a]Conditions: (a) THF, AgBF$_4$ or [TEMPO][BF$_4$] or AgPF$_6$ or FcPF$_6$ or [Ph$_3$C][PF$_6$]. (b) THF, CuI or AgI or I$_2$ or HgI$_2$.

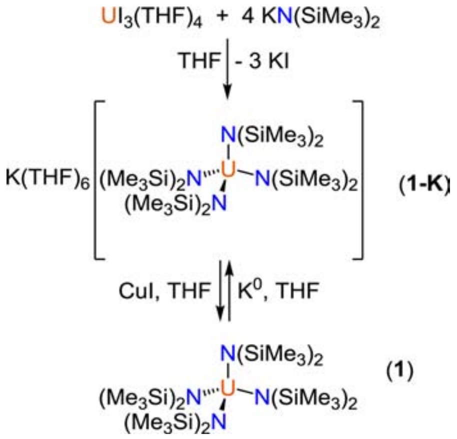
**Received:** May 11, 2013
**Published:** June 7, 2013

polymerized the solvent at varying rates, typically leading to solidification of the reaction mixture within 30 min to 1 h. $PF_5$,[7] and to a lesser extent $BF_3$,[8] are capable of initiating the ring-opening polymerization of THF, however we observed THF polymerization even when we did not detect the expected fluorine abstraction product $UF[N(SiMe_3)_2]_3$.[9] The formation of **1** under these conditions is attributed to ligand redistribution.

Unlike the oxidants comprising the noncoordinating $BF_4^-$ and $PF_6^-$ anions, iodide-based oxidants, including CuI, AgI, $I_2$, and $HgI_2$, generated a mixture of **1** and $UI[N(SiMe_3)_2]_3$,[10] which were in practice inseparable. This product distribution is attributed to the reaction of the iodide-based reagents as either inner sphere or outer sphere oxidants. An inner sphere oxidation pathway would form the uranium(IV)-iodide complex while the outer sphere oxidation leads to the formation of **1** through ligand redistribution.

Since the synthesis of **1** through oxidative ligand-redistribution proceeded in inherently low yield, we pursued a more rational approach. We reasoned that direct oxidation of **1-K** would provide a convenient pathway for the synthesis of **1** (Scheme 2). The synthesis of **1-K** has been previously reported through the reduction of $U[N(SiMe_3)_2]_3$ with $KC_8$ in THF under $N_2$; however, no yield was provided for **1-K**.[4] The addition of 4 equiv of $KN(SiMe_3)_2$ to $UI_3(THF)_4$ in THF led to the formation of **1-K** as the sole uranium containing product, which was easily separated due to its high solubility in pentane, allowing for its isolation in 76% yield. Importantly, no evidence for a cyclometalated product was observed in this reaction.

**Scheme 2. Stepwise Synthesis of 1 and 1-K**



Variable amide coordination with different alkali-metal salts of the $N(SiMe_3)_2^-$ ligand has been observed previously in the synthesis of uranyl complexes.[11] The $^1H$ NMR spectrum of **1-K** displayed variable peak positions among different samples, which prompted further investigation. The $-SiMe_3$ protons appeared between −6 and −10 ppm in $C_6D_6$, and a varying amount of $KN(SiMe_3)_2$ was observed from solutions of **1-K**. Interestingly, exposure of solid **1-K** to a dynamic vacuum for several hours resulted in complete conversion to $U[N(SiMe_3)_2]_3$ and $KN(SiMe_3)_2$ with a loss of the associated THF resonances.

The direct oxidation of **1-K** with a mild oxidant such as CuI led to quantitative formation of **1**. Conversely, the reaction of **1** with $K^0$ in THF produced **1-K**. The CuI oxidation of **1-K** formed *in situ* from $UI_3(THF)_4$ allowed for the direct one-pot synthesis of **1** in 94% yield. We also attempted to prepare **1** directly from a uranium(IV) precursor. The reaction of $UCl_4$ with 4 equiv of $NaN(SiMe_3)_2$ is reported to form the metallacycle $U[N(SiMe_3)_2]_2(CH_2SiMe_2NSiMe_3)$ (**2**).[12] In our hands no evidence for the formation of **1** was observed under these reaction conditions. We also attempted the reaction of $UI_4(OEt_2)_2$ with 4 equiv of $NaN(SiMe_3)_2$, which also rapidly produced **2** without the formation of **1**, as judged by $^1H$ NMR spectroscopy. In contrast, the reaction of $UI_4(OEt_2)_2$ with 4 equiv of $KN(SiMe_3)_2$ generated an approximately equimolar mixture of **1** and **2**, as judged by $^1H$ NMR, that was not easily separated.

The steric bulk provided by the four bis(trimethylsilylamide) ligands prevents further reactivity at the metal center in **1**. Notably, cyclometalation to form **2** through the loss of $HN(SiMe_3)_2$ was not observed at room temperature, though complete conversion to form **2** was observed after refluxing **1** in toluene for 2 h. We may therefore reasonably rule out **1** as an intermediate in the room temperature formation of **2**.[13] It was recently shown that $U[N(SiMe_3)_2]_3$ slowly disproportionates in arene solvent to form $\{U[N(SiMe_3)_2]_2\}_2(\mu{-}\eta^6{:}\eta^6\text{-arene})$ and **2**.[3n] On the basis of our observations, it is likely that **1** initially forms in this reaction, then converts into **2** upon heating. In this context, DFT calculations were performed to assess the relative stability of **1** and **2**. Indeed, the conversion of **1**→**2** was found to be exothermic, with $\Delta G_{rxn} = -38.9$ kcal/mol (see Supporting Information for details).

Despite the strong thermodynamic driving force for cyclometalation, experimentally the stability of **1** was greater than anticipated. For example, exposing a solution of **1-K** to air led to immediate formation of **1** as judged by $^1H$ NMR. A $CDCl_3$ solution of **1** left open to ambient atmosphere was quite stable and exhibited approximately 50% decomposition to $HN(SiMe_3)_2$ over the course of 24 h, indicating that the complex decomposes only slowly in the presence of water but is stable to oxygen. Additionally, **1** was found to be stable on alumina. Although not strictly necessary given the high yield on recrystallization of **1** from pentane, it is remarkable that the use of flash chromatography through alumina is a viable means of purification of the complex.

The high stability of **1** and its persistence as a product of the redox chemistry of $U[N(SiMe_3)_2]_3$ prompted us to perform complete characterization of the complex (see Supporting Information for details). Electrochemical measurements were carried out on **1** to assess its redox stability (Figure S1). In the cyclic voltammogram of **1** performed in $CH_3CN$, two sets of waves were observed, assigned to the $U^{V/IV}$ couple at +0.49 V and the $U^{IV/III}$ couple at −2.05 V versus $Fc/Fc^+$. The $U^{IV/III}$ reduction potential is shifted to a more negative potential than the reported $U^{IV/III}$ couple of $U[N(SiMe_3)_2]_3$ at −1.24 V,[14] consistent with the greater stabilization of the uranium(IV) oxidation state upon coordination of a fourth amide ligand. Despite the electrochemically accessible 5+ oxidation state, none of the oxidants that were used to produce **1** further oxidized the complex. Attempts to collect electrochemical data on **1-K** were hindered by the poor stability of the complex under the conditions of the experiment. Temperature dependent magnetic susceptibility measurements carried out on **1** yielded a room temperature moment $\mu_{eff} = 2.94\ \mu_B$ (Figure 2, top). The data showed a substantial decrease in the moment at low temperature and no saturation of the moment in the field dependent measurement at 2 K, features characteristic of a uranium(IV) ion.[15] The near-IR spectrum of **1** in toluene

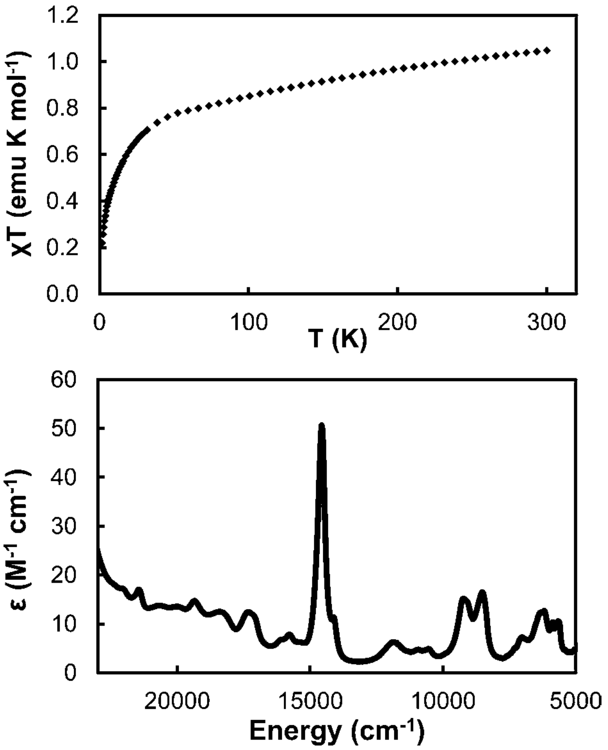


**Figure 2.** Temperature dependent magnetic behavior of **1** at an applied field of 2 T (top) and near-IR spectrum of **1** as a 59.5 mM solution in toluene (bottom).

exhibited numerous transitions within a 5f state manifold (Figure 2, bottom).[16] Together the characterization data are consistent with signatures of a 5f$^2$ uranium(IV) ion.

In conclusion, we have demonstrated the synthesis of the homoleptic uranium(IV) amide complex U[N(SiMe$_3$)$_2$]$_4$ through a rational synthetic route and as a common product to various oxidation reactions. The compound is a rare example of a coordination environment with four bis(trimethylsilylamide) ligands at a single metal ion. We expect the characterization data for the complex will be of interest given the ubiquitous use of U[N(SiMe$_3$)$_2$]$_3$ in uranium chemistry.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Synthetic details and characterization, electrochemical data, UV−vis data, magnetism data, and X-ray crystal structure data (.cif). This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: schelter@sas.upenn.edu.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

E.J.S. acknowledges the University of Pennsylvania for financial support. We thank the U.S. National Science Foundation for support of the X-ray diffractometer used in this work (CHE-0840438). This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number OCI-1053575. We thank Prof. Christopher R. Graves (Albright College) for helpful discussion.

## ■ REFERENCES

(1) (a) Castro-Rodriguez, I.; Nakai, H.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *Science* **2004**, *305*, 1757. (b) Lam, O. P.; Anthon, C.; Meyer, K. *Dalton Trans.* **2009**, 9677. (c) King, D. M.; Tuna, F.; McInnes, E. J. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Science* **2012**, *337*, 717. (d) King, D. M.; Tuna, F.; McInnes, E. J.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Nat. Chem.* **2013**, *5*, 482.

(2) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1507.

(3) (a) Zalkin, A.; Brennan, J. G.; Andersen, R. A. *Acta Crystallogr., Sect. C* **1988**, *44*, 1553. (b) Burns, C. J.; Smith, W. H.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 3237. (c) Berg, J. M.; Clark, D. L.; Huffman, J. C.; Morris, D. E.; Sattelberger, A. P.; Streib, W. E.; Van der Sluys, W. G.; Watkin, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 10811. (d) Clark, D. L.; Miller, M. M.; Watkin, J. G. *Inorg. Chem.* **1993**, *32*, 772. (e) Stewart, J. L.; Andersen, R. A. *New J. Chem.* **1995**, *19*, 587. (f) Nakai, H.; Hu, X.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *Inorg. Chem.* **2004**, *43*, 855. (g) Roger, M.; Barros, N.; Arliguie, T.; Thuéry, P.; Maron, L.; Ephritikhine, M. *J. Am. Chem. Soc.* **2006**, *128*, 8790. (h) Fortier, S.; Wu, G.; Hayton, T. W. *Dalton Trans.* **2010**, *39*, 352. (i) Fortier, S.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2010**, *132*, 6888. (j) Arnold, P. L.; Turner, Z. R.; Bellabarba, R. M.; Tooze, R. P. *Chem. Sci.* **2011**, *2*, 77. (k) Fortier, S.; Kaltsoyannis, N.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2011**, *133*, 14224. (l) Fortier, S.; Walensky, J. R.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2011**, *133*, 6894. (m) Lewis, A. J.; Nakamaru-Ogiso, E.; Kikkawa, J. M.; Carroll, P. J.; Schelter, E. J. *Chem. Commun.* **2012**, *48*, 4977. (n) Arnold, P. L.; Mansell, S. M.; Maron, L.; McKay, D. *Nat. Chem.* **2012**, *4*, 668.

(4) Evans, W. J.; Lee, D. S.; Rego, D. B.; Perotti, J. M.; Kozimor, S. A.; Moore, E. K.; Ziller, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 14574.

(5) Shannon, R. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(6) Mansell, S. M.; Perandones, B. F.; Arnold, P. L. *J. Organomet. Chem.* **2010**, *695*, 2814.

(7) Sims, I. D. *J. Chem. Soc.* **1964**, 864.

(8) Burrows, R. C.; Crowe, B. F. *J. Appl. Polym. Sci.* **1962**, *6*, 465.

(9) Stewart, J. L. *Tris[bis(trimethylsilyl)amido]uranium: compounds with tri-, tetra-, and pentavalent uranium*; Lawrence Berkeley National Laboratory: Berkeley, CA, 1988.

(10) Fortier, S.; Brown, J. L.; Kaltsoyannis, N.; Wu, G.; Hayton, T. W. *Inorg. Chem.* **2012**, *51*, 1625.

(11) Burns, C. J.; Clark, D. L.; Donohoe, R. J.; Duval, P. B.; Scott, B. L.; Tait, C. D. *Inorg. Chem.* **2000**, *39*, 5464.

(12) (a) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991. (b) Dormond, A.; El Bouadili, A.; Aaliti, A.; Moise, C. *J. Organomet. Chem.* **1985**, *288*, C1. (c) Bénaud, O.; Berthet, J.-C.; Thuéry, P.; Ephritikhine, M. *Inorg. Chem.* **2010**, *49*, 8117.

(13) Kaltsoyannis, N.; Scott, P. *The f Elements*; Oxford University Press: Oxford, U. K.,1999.

(14) Avens, L. R.; Barnhart, D. M.; Burns, C. J.; McKee, S. D.; Smith, W. H. *Inorg. Chem.* **1994**, *33*, 4245.

(15) (a) Castro-Rodriguez, I.; Olsen, K.; Gantzel, P.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 4565. (b) Lewis, A. J.; Williams, U. J.; Kikkawa, J. M.; Carroll, P. J.; Schelter, E. J. *Inorg. Chem.* **2012**, *51*, 37.

(16) (a) Roussel, P.; Alcock, N. W.; Boaretto, R.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Scott, P. *Inorg. Chem.* **1999**, *38*, 3651. (b) Yin, H.; Lewis, A. J.; Williams, U. J.; Carroll, P. J.; Schelter, E. J. *Chem. Sci.* **2013**, *4*, 798.