JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
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Synthesis of Uranium–Ligand Multiple Bonds by Cleavage of a Trityl Protecting Group

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Supporting Information

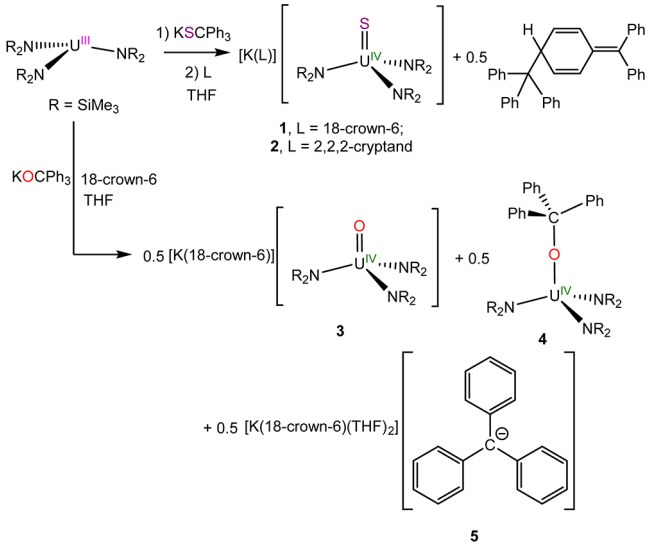
ABSTRACT: Addition of $KSCPh_3$ to $[U(NR_2)_3]$ (R = $SiMe_3$) in tetrahydrofuran, followed by addition of 18-crown-6, results in formation of the U(IV) sulfide, $[K(18\text{-crown-6})][U(S)(NR_2)_3]$ (**1**) and Gomberg's dimer. Similarly, addition of $KOCPh_3$ to $[U(NR_2)_3]$ in tetrahydrofuran, followed by addition of 18-crown-6, results in formation of the U(IV) oxide, $[K(18\text{-crown-6})][U(O)(NR_2)_3]$ (**3**). Also observed in this transformation are the triphenylmethyl anion, $[K(18\text{-crown-6})(THF)_2][CPh_3]$ (**5**), and the U(IV) alkoxide, $[U(OCPh_3)(NR_2)_3]$ (**4**).

There is significant interest in the synthesis and study of complexes with actinide–ligand multiple bonds, due in part to the need for a better understanding of covalency and f-orbital participation in actinide–ligand bonding.[1−6] Recently, significant progress has been made toward the synthesis and characterization of f-element oxos,[7−10] imidos,[11−15] and nitridos.[16−19] Despite this progress, however, there still exist several unanswered challenges in the synthesis of actinide–ligand multiple bonds. For example, alkylidene and phosphido complexes of the actinides remain unknown, despite several attempts toward their isolation.[20,21] In addition, only a few terminal chalcogenido (E = S, Se, Te) complexes are known, and their isolated yields are often low.[22−24] This suggests that new methods for the installation of these functional groups are needed to permit the further development of this field.

The triphenylmethyl (trityl) moiety is a common protecting group for alcohols, thiols, and amines in organic synthesis.[25] Selective removal of the trityl group is possible using a variety of conditions, including reductive cleavage with Li/naphthalene in THF.[26,27] Yet, while relatively common in organic chemistry, there are only a few instances of the trityl protecting group being used as a leaving group in inorganic synthesis.[28] For example, Kitajima and co-workers reported the formation of a bimetallic Cu(II) disulfide, $[Tp'Cu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2)$ (Tp′ = $HB(3,5\text{-}^iPr_2pz)_3$), along with formation of Gomberg's dimer[29,30] via thermal C–S bond homolysis in a Cu(I) trityl–thiolate complex, $[Tp'Cu(SCPh_3)]$.[31] Riordan and co-workers reported the formation of a Ni(II) $\mu\text{-}\eta^2\text{:}\eta^2$ disulfide by a similar procedure.[32]

Inspired by the results of the Kitajima and Riordan groups, we explored the use of trityl as a leaving group for actinide–ligand multiple bond formation. Thus, addition of 1 equiv of $KSCPh_3$ to a cold (−25 °C) solution of $[U(NR_2)_3]$ (R = $SiMe_3$) in tetrahydrofuran-d_8 results in an immediate color change from dark purple to vibrant orange. The ^1H NMR spectrum of the reaction mixture displays a broad resonance at −2.48 ppm assignable to a new uranium(IV) sulfide complex, in addition to resonances at 5.21, 5.98, and 6.23 ppm, assignable to the allylic and vinylic protons of Gomberg's dimer (Figure S1 in Supporting Information [SI]).[33] On a preparative scale, reaction of $KSCPh_3$ with $[U(NR_2)_3]$, followed by addition of 18-crown-6, affords $[K(18\text{-crown-6})][U(S)(NR_2)_3]$ (**1**) as yellow-orange blocks in 48% yield after crystallization from diethyl ether (Scheme 1). Similarly,

Scheme 1



utilization of 2,2,2-cryptand in place of 18-crown-6 affords $[K(2,2,2\text{-cryptand})][U(S)(NR_2)_3]$ (**2**) as yellow-orange needles in 45% yield after crystallization (Scheme 1). Notably, in a related transformation Arnold and co-workers showed that oxidation of $[U(NR_2)_3]$ with $ClCPh_3$ also resulted in Gomberg's dimer formation, along with the U(IV) chloride, $[U(Cl)(NR_2)_3]$.[34]

The connectivities of complexes **1** and **2** were verified by X-ray crystallography (Figures 1 and S27; see SI for complete structural details of complex **2**). Complex **1** crystallizes with two molecules in the asymmetric unit, one of which is omitted for clarity. In both complexes, the $[U(S)(NR_2)_3]^-$ anion features a pseudotetrahedral geometry, similar to that observed previously for this moiety.[23] Also of note, the sulfide ligand in **1**

Received: November 8, 2013
Published: December 18, 2013

   dx.doi.org/10.1021/ja411423a | J. Am. Chem. Soc. 2014, 136, 96–99

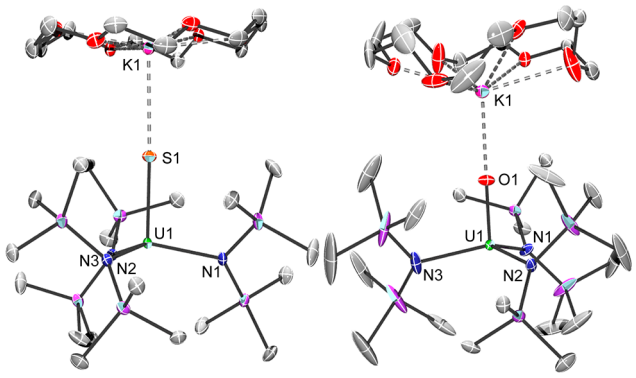


Figure 1. Solid-state molecular structure of **1** (left) and **3** (right), with 50% probability ellipsoids. One molecule of **1** and hydrogen atoms are omitted for clarity. **1**: U1−S1 = 2.4463(6) Å, S1−K1 = 3.0684(8) Å; **3**: U1−O1 = 1.890(5) Å, O1−K1 = 2.640(5) Å.

is coordinated by the K^+ ion of the $[K(18\text{-crown-6})]^+$ moiety, whereas complex **2** exists as a discrete cation/anion pair. The U−S bond lengths in **1** (2.4463(6) and 2.4513(6) Å) and **2** (2.4423(16) Å) are identical by the 3σ criterion, and are slightly shorter than those reported for the U(IV) terminal sulfides, $[Ph_3PCH_3][U(S)(NR_2)_3]$ (U−S = 2.4805(5) Å)[23] and [Na-(18-crown-6)][$U(Cp^*)_2(S^tBu)(S)$] (U−S = 2.462(2) and 2.477(2) Å).[24] The S−K distances in **1** (3.0684(8) and 3.1551(8) Å) are long and comparable to the S−Na interaction in [Na(18-crown-6)][$U(Cp^*)_2(S^tBu)(S)$] (S−Na = 3.135(4) Å).[24] The S−K interaction in **1** is likely quite weak, a hypothesis that is supported by the nearly identical U−S bond lengths in complexes **1** and **2**.

The ^{1}H NMR spectrum of **1** in benzene-d_6 exhibits two broad resonances at −2.02 and −1.11 ppm, assignable to the methyl groups of the silylamide ligands and the methylene groups of the 18-crown-6 moiety, respectively (Figure S2, SI). The latter resonance is paramagnetically shifted, suggesting that the $[K(18\text{-crown-6})]^+$ cation is in close contact with the $[U(S)(NR_2)_3]^-$ anion in this solvent. Upon dissolution of **1** in tetrahydrofuran-d_8, the resonance assignable to the 18-crown-6 moiety shifts to 1.46 ppm, closer to that of free 18-crown-6 (3.57 ppm in tetrahydrofuran-d_8),[35] suggesting the formation of better separated cation/anion pairs in this donating solvent (Figure S3, SI). The ^{1}H NMR spectrum of **2** in pyridine-d_5 exhibits a broad resonance at −2.33 ppm, assignable to the methyl groups of the silylamide ligands, and three resonances at 2.25, 3.25, and 3.29 ppm, assignable to the three proton environments of the 2,2,2-cryptand moiety (Figure S5, SI). In addition, the UV−vis/NIR spectra of **1** and **2** are consistent with the presence of U(IV) centers (Figures S37 and S38, SI).[7,23,36−39]

After successful demonstration of terminal sulfide formation via trityl radical elimination, we explored the viability of this method for the synthesis of the analogous terminal oxide. Thus, addition of 1 equiv of $KOCPh_3$ to a cold (−25 °C) solution of $[U(NR_2)_3]$ in benzene-d_6, in the presence of 18-crown-6, results in an immediate color change to deep red, concomitant with the deposition of a red solid. Surprisingly, the ^{1}H NMR spectrum of this reaction mixture revealed no evidence for formation of Gomberg's dimer (Figure S6, SI). However, the spectrum did reveal formation of a U(IV) terminal oxo, [K(18-crown-6)][$U(O)(NR_2)_3$] (**3**), as evidenced by the broad resonance at −4.87 ppm, assignable to the methyl groups of the silylamide ligands. In addition, the U(IV) alkoxide, $[U(OCPh_3)(NR_2)_3]$ (**4**), was also observed in the reaction mixture, as evidenced by the aryl C−H resonances at 7.44, 8.57, and 17.28 ppm. Finally, the red precipitate was identified as $[K(18\text{-crown-6})(THF)_2][Ph_3C]$ (**5**) by X-ray crystallography (Scheme 1). Its identity was further supported by a comparison of its ^{1}H NMR spectrum with previously reported spectral data for the trityl anion,[40] and by its independent synthesis, via the reduction of triphenylmethane with KC_8 in the presence of 18-crown-6 (Scheme S5, SI).

The terminal oxo complex, [K(18-crown-6)][$U(O)(NR_2)_3$] (**3**), can be independently synthesized by reduction of the previously reported U(V) oxo $[U(O)(NR_2)_3]$[7] with KC_8, followed by the addition of 18-crown-6. Crystallization from diethyl ether affords **3** as pale-purple blocks in 50% yield (Scheme S3, SI). Complex **3** can also be formed by reaction of $[U(O)(NR_2)_3]$ with **5**, concomitant with formation of Gomberg's dimer, as revealed by ^{1}H NMR spectroscopy (Figure S21, SI).

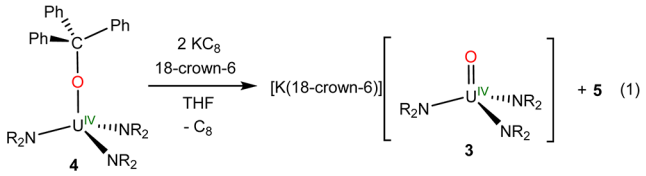
The ^{1}H NMR spectrum of **3** in benzene-d_6 exhibits two broad resonances at −4.91 and 16.15 ppm, assignable to the methyl groups of the silylamide ligands and the methylene groups of the 18-crown-6 moiety, respectively (Figure S9, SI). Complex **3** is isostructural with complex **1** in the solid state; as with **1**, complex **3** features a dative interaction between the chalcogenido ligand and the $[K(18\text{-crown-6})]^+$ moiety. The U−O bond length in **3** (1.890(5) Å) is statistically equivalent to that of the previously reported $[Cp^*_2Co][U(O)(NR_2)_3]$ (U−O = 1.878(5) Å),[23] which features the identical $[U(O)(NR_2)_3]^-$ anion. Finally, the E1−K1 distance in **3** (2.640(5) Å) is shorter than that of **1**, consistent with the smaller ionic radii of O^{2-} vs S^{2-}.

The U(IV) alkoxide, $[U(OCPh_3)(NR_2)_3]$ (**4**), can also be independently synthesized via reaction of $[U(I)(NR_2)_3]$[7] with 1 equiv of $KOCPh_3$. This complex can be isolated as pale-purple plates in 38% yield after crystallization from a concentrated diethyl ether solution (Scheme S4, SI). Its ^{1}H NMR spectrum in benzene-d_6 consists of four resonances at −4.85, 7.74, 8.56, and 17.22 ppm, in a 54:3:6:6 ratio, respectively, corresponding to the methyl groups of the silylamide ligands and the *p*-, *m*-, and *o*-aryl protons of the trityl−alkoxide ligand (Figure S10, SI). Importantly, the resonances for the aryl protons match those seen in the reaction between $[U(NR_2)_3]$ and $KOCPh_3$, and confirm the presence of **4** in that transformation.

In order to gain further mechanistic insight into the formation of complexes **3**, **4**, and **5**, we monitored the reaction of $[U(NR_2)_3]$ with $KOCPh_3$ in THF-d_8, in the presence of 18-crown-6, by ^{1}H NMR spectroscopy. A ^{1}H NMR spectrum of this solution, after standing at −25 °C for 30 min, reveals the formation of a new species that we have tentatively assigned as the U(III) alkoxide, [K(18-crown-6)][$U(OCPh_3)(NR_2)_3$] (**6**). The presence of **6** is supported by resonances at −8.37, 7.57, 8.33, and 17.02, in a 54:6:3:6 ratio (Figure S7, SI), which correspond to the methyl groups of the silylamide ligands and the *m*-, *p*-, and *o*-aryl protons of the trityl−alkoxide ligand, respectively. Upon warming this solution to 25 °C, the resonances assigned to **6** disappear (Figure S8, SI), while those assigned to **3** and **4** grow in intensity. To account for these observations, we propose that **6** undergoes a disproportionation reaction, instead of C−O bond homolysis, wherein one molecule of the U(III) alkoxide reduces the triphenylmethyl fragment of a second molecule. The first molecule is thereby oxidized, accounting for the formation of **4**, while reduction of the triphenylmethyl group on the second

dx.doi.org/10.1021/ja411423a | J. Am. Chem. Soc. 2014, 136, 96−99

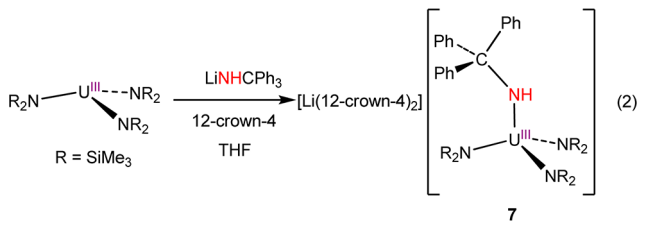
molecule results in heterolytic cleavage of the C−O bond and formation of both **3** and **5** (Scheme S1, SI). If true, this mechanism suggests that the trityl group of the $[OCPh_3]^-$ ligand could be selectively removed by reduction with an external reducing agent. Gratifyingly, reduction of **4** with KC_8, in the presence of 18-crown-6, results in the formation of both **3** and **5**, which are isolated in 36% and 52% yield, respectively (eq 1) (Figures S19 and S20, SI). To our knowledge, this is the



first example of reductive deprotection of trityl to form an oxo ligand and demonstrates that traditional organic deprotection protocols[25] can be applied to inorganic synthesis.

Alternately, the formation of **3**, **4**, and **5** from the reaction of $[U(NR_2)_3]$ and $KOCPh_3$ could arise via formation of a U(V) oxo intermediate, $[U(O)(NR_2)_3]$. In this scenario, complex **6** undergoes a heterolytic C−O bond cleavage, resulting in the formation of **5** and $[U(O)(NR_2)_3]$. This U(V) species could then be reduced by another molecule of **6**, resulting in concomitant formation of **3** and **4** (Scheme S2, SI). However, we suggest that this pathway is not operative, as the reaction of $[U(O)(NR_2)_3]$ with **5**, the microscopic reverse of the first step, results in the formation of **3** and Gomberg's dimer (Figure S21, SI). Given the absence of any evidence for the presence of $[U(O)(NR_2)_3]$ or Gomberg's dimer in the reaction mixture, we suggest that the first pathway is more likely.

We also endeavored to synthesize a U(IV) imido complex using the trityl deprotection protocol. Thus, reaction of $[U(NR_2)_3]$ with 1 equiv of $LiNHCPh_3$,[41] in the presence of 2 equiv of 12-crown-4, in tetrahydrofuran results in formation of a dark red−brown solution. Crystallization from diethyl ether affords $[Li(12\text{-crown-}4)_2][U(NHCPh_3)(NR_2)_3]$ (**7**) as a dark red−brown microcrystalline solid in 42% yield (eq 2).



Unlike the analogous reactions with the sulfur and oxygen derivatives, no evidence for the formation of Gomberg's dimer or the trityl anion was observed in the reaction mixture (Figure S14, SI). The ^{1}H NMR spectrum of **7** features five distinct resonances at −7.41, 3.64 6.22, 7.36, and 12.23 ppm, corresponding to the methyl groups of the silyamide ligands, the methylene groups of the 12-crown-4 moiety, and the *p*-, *m*-, and *o*-aryl protons of the trityl group, respectively (Figure S15, SI). While the NH resonance of the $[NHCPh_3]^-$ ligand was not definitively identified in the ^{1}H NMR spectrum, the UV−vis/NIR spectrum of **7** is consistent with the presence of a U(III) center (Figure S41, SI).[42] In the solid state, complex **7** crystallizes as a discrete cation/anion pair. The U−N_{trityl} bond length (2.342(4) Å) and U−N−C angle (151.2(3)°) are similar to those observed in the related U(III) amide, $[K(THF)_2]_2[U(NH\text{-}2,6\text{-}{}^i Pr_2C_6H_3)_5]$,[43] consistent with the presence of a primary amide ligand. The long U−N_{trityl} bond length also rules out the presence of an imido ligand, as U(IV)−N_{imido} bond lengths are typically much shorter (1.95−2.05 Å)[20,21]

Undoubtedly, trityl release during the formation of complexes **1**, **2**, and **3** is driven, in part, by the highly reducing U(III/IV) redox potential. However, we suggest that the C−E bond dissociation enthalpies and the strength of the new U−E bond being formed also play a role in determining the reaction outcome. While BDE data is not readily available for triphenylmethyl−heteroatom bonds, C−E BDE data is known for the benzyl derivatives, $PhCH_2EH$ (E = S, 60.4 kcal/mol; O, 81 kcal/mol; NH, 74.0 kcal/mol).[44,45] Accordingly, the spontaneous C−S bond cleavage observed in the $KSCPh_3$ reaction can be explained by the relatively weak C−S bond. The weak C−S bond should also result in a low kinetic barrier for trityl release. In contrast, the stronger C−E bonds for the oxygen and nitrogen trityl precursors render trityl radical release less favorable, both thermodynamically and kinetically. In the case of the oxygen analogue, however, an alternate pathway for trityl release is operative (e.g., disproportionation), no doubt because the highly oxophilic nature of uranium greatly favors the formation of U−O multiple bonds,[46] whereas in the case of nitrogen, the weaker U−N multiple bond does not outweigh the energy required to break the C−N bond in $[Ph_3CNH]^-$.

In summary, we have demonstrated the syntheses of a terminal oxo and a terminal sulfido complex of uranium by release of the trityl protecting group. Importantly, the trityl group can be cleaved from the heteroatom by two different mechanisms: spontaneous loss of trityl radical or reductive cleavage of the trityl group and loss of the trityl anion. Intriguingly, $KSCPh_3$ is acting as a $1e^-$ oxidant in its reaction with $[U(NR_2)_3]$, converting the U(III) precursor into a U(IV) terminal sulfide. This is significant because most chalcogen atom transfer reagents are $2e^-$ oxidants, suggesting that with a trityl-based chalcogen source, any $1e^-$ metal redox couple could be harnessed to synthesize a terminal chalcogenide ligand. Accordingly, this protocol could have wide synthetic utility in inorganic chemistry, as most first row transition metals, and all of the lanthanides, are resistant to $2e^-$ redox chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, crystallographic details (as CIF files) and spectral data for complexes **1**−**5**, and **7**. 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.

■ ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences, Biosciences, and Geosciences Division under Contract No. DE-FG02-09ER16067.

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