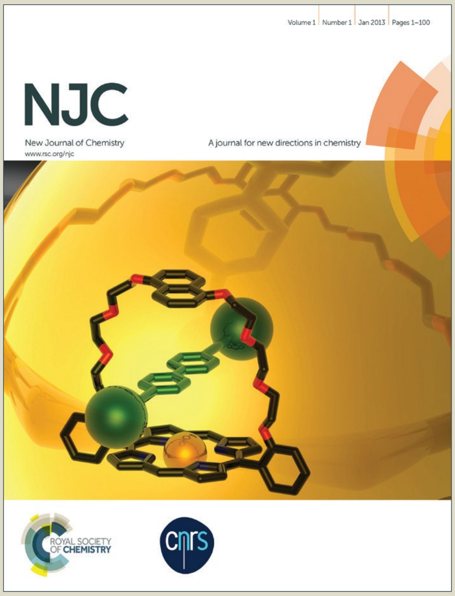
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Reactivity of $[U(CH_2SiMe_2NSiMe_3)(NR_2)_2]$ (R = $SiMe_3$) with elemental chalcogens: Towards a better understanding of chalcogen atom transfer in the actinides

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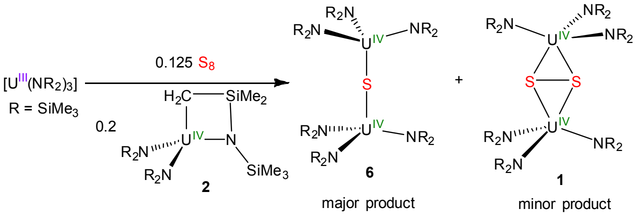
The reaction of the U(IV) metallacycle, $[U(CH_2SiMe_2NSiMe_3)(NR_2)_2]$ (R = $SiMe_3$) with the elemental chalcogens, E (E = S, Se, Te) affords the insertion products, $[U(ECH_2SiMe_2NSiMe_3)(NR_2)_2]$, in good yields. All three can transfer the chalcogen atom to $[U(NR_2)_3]$ to give the bridged mono-chalcogenides $[U(NR_2)_3](\mu\text{-E})$ (E = S, Se, Te) and regenerate $[U(CH_2SiMe_2NSiMe_3)(NR_2)_2]$. Additionally, the reaction of $[U(Cl)(NR_2)_3]$ with 2 equiv of $KSCPh_3$ affords the di-sulfide, $[K(Et_2O)_2][U(S_2)(NR_2)_3]$.

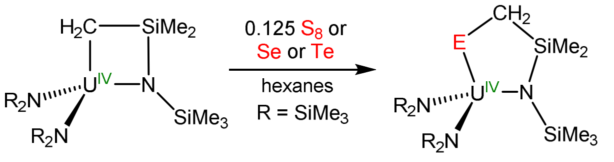
There has been a resurgence of interest in the chemistry of actinide chalcogenides over the past decade,[1-3] and great progress has been made in the synthesis and isolation of this class of molecules. While complexes bearing bridging chalcogenide ligands remain the most common,[4-9] recently, several actinide complexes containing the terminal chalcogenide moiety have been synthesized.[9-12] A variety of chalcogen sources have been utilized for the installation of these ligands.[13-15] For example, Ryan and co-workers synthesized the thorium polysulfide, $[(Cp^*)_2Th(S_5)]$, via the reaction of Li_2S_5 with $[(Cp^*)_2ThCl_2]$,[16] and more recently we reported the synthesis of several uranium mono- and di-chalcogenides, using similar polychalcogenides as the chalcogen source.[17] The phosphine chalcogenides, $R_3P{=}E$, have also been used for chalcogen atom transfer in the actinides.[9, 18] Despite these examples, by far the most commonly used chalcogen sources in actinide chemistry are the elemental chalcogens (e.g., S_8, Se, Te).[4, 5, 7, 9, 12] However, a major drawback to their use is the lack of control over the reaction outcome. For example, we recently reported the synthesis of the U(IV) bridged chalcogenides complexes, $[U(NR_2)_3](\mu\text{-E})$ (E = S, **6**; Se, **7**; Te, **8**; R = $SiMe_3$), via reaction of the U(III) amide, $[U(NR_2)_3]$, with the corresponding chalcogen source.[7] However, when S_8 was utilized as the sulfur source, the formation of the bridged di-sulfide complex, $[U(NR_2)_3]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)$ (**1**), was also observed in the reaction mixture (Scheme 1). This complex was isolated in low to moderate yields, and its formation was found to be highly batch dependent.[7]

During these investigations we observed a correlation between the formation of complex **1** and the presence of a U(IV) metallacycle impurity, $[U(CH_2SiMe_2NSiMe_3)(NR_2)_2]$ (**2**), in the U(III) starting material (Scheme 1).[7] Complex **2** is a common impurity in $[U(NR_2)_3]$, with some batches containing as much as 20% of this material. Thus, we hypothesized that complex **2** somehow catalysed the formation of **1**, possibly via the S-atom insertion product, $[U(S_2CH_2SiMe_2NSiMe_3)(NR_2)_2]$. Further support for this proposed mechanism comes from the observation that several substrates, including nitriles and ketones, are able to insert into the U-C bond of **2**.[19, 20] Accordingly, we deemed the S-atom insertion hypothesis plausible. In this contribution we describe our efforts to evaluate the proposed mechanism for the formation of **1**, and develop a rational synthetic route to this complex.

Scheme 1



To probe the proposed mechanism, we began by exploring the reactivity of **2** with chalcogens and chalcogen sources. The addition of 0.125 equiv of S_8 to a cold (-25 °C) solution of **2**, in hexanes, results in the formation of a yellow-brown solution over the course of 30 min. Crystallization from hexanes affords the thiolate complex, $[U(SCH_2SiMe_2NSiMe_3)(NR_2)_2]$ (**3**), in 62% yield (eq 1). As anticipated, complex **3** exhibits a ^1H NMR spectrum similar to that of complex **2**. The ^1H NMR spectrum of **3**, in benzene-d_6, consists of four broad resonances at -11.44, -9.97, -4.22, and 3.38 ppm, in a 9:2:36:6 ratio, respectively, corresponding to the single methylene environment and three methyl environments (Figure S1). Importantly, addition of excess sulfur to **2** did not result in the formation of a polysulfide complex; this reaction results in the formation of **3** as the only uranium containing product.



(1)

2

E = S, **3**; E = Se, **4**; E = Te, **5**

Complex **3** can also be synthesized with other sulfur sources. For example, the reaction of **2** with 1 equiv of ethylene sulfide, in benzene-d_6, was monitored by ^{1}H NMR spectroscopy. The formation of complex **3** was observed over the course of 24 h, concomitant with the consumption of complex **2**. Also observed in the in-situ ^{1}H NMR spectrum was a single resonance at 5.26 ppm, which is assignable to ethylene (Figure S5).[21] On a preparative scale, reaction of **2** with 1 equiv of ethylene sulfide in hexanes affords complex **3** as a yellow-brown powder in 93% yield, after work-up. This material is identical to that formed upon reaction of **2** with S_8, according to ^{1}H NMR spectroscopy (Figure S2).

Similar to its reactivity with elemental sulfur, addition of elemental selenium or tellurium to cold (-25 °C) solutions of **2**, in hexanes, yields either a yellow-brown or red solution, respectively. Crystallization of these materials from hexanes affords the chalcogenate complexes, $[U(ECH_2SiMe_2NSiMe_3)(NR_2)_2]$ (E = Se, **4**; E= Te, **5**), in 60% and 51% yields, respectively (eq 1).

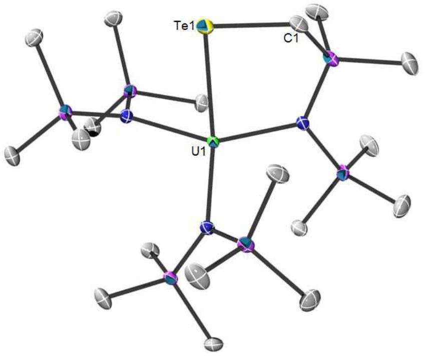


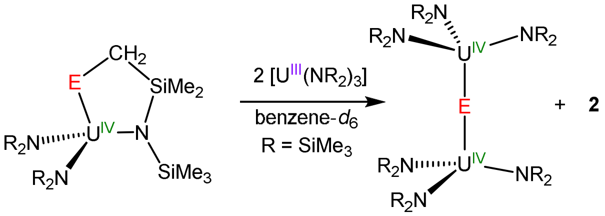
Fig. 1. Solid state molecular structure of **5** with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): U1-Te1 = 3.0185(1), Te1-C1 = 2.171(2), U-N (av.) = 2.250.

Crystals of complexes **3-5** suitable for X-ray diffraction analysis were grown from concentrated hexanes solutions. In the solid state, complexes **3** and **4** both crystallize in the trigonal space group $P\overline{3}\,1c$. As a result of the high symmetry, their structures exhibit considerable positional disorder that only allowed for the confirmation of their connectivities. Complex **5** crystallizes in the triclinic space group $P\overline{1}$, and its solid state molecular structure is shown in Figure 1. Complex **5** features a distorted tetrahedral geometry about the uranium centre. Its most interesting structural feature is the 5-membered ring formed via insertion of a Te atom into the U-C bond. The U-Te (3.0185(1) Å) distance is comparable to those previously reported for complexes with U-Te single bonds.[7, 13, 14] In addition, the U-N distances (av. = 2.250 Å), are similar to those of other U(IV) complexes bearing the $[N(SiMe_3)_2]^-$ ligand.[7, 12, 17, 22]

Both complexes **4** and **5** were characterized by ^{1}H NMR spectroscopy. In benzene-d_6, complex **4** exhibits four broad resonances at -12.24, -7.18, -3.69, and 4.67 ppm, in a 9:2:36:6 ratio, respectively, assignable to the methyl and methylene environments of the silylamide ligands (Figure S3). Complex **5** displays a ^{1}H NMR spectrum, in benzene-d_6, similar to those of complexes **3** and **4**, again consisting of four broad resonances (Figure S4). Notably, the unique $N(SiMe_3)$ resonance for this series of compounds shifts upfield on moving from S to Se to Te. A similar, but downfield, trend was observed for the Cp* resonances in the $Cp^*{}_2U(EPh)_2$ (E = S, Se, Te).[13, 23, 24] Finally, the near-IR spectra of **3**, **4**, and **5** are all consistent with the presence of a U(IV) metal ion (Figures S21-S23), confirming that no metal redox chemistry has taken place upon chalcogen insertion.[7, 12, 17, 25]

With these chalcogenate complexes in hand we then investigated their ability to perform chalcogen atom transfer. Thus, we monitored the reaction of $[U(NR_2)_3]$ with **3** by ^{1}H NMR spectroscopy. Addition of 1 equiv of $[U(NR_2)_3]$ to a solution of **3** in benzene-d_6 affords an orange solution. A ^{1}H NMR spectrum of the reaction mixture, recorded after 2 h, reveals the formation of the previously reported bridging mono-sulfide, $[U(NR_2)_3]_2(\mu\text{-}S)$ (**6**),[7] along with the formation of complex **2** (eq 2). A decrease in the intensity of the resonances assignable to complex **3** is also observed (Figure S6). Addition of a second equiv of $[U(NR_2)_3]$ to this solution results in complete consumption of complex **3**, as well as an increase in the intensity of the resonances assignable to complexes **2** and **6** (Figure S7). Notably, the disulfide complex, **1**, was not observed in the reaction mixture, suggesting that complex **2** is not involved in its formation, and calling into question our proposed mechanism for the formation of complex **1**.[7]

Complexes **4** and **5** also function as chalcogen transfer reagents. Thus, reaction of **4** or **5** with 2 equiv of $[U(NR_2)_3]$ results in clean formation of the bridging mono-chalcogenide complexes, $[U(NR_2)_3]_2(\mu\text{-}E)$ (E = Se, **7**; E = Te, **8**) (eq 2),[7] along with formation of complex **2** (Figures S8-S11).



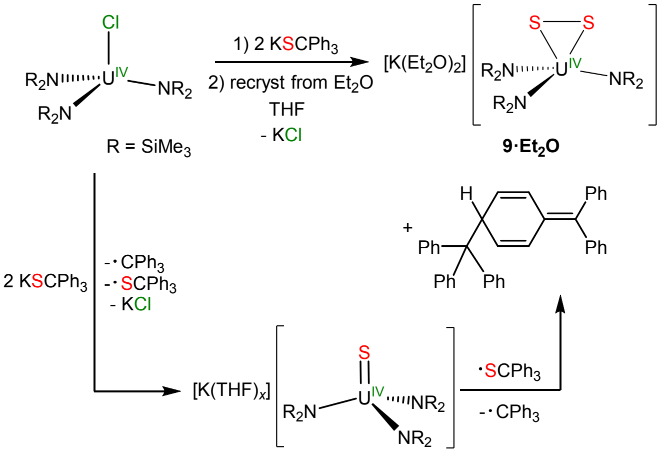
(2)

E = S, **3**; E = Se, **4**; E = Te, **5**

E = S, **6**; E = Se, **7**; E = Te, **8**

The inability to generate complex **1** from the reaction of **3** with $[U(NR_2)_3]$ led us to explore different routes towards its rational preparation. Previously, we reported the synthesis of a U(IV) terminal mono-sulfide, $[K(18\text{-crown-}6)][U(S)(NR_2)_3]$, via reaction of $[U(NR_2)_3]$ with $KSCPh_3$.[22] Inspired by this result, we explored the reactivity of $KSCPh_3$ with the previously reported U(IV) chloride, $[U(Cl)(NR_2)_3]$.[26] Interestingly, reaction of $[U(Cl)(NR_2)_3]$ with two equiv of $KSCPh_3$, in THF, affords the new U(IV) disulfide, $[K(Et_2O)_2][U(S_2)(NR_2)_3]$ (**9·Et₂O**), in 44% yield after recrystallization in Et_2O (Scheme 2).

Scheme 2.



We hypothesize that this complex is formed via a stepwise mechanism (Scheme 2), whereby reaction of $[U(Cl)(NR_2)_3]$ with 1 equiv of $KSCPh_3$ results in the transient formation of the U(V) mono-sulfide, $[U(S)(NR_2)_3]$, and trityl radical. The putative U(V) sulfide then reacts with a second equiv of $KSCPh_3$, resulting in the reduction of the metal centre back to U(IV), and formation of the $Ph_3CS·$ radical. The latter then functions as a sulfur source, resulting in S-atom transfer and formation of the S-S bond.[27] The *in situ* ^1H NMR spectrum of the reaction mixture supports this hypothesis. For example, a ^1H NMR spectrum of the reaction between $[U(Cl)(NR_2)_3]$ and 1 equiv of $KSCPh_3$ in THF-d_8 exhibits resonances assignable to $[K(THF)_x][U(S_2)(NR_2)_3]$ (**9·THF**), Gomberg's dimer,[22, 28] and unreacted $[U(Cl)(NR_2)_3]$, fully consistent with the proposed stoichiometry (Figure S13). Moreover, at short reaction times a third uranium-containing species is also present, as indicated by a broad resonance at -2.06 ppm (Figure S12), which we have tentatively identified as $[K(THF)_x][U(S)(NR_2)_3]$.[22] In further support of this mechanism, the reaction of independently prepared $[K(18\text{-crown-}6)][U(S)(NR_2)_3]$ with $Ph_3CSSCPh_3$ results in formation of $[K(18\text{-crown-}6)][U(S_2)(NR_2)_3]$ (**9·18-crown-6**) and Gomberg's dimer (Figure S15).

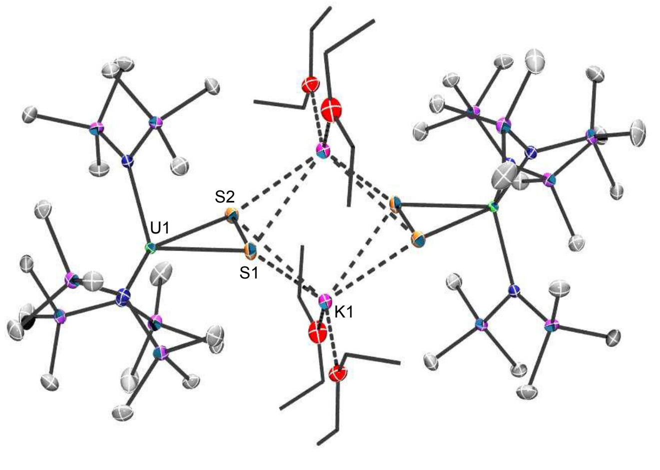
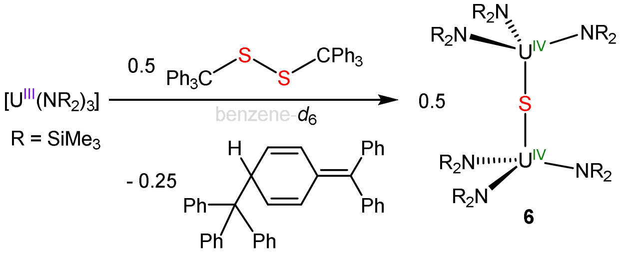


Fig. 2 Solid state molecular structure of **9·Et₂O** with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): U1-S1 = 2.6984(5), U1-S2 = 2.7448(5), S1-S2 = 2.1031(7).

Complex **9·Et₂O** crystallizes in the monoclinic spacegroup $P2_1/c$, and its solid state molecular structure is shown in Figure 2. In the solid state, **9·Et₂O** exists as a dimer and features two bridging $[K(Et_2O)_2]^+$ cations. The structure sits on a crystallographically imposed inversion centre that results in half of the dimer being generated by symmetry. Complex **9·Et₂O** features a distorted tetrahedral geometry about uranium with N-U-N angles [N1-U1-N2 = 107.99(5)°, N2-U1-N3 = 101.21(5)°, N2-U1-N3 = 123.15(5)°] similar to those previously seen for the $[U(S_2)(NR_2)_3]^-$ anion.[27] The U-S distances in **9·Et₂O** (U1-S1 = 2.6984(5) Å and U1-S2 = 2.7448(5) Å) are also similar to those reported for **9·18-crown-6**.[27] Finally, the S-S distance (S1-S2 = 2.1031(7) Å) in **9·Et₂O** is comparable to those of **9·18-crown-6** and other uranium disulfides.[9, 11, 27, 29-31]

Complex **9·Et₂O** exhibits a broad resonance at -7.08 ppm, in benzene-d_6, in its ^1H NMR spectrum. This resonance is assignable to the methyl groups of the silylamide ligands (Figure S14). The addition of 18-crown-6 to this sample readily converts **9·Et₂O** into the previously reported complex, **9·18-crown-6**. This was revealed by an upfield shift of the resonance, assignable to the methyl groups of the silylamide ligands, to -7.41 ppm, consistent with the ^1H NMR spectrum previously reported for this species.[27]

We also explored the reaction of $[U(NR_2)_3]$ with $Ph_3CSSCPh_3$,[32, 33] which we hypothesized could function as an "S_2" transfer reagent. Thus, 0.5 equiv of $Ph_3CSSCPh_3$ was added to a solution of $[U(NR_2)_3]$ in benzene-d_6 (eq 3). A ^1H NMR spectrum of the reaction mixture reveals clean formation of complex **6** and Gomberg's dimer, along with the presence of unreacted $Ph_3CSSCPh_3$ (Figure S17). While complex **1** was not generated during the reaction, we nonetheless demonstrated that $Ph_3CSSCPh_3$ is also a competent S-atom transfer reagent for U(III).



(3)

In summary, we have demonstrated that the U(IV) metallacycle, $[U(CH_2SiMe_2NSiMe_3)(NR_2)_2]$, readily reacts with elemental S, Se and Te, to form the new U(IV) chalcogenates, $[U(ECH_2SiMe_2NSiMe_3)(NR_2)_2]$ (E = S, Se, Te), which are themselves competent chalcogen atom transfer reagents. In addition, reaction of $KSCPh_3$ with $[U(Cl)(NR_2)_3]$ provides a new route to the di-sulfide, $[K(Et_2O)_2][U(S_2)(NR_2)_3]$. We hypothesize that this reaction proceeds via a transiently formed U(IV) terminal sulfide. While a rational synthesis of the di-sulfide complex, $[U(NR_2)_3]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2)]$, remains elusive, we have discovered a new mode a reactivity of $KSCPh_3$ and have demonstrated that $Ph_3CSSCPh_3$ can function as a S-atom transfer reagent in the actinides. Ultimately, this work provides us with a better understanding of chaclogen atom transfer in the actinides, information that we hope will lead towards greater kinetic and thermodynamic control over the formation of actinide-chalcogen bonds.

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