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C−H and C−S Bond Cleavage in Uranium(III) Thiolato Complexes

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Reduction of the uranium(IV) thiolates $Cp^*_2U(SR)_2$ ($Cp^* = \eta$-C_5Me_5, R = Ph, Me, ^{i}Pr or ^{t}Bu) with sodium amalgam afforded the corresponding U(III) complexes $Na[Cp^*_2U(SR)_2]$ (R = Ph, **2a**; Me, **2b**; ^{i}Pr, **2c**) or the U(IV) sulfide $Na[Cp^*_2U(S^tBu)(S)]$. C−S bond cleavage of a thiolate ligand was also observed during the thermal decomposition of **2c** into the sulfide $Na[Cp^*_2U(S^iPr)(S)]$, whereas **2b** was transformed in refluxing THF into the thiametallacyclopropane complex $Na[Cp^*_2U(SMe)(SCH_2)]$, resulting from C−H bond activation of a SMe group. The X-ray crystal structures of $[Na(18\text{-crown-}6)(THF)_2][Cp^*_2U(S^iPr)_2]$, $[Na(18\text{-crown-}6)][Cp^*_2U(S^tBu)(S)]$, and $[Na(18\text{-crown-}6)(THF)_2][Cp^*_2U(SMe)(SCH_2)]$ have been determined.

Introduction

Thiolate compounds of the d-transition metals are of great interest in various domains of chemistry. Their importance in biological systems[1] and industrial processes such as desulfurization[2] has been known for a long time, while their potential in the synthesis of organosulfur compounds[3,4] or metal sulfide materials has been recognized more recently.[5] As a result, many efforts have been devoted to the synthesis of thiolate complexes, revealing their large structural diversity and rich reactivity which are due to the flexibility and bridging ability of the SR ligand and the presence of three active sites, i.e., the metal−sulfur, carbon−sulfur, and carbon−hydrogen bonds.[6]

By comparison, the chemistry of thiolate compounds of the f-elements, in particular uranium, was much less developed, certainly because these complexes have been long reputed to be unstable. This presumption was invalidated with the synthesis of the homoleptic complexes $U(SR)_4$[7] and $Na_2U(SR)_6$[8] and of the organometallic derivatives $(COT)U(SR)_2$ ($COT = \eta$-C_8H_8),[9] $Cp_3U(SR)$ ($Cp = \eta$-C_5H_5),[10] and $Cp^*_2U(SR)_2$ ($Cp^* = \eta$-C_5Me_5).[11] First reactivity studies were focused on the uranium(IV) thiolates $U(S^iPr)_4$,[7] $Cp_3U(S^iPr)$,[10] and $Cp^*_2U(S^tBu)_2$;[11] they showed that the SR ligand could undergo substitution reactions and that unsaturated molecules such as CO_2 and CS_2 could be inserted into the U−S bond.

Here we report on the reduction reactions of the bisthiolate compounds $Cp^*_2U(SR)_2$ (R = Ph, Me, ^{i}Pr, and ^{t}Bu).[12] The stability of the corresponding U(III) anions $[Cp^*_2U(SR)_2]^-$ and their oxidation following C−S or C−H bond cleavage were found to depend markedly on the nature of the R group. The uranium(III) complexes $Na[Cp^*_2U(SPh)_2]$ and $[Na(18\text{-crown-}6)][Cp^*_2U(SR)_2]$ (R = Me, ^{i}Pr) could be isolated; the isopropyl thiolate derivative is the first thiolate of U(III) to have been crystallographically characterized. The uranium(IV) complexes $[Na(18\text{-crown-}6)][Cp^*_2U(S^tBu)(S)]$ and $[Na(18\text{-crown-}6)(THF)_2][Cp^*_2U(SMe)(SCH_2)]$, also characterized by their X-ray crystal structure, are the first f-element compounds containing respectively a metal−sulfur double bond and a thiametallacyclopropane ring.

Results and Discussion

Reduction reactions of the uranium(IV) bisthiolates $Cp^*_2U(SR)_2$ **(1)** with sodium amalgam and thermolysis

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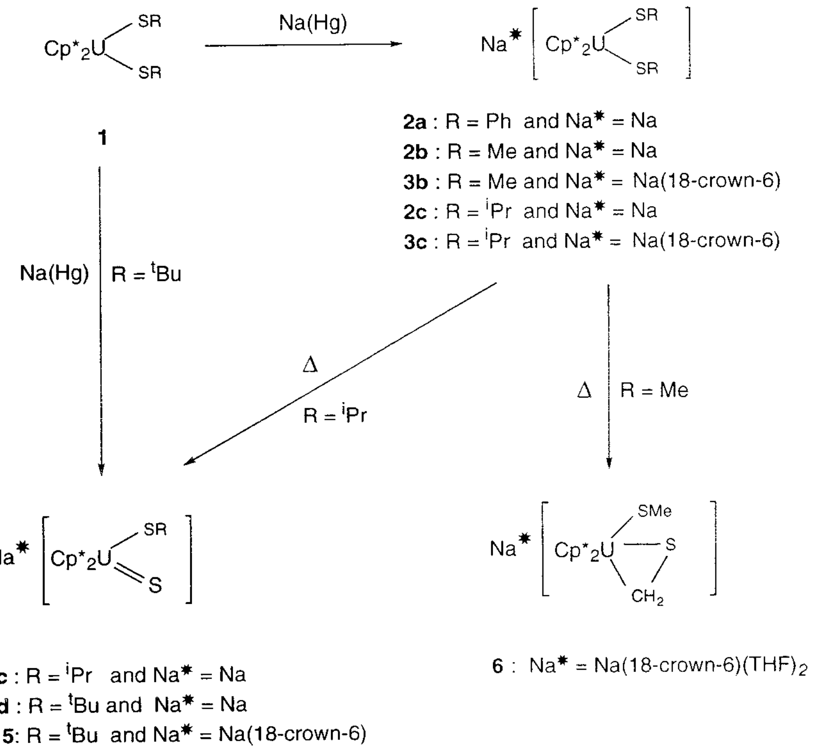
Scheme 1



reactions of the corresponding U(III) compounds Na[$Cp^*_2U(SR)_2$] (**2**) are summarized in Scheme 1.

Treatment of $Cp^*_2U(SPh)_2$ (**1a**) with 1 equiv of sodium amalgam in tetrahydrofuran (THF) gave the corresponding anionic uranium(III) compound Na[$Cp^*_2U(SPh)_2$] (**2a**). After stirring for 20 h at 20 °C, the solution was filtered and evaporated to dryness, leaving **2a** as a dark green powder in 93% yield. Complex **2a** is thermally stable in solution.

In contrast, Na(Hg) reduction of $Cp^*_2U(SMe)_2$ (**1b**) or $Cp^*_2U(S^iPr)_2$ (**1c**) was not so clean, and the compounds Na[$Cp^*_2U(SR)_2$] (R = Me, **2b**, and R = ^{i}Pr, **2c**) could not be obtained pure because of slow decomposition in solution (vide infra). However, in the presence of 18-crown-6, green microcrystalline powders of [Na(18-crown-6)][$Cp^*_2U(SR)_2$] (R = Me, **3b**, and R = ^{i}Pr, **3c**) have been isolated. The ^{1}H NMR spectra of compounds **2** and **3** exhibit signals corresponding to two Cp* and two SR ligands; these resonances are broader (30–50 Hz) than those of the U(IV) precursor (10–20 Hz), in accordance with the +3 oxidation state of uranium. Reactions of **3** with $AgBPh_4$ gave back the U(IV) complexes **1** in almost quantitative yield (NMR experiments).

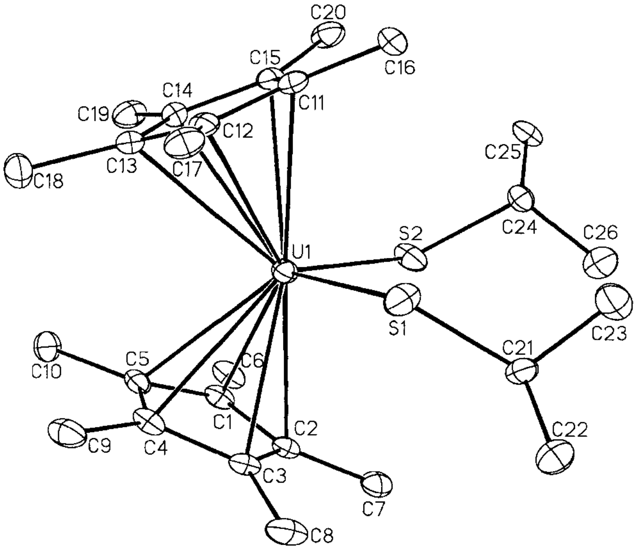


Figure 1. View of the crystal structure of the anion [$Cp^*_2U(S^iPr)_2$]$^-$ with displacement ellipsoids drawn at the 20% level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for [Na(18-crown-6)(THF)$_2$][$Cp^*_2U(S^iPr)_2$]

U(1)–C(1)	2.817(3)	U(1)–C(2)	2.819(3)	U(1)–C(3)	2.812(3)
U(1)–C(4)	2.812(3)	U(1)–C(5)	2.823(3)	U(1)–C(11)	2.814(3)
U(1)–C(12)	2.786(3)	U(1)–C(13)	2.793(3)	U(1)–C(14)	2.793(3)
U(1)–C(15)	2.813(3)	U(1)–S(1)	2.791(1)	U(1)–S(2)	2.777(1)
S(1)–C(21)	1.843(4)	S(2)–C(24)	1.840(3)		
S(1)–U(1)–S(2)	107.65(3)	U(1)–S(1)–C(21)	109.3(1)		
U(1)–S(2)–C(24)	117.9(1)				

After the triscyclopentadienyl derivatives Na[$Cp_3U(SR)$],[10] **2** and **3** are new examples of uranium(III) thiolates, and [Na(18-crown-6)(THF)$_2$][$Cp^*_2U(S^iPr)_2$], obtained by crystallization of **3c** from THF–pentane, is the only one to have been crystallographically characterized. The crystals are composed of discrete cation–anion pairs. The cation displays the expected structural parameters;[13] a view of the anion is shown in Figure 1, and selected bond distances and angles are listed in Table 1. The uranium coordination geometry is the pseudo-tetrahedral arrangement, which is typical of the $Cp^*_2MX_2$ fragment. The U–S bond distances of 2.791(1) and 2.777(1) Å are 0.1 Å longer than in $Cp^*_2U(SMe)_2$

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[2.640(5) Å],[11] in agreement with the difference of ionic radii between the U(III) and U(IV) centers.[14]

Reaction of $Cp^*_2U(S^tBu)_2$ (**1d**) with sodium amalgam was quite different from that of **1a**−**c** since the corresponding U(III) anion could not be detected by NMR, which revealed instead the ready formation of a product containing two Cp* ligands for only one S^tBu group; the narrow resonances (10−20 Hz) suggested that this complex was in the +4 oxidation state. NMR and GLC analyses also revealed the formation of isobutene and isobutane, which certainly resulted from dismutation of a *tert*-butyl radical. These facts suggested that the likely intermediate $Na[Cp^*_2U(S^tBu)_2]$ was oxidized into $Na[Cp^*_2U(S^tBu)(S)]$ **(4d)** by facile homolytic C−S bond cleavage of a S^tBu ligand. Complex **4d** was alternatively synthesized by treating the U(III) chloride $[Na(THF)_{1.5}][Cp^*_2UCl_2]$[15] with NaS^tBu in THF, and here again, concomitant formation of isobutene and isobutane was observed. The reaction mixture was stirred for 18 h at 20 °C, and after filtration and evaporation of the red solution, the ochre powder of **4d** was extracted in pentane and recovered in 95% yield. In the presence of 18-crown-6, crystallization of **4d** from THF−pentane afforded red needles of $[Na(18\text{-crown-}6)][Cp^*_2U(S^tBu)(S)]$ (**5**). The X-ray crystal structure of this molecular heterobimetallic compound was presented in our preliminay communication,[12] and only the two most salient features will be recalled here: the unsupported U−S−Na linkage and the shortest U−S distance ever observed, 2.462(2) Å, which is consistent with a formal U═S double bond. Compound **5** can therefore be viewed as the adduct of the terminal sulfide $[Cp^*_2U(S^tBu)(S)]^-$ to $[Na(18\text{-crown-}6)]^+$. Among the rare heterobimetallics containing an unsupported M−S−M′ linkage,[16] the tantalum compound $Cp^*_2Ta(H)(\mu\text{-}S)W(CO)_5$ is the only one to exhibit such a dative coordination of a sulfur lone pair of the Ta═S bond.[16a]

Carbon−sulfur bond cleavage of thiolate ligands, especially S^tBu, constitutes a classical route to metal sulfides.[7,17−20] However, the propensity of the sulfide group to bridge metal atoms is a current obstacle in the synthesis of complexes containing M═S multiple bonds, and formation of clusters is frequently observed. This behavior is illustrated with the facile thermal decomposition of $M(S^tBu)_4$ into the trinuclear derivative $M_3S(S^tBu)_{10}$ (M = Zr,[20] U[7]). The stability of **4**, the first f-element compound containing a metal−sulfur double bond, is likely favored by the negative charge of the complex and the sterically demanding Cp* ligands which impede dimerization via U−S−U bridges.[18,19]

Not surprisingly, the bis thiolates **2a**−**c** were found to be much more stable than $Na[Cp^*_2U(S^tBu)_2]$, in accordance with the rate at which the C−S bond rupture occurs in M−SR complexes, depending on the structure of R and following the sequence $^tBu \gg {}^iPr > Me \gg Ph$. As already noted, slow decomposition of **2c** took place in THF at room temperature. After 4 h at 65 °C, **2c** was completely decomposed, giving $Na[Cp^*_2U(S^iPr)(S)]$ (**4c**) as the major product (ca. 85%, NMR experiments); concomitant formation of propane, propene, and 2,3-dimethylbutane confirmed that **2c** underwent C−S bond cleavage of a S^iPr group. Encapsulation of the Na^+ cation into the crown-ether confers to the uranium(III) thiolato complexes a greater stability, as shown by the decomposition of **3c** in THF, which was complete after 15 h at 65 °C, instead of 4 h for **2c**. This distinct behavior of **2c** and **3c** suggests that conversion of the anion $[Cp^*_2U(SR)_2]^-$ into $[Cp^*_2U(SR)(S)]^-$ (R = ^iPr or ^tBu) proceeded by initial formation of the neutral species $Cp^*_2U(SR)$, resulting from dissociation of a thiolate group, followed by C−S bond activation and readdition of the SR ligand to the sulfide $Cp^*_2U(S)$. Moreover, the facility with which the U(III) anions $[Cp^*_2U(SR)_2]^-$ (R = ^iPr, ^tBu) decompose is in striking contrast to the thermal stability of their U(IV) precursors. While it has been noted that reduction of the Ti(IV) thiolate $CpTi(OC_6H_3\text{-}2,6\text{-}^iPr_2)(Cl)(S^tBu)$ promotes the C−S bond rupture of the S^tBu group,[3] the results reported here allow for the first time a direct comparison between the C−S bond cleavage reactions of analogous metal thiolates in different oxidation states. Contrary to previous indications which suggested that activation of the SR ligand requires the formation of a *μ*-thiolate ligand in a polymetallic species[21] and that sulfur abstraction is favored by a highly oxidized and electrophilic metal center,[20] the results show that low-valent, coordinatively unsaturated species could facilitate the C−S bond cleavage reaction, which is of great importance in catalytic desulfurization processes.

Thermolysis of **2b** in refluxing THF was much less rapid than that of **2c** and required 2 days to go to completion. Here again, the slowing effect of 18-crown-6 was observed, **3b** being totally decomposed after 6 days at 65 °C. Formation of methane, detected by GLC and MS, confirmed that C−S bond cleavage did occur; the absence of dimethyl sulfide indicated that this rupture did not proceed via S_N2 attack of SMe^- onto the coordinated SMe group. However, the NMR spectra showed that the major product, formed in ca. 50% yield, was not $Na[Cp^*_2U(SMe)(S)]$ since, in addition to the two signals attributed to two Cp* and one SMe ligand, another resonance corresponding to a CH_2 group was also visible. In the presence of 18-crown-6, dark red crystals were obtained from THF−pentane, and X-ray diffraction analysis revealed the structure of the thiametallacycle $[Na(18\text{-crown-}6)(THF)_2][Cp^*_2U(SMe)(SCH_2)]$ **(6)** (vide infra). Protonation of **6** with $NHEt_3BPh_4$ led to the quantitative formation of **1b** (NMR experiments).

Formation of **6** obviously resulted from C−H bond activation of a SMe ligand of **3b**; mechanistic studies of

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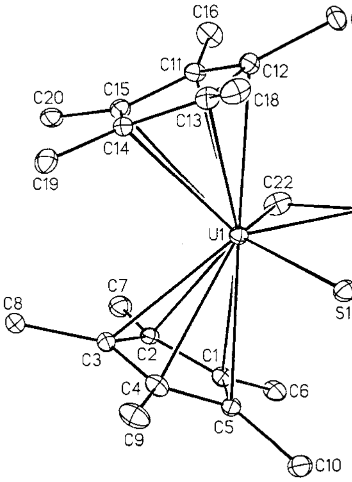

Figure 2. View of the crystal structure of the anion $[Cp^*_2U(SMe)(SCH_2)]^-$ with displacement ellipsoids drawn at the 10% level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Na(18\text{-crown-}6)(THF)_2][Cp^*_2U(SMe)(SCH_2)]$

U(1)−C(1)	2.798(9)	U(1)−C(2)	2.751(8)	U(1)−C(3)	2.795(9)
U(1)−C(4)	2.788(9)	U(1)−C(5)	2.790(9)	U(1)−C(11)	2.794(9)
U(1)−C(12)	2.813(9)	U(1)−C(13)	2.813(9)	U(1)−C(14)	2.800(9)
U(1)−C(15)	2.807(9)	U(1)−C(22)	2.44(1)	U(1)−S(1)	2.753(3)
U(1)−S(2)	2.613(3)	C(21)−S(1)	1.85(1)	C(22)−S(2)	1.74(1)

C(22)−U(1)−S(2)	40.0(3)	S(2)−U(1)−S(1)	88.42(9)
C(22)−U(1)−S(1)	127.8(3)	U(1)−S(2)−C(22)	64.7(3)
U(1)−S(1)−C(21)	108.1(3)		

this process were impeded by the occurrence of the many side reactions. Such syntheses of thiametallacyclopropane compounds involving C−H bond activation of a thiolate ligand are very rare, and these consist in the thermal decomposition of (alkylthio)methyl complexes of titanium and zirconium. Thus were obtained the dimeric compounds $[CpTi(OC_6H_3\text{-}2,6\text{-}{}^iPr_2)(SCHMe)]_2$[3] and $[CpTi(SCHCH_2CH_2S)]_2$[4] and the mononuclear derivative $Cp_2Zr(PMe_3)(SCHR)$ (R = Me, Ph).[22] Kinetic data on the decomposition of $Cp_2Zr(Me)(SCH_2R)$ in the presence of PMe_3 were consistent with intramolecular loss of methane via a concerted four-center cyclometalation process.[23] Complex **6** is the first unsubstituted thiametallacyclopropane obtained by this M(SMe) → $M(SCH_2)$ transformation. Other thiametallacyclopropanes, often considered as η^2-thioformaldehyde complexes, have been prepared by a variety of methods including reactions of methylidene compounds with alkene sulfides,[24−26] hydrogenation and fragmentation of CS_2,[27] hydrogenation of thiocarbonyl ligands,[28] treatment of iodomethyl iodo metal complexes with NaSH,[29] and reactions of diazomethane with sulfido metal compounds.[30]

Crystals of **6** are composed of discrete cation−anion pairs. The cation exhibits the expected geometry;[13] a view of the anion is represented in Figure 2, and selected bond distances and angles are listed in Table 2. The anion of **6** adopts the familiar bent metallocene structure. The U(1), C(22), S(1), and S(2) atoms are practically coplanar (within ±0.08 Å) and lie in the equatorial plane that bisects the dihedral angle formed by the Cp* ligands. The S(1)−U−S(2) angle is equal to 88.42(9)°, and the S(1)···S(2) distance is 3.743(4) Å; the corresponding values in **3c** are 107.65(3)° and 4.495(3) Å. The thiauranacyclopropane ring is very strained, as shown by the C(22)−U(1)−S(2) and U(1)−S(2)−C(22) angles of 40.0(3)° and 64.7(3)°, respectively. The U(1)−C(22) bond distance of 2.44(1) Å is within the range typically found for other uranium−carbon σ bonds (2.4−2.6 Å).[31] The U(1)−S(2) bond length of 2.613(3) Å is shorter than the U(1)−S(1) distance of 2.753(3) Å; these values are at the limits of the range of those determined for terminally coordinated thiolate ligands, which vary from 2.58(1) Å in $U_3(S)(S^tBu)_{10}$[7a] to 2.759(3) Å in $[NEt_2H_2]_2[U(SPh)_6]$.[8a] The C(22)−S(2) bond length of 1.737(12) Å can be compared to those found in the other mononuclear thiametallacyclopropanes: 1.744(3) Å in $Cp_2Ti(PMe_3)(SCH_2)$,[25] 1.739(13) and 1.785(11) Å in the two independent molecules of $Cp_2Zr(PMe_3)(SCHMe)$,[22] and 1.742(9) Å in $[CpRe(NO)(PPh_3)(SCH_2)][PF_6]$.[24] It has been generally considered that these distances, which are intermediate between that determined in $H_2C{=}S$ (1.6108(9) Å)[32] and typical C−S single bonds (1.80−1.82 Å;[33] C(1)−S(1) = 1.847(10) Å in **6**), would reflect some contribution of the $M(\eta^2\text{-}S{=}CHR)$ resonance form in the actual structure. Such π-coordination of a thioformaldehyde ligand would confer to the central metal of **6** the +2 oxidation state. Although the formally divalent uranium compound $(\mu\text{-}C_7H_8)[U(N[Ad]Ar)_2]_2$ (Ad = adamantyl; Ar = 3,5-$C_6H_3Me_2$) has been isolated recently,[34] this valency seems most unlikely in the case of **6**, in view of the strong reducing character of low-valent uranium complexes and their great reactivity toward carbonyl groups.

Experimental Section

All preparations and reactions were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use; THF-d_8 was dried over Na−K alloy.

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Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The GLC analyses were performed on a Chrompack CP 9002 apparatus equipped with a capillary CP Wax 57 CB column. The mass spectra were obtained using a CEA instrument (electron impact). Sodium amalgam (2.0% Na) was prepared by adding small pieces of sodium to mercury under argon at 20 °C; NaS^{t}Bu was obtained as a white powder after the reaction of sodium and a slight excess of ^{t}BuSH (1.1 equiv) in THF; the salts $NHEt_3BPh_4$ and $AgBPh_4$ precipitated by mixing $NHEt_3Cl$ or $AgNO_3$ and $NaBPh_4$ in water. The compounds $Cp*_2U(SR)_2$[11] and [Na(THF)$_{1.5}$][$Cp*_2UCl_2$][15] were synthesized by published methods.

Na[Cp*$_2$U(SPh)$_2$] (2a). A flask was charged with **1a** (262 mg, 0.36 mmol) and 2% Na(Hg) (414.5 mg, 0.36 mmol), and THF (50 mL) was condensed in. The reaction mixture was stirred at 20 °C for 20 h. After filtration, the solvent was evaporated off, leaving the product as a dark green powder (252 mg, 93%). Anal. Calcd for $C_{32}H_{40}NaS_2U$: C, 51.26; H, 5.38; S, 8.55. Found: C, 51.02; H, 5.46; S, 8.36. ^{1}H NMR (THF-d_8): δ −18.8 (s, 4 H, *o*-Ph), −3.5 (s, 30 H, Cp*), 2.4 (s, 4 H, *m*-Ph), 3.1 (t, $J = 6$ Hz, 2 H, *p*-Ph).

[Na(18-crown-6)][Cp*$_2$U(SMe)$_2$] (3b). A flask was charged with **1b** (212 mg, 0.35 mmol) and 2% Na(Hg) (405 mg, 0.35 mmol), and THF (50 mL) was condensed in. After 15 h at 20 °C, the solution was filtered and evaporated to dryness. The ^{1}H NMR spectrum of the green powder in THF-d_8 showed that **2b** was contaminated with ca. 10% of Na[Cp*$_2$U(SMe)(SCH$_2$)]. Crystallization of the green powder (170 mg) in the presence of 18-crown-6 (71 mg, 0.27 mmol) from THF−pentane afforded a green microcrystalline powder in an orange solution. After filtration, the powder was washed with pentane (50 mL) and dried under vacuum (168 mg, 54%). Anal. Calcd for $C_{34}H_{60}NaO_6S_2U$: C, 45.88; H, 6.79; S, 7.20. Found: C, 41.69; H, 6.39; S, 6.92 (similar low percentages have been obtained with distinct samples of **3b**, possibly reflecting the difficult combustion of the product). ^{1}H NMR (THF-d_8): δ −21.5 (s, 6 H, Me), 3.4 (s, 24 H, 18-crown-6), 10.85 (s, 30 H, Cp*).

[Na(18-crown-6)][Cp*$_2$U(S^{i}Pr)$_2$] (3c). A flask was charged with **1c** (211 mg, 0.32 mmol), 18-crown-6 (86.5 mg, 0.33 mmol), and 2% Na(Hg) (369 mg, 0.32 mmol), and THF (100 mL) was condensed in. The reaction mixture was stirred at 20 °C for 24 h, and after filtration, the solution was evaporated to dryness. The dark green product was washed with toluene (20 mL) and dried under vacuum (243 mg, 80%). Anal. Calcd for $C_{38}H_{68}NaO_6S_2U$: C, 48.24; H, 7.24; S, 6.78. Found: C, 47.98; H, 7.09; S, 6.94. ^{1}H NMR (THF-d_8): δ −10.3 (s, 12 H, Me), −6.0 (s, 2 H, CH), −4.2 (s, 30 H, Cp*), 3.8 (s, 24 H, 18-crown-6).

Reactions of 3b and 3c with AgBPh$_4$. An NMR tube was charged with **3b** (6.0 mg, 6.7 10^{-3} mmol) and $AgBPh_4$ (2.9 mg, 6.7 10^{-3} mmol) in THF-d_8 (0.4 mL). After 15 min at 20 °C, the spectrum showed the quantitative formation of **1b**. A similar reaction with **3c** gave **1c**.

Sodium Amalgam Reduction of 1b and Thermolysis of 2b. A flask was charged with **1a** (258 mg, 0.43 mmol) and 2% Na(Hg) (492 mg, 0.43 mmol), and THF (50 mL) was condensed in. After stirring for 15 h at 20 °C, the solution was filtered and evaporated to dryness. The ^{1}H NMR spectrum of the green powder showed that **1b** was completely transformed into a mixture containing **2b** and Na[Cp*$_2$U(SMe)(SCH$_2$)] in the relative proportions of 92:8, and minor impurities (ca 5%). ^{1}H NMR of **2b** (THF-d_8): δ −11.7 (s, 6 H, Me), −5.2 (s, 30 H, Cp*). The tube was heated for 2 days at 65 °C, and the spectrum showed that **2b** was totally decomposed, giving Na[Cp*$_2$U(SMe)(SCH$_2$)] as the major product (ca. 50%). ^{1}H NMR (THF-d_8): δ −0.4 (s, 30 H, Cp*), 22.3 (s, 2 H, CH$_2$), 32.8 (s, 3 H, Me). The NMR spectrum also showed the formation of Cp*H and a number of unidentified compounds. Methane was detected by GLC.

Sodium Amalgam Reduction of 1c and Thermolysis of 2c. An NMR tube was charged with **1c** (7.3 mg, 11 10^{-3} mmol) and 2% Na(Hg) (12.7 mg, 11 10^{-3} mmol) in THF-d_8 (0.4 mL). After stirring for 24 h at 20 °C, the spectrum showed that **1c** was completely transformed into a mixture containing **2c** and **4c** in the relative proportions of 94:6. ^{1}H NMR of **2c** (THF-d_8): δ −13.8 (s, 12 H, Me), −12.1 (s, 2 H, CH), −3.5 (s, 30 H, Cp*). After heating for 4 h at 65 °C, the spectrum showed that **2c** was totally decomposed, giving **4c** as the major product (ca. 85%). ^{1}H NMR (THF-d_8): δ −46.7 (s, 1 H, CH), −19.1 (s, 6 H, Me), 3.12 (s, 30 H, Cp*). Pentamethylcyclopentadiene, propane, 2,3-dimethylbutane, and a trace of propene were detected by NMR and GLC-MS.

Sodium Amalgam Reduction of 1d. An NMR tube was charged with **1d** (11.2 mg, 16.3 10^{-3} mmol) and 2% Na(Hg) (18.8 mg, 16.3 10^{-3} mmol) in THF-d_8 (0.4 mL). After stirring for 4 h at 20 °C, the spectrum showed that **1d** was completely transformed into **4d** in almost quantitative yield. ^{1}H NMR (THF-d_8): δ −19.5 (s, 9 H, ^{t}Bu), 4.3 (s, 30 H, Cp*). Isobutane and isobutene were detected by NMR and GLC.

[Na(18-crown-6)][Cp*$_2$U(S^{t}Bu)(S)] (5). A flask was charged with [Na(THF)$_{1.5}$][Cp*$_2$UCl$_2$] (560 mg, 0.79 mmol) and NaS^{t}Bu (313 mg, 2.8 mmol), and THF (50 mL) was condensed in. After stirring for 18 h at 20 °C, the red solution was filtered and evaporated to dryness. The residue was extracted in pentane (50 mL), and the ochre powder of **4d** was obtained after evaporation (482 mg, 95%). Crystallization of this powder in the presence of 18-crown-6 (198 mg, 0.75 mmol) from THF−pentane afforded red needles of **5**, which were filtered off and dried under vacuum (521 mg, 77%). Anal. Calcd for $C_{36}H_{63}NaO_6S_2U$: C, 47.16; H, 6.92; S, 6.99. Found: C, 46.91; H, 6.78; S, 6.74. ^{1}H NMR (THF-d_8): δ −17.2 (s, 9 H, ^{t}Bu), 2.3 (s, 30 H, Cp*), 4.5 (s, 24 H, 18-crown-6). The same reaction was monitored by NMR, showing concomitant formation of isobutane and isobutene.

[Na(18-crown-6)(THF)$_2$][Cp*$_2$U(SMe)(SCH$_2$)] (6). A flask was charged with **1b** (268 mg, 0.44 mmol) and 2% Na(Hg) (511 mg, 0.44 mmol), and THF (25 mL) was condensed in. After stirring for 12 h at 20 °C, the green solution of **2b** was filtered and heated at 65 °C for 40 h. The brown solution was filtered and evaporated to dryness; 18-crown-6 (58.7 mg, 0.22 mmol) was added and THF (25 mL) was condensed into the flask. After filtration and evaporation to dryness, the brown powder was washed with pentane (30 mL) and extracted with THF (25 mL). Dark red crystals of **6** were obtained by crystallization from THF−pentane; these were filtered off and dried under vacuum (206 mg, 45%). Anal. Calcd for $C_{42}H_{75}NaO_8S_2U$: C, 48.82; H, 7.32; S, 6.21. Found: C, 48.91; H, 7.34; S, 6.38. ^{1}H NMR (THF-d_8): δ −2.4 (s, 30 H, Cp*), 3.1 (s, 24 H, 18-crown-6); 15.2 (s, 3 H, Me); 67.2 (s, 2 H, CH$_2$).

Protonation of 6 with NHEt$_3$BPh$_4$. An NMR tube was charged with **6** (8.7 mg, 8.4 10^{-3} mol) and $NHEt_3BPh_4$ (3.9 mg, 9.2 10^{-3} mol) in THF-d_8 (0.4 mL). After 5 min at 20 °C, the spectrum showed the quantitative formation of **1b**.

X-ray Data Collection, Structure Determination, and Refinement for [Na(18-crown-6)(THF)$_2$][Cp*$_2$U(S^{i}Pr)$_2$]. Green crystals were obtained by crystallization of **3c** from THF−pentane. A selected crystal was introduced into a Lindemann glass capillary. Data were collected on a Nonius Kappa-CCD area detector diffractometer.[35] The lattice parameters were determined from 10 frames (Φ-scans, 1° steps) and later refined on all data. A 180° Φ-range was scanned with 2° steps with a crystal-to-detector distance fixed at 28 mm. Data were processed and corrected for Lorentz polarization effects with DENZO-SMN.[36] The structure was solved by the heavy-

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Table 3. Crystal Data and Summary of Data Collection and Refinement for [Na(18-crown-6)(THF)$_2$][Cp*$_2$U(S^{i}Pr)$_2$] and [Na(18-crown-6)(THF)$_2$][Cp*$_2$U(SMe)(SCH$_2$)]

	3c·2THF	**6**
formula	$C_{46}H_{84}NaO_8S_2U$	$C_{42}H_{75}NaO_8S_2U$
fw	1090.27	1033.16
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	17.052(3)	10.7635(11)
b (Å)	13.883(3)	21.759(2)
c (Å)	22.560(5)	19.8422(12)
β (deg)	102.14(3)	94.511(6)
V (Å^3)	5221.2(2)	4632.7(7)
Z	4	4
D(calcd) (g/cm^3)	1.387	1.481
μ (mm^{-1})	3.242	3.650
cryst size (mm)	0.15 × 0.15 × 0.10	0.25 × 0.20 × 0.15
radiation type	Mo Kα	Mo Kα
temp (K)	123(2)	100(2)
θ range, deg	4.1−20.8	3.5−25.7
no. of reflns collected	20 168	30 124
no of reflns merged	5423	8443
no of reflns obsd	4522	4554
observn criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$
no of params refined	527	501
R^a	0.044	0.058
$R_w{}^b$	0.102	0.117
goodness of fit	1.198	1.008

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$.

atom method and subsequent Fourier-difference synthesis and refined by full matrix least-squares on F^2 with SHELXL-97.[37] No absorption correction was done. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced at calculated positions as riding atoms with an isotropic displacement parameter equal to 1.2(CH, CH$_2$) or 1.5(CH$_3$) times that of the parent carbon atom. The molecular plot was done with SHELXTL.[38] All calculations were performed on a Silicon Graphics station. Crystal data and summary of data collection and refinement are given in Table 3.

X-ray Data Collection, Structure Determination, and Refinement for [Na(18-crown-6)(THF)$_2$][Cp*$_2$U(SMe)(SCH$_2$)] (6). A selected crystal was introduced into a Lindemann glass capillary with a protecting Paratone oil (Exxon Chemical Ltd.) coating. Data were collected on a Nonius Kappa-CCD area detector diffractometer.[35] The lattice parameters were determined from 10 frames (Φ-scans, 2° steps) and later refined on all data. A 180° Φ-range was scanned with 2° steps with a crystal-to-detector distance fixed at 28 mm. Data were processed and corrected for Lorentz polarization effects with DENZO-SMN.[36] The structure was solved by direct methods with SHELXS-97[37] and subsequent Fourier-difference synthesis and refined by full matrix least-squares on F^2 with SHELXL-97.[37] Absorption effects were corrected empirically with the program DELABS from PLATON[39] ($T_{\min} = 0.369$, $T_{\max} = 0.578$). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced at calculated positions as riding atoms with an isotropic displacement parameter equal to 1.2(CH, CH$_2$) or 1.5(CH$_3$) times that of the parent carbon atom. The molecular plot was done with SHELXTL.[38] All calculations were performed on a Silicon Graphics station. Crystal data and summary of data collection and refinement are given in Table 3.

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Supporting Information Available: Tables giving data collection and refinement details, atomic coordinates, thermal parameters, and bond lengths and bond angles of the crystallographically characterized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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