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Organouranium Complexes with Phosphinine-Based SPS Pincer Ligands. Variations with the Substituent at the Phosphorus Atom

Thérèse Arliguie,*^,†^ Matthias Blug,[‡] Pascal Le Floch,[‡] Nicolas Mézailles,*^,‡^ Pierre Thuéry,[†] and Michel Ephritikhine*^,†^

Service de Chimie Moléculaire, DSM, IRAMIS, CNRS URA 331, CEA/Saclay, 91191 Gif-sur-Yvette, France, and Laboratoire “Hétéroéléments et Coordination”, CNRS UMR 7653, Ecole Polytechnique, 91128, Palaiseau Cédex, France

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Reaction of [K(Et$_2$O)][SPS^{Me}] with [U(Cp*)(BH$_4$)$_3$] or [U(COT)(BH$_4$)$_2$(THF)] in THF gave the expected substitution products [U(Cp*)(BH$_4$)$_2$(SPS^{Me})] (**1**) and [U(COT)(BH$_4$)(SPS^{Me})] (**2**), respectively. Protonolysis of **2** with [NEt$_3$H][BPh$_4$] afforded the cationic complex [U(COT)(SPS^{Me})(NEt$_3$)][BPh$_4$] (**3**), which was transformed into [U(COT)(SPS^{Me})(L)][BPh$_4$] [L = OPPh$_3$ (**4**) or HMPA (**5**)]. Changing [K(Et$_2$O)][SPS^{Me}] with [Na][SPS^{OMe}] in its reaction with [U(COT)(BH$_4$)$_2$(THF)] afforded a mixture of complexes, among which [U(COT)(BH$_4$)(SPS^H)] (**6**) was deposited as red crystals of a THF solvate. Complex **6** was isolated in 79% yield from the reaction of [U(COT)(BH$_4$)$_2$(THF)] and SPS in the presence of a catalytic amount of NaBH$_4$; the key intermediate of the reaction is [Na(THF)$_x$][SPS^H·BH$_3$], formed by addition of NaBH$_4$ to SPS, which reacts with [U(COT)(BH$_4$)$_2$(THF)] to give **6** and NaBH$_4$. The X-ray crystal structures of **1**·4.5C$_6$H$_{12}$, **2**·THF, **5**·Et$_2$O, and **6**·1.5THF indicate that the central moiety of the SPS ligand can be considered as a classical phosphine, the anionic charge being stabilized by delocalization over the five carbon atoms of the phosphahexadienyl anion and negative hyperconjugation into the two Ph$_2$PS pendant arms. The X-ray crystal structures of [{U(COT)(S$_2$PPh$_2$)(μ-OMe)}$_2$] and [{U(COT)}$_4${U(THF)$_3$}$_2$(μ_3-S)$_8$], which resulted from decomposition of the SPS ligand, are also presented.

Introduction

Pincer ligands have gained a prominent position in coordination chemistry, justified by their structural rigidity, which provides a significant thermodynamic stability to their complexes, and the easy modification of their steric and electronic properties through changes to the substituents of the central and peripheral binding sites.[1–4] Besides the number of terdentate pincer ligands of XCX or XNX type, in which a central aromatic benzene or pyridine ring is substituted by two chelating pendant arms with a variety of donor heteroatom combinations (X = C, N, O, P, and S),[5] the unique SPS^R ligand, featuring a central λ^4-phosphinine unit and two lateral phosphinosulfide groups, was found to endow a series of d transition metals with attractive structures and reactions.[6–14] The softness of both the phosphorus and sulfur centers of this SPS pincer was not an obstacle to its coordination to the hard f elements, as shown recently with the synthesis, from the borohydride precursors [Ln(BH$_4$)$_3$], of the lanthanide derivatives [Ln(BH$_4$)$_2$(SPS^{Me})(THF)$_2$] and of the homoleptic complexes [Ln(SPS^{Me})$_3$] (Ln = Nd, Ce), the formation of which was clearly favored by the flexibility of the tridentate ligand.[15] In contrast, reactions of UX$_4$ (X = Cl, BH$_4$) and the lithium or potassium salts of the [SPS^{Me}]$^-$ anion afforded the uranium compounds [UX$_2$(SPS^{Me})$_2$] as the sole products.[15] In order to extend this work and learn more about the uranium complexes with SPS^R ligands, we turned our investigations toward the organometallic compounds, considering the most familiar classes of tris(cyclopentadienyl) [U(Cp)$_3$], mono- and bis(pentamethylcyclopentadienyl) [U(Cp*)] and [U(Cp*)$_2$], and mono(cyclooctatetraenyl) [U(COT)] derivatives. A series of neutral and cationic compounds with the SPS^{Me} ligand were isolated from [U(Cp*)(BH$_4$)$_3$] and [U(COT)(BH$_4$)$_2$(THF)]. Of special interest was the reaction of [U(COT)(BH$_4$)$_2$(THF)] and [Na][SPS^{OMe}], which gave a mixture of products including the SPS^H complex [U(COT)(BH$_4$)(SPS^H)] (**6**). Here we report first on the preparation and characterization of these compounds. Second, we propose a mechanism for the formation of **6**, which is supported by a straightforward and clean synthesis of this complex. Finally, we also describe the X-ray crystal structures

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* Corresponding authors. E-mail (N.M.): mezaille@poly.polytechnique.fr.

[†] Service de Chimie Moléculaire, DSM, IRAMIS, CNRS URA 331.

[‡] Laboratoire “Hétéroéléments et Coordination”, CNRS UMR 7653.

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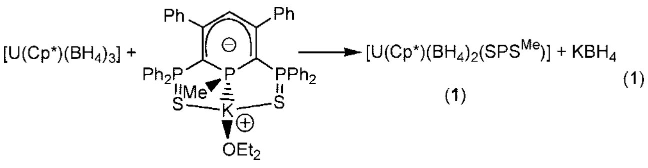
of complexes resulting from decomposition of the SPS^R ligand in the coordination sphere of U.

Results and Discussion

Complexes with the SPS^{Me} Ligand. Reactions of the tris(cyclopentadienyl) and bis(pentamethylcyclopentadienyl) uranium(IV) compounds $[U(Cp)_3Cl]$ and $[U(Cp^*)_2X_2]$ (X = Cl, BH_4) with the lithium or potassium salt of the $[SPS^{Me}]^-$ anion were quite sluggish, and no product was identified. This lack of reactivity can be explained by the steric hindrance of the reagents and the electron richness of the uranium center impeding the approach of the anionic tridentate ligand. Treatment of the trivalent uranium metallocene $[U(Cp)_3(THF)]$ with $[M(Et_2O)][SPS^{Me}]$ (M = Li or K) led to the formation of dark red crystals, which were found to be the bridging sulfide compound $[\{U(Cp)_3\}_2(\mu\text{-S})]$ by X-ray diffraction analysis (only a rough model could be obtained, see Experimental Section). The crystal structure and formation of this complex are reminiscent of those of $[\{U(C_5H_4Me)_3\}_2(\mu\text{-S})]$, which was synthesized by oxidation of $[U(C_5H_4Me)_3]$ with $Ph_3P{=}S$.[16] Obviously, electron-rich U(III) centers are efficient reducing agents for phosphine sulfide derivatives.

The mono(pentamethylcyclopentadienyl) compound $[U(Cp^*)(BH_4)_3]$ readily reacted with 1 molar equiv of $[K(Et_2O)][SPS^{Me}]$ in THF to give $[U(Cp^*)(BH_4)_2(SPS^{Me})]$ (**1**) (eq 1); after filtration and evaporation, **1** was extracted in cyclohexane and crystallized from this solvent as an orange solvate in 70% yield. Complex **1** is, after the mixed-ring compound $[U(Cp^*)(C_4Me_4P)(BH_4)_2]$, the only other derivative of $[U(Cp^*)(BH_4)_3]$ obtained by substitution of a BH_4 ligand.[17] One may note here the stability of the SPS^{Me} ligand in the presence of a borohydride derivative, unlike the SPS^{OMe} analogue (*vide infra*).



(1)

A view of complex **1** is shown in Figure 1, while selected bond lengths and angles are listed in Table 1. The uranium atom is in the familiar *fac* pseudo-octahedral configuration with the Cp* ligand and the central P(1) atom of the SPS ligand in *trans* axial positions and the two B and two S atoms defining the equatorial plane (rms deviation 0.025 Å). The U atom is displaced by 0.556(4) Å from this plane toward the Cp* ligand. The short U···B distances of 2.577(8) and 2.575(10) Å are identical to that of 2.58(3) Å in $[U(Cp^*)_2(BH_4)_2]$[17] and indicate a tridentate ligation mode of the BH_4 ligands, in keeping with the positions found for the hydrogen atoms. The coordination geometry of the SPS^{Me} ligand in **1** can be compared with that in $[UCl_2(SPS^{Me})_2]$, the other uranium SPS compound to have been crystallographically characterized.[15] The flexible SPS^{Me} ligand in **1** adopts a facial coordination mode, with the U atom at a distance of 2.1145(11) Å from the P(1)−S(1)−S(2) plane and the S(1)−U−S(2) angle equal to 77.95(5)°. This geometry is similar to that of one of the two SPS^{Me} ligands of $[UCl_2(SPS^{Me})_2]$, the other one being closer to the planar geometry, with the U atom less displaced from the P(1)−S(1)−S(2) plane, at 0.2032(13) Å, and a larger S−U−S angle of 139.53(3)°. The two U−S distances in **1** are identical, 2.8793(19) and 2.8781(18) Å, and the U−P(1) distance is 2.9853(18) Å, in line with the corresponding average distances of 2.88(8) and 2.98(2) Å in $[UCl_2(SPS^{Me})_2]$. It has been already noted, after comparison of the U−P distances with the $U{-}P_{phosphido}$ and $U{-}P_{phosphino}$ bond lengths in uranium(IV) complexes, that the SPS^{Me} ligand is better described as containing a tertiary phosphine functionality.[15] This bonding situation will be confirmed after consideration of the bond lengths within the SPS ligands in all the organouranium complexes (*vide infra*).

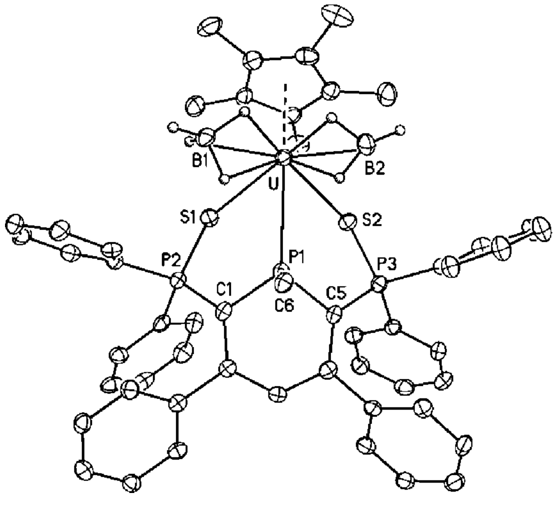
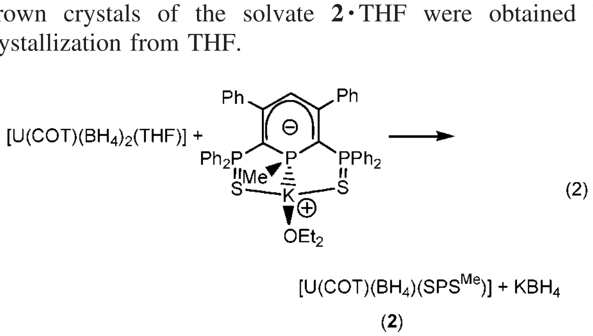


Figure 1. View of complex **1**. The hydrogen atoms (except those of the borohydride groups) have been omitted. Displacement ellipsoids are drawn at the 30% probability level.

Attempts at the synthesis of derivatives of **1** were disappointing. Complex **1** was inert in the presence of an excess of $[K(Et_2O)][SPS^{Me}]$, likely reflecting unfavorable steric and electronic effects, as noted in the tris(Cp) and bis(Cp*) series. Reduction of **1** with sodium amalgam led to the formation of $[U(Cp^*)(BH_4)_3]^-$ as the sole identified complex, in ca. 40% yield; it is possible that the latter resulted from ligand redistribution reaction of the expected anion $[U(Cp^*)(BH_4)_2(SPS^{Me})]^-$.

Reaction of $[U(COT)(BH_4)_2(THF)]$ with 1 molar equiv of $[M(Et_2O)][SPS^{Me}]$ in THF at 20 °C readily afforded the expected substitution product $[U(COT)(BH_4)(SPS^{Me})]$ (**2**) (eq 2); after usual workup, **2** was isolated as a microcrystalline brown powder in 80% or 94% yield for M = Li or K, respectively. Brown crystals of the solvate **2**·THF were obtained by crystallization from THF.



(2)

(**2**)

A view of **2** is shown in Figure 2, while selected bond lengths and angles are listed in Table 1. The five-coordinate uranium atom can be seen in a distorted square-pyramidal arrangement if the COT ligand is considered as monodentate. The U atom is 1.455(4) Å above the basal plane defined by the B, P(1), S(1), and S(2) atoms (rms deviation 0.336 Å), which is almost parallel to the planar C_8H_8 ring, with a dihedral angle of 1.3(2)°.

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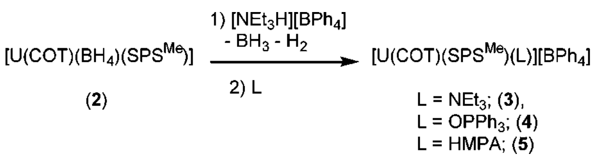
Table 1. Selected Bond Lengths (Å) and Angles (deg) in Complexes 1, 2, 5, and 6

	[U(Cp*)(BH$_4$)$_2$(SPS^{Me})] (**1**)	[U(COT)(BH$_4$)(SPS^{Me})] (**2**)	[U(COT)(SPS^{Me})(HMPA)][BPh$_4$] (**5**)	[U(COT)(BH$_4$)(SPS^H)] (**6**)
<U−C>	2.758(9)	2.680(11)	2.665(16)	2.668(13)
U−S(1)	2.8793(19)	2.919(3)	2.7940(6)	2.899(4)
U−S(2)	2.8781(18)	2.931(3)	2.7986(7)	2.873(3)
U−P(1)	2.9853(18)	2.965(3)	3.0425(7)	3.018(3)
U···B or U−O	2.577(8); 2.575(10)	2.571(12)	2.2567(16)	2.49(2)
P(1)−C(1)	1.794(7)	1.810(10)	1.800(3)	1.772(13)
P(1)−C(5)	1.792(7)	1.784(11)	1.805(3)	1.770(12)
P(1)−C(6)	1.826(7)	1.854(10)	1.840(3)	
P(2)−C(1)	1.753(7)	1.755(11)	1.769(2)	1.788(12)
P(3)−C(5)	1.778(7)	1.764(10)	1.760(3)	1.776(12)
P(2)−S(1)	2.011(2)	2.023(4)	2.0181(9)	2.012(4)
P(3)−S(2)	2.011(3)	2.008(4)	2.0204(10)	2.013(4)
P(1)−U−S(1)	69.70(5)	65.61(8)	71.825(18)	66.63(9)
P(1)−U−S(2)	70.48(5)	69.80(8)	72.15(2)	68.96(9)
S(1)−U−S(2)	77.95(5)	129.86(8)	95.43(2)	116.42(10)

The U···B distance of the tridentate BH$_4$ group, 2.571(12) Å, is quite identical to those in **1** and [{U(COT)(BH$_4$)(μ-OEt)}$_2$] [2.594(8) Å].[18] The U−S and U−P distances in **2** seem to be respectively 0.05 Å larger and 0.02 Å smaller than the corresponding distances in **1**, but the major difference between the SPS^{Me} ligands of the two complexes concerns their coordination geometry, which is closer to planar in **2**. This change in the coordination mode of the SPS^{Me} ligand, which should be related to the distinct configuration, octahedral and square pyramidal, of complexes **1** and **2** is shown by the smaller distance of the U atom from the P(1)−S(1)−S(2) plane, 0.845(3) Å, and the larger S(1)−U−S(2) angle of 129.86(8)°. However, the conformation of the SPS^{Me} ligand in **2** is different from that of the planar ligand in [UCl$_2$(SPS^{Me})$_2$], where the S(1) and S(2) atoms are located on the same side of the plane defined by the five carbon atoms of the central ring, whereas they are on either side of this plane in **2**. The COT ligation in **2**, as well as in the other (mono)cyclooctatetraenyl complexes presented hereafter, is unexceptional.

Protonolysis of M−BH$_4$ bonds by the acidic ammonium salt [NEt$_3$H][BPh$_4$] proved to be a convenient route to cationic complexes, as shown in particular by the synthesis of [U(COT)(BH$_4$)(THF)$_2$][BPh$_4$] and [U(COT)(HMPA)$_3$][BPh$_4$]$_2$ [HMPA = O=P(NMe$_2$)$_3$] from [U(COT)(BH$_4$)$_2$(THF)].[19] Complexes **1** and **2** were then considered as precursors of cationic SPS^{Me} compounds. Treatment of [U(Cp*)(BH$_4$)$_2$(SPS^{Me})] (**1**) with [NEt$_3$H][BPh$_4$] led to a slow protonolysis reaction, as shown by the formation of free amine NEt$_3$, but no product could be identified. In contrast, [U(COT)(BH$_4$)(SPS^{Me})] (**2**) was cleanly transformed into [U(COT)(SPS^{Me})(NEt$_3$)][BPh$_4$] (**3**), which, after filtration and evaporation, was isolated as a brown powder in 94% yield (eq 3).



$$\underset{(\mathbf{2})}{[\mathrm{U(COT)(BH_4)(SPS^{Me})}]} \xrightarrow[\text{2) L}]{\text{1) [NEt}_3\text{H][BPh}_4\text{]} \; - \mathrm{BH_3} - \mathrm{H_2}} [\mathrm{U(COT)(SPS^{Me})(L)}][\mathrm{BPh_4}] \qquad (3)$$

L = NEt$_3$; (**3**),
L = OPPh$_3$; (**4**)
L = HMPA; (**5**)

Successive evaporations of THF solutions of **3** did not permit the elimination of the NEt$_3$ ligand, which was however easily replaced with OPPh$_3$ or HMPA to give the brown adducts [U(COT)(SPS^{Me})(L)][BPh$_4$] [L = OPPh$_3$ (**4**) or HMPA (**5**)] in almost quantitative yield; crystals of **5**·Et$_2$O were obtained by slow diffusion of diethyl ether into a THF solution of **5**. A view of **5** is shown in Figure 3, and selected bond lengths and angles are listed in Table 1. By comparison with the structure of **2**, the SPS^{Me} ligand in **5** adopts a more facial conformation, with a larger distance of the U atom from the P(1)−S(1)−S(2) plane, 1.8521(5) Å, and a smaller S(1)−U−S(2) angle of 95.43(2)°. The average U−S and the U−P distances of 2.796(2) and 3.0425(7) Å are respectively the smallest and largest ever observed in uranium SPS compounds. These features can be tentatively explained by the stronger interaction between the cationic metal center and the negatively charged sulfur atoms of the SPS^{Me} ligand, in line with the contribution of the resonance hybrid structure C shown in Scheme 2 to the real

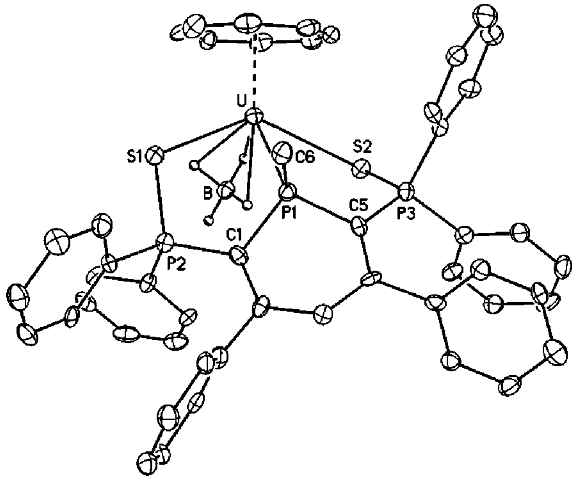


Figure 2. View of complex **2**. The hydrogen atoms (except those of the borohydride group) have been omitted. Displacement ellipsoids are drawn at the 30% probability level.

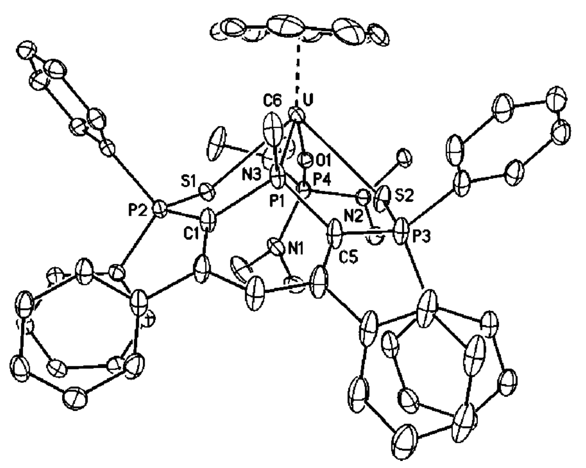


Figure 3. View of the cation of complex **5**. The hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 30% probability level.

structure (*vide infra*). The U−O distance of 2.2567(16) Å is unexceptional; it can be compared with that of 2.27(1) Å in $[\mathrm{U(COT)(BH_4)_2(OPPh_3)}]$[20] and 2.22(1) Å (average value) in $[\mathrm{U(COT)(HMPA)_3}][\mathrm{BPh_4}]_2$.[19]

Formation of the $[\mathrm{SPS^H \cdot BH_3}]^-$ Anion and Synthesis of $[\mathrm{U(COT)(BH_4)(SPS^H)}]$. By comparison with the $[\mathrm{SPS^{Me}}]^-$ anion, the $[\mathrm{SPS^{OMe}}]^-$ analogue has only seldom been studied.[21] Changing $[\mathrm{M(Et_2O)}][\mathrm{SPS^{Me}}]$ (M = Li, K) with $[\mathrm{Na}][\mathrm{SPS^{OMe}}]$ in its reaction with $[\mathrm{U(COT)(BH_4)_2(THF)}]$ led to a complicated mixture of products, among which $[\mathrm{U(COT)(BH_4)(SPS^H)}]$ (**6**) was deposited as red crystals of the THF solvate **6**·1.5THF. Complex **6**, the first compound with the $\mathrm{SPS^H}$ ligand, was isolated in good yield from reaction of $[\mathrm{U(COT)(BH_4)_2(THF)}]$ with SPS and $\mathrm{NaBH_4}$ (*vide infra*). The crystal structure of **6**, which revealed the presence of the $\mathrm{SPS^H}$ ligand resulting from P−O bond cleavage of the $[\mathrm{SPS^{OMe}}]^-$ anion, is quite similar to that of **2**; a view of **6** is shown in Figure 4, and selected bond lengths and angles are listed in Table 1. The most significant differences seem to concern the U−P(1) and U−B distances, which are respectively 0.05 Å larger and 0.08 Å smaller in **6**. The U−B bond length in **6** can be compared with those of 2.45(5) Å in $[\mathrm{U(Cp)(BH_4)_3}]$[22] and 2.48 Å in $[\mathrm{U(Cp)_3(BH_4)}]$.[23] It is possible that the shorter U−P(1) bond in **2** results from both the steric and electronic effects of the methyl substituent, whose interaction with the COT ring brings the $\mathrm{SPS^{Me}}$ ligand closer to the metal center and which increases the Lewis basicity of the phosphorus atom. As a consequence, the bond between the anionic $\mathrm{BH_4}$ ligand and the more electron-rich metal center of **2** would be weaker, as reflected by the larger U−B distance.

In one experiment, the reaction mixture of $[\mathrm{U(COT)(BH_4)_2(THF)}]$ and $[\mathrm{Na}][\mathrm{SPS^{OMe}}]$ was heated at 60 °C, leading to the formation of red crystals, which were found by X-ray diffraction analysis to be the dithiophosphinate complex $[\{\mathrm{U(COT)(S_2PPh_2)}(\mu\text{-OMe})\}_2]$, which obviously resulted from decomposition of the pincer ligand. It is quite striking to observe here again the facile elimination of the methoxide fragment from the ligand. A view of the centrosymmetric methoxy-bridged dimer is presented in Figure 5, together with selected bond lengths and angles. The uranium atom is in a square-pyramidal environment, if the COT ligand is considered to occupy a single coordination site, the basal plane defined by the O and S atoms with an rms deviation of 0.152 Å forming a dihedral angle of 5.4(2)° with the planar COT ligand. The U−O distances of 2.262(4) and 2.348(4) Å can be compared with those in $[\{\mathrm{U(COT)(BH_4)}(\mu\text{-OEt})\}_2]$ and $[\{\mathrm{U(COT)(O^iPr)}(\mu\text{-O^iPr})\}_2]$,[18] which vary from 2.296(5) to 2.317(6) Å, and the U−S distances of 2.8824(16) and 2.9435(16) Å can be compared with those of 2.845(3)−2.871(3) Å measured in $[\{\mathrm{U(S_2PMe_2)_2(OSPMe_2)}(\mu\text{-O_2PMe_2})\}_2]$, the only other dithiophosphinate complex of uranium(IV) to have been crystallographically characterized.[24]

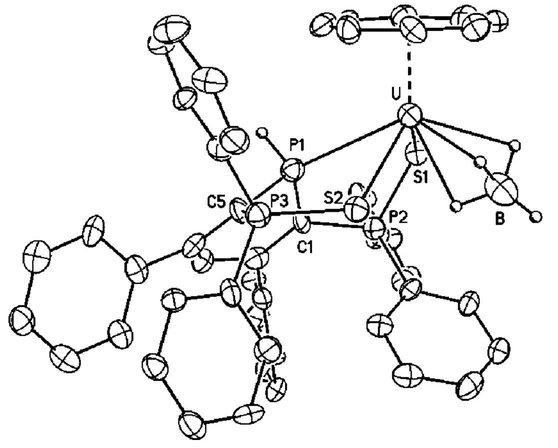


Figure 4. View of the cation of complex **6**. Carbon-bound hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 30% probability level.

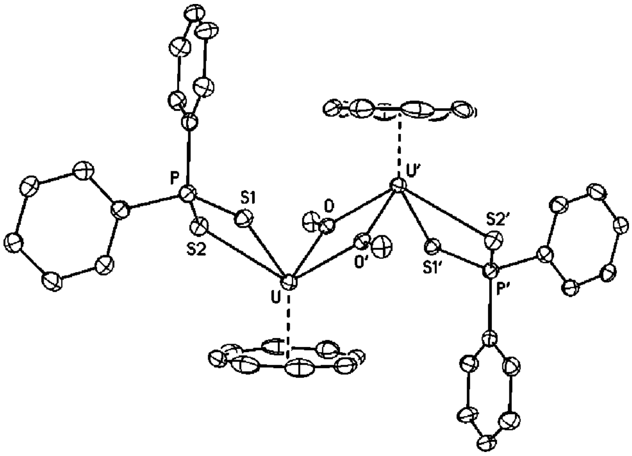


Figure 5. View of the complex $[\{\mathrm{U(COT)(S_2PPh_2)}(\mu\text{-OMe})\}_2]$. The hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): <U−C> 2.676(17), U−S(1) 2.8824(16), U−S(2) 2.9435(16), U−O 2.262(4), U−O′ 2.348(4), O−U−O′ 67.00(16), S(1)−U−S(2) 69.63(4). Symmetry code: ′ = −*x*, 1 − *y*, −*z*.

To have a better insight into the highly unusual behavior of the $\mathrm{SPS^{OMe}}$ ligand, the reaction of $[\mathrm{U(COT)(BH_4)_2(THF)}]$ and $[\mathrm{Na}][\mathrm{SPS^{OMe}}]$ was monitored by ^{1}H NMR spectroscopy. The spectra showed the simultaneous formation of three "U(COT)" complexes, easily noticed by their specific chemical shifts. The first of these is the known $[\mathrm{U(COT)(BH_4)_3}]^-$ complex (47% of the complexes), characterized by the signals at δ −25.5 and +60 for the COT and $\mathrm{BH_4}$ ligands, respectively. The second complex (31%), also present at the beginning of the reaction, is characterized by a COT resonance at δ −30.4 as well as a signal at δ 155.7 integrating for 3H. This latter signal is consistent with the low-field resonance corresponding to the alkoxide ligand in [U(COT)(OR)X] compounds.[22] As this complex also featured a $\mathrm{SPS^H}$ fragment, it was formulated as $[\mathrm{U(COT)(OMe)(SPS^H)}]$, but not isolated from the reaction mixture. The last complex, **6**, is characterized by the signals at δ −32.7 for the COT ligand and +245 for the $\mathrm{BH_4}$ ligand. Finally, the mixture also contained a $\mathrm{SPS^H}$ anionic fragment, not coordinated to a U center. The coexistence of these species can be explained by the following sequence. The expected reaction of $[\mathrm{U(COT)(BH_4)_2(THF)}]$ and $[\mathrm{Na}][\mathrm{SPS^{OMe}}]$ would give the unstable complex "$[\mathrm{U(COT)(BH_4)(SPS^{OMe})}]$" and $\mathrm{NaBH_4}$. The presence of $\mathrm{NaBH_4}$ in solution is the key to the formation of the other products. Indeed, it may react with $[\mathrm{U(COT)(BH_4)_2(THF)}]$ to form the observed $[\mathrm{U(COT)(BH_4)_3}]^-$

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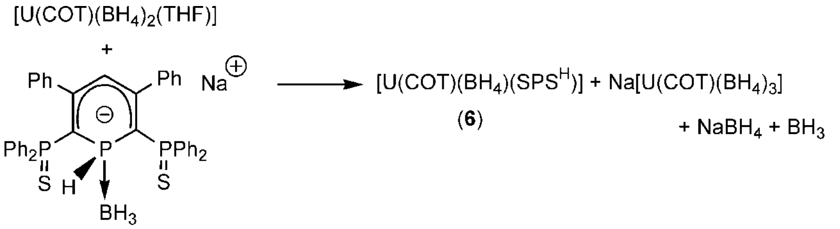
complex. In parallel, it also appeared to have reacted with the SPS^{OMe} fragment to form the SPS^{H} fragment. This substitution reaction is unprecedented, although it may be rationalized in light of our recent DFT study on SPS^{R} anionic derivatives.[25] Indeed, we showed in this study that the overall anionic charge is stabilized both by delocalization in the carbon ring and by negative hyperconjugation in σ^* antibonding orbitals of appropriate energy and symmetry (Scheme 1).

Should this be the case, the P−R bond would be longer than usual, which was verified experimentally with R = Me. In the particular case discussed here, the P−OMe derivative lies quite lower in energy, which leads to an enhanced leaving ability of the MeO group.

Our efforts were then concentrated on the straightforward and clean synthesis of **6** from $[U(COT)(BH_4)_2(THF)]$ and $[Na(THF)_x][SPS^{H}\cdot BH_3]$. Addition of 1 molar equiv of $NaBH_4$ to a THF solution of SPS led to the immediate formation of $[Na(THF)_x][SPS^{H}\cdot BH_3]$ in ca. 50% yield; total conversion of SPS into $[SPS^{H}\cdot BH_3]^-$ was observed upon addition of 18-crown-6. The ^{11}B and ^{31}P NMR spectra of this compound are similar to those of the methyl derivative $[K(Et_2O)][SPS^{Me}\cdot BH_3]$,[25] the high-field signal of the central phosphorus atom being here a doublet at δ −18.45 with $^1J(H-P) = 380$ Hz. Not surprisingly, treatment of $[Li(THF)_x][SPS^{H}]$[25] with $Me_2S\cdot BH_3$ also afforded the $[SPS^{H}\cdot BH_3]^-$ anion as its lithium salt, which was found to be in equilibrium with SPS and $LiBH_4$. The $[SPS^{H}\cdot BH_3]^-$ anion was not stable in THF solution and decomposed progressively into a product resulting from cleavage of a Ph_2PS arm of the pincer ligand and containing two phosphorus atoms, as shown by the ^{31}P NMR spectra, which exhibit a pair of doublets with $^2J(P-P) = 109$ Hz.

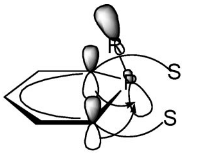


(4)

$$[U(COT)(BH_4)_2(THF)] + SPS \longrightarrow \text{"}[U(COT)(BH_4)_2(SPS)]\text{"} \longrightarrow [U(COT)(BH_4)(SPS^{H})]\ (\mathbf{6}) + BH_3 \qquad (5)$$

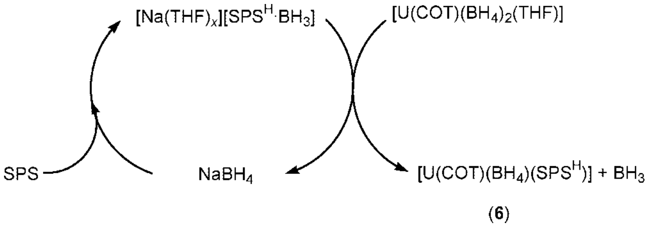
Attempts at the synthesis of **6** by reaction of $[U(COT)(BH_4)_2(THF)]$ with 1 molar equiv of $[Na(THF)_x][SPS^{H}\cdot BH_3]$, as a freshly prepared solution of $NaBH_4$ and SPS, gave a mixture of **6** and $[Na(THF)_x][U(COT)(BH_4)_3]$ in relative proportions of 10:90; this ratio changed to 25:75 after heating for 2 h at 80 °C. The formation of the $[U(COT)(BH_4)_3]^-$ anion, which was also observed in the reaction of $[U(COT)(BH_4)_2(THF)]$ and $[Na][SPS^{OMe}]$, was obviously caused by the presence of $NaBH_4$, which is in equilibrium with $[Na(THF)_x][SPS^{H}\cdot BH_3]$ and is produced in the synthesis of **6** by the substitution reaction (eq 4).

Scheme 1



stabilization of the anionic charge
in the sigma* P-R orbital

Scheme 2



Since the quantity of $NaBH_4$, which is necessary for making $[Na(THF)_x][SPS^{H}\cdot BH_3]$ from SPS, is recovered during the synthesis of **6** (eq 4), the latter could be prepared by reaction of $[U(COT)(BH_4)_2(THF)]$ and SPS in the presence of a catalytic amount of $NaBH_4$, thus avoiding the competitive formation of $[Na(THF)_x][U(COT)(BH_4)_3]$. The synthesis of **6** is described by the catalytic cycle shown in Scheme 2. Complex **6** was obtained in a 70% yield after 2 h at 80 °C, and its formation was complete when NEt_3 was added to the reaction mixture, for trapping BH_3 as the borane adduct $Et_3N\cdot BH_3$ (NMR observations). In a preparative scale synthesis, analytically pure **6** was isolated in 79% yield as a red microcrystalline powder after evaporation of the solvent and washing with diethyl ether.

An alternative to this mechanism was envisaged. It involves the reaction of neutral SPS with $[U(COT)(BH_4)_2(THF)]$, to form an intermediate species "$[U(COT)(BH_4)_2(SPS)]$", from which an intramolecular hydride transfer from the BH_4 ligand to the SPS would lead directly to **6** with the concomitant release of BH_3 (eq 5).

In practice, treatment of $[U(COT)(BH_4)_2(THF)]$ with SPS in THF indeed provided the desired complex **6**, yet with a low yield of 10% after 24 h at 20 °C (eq 5). Heating the reaction mixture led to a number of unidentified products, including a $[U(COT)(BH_4)X]$ compound characterized by its ^1H NMR signals at δ −34.76 (8H) and 273.23 (4H); this product was not observed in the reaction of $[U(COT)(BH_4)_2(THF)]$ and $[Na][SPS^{OMe}]$. In one experiment, black crystals were deposited from the reaction mixture and were found by X-ray diffraction analysis to be the hexanuclear complex $[\{U(COT)\}_4\{U(THF)_3\}_2(\mu_3\text{-}S)_8]$, a view of which is presented in Figure 6 together with selected bond lengths and angles. The plane defined by the U(2), U(2′), U(3), and U(3′) atoms is a mirror plane for the centrosymmetric complex. The structure exhibits an octahedron-like skeleton of uranium atoms that are held together with triply bridging sulfur atoms located above each face of the octahedron. The U_6S_8 core of the complex is a tetrakis hexahedron, that is, a cube of S atoms each face of which is covered by a square pyramid with a uranium atom at the apex. The U−S distances vary from 2.662(4) to 2.810(3) Å with an average value of 2.74(5) Å, which is similar to those of 2.74(1) and 2.75(2) Å in the trinuclear compounds $[U_3(\mu_3\text{-}S)(SBu^t)_{10}]$[26] and $[\{U(Cp^*)I_2\}_3(\mu_3\text{-}I)(\mu_3\text{-}S)]$,[27] respectively; the average U···U distance between proximal metal centers is 4.25(8) Å. While octahedral thiolato

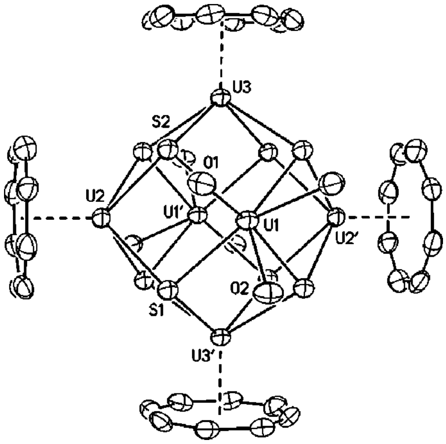
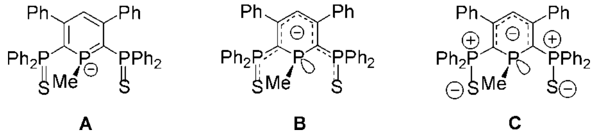


Figure 6. View of the complex $[\{U(COT)\}_4\{U(THF)_3\}_2(\mu_3\text{-}S)_8]$. The hydrogen atoms and carbon atoms of the THF molecules have been omitted. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): <U(1)−O> 2.547(16), <U(2)−C> 2.715(17), <U(3)−C> 2.71(2), U(1)−S(1) 2.662(4), U(1)−S(2) 2.684(3), U(2)−S(1) 2.810(3), U(2)−S(2) 2.752(4), U(3)−S(2) 2.756(3), U(3)−S(1′) 2.791(4). Symmetry code: ′ = 2 − *x*, 1 − *y*, 1 − *z*.

clusters of the type M_6S_8 are quite common for d transition metals, especially for M = Re, Mo, and W,[28–30] such compounds of the f elements have, to the best of our knowledge, not been reported.

Bonding Situation in the Organouranium SPS Complexes. The bonding mode of the SPS ligand was assessed by consideration of its geometrical parameters. As previously observed in the crystal structure of $[UCl_2(SPS^{Me})_2]$,[15] the internal P(1)−C(1) and P(1)−C(5) distances of the SPS ligands in complexes **1**, **2**, **5**, and **6**, which vary from 1.770(12) to 1.810(10) Å and average 1.791(14) Å, are larger than those in the neutral λ^3-phosphinine SPS [av 1.743(2) Å][8] and similar to those in the $[SPS^{Me}]^-$ and $[SPS^{OMe}]^-$ anions [av 1.808(9) and 1.793(2) Å, respectively];[8,25] these bond lengths are typical for classical phosphine ligands. In turn, the external P(2)−C(1) and P(3)−C(5) distances, which range from 1.753(7) to 1.788(12) Å and average 1.768(11) Å, are smaller than those in SPS [av 1.830(6) Å] and are similar to those in $[SPS^{Me}]^-$ and $[SPS^{OMe}]^-$ [av 1.777(6) and 1.78(1) Å, respectively]. The average P−S distance of 2.015(5) Å in complexes **1**, **2**, **5**, and **6** is larger than in SPS [1.954(2) Å], even larger than the mean P−S bond lengths of 1.977(5) and 1.971(4) Å in $[SPS^{Me}]^-$ and $[SPS^{OMe}]^-$, respectively, and is identical to that of 2.013(9) Å in $[UCl_2(SPS^{Me})_2]$.[15] These variations in the bond lengths, together with the pyramidalization and sp^3-type hybridization of the central P atom, clearly indicate that the central moiety of the SPS^R ligand can be considered as a classical phosphine and are in agreement with the resonance structure B in Scheme 3, where the negative charge is delocalized from one sulfur atom to the other. However, DFT calculations and NBO (natural bond orbital) analysis of the $[SPS^{Me}]^-$ anion showed that the electronic structure would be better described by the canonical form C, where the anionic charge is not fully delocalized but is stabilized by both delocalization over the five carbon atoms of the phosphahexadienyl anion and negative hyperconjugation into the two Ph_2PS pendant arms.[25] As noted before, the short U−S bonds suggest that form C contributes significantly to the true structure of the SPS^{Me} ligand in the cationic complex **5**.

Scheme 3



Conclusion

The first organo-f-element compounds with a phosphinine-based SPS pincer ligand, $[U(Cp^*)(BH_4)_2(SPS^{Me})]$ and $[U(COT)(BH_4)(SPS^{Me})]$, were synthesized by reaction of the uranium borohydride precursors with the lithium or potassium salt of the $[SPS^{Me}]^-$ anion. Treatment of $[U(COT)(BH_4)_2(THF)]$ with $[Na][SPS^{OMe}]$ led to the formation of $[U(COT)(BH_4)(SPS^H)]$ (**6**), the first compound with the SPS^H ligand. Attempts to devise a more rational synthesis of this complex via the independent formation of a "$M[SPS^H]$" species was hampered by the existence of an equilibrium between MBH_4 and neutral SPS to form $M[SPS^H\cdot BH_3]$. Anyhow, the latter observation pointed to the potential catalytic use of $NaBH_4$ in the synthesis. Eventually, synthesis of **6** was achieved by the reaction of $[U(COT)(BH_4)_2(THF)]$ with SPS in the presence of a catalytic amount of $NaBH_4$. In terms of geometrical and electronic properties of the tridentate anionic derivatives $[SPS^R]^-$ (R= Me, H), this study once again points up the flexibility of the ligand, which can be better seen as a central phosphine moiety with the anionic charge stabilized by both delocalization over the five carbon atoms of the heterocycle and negative hyperconjugation into the two Ph_2PS pendant arms.

Experimental Section

All 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 dried by standard methods and distilled immediately before use. Nuclear magnetic resonance spectra were recorded on a Bruker DPX 200 instrument operating at 200 MHz for ^1H, 64.2 MHz for ^{11}B, and 81 MHz for ^{31}P. The ^1H NMR spectra were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference, and ^{11}B chemical shifts are relative to a BF_3 external reference. The spectra were recorded at 23 °C when not otherwise specified. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The organouranium complexes $[U(Cp)_3(THF)]$,[31] $[U(Cp^*)(BH_4)_3]$,[32] $[U(COT)(BH_4)_2(THF)]$[20] and SPS,[6] $[M(Et_2O)][SPS^{Me}]$ (M = Li, K),[15] $[Li(THF)_x][SPS^H]$,[25] and $[Na][SPS^{OMe}]$[8] were prepared as previously reported; $[NEt_3H][BPh_4]$ was made by mixing NEt_3HCl and $NaBPh_4$ in water. IR samples were prepared as Nujol mulls between KBr round cell windows and the spectra recorded on a Nicolet Magna-IR 860 spectrometer.

Reaction of $[U(Cp)_3(THF)]$ and $[Li(Et_2O)][SPS^{Me}]$. An NMR tube was charged with the uranium complex (10.0 mg, 0.020 mmol)

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Table 2. Crystal Data and Structure Refinement Details

	1·4.5cyclohexane	**2**·THF	**5**·Et_2O	**6**·1.5THF	$[\{U(COT)(S_2PPh_2)(\mu\text{-}OMe)\}_2]$	$[\{U(COT)\}_4\{U(THF)_3\}_2(\mu_3\text{-}S)_8]$
empirical formula	$C_{79}H_{111}B_2P_3S_2U$	$C_{54}H_{54}BOP_3S_2U$	$C_{84}H_{90}BN_3O_2P_4S_2U$	$C_{55}H_{55}BO_{1.5}P_3S_2U$	$C_{42}H_{42}O_2P_2S_4U_2$	$C_{56}H_{80}O_6S_8U_6$
M_r	1477.36	1124.84	1610.43	1145.86	1245.00	2533.86
cryst syst	triclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/m$
a/Å	11.4079(7)	13.3300(15)	12.9649(3)	12.596(2)	12.8051(10)	15.0680(13)
b/Å	13.8663(8)	16.0507(10)	15.8235(4)	13.3444(19)	9.1321(7)	17.7057(18)
c/Å	24.1144(16)	22.223(2)	19.9331(4)	17.325(2)	17.4375(16)	13.0618(13)
α/deg	96.727(2)	90	94.930(2)	68.359(9)	90	90
β/deg	91.573(3)	97.554(4)	104.712(3)	88.154(9)	96.989(6)	95.326(6)
γ/deg	100.436(5)	90	93.076(2)	66.305(9)	90	90
V/Å^3	3721.0(4)	4713.4(8)	3928.47(17)	2455.6(6)	2023.9(3)	3469.7(6)
Z	2	4	2	2	2	2
D_{calcd}/g cm^{-3}	1.319	1.585	1.361	1.550	2.043	2.425
μ(Mo Kα)/mm^{-1}	2.343	3.674	2.248	3.528	8.313	14.234
F(000)	1528	2240	1640	1142	1176	2288
no. of rflns collected	22 588	30 900	159 481	16 056	13 311	13 095
no. of indep rflns	12 539	8716	14 905	8372	3801	3374
no. of obsd rflns ($I > 2\sigma(I)$)	10 037	5084	13 435	4377	2989	2451
R_{int}	0.065	0.113	0.039	0.135	0.075	0.087
no. of params refined	790	560	883	577	236	189
R1	0.059	0.066	0.025	0.072	0.033	0.054
wR2	0.137	0.138	0.065	0.159	0.073	0.123
S	1.079	1.006	1.067	0.955	1.005	1.052
$\Delta\rho_{min}$/e Å^{-3}	−1.22	−1.12	−0.94	−1.22	−0.91	−1.54
$\Delta\rho_{max}$/e Å^{-3}	1.58	1.54	0.60	0.97	0.85	1.37

and the lithium salt (15.4 mg, 0.020 mmol) in THF-d_8 (0.35 mL). After 20 h at 20 °C, dark red crystals of $[\{U(Cp)_3\}_2(\mu\text{-}S)]$ were deposited.

Synthesis of $[U(Cp^*)(BH_4)_2(SPS^{Me})]$ (1). A flask was charged with $[U(Cp^*)(BH_4)_3]$ (106 mg, 0.25 mmol) and $[K(Et_2O)][SPS^{Me}]$ (203 mg, 0.25 mmol), and THF (20 mL) was condensed in. The reaction mixture was stirred for 12 h at 20 °C; the solvent was evaporated off and the residue extracted in toluene (20 mL). After filtration, the volume of the brown solution was reduced to 2 mL, and addition of pentane led to the precipitation of a brown powder, which was filtered off and dried under vacuum. The powder was extracted with THF (10 mL), and after filtration, the solution was evaporated to dryness, leaving a brown-orange solid, which was extracted with cyclohexane (10 mL). Filtration and evaporation to dryness of the orange cyclohexane solution afforded the orange powder of **1**·C_6H_{12}. Yield: 208.6 mg (70%). Anal. Calcd for $C_{58}H_{69}B_2P_3S_2U$: C, 58.89; H, 5.88; P, 7.85; S, 5.42. Found: C, 58.62; H, 5.65; P, 7.81; S, 5.56. ^{1}H NMR (THF-d_8): δ 41.26 (s, 3 H, Me), 35.3 (br, $w_{1/2}$ = 260 Hz, 8 H, BH_4), 11.53 (s, 1 H, H^4), 10.35 (br, 4 H, CH of Ph), 9.97 (s, 15 H, Cp*), 9.01 (br t, J = 9.8 Hz, 4 H, CH of Ph), 7.70 (m, 6 H, CH of Ph), 6.20 (t, J = 7.3 Hz, 4 H, CH of Ph), 5.62 (t, J = 7.3 Hz, 2 H, CH of Ph), 4.98 (t, J = 7.3 Hz, 2 H, CH of Ph), 4.30 (t, J = 7.6 Hz, 4 H, CH of Ph), 1.43 (s, 12 H, C_6H_{12}), 0.47 (br t, J = 9.7 Hz, 4 H, CH of Ph). IR (Nujol): $\nu(BH_4)$ 2461(s), 2214(s), 2177(s) cm^{-1}.

Synthesis of $[U(COT)(BH_4)(SPS^{Me})]$ (2). Method a. A flask was charged with $[U(COT)(BH_4)_2(THF)]$ (52.9 mg, 0.119 mmol) and $[K(Et_2O)][SPS^{Me}]$ (96.5 mg, 0.119 mmol), and THF (50 mL) was condensed in. The color of the solution turned from bright red to brown. After stirring for 1 h at 20 °C, THF was evaporated off and the orange-brown residue was extracted in THF (30 mL), leaving a white precipitate of KBH_4; the orange-brown solution was filtered and evaporated to dryness, leaving a brown microcrystalline powder of **2**. Yield: 118 mg (94%). Anal. Calcd for $C_{50}H_{46}BP_3S_2U$: C, 57.04; H, 4.40; S, 6.09; P, 8.83. Found C, 57.02; H, 4.51; S, 5.83; P, 8.71. ^{1}H NMR (THF-d_8): δ 255 (br s, $w_{1/2}$ = 240 Hz, 4 H, BH_4), 17.54 (br t, $w_{1/2}$ = 24 Hz, 4 H, CH of Ph), 15.17 (t, J = 7.3 Hz, 4 H, CH of Ph), 14.37 (t, J = 7.3 Hz, 2 H, CH of Ph), 6.33 (t, J = 7.3 Hz, 2 H, CH of Ph), 6.16 (m, $w_{1/2}$ = 30 Hz, 4 H, CH of Ph), 5.78 (t, J = 7.3 Hz, 4 H, CH of Ph), 4.84 (t, J = 7.3 Hz, 4 H, CH of Ph), 3.35 (s, 1H, H^4), 1.69 (br, masked by the THF resonance, 2 H, CH of Ph), −0.43 (br t, J = 9.8 Hz, 4 H, CH of Ph), −21.09 (s, 3 H, Me), −32.31 (s, 8 H, COT). ^{31}P NMR (THF-d_8): δ 2113 (br, $w_{1/2}$ = 415 Hz, PMe), −320.5 (br, $w_{1/2}$ = 165 Hz, PPh_2). ^{11}B NMR (THF-d_8): δ 276 (br s, $w_{1/2}$ = 290 Hz, BH_4). IR (Nujol): $\nu(BH_4)$ 2491(s), 2198(s), 2165(s) cm^{-1}.

Method b. A flask was charged with $[U(COT)(BH_4)_2(THF)]$ (175 mg, 0.394 mmol) and $[Li(Et_2O)][SPS^{Me}]$ (306.2 mg, 0.394 mmol), and THF (50 mL) was condensed in. The reaction mixture was stirred for 1 h at 20 °C, and THF was evaporated off. The orange-brown powder of **2** was washed with diethyl ether (2 × 30 mL) and dried under vacuum. Yield: 330 mg (80%). The absence of $LiBH_4$ in the product was checked by ^{11}B NMR spectroscopy.

Synthesis of $[U(COT)(SPS^{Me})(NEt_3)][BPh_4]$ (3). A flask was charged with **2** (69 mg, 0.066 mmol) and $[NEt_3H][BPh_4]$ (30 mg, 0.07 mmol), and THF (100 mL) was condensed in. The reaction mixture was stirred at 80 °C for 90 min, and after filtration, the solution was evaporated to dryness, leaving **3** as a light brown powder. Yield: 198.4 mg (94%). Anal. Calcd for $C_{80}H_{77}BNP_3S_2U$: C, 65.88; H, 5.28; S, 4.39. Found: C, 64.08; H, 5.33; S, 4.25. ^{1}H NMR (THF-d_8): δ 19.75 (br t, $w_{1/2}$ = 25 Hz, 4 H, CH of Ph), 12.35 (t, J = 7.3 Hz, 4 H, CH of Ph), 11.01 (t, J = 7.3 Hz, 2 H, CH of Ph), 8.2−6.8 (m, 16 H, CH of Ph], 6.72 (m, $w_{1/2}$ = 16 Hz, 8 H, CH of BPh_4), 6.39 (t, J = 7.3 Hz, 8 H, CH of BPh_4), 6.26 (t, J = 7.3 Hz, 4 H, CH of BPh_4), 5.60 (t, J = 7.3 Hz, 4 H, CH of Ph), 2.68 (q, J = 7.2 Hz, 6 H, NCH_2CH_3), 1.11 (t, J = 7.2 Hz, 9 H, NCH_2CH_3), −18.51 (s, 3 H, PMe), −35.89 (s, 8 H, COT). ^{31}P NMR (THF-d_8): δ 2638 (br, $w_{1/2}$ = 390 Hz, Pme), −242.6 [d, ^2J(P−P) = 127 Hz, PPh_2].

Synthesis of $[U(COT)(SPS^{Me})(OPPh_3)][BPh_4]$ (4). An NMR tube was charged with **3** (10.3 mg, 0.007 mmol) and $OPPh_3$ (2.0 mg, 0.007 mmol) in THF-d_8 (0.4 mL). The spectrum showed the immediate and quantitative formation of **4**. ^{1}H NMR (THF-d_8): δ 13.43 (dt, J = 7.3 and 4.6 Hz, 4 H, CH of Ph), 12.12 (m, $w_{1/2}$ = 28 Hz, 6 H, CH of Ph), 11.12 (t, J = 7.3 Hz, 4 H, CH of Ph), 10.47 (t, J = 7.3 Hz, 2 H, CH of Ph), 7.7−6.5 (m, 35 H, CH of OPh_3 and BPh_4), 5.91 (dt, J = 7.3 and 4.6 Hz, 4 H, CH of Ph), 5.41 (m, $w_{1/2}$ = 26 Hz, 3 H, CH of Ph and H^4), 4.28 (t, J = 7.3 Hz, 4 H, CH of Ph), −2.91 (dt, J = 7.3 and 4.6 Hz, 4 H, CH of Ph), −12.42 (s, 3 H, PMe), −33.71 (s, 8 H, COT). ^{31}P NMR (THF-d_8): δ 2216 (br, $w_{1/2}$ = 395 Hz, PMe), 61.84 (s, $OPPh_3$), −285.1 [d, ^2J(P−P) = 130 Hz, PPh_2].

Synthesis of $[U(COT)(SPS^{Me})(HMPA)][BPh_4]$ (5). A flask was charged with **3** (77 mg, 0.052 mmol) in THF (25 mL), and HMPA (9.1 μL, 0.052 mmol) was added via a microsyringe. The solution was evaporated to dryness, leaving a brown powder of **5**. Yield: 80 mg (99%). Anal. Calcd for $C_{80}H_{80}BN_3OP_4S_2U$: C, 62.44; H, 5.25; S, 4.17; P, 8.06. Found: C, 61.98; H, 5.13; S, 3.92; P, 7.85. ^{1}H NMR (THF-d_8): δ 9.80 (dt, J = 7.3 and 5.1 Hz, 4 H, CH of Ph), 9.62 (t, J = 7.3 Hz, 4 H, CH of Ph), 9.40 (d, J = 9.5 Hz, 18 H, HMPA), 9.31 (t, J = 7.3 Hz, 2 H, CH of Ph), 7.45 (br s, $w_{1/2}$ = 16 Hz, 8 H, CH of BPh_4), 6.97 (m, 8 H + 6 H, CH of BPh_4 + CH of Ph), 6.76 (t, J = 7.3 Hz, 4 H, CH of BPh_4), 5.68 (t, J = 7.3 Hz, 2 H, CH of Ph), 5.37 (t, J = 7.3 Hz, 2 H, CH of Ph), 4.73 (br, $w_{1/2}$ = 28 Hz, 3 H, CH of Ph and H^4), 3.88 (t, J = 7.3 Hz, 4 H, CH of Ph), −4.50 (dt, J = 7.3 and 5.1 Hz, 4 H, CH of Ph), −6.41 (s, 3 H, PMe), −32.65 (s, 8 H, COT). ^{31}P NMR (THF-d_8): δ 2064 (br, $w_{1/2}$ = 410 Hz, PMe), 142.4 (br, $w_{1/2}$ = 20 Hz, HMPA), −286.51 [d, ^2J(P−P) = 132 Hz, PPh_2].

Reaction of [U(COT)$(BH_4)_2$(THF)] and [Na][SPS^{OMe}]. An NMR tube was charged with the uranium compound (9.0 mg, 0.020 mmol) and the sodium salt (14.9 mg, 0.020 mmol) in THF-d_8 (0.35 mL). After 15 min at 20 °C, the spectrum showed the formation of three U(COT) complexes: the anionic derivative [U(COT)$(BH_4)_3$]$^-$ (47%), complex **3** (21%), and another complex formulated as [U(COT)(OMe)(SPS^H)] (31%). ^{1}H NMR (THF-d_8): δ 155.7 (s, 3 H, OMe), 9.75 (t, J = 7.2 Hz, 2 H, CH of Ph), 9.14 (t, J = 7.2 Hz, 4 H, CH of Ph), 5.58 (t, J = 7.2 Hz, 4 H, CH of Ph), 3.79 (t, J = 7.2 Hz, 2 H, CH of Ph), 2.93 (t, J = 7.7 Hz, 4 H, CH of Ph), −0.57 (d, J = 7.6 Hz, 4 H, CH of Ph), −4.04 (s, 1 H, H^4), −4.87 (dd, J = 12 and 8 Hz, 4 H, CH of Ph), −30.38 (s, 8 H, COT); other signals should be masked by solvent and other complexes' resonances. The ^{1}H NMR spectrum of the reaction mixture also exhibits the signals of [Na(THF)$_x$][SPS^H·BH_3].

Formation of the [SPS^H·BH_3]$^-$ Anion. (a) An NMR tube was charged with SPS (10.8 mg, 0.016 mmol), $NaBH_4$ (0.6 mg, 0.016 mmol), and THF-d_8 (0.4 mL). The color of the solution immediately turned dark pink. The spectrum showed that 50% of SPS was transformed into the [SPS^H·BH_3]$^-$ anion. ^{1}H NMR (THF-d_8): δ 8.0−6.6 (m, 30 H, CH of Ph), 5.44 [hextuplet, ^2J(H−B) = ^3J(H−P) = 6.3 Hz, 0.5 H, PH] (the other half of the signal is masked by either the Ph or the THF resonances), 5.18 [t, ^4J(H−P) = 4.8 Hz, 1 H, H^4], 1.0 (br, $w_{1/2}$ = 220 Hz, 3 H, BH_3). ^{31}P NMR (THF-d_8): δ 37.67 [d, ^2J(P−P) = 23 Hz, PPh_2], −18.45 [br d, ^1J(P−H) = 380 Hz, PH]. ^{11}B NMR (THF-d_8): −37.3 (br s, $w_{1/2}$ = 270 Hz, BH_3). Addition of 18-crown-6 (4.1 mg, 0.06 mmol) to the reaction mixture led to the complete conversion of SPS into [SPS^H·BH_3]$^-$. After 1 h at 20 °C, the spectrum showed that [SPS^H·BH_3]$^-$ decomposed into a product resulting from cleavage of a Ph_2PS arm of the pincer ligand and containing two phosphorus atoms, as indicated by the ^{31}P NMR spectrum, which exhibited a pair of doublets at δ 228.80 and 40.69 with ^2J(P−P) = 109 Hz.

(b) An NMR tube was charged with SPS (10.6 mg, 0.016 mmol) in THF-d_8 (0.4 mL), and ^{t}BuLi (9.6 μL of a 1.7 M solution in pentane, 0.016 mmol) was added via a microsyringe, giving a deep red solution of [Li(THF)$_x$][SPS^H]. After 20 min at 20 °C, $Me_2S·BH_3$ (7.8 μL of a 2 M solution in Et_2O, 0.016 mmol) was introduced into the tube via a microsyringe. The ^{1}H, ^{31}P, and ^{11}B spectra of the deep pink solution showed the formation of [Li(THF)$_x$][SPS^H·BH_3] in equilibrium with SPS and $LiBH_4$.

Synthesis of [U(COT)(BH_4)(SPS^H)] (6). A flask was charged with [U(COT)$(BH_4)_2$(THF)] (180 mg, 0.405 mmol), $NaBH_4$ (1.0 mg, 0.027 mmol), NEt_3 (56 μL, 0.405 mmol), and SPS (276 mg, 0.405 mmol), and THF (50 mL) was condensed in. The red solution was heated for 1 h at 80 °C. The solvent was evaporated off and the red precipitate washed with diethyl ether (2 × 30 mL) and dried under vacuum. Yield: 333 mg (79%). Anal. Calcd for $C_{49}H_{44}BP_3S_2U$: C, 56.66; H, 4.27; S, 6.17; P, 8.94. Found: C, 56.38; H, 4.42; S, 5.98; P, 8.63. ^{1}H NMR (THF-d_8): δ 245 (br, $w_{1/2}$ = 240 Hz, 8 H, BH_4), 14.73 (dt, J = 7.3 and 4.8 Hz, 4 H, CH of Ph), 13.42 (t, J = 7.3 Hz, 4 H, CH of Ph), 12.79 (t, J = 7.3 Hz, 2 H, CH of Ph), 6.71 (t, J = 7.3 Hz, 2 H, CH of Ph), 5.88 (t, J = 7.3 Hz, 2 H, CH of Ph), 5.49 (m, 8 H, CH of Ph), 4.21 (m, 3 H, CH of Ph + H^4), 1.15 (br s, 2 H, CH of Ph), −1.15 (dt, J = 7.3 and 4.8 Hz, 4 H, CH of Ph), −32.73 (s, 8 H, COT), −35 (br d, J = 267 Hz, 1 H, PH). ^{31}P NMR (THF-d_8): δ 2139 (br, $w_{1/2}$ = 490 Hz, PH), −325.5 [d, ^2J(P−P) = 90 Hz, PPh_2]. ^{11}B NMR (THF-d_8): δ 263 (br, $w_{1/2}$ = 240 Hz, BH_4). IR (Nujol): $\nu(BH_4)$ 2454(s), 2199(s), 2156(s) cm^{-1}.

Reaction of [U(COT)$(BH_4)_2$(THF)] and SPS. An NMR tube was charged with [U(COT)$(BH_4)_2$(THF)] (8.5, 0.019 mmol) and SPS (12.9 mg, 0.019 mmol) in THF-d_8 (0.4 mL). After 24 h at 20 °C, the spectrum showed that 10% of [U(COT)$(BH_4)_2$(THF)] was transformed into **6**. After heating for 30 min at 80 °C, the spectrum showed the formation of unidentified products, including a [U(COT)(BH_4)X] compound characterized by two signals at δ −34.76 (8H) and 273.23 (4H).

Crystallographic Data Collection and Structure Determination. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[33] with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were introduced into glass capillaries with a protective "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames and then refined on all data. The data were processed with HKL2000.[34] The structures were solved by direct methods or by Patterson map interpretation with SHELXS97, expanded by subsequent Fourier-difference synthesis, and refined by full-matrix least-squares on F^2 with SHELXL97.[35] Absorption effects were corrected empirically with DELABS[36] or SCALEPACK.[34] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom bound to phosphorus in **6** and those of the borohydride groups in **1**, **2**, and **6** were found on Fourier-difference maps (only two were found for the borohydride group in **2** and the two others were introduced at calculated positions), and the carbon-bound hydrogen atoms were introduced at calculated positions; all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (BH_4, CH, CH_2) or 1.5 (CH_3) times that of the parent atom. Special details are as follows:

[U(COT)(SPS^{Me})(HMPA)][BPh_4]·Et_2O (5·Et_2O). Some voids in the lattice (about 90 Å^3 per asymmetric unit) probably contain very disordered solvent molecules that could not be resolved. The corresponding electronic density was taken into account with the program SQUEEZE.[36]

[U(COT)(BH_4)(SPS^H)]·1.5THF (6·1.5THF). One solvent THF molecule was found to be disordered around a symmetry center and could only be modeled with six atoms. Some restraints on displacement parameters were applied for some badly behaving atoms, particularly in the solvent molecules.

[{U(COT)}$_4${U(THF)$_3$}$_2$(μ_3-S)$_8$]. Two C atoms of one THF molecule are disordered around a mirror plane. Some voids in the lattice (about 64 Å^3 per asymmetric unit) probably contain very disordered solvent molecules that could not be resolved.

[{U(Cp)$_3$}$_2$(μ-S)]. The low quality of the crystals permitted only a rough model to be determined, which could not be refined. Crystal data: monoclinic, space group Cc, a = 8.21 Å, b = 14.31 Å, c = 43.23 Å, β = 91.73°.

Crystal data and structure refinement details are given in Table 2. The molecular plots were drawn with SHELXTL.[35]

Supporting Information Available: Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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