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Exploring the Uranyl Organometallic Chemistry: From Single to Double Uranium−Carbon Bonds

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S *Supporting Information*

ABSTRACT: Uranyl organometallic complexes featuring uranium(VI)−carbon single and double bonds have been obtained from uranyl UO_2X_2 precursors by avoiding reduction of the metal center. X-ray diffraction and density functional theory analyses of these complexes showed that the U−C and U═C bonds are polarized toward the nucleophilic carbon.

Compounds containing the hexavalent uranyl ion UO_2^{2+} have flourished considerably during the last years, enlarging a very active domain of coordination chemistry. The most notable advances, which have been described as nothing else than a revolution,[1] concern uranyl-based supramolecular assemblies and materials with unprecedented shapes, topologies, and potential applications, such as uranyl nanotubules[2] and nanospheres,[3] which have been built using organic templates and other metal cations under hydrothermal conditions. Other major progress is related to the synthesis of new precursors and their use in anhydrous organic solvents,[4] leading to the discovery of structural and chemical features[5] that have changed generally accepted ideas concerning the coordination geometry and stability of the UO_2^{2+} ion. In this context, it is noteworthy that the synthesis of uranyl compounds with metal−carbon bonds remains a challenging goal, and only a handful of such complexes can be identified among the thousands of uranyl derivatives that have been structurally characterized. The first attempts at their preparation date back to the 19th century with reactions of $[UO_2Cl_2]$ and Frankland or Grignard reagents,[6] and much later attempts employed organolithium reagents;[7] however, they consistently failed to access uranyl organometallic species. The reasons behind this behavior are now better understood and mainly arise from the reduction of U^{VI} to U^{V} by the alkyl ligand.[5d] Thus, only two uranyl complexes with alkyl or π-organometallic ligands have been observed to date: the cyclopentadienyl compound $[NEt_4]_2[UO_2(C_5Me_5)(CN)_3]$[8] and the bis(iminophosphoranyl) complex $[UO_2(\text{H-bipm})Cl]_2$ and its derivatives $[H_2\text{-bipm} = H_2C(Ph_2PNSiMe_3)_2]$.[9] Interestingly, the cyclopentadienyl uranyl complex was not synthesized by treatment of a $[UO_2X_2]$ precursor with the $[C_5Me_5]^-$ anion, a reaction that instead provides a convenient route to the corresponding pentavalent $[UO_2X]$ derivative,[5d] but was isolated from the reaction of the linear metallocene $[NEt_4]_3[U(C_5Me_5)_2(CN)_5]$ and pyridine *N*-oxide.[8] In view of the general utility of alkyl complexes in the synthesis of functional derivatives, there is a large gap in uranium coordination chemistry to fill.

Reasoning that stable uranyl organometallic complexes would require the use of alkyllithium compounds with high oxidation potentials, we investigated the coordination chemistry of bis(thiophosphinoyl)methane anions with uranyl(VI) salts. Both the $[CH(Ph_2PS)_2]^-$ monoanion ($[SCHS]^-$) and the $[C(Ph_2PS)_2]^{2-}$ dianion ($[SCS]^{2-}$) are available, and importantly, the geminal dianion and its nitrogen counterparts, bis(iminophosphorano)methanediides, have proven useful for the synthesis of a new type of metal carbene complex wherein the four electrons of the formal M═C double bond are provided by the sole carbenic precursor.[10,11]

Addition of $[UO_2(OTf)_2]$[4b] to 1 molar equiv of Li[SCHS] in diethyl ether immediately gave a red solution that deposited red crystals of $[UO_2(SCHS)(OTf)(OEt_2)]$ (**1**); after filtration and successive washings with toluene and Et_2O, pure **1** was obtained in 65% yield. A similar reaction of $[UO_2(OTf)_2]$ and 2 molar equiv of Li[SCHS] in tetrahydrofuran (THF) afforded red crystals of the bis(methanide) complex $[UO_2(SCHS)_2]\cdot$THF (**2**·THF), which were isolated in 85% yield after the usual workup. Complex **2** was alternatively prepared in 64% yield from a 1:2 mixture of $[UO_2I_2(THF)_3]$[4c] and K[SCHS] in THF. The comproportionation reaction of $[UO_2(OTf)_2]$ and **2** in THF led to the quantitative formation of $[UO_2(SCHS)(OTf)(THF)]$, which was also obtained by dissolving **1** in THF (Scheme 1).

The crystal structure of **1** is shown in Figure 1. The complex adopts the classical pentagonal bipyramidal configuration, with the equatorial plane defined by the U, C1, S1, S2, O3, and O6 atoms [root-mean-square (rms) deviation 0.095 Å] perpendicular to the linear UO_2 moiety. The displacement of the central carbon C1 from the plane containing the metal and the other four coordinating atoms in the equatorial plane, 0.327(13) Å, is much smaller than the value of 0.88 Å observed in $[UO_2(\text{H-bipm})Cl]_2$ and its derivatives,[9] a difference that likely reflects the smaller steric hindrance of the SCHS ligand in comparison with H-bipm. The almost planar U−S−P−C−P−S core in **1** contrasts with the boat conformation adopted by the H-bipm ligands in the aforementioned uranyl compounds and by the SCHS ligand in $[U(SCS)(SCHS)(NEt_2)]$,[11c] the only other uranium compound with this ligand. The U−C1 distance of 2.647(12) Å is smaller than those measured in the H-bipm uranyl compounds, which vary from 2.691(8) to 2.707(3) Å,[9] and that of 2.819(5) Å found for the SCHS ligand of the uranium(IV) complex.[11c] The average U−S distances of the SCHS ligand in

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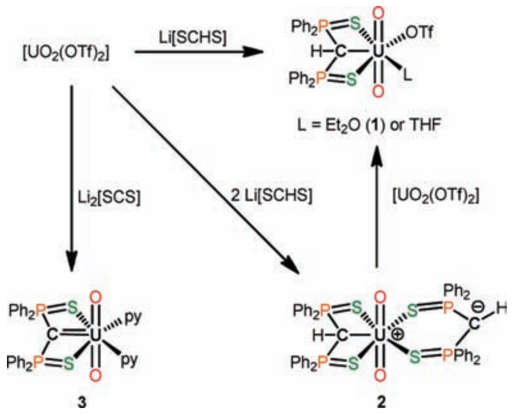
Scheme 1. Synthesis of Uranyl Organometallic Complexes 1−3



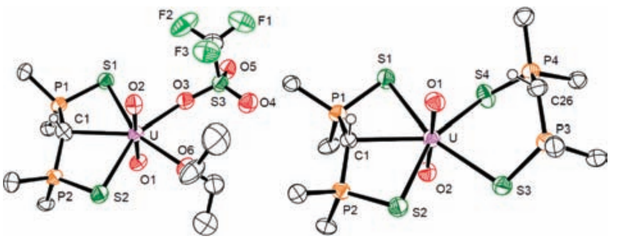


Figure 1. X-ray structures of (left) **1** and (right) **2** with 50% probability ellipsoids. Phenyl rings have been omitted for clarity.

the uranium(IV) and uranyl complexes are identical, with values of 2.889(9) and 2.882(6) Å, respectively.

While a few compounds of Ca^{2+}, Ba^{2+}, Sm^{2+}, Eu^{2+}, and Nd^{3+} with two bis(iminophosphorano)methanide ligands have been crystallographically characterized,[12] **2** is the first bis(methanide) complex of uranium(VI). Its crystal structure is shown in Figure 1. The two SCHS ligands are very distinct. One is similar to that in **1**, having an almost planar conformation with the central C1 atom in the equatorial plane of the UO$_2$ fragment, which also contains the U and four S atoms (rms deviation 0.063 Å); the U−C1 distance is equal to 2.656(3) Å. The other SCHS ligand adopts a boat conformation and a bidentate ligation mode, as the U−C26 distance of 3.863(3) Å is too large to define a direct U−C interaction. Therefore, complex **2** exhibits a zwitterionic structure with cationic U and anionic C26 separation. The distinct charge distributions within the two SCHS ligands and their distinct coordination modes induce variations in the interatomic distances and S−U−S angles; in particular, the U−S1 and U−S2 bonds [av 2.914(10) Å] are longer than the U−S3 and U−S4 bonds [av 2.824(8) Å], whereas the S1−U−S2 angle of 128.13(2)° is much larger than S3−U−S4 [86.59(3)°]. The ^{1}H and ^{13}C NMR spectra of **2** in THF-d_8 at 25 °C indicated complete equivalence of the two SCHS ligands on the NMR time scale. A single triplet corresponding to the methine protons was visible at δ 2.60; decoalescence of this signal and broadening of the phenyl resonances were observed at −107 °C, but the slow-limit spectrum could not be attained. These results can be explained by an intramolecular dynamic process leading to interchange of the tri- and bidentate SCHS ligands in solution, reflecting the hemilabile nature of the methanide carbon−uranium interaction.[12c]

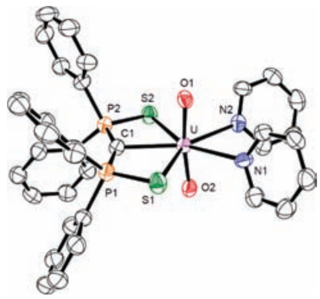


Figure 2. X-ray structure of **3** with 50% probability ellipsoids.

The successful stabilization of the uranyl(VI) alkyl complexes **1** and **2** prompted us to investigate the coordination chemistry of the more reducing dianionic [SCS]$^{2-}$ species as an entry to the first uranyl carbene complexes. Treatment of an equimolar mixture of [UO$_2$(OTf)$_2$] and CH$_2$(Ph$_2$PS)$_2$ with an excess of LiNEt$_2$ in pyridine afforded the uranyl carbene complex [UO$_2$(SCS)(py)$_2$] (**3**). After the reaction mixture was stirred for 12 h at 20 °C and then evaporated to dryness, **3** was extracted with toluene and isolated as an orange powder in 95% yield. Complex **3** was alternatively obtained in almost quantitative yield from a 1:1 mixture of [UO$_2$(OTf)$_2$(py)$_3$] and Li$_2$SCS in toluene; the LiOTf byproduct was discarded by filtration, and **3** was recovered after solvent evaporation. Finally, the protonolysis reaction of the uranyl amide [UO$_2${N(SiMe$_3$)$_2$}$_2$(THF)$_2$][13] with CH$_2$(Ph$_2$PS)$_2$ in pyridine also led to the formation of **3**; the solution was heated at 60 °C for 6 h and then evaporated to dryness, after which crystallization of the residue from pyridine/pentane gave dark-orange crystals of **3** together with dark-brown crystals of **3**·0.5py (50% yield).

The crystal structure of **3** is shown in Figure 2. The equatorial plane of the pentagonal bipyramidal complex defined by the U, S, N and C1 atoms also contains the P atoms, with an rms deviation of 0.076 Å. While the U−S−P−C−P−S core of the SCS ligand is slightly less planar in **3**·0.5py than in **3** (rms deviation of 0.147 vs 0.062 Å), the distances and angles are quite identical in both structures. The U−C distances of 2.430(6) Å in **3** and 2.420(3) Å in **3**·0.5py are 0.2 Å smaller than those of the methanide SCHS ligands of **1** and **2** and also that of the NHC ligand of [UO$_2$Cl$_2$(IMes)$_2$] (IMes =1,3-dimesitylimidazole-2-ylidene).[9] However, this distance is 0.1 Å larger than those measured in the U^{IV} carbenes [U(SCS)(BH$_4$)$_2$(THF)$_2$][11a] and [U(C$_5$H$_5$)$_2$U(SCS)],[11b] and the U−S distances, with an average value of 2.872(7) Å for both **3** and **3**·0.5py, are quite identical to those found in these same complexes, while the ionic radius of the UO$_2^{2+}$ ion is ~0.2 Å smaller than that of U^{4+}.[14] These features suggest that the multiple bond character of the U−C bond is less pronounced in **3** than in the U^{IV} compounds. The deviation from linearity of the UO$_2$ fragment, which displays angles of 171.8(2)° in **3** and 168.5(1)° in **3**·0.5py, is among the largest ever measured, whereas the U═O bond lengths remain unexceptional.[8,15] This severe bending likely results from repulsion between the negatively charged oxo groups and the electron-rich ligands, as previously observed in [NEt$_4$]$_2$[UO$_2$(C$_5$Me$_5$)(CN)$_3$].[8] The peculiar structural parameters of **3** (i.e., the relatively long U−C bond and the bent UO$_2$ unit) were subjected to density functional theory (DFT) analysis.

Because of the paucity of uranyl organometallic species, a relativistic DFT analysis of model complexes was performed to gain further insights into the electronic nature of the U−C and U═C bonds in complexes **1**−**3** (see the Supporting Information

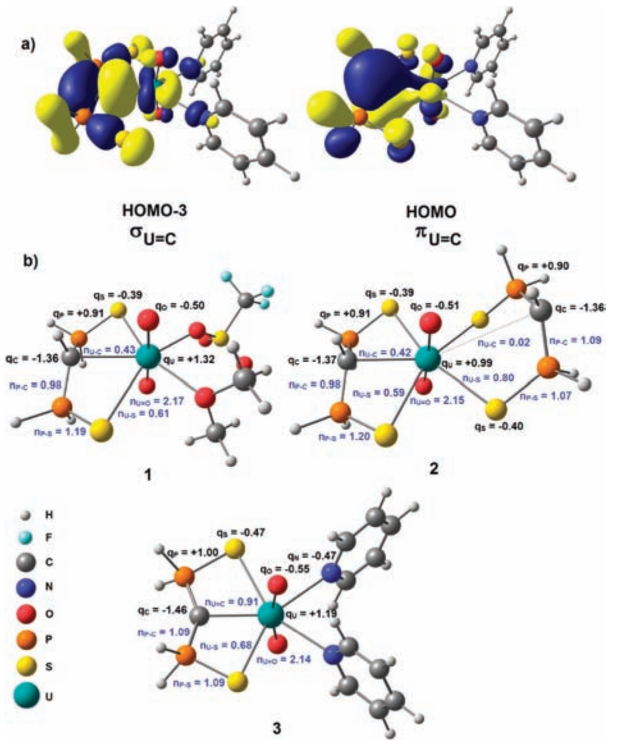


Figure 3. (a) Selected Kohn–Sham orbitals of **3**. (b) Results of NBO analysis [charges (q) and Wiberg bond indices (n)] of **1**, **2**, and **3**.

for computational details). The optimized geometries compared well with those observed experimentally by X-ray diffraction. For example, in **3**, the U═C bond distance was calculated as 2.41 Å [vs 2.430(6) Å experimentally], and the bending of the O═U═O backbone was well-reproduced [165.8° calcd vs 171.81(18)° exptl]. Inspection of the Kohn–Sham orbitals of **1**, **2**, and **3** revealed that the highest occupied molecular orbitals (HOMOs) describe the interaction between the uranium(VI) ion and the SCS and SCHS ligands, whereas the MOs for the U═O "yl" interactions are lower in energy. The HOMO–3 orbital in **3** describes the U═C σ bond, while the π bond was found to be the HOMO of the complex (Figure 3). Importantly, these two MOs exhibit small antibonding interactions between the uranium ion and the oxo atoms, accounting for the bending of the O═U═O backbone. Natural bond orbital (NBO) analysis of **1**–**3** was then undertaken in order to avoid the overestimation of covalency usually encountered in Mulliken population analysis (Figure 3). Alkyl complexes **1** and **2** exhibited only a single U–C bond described by a polarized NBO resulting from the donation of the carbon lone pair of the SCHS$^-$ ligand (~86%, with 12% 2s character and 88% 2p character) to a vacant metal orbital (~14%) having 30% 6d character and 25% 5f character. In contrast, the U═C interaction in **3** is properly described by two distinct NBOs, as expected from prior studies on U^{IV} and Zr^{IV} complexes.[11] Donation from a carbon sp$^{2.30}$ lone pair (80.6%) to a uranium hybrid orbital (19.4%) having 24.0% 6d and 30.2% 5f character forms the U═C σ bond. On the other hand, the U═C π bond is made of a carbon pure 2p orbital (87.3%) and a metal hybrid orbital (12.7%) having 23.3% 6d and 68.1% 5f character. These data clearly support the formation of a polarized U═C bond and show the contribution of the uranium 5f orbitals in establishing the double bond. As a result, the four electrons of the U═C bond in **3** are polarized as follows: while 3.36 electrons remain located on the carbon atom of the [SCS]$^{2-}$ carbenic precursor, 0.64 electron is transferred to the uranium atom. Overall, the formation of the U═C π bond upon conversion of **1** and **2** to **3** is clearly reflected by the change in the uranium–carbon Wiberg bond order, which increases from 0.43 in alkyl complexes **1** and **2** to 0.91 in **3**.

Interestingly, the U═C double bond in **3** remains polarized toward the nucleophilic carbon, as illustrated by the reaction of **3** with benzophenone to give the alkene $Ph_2C{=}C(Ph_2PS)_2$.[11a] The U═C bond polarization in **3** is even more marked than in U^{IV} complexes.[11] This result is surprising in view of the greater electrophilicity of U^{VI} relative to U^{IV}, which was expected to maximize the U═C interaction and therefore electron donation from the [SCS]$^{2-}$ ligand to uranium. However, inspection of the U═O Wiberg bond indexes and q_O charges in **1**, **2**, and **3** showed that the uranium–oxo interactions are only slightly perturbed by the formation of the U═C double bond. In other words, among the three double bonds present in the uranium coordination sphere (one U═C and two U═O bonds), the metal ion preferentially stabilizes the oxo ligands, leaving a nucleophilic carbene center. Interestingly, in the absence of oxo ligands, the expected shortening and decrease in the polarized character of the U═C bond were observed upon oxidation of U^{IV} to U^{V} in [UCl$_3$(bipm)]$^-$.[11d]

In summary, the use of the anions [SCHS]$^-$ and [SCS]$^{2-}$ has allowed us to access rare uranyl organometallic species, especially the first uranyl carbene complex, by avoiding reduction of the metal ion. Both uranium–carbon single and double bonds were stabilized, pushing back the limits of stable uranyl(VI) complexes with reducing ligands. Reactivity studies to introduce unusual functional groups in the coordination sphere of uranyl and isolate the pentavalent organouranyl derivatives are now under scrutiny.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data (CIF) and experimental and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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