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The U═C Double Bond: Synthesis and Study of Uranium Nucleophilic Carbene Complexes

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Abstract: Treatment of $U(BH_4)_4$ with 1 or 3 equiv of $Li_2(SCS)\cdot 1.5Et_2O$, **1**, afforded the actinide carbene complexes $U(\mu\text{-}SCS)_3[U(BH_4)_3]_2$ (**4**) and $U(\mu\text{-}SCS)_3[Li(Et_2O)]_2$ (**6**), respectively [SCS = $(Ph_2P = S)_2C$]. In THF, complex **4** was transformed into the mononuclear derivative $(SCS)U(BH_4)_2(THF)_2$ (**5**). The multiple bond character of the uranium−carbon bond was first revealed by the X-ray crystal structures of the three complexes. The U═C bond in these complexes present a nucleophilic character, as shown by their reaction with a carbonyl derivative. Finally, DFT calculations prove the involvement of both 5f and 6d orbitals in both the σ and the π U−C bonds.

Introduction

By comparison with the considerable amount of work devoted to the carbene complexes of d transition metals,[1] the chemistry of such compounds with f elements remains largely underdeveloped. Imidazol-2-ylidene molecules were used in the past few years to prepare lanthanide and uranium complexes with *N*-heterocyclic carbene (NHC) ligands, yet these carbene complexes are considered as simple Lewis base adducts without significant M─C double bond character.[2] Carbene complexes of f elements which are not simple adducts of free stable carbene ligands are very rare, a fact which can be related to intrinsic electronic properties of these metals, since the carbenic center can hardly be stabilized by π-back-donation from the metal fragment. However, access to this class of complexes in the lanthanide and actinide series would be of great interest to probe the involvement of 4f and 5f orbitals (respectively) in such a formally M─C multiple bond. If involved, these orbitals would participate in the stabilization of carbene fragments unstable in the free state by covalency. If possible, access to analogous complexes with 4f and 5f elements would allow a direct comparison of the bonding situation. Few examples of such species have been reported. In fact, very reactive intermediates such as the methylidene complexes $[M]{=}CH_2$ (M = Ce, Nd, Th, U) were detected by IR spectroscopy in reactions of excited metal atoms with methane or methyl halides in solid argon,[3] and carbenoid $[U]{=}CR_2$ nucleophilic species were evidenced in McMurry type reactions of sterically hindered ketones with the UCl_4/Li(Hg) system.[4] The phosphoylide uranium compounds $Cp_3U{=}CHPR_3$ reported by Gilje et al. were in fact the first actinide carbenes to be structurally characterized,[5] while, in 2000, Cavell et al. obtained the first structurally characterized Sm(III) carbene complex from *in situ* double deprotonation of a neutral bis(iminophosphorane) coordinated to $[Sm(NCy_2)_3(THF)]$.[6] More recently, Cavell et al. and some of us devised a new strategy toward transition metal carbene complexes, which relies on the potential four-electron donation of stable geminal dianions to an electron-deficient metal center to yield an M═C double bond (Scheme 1).[7] This strategy was successfully employed to synthesize lanthanide (Sm, Tm) complexes presenting a lanthanide−carbon double bond.[7] Among them the homoleptic bis-carbene complexes of Sm(III)[8a] and Tm(III)[8b] were isolated. The highly nucleophilic reactivity of these compounds toward ketones and aldehydes is reminiscent of Schrock type alkylidene complexes. Lastly, triply bridging methylidene complexes $Cp^*_3Ln_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)(\mu_3\text{-}CH_2)(THF)_3$ (Ln = Y, La), obtained by proton abstraction reactions involving $[Ln(AlMe_4)Cl]$ moieties, were reported in 2006.[9] It is noticeable that, in these complexes, the highly reactive CH_2 fragment is

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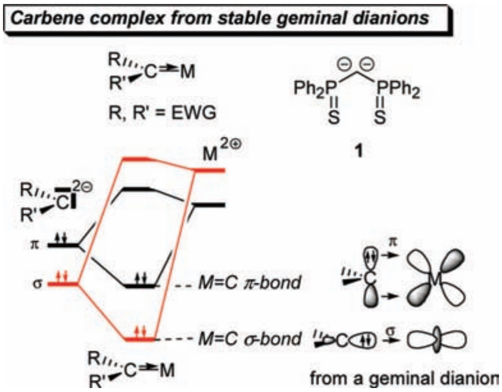
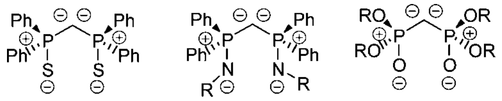
Scheme 1. Strategy to Access f-Elements Carbene Complexes Using a Stable Geminal Dianion



Scheme 2. Most Accurate Lewis Structure to Describe the Electronic Structure of the Geminal Dianions **1**−**3**


1 **2** **3**

stabilized by three metal centers instead of one, therefore pointing to a stabilization ensured by Ln−C σ-bonds only rather than σ- and π-bonds. None of these reports were concerned with the nature of the bonding between the carbene fragment and the metal center.

Considering the lack of information regarding the U═C double bond, we decided to extend our strategy to the 5f element U by using the SCS (bis-(diphenylthiophosphinoyl)methane) dianionic ligand **1** (Scheme 2), with the aim of studying the nature of the uranium−carbon bond in terms of electronic structure and reactivity. Here we report on the synthesis and crystal structures of U(IV) carbene compounds, including the first homoleptic tris-carbene complex. Preliminary reactivity studies confirmed the nucleophilicity of the carbene complexes. Finally, DFT calculations prove the involvement of the 5f and 6d orbitals of the uranium center in stabilizing the U═C double bond.

Results and Discussion

Choice of the Dianionic Ligand. As shown in Scheme 1, our strategy for U═C carbene complexes relies on the use of an isolated, well-defined, and stable geminal dianion (**1**). Very few such stable dianions have been reported in the literature,[10] and among them, only three have been used as ligands (Scheme 2). Cavell et al. have first developed in 2000 the use of a dianion of a bis-iminophosphorane compound, ligand **2**, toward Zr and Pt.[11,12] Starting from 2003, we have been using ligand **1** with a range of metal centers (Pd to Ln).[8,13] We have performed DFT calculations to understand precisely how the two charges may be accommodated on the same carbon center, in ligand **1** as well as on the bisphosphonate derivative **3** (first reported in 2005).[10] Briefly, the NBO analysis for **1** and **3** shows that both the S−Li and C−Li interactions are electrostatic in nature in each dianion. It also points to a Lewis structure which involves two lone pairs at the carbon center and three lone pairs at each sulfur atom. The best Lewis structure is therefore shown in Scheme 2 with anionic charges on both sulfur and carbon and cationic charges on each phosphorus atom. The P−S and P−C bonds are described by single bonds although very short bond distances are measured in the crystal (1.687 Å vs 1.673 Å in $HP{=}CH_2$ with a "true" P═C system), resulting from negative hyperconjugative interactions aimed at stabilizing the S and C lone pairs. Therefore, delocalization forms which involve P═C or P═S double bonds are not accurate to describe these systems as they would involve the p_π−d_π bonding scheme abandoned for over 10 years,[14] although P═S, P═O, P═N (in $R_3P{=}X$ compounds), and P═C bonds are still drawn in this manner for the sake of simplicity. More recently, a similar electronic structure was reported for the bis-iminophosphorane analogue. In these dianionic systems, the presence of two lone pairs at C and three lone pairs at X leads to a tridentate coordination mode. This bonding mode will have crucial implications on the geometry adopted by the ligand in the metal complex and on its overall electronic structure. Indeed, to favor the π donation from the carbon atom to the metal center and therefore the establishment of the M═C π bond, the X, P, C, and M atoms have to be coplanar. In other words, the sum of the angles at C has to be as close as possible to 360°. One may note here that the P−N bond length of an iminophosphorane moiety is close to 1.6 Å, whereas the P−S bond lengths in phosphine sulfide amount to 2.0 Å. The short P═N bond, conjugated to the tridentate coordination, leads to strong geometrical constraints. It was shown to be compatible with the formation of M═C bonds in the transition metal series, but it also precluded the coplanar arrangement upon coordination to the lanthanide Sm or group 3 element Y.[12a,15] The geometry at C in these systems is strongly pyramidalized, resulting in unfavorable overlap with orbitals at the metal (the orbital at C points in the "wrong" direction), and in turn leading to the formation of an M−C single bond, with a localized lone pair on the C atom. On the other hand, we have shown in several instances with the P═S system that the planar arrangement is favored (for the transition metals and lanthanides), which makes dianion **1** an optimal candidate for the desired establishment of the multiple bond between U and C.

Synthesis of the Complexes. We first tried to prepare uranium carbene complexes by treating UCl_4 with the lithium salt of the SCS dianion in toluene or diethyl ether, but the reactions were not straightforward, likely because of the poor solubility of the

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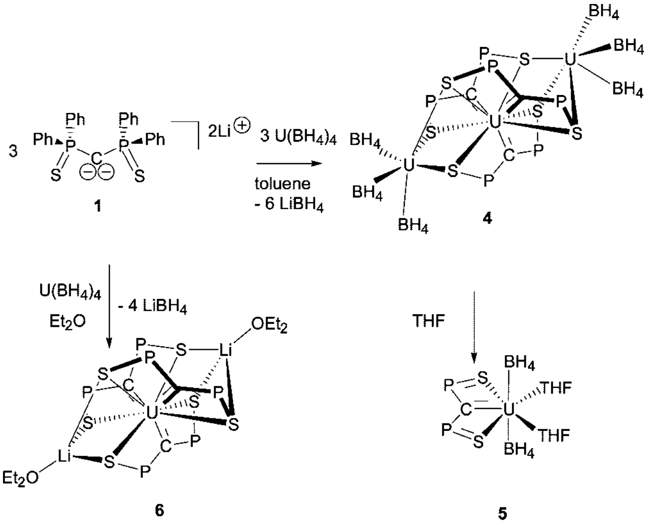
Scheme 3. Synthesis of Complexes **4**−**6**[a]



[a] The phenyl rings on the phosphorus atoms are omitted for clarity.

uranium chloride; THF was not appropriate because the SCS dianion is transformed into the corresponding monoanion in this solvent.[10] We then used the borohydride $U(BH_4)_4$ which is soluble in organic solvents and was shown to be a valuable precursor of various inorganic and organometallic derivatives.[16] The dianionic reagent $Li_2(SCS)$, **1**, was utilized as the solid solvate $Li_2(SCS)\cdot1.5Et_2O$ obtained after evaporation of a diethyl ether solution. The syntheses of the complexes are summarized in Scheme 3.

In a first attempt to prepare a mono carbene complex, the reaction of $U(BH_4)_4$ with 1 equiv of **1** in toluene was attempted. During the course of this reaction, brown crystals rapidly deposited in addition to an off-white solid of $LiBH_4$. The reaction, followed both by ^{31}P NMR and ^{11}B NMR spectroscopies, showed the complete disappearance of the dianion **1** and uranium starting complex, without appearance of any signal for a new uranium complex, showing the insolubility of complex **4** in the reaction mixture. After filtration and elimination of the $LiBH_4$ salts by washings with Et_2O, a brown powder was collected. This new complex **4** was characterized by elemental analysis showing the expected ligand/U ratio of 1:1. Characterization by usual NMR techniques in THF-d_8 was somewhat hampered by the slow transformation of complex **4** into a single new complex **5** (vide infra). However, this transformation is slow enough to allow the in situ characterization. Complex **4** is characterized by two singlets at −329 ppm (s, $w_{1/2} = 260$ Hz) and at 157 ppm (br, $w_{1/2} = 840$ Hz) in the ^{31}P and ^{11}B NMR spectra. The BH_4 ligands are seen as two broad singlets at 118 and 103 ppm in the ^1H NMR spectrum indicating a fluxional behavior. Finally, this complex was characterized by X-ray diffraction, and its displacement ellipsoid plot is presented in Figure 1, while significant bond lengths and angles are listed in Table 1. This complex appeared not to be the expected mono carbene complex but rather a trimetallic species in which the central U center is coordinated to three ligands **1**, making this fragment formally overall dianionic. This charge is compensated by two "$U(BH_4)_3^+$" fragments. These three fragments are held together by all the sulfur atoms which act as bridging ligands.

The transformation of complex **4** in THF-d_8 was followed by NMR spectroscopy. As mentioned above, this reaction is slow at room temperature, being achieved after 16 days, yet a single new complex, **5**, is formed. Heating the solution at 80 °C resulted in the complete formation of **5** after 0.5 h. This complex was fully characterized by usual NMR techniques as well as elemental analyses and X-ray diffraction. Singlet signals are found in the ^{31}P and ^{11}B NMR spectra at −524 and +177 ppm, respectively, pointing to a structure of overall C_s or C_2 symmetry. The change in chemical shifts is very significant ($\Delta\delta$ of −195 ppm in ^{31}P NMR) which is likely attributable to the presence of two paramagnetic U^{IV} centers coordinated to each sulfur atom in complex **4**. The ^1H NMR spectra indicate that the phenyl groups of complex **5** are magnetically equivalent. This **4** → **5** rearrangement is quite interesting as the dianion **1** itself is unstable in THF, leading to instantaneous formation of the monoanion, as mentioned above. It proves that the free dianion is not released in the THF solution. Most likely, the three ligands bound to the central U of the trimetallic complex redistribute in the coordination sphere. This reaction represents the only way to synthesize the mono carbene complex **5**. Finally, this complex was characterized by X-ray diffraction, and its displacement ellipsoid plot is presented in Figure 2, while significant bond lengths and angles are listed in Table 2.

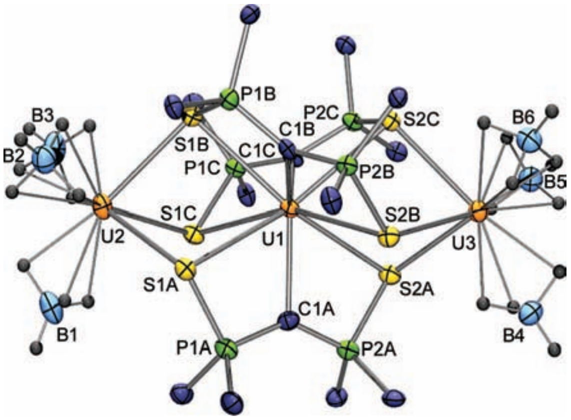


Figure 1. View of complex **4**. The hydrogen atoms (except those of the borohydride groups) have been omitted. Displacement ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex **4**·3.5toluene

	ligand A	ligand B	ligand C
U(1)−C(1)	2.444(4)	2.430(4)	2.451(4)
U(1)−S(1)	3.0442(11)	3.0311(12)	3.1378(11)
U(1)−S(2)	3.0847(12)	3.0582(11)	3.0759(10)
C(1)−P(1)	1.683(4)	1.675(5)	1.674(4)
C(1)−P(2)	1.669(5)	1.691(4)	1.675(4)
P(1)−S(1)	2.0547(16)	2.0605(16)	2.0662(15)
P(2)−S(2)	2.0560(15)	2.0586(16)	2.0621(16)
U(2)−S(1)	2.8531(12)	2.9108(11)	2.8715(12)
U(3)−S(2)	2.8606(11)	2.8701(11)	2.9013(11)
S(1)−U(1)−S(2)	126.25(3)	126.69(3)	124.89(3)
C(1)−U(1)−S(1)	63.45(11)	63.70(10)	62.01(10)
C(1)−U(1)−S(2)	62.80(11)	62.99(10)	62.88(10)
U(1)−C(1)−P(1)	111.1(2)	111.6(2)	112.91(19)
U(1)−C(1)−P(2)	112.1(2)	112.7(2)	111.6(2)
P(1)−C(1)−P(2)	136.7(3)	135.6(3)	135.5(3)

Finally, in a more rational synthesis of the tris(carbene) fragment "$U(SCS)_3$" found in **4**, addition of 3 equiv of **1** to $U(BH_4)_4$ in Et_2O led to the immediate precipitation of the yellow powder of $U(\mu\text{-}SCS)_3[Li(Et_2O)]_2$ (**6**) which was subsequently isolated in an excellent 83% yield. The ^{31}P NMR spectrum of

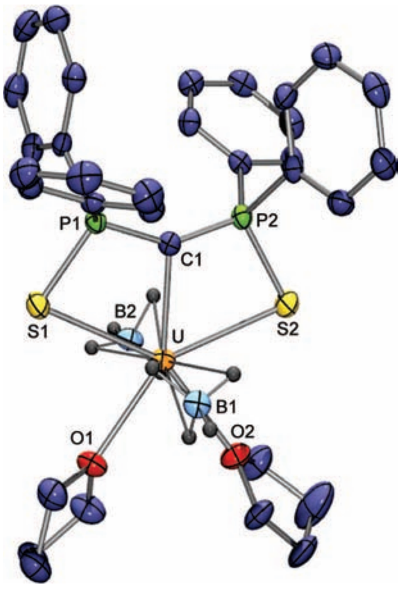


Figure 2. View of complex **5**. The hydrogen atoms (except those of the borohydride groups) have been omitted. Displacement ellipsoids are drawn at the 50% probability level.

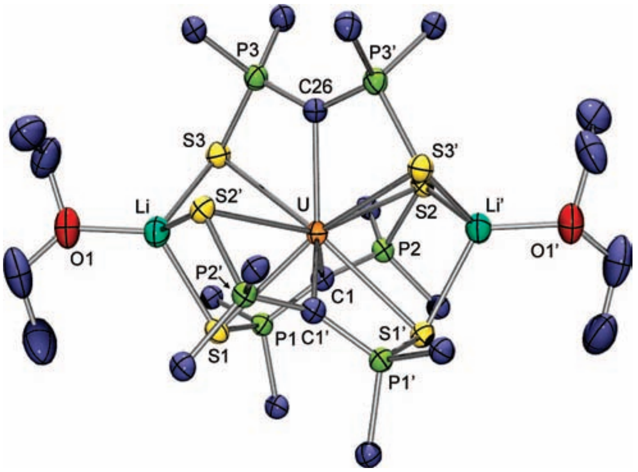


Figure 3. View of complex **6**. Only the *ipso* carbon atoms of the phenyl rings are represented. The hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: $' = 1 - x, y, {}^{3}/_{2} - z$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **5**

U−C(1)	2.327(3)		
U−S(1)	2.9009(7)	U−S(2)	2.8685(8)
U−B(1)	2.599(3)	U−B(2)	2.609(3)
U−O(1)	2.504(2)	U−O(2)	2.583(2)
C(1)−P(1)	1.683(3)	C(1)−P(2)	1.684(3)
P(1)−S(1)	2.0282(11)	P(2)−S(2)	2.0279(12)
C(1)−U−S(1)	67.89(6)	C(1)−U−S(2)	68.10(6)
O(1)−U−S(1)	77.07(5)	O(2)−U−S(2)	71.65(5)
S(1)−U−S(2)	135.64(3)	O(1)−U−O(2)	75.59(7)
B(1)−U−B(2)	170.65(12)	P(1)−C(1)−P(2)	147.2(2)
U−C(1)−P(1)	106.23(15)	U−C(1)−P(2)	106.09(13)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **6**[a]

U−C(1)	2.484(3)	U−C(26)	2.440(4)
U−S(1)	3.0086(7)	U−S(2)	3.0836(7)
U−S(3)	3.1168(7)		
Li−O(1)	1.941(6)	Li−S(1)	2.418(5)
Li−S(2′)	2.438(5)	Li−S(3)	2.450(5)
C(1)−P(1)	1.671(3)	C(1)−P(2)	1.666(3)
C(26)−P(3)	1.6769(17)	P(1)−S(1)	2.0353(10)
P(2)−S(2)	2.0316(10)	P(3)−S(3)	2.0293(11)
C(1)−U−S(1)	64.04(6)	C(1)−U−S(2)	63.29(6)
C(26)−U−S(3)	62.703(14)	S(1)−U−S(2)	127.329(18)
S(3)−U−S(3′)	125.41(3)		
P(1)−C(1)−P(2)	142.37(17)	P(3)−C(26)−P(3′)	137.0(3)
U−C(1)−P(1)	108.30(12)	U−C(1)−P(2)	109.28(13)
U−C(26)−P(3)	111.52(14)		

[a] Symmetry code: $' = 1 - x, y, {}^{3}/_{2} - z$.

6 exhibits a signal at −562 ppm, close to that of **5** (at −524 ppm). Brown crystals of **6** and yellow crystals of **6**·3toluene were formed by crystallization from a 1:1 and 5:1 mixture of toluene and diethyl ether, respectively. A view of **6** is shown in Figure 3; selected bond lengths and angles are listed in Table 3.

Crystal Structures of the Complexes. The trinuclear complex **4** (**6** respectively) is built up of a central $U(SCS)_3$ fragment connected to two $U(BH_4)_3$ units ($Li(OEt_2)$ respectively) via one S atom of each of the three SCS ligands labeled A, B, and C (Figure 1). The S atoms form around U(1) a very distorted trigonal prism which is capped on its rectangular faces by the carbene C(1) atoms of the SCS ligands which adopt the classical *mer*-stereochemistry of the M(tridentate ligand)$_3$ complexes.[17] The equilateral triangle of C(1) atoms is almost parallel to the trigonal faces of the prism defined by the S(1) and S(2) atoms, with dihedral angles of 1.56(15)° and 1.07(15)°, respectively. The coordination geometry of the $U(SCS)_3$ fragment is quite similar to that of the uranium(III) imidodiphosphinosulfide compound $U(SNS)_3$ [SNS = $(Ph_2P{=}S)_2N$].[18] The U(2) and U(3) atoms are in a *fac*-octahedral configuration, if the BH_4 groups are considered to occupy a single coordination site; the face of S atoms is shared with the trigonal prism around U(1). In fact, the borohydride groups adopt a tridentate ligation mode, as shown by the short U···B distances, in keeping with the positions found for the hydrogen atoms. The average U···B distance of 2.525(7) Å can be compared with those of 2.49(6) Å in $CPU(BH_4)_3$,[16d] 2.52(2) Å in $(2,4\text{-}Me_2C_5H_5)U(BH_4)_3$,[16d] and 2.59(4) Å in $[(BH_4)_3U(\mu\text{-}C_7H_7)U(BH_4)_3]^-$;[16c] the U−H bond lengths are in the range 2.17−2.46 Å with an average value of 2.31(8) Å, and the B−H bond lengths (involving coordinated H atoms) are in the range 1.01−1.30 Å with an average value of 1.17(7) Å. The U(1)−S distances are larger than U(2)−S and U(3)−S, with average values of 3.07(3) and 2.88(2) Å, respectively, reflecting the variation in the coordination number. These values are larger than those found in the eight- and six-coordinate dithiolene complexes $[Na_4(THF)_8U(dddt)_4]_n$ (2.83(3) Å), $[U(dddt)_3]^{2-}$ (2.74(1) Å), $[Na\{U(dddt)_3\}_2]^{3-}$ (2.74(2) Å) (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate),[19] the series of uranium hexathiolates (2.72−2.75 Å),[20] and the eight-coordinate compound $(SPS^{Me})_2UCl_2$ (2.88(8) Å) where SPS^{Me} is a pincer

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ligand featuring a central λ^4-phosphinine unit and two pendant phosphinosulfide groups,[21] but they are close to that of 2.9956(5) Å in the imidodiphosphidosulfide compound $U(SNS)_3$.[18]

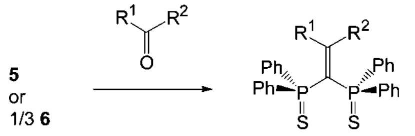
The uranium environment in **5** is a pentagonal bipyramid with the S, P, and C(1) atoms of the pincer ligand and the O atoms of the THF molecules lying in the equatorial plane [rms deviation 0.075 Å] and the BH_4 groups in axial positions (Figure 2). The borohydride ligands are tridentate, the U···B distances of 2.599(3) and 2.609(3) Å being slightly larger than those in **4**, but similar to those in $U(BH_4)$(18-crown-6)(μ-O)$U(BH_4)_5$, which vary from 2.595(10) to 2.652(11) Å;[22] the U−H and B−H bond lengths average 2.38(5) and 1.02(9) Å, respectively. The U−S distances of 2.8685(8) and 2.9009(7) Å are smaller than the U(1)−S distances in **1**, in line with the smaller coordination number and the nonbridging nature of the SCS ligand.

The structure of **6** resembles that of **4**, the $U(BH_4)_3$ moieties being replaced with $Li(Et_2O)$ units (Figure 3). In both **6** and **6**·3toluene, which differ by the presence in the former of a crystallographically imposed C_2 axis of symmetry passing though the uranium atom and one of the three carbene carbon atoms, the average U−S distance of 3.08(4) Å is identical to the mean U(1)−S bond length in **4**, and the average Li−S distance of 2.44(2) Å is identical to that of 2.46(2) Å in $[Li_2(Et_2O)(SCS)]_2$.[10]

It is interesting to note that, in the trinuclear complexes **4** and **6**, the phenyl groups of the SCS ligands can be divided into two groups, those which have their *ipso* carbon atoms [C(2) and C(14) in **1**] in the mean plane defined by the carbene C(1) atom and the three metal centers, and those which have their *ipso* carbon atoms [C(8) and C(20) in **1**] located on each side of this plane, at a distance of ca. 2.2 Å. The solid state structure of **6** is retained in solution, as shown by the ^{1}H NMR spectra, which exhibit two sets of phenyl signals; also in agreement with the crystal structure, the spectra of **5** show that the phenyl rings are equivalent.

The most salient structural features of **4**−**6** concern the metrical parameters of the SCS ligands. U—C bond distances of 2.327(3) Å in **5** and of 2.46(2) Å (average) in **4** and **6** were found. The short U—C(1) distance in **5** is similar to those measured in the phosphoylide complexes $Cp_3U{=}CHPMe_2R$, 2.29(3) Å for R = Ph (X-ray diffraction)[5b] and 2.293(1) Å for R = Me (neutron diffraction).[5c] The U—C distances in **4** and **6** are larger, in line with the greater coordination number, and fall in the range of the σ U—C bond lengths (2.4−2.5 Å) of uranium(IV) alkyl compounds, for example 2.41(1) Å in $Cp^*_2UMe_2$[23] or 2.426(23) Å in Cp_3U^nBu.[24] These values are smaller than that of 2.60(1) Å for the U—C(ylide) distances in the complexes $Cp^*_2UCl(CH_2)(CH_2)PPhR$ (R = Ph, Me) containing chelating phosphoylide ligands.[25] U—C bond distances of 2.383(6) and 2.485(9) Å were found for the only two known carbon monoxide uranium complexes $Cp'_3U(CO)$ (Cp′ = tetramethylcyclopentadienyl)[26a] and $Cp^*_3U(CO)$ (Cp* = pentamethylcyclopentadienyl)[26b] respectively. Finally, the bond distances in **4**−**6** are significantly smaller than those found in uranium(IV) complexes with *N*-heterocyclic carbene ligands, 2.58(1) Å in the pincer dicarbene compound $(CNC)UCl_4$ [CNC = 2,6-bis(arylimidazo-2-ylidene)pyridine; aryl = 2,6-$^iPr_2C_6H_3$],[27] 2.636(9) Å in $Cp^*_2U(O)(C\{NMeCMe\}_2)$,[28] and 2.75(5) Å in $U(OCMe_2CH_2\{1\text{-}C(NCHCHN^iPr)\})_4$.[29] In all the complexes, the P—C distances [av. 1.676(7) Å] are short and identical to those measured in $[Li_2(Et_2O)(SCS)]_2$, suggesting a participation of the Ph_2PS arms in the stabilization of an important electron density on the carbon atom via negative hyperconjugation.[10] The U—S—P—C—P—S cores are planar, with an rms deviation of 0.095 Å at most; the planarity at the carbene carbon atoms, also demonstrated by the sums of the P—C—P and U—C—P angles which are equal to 360°, shows the donation of both lone pairs from the dianionic fragment to the metal center.

Scheme 4. Reactivity of the Complexes with Carbonyl Derivatives



7: R^1 = H, R^2 = 9-anthracenyl
8: R^1 = R^2 = Ph

Reactivity Studies. The chemical nature of the multiple uranium−carbon bonds in complexes **4**−**6** was further established via reactivity studies. Gilje et al. studied the reactivity of $Cp_3U{=}CHPR_3$ toward small molecules, such as CO, isonitrile, or nitrile, resulting in the formation of new ligands in the coordination sphere of the U center via insertion.[5] We focused on the reactivity of the carbene complexes **5** and **6** toward ketone and aldehyde molecules, clearly demonstrating their nucleophilic character. Indeed, reactions of 9-anthracene carboxaldehyde or benzophenone with either 1 equiv of **5** in THF or $^1/_3$ equiv of **6** in toluene at 20 °C afforded the trisubstituted olefin **7** and the tetrasubstituted olefin **8**, respectively, in almost quantitative yield (Scheme 4). As observed with $(SCS)ZrCl_2(py)_2$,[13c] benzophenone reacted less rapidly than 9-anthracene carboxaldehyde to give the expected geminal bis(diphenylthiophosphinoyl) olefin **8**. Note that the dianion **1** itself does not react with the carbonyl derivatives to form the alkene derivatives.[8a,30]

We had shown previously, in the case of the lanthanide-carbene derivatives, that the carbonyl derivative was coordinated to the metal center prior to the formation of the new C−C bond in the coordination sphere. An open metallacycle could be isolated.[8a] In the present cases, the reactions are very rapid, and no intermediate was observed. In particular, it was a surprise to observe the full transfer of the three carbene moieties from **6**. It is noteworthy that the SCS ligand was more reactive than the BH_4 groups in **5** since complete formation of **7** or **8** was achieved by using the stoichiometric amount of the carbonyl reagent. These reactions clearly demonstrate the nucleophilic character of the uranium−carbon double bond.

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(24) Perego, G.; Cesari, M.; Farina, F.; Lugli, G. *Acta Crystallogr., Sect. B* **1976**, *32*, 3034.

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(26) (a) Parry, J.; Carmona, E.; Coles, S.; Hursthouse, M. *J. Am. Chem. Soc.* **1995**, *117*, 2649. (b) Evans, W. J.; Kozimor, S. A.; Nyce, G. W.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 13831.

(27) Pugh, D.; Wright, J. A.; Freeman, S.; Danopoulos, A. A. *Dalton Trans.* **2006**, 775.

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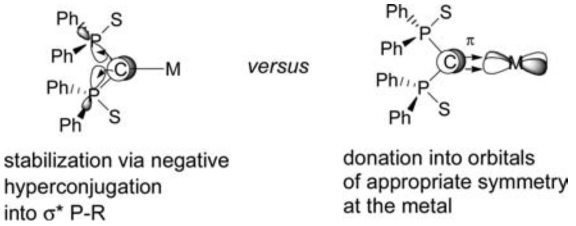
(29) Arnold, P. L.; Blake, A. J.; Wilson, C. *Chem.—Eur. J.* **2005**, *11*, 6095.

(30) We have also verified that the monoanion SCS^-, potentially acting as a soft anion, does not react with the carbonyl derivatives.

Scheme 5. Two Extreme Stabilization Structures of the M(SCS) Moiety



Yet, at this point, two pictures for these species can still be postulated, which are two extreme stabilization structures of the same complex (Scheme 5). The first one corresponds only to the donation of the lone pair at the carbon in the σ^* orbitals at P, like in the dianion **1** itself. The second corresponds to a donation to orbitals of the appropriate symmetry and energies at the U center. If it is obvious for transition metals that orbitals of both appropriate symmetry and energies are accessible, the case is much more delicate for U. Indeed, it has been shown that some degree of covalency may be found in σ type "ligand−U" interactions, but the question here pertains not only to σ but also to π type interactions.

Therefore, DFT calculations using the Gaussian suite of programs[31] were performed to gain both a qualitative and a quantitative picture of the "dianionic ligand **1**−U center" interaction and in particular on the nature of the uranium−carbon interaction.

Theoretical Calculations. Previous studies have shown that the free geminal dianion **1** features two lone pairs centered on the carbon atom. The lowest in energy presents an sp^2 hybridization state and belongs to the P−C−P plane of the ligand (Scheme 5). The second lone pair is a pure 2p orbital.[32] Upon coordination to a transition metal or a lanthanide, ligand **1** was shown to behave as a carbene center as donation of both carbon lone pairs to metal-centered vacant orbitals leads to the formation of an M=C double bond (Scheme 6).

The electronic structure of the uranium complexes **4**−**6** has been investigated using DFT approaches.[33] For the sake of simplicity, complex **I**, the parent model of **5**, was chosen so as to understand the U=C bonding scheme in these new complexes.[34] The optimized structure of **I** is in very good agreement with that obtained by X-ray diffraction analysis for complex **5** (Figure 4). For example the calculated U−C bond length is 2.32 Å, compared to 2.327(3) Å for the experimental value. Although the U−S bond lengths are overestimated by 0.08 Å, the interatomic bond lengths within the ligand framework are well reproduced (deviations lower than 0.01 Å).

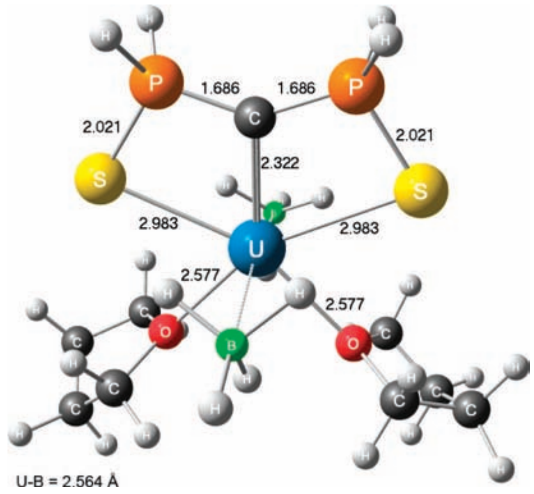
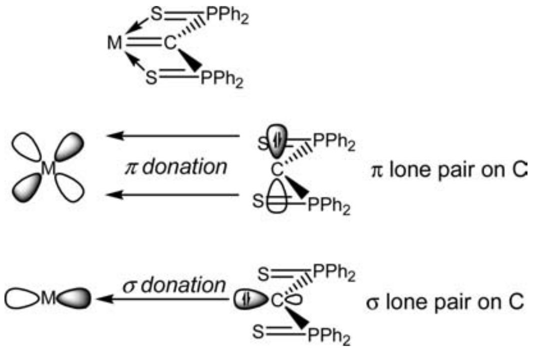


Figure 4. Optimized structure for **I**.

Scheme 6. Formation of a M=C Double Bond upon Coordination of the Geminal Dianion **1** to an Electron Deficient Metal Center



The highest occupied molecular orbitals (HOMOs) for complex **I** describe the U^{4+} ↔ SCS^{2-} interaction (Figures 5 and 6). The DFT results reveal the presence of 2.15 unpaired electrons on the uranium atom consistent with a U^{IV} metal center of high spin 6d^0 5f^2 configuration (residual spin density on the ligands is negligible). In fact, the two HOMOs (HOMO-1 and HOMO) are almost pure 5f AOs (%5f > 78%), with a small antibonding interaction with the sulfur atoms on the SCS ligand. The MO diagram of **I** possesses a good σ/π separation that allows for a simplified description of the bonding scheme. So as to respect the synthetic scheme used to synthesize **5**, the fragmentation [(THF)$_2$(BH$_4$)$_2$U^{2+}] + [SCS^{2-}] was chosen to study this diagram. First, the $\sigma_{\text{U-SCS}}$ interaction is made of the donation of the three occupied fragment orbitals σ_1, σ_2, and σ_3 on the SCS^{2-} ligand to vacant orbitals on the metal fragment. HOMO-7 and HOMO-4 describe the two U−S σ-bonds. The participation of uranium to these MOs is in the range 9.5−12.8% with an equivalent amount of 6d and 5f contributions. Interestingly HOMO-6 clearly describes the U−C σ-bond. This results from the donation of the carbon sp^2 lone pair (65.0% σ_3 + 7.0% σ_1) to a vacant hybrid orbital on U (15.4%) which breaks down to 7.1% 6d and 6.0% 5f.

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(31) Frisch, M. J. et al. *Gaussian 03*; Gaussian Inc.: Wallingford, CT, 2004.

(32) This description arises from a localized NBO analysis at DFT level of theory. In the Kohn−Sham MO diagram of the ligand, these two lone pairs are found with an admixture of the sulfur lone pairs, see σ_1, σ_3, π_1, and π_3 in Figure 5 and ref 10.

(33) For recent examples of the use of DFT calculcations to elucidate the electronic structures of actinide complexes or the rationalization of their reactivities, see:(a) Summerscales, O. T.; Cloke, F. G. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. *J. Am. Chem. Soc.* **2006**, *128*, 9602. (b) Lyon, J. T.; Andrews, L.; Malmqvist, P.-A.; Roos, B.; O.; Yang, T.; Bursten, B. E. *Inorg. Chem.* **2007**, *46*, 4917. (c) Evans, W. J.; Kozimor, S. A.; Ziller, J. W.; Kaltsoyannis, N. *J. Am. Chem. Soc.* **2004**, *126*, 14533. (d) Castro-Rodriguez, I.; Nakai, H.; Gantzel, P.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 15734. (e) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M *J. Am. Chem. Soc.* **2008**, *130*, 2930. (f) Graves, C. R.; Yang, P.; Kozimor, S. A.; Vaughn, A. E.; Clark, D. L.; Conradson, S. D.; Schelter, E. J.; Scott, B. L.; Thompson, J. D.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 5272. (g) Li, J.; Bursten, B. E.; Zhou, M.; Andrews, L. A *Inorg. Chem.* **2001**, *40*, 5448. (h) Yang, P.; Warnke, I.; Martin, R. L.; Hay, P. J. *Organometallics* **2008**, *27*, 1384.

(34) The substitution of the phenyl groups on the P atoms by H atoms has previously proven its accuracy in related transition metal and actinide systems: see for exemple refs 10, 13, and (a) Ingram, K. I. M.; Tassell, M. J.; Gaunt, A. J.; Kaltsoyannis, N. *Inorg. Chem.* **2008**, *47*, 7824.

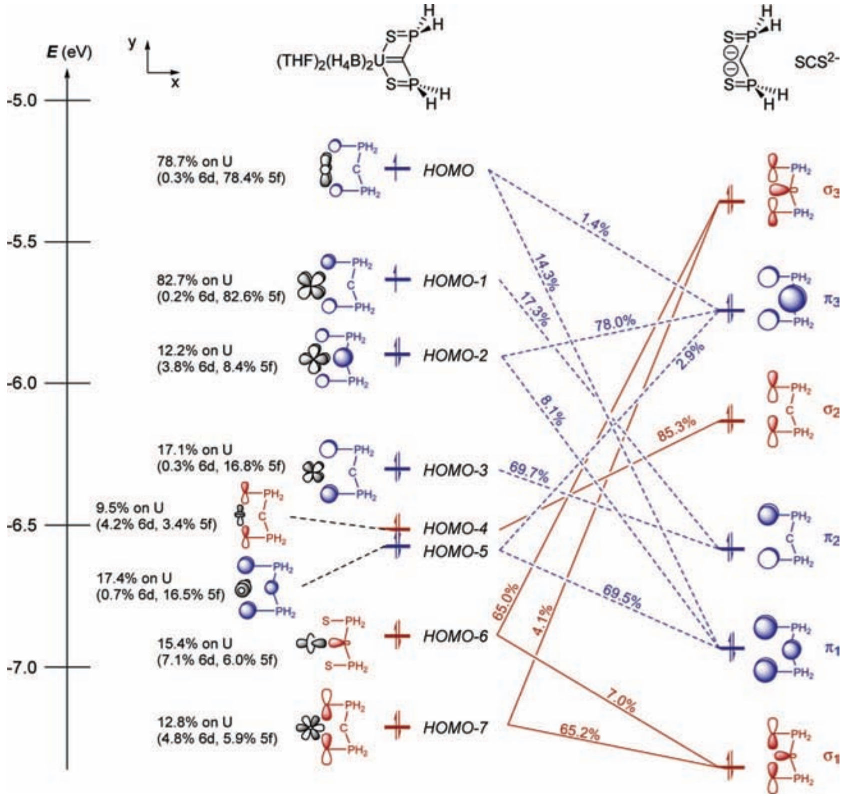

Figure 5. MO diagram of the HOMOs in complex **I**. The σ-bonds are depicted in red, and the π-bonds in blue. For each MO the total contribution of the metal is indicated (and the 6d/5f breakdown) as well as the contribution from the SCS^{2-} fragment orbitals. For example, HOMO-3 results from the donation of the π_2 orbital on the ligand (69.7%) to a metal vacant orbital. The contribution of the uranium center to this MO reaches 17.1% with 0.3% 6d and 16.8% 5f character.

The π-system of this MO diagram is of particular interest since it contains the description of the U−C π-bond. It arises from the interaction of the occupied π_1, π_2, and π_3 orbitals on the SCS^{2-} ligand with vacant orbitals on the uranium fragment. HOMO-3 clearly describes a U−S π-bonding interaction (with no coefficient on the C atom). HOMO-5 and HOMO-2 together account for the second U−S π-bond and the U−C π-bond. HOMO-5 is mainly polarized on the S atoms (69.5% π_1 + 2.9% π_3) and accounts only for a small U−C π-bond character. However HOMO-2 mainly corresponds to a U−C π-bond, polarized on the C atom (78.0% π_3 + 8.1% π_1 and 12.2% contribution on U (3.8% 6d and 8.4% 5f character)). The Mulliken analysis finally gives an overall electronic configuration of $(7s,7p)^{0.58}$ $(6d)^{1.87}$ $(5f)^{2.87}$ for uranium. The metal atom bears a charge of +0.67. This deviation from the purely ionic U^{4+} image reflects the important electronic transfer from the SCS^{2-} ligand.[35]

To summarize, the MO diagram of complex **I** shows a significant involvement of the uranium 6d and 5f AOs in stabilizing the occupied σ and π orbitals of geminal dianion **1**. By engaging covalent interaction with this carbene precursor, the metal center promotes an important electronic transfer from the ligand to the metal that results in the formation of U═C and U═S double bonds.[36]

As depicted in the MO diagram of complex **I**, the valence MOs are delocalized over the metal and the ligands so that chemical bonds (such as the U−C σ and π-bonds) are described by a combination of Kohn−Sham molecular orbitals. In particular, interaction of the carbon lone pairs with the sulfur lone pairs in the geminal dianion SCS^{2-} leads to a strong mixing of the C and S contributions to the bonding interaction with the metal center (see HOMO-5 and HOMO-2 for examples). A Natural Bond Orbital (NBO) analysis was performed to give a more localized and chemically relevant picture (in the sense of giving a pertinent Lewis structure) of the U═C interaction. Additionally, this population analysis gives a more ionic image of the electronic structure that should be compared to the Mulliken analysis to explore covalency. According to the NBO analysis, the most accurate Lewis structure of **I** involves a U═C double bond. The Lewis structure describing the U−C interaction by a U−C σ-bond with an additional lone pair on the C atom (no U−C π-bond) would result in an additional 39.9 kcal/mol increase in energy and an additional deviation of 0.31 electron compared to the completely delocalized molecule. This latter resonance structure has therefore a much weaker weight than the one relying on a U═C double bond. The NBOs describing the two U−C σ and π-bonds are presented in Figure 7. The U−C σ-bond comes from the interaction of the C sp^2 lone pair (80.7%) with a uranium hybrid orbital (19.3%) of 52.6% 5f and 37.0% 6d character. The U−C π-bond is made of a carbon 2p pure lone pair (82.9%) and a metal hybrid orbital (17.1%) of 59.0% 5f and 40.9% 6d character. This bonding scheme shows that the U═C double bond is polarized toward the carbon atom, in agreement with the Mulliken analysis. The charge on the C atom is indeed negative ($q_C = -1.52$ vs $q_U = +0.98$) and accounts very well for the observed nucleophilicity

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(35) The charge on uranium in the $[(THF)_2(BH_4)_2U^{2+}]$ fragment is +1.21.

(36) The singly occupied HOMO-1 and HOMO being antibonding between the uranium and sulfur atoms, the bond orders for the U═S bonds is formally lower than 2.

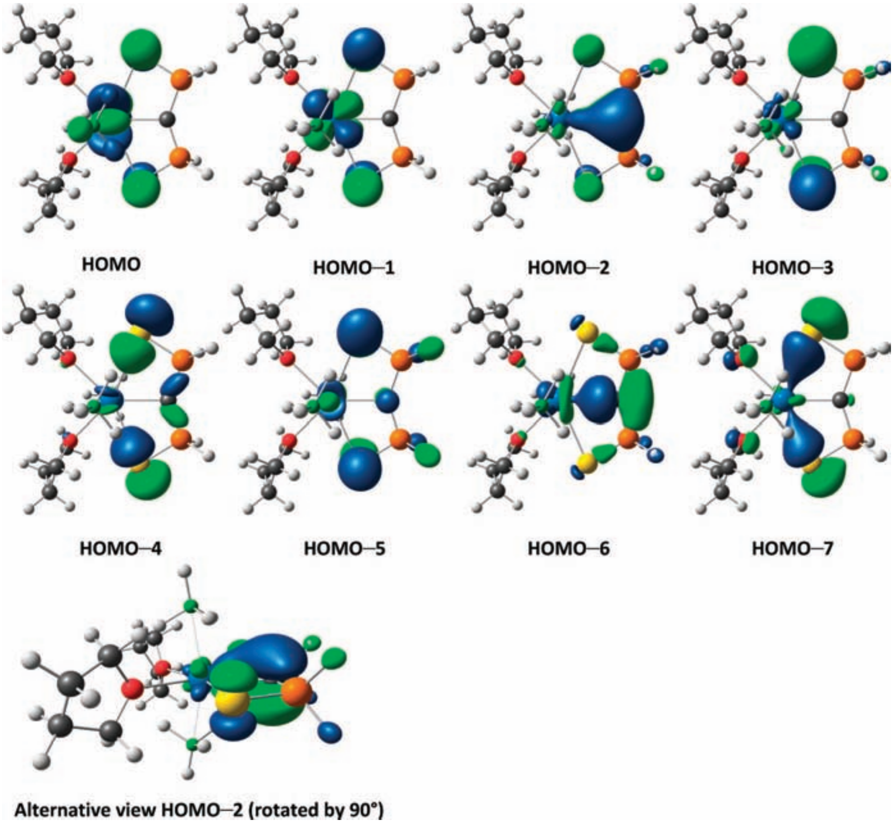

Figure 6. Plots of the HOMOs for **I**.

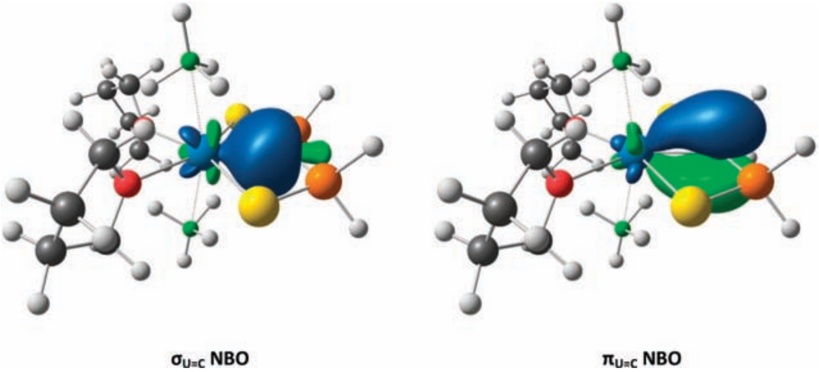

Figure 7. Plots of the NBOs describing the U=C double bond.

of the carbene center (*vide infra*). The polarization of the U=C double bond is not only due to the greater electronegativity of carbon compared to uranium but also to the presence of two thiophosphinoyl groups attached to the carbene center. The two lone pairs on the carbon atom are indeed stabilized by negative hyperconjugation (delocalization into the vacant σ^*_{P-R} and σ^*_{P-S} orbitals) in the free SCS^{2-} ligand. The same occurs also, but to a lower extent, in the complex. Upon coordination to the metal fragment, the charge of the carbon atom drops from −1.90 in the free ligand **1** to −1.52 in complex **I**. This is diagnostic of a significant electron transfer from the two carbon lone pairs to the U^{IV} metal center that establishes the U=C double bond. This NBO analysis also confirms the important involvement of the uranium 5f orbitals in stabilizing the U=C double bond. Overall, we note that the contribution of the uranium 5f orbitals is somewhat higher than that of the 6d orbitals in the U=C interaction. Though the 5f orbitals are more radially contracted than the 6d AOs, the 5f AOs are indeed lower in energy in uranium and can lead to greater angular overlaps where symmetry constraints are high (such as in HOMO-2).[37]

Based on these calculations it is important to accurately define these new complexes. In the transition metal series, complexes featuring an M=C double bond have been classified commonly into two categories namely alkylidene and carbene complexes. Alkylidene complexes (or Schrock-type complexes) are characterized by a carbon center possessing two alkyl substituents, and the complexes usually present a marked nucleophilic character. According to the reactivity of complexes **5** and **6** toward ketones and aldehydes, these complexes could be described in an analogous manner. However, the stabilization of the carbene center in alkylidene complexes is exclusively ensured by the metal center, the substituents on the C atom being electronically "neutral" (alkyl groups). Though we have shown that the uranium atom was clearly involved in stabilizing the

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[37] Li, J.; Bursten, B. E. *J. Am.Chem. Soc.* **1997**, *119*, 9021.

carbene center in model compound **I**, the electron withdrawing thiophosphinoyl arms also stabilize some electronic density on the carbon atom. To this respect we believe that the name alkylidene should be avoided to describe complexes **4**−**6**. On the other hand, carbene complexes (or Fischer-type complexes) usually correspond to the coordination of a neutral carbene ligand to an electron-rich metal center. In this case, the stabilization of the carbene center is provided both by the metal (*via* π-backdonation) and by π-donor substituents on the C atom. These complexes exhibit an electrophilic character due to the low energy of the M=C π^*-orbital which is polarized on the carbon center. Complexes **4**−**6** resemble carbene complexes as the stabilization is brought about by both the uranium ion and the $R_2P{=}S$ substituents. Nevertheless, their reactivity totally differs from carbene complexes since the $\pi_{U=C}$ MO, instead of the $\pi^*_{U=C}$ MO, is polarized on the C atom (see Figure 7) and the carbene center is nucleophilic. Consequently, the term "*nucleophilic carbene complexes*" would be more appropriate for complexes **4**−**6**.

Conclusion

In conclusion, we have applied successfully the general strategy relying on the use of a stable geminal dianion **1** to form carbene complexes of the 5f element U, including the first homoleptic actinide carbene derivative **6**. The short U−C distances and the planarity at the carbene centers favor the donation of the two lone pairs of carbon to the uranium center leading to the desired double bond character. DFT calculations have been performed to specify the electronic transfer from the carbon to the uranium center. The results show clearly the involvement of the 5f and 6d orbitals in both the U−C σ-bond and U−C π-bond. The U orbitals amount to 19.3% and 17.1% in the orbitals describing these bonds, respectively. This bonding scheme shows that the U=C double bond is polarized toward the carbon atom, as was anticipated from the use of a stable dianion and an electropositive metal center. The complexes **5** and **6** showed nucleophilic character of the U=C bond similarly to Schrock-type alkylidene complexes. However, based on the substituents at the carbon center, the denomination "*nucleophilic carbene complexes*" seems more appropriate for complexes **4**−**6** described in this study.

Experimental Section

Syntheses. 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. The ^{1}H, ^{11}B, and ^{31}P NMR spectra were recorded on a Bruker DPX 200 spectrometer operating at 200.0 MHz for ^{1}H, 64.2 MHz for ^{11}B, and 81.0 MHz for ^{31}P; the ^{1}H NMR spectra are referenced internally using the residual proton solvent resonances relative to tetramethylsilane (δ 0), and the ^{11}B and ^{31}P NMR chemical shifts are given relative to $BF_3 \cdot Et_2O$ and an 85% H_3PO_4 external reference, respectively. When not specified, NMR signals have half-height widths of 20−35 Hz. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). Benzophenone and 9-anthracene carboxaldehyde (Aldrich) were dried under vacuum; $U(BH_4)_4$[38] and $Li_2(SCS) \cdot 1.5Et_2O$[10] were prepared according to published methods.

Synthesis of $U(\mu\text{-}SCS)_3[U(BH_4)_3]_2$ (4). A flask was charged with $U(BH_4)_4$ (79.8 mg, 0.27 mmol), and toluene (30 mL) was condensed in it. The color of the solution turned immediately from green to brown upon addition of $Li_2(SCS) \cdot 1.5Et_2O$ (152.8 mg, 0.27 mmol), and brown microcrystals and an off-white powder were deposited. The reaction mixture was stirred for 2 h at 20 °C and allowed to stand for 12 h, after which the solution was filtered off. After washing with Et_2O (25 mL), the light brown powder of **4** was dried under vacuum (59% yield, 114 mg). Anal. Calcd for $C_{75}H_{84}B_6P_6S_6U_3$: C, 42.04; H, 3.95; P 8.67; S, 8.98. Found C, 41.74; H, 3.82; P 8.47; S, 9.10. The insolubility of **4** in toluene precluded recording the NMR spectra. Complex **4** was soluble in THF but was slowly transformed into **5** in this solvent; this reaction was complete after 16 days at room temperature. Therefore, the NMR spectra of **4** in THF also exhibit the signals corresponding to **5**. ^{1}H NMR (200 MHz, THF-d_8, 23 °C): δ 118 (br, $w_{1/2}$ = 1490 Hz, 16 H, BH_4), 103 ppm [broad s, $w_{1/2}$ = 680 Hz, 8H, BH_4], 25.2 (s, 48 H, Ph), 12.6 (s, 6 H, Ph), 11.3 (t, J = 8 Hz, 6 H, Ph). ^{11}B NMR (64.2 MHz, THF-d_8, 23 °C): δ 157 (br, $w_{1/2}$ = 840 Hz). ^{31}P NMR (81.0 MHz, THF-d_8, 23 °C): δ −329 (s, $w_{1/2}$ = 260 Hz). Brown crystals of **4**·3.5toluene were obtained upon addition of $Li_2(SCS) \cdot 1.5Et_2O$ (11.9 mg, 0.021 mmol) to a solution of $U(BH_4)_4$ (6.2 mg, 0.021 mmol) in toluene (0.4 mL). Crystals were inserted in a *Lindemann tube* filled with mother liquor as to prevent evaporation of the solvent, and subsequent loss of solvent molecules form the crystal.

Synthesis of $(SCS)U(BH_4)_2(THF)_2$ (5) Method a. A flask was charged with $U(BH_4)_4$ (132.5 mg, 0.446 mmol) in toluene (30 mL), and $Li_2(SCS) \cdot 1.5Et_2O$ (254.7 mg, 0.446 mmol) was added into the green solution. The mixture was stirred for 12 h at 20 °C, and the brown solution was filtered off. The brown powder of **4** was washed with Et_2O (2 × 20 mL), dried under vacuum, and dissolved in THF (30 mL). The solution was heated at 80 °C for 30 min, turning from brown to red. The volume of the solution was reduced to ca. 1 mL, and Et_2O (30 mL) was added. After vigorous stirring, the solvents were evaporated off, leaving an orange-red powder of **5** (41% yield, 157 mg). Anal. Calcd for $C_{33}H_{44}B_2O_2P_2S_2U$: C, 46.17; H, 5.17; S, 7.47; P, 7.22. Found: C, 45.98; H, 5.05; S, 7.49; P, 7.06. ^{1}H NMR (200 MHz, THF-d_8, 23 °C): δ 81.4 (br, $w_{1/2}$ = 850 Hz, 8 H, BH_4), 20.3 (s, 8 H, Ph), 11.7 (s, 8 H, Ph), 10,5 (s, 4 H, Ph). ^{31}P NMR: (81.0 MHz, THF-d_8, 23 °C): δ −546 (br, $w_{1/2}$ = 530 Hz). ^{11}B NMR (64.2 MHz, THF-d_8, 23 °C): δ (br, $w_{1/2}$ = 580 Hz). Orange crystals of **5** were obtained upon addition of diethyl ether (3 mL) into a solution of **5** (ca. 10 mg) in THF (0.5 mL).

Method b. A flask was charged with **4** (99.8 mg, 0.046 mmol), and THF (30 mL) was condensed in. The solution was heated at 80 °C for 30 min, turning from brown to red. THF was evaporated off, and Et_2O (30 mL) was added. After vigorous stirring, the solvents were removed under vacuum, leaving an orange-red powder of **5** (66% yield, 79 mg).

Synthesis of $U(\mu\text{-}SCS)_3[Li(Et_2O)]_2$ (6). A flask was charged with $U(BH_4)_4$ (90.8 mg, 0.31 mmol) in Et_2O (30 mL), and $Li_2(SCS) \cdot 1.5Et_2O$ (541 mg, 0.95 mmol) was added into the green solution. An orange suspension formed readily and was stirred for 12 h at 20 °C. Complex **6** was filtered, washed with Et_2O (2 × 30 mL), and obtained as a yellow powder after drying under vacuum (83% yield, 441 mg). Anal. Calcd for $C_{83}H_{80}Li_2O_2P_6S_6U$: C, 57.30; H, 4.63; S, 11.06. Found: C, 57.20; H, 4.51; S, 10.99. ^{1}H NMR (200 MHz, THF-d_8, 23 °C): δ 19.78 (s, 12 H, *o*-Ph), 11.89 (t, J = 7 Hz, 12 H, *m*-Ph), 10.59 (t, J = 7 Hz, 6 H, *p*-Ph), 9.61 (s, 12 H, *o*-Ph], 6.54 (t, J = 7 Hz, 12 H, *m*-Ph), 6.40 (t, J = 7 Hz, 6 H, *p*-Ph), 3.42 (q, J = 7 Hz, 8 H, Et_2O), 1.16 (t, J = 7 Hz, 12 H, Et_2O). ^{31}P NMR: (81.0 MHz, THF-d_8, 23 °C): δ −562 (br, $w_{1/2}$ = 120 Hz). Brown crystals of **6** and yellow crystals of **6**·3toluene were formed by crystallization from a 1:1 and 5:1 mixture of toluene and diethyl ether, respectively.

Reactivity of Complex 5 and 6 toward Carbonyl Derivatives. Reaction of Complex 5 with 9-Anthracene Carboxaldehyde. An NMR tube was charged with **5** (7.2 mg, 8.39 μmol) and 9-anthracene carboxaldehyde (1.9 mg, 9.22 μmol) in THF-d_8 (0.4 mL). A color change of the solution from orange to yellow was immediately observed, and the ^{1}H and ^{31}P NMR spectra showed the almost quantitative formation of **7**.[13c]

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Reaction of Complex 5 with Benzophenone. An NMR tube was charged with **5** (22.4 mg, 0.026 mmol) and Ph_2CO (4.8 mg, 0.026 mmol) in THF-d_8 (0.4 mL). A color change of the solution from orange to yellow was immediately observed, and the ^1H and ^{31}P NMR spectra showed the almost quantitative formation of **8**.[8a]

Reaction of Complex 6 with 9-Anthracene Carboxaldehyde. An NMR tube was charged with **6** (6.6 mg, 3.45 μmol) and 9-anthracene carboxaldehyde (2.1 mg, 10.2 μmol) in toluene-d_8 (0.4 mL). After 30 min at 20 °C, the ^1H and ^{31}P NMR spectra of the brown solution showed the almost quantitative formation of **7**.[13c]

Reaction of Complex 6 with Benzophenone. An NMR tube was charged with **6** (6.0 mg, 3.79 μmol) and 9-anthracene carboxaldehyde (2.5 mg, 11.5 μmol) in toluene-d_8 (0.4 mL). After 6 h at 80 °C, the ^1H and ^{31}P NMR spectra showed the almost quantitative formation of **8**.[8a]

Crystallographic Data Collection and Structure Determination. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[39] with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ 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 (φ and ω scans with 2° steps giving complete data sets up to $\theta = 25.7°$ and a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[40] 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.[41] Absorption effects were corrected empirically with SCALEPACK.[40] All non-hydrogen atoms were refined with anisotropic displacement parameters. The borohydride protons in **4**·3.5toluene and **5** were found on Fourier-difference maps and either refined (**4**·3.5toluene) or treated as riding atoms (**5**) with an isotropic displacement parameter equal to 1.2 times that of the parent atom. The carbon-bound hydrogen atoms were introduced at calculated positions and were treated 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 atom. One toluene molecule in **4**·3.5toluene is disordered around an inversion center, and two carbon atoms of one THF molecule in **5** are disordered over two positions which were refined with occupancy factors constrained to sum to unity.

Selected bond distances and angles are given in Tables 13. The molecular plots were drawn with ORTEP-3/POV-Ray.[42]

Computational Methods. The B3PW91 hybrid density functional was employed to optimize the equilibrium molecular structure of the model complex **I**. The Stuttgart RSC 1997 ECP was employed for uranium, which incorporates scalar relativistic effects and replaces 60 core electrons (complete shells 1s through 4f). The valence electrons are represented as [8s/7p/6d/4f]; 6−31G* basis sets were used for carbon, hydrogen, boron, oxygen, phosphorus, and sulfur. Harmonic vibrational analysis was performed to confirm that the structure was a minimum. All calculations were carried out using the *Gaussian03* suite of codes.[31] The Mulliken population analysis was performed using the AOMIX suite of programs.[43,44]

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Supporting Information Available: Atomic positions and displacement parameters, anisotropic displacement parameters, bond lengths and bond angles in CIF format; Table of crystal data, complete ref 31, computed Cartesian coordinate for complex **I**. This material is available free of charge via the Internet at http://pubs.acs.org.

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