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Uranium(IV) Nucleophilic Carbene Complexes

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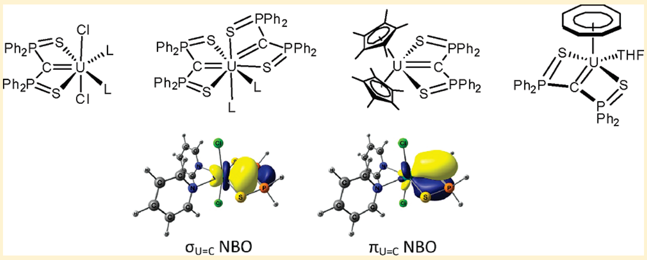
S *Supporting Information*

ABSTRACT: The mono-, bis-, and tris-carbene uranium complexes $[Li(THF)_2U(SCS)Cl_3(THF)]$ (**2a**), $[U(SCS)_2(THF)_2]$ (**3a**), and $[\{Li(OEt_2)\}_2U(SCS)_3]$ (**1**) were synthesized in good yields by reactions of UCl_4 and the stoichiometric amount of $Li_2(SCS)$ $[(SCS)^{2-} = [Ph_2P({=}S)]_2C^{2-}]$. Complex **3a** was also obtained by comproportionation reaction of **1** and 0.5 molar equiv of UCl_4 and further reacted with 1 molar equiv of UCl_4 to give the neutral mono-carbene $[U(SCS)Cl_2(THF)_2]$ (**5a**). Treatment of $U(NEt_2)_4$ with $H_2C(Ph_2PS)_2$ in THF led to a mixture of **3a** and $[U(SCS)(NEt_2)_2]$ (**6**), while the same reaction in Et_2O gave the mixed alkyl-carbene compound $[U(SCS)(SCHS)(NEt_2)]$ (**7**) in 85% yield. The cationic uranium carbene complex $[U(SCS)(NEt_2)(THF)_3][BPh_4]$ (**9**) was isolated in almost quantitative yield from reaction of $[U(NEt_2)_3][BPh_4]$ and $H_2C(Ph_2PS)_2$. Mono-carbenes **2a**, **5a**, and **9** were used as precursors for the synthesis of Cp and COT derivatives (Cp = C_5H_5, COT = C_8H_8). Treatment of **2a** with 1 or 2 molar equiv of TlCp gave $[Tl\{U(Cp)(SCS)\}_2(\mu\text{-}Cl)_3]$ (**10**) and $[U(Cp)_2(SCS)]$ (**11**) in 90% and 79% yield, respectively, whereas $[U(Cp^*)_2(SCS)]$ (**12**) (Cp* = C_5Me_5) was obtained only by reaction of $[U(Cp^*)_2Cl_2]$ and $Li_2(SCS)$. Reactions of **5a** or **9** with K_2COT gave $[U(COT)(SCS)(THF)]$ (**13**) in 78% and 99% yield, respectively. **2a**, $[Li(THF)(Et_2O)U(SCS)(\mu\text{-}Cl)_3]_2$ (**2b**), $[U(SCS)_2(py)_2]\cdot1.5py\cdot0.5THF$ (**3b**·1.5py·0.5THF), $[U(SCS)\{CS(Ph_2PS)_2\}(py)]$ (**4**), **7**·toluene, $[Li(THF)_2U(SCS)(NEt_2)(\mu\text{-}O)]_2$ (**8**), **10**·2toluene, **11**, **12**, and **13**·0.5pentane were characterized by X-ray diffraction. The crystal data revealed that, in contrast to transition metal complexes, changes in the coordination sphere of the U(IV) center have little influence on the U=C bond. This feature was explained by DFT analysis of analogous U(IV) and Zr(IV) compounds $[M(SCS')Cl_2(py)_2]$ and $[M(SCS')(Cp)_2]$ [M = U, Zr; SCS′ = $C(H_2PS)_2$]. Although the 5f orbitals are more radially contracted than the 6d atomic orbitals, the 5f AOs are lower in energy in uranium and can lead to greater angular overlaps in symmetry-constrained systems. As a result, the seven 5f orbitals play a "buffer" role by engaging in covalent interactions with the carbon center to stabilize the nucleophilic carbene lone pairs.



INTRODUCTION

Carbene complexes of the d-transition metals occupy a prominent position in coordination chemistry due to their fundamental aspects and their extensive utility in organic synthesis and catalytic processes.[1] In these complexes, classified as Fischer- or Schrock-type carbenes depending on the electrophilic or nucleophilic character of the CR_2 moiety, both the carbenic and metal fragments bring two electrons to the M=C interaction.[1] In contrast, the carbene complexes that are not simple adducts of free stable N-heterocyclic carbene (NHC) ligands[2] are very rare in the f-element series.[3,4] This situation is related to the strong ionic character of the metal–ligand bonding, with poor covalent contribution and unlikely stabilization of the carbenic center by π-back-donation from the metal fragment. In recent years, a new class of metal carbene complexes was designed and developed with the use of geminal carbon dianions stabilized by phosphorus(V) substituents (Scheme 1).[5] In these complexes, the four electrons of the formal M=C double bond are provided by the sole ligand, in contrast to the Fischer- and Schrock-type carbenes.[1] The bis-phosphorus-stabilized carbene compounds could therefore be constructed from any electron-deficient metal center and, most notably, from oxidized f-element ions.[5]

Three different types of geminal dianions, namely, bis(iminophosphoranyl) methanediides ($[Ph_2P({=}NR)]_2C^{2-}$, named $(^{R}NCN)^{2-}$ hereafter), bis(thiophosphinoyl)methanediides ($[Ph_2P({=}S)]_2C^{2-}$, named $(SCS)^{2-}$ hereafter), and bis(phosphonate)methanediides ($[(RO)_2P({=}O)]_2C^{2-}$) ligands, were used as precursors for the synthesis of carbene complexes. The use of these ligands for the formation of f-element carbene complexes was first explored for the lanthanide series with the synthesis by Cavell et al. of the first structurally characterized samarium(III) alkylidene complex $[Sm\{C(Ph_2PNSiMe_3)_2\}$

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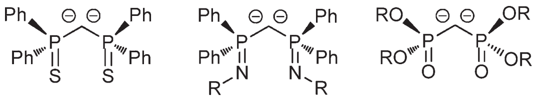
Scheme 1. Phosphorus-Stabilized Geminal Dianions



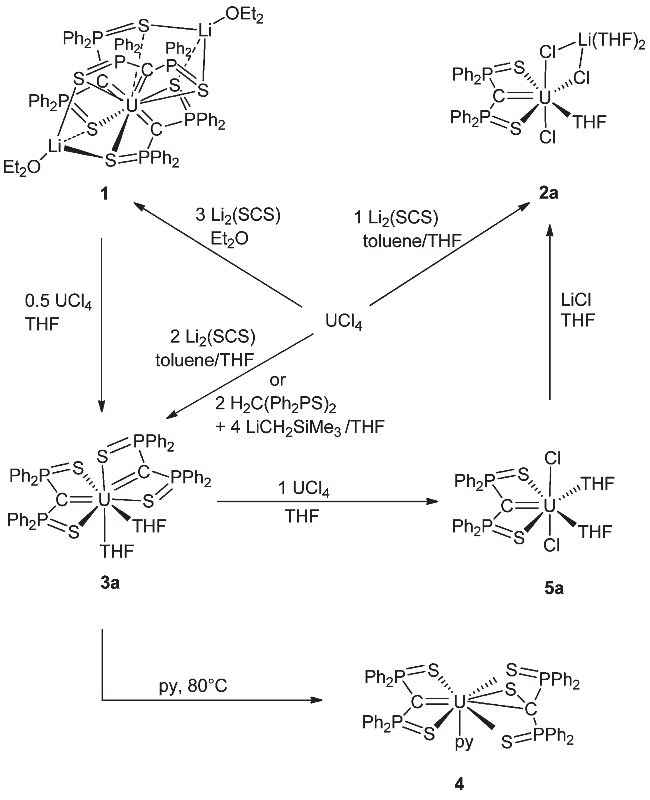
(NCy$_2$)(THF)], by double deprotonation of the methylene backbone of $H_2C(Ph_2PNSiMe_3)_2$ with the tris-amide [Sm(NCy$_2$)$_3$(THF)].[6] This chemistry was then extended to samarium(III), thulium(III), and scandium(III) mono- and bis-carbene complexes by Le Floch and co-workers,[7,8] using the SCS^{2-} ligand and, later on, to yttrium(III), erbium(III), and dysprosium(III) alkyl-carbene complexes[9−11] and to larger rare earth (Ln = La, Ce, Pr, Nd, Sm, and Gd) carbene complexes by the Liddle and Le Floch groups, using the bis(iminophosphoranyl) methanediide backbone.[12−15]

Recently, the (SCS)$^{2-}$ and (^{Mes}NCN)$^{2-}$ dianions proved to be excellent precursors to uranium(IV) nucleophilic carbene complexes, a class of coordination compounds then limited to tris(cyclopentadienyl) uranium phosphoylide compounds [Cp$_3$U{CHP(Me)RR′}] (Cp = η-C_5H_5), discovered by Gilje et al in 1981.[3] The bis(thiophosphinoyl)- and bis(iminophosphoranyl)methanediides (SCS)$^{2-}$ and (^{Mes}NCN)$^{2-}$ have been coordinated to uranium(IV) by reactions of their dilithium salts with $U(BH_4)_4$ and $UI_3(THF)_4$, which gave [M_2U(SCS)$_3$] [M = $U(BH_4)_3$ or Li(OEt$_2$)], [U(SCS)(BH$_4$)$_2$(THF)$_2$],[16] and [U(^{Mes}NCN)$_2$] respectively.[17] However, these synthetic routes suffer from major drawbacks that are, for the former,[16] the use of uranium tetraborohydride as the starting material, whose preparation is somewhat tedious and skill-demanding,[18] and, for the latter, the poor yield, which was accounted for by the detrimental waste of uranium metal following disproportionation of the U(III) intermediate.[17] In this context, our first objective was to find easy and efficient routes to uranium(IV) carbenes, stemming from practical starting materials. A second objective was to access functionalized derivatives in order to investigate the influence of ancillary ligands in the coordination sphere of the metal ion on the U^{IV}═C multiple bond. Here we report on the synthesis of neutral, anionic, and cationic mono-, bis-, and tris-carbene uranium complexes from UCl_4, $U(NEt_2)_4$, and [U(NEt$_2$)$_3$][BPh$_4$] and their transformation into cyclopentadienyl and cyclooctatetraenyl derivatives.[19] We describe the crystal structures of [Li(THF)$_2$U(SCS)Cl$_3$(THF)], [Li(THF)(Et$_2$O)U(SCS)(μ-Cl)$_3$]$_2$, [U(SCS)$_2$(py)$_2$], [U(SCS){CS(Ph$_2$PS)$_2$}(py)], [U(SCS)(SCHS)(NEt$_2$)] [SCHS = CH(Ph$_2$PS)$_2$], [Li(THF)$_2$U(SCS)(NEt$_2$)(μ-O)]$_2$, [Tl{U(C$_5$H$_5$)(SCS)}$_2$(μ-Cl)$_3$], [U(C$_5$R$_5$)$_2$(SCS)] (R = H, Me), and [U(C$_8$H$_8$)(SCS)(THF)]; we compare the structure of the bis(cyclopentadienyl) complex with that of the zirconium analogue[20] and analyze the role of the f electrons in the U═C interaction by relativistic density functional theory (DFT) calculations.

■ RESULTS AND DISCUSSION

Carbene Complexes from UCl_4. In contrast to UCl_4, uranium tetraborohydride, $U(BH_4)_4$, is quite soluble in toluene and diethyl ether and was for this reason first considered as a precursor for the synthesis of bis(thiophosphinoyl)methanediide complexes. The lithium salt of the dianion (SCS)$^{2-}$ is indeed very stable in these solvents, whereas it is converted into the corresponding monoanion [CH(Ph$_2$PS)$_2$]$^-$ ((SCHS)$^-$) in THF, the solvent usually employed for reactions with UCl_4. The mono- and tris-carbene complexes [U(SCS)(BH$_4$)$_2$(THF)$_2$] and [M_2U(SCS)$_3$] [M = $U(BH_4)_3$ or Li(OEt$_2$)] were thus obtained from uranium tetraborohydride.[16] Because of the tedious preparation of $U(BH_4)_4$, these complexes cannot be considered as practical starting materials for the synthesis of functional derivatives.

Scheme 2. Syntheses of Carbene Complexes from UCl_4



The reaction chemistry between the lithium salt of (SCS)$^{2-}$ and UCl_4 has been explored, and the syntheses of the corresponding carbene compounds are summarized in Scheme 2. Despite its poor solubility in diethyl ether, UCl_4 was found to react with 1 or 2 molar equiv of Li$_2$(SCS), prepared *in situ* from $H_2C(Ph_2PS)_2$ and MeLi in Et_2O or toluene. After stirring for 2 days at 20 °C, the tris-carbene complex [{Li(OEt$_2$)}$_2$U(SCS)$_3$] (**1**) was the sole uranium-containing product observed. By using the correct 1:3 stoichiometry, the yellow powder of **1** was isolated with a 84% yield after evaporation of the solvent and extraction in toluene; this yield is identical to that obtained for the previously reported synthesis of **1** from $U(BH_4)_4$.[16] In order to avoid the detrimental conversion of (SCS)$^{2-}$ into (SCHS)$^-$ in THF,[15] the synthesis of the mono- and bis-carbene complexes was attempted by addition of a toluene solution of the lithium methanediide Li$_2$(SCS) to a concentrated THF solution of the uranium chloride, in a ca. 5:1 volume ratio. The brown solution obtained from equimolar amounts of UCl_4 and Li$_2$(SCS) afforded a unique brown product after evaporation to dryness, which was formulated as the "ate" compound [Li$_2$(THF)$_4$U(SCS)Cl$_4$] (**2**) because of the failure to eliminate LiCl. Crystallization of this complex from a mixture of THF and pentane gave red-brown crystals of [Li(THF)$_2$U(SCS)Cl$_3$(THF)] (**2a**), while red crystals of the dimeric complex

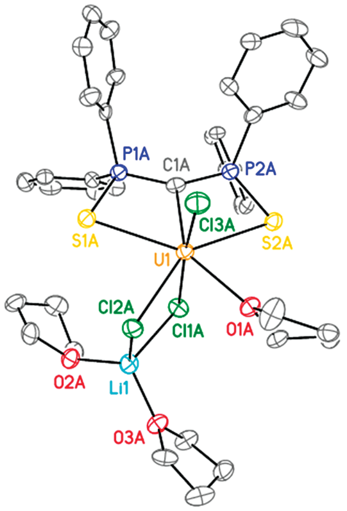


Figure 1. View of one of the two independent and quite identical molecules of **2a** with displacement ellipsoids at the 30% probability level. The hydrogen atoms have been omitted.

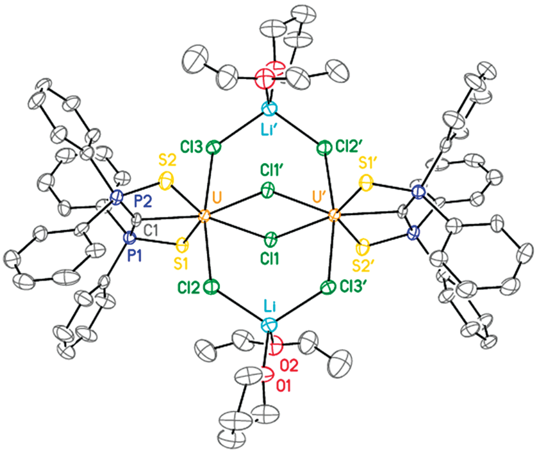


Figure 2. View of **2b** with displacement ellipsoids at the 30% probability level. The hydrogen atoms have been omitted. Symmetry code: ′ = 1 − *x*, 2 − *y*, −*z*.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 2a and 2b

2a[a]			
U(1)−C(1A)	2.344(13)	U(1)−Cl(3A)	2.612(4)
U(1)−S(1A)	2.868(4)	P(1A)−C(1A)	1.663(15)
U(1)−S(2A)	2.865(4)	P(2A)−C(1A)	1.690(15)
U(1)−Cl(1A)	2.718(4)	P(1A)−S(1A)	2.012(5)
U(1)−Cl(2A)	2.745(4)	P(2A)−S(2A)	2.026(5)
C(1A)−U(1)−S(1A)	67.7(4)	Cl(2A)−U(1)−Cl(3A)	94.24(13)
C(1A)−U(1)−S(2A)	68.4(4)	O(1A)−U(1)−Cl(2A)	76.6(3)
S(1A)−U(1)−S(2A)	136.02(10)	U(1)−C(1A)−P(1A)	106.0(7)
Cl(1A)−U(1)−Cl(2A)	142.4(4)	U(1)−C(1A)−P(2A)	105.5(6)
Cl(1A)−U(1)−Cl(3A)	171.95(12)	P(1A)−C(1A)−P(2A)	148.4(9)
2b			
U−C(1)	2.321(6)	U−Cl(2)	2.6737(19)
U−S(1)	2.809(2)	U−Cl(3)	2.6841(19)
U−S(2)	2.826(2)	P(1)−C(1)	1.676(8)
U−Cl(1)	2.8275(18)	P(2)−C(1)	1.682(7)
U−Cl(1′)[b]	2.7924(19)	P(1)−S(1)	2.032(3)
		P(2)−S(2)	2.014(3)
C(1)−U−S(1)	69.43(19)	Cl(2)−U−Cl(3)	167.92(6)
C(1)−U−S(2)	68.33(19)	Cl(1)−U−Cl(1′)	75.76(6)
S(1)−U−S(2)	137.46(6)	U−C(1)−P(1)	104.9(3)
Cl(1)−U−Cl(2)	84.29(6)	U−C(1)−P(2)	106.0(3)
Cl(1)−U−Cl(3)	87.31(6)	P(1)−C(1)−P(2)	148.5(4)

[a] Data for one of the two independent and quite identical molecules. [b] Symmetry code: ′ = 1 − *x*, 2 − *y*, −*z*.

$[Li(THF)(Et_2O)U(SCS)(\mu\text{-}Cl)_3]_2$ (**2b**) were obtained by crystallization from diethyl ether. Similar treatment of UCl_4 with 2 molar equiv of $Li_2(SCS)$ led to the formation of the first actinide bis-carbene compound, $[U(SCS)_2(THF)_2]$ (**3a**), which was isolated after extraction in toluene as a dark orange powder in 95% yield. These syntheses of **2** and **3a** in THF were successful because the reaction of the *in situ* generated $(SCS)^{2-}$ dianion with UCl_4 is much faster than its protonation into the corresponding methanide monoanion. In order to circumvent the problematic instability of $(SCS)^{2-}$ in THF and avoid the use of solvent mixtures, complex **3a** was prepared in a more convenient way and in almost quantitative yield by *in situ* deprotonation of $H_2C(Ph_2PS)_2$, that is, treatment of a 1:2 mixture of UCl_4 and $H_2C(Ph_2PS)_2$ with 4 molar equiv of $LiCH_2SiMe_3$ in THF. Orange crystals of a solvate of $[U(SCS)_2(py)_2]$ (**3b**) were obtained by crystallization of **3a** from a mixture of pyridine and THF. Interestingly, complex **3a** was found to be heat sensitive and to decompose when heated in THF or pyridine solution. Dark orange crystals deposited in one experiment and revealed the formation of $[U(SCS)\{CS(Ph_2PS)_2\}(py)]$ (**4**), which formally results from the addition of a sulfur atom to the U=C bond.

The bis-carbene complex **3a** was also obtained in almost quantitative yield from a 1:2 mixture of UCl_4 and **1** in THF; after 4 h at 20 °C, the solvent was evaporated off and **3a** was separated from LiCl by extraction in toluene. Under the same conditions, the comproportionation reaction between **3a** and UCl_4 in a 1:1 molar ratio led to the quantitative formation of the neutral monocarbene compound $[U(SCS)Cl_2(THF)_2]$ (**5a**), which was isolated as an orange powder after evaporation of THF. The pyridine adduct $[U(SCS)Cl_2(py)_2]$ (**5b**) was obtained by dissolving **5a** in this solvent. Complex **5a** was readily transformed into the "ate" derivative **2** upon addition of 2 molar equiv of LiCl (NMR experiment).

A view of one of the two independent yet similar molecules in the crystal of **2a** and a view of **2b** are presented in Figures 1 and 2, respectively, and selected bond lengths and angles are listed in Table 1. The uranium environment in **2a** is a slightly distorted pentagonal bipyramid with the S, P, and central C(1) atoms of the carbene ligand and Cl(2) and O(1) atoms lying in the equatorial plane (rms deviation 0.14−0.15 Å) and Cl(1) and Cl(3) in axial positions. The planarity of the carbenic fragment is demonstrated by the sum of the P−C−P and U−C−P angles, which is equal to 360°. The average U−C and U−S distances of 2.349(5) and 2.857(10) Å, respectively, are similar to those of 2.323(3) and 2.88(2) Å found in $[U(SCS)(BH_4)_2(THF)_2]$.[16] The uranium atom in the centrosymmetric dimer **2b** is also in a pentagonal bipyramidal environment with the S, P, and central

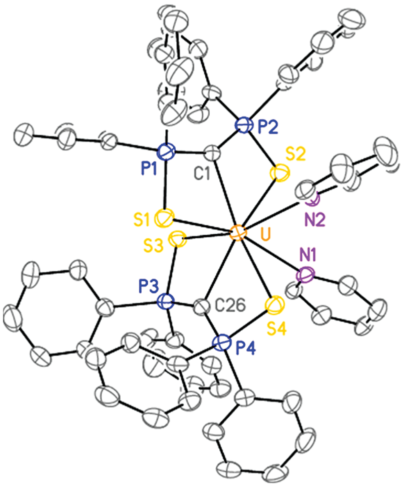


Figure 3. View of **3b**·1.5py·0.5THF with displacement ellipsoids at the 40% probability level. The hydrogen atoms and lattice solvent molecules have been omitted.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 3b·1.5py·0.5THF, 4, and 7·toluene

	3b	4	7
U−C(1)	2.399(7)	2.374(7)	2.395(5)
U−C(26)	2.390(8)	2.636(7)	2.819(5)
U−S(1)	2.892(2)	2.8634(18)	2.8533(14)
U−S(2)	2.940(2)	2.865(2)	2.8556(15)
U−S(3)	2.876(2)	2.865(2)	2.8824(14)
U−S(4)	2.951(2)	2.964(2)	2.8994(17)
U−S(5)		2.7021(19)	
U−N(1)	2.670(7)	2.569(6)	2.159(6)
U−N(2)	2.683(6)		
P(1)−C(1)	1.658(8)	1.679(7)	1.662(6)
P(2)−C(1)	1.680(8)	1.686(7)	1.668(6)
P(3)−C(26)	1.681(8)	1.744(8)	1.751(6)
P(4)−C(26)	1.663(8)	1.753(7)	1.758(6)
P(1)−S(1)	2.015(3)	2.025(3)	2.036(2)
P(2)−S(2)	2.019(3)	2.027(3)	2.038(2)
P(3)−S(3)	2.031(3)	2.008(3)	2.004(2)
P(4)−S(4)	2.014(3)	1.999(3)	2.003(2)
C(1)−U−S(1)	66.44(18)	67.92(16)	68.06(13)
C(1)−U−S(2)	66.49(19)	67.79(17)	68.65(13)
C(26)−U−S(3)	67.24(19)	67.00(17)	65.73(12)
C(26)−U−S(4)	65.79(19)	65.54(16)	65.80(12)
S(1)−U−S(2)	132.88(6)	135.71(6)	135.37(4)
S(3)−U−S(4)	132.72(6)	126.04(6)	85.49(5)
P(1)−C(1)−P(2)	147.6(5)	148.9(5)	150.0(4)
P(3)−C(26)−P(4)	146.5(5)	136.9(4)	123.7(3)
U−C(1)−P(1)	106.0(3)	105.3(3)	104.7(2)
U−C(1)−P(2)	106.2(4)	105.6(3)	103.7(2)
U−C(26)−P(3)	106.1(4)	98.5(3)	92.0(2)
U−C(26)−P(4)	107.4(4)	100.6(3)	93.6(2)

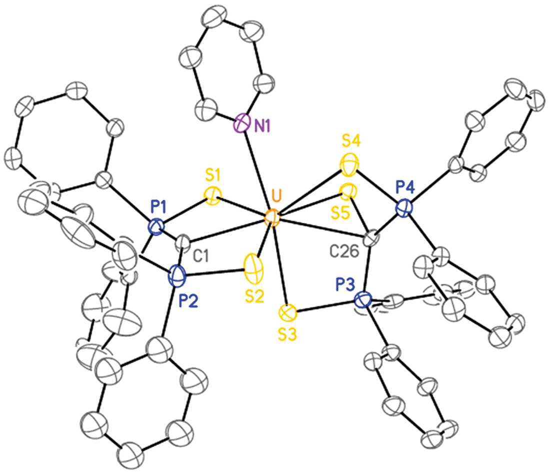


Figure 4. View of **4** with displacement ellipsoids at the 30% probability level. The hydrogen atoms have been omitted.

C(1) atoms of the carbene ligand and the bridging Cl(1) and Cl(1′) atoms in the equatorial plane (rms deviation 0.083 Å) and Cl(2) and Cl(3) in axial positions. The structural parameters of the planar tridentate carbene ligand are quite identical to those in **2a**, with a U−C bond length of 2.321(6) Å. The Li−Cl bond lengths, which average 2.390(10) Å in **2a** and 2.438(8) Å in **2b**, are smaller than those measured in $[LiCl(THF)_2\{U(C_5H_4CH_2C_5H_4)Cl_2\}_2]$[21a] [average 2.7(1) Å] and $[\{Li(TMEDA)\}_2U(C_5Me_4SiMe_2C_5Me_4)Cl_4]$[21b] [average 2.49(2) Å], where the lithium atoms are linked to four and three Cl atoms, respectively, and are similar to those found in solvated LiCl structures (2.33−2.42 Å).[22]

The crystal structure of **3b**·1.5py·0.5THF was described in a preliminary communication,[19] and only the major geometrical parameters will be recalled here and compared with those of the recently reported uranium(IV) bis-carbene compound $[U(^{Mes}NCN)_2]$.[17] A view of **3b** is presented in Figure 3, and selected bond lengths and angles are listed in Table 2. The U−C distances of 2.399(7) and 2.390(8) Å in this eight-coordinate compound, which are intermediate between those measured in the seven- and nine-coordinate complexes $[U(SCS)(BH_4)_2(THF)_2]$ and **1**[16] [2.323(3) and 2.47(2) Å (average), respectively], are shorter than those of 2.427(8) and 2.448(9) Å measured in the six-coordinate complex $[U(^{Mes}NCN)_2]$.[17] While the U−S−P−C−P−S cores are planar in **3b** (rms deviations 0.081 and 0.062 Å), the two four-membered C−P−N−U rings in each carbene ligand of $[U(^{Mes}NCN)_2]$ adopt "open book" conformations with a dihedral angle of ca. 47°. These differences likely reflect the much greater steric constraints imposed by the $C(Ph_2PNMes)_2$ vs $C(Ph_2PS)_2$ ligand, due to U−N and P−N bonds much shorter than U−S and P−S bonds and to the presence of bulky Mes substituents (Mes = 2,4,6-$Me_3C_6H_2$) on the coordinated N atoms. Even though the nonplanarity of the bis(iminophosphoranyl) group suggested that the formation of U═C double bonds was unlikely, the manifestation of both σ and weak π components in these bonds was proposed on the basis of DFT calculations.[17]

A view of **4** is shown in Figure 4, while selected bond lengths and angles are listed in Table 2. The eight-coordinate uranium atom is in a very distorted square-antiprismatic environment, the square bases defined by the N(1)−C(1)−S(2)−S(4) and S(1)−S(3)−C(26)−S(5) atoms (rms deviations 0.33 and 0.29 Å), forming a dihedral angle of 17.2(2)°. The geometry of the planar carbene ligand is identical to that found in **2a**, **2b**, and **3b** with a U−C(1) distance of 2.374(7) Å. The U−C(26) bond length of 2.636(7) Å is much larger, at the upper limit of the range of typical σ U−C distances (2.4−2.6 Å) of uranium(IV) alkyl compounds,[23] and can be compared with that of 2.44(1) Å in the thiametallacyclopropane $[U(C_5Me_5)_2(SMe)(SCH_2)]^-$.[24] The U−S distances of the thiophosphinoyl groups average 2.89(5) Å and are quite similar to those found in **2a**, **2b**, and **3b** [2.91(3) Å]. The smaller U−S(5) distance of 2.702(2) Å is in the range of those determined for terminally coordinated thiolate ligands, which vary from 2.58(1) Å in $[U_3(S)(S^tBu)_{10}]$[25] to 2.759(3) Å in $[NEt_2H_2][U(SPh)_6]$.[26] The U−S(5)−C(26) ring is very strained, as shown by the C−U−S and U−S−C angles of 39.59(14)° and 68.2(2)°, respectively, which are similar to the corresponding angles of 40.0(3)° and 64.7(3)° of the $U(SCH_2)$ fragment in $[U(C_5Me_5)_2(SMe)(SCH_2)]^-$,[24] while the planar U−S(3)−P(3)−C(26) and U−S(4)−P(4)−C(26) rings form a dihedral angle of 28.29(14)°. The P−C(1) and P−S distances in the SCS ligand, with average values of 1.683(4) and 2.026(1) Å, are respectively 0.06 Å smaller and 0.02 Å larger than the P−C(26) and P−S distances in the $CS(Ph_2PS)_2$ fragment. Such variations, which were also measured between the $P-C_{central}$ and P−N bond lengths of the alkyl and carbene ligands in $[Ln\{C(Ph_2PNSiMe_3)_2\}\{CH(Ph_2PNSiMe_3)_2\}]$[11] and $[Nd\{C(Ph_2PN^iPr)_2\}\{CH(PPh_2N^iPr)_2\}]$,[14] reflect the stabilization of the two anionic charges of the methanediide ligand by negative hyperconjugation in the vacant antibonding σ* P−N, P−Ph, and P−S orbitals.[15]

Mixed Amide-Carbene Complexes from $U(NEt_2)_4$ and $[U(NEt_2)_3][BPh_4]$. Uranium nucleophilic carbene complexes featuring the (^{R}NCN) and (SCS) ligands are limited to date to mixed halide-carbene or homoleptic carbene complexes. It is now of interest to access functional derivatives where the uranium ion is coordinated to nucleophilic carbene ligands and to other reactive functions such as amides, organometallic ligands, etc. In this context, the reaction chemistry between uranium amide complexes ($U(NEt_2)_4$ and $[U(NEt_2)_3][BPh_4]$) and the neutral $H_2C(Ph_2PS)_2$ ligand was investigated (Scheme 3).[27] In contrast to $[Sm\{C(Ph_2PNSiMe_3)_2\}(NCy_2)(THF)]$[6] and $[Hf\{C(R_2PNSiMe_3)_2\}Cl_2]$ (R = Cy, Ph),[28] which were obtained by protonolysis of the $M-NR_2$ bonds of $[Sm(NCy_2)_3(THF)]$ and $[Hf\{N(SiMe_3)_2\}_2Cl_2]$ with $H_2C(R_2PNSiMe_3)_2$ (R = Cy, Ph) in hot toluene, the bis-carbene complex **3a** could not be isolated pure from the reaction of $U(NEt_2)_4$ with 2 molar equiv of $H_2C(Ph_2PS)_2$ in toluene or THF. After 5 h at 60 °C in THF, a mixture of **3a** and the monocarbene complex $[U(SCS)(NEt_2)_2]$ (**6**) in relative proportions of 73:27 was obtained (NMR experiments). The structure of the products appeared to strongly depend on the nature of the solvent. A similar reaction carried out in diethyl ether gave a yellow microcrystalline powder of $[U(SCS)(SCHS)(NEt_2)]$ (**7**) in 85% yield, after 2 days at 20 °C. Recrystallization from a toluene/pentane mixture afforded dark yellow crystals of **7**·toluene. Complex **7** is a novel example, the first with an actinide element, of a mixed alkyl-carbene compound with both methanide and methanediide ligands. This compound is not stable in THF, being readily converted almost quantitatively into the bis-carbene **3a**, with loss of free $HNEt_2$. Attempts to isolate the mono-carbene **6** from reactions of $U(NEt_2)_4$ or $[U(NEt_2)_3][BPh_4]$ with $H_2C(Ph_2PS)_2$ or $Li_2(SCS)$, respectively, were unsuccessful. In one of these latter experiments, bright red crystals of the μ-oxo derivative $[Li(THF)_2U(SCS)(NEt_2)(\mu\text{-}O)]_2$ (**8**) were deposited, obviously resulting from the presence of adventitious water.

In contrast to the reactions of $U(NEt_2)_4$ and $H_2C(Ph_2PS)_2$, reaction of the cationic uranium tris-amide $[U(NEt_2)_3][BPh_4]$

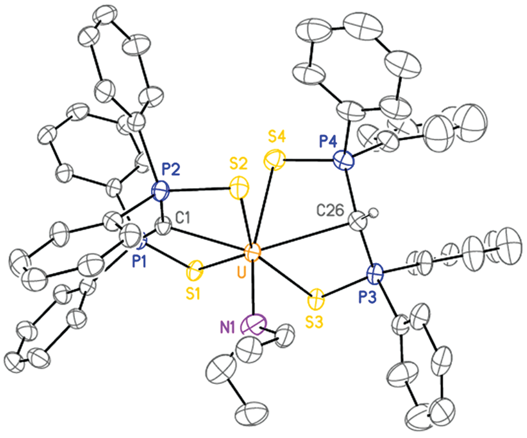
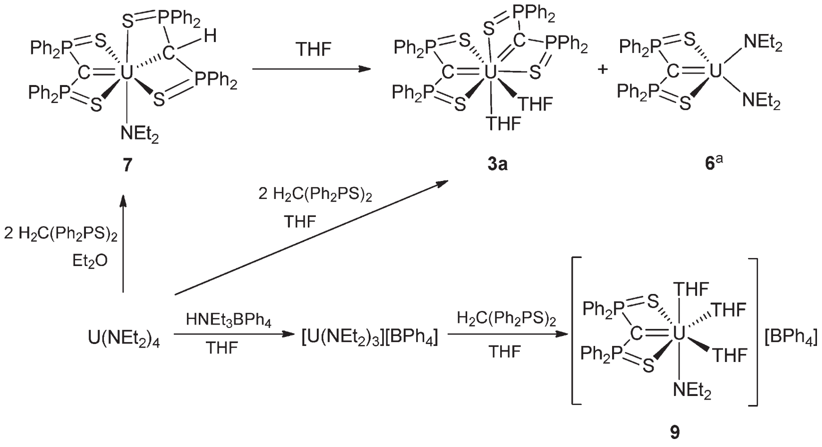


Figure 5. View of **7**·toluene with displacement ellipsoids at the 30% probability level. The hydrogen atoms [except on C(26)] and lattice solvent molecules have been omitted.

Scheme 3. Syntheses of Carbene Complexes from $U(NEt_2)_4$ and $[U(NEt_2)_3][BPh_4]$[a]



[a] Complex **6** was formed only in reaction of $U(NEt_2)_4$ and $H_2C(Ph_2PS)_2$ in THF.

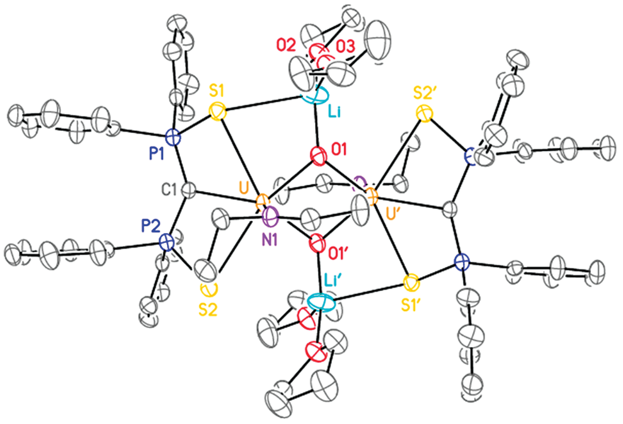


Figure 6. View of **8** with displacement ellipsoids at the 30% probability level. The hydrogen atoms have been omitted. Symmetry code: ′ = 1 − *x*, 2 − *y*, 1 − *z*.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 8

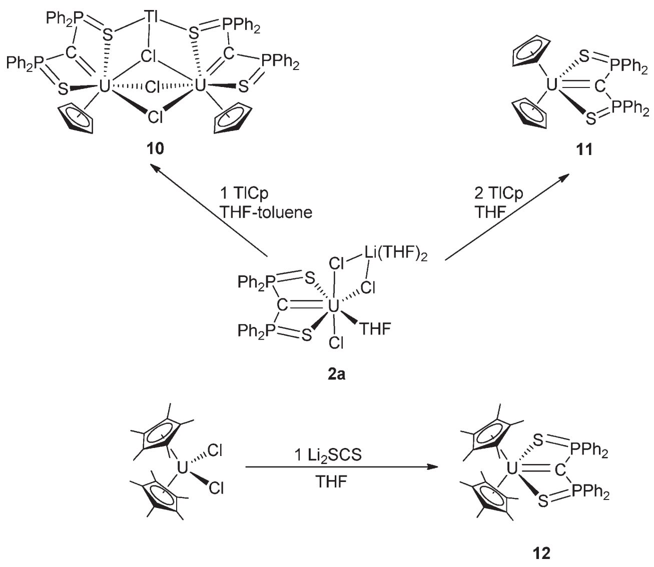
U−C(1)	2.544(5)	P(1)−C(1)	1.681(5)
U−S(1)	2.9509(14)	P(2)−C(1)	1.662(5)
U−S(2)	2.9180(13)	P(1)−S(1)	2.0349(16)
U−N(1)	2.230(4)	P(2)−S(2)	2.033(2)
U−O(1)	2.177(3)	Li−O(1)	1.828(12)
U−O(1′)[a]	2.152(3)	Li−S(1)	2.890(12)
C(1)−U−S(1)	67.18(10)	S(2)−U−N(1)	92.27(11)
C(1)−U−S(2)	66.75(12)	O(1)−U−N(1)	106.49(12)
S(1)−U−S(2)	122.24(3)	O(1)−U−O(1′)	72.28(15)
S(1)−U−O(1)	80.00(9)	P(1)−C(1)−P(2)	138.3(2)
S(2)−U−O(1′)	83.20(8)	U−C(1)−P(1)	101.28(18)
S(1)−U−N(1)	87.97(12)	U−C(1)−P(2)	102.0(2)

[a] Symmetry code: ′ = 1 − *x*, 2 − *y*, 1 − *z*.

with 1 molar equiv of $H_2C(Ph_2PS)_2$ in THF was straightforward, leading to the immediate formation of $[U(SCS)(NEt_2)(THF)_3][BPh_4]$ (**9**), which was isolated as a red powder in almost quantitative yield. Complex **9** is the first example of a cationic uranium carbene complex.

A view of **7** is shown in Figure 5, and selected bond lengths and angles are presented in Table 2. The complex adopts a distorted pentagonal-bipyramidal configuration; the equatorial plane defined by the C(1), C(26), S(1), S(2), and S(3) atoms also contains the P(1) and P(2) atoms of the planar carbene ligand, and the N(1) and S(4) atoms occupy the axial positions, forming a N(1)−U−S(4) angle of 167.15(17)°. The U−C(26) bond of the alkyl ligand is much longer, by 0.42 Å, than the U−C(1) bond of the carbene ligand, whose length of 2.395(5) Å is quite similar to those found in the other [U](SCS) compounds. This difference is comparable to the 0.54 and 0.27 Å differences between the Ln−C distances in the lanthanide complexes $[Ln\{C(Ph_2PNSiMe_3)_2\}\{CH(Ph_2PNSiMe_3)_2\}]$ (Ln = La, Ce, Pr, Sm, Gd)[11] and $[Nd\{C(Ph_2PN^iPr)_2\}\{CH(PPh_2N^iPr)_2\}]$,[14] respectively. In analogy with these complexes, the average P−S distance in the monoanionic fragment is measured at 2.0035(5) vs 2.037(1) Å in the dianionic unit, and the P−C(1) distances are shorter in the methanediide than the P−C(26) in the methanide fragment, with average values of 1.665(3) and 1.755(4) Å, respectively. These features are explained by the stabilization of the two lone pairs at C(1) by negative hyperconjugation into the thiophosphoranyl groups and by electron donation to the metal center, this latter interaction accounting for the double-bond character of U−C(1) and its reduced bond length compared to U−C(26).[15]

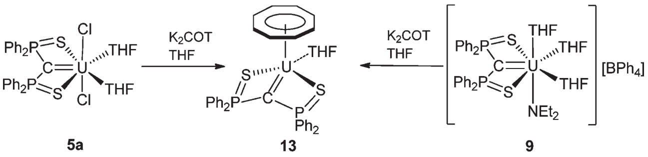
Scheme 4. Syntheses of Cyclopentadienyl Uranium Carbene Complexes



A view of the centrosymmetric dimer **8** is shown in Figure 6, and selected bond lengths and angles are listed in Table 3. The carbene ligand is not planar, the two U−S−P−C(1) rings adopting an "open book" conformation with an interplanar angle of 35.71(10)°, and the U−C(1) distance is larger, by ca. 0.15 Å, than in the other planar U(SCS) complexes. This difference can be tentatively explained by the greater electron richness of the metal center, related to the presence of the electron-donating oxo and amide ligands, with driving of the negative charge onto the C(1) atom. The average U−O distance of 2.165(12) Å can be compared with those of 2.12(1) Å in $[(C_5H_3{}^tBu_2)_2U(\mu\text{-}O)]_2$[29] and 2.18(2) Å in $[\{(Ph_2N)_2U(\mu\text{-}O)\}]_2$.[30] The Li−O(1) distance of 1.828(12) Å is similar to those of 1.932(10) and 2.013(10) Å in $[U(Me_2calix)(\mu\text{-}O)LiCl(THF)]_2$ [H_2Me_2calix = 25,27-dimethoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene].[31] The Li−S(1) bonding interaction distance is very long, at 2.890(12) Å, being similar to that of 2.894(5) Å found in $[Li(12\text{-crown-}4)(NC_5H_4S\text{-}2)]$.[32]

Cyclopentadienyl and Cyclooctatetraenyl Uranium Carbene Complexes. The isolation of the mixed alkyl-carbene complex **7** demonstrated that uranium(IV) carbene complexes could support σ-bound organometallic ligands. From this result, we tried to extend the synthesis of mixed uranium carbene complexes to π-organometallic compounds. Mono-carbenes **2**, **5a**, and **9** were used as precursors for the synthesis of Cp and COT derivatives (Cp = $\eta\text{-}C_5H_5$, COT = $\eta\text{-}C_8H_8$); the syntheses are summarized in Schemes 4 and 5. Treatment of the "ate" complex **2** with 1 molar equiv of freshly sublimed TlCp in THF gave the trinuclear compound $[Tl\{U(Cp)(SCS)\}_2(\mu\text{-}Cl)_3]$ (**10**), which was isolated as a red powder in 90% yield. Red crystals of **10**·2toluene were obtained by slow diffusion of pentane into a toluene solution. Complex **10** can be seen as

Scheme 5. Syntheses of the Monocyclooctatetraenyl Uranium Carbene Complex 13



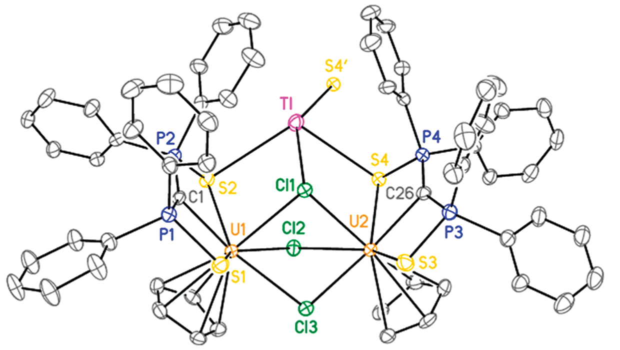


Figure 7. View of **10**·2toluene with displacement ellipsoids at the 30% probability level. The hydrogen atoms and lattice solvent molecules have been omitted. Symmetry code: ′ = −*x*, 1 − *y*, −*z*.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 10·2toluene

U(1)−C(1)	2.359(6)	U(2)−C(26)	2.379(6)
U(1)−S(1)	2.8804(17)	U(2)−S(3)	2.8908(18)
U(1)−S(2)	2.9237(16)	U(2)−S(4)	2.9341(16)
⟨U(1)−C(Cp)⟩	2.731(5)	⟨U(2)−C(Cp)⟩	2.737(14)
U(1)−Cl(1)	2.8565(15)	U(2)−Cl(1)	2.8468(15)
U(1)−Cl(2)	2.8631(15)	U(2)−Cl(2)	2.8510(16)
U(1)−Cl(3)	2.8422(15)	U(2)−Cl(3)	2.8440(15)
Tl−S(2)	3.2576(16)	Tl−S(4)	3.2132(16)
Tl−Cl(1)	3.0579(16)	Tl−S(4′)[a]	3.4511(16)
P(1)−C(1)	1.673(6)	P(3)−C(26)	1.692(6)
P(2)−C(1)	1.684(6)	P(4)−C(26)	1.667(6)
P(1)−S(1)	2.018(2)	P(3)−S(3)	2.016(2)
P(2)−S(2)	2.030(2)	P(4)−S(4)	2.043(2)
C(1)−U(1)−S(1)	67.15(15)	C(26)−U(2)−S(3)	67.02(16)
C(1)−U(1)−S(2)	66.67(15)	C(26)−U(2)−S(4)	66.12(16)
S(1)−U(1)−S(2)	132.56(5)	S(3)−U(2)−S(4)	132.46(5)
P(1)−C(1)−P(2)	145.4(4)	P(3)−C(26)−P(4)	146.8(4)
U(1)−C(1)−P(1)	105.9(3)	U(2)−C(26)−P(3)	104.6(3)
U(1)−C(1)−P(2)	107.3(3)	U(2)−C(26)−P(4)	108.5(3)
U(1)−Cl(1)−U(2)	93.31(5)	U(1)−Cl(2)−U(2)	93.08(5)
U(1)−Cl(3)−U(2)	93.68(4)	S(2)−Tl−S(4)	112.02(4)
Cl(1)−Tl−S(2)	74.94(4)	Cl(1)−Tl−S(4)	75.72(4)

[a] Symmetry code: ′ = −*x*, 1 − *y*, −*z*.

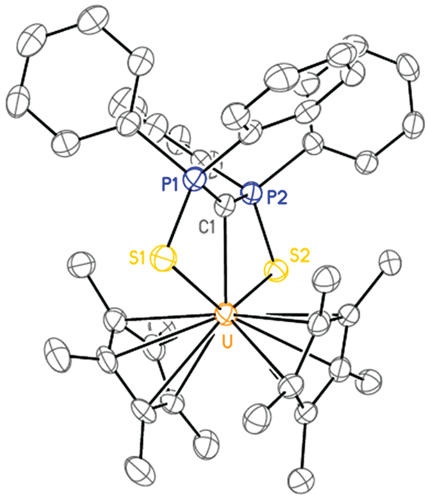


Figure 8. View of **12** with displacement ellipsoids at the 50% probability level. The hydrogen atoms have been omitted.

the assemblage of the expected monocyclopentadienyl uranium carbene [U(Cp)(SCS)Cl] with half the quantity of the byproduct TlCl. The same reaction with 2 molar equiv of TlCp gave a pale orange powder of the biscyclopentadienyl complex [U(Cp)$_2$(SCS)] (**11**) in 79% yield, and pale orange crystals of **11**·toluene were deposited from a toluene solution. In contrast, the bis(pentamethylcyclopentadienyl) analogue [U(Cp*)$_2$(SCS)] (**12**) could not be obtained by treatment of **2** with KCp* or Mg(Cp*)Cl, but was synthesized by reaction of [U(Cp*)$_2$Cl$_2$] and Li$_2$(SCS) in diethyl ether and isolated as red crystals in 87% yield.

A view of **10** is shown in Figure 7, and selected bond lengths and angles are presented in Table 4. The two U(Cp)(SCS) units are bridged by the three Cl atoms, and the thallium atom is attached to Cl(1) and the S(2) and S(4) atoms of the SCS ligands. The plane defined by Tl, Cl(1), Cl(2), and Cl(3) is a pseudo plane of symmetry (rms deviation 0.005 Å), which is perpendicular to the plane defined by U(1), U(2), Cl(1), C(1), and C(26) (rms deviation 0.029 Å); the latter is another pseudo plane of symmetry of the complex with the exception of the Tl atom, which is out of this plane at a distance of 2.978(5) Å and is linked to the S(4′) atom of an adjacent complex. Such compounds where thallium(I) coordinates to metal-bound halide ions to form soluble coordination compounds are quite uncommon and have been obtained by serendipity.[33] The Tl−Cl(1) distance of 3.0579(16) Å compares with those of 3.0556(11) and 3.0260(11) Å in [TlCr(C$_5$Ph$_5$)Cl(μ-Cl)$_2$]$_2$[33] and 2.9157(13) Å in [Tl{Ru(C≡C^{t}Bu)(dcypb)}$_2$(μ-Cl)$_3$] (dcypb = 1,4-bis(dicyclohexylphosphino)butane).[34] The Tl−S distances of 3.2132(16), 3.2576(16), and 3.4511(16) Å are similar to those measured in the polysufide Tl$_2$(S$_5$),[35] which vary from 3.04(3) to 3.47(3) Å. The uranium atoms are heptacoordinate, considering that the Cp ring occupies a single coordination site, and the environment geometry is a distorted pentagonal bipyramid, with Cl(2), Cl(3), and the S and C atoms of their SCS ligand defining the equatorial basis, and Cl(1) and the ring centroid are in axial positions. The geometrical parameters of the planar SCS ligands are identical to those previously observed. The U−C(Cp) and bridging U−Cl distances, which average 2.734(11) and 2.851(7) Å, respectively, are unexceptional and can be compared with those of 2.67(2) and 2.78(3) Å in the hexacoordinate anion [{U(Cp)Cl$_2$}$_2$(μ-Cl)$_3$]$^-$ or those of 2.73(3) and 2.83(6) Å in the hexacoordinate cation [{U(Cp)$_2$(μ-Cl)}$_3$(μ_3-Cl)$_2$].[36]

The crystal structure of **12**, shown in Figure 8, is quite similar to that of **11**, which was described in a preliminary communication,[19] with the planar U−S−P−C−P−S core

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complexes **11** and **12**

	11	**12**
U−C(1)	2.336(4)	2.396(4)
U−S(1)	2.8656(11)	2.8637(10)
U−S(2)	2.8694(12)	2.8588(11)
⟨U−C(Cp)⟩	2.73(3)	2.79(2)
P(1)−C(1)	1.684(4)	1.674(4)
P(2)−C(1)	1.678(5)	1.681(4)
P(1)−S(1)	2.0344(16)	2.0235(16)
P(2)−S(2)	2.0352(16)	2.0232(14)
C(1)−U−S(1)	68.29(11)	67.49(10)
C(1)−U−S(2)	67.90(11)	67.91(10)
S(1)−U−S(2)	135.33(3)	135.35(3)
centroid−U−centroid	119.7	127.3
P(1)−C(1)−P(2)	147.1(3)	150.7(3)
U−C(1)−P(1)	106.1(2)	104.91(19)
U−C(1)−P(2)	106.7(2)	104.38(18)

(rms deviation 0.075 Å) lying in the equatorial girdle of the bent-sandwich U(Cp*)$_2$ fragment. The geometrical parameters (Table 5) reveal only two significant differences concerning the U−C(carbene) and U−C(ring) distances, which are ca. 0.05 Å larger in **12**; these variations obviously reflect the greater steric hindrance and electron-donating capacity of the Cp* ligand compared to the Cp ring. It is noteworthy that the U−C(1) (2.336(4) Å) and U−S distances (2.87 Å av) in **11** are respectively only 0.08 and 0.11 Å larger than the Zr−C(1) and Zr−S distances in the isostructural zirconium analogue,[20] while the ionic radius of U^{4+} is 0.26 Å larger than that of Zr^{4+}.[37] A purely ionic bond model cannot account for such differences and would predict a U═C bond distance of about 2.52 Å. In addition, the U═C bond length in **11** is equivalent to that measured in the other uranium(IV) monocarbene complexes **2a**, **2b**, **4**, **7**, **10**, and **13** (2.36 Å av), showing that the ligand field around the uranium(IV) ion has no influence on the U═C bond. In contrast, a bond elongation of 0.08 Å was observed upon replacing the chloride ligands in [Zr(SCS)Cl$_2$(py)$_2$] (Zr−C = 2.172(2) Å) by cyclopentadienyl ligands (Zr−C = 2.251(2) Å in [Zr(Cp)$_2$(SCS)]), pointing to a noticeable influence of the coordination sphere in the transition metal complexes. These findings prompted us to carry out a theoretical study on the bonding interactions in analogous uranium(IV) and zirconium(IV) complexes (*vide infra*).

Although the chemistry of the monocyclooctatetraenyl uranium compounds has been significantly developed during the last years,[38] dialkyl complexes of general formula [U(COT)R$_2$] remain very rare.[39] It was thus of interest to introduce the carbene ligand in the series of monoCOT uranium complexes. The monocyclooctatetraenyl compound [U(COT)(SCS)(THF)] (**13**) was synthesized by metathesis reaction of **5a** and K$_2$COT in THF (Scheme 5); after filtration, evaporation of the solvent, and extraction in toluene, the red-brown powder of **13** was isolated with a 78% yield, and red-orange crystals of **13**·0.5pentane were obtained from a mixture of THF and pentane. Complex **13** was alternatively prepared in almost quantitative yield by treatment of **9** with K$_2$COT in THF. Reaction of **2** with 1 molar equiv of K$_2$COT in THF led to the formation of a compound formulated as the "ate" complex [Li(THF)$_x$U(COT)(SCS)Cl] since it was also formed from **13** upon addition of LiCl.

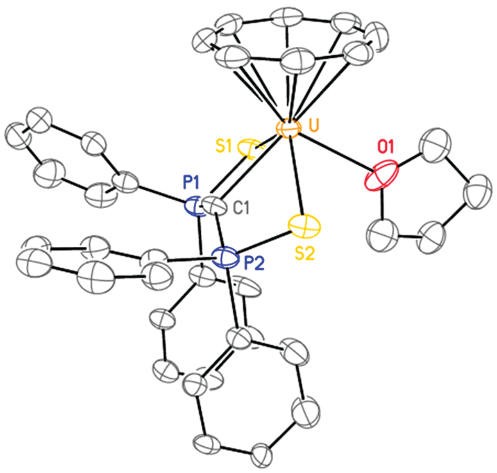


Figure 9. View of **13**·0.5pentane with displacement ellipsoids at the 30% probability level. The hydrogen atoms and lattice solvent molecules have been omitted.

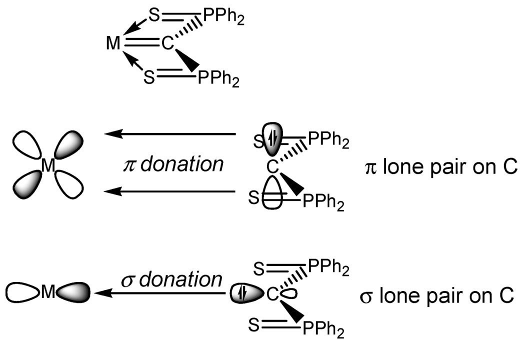
Table 6. Selected Bond Lengths (Å) and Angles (deg) for Complex **13**·0.5pentane

U−C(1)	2.351(8)	P(1)−C(1)	1.686(8)
U−S(1)	2.909(2)	P(2)−C(1)	1.692(8)
U−S(2)	2.906(2)	P(1)−S(1)	2.027(3)
⟨U−C(COT)⟩	2.70(2)	P(2)−S(2)	2.017(3)
U−O(1)	2.475(6)		
C(1)−U−S(1)	67.68(19)	S(1)−U−S(2)	126.04(6)
C(1)−U−S(2)	67.80(19)	P(1)−C(1)−P(2)	139.6(5)
U−C(1)−P(1)	106.2(3)	U−C(1)−P(2)	105.8(4)

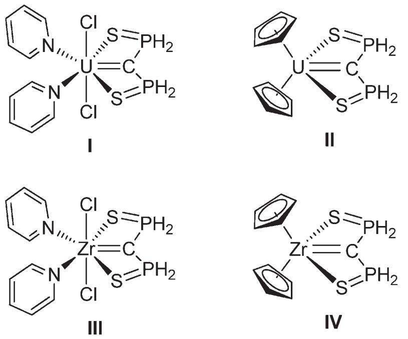
A view of **13** is shown in Figure 9, and selected bond lengths and angles are listed in Table 6. The uranium atom is in a distorted square-pyramidal arrangement, considering the C_8H_8 ring as a monodentate ligand, a configuration that is classical for five-coordinate monoCOT uranium compounds.[40] The square base defined by C(1), O(1), S(1), and S(2) (rms deviation 0.108 Å) forms a dihedral angle of 5.1(4)° with the planar COT ligand (rms deviation 0.011 Å). As observed with **8** and in contrast to the other U(SCS) complexes, the U−S−P−C−P−S core in **13** deviates from planarity, with a dihedral angle of 30.62(12)° between the two U−S−P−C(1) rings of the carbene ligand. However, the U−C(1) and U−S distances, as well as the P−C(1) and P−S distances, are not significantly different from those measured in the other planar carbene complexes reported here and are in favor of the covalent nature of the metal−carbene interaction. The average U−C(COT) and the U−O(1) distances of 2.70(2) and 2.475(6) Å are unexceptional.

Theoretical Investigation. Previous studies have shown that the geminal dianion (SCS)$^{2-}$ behaves as a carbene precursor because of the presence of two lone pairs on the central carbon atom able to transfer electron density upon coordination to an electron-deficient metal center (such as zirconium(IV) or uranium(IV)).[5] Donation from the sp^2 lone pair to a metal vacant orbital accounts for the establishment of the M═C σ-bond, whereas the M═C π-bond results from an electron transfer from the carbon 2p lone pair (Scheme 6). The complexes formed from coordination of the $(SCS)^{2-}$ ligand to an oxidized metal center therefore present a metal–carbon multiple bond. Detailed descriptions of the chemical bonding in geminal dianions and their complexes are available in the literature.[5–20] Because the two carbon lone pairs are stabilized by the phosphorus(V) centers (by electrostatic interactions and negative hyperconjugation) in the geminal dianion $(SCS)^{2-}$ and its complexes, the complexes are better described as *carbene complexes* rather than alkylidene complexes. Indeed, for carbene complexes, the carbene center is stabilized by the metal ion and donation from the substituents on the C atom. In contrast, in alkylidene complexes stability of the carbene center is completely ensured by the sole metal ion. Since carbene complexes usually refer to Fisher-type complexes that are electrophilic, we named complexes resulting from coordination of geminal dianions, such as $(SCS)^{2-}$, "*nucleophilic carbene complexes*" to mark the difference in reactivity between the different types of carbene complexes.[16]

Scheme 6. Formation of a M═C Double Bond upon Coordination of the Geminal Dianion $(SCS)^{2-}$ to an Electron-Deficient Metal Center



Scheme 7. The Model Compounds I–IV



In order to gain insight into the bonding scheme between the uranium ion and the SCS^{2-} ligand in the new uranium(IV) complexes **1**–**13**, the electronic structure of model uranium complexes was studied computationally, using density functional theory methods. This investigation is aimed at answering two fundamental questions: (i) How does the U═C bonding interaction in the uranium complexes compare with that in analogous transition metal complexes? (ii) Why is the U═C left unchanged upon modification of the coordination sphere around the metal ion?

For comparing the electronic structure of these new uranium(IV) nucleophilic carbene complexes with transition metal analogues, the electronic structure of complexes **I**–**IV**, in which the phenyl rings were replaced by H atoms, was investigated (Scheme 7). This simplification was validated in the past for transition metal and actinide complexes.[16,20] Two different ligand sets were chosen to explore the influence of the coordination environment around the metal on the U═C double bond, namely, a bis-cyclopentadienyl backbone (complexes **II** and **IV**) and a dichloro/bis-pyridine set (complexes **I** and **III**). The choice of zirconium(IV) (complexes **III** and **IV**) was motivated by an s/p/d valence electronic distribution similar to uranium(IV) (Zr^{IV}: $5s^0/5p^0/4d^0$ vs U^{IV}: $7s^0/7p^0/6d^0/5f^2$) and the availability of experimental (including X-ray structures) and theoretical data for complexes analogous to **5** and **11**.[19] Complex **5b** was not characterized by X-ray diffraction analysis; however, we assume

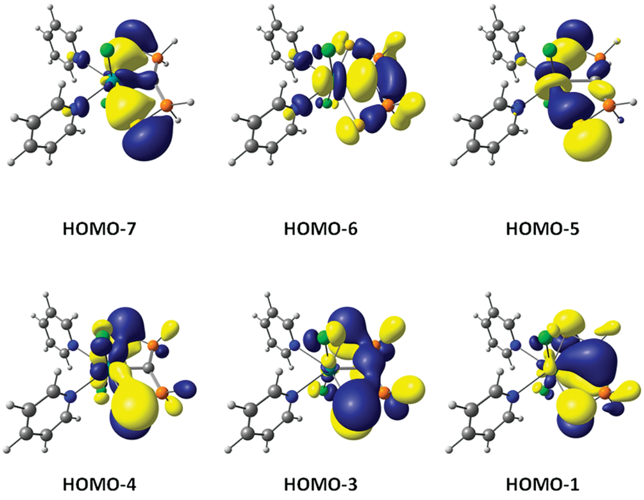


Figure 10. Selected Kohn–Sham HOMOs in **I**.

Table 7. Selected Structural Parameters for I–IV

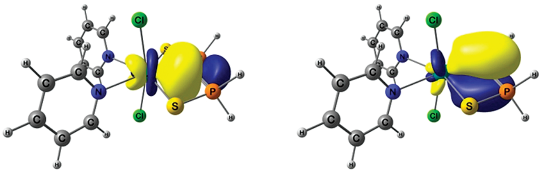
	M–C bond length (Å)		P–C bond length (Å)		P–S bond length (Å)		M–S bond length (Å)		P–C–P bond angle (deg)	
	DFT	X-ray	DFT	X-ray	DFT	X-ray	DFT	X-ray	DFT	X-ray
I[a]	2.33	2.344(13)	1.69	1.68(av)	2.04	2.02(av)	2.94	2.87(av)	144.9	148.4(9)
II[b]	2.36	2.336(4)	1.68	1.68(av)	2.05	2.03(av)	2.93	2.87(av)	146.7	147.1(3)
III[c]	2.21	2.172(2)	1.69	1.68(av)	2.04	2.02(av)	2.78	2.69(av)	145.4	145.7(1)
IV[d]	2.27	2.251(2)	1.68	1.67(av)	2.04	2.02(av)	2.88	2.77(av)	143.1	145.7(1)

[a–d] The structures of **I**–**IV** are compared respectively to the X-ray crystal structures of **2a** (a), **11** (b),[19] $[Zr(SCS)Cl_2(py)_2]$ (c),[20] and $[Zr(Cp)_2(SCS)]$ (d).[20]

Table 8. Mulliken and NBO Analysis for I−IV[a]

	metal electronic configuration		Mulliken charges		NBO charges		M=C Wiberg bond index	$\sigma_{M=C}$ NBO breakdown		$\pi_{M=C}$ NBO breakdown	
	Mulliken	NBO	q_M	q_C	q_M	q_C		metal	carbon	metal	carbon
I	$(7s,7p)^{0.31}(6d)^{1.75}(5f)^{2.75}$	$(7s,7p)^{0.62}(6d)^{1.54}(5f)^{2.88}$	+1.2	−0.6	+0.9	−1.6	0.88	18.3% (29.4% 6d, 52.0% 5f)	81.7% ($sp^{2.34}$)	15.7% (47.6% 6d, 41.7% 5f)	84.3% (pure p)
II	$(7s,7p)^{0.41}(6d)^{1.86}(5f)^{2.82}$	$(7s,7p)^{0.55}(6d)^{1.54}(5f)^{2.89}$	+0.9	−0.7	+1.0	−1.6	0.86	17.4% (28.3% 6d, 45.9% 5f)	82.6% ($sp^{2.28}$)	15.5% (47.0% 6d, 48.3% 5f)	84.5% (pure p)
III	$(5s,5p)^{2.13}(4d)^{2.5}$	$(5s,5p)^{0.98}(4d)^{2.51}$	−0.64	−0.5	+0.5	−1.5	0.89	18.2% (53.6% 4d)	81.8% ($sp^{1.52}$)	17.0% (53.6% 4d)	83.0% (pure p)
IV	$(5s,5p)^{1.31}(4d)^{2.56}$	$(5s,5p)^{0.81}(4d)^{2.50}$	+0.1	−0.9	+0.7	−1.5	0.79	19.2% (54.4% 4d)	80.8% ($sp^{1.62}$)	9.6% (47.0% 4d)	90.4% (pure p)

[a] For each M=C NBO (M = U, Zr), the contributions (%) of M and C are given together with the orbital participation (%). For example, the $\sigma_{U=C}$ bond in I results from the interaction between a uranium hybrid orbital (18.3%) having 29.4% 6d character and 52.0% 5f character and a carbon $sp^{2.34}$ hybrid orbital (81.7%).



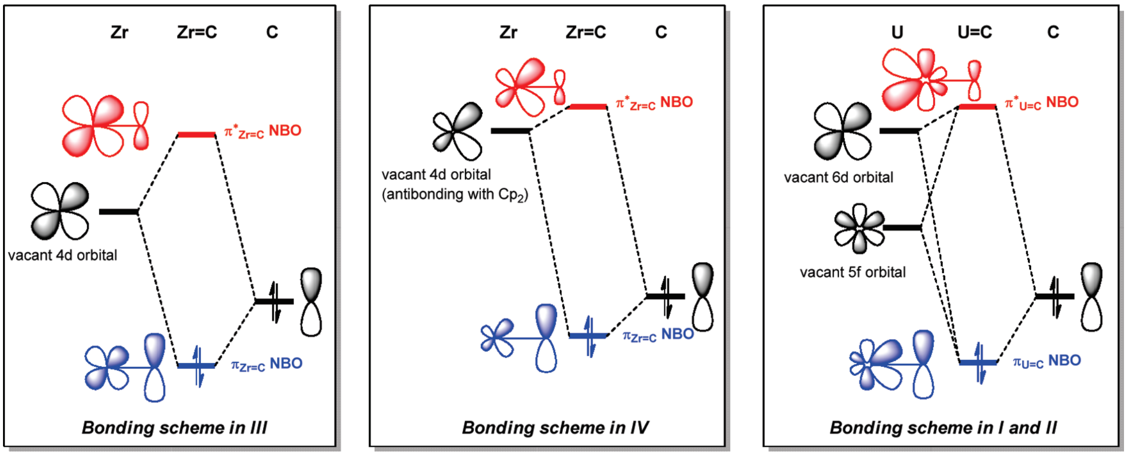
$\sigma_{U=C}$ NBO $\pi_{U=C}$ NBO

Figure 11. Natural bond orbitals of the U=C double bond in **I**.

that the geometric and electronic structures are very similar to that of **2a** given that the ligand environment was observed to have little influence on the U=C bond in complexes **2**−**5**. The optimized geometries for complexes **I**−**IV** compare very well with experimental structures derived from X-ray diffraction (Table 7).

The electronic structure of **I** is closely related to that of $[U(SCS)(BH_4)_2(THF)_2]$, reported previously.[16] The highest occupied molecular orbitals (HOMO and HOMO−2) are singly occupied and mostly 5f in character, as expected for a uranium(IV) complex with a high-spin $6d^0 5f^2$ configuration. The other HOMOs are all doubly occupied and describe the interaction between the SCS ligand and the $UCl_2(py)_2$ fragment: HOMO−7, HOMO−6, and HOMO−5 account for the two U−S and the U−C σ-bonds, whereas HOMO−4, HOMO−3, and HOMO−1 describe the U−S and U−C π-bonds (Figure 10). Overall, the electron donation from the chloride, pyridine, and SCS ligands to the U^{IV} metal center results in a Mulliken charge of +1.2 for the metal ion (vs −0.6 for the carbenic center) with a $(7s,7p)^{0.31}(6d)^{1.75}(5f)^{2.75}$ electronic configuration (Table 8). These charges point to a covalent participation of the uranium ion in the stabilization of the carbene σ and π lone pairs. As depicted in Figure 10, the Kohn−Sham orbitals describing the uranium−carbon interaction show an important admixture of the sulfur lone pairs (see HOMO−4 for example), making it difficult to clearly investigate the involvement of the uranium valence orbitals in the U=C double bond. A natural bond orbital (NBO) analysis was thus performed so as to provide a more localized and chemically relevant picture of the U=C interaction and to avoid the overestimation of covalency usually encountered in Mulliken population analysis. As in $[U(SCS)(BH_4)_2(THF)_2]$, the Lewis structure involving a uranium−carbon double bond is the closest structure to the fully delocalized complex. The NBOs describing the U=C double bond involve the two lone pairs on the carbon atom and uranium hybrid valence orbitals (Figure 11). Donation from a carbon $sp^{2.34}$ lone pair (81.7%) to a uranium vacant orbital (18.3%) having 29.4% 6d character and 52.0% 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 (84.3%) and a metal hybrid orbital (15.7%) of 47.6% 6d and 41.7% 5f character. These data clearly support the formation of a polarized double bond. Interestingly, the participation of the metal orbitals is similar in the σ- and the π-bond, showing that both bonds exhibit the same amount of covalency. The 5f and 6d uranium orbitals have equal weights in the π-bond with the carbene center (about 45%), whereas the involvement of 6d orbitals in the U=C σ-bond is less pronounced (about 28% vs 50% 5f character in the metal hybrid orbital). On the basis of these results, the four electrons of the U=C double bond distribute as follows in complex **I**: 0.68 electron is located on uranium, whereas the other 3.32 electrons are brought by the carbon atom. As the carbon atom retains most

Scheme 8. Schematic Representation of the Metal−Carbon Double Bond in Zirconium and Uranium Complexes I−IV



of the electron density, the carbene center is nucleophilic (q_C = −1.6 vs q_U = +0.9). The Wiberg bond index for the U═C bond of 0.88 confirms that, despite the bond polarization, the bond order is greater in **I** than in uranium(IV) alkyl complexes (for example the U−C Wiberg bond index in $[U(Cp)_2(CH_3)_2]$ is 0.70).

The electronic structure of **I** can be compared with that of its zirconium(IV) analogue **III**, which is a model for $[Zr(SCS)Cl_2(py)_2]$.[20] Results from the Mulliken and NBO analyses are summarized in Table 8. The Zr═C Wiberg bond index of 0.89 in **III** clearly suggests similar bonding schemes in the two complexes. This is further confirmed by the participation of the carbon and metal valence orbitals in the M═C (M = Zr, U) σ and π NBOs. Indeed, the U═C π-bond in **I** has a similar polarization to the Zr═C π-bond in **III**, the absence of f orbitals in the valence shell of zirconium being balanced by a greater involvement of the metal 4d, 5s, and 5p orbitals.

The influence of the coordination environment around the metal ion on the metal−carbene interaction has been investigated by studying the effects of replacing the chloride and pyridine ligands in **I** and **III** by a bis-cyclopentadienyl backbone (**II** and **IV**, respectively). The Mulliken and NBO analyses point out the resistance of the U═C bonding scheme to changes in the metal coordination sphere: the U═C Wiberg bond index (0.88 in **I** vs 0.86 in **II**), the bond polarization, and the 5f/6d uranium participation remain unchanged (Table 8). As a result, the uranium carbon bond distance is left unchanged from **I** (2.33 Å) to **II** (2.36 Å), in excellent agreement with the data collected by X-ray diffraction for **2a** and **11** (Table 7). In contrast, the same change in coordination environment at the zirconium center induces an elongation of the Zr−C bond from 2.172(2) Å in $[Zr(SCS)Cl_2(py)_2]$ to 2.251(2) Å in **IV**. Computationally, this stretch is well reproduced (Zr−C = 2.21 Å in **III** vs 2.27 Å in **IV**) and the Zr═C Wiberg bond index drops by 10% from **III** to **IV**, pointing to a significant sensitivity of the Zr═C under coordination changes. Importantly, this stimulus has no effect on the Zr═C σ-bond; the $\sigma_{Zr=C}$ NBO is even slightly more covalent in **IV** than in **III** with a greater participation of zirconium orbitals (19.2% in **IV** vs 18.2% in **III**). However, the Zr═C π-bond is clearly weakened in **IV**, with 90.4% of the corresponding electron density localized on the C atom (compared to 83.0% in **III**). This decrease in covalency was attributed to the presence of the cyclopentadienyl ligands that destabilize the vacant orbital involved in the electron donation from the 2p lone pair on the carbene center to the zirconium(IV) ion (Scheme 8).[20] The electron transfer from the dianionic carbene ligand to the d^0 metal ion is responsible for the formation of the metal−carbon double bond. As such, the strength of the double bond depends on the electron withdrawing character of the metal fragment. The experimental study of complexes **1**−**13** and the electronic structure analysis of model complexes **I**−**IV** clearly show that this rule applies to zirconium(IV) but not to uranium(IV). Although the 5f orbitals are more radially contracted than the 6d atomic orbitals, the 5f AOs are lower in energy in uranium and can lead to greater angular overlaps in symmetry-constrained systems. As a result, the seven 5f orbitals play a "buffer" role by engaging covalent interactions with the carbon center to stabilize the nucleophilic carbene lone pairs (Scheme 8, right-hand side).

■ CONCLUSION

In this contribution, we have described simple routes to new uranium(IV) nucleophilic carbene complexes, from readily available UCl_4. Examples include mixed carbene-halide, carbene-amide, and carbene-organometallic complexes. Together with crystal data, theoretical calculations show that the U═C multiple bond presents a covalent character similar to the bonding situation in transition metal complexes. In addition, the vacant 5f atomic orbitals on the actinide ion engage in covalent interactions with the carbene center, so as to better stabilize the carbene valence orbitals. As a result, and in contrast with transition metal complexes, changes in the coordination sphere of the uranium(IV) center have little influence on the U═C bond. Having in hand a variety of functional carbene complexes, future developments will focus on their reactivity, with special attention to their oxidation.

■ EXPERIMENTAL SECTION

All reactions were carried out under argon with the rigorous exclusion of air and water (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum line techniques or in a glovebox. Solvents were thoroughly dried by standard methods and distilled immediately before use. The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DPX 200 or DRX 300 instrument; the ^{1}H NMR spectra are referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0), and the ^{31}P NMR chemical shifts are given relative to an 85% H_3PO_4 external reference; the spectra were recorded in THF-d_8 at 23 °C when not otherwise specified. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). UCl_4,[41] $U(NEt_2)_4$,[42] $[U(NEt_2)_3][BPh_4]$,[43] $[U(Cp^*)_2UCl_2]$,[44] $H_2C(Ph_2PS)_2$,[15] and solutions of $Li_2(SCS)$ in diethyl ether or toluene[15] were prepared according to published methods.

Synthesis of $[\{Li(OEt_2)\}_2U(SCS)_3]$ (1). A flask was charged with UCl_4 (282.3 mg, 0.74 mmol) and an Et_2O solution (50 mL) of $Li_2(SCS)$ prepared *in situ* from $H_2C(Ph_2PS)_2$ (1000 mg, 2.23 mmol) and LiMe (2.79 mL of a 1.6 M solution in Et_2O, 4.46 mmol). The reaction mixture was stirred for 2 d at 20 °C. After evaporation of the solvent, **1** was extracted with toluene (50 mL) and isolated as a yellow powder after drying under vacuum. Yield: 1086 mg (84%). Complex **1** was characterized by its elemental analyses, ^{1}H and ^{31}P NMR spectra, and X-ray crystal structure.[16] 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: δ 19.78 (s, 12H, *o*-Ph), 11.89 (t, J = 7 Hz, 12H, *m*-Ph), 10.59 (t, J = 7 Hz, 8H, *p*-Ph), 9.61 (s, 12H, *o*-Ph), 6.54 (t, J = 7 Hz, 12H, *m*-Ph), 6.40 (t, J = 7 Hz, 6H, *p*-Ph), 3.42 (q, J = 7 Hz, 8H, Et_2O), 1.16 (t, J = 7 Hz, 12H, Et_2O). ^{31}P{^{1}H} NMR: δ −562 ($w_{1/2}$ = 120 Hz).

Synthesis of $[Li_2(THF)_4U(SCS)Cl_4]$ and Crystals of $[Li(THF)_2U(SCS)Cl_3(THF)]$ (2a) and $[Li(THF)(Et_2O)U(SCS)(\mu\text{-}Cl)_3]_2$ (2b). A solution of $Li_2(SCS)$ (60 mg, 0.13 mmol) in toluene (20 mL) was poured with stirring into a solution of UCl_4 (50 mg, 0.13 mmol) in THF (4 mL). After 5 min at 20 °C, the solvents were evaporated off, leaving the dark brown powder of $[Li_2(THF)_4U(SCS)Cl_4]$. Yield: 143 mg (98%). Despite several attempts, satisfactory elemental analyses were not obtained; the low values suggest incomplete combustion of the sample. Anal. Calcd for $C_{41}H_{52}Li_2O_4P_2S_2U$: C, 43.63; H, 4.64; S, 5.68. Found: C, 34.75; H, 3.88; S, 5.28. ^{1}H NMR: δ 21.3 (br s, $w_{1/2}$ = 215 Hz, 8H, *o*-Ph), 11.68 (s, $w_{1/2}$ = 30 Hz, 8H, *m*-Ph), 10.50 (s, $w_{1/2}$ = 30 Hz, 4H, *p*-Ph). ^{31}P{^{1}H} NMR: the signal was not detected. Red-brown crystals of **2a** were obtained by slow diffusion of pentane into a THF solution of this powder, and red crystals of **2b** were formed by recystallization from diethyl ether.

Synthesis of $[U(SCS)_2(THF)_2]$ (3a) and Crystals of $[U(SCS)_2(py)_2]\cdot1.5py\cdot0.5THF$ (3b·1.5py·0.5THF). (a) A solution of $Li_2(SCS)$ (600 mg, 1.3 mmol) in toluene (100 mL) was poured with stirring into a solution of UCl_4 (250 mg, 0.65 mmol) in THF (20 mL). After 5 min at 20 °C, the solvents were evaporated off, and **3a** was extracted with toluene (30 mL) and isolated as a dark orange powder after evaporation under vacuum. Yield: 0.804 g (96%). Anal. Calcd for $C_{58}H_{56}O_2P_4S_4U$: C, 54.63; H, 4.43; S, 10.06. Found: C, 55.16; H, 4.53; S, 9.94. ^{1}H NMR: δ 25.72 (s, 16H, *o*-Ph), 12.77 (s, 16H, *m*-Ph), 11.41 (s, 8H, *p*-Ph). ^{31}P{^{1}H} NMR: δ −324 ($w_{1/2}$ = 290 Hz).

(b) A flask was charged with UCl_4 (100.0 mg, 0.23 mmol) and $H_2C(Ph_2PS)_2$ (263.2 mg, 0.46 mmol) in THF (25 mL), and $LiCH_2SiMe_3$ (104.1 mg, 1.10 mmol) was added to the green solution. After stirring for 3 h at 20 °C, the reaction mixture was evaporated to dryness and the orange residue was extracted in toluene (3 × 10 mL). The solvent was evaporated off, leaving the dark orange powder of **3a**. Yield: 534 mg (98%).

(c) A flask was charged with **1** (500 mg, 0.29 mmol) and UCl_4 (54.6 mg, 0.14 mmol) in THF (30 mL). After 4 h at 20 °C, the solvent was evaporated off, and **3a** was extracted in toluene (3 × 20 mL) and isolated as a brown powder after evaporation to dryness. Yield: 534 mg (97%). Orange crystals of $[U(SCS)_2(py)_2]\cdot1.5py\cdot0.5THF$ (**3b**·1.5py·0.5THF) were formed by crystallization of **3a** from a mixture of pyridine and THF, while a few dark orange crystals of $[U(SCS)\{CS(Ph_2PS)_2\}(py)]$ (**4**) were obtained when a pyridine solution of **3a** was heated for 4 h at 80 °C.

Synthesis of $[U(SCS)Cl_2(THF)_2]$ (5a) and $[U(SCS)Cl_2(py)_2]$ (5b). (a) A flask was charged with **3a** (100 mg, 0.078 mmol) and UCl_4 (29.78 mg, 0.078 mmol) in THF (15 mL). After 3 h at 20 °C, the solvent was evaporated off, leaving **5a** as an orange powder. Yield: 137 mg (98%). Anal. Calcd for $C_{33}H_{36}Cl_2O_2P_2S_2U$: C, 44.05; H, 4.03; S, 7.13. Found: C, 43.94; H, 4.17; S, 6.95. ^{1}H NMR: δ 17.04 (s, 8H, *o*-Ph), 10.87 (t, J = 7 Hz, 8H, *m*-Ph), 9.88 (t, J = 7 Hz, 4H, *p*-Ph). ^{31}P{^{1}H} NMR: δ −600.1. An NMR tube was charged with **5a** (10.5 mg, 0.011 mmol) and LiCl (0.5 mg, 0.023 mmol) in THF-d_8 (0.4 mL), and the NMR spectrum showed the immediate formation of $[Li_2(THF)_4U(SCS)Cl_4]$. (b) An NMR tube was charged with **5a** (10 mg, 0.011 mmol) in pyridine (1 mL), and after 10 min at 20 °C, the solvent was evaporated off. The spectrum of the orange residue in Tol-d_8 showed the quantitative formation of $[U(SCS)Cl_2(py)_2]$ (**5b**). ^{1}H NMR (Tol-d_8): δ 13.01 (br s, $w_{1/2}$ = 56 Hz, 8H, *o*-Ph), 9.71 (t, J = 7.2 Hz, 8H, *m*-Ph), 8.66 (t, J = 6.6 Hz, 4H, *p*-Ph), 7.74 (m, 1H, py), 7.41 (m, 2H, py), 7.23 (s, 2H, py).

Reaction of $U(NEt_2)_4$ and $H_2C(Ph_2PS)_2$. An NMR tube was charged with $U(NEt_2)_4$ (10.8 mg, 0.020 mmol) and $H_2C(Ph_2PS)_2$ (18.4 mg, 0.041 mmol) in THF (0.35 mL). After 5 h at 60 °C, the ^{1}H NMR spectrum of the brown solution showed the presence of **3a** and $[U(SCS)(NEt_2)_2]$ (**6**) in the ratio 73:27. ^{1}H NMR of **6**: δ 49.00 (s, 12H, Me), 18.17 (s, 8H, *o*-Ph), 14.32 (s, 8H, *m*-Ph), 12.58 (s, 4H, *p*-Ph), −17.53 (s, 8H, CH_2). ^{31}P{^{1}H} NMR: δ −404.1.

Synthesis of $[U(SCS)(SCHS)(NEt_2)]$ (7). A flask was charged with $U(NEt_2)_4$ (17.3 mg, 0.032 mmol) and $H_2C(Ph_2PS)_2$ (29.2 mg, 0.065 mmol) in Et_2O (5 mL). After stirring for 2 h at 20 °C, the volume of the orange solution was reduced to 3 mL. The yellow microcrystalline powder of **7**, which was deposited after 2 d at 20 °C, was filtered off and dried under vacuum. Yield: 32.7 mg (85%). Anal. Calcd for $C_{54}H_{51}NP_4S_4U$: C, 53.86; H, 4.27; N, 1.16. Found: C, 53.53; H, 4.51; N, 1.06. ^{1}H NMR: δ 63.47 (s, 2H, CH_2), 45.12 (s, 2H, CH_2), 42.63 (s, 6H, CH_3), 20.14 (s, 8H, *o*-Ph), 12.18 (s, 8H, *m*-Ph), 11.92 (s, 8H, *o*-Ph), 10.48 (s, 4H, *p*-Ph), 9.06−6.11 (m, 12H, *m*- and *o*-Ph); the methanide proton of SCHS was not detected. ^{31}P{^{1}H} NMR: δ 43.17 (P of SCHS), −495 ($w_{1/2}$ = 219 Hz, P of SCS). Dark yellow crystals of **7**·toluene were obtained by slow diffusion of pentane into a toluene solution. An NMR tube was charged with **7** (10 mg) in THF-d_8 (0.4 mL), and after 48 h at 20 °C, the spectrum showed the almost quantitative formation of **3a** with concomitant elimination of $HNEt_2$.

Crystals of $[Li(THF)_2U(SCS)(NEt_2)(\mu\text{-}O)]_2$ (8). An NMR tube was charged with $[U(NEt_2)_3][BPh_4]$ (10.1 mg, 0.013 mmol) in toluene (0.3 mL), and a solution of $Li_2(SCS)$ (6.0 mg, 0.013 mmol) in toluene (0.1 mL) was added. The tube was immersed for 2 h in an ultrasound bath (70 W, 42 kHz), and a brown precipitate was deposited from the orange solution. After evaporation to dryness, the residue was dissolved in THF-d_8 (0.4 mL), and the NMR spectrum showed the formation of unidentified products. Bright red crystals of **8** were formed after 1 week.

Synthesis of $[U(SCS)(NEt_2)(THF)_3][BPh_4]$ (9). A flask was charged with $[U(NEt_2)_3][BPh_4]$ (200 mg, 0.25 mmol) and $H_2C(Ph_2PS)_2$ (115.8 mg, 0.25 mmol) in THF (30 mL). After stirring for 5 min at 20 °C, the red solution was evaporated to dryness, leaving the red powder of **9**. Yield: 330 mg (99%). Anal. Calcd for $C_{65}H_{74}BNO_3P_2S_2U$: C, 60.42; H, 5.77; S, 4.96. Found: C, 59.70; H, 5.69; S, 4.82. ^{1}H NMR: δ 137.90 (s, 4H, CH_2), 53.80 (s, 6H, CH_3), 29.98 (s, 8H, *o*-Ph), 14.03 (s, 8H, *m*-Ph), 12.14 (s, 4H, *p*-Ph). ^{31}P{^{1}H} NMR: δ −122.4.

Synthesis of $[Tl\{U(C_5H_5)(SCS)\}_2(\mu\text{-}Cl)_3]$ (10). An NMR tube was charged with UCl_4 (25.1 mg, 0.065 mmol) in THF (0.2 mL), and a solution of $Li_2(SCS)$ (30 mg, 0.065 mmol) in toluene (3 mL) was added. After stirring for 5 min at 20 °C, TlCp (17.7 mg, 0.065 mmol) was added. The tube was immersed for 1 h in the ultrasound bath, and after 8 h at 20 °C, the solution was filtered and evaporated to dryness, leaving the red powder of **10**. Yield: 52.9 mg (90%). Red crystals of **10**·2toluene were obtained by slow diffusion of pentane into a toluene solution. Anal. Calcd for $C_{74}H_{66}Cl_3P_4S_4TlU_2$: C, 44.56; H, 3.31; S, 6.42. Found: C, 45.09; H, 3.69; S, 6.01. ^{1}H NMR: δ 21.11 (s, 8H, *o*-Ph), 11.61 (s, 8H, *m*-

Table 9. Crystal Data and Structure Refinement Details

	2a	**2b**	**4**	**7**·toluene	**8**	**10**·2toluene	**12**	**13**·0.5pentane
chemical formula	$C_{37}H_{44}Cl_3LiO_3P_2S_2U$	$C_{66}H_{76}Cl_6Li_2O_4P_4S_4U_2$	$C_{55}H_{45}NP_4S_5U$	$C_{61}H_{59}NP_4S_4U$	$C_{74}H_{92}Li_2N_2O_6P_4S_4U_2$	$C_{74}H_{66}Cl_3P_4S_4TlU_2$	$C_{45}H_{50}P_2S_2U$	$C_{39.5}H_{42}OP_2S_2U$
M (g mol^{-1})	1014.10	1888.03	1242.13	1296.24	1847.56	1994.17	954.94	896.82
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a (Å)	36.441(3)	11.5147(7)	38.644(3)	11.6055(5)	11.8930(13)	12.8993(6)	17.6971(12)	12.2184(10)
b (Å)	19.0149(8)	28.371(2)	13.7549(8)	12.4377(9)	13.3571(10)	16.7058(10)	12.2271(9)	15.2045(8)
c (Å)	11.6868(9)	11.5957(11)	20.2815(9)	22.3380(15)	13.8449(12)	18.2890(13)	19.7485(9)	21.5057(19)
α (deg)	90	90	90	102.783(3)	72.795(5)	84.286(4)	90	90
β (deg)	92.213(4)	98.252(5)	113.383(3)	91.916(3)	87.145(4)	82.550(4)	109.576(4)	102.369(5)
γ (deg)	90	90	90	114.428(4)	63.896(5)	70.172(3)	90	90
V (Å^3)	8092.0(10)	3748.9(5)	9895.1(11)	2834.5(3)	1878.3(3)	3669.7(4)	4026.3(5)	3902.5(5)
Z	8	2	8	2	1	2	4	4
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	100(2)	150(2)
D_{calcd} (g cm^{-3})	1.665	1.673	1.668	1.519	1.633	1.805	1.575	1.526
μ(Mo Kα) (mm^{-1})	4.426	4.768	3.661	3.163	4.553	6.943	4.245	4.376
F(000)	3984	1840	4912	1296	912	1900	1896	1764
reflns collcd	139 865	104 969	150 132	106 296	82 532	161 388	72 714	112 249
indep reflns	15 247	7097	9364	10 730	7122	13 926	7638	7391
obsd reflns [$I > 2\sigma(I)$]	9492	4800	6721	8619	5803	10 245	5905	4956
R_{int}	0.083	0.063	0.065	0.059	0.074	0.052	0.052	0.068
params refined	883	399	583	619	436	795	461	435
R1	0.084	0.052	0.049	0.042	0.033	0.037	0.033	0.050
wR2	0.230	0.086	0.121	0.105	0.065	0.081	0.066	0.130
S	1.057	1.033	1.031	1.049	0.971	0.947	0.975	1.032
$\Delta\rho_{min}$ (e Å^{-3})	−2.30	−1.25	−1.70	−1.02	−1.14	−1.30	−1.09	−1.34
$\Delta\rho_{max}$ (e Å^{-3})	4.31	1.02	1.74	1.30	0.90	2.92	0.72	1.77

Ph), 10.47 (s, 4H, *p*-Ph), −17.27 (s, 5H, Cp). $^{31}P\{^1H\}$ NMR: δ −375 ($w_{1/2}$ = 54 Hz).

Synthesis of [U(Cp)$_2$(SCS)] (11). TlCp (283.8 mg, 1.06 mmol) was added into a flask containing a solution of [Li_2(THF)$_4$U(SCS)Cl_4] prepared from UCl_4 (200 mg, 0.53 mmol) in THF (10 mL) and Li_2(SCS) (30.9 mg, 0.53 mmol) in toluene (50 mL). After 6 h at 20 °C, the solvents were evaporated off and **11** was extracted with toluene (50 mL) and isolated as a pale orange powder after evaporation under vacuum. Yield: 339 mg (79%). Anal. Calcd for $C_{35}H_{30}P_2S_2U$: C, 51.60; H, 3.71; P, 7.60. Found: C, 51.17; H, 3.94; P, 7.25. ^1H NMR: δ 20.63 (t, *J* = 7.2 Hz, 8H, *o*-Ph), 11.14 (t, *J* = 7.2 Hz, 8H, *m*-Ph), 9.94 (t, *J* = 7.2 Hz, 4H, *p*-Ph), −13.60 (s, 10H, Cp). $^{31}P\{^1H\}$ NMR: δ −361.4. Pale orange crystals of **11**·toluene were deposited from a toluene solution.

Synthesis of [U(Cp*)$_2$(SCS)] (12). A flask was charged with $H_2C(Ph_2PS)_2$ (77 mg, 0.17 mmol) in Et_2O (2 mL), and LiMe (216 μL of a 1.6 M solution in Et_2O, 0.34 mmol) was added. To this solution of Li_2(SCS) was added [U(Cp*)$_2Cl_2$] (100 mg, 0.17 mmol) dissolved in Et_2O (20 mL). The flask was immersed in the ultrasound bath for 20 min, and, after filtration, the volume of the solution was reduced to 10 mL. After 1 d at 20 °C, the red crystals of **12** that were deposited were filtered off and dried under vacuum. Yield: 141.2 mg (87%). Anal. Calcd for $C_{45}H_{50}P_2S_2U$: C, 56.60; H, 5.28; S, 6.72. Found: C, 55.85; H, 5.28; S, 6.38. ^1H NMR: δ 13.30 (s, 8H, *o*-Ph), 9.75 (s, 8H, *m*-Ph), 9.28 (t, *J* = 7.2 Hz, 4H, *p*-Ph), 5.70 (s, 15H, Cp*). $^{31}P\{^1H\}$ NMR: δ −665.6.

Synthesis of [U(COT)(SCS)(THF)] (13). (a) A flask was charged with **5a** (200 mg, 0.22 mmol) in THF (50 mL), and a solution of K_2COT (40.4 mg, 0.22 mmol) in THF (10 mL) was slowly added. After 4 h at 20 °C, the solution was filtered to eliminate a small quantity of green [U(COT)$_2$] and evaporated to dryness. The red powder was extracted with toluene (20 mL). After filtration and evaporation, the red powder of **13** was washed with diethyl ether (15 mL) and dried under vacuum. Yield: 152.5 mg (80%). Anal. Calcd for $C_{37}H_{36}OP_2S_2U$: C, 51.63; H, 4.22; S, 7.45. Found: C, 49.94; H, 4.39; S, 7.29. ^1H NMR: δ 22.68 (s, 8H, *o*-Ph), 11.29 (s, 8H, *m*-Ph), 10.22 (s, 4H, *p*-Ph), −32.72 (s, 8H, COT). $^{31}P\{^1H\}$ NMR: δ −230.6.

(b) A flask was charged with **9** (81.5 mg, 0.064 mmol) in THF (20 mL), and K_2COT (11.8 mg, 0.064 mmol) was added. After stirring for 2 h, the solution was filtered to eliminate the released salts $KNEt_2$ and $KBPh_4$ and then evaporated to dryness, leaving the red powder of **13**. Yield: 55 mg (99%).

(c) To a flask containing a toluene/THF solution of [Li_2(THF)$_4$U(SCS)Cl_4] (145 mg, 0.13 mmol), prepared as described above, was slowly added a solution of K_2COT (23.9 mg, 0.13 mmol) in THF (3 mL). The flask was immersed for 10 min in the ultrasound bath, the solvents were evaporated off, and the residual red powder was extracted with toluene (10 mL). The solution was further filtered to eliminate a small quantity of [U(COT)$_2$] and then evaporated to dryness. The red powder formulated as [Li(THF)$_x$U(COT)(SCS)Cl] was washed with diethyl ether (15 mL) and dried under vacuum. Yield: 75.6 mg (60% with $x = 2$). The same product was formed upon addition of LiCl into a solution of **13** in THF-d_8. ^1H NMR: δ 24.21 (s, 4H, Ph), 16.61 (s, 4H, Ph), 13.42 (s, 4H, Ph), 11.84 (s, 2H, Ph), 8.32 (s, 4H, Ph), 7.18 (s, 2H, Ph), −30.91 (s, 8H, COT). $^{31}P\{^1H\}$ NMR: δ −352.1.

Crystallography. The data were collected on a Nonius Kappa-CCD area detector diffractometer[45] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were introduced into glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames, then refined on all data. The data (combinations of φ- and ω-scans giving complete data sets up to θ = 25.7° and a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[46] Absorption effects were corrected empirically with the program SCALEPACK.[46] All structures were solved by direct methods with SHELXS-97,[47] except for those of **2b** and **7**·toluene, which were solved by Patterson map interpretation, and expanded by subsequent Fourier-difference synthesis. All structures were refined by full-matrix least-squares on F^2 with SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The 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. Crystal data and structure refinement parameters are given in Table 9. The molecular plots were drawn with SHELXTL.[47] Special details are as follows:

Compound ***2a****.* Restraints on bond lengths and/or displacement parameters were applied for the carbon atoms of one THF in molecule B.

Compound ***2b****.* Restraints on bond lengths and/or displacement parameters were applied for some atoms in the THF and diethyl ether molecules.

Compound ***4****.* One aromatic ring was refined as an idealized hexagon, and restraints on displacement parameters were applied for some aromatic carbon atoms.

Compound ***7****·toluene.* Restraints on displacement parameters were applied for some atoms in the aromatic rings. Two aromatic rings (one in a ligand and the solvent toluene molecule) were refined as idealized hexagons. The hydrogen atom bound to C26 was introduced as found on a Fourier-difference map.

Compound ***8****.* One carbon atom in one THF molecule is disordered over two positions, which were refined with occupancy parameters constrained to sum to unity.

Compound ***10****·2toluene.* Some voids in the lattice likely indicate the presence of other, unresolved solvent molecules.

Compound ***13****·0.5pentane.* The pentane solvent molecule was given an occupancy factor of 0.5 in order to retain acceptable displacement parameters. Restraints on bond lengths and displacement parameters were applied for the atoms of the THF and pentane molecules.

Computational Details. The B3LYP 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. The LANL2DZ basis set was used for Zr.[48] Harmonic vibrational analysis was performed to confirm that the structure was a minimum. All calculations were carried out using the Gaussian03 suite of codes.[49] The Mulliken population analysis was performed using the AOMIX suite of programs.[50,51]

■ ASSOCIATED CONTENT

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

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■ DEDICATION

This article is dedicated to the memory of our friend Pascal Le Floch.

■ REFERENCES

(1) (a) Nugent, W. A.; Mayer, J. M. *Metal—Ligand Multiple Bonds*; Wiley—Interscience: New York, 1988. (b) Hill, A. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 7, p 299. (c) Che, C. M.; Ho, C. M.; Huang, J. S. *Coord. Chem. Rev.* **2007**, *251*, 2145, and references therein. (d) Vignolle, J.; Catton, X.; Bourissou, D. *Chem. Rev.* **2009**, *109*, 3333. (e) Öfele, K.; Tosh, E.; Taubmann, C.; Herrmann, W. A. *Chem. Rev.* **2009**, *109*, 3408. (f) Herndon, J. W. *Coord. Chem. Rev.* **2000**, *206—207*, 237.

(2) (a) Arnold, P. L.; Liddle, S. T. *Chem. Commun.* **2006**, 3959. (b) Giesbrecht, G. R.; Gordon, J. C. *Dalton Trans.* **2004**, 2387.

(3) (a) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 3589. (b) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1983**, *2*, 1336. (c) Cramer, R. E.; Bruck, M. A.; Edelman, F.; Afzal, D.; Gilje, J. W. *Chem. Ber.* **1988**, *121*, 417. (d) Stevens, R. C.; Bau, R.; Cramer, R. E.; Afzal, D.; Gilje, J. W.; Koetzle, T. F. *Organometallics* **1990**, *9*, 694.

(4) (a) Andrews, L.; Cho, H. G. *Organometallics* **2006**, *25*, 4040. (b) Lyon, J. T.; Andrews, L.; Hu, H. S.; Li, J. *Inorg. Chem.* **2008**, *47*, 1435. (c) Villiers, C.; Ephritikhine, M. *Chem.—Eur. J.* **2001**, *7*, 3043. (d) Villiers, C.; Vandais, A.; Ephritikhine, M. *J. Organomet. Chem.* **2001**, *617—618*, 744.

(5) Cantat, T.; Mézailles, N.; Auffrant, A; Le Floch, P. *Dalton Trans.* **2008**, 1957.

(6) Aparna, K.; Ferguson, M.; Cavell, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 726.

(7) (a) Cantat, T.; Jaroschik, F.; Nief, F.; Ricard, L.; Mézailles, N.; Le Floch, P. *Chem. Commun.* **2005**, 5178. (b) Cantat, T.; Jaroschik, F.; Ricard, L.; Le Floch, P.; Nief, F.; Mézailles, N. *Organometallics* **2006**, *25*, 1329.

(8) Fustier, M.; Le Goff, X.-F.; Le Floch, P.; Mézailles, N. *J. Am. Chem. Soc.* **2010**, *132*, 13108.

(9) Liddle, S. T.; McMaster, J.; Green, J. C.; Arnold, P. L. *Chem. Commun.* **2008**, 1747.

(10) Mills, D. P.; Cooper, O. J.; McMaster, J.; Lewis, W.; Liddle, S. T. *Dalton Trans.* **2009**, 4547.

(11) Wooles, A. J.; Mills, D. P.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Dalton Trans.* **2010**, *39*, 500.

(12) Wooles, A. J.; Cooper, O. J.; McFaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Organometallics* **2010**, *29*, 2315.

(13) Mills, D. P.; Wooles, A. J.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Organometallics* **2009**, *28*, 6771.

(14) Buchard, A.; Auffrant, A.; Ricard, L.; Le Goff, X.; Platel, R. H.; Williams, C. K.; Le Floch, P. *Dalton Trans.* **2009**, 10219.

(15) Cantat, T.; Ricard, L.; Le Floch, P.; Mézailles, N. *Organometallics* **2006**, *25*, 4965.

(16) Cantat, T.; Arliguie, T.; Noël, A.; Thuéry, P.; Ephritikhine, M.; Le Floch, P.; Mézailles, N. *J. Am. Chem. Soc.* **2009**, *131*, 963.

(17) Cooper, O. J.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Dalton Trans.* **2010**, *39*, 5074.

(18) Volkov, V. V.; Myakishev, K. G. *Radiokhimiya* **1980**, *22*, 745.

(19) Preliminary communication: Tourneux, J. C.; Berthet, J. C.; Thuéry, P.; Mézailles, N.; Le Floch, P.; Ephritikhine, M. *Dalton Trans.* **2010**, *39*, 2494.

(20) Cantat, T.; Ricard, L.; Mézailles, N.; Le Floch, P. *Organometallics* **2006**, *25*, 6030.

(21) (a) Secaur, C. A.; Day, V. W.; Ernst, R. D.; Kennelly, W. J.; Marks, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 3713. (b) Schnabel, R. C.; Scott, B. L.; Smith, W. H.; Burns, C. J. *J. Organomet. Chem.* **1999**, *591*, 14.

(22) Durant, F.; Piret, P.; van Meerssche, M. *Acta Crystallogr.* **1967**, *22*, 52.

(23) Hall, S. W.; Huffman, J. C.; Miller, M. M.; Avens, L. R.; Burns, C. J.; Arney, D. S. J.; England, A. F.; Sattelberger, A. P. *Organometallics* **1993**, *12*, 752.

(24) Arliguie, T.; Lescop, C.; Ventelon, L.; Leverd, P. C.; Thuéry, P.; Nierlich, M.; Ephritikhine, M. *Organometallics* **2001**, *20*, 3698.

(25) Leverd, P. C.; Arliguie, T.; Ephritikhine, M.; Nierlich, M.; Lance, M.; Vigner, J. *New J. Chem.* **1993**, *17*, 769.

(26) Leverd, P. C.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1993**, 2251.

(27) Berthet, J. C.; Ephritikhine, M. *Coord. Chem. Rev.* **1998**, *178—180*, 83.

(28) Babu, R. P. K.; Cavell, R. G.; McDonald, R. *Chem. Commun.* **2000**, 481.

(29) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 1090.

(30) Lukens, W. W.; Allen, P. G.; Bucher, J. J.; Edelstein, N. M.; Hudson, E. A.; Shuh, D. K.; Reich, T.; Andersen, R. A. *Organometallics* **1999**, *18*, 1253.

(31) Salmon, L.; Thuéry, P.; Asfari, Z.; Ephritikhine, M. *Dalton Trans.* **2006**, 3006.

(32) Chadwick, S.; Ruhlandt-Senge, K. *Chem.—Eur. J.* **1998**, *4*, 1768.

(33) Davis, K. B.; Harris, T. D.; Castellani, M. P.; Golen, J. A.; Rheingold, A. L. *Organometallics* **2007**, *26*, 4843.

(34) Drouin, S. D.; Foucault, H. M.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2004**, *23*, 2583.

(35) Leclerc, B.; Kabre, T. S. *Acta Crystallogr., Sect. B* **1975**, *31*, 1675.

(36) Arliguie, T.; Ephritikhine, M.; Lance, M.; Vigner, J.; Nierlich, M. *J. Organomet. Chem.* **1994**, *484*, 195.

(37) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(38) (a) Seyferth, D. *Organometallics* **2004**, *23*, 3562. (b) Ephritikhine, M. *Dalton Trans.* **2006**, 2501.

(39) Arliguie, T.; Baudry, D.; Berthet, J. C.; Ephritikhine, M.; Le Maréchal, J. F. *New J. Chem.* **1991**, *15*, 569.

(40) (a) Arliguie, T.; Baudry, D.; Ephritikhine, M.; Nierlich, M.; Lance, M.; Vigner, J. *J. Chem. Soc., Dalton Trans.* **1992**, 1019. (b) Leverd, P. C.; Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1992**, 501. (c) Boisson, C.; Berthet, J. C.; Ephritikhine, M.; Lance, M.; Nierlich, M. *J. Organomet. Chem.* **1996**, *522*, 249. (d) Arliguie, T.; Fourmigué, M.; Ephritikhine, M. *Organometallics* **2000**, *19*, 109. (e) Berthet, J. C.; Nierlich, M.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2002**, 850. (f) Arliguie, T.; Thuéry, P.; Fourmigué, M.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2004**, 4502. (g) Arliguie, T.; Blug, M.; Le Floch, P.; Mézailles, N.; Thuéry, P.; Ephritikhine, M. *Organometallics* **2008**, *27*, 4158.

(41) Hermann, J. A.; Suttle, J. F. *Inorg. Synth.* **1957**, *5*, 143.

(42) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M.; Templeton, L. K. *Inorg. Chem.* **1976**, *15*, 2498.

(43) Berthet, J. C.; Boisson, C.; Lance, M.; Vigner, J.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3019.

(44) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.

(45) Hooft, R. W. W. *COLLECT*; Nonius BV: Delft, The Netherlands, 1998.

(46) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(47) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(48) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

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

(50) Gorelsky, S. I. *AOMix: Program for Molecular Orbital Analysis*, version 6.35; University of Ottawa: Ottawa, Canada, 2007.

(51) Gorelsky, S. I.; Lever, A. B. P. *J. Organomet. Chem.* **2001**, *635*, 187.