Easy access to uranium nucleophilic carbene complexes[†]

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Metathesis reactions of UCl₄ with $Li_2C(Ph_2PS)_2$ in Et_2O only afforded the tris-carbene complex $[{Li(OEt_2)}_2 U{=C(Ph_2PS)_2}_{3}$ (1), while the bis- and mono-carbene compounds $[U{=C(Ph_2PS)_2}_2(THF)_2]$ (2) and $[{Li(THF)_2}_2U{=}$ $C(Ph_2PS)_2$ Cl₄ (3) were obtained by treatment of UCl₄ with $Li_2C(Ph_2PS)_2$ in a mixture of THF and toluene. The bis-carbene complex 2 was also obtained either from the comproportionation reaction of 1 and UCl₄ or protonolysis reaction of U(NEt₂)₄ with H₂C(Ph₂PS)₂ and was transformed into the mono-carbene complex $[U{=C(Ph_2PS)_2}Cl_2(THF)_2]$ (4) by further reaction with UCl_4 . The utility of these complexes as precursors is illustrated by the synthesis of the biscyclopentadienyl derivative $[Cp_2U{=C(Ph_2PS)_2}]$ (5) by treatment of 3 with TlCp. The crystal structures of $[U{=C(Ph_2PS)_2}_2(py)_2]$ 1.5py 0.5THF and 5 toluene are reported.

Actinide carbene complexes with significant metal-carbon multiple bond character are very rare. These were limited to the tris(cyclopentadienyl) uranium phosphoylide compounds $[Cp_3U=CHP(Me)RR']$ (Cp = η -C₅H₅), discovered by Gilje et al. in 1981 and prepared by treatment of [Cp₃UCl] with Li(CH₂)(CH₂)PRR',¹ until we recently reported on the synthesis of the bis(thiophosphinoyl)methanediide complexes $[M_2U{=C(Ph_2PS)_2}_3]$ $[M = U(BH_4)_3$ or Li(OEt₂)] and $[U{=C(Ph_2PS)_2}(BH_4)_2(THF)_2]^2$ These nucleophilic carbene complexes were isolated from $U(BH_4)_4$ and the geminal dianionic reagent Li₂C(Ph₂PS)₂. However, this synthetic route suffers from a major drawback, that is the use of the uranium borohydride as the starting material, whose preparation by the solvent-free reaction of finely powdered UCl₄ and LiBH₄ in a vacuum vibration ball mill, followed by sublimation, is somewhat tedious and skill-demanding.3 As such, these uranium carbene complexes have a limited utility and more practical precursors for the development of this class of compounds were clearly desirable. Here we report on (a) the easy and efficient syntheses of the tris-, bis- and mono-carbene complexes $[{Li(OEt_2)}_2U{=C(Ph_2PS)_2}_3]$ (1), $[U{=C(Ph_2PS)_2}_2(L)_2]$ (L = THF, 2 or L = py, 2'), $[{Li(THF)_2}_2U{=C(Ph_2PS)_2}Cl_4]$ (3) and $[U{=C(Ph_2PS)_2}Cl_2(THF)_2]$ (4) from UCl₄, the most familiar

starting material in uranium chemistry, (b) the utility of these complexes as precursors with the synthesis of $[Cp_2U{=C(Ph_2PS)_2}]$ (5), (c) the crystal structures of solvates of 2' and 5, first examples of uranium bis-carbene and bis(cyclopentadienyl) uranium carbene compounds, and (d) the reaction of $U(NEt_2)_4$ and $H_2C(Ph_2PS)_2$ which afforded a mixture of 2 and the mono-carbene complex $[U{=C(Ph_2PS)_2}(NEt_2)_2]$ (6).

The syntheses are summarized in Scheme 1.[‡] The geminal dianionic reagent Li₂C(Ph₂PS)₂ was so far used in diethyl ether or toluene, but not in THF where it is converted into the corresponding monoanion [HC(Ph₂PS)₂]^{-.4} Despite its poor solubility in Et₂O, the green solid of UCl₄ was reacted with 3 mol equivalents of Li₂C(Ph₂PS)₂ and after stirring for 2 days at 20 °C, was transformed into the yellow powder of 1.² After evaporation of the solvent, extraction with toluene in which it is more soluble, complex 1 was isolated in 84% yield. Mono- and bis-carbene complexes were not obtained by treating UCl₄ with 1 or 2 mol equivalents of $Li_2C(Ph_2PS)_2$ in Et_2O as these reactions led to the sole formation of 1. However, the desired mono- and bis-carbene compounds could be synthesized by addition of a toluene solution of Li₂C(Ph₂PS)₂ to a concentrated solution of UCl₄ in THF, in a volume ratio of 5:1. Under these conditions, the reactions were immediate and much faster than the detrimental conversion of $[C(Ph_2PS)_2]^{2-}$ into $[HC(Ph_2PS)_2]^{-}$. Thus, the bis-carbene complex 2 was readily synthesized from UCl_4 and $Li_2C(Ph_2PS)_2$ in the molar ratio of 1:2; following usual work-up, the dark orange powder of 2 was obtained in 95% yield. Similar treatment of UCl_4 with 1 mol equivalent of $Li_2C(Ph_2PS)_2$ afforded a unique



Scheme 1 Synthesis of the complexes: (i) 3 $Li_2C(Ph_2P)_2$, Et_2O ; (ii) 2 $Li_2C(Ph_2P)_2$, THF-toluene 1:5; (iii) 1 $Li_2C(Ph_2P)_2$, THF-toluene 1:5; (iv) 0.5 UCl₄, THF; (v) 1 UCl₄, THF; (vi) 2 LiCl, THF; (vii) 2 H₂C(Ph₂PS)₂, THF; (viii) 2 TICp, THF. X = Cl except for (vii) X = NEt₂. The phenyl rings on the phosphorus atoms are omitted.

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brown compound which was formulated as the mono-carbene "ate" complex **3** because of the failure to eliminate LiCl and in view of the reactions described hereafter.

The bis-carbene complex **2** was also obtained from a 1:2 mixture of UCl₄ and **1** in THF; after 4 h at 20 °C, the solvent was evaporated off and **2** was separated from LiCl by extraction in toluene; the yield was almost quantitative. Under the same conditions, the comproportionation reaction between **2** and UCl₄ in the 1:1 molar ratio quantitatively yielded the mono-carbene compound **4** which was isolated as an orange powder after evaporation of THF. Complex **4** was readily transformed into the "ate" derivative **3** upon addition of 2 mol equivalents of LiCl (NMR experiment). The structure of **4** is likely to be similar to that of the borohydride analogue;² a plausible structure of **3** is presented in Scheme 1.

An alternative preparation of **2** was attempted with the reaction of the tetraamide precursor $U(NEt_2)_4^5$ with 2 mol equivalents of $H_2C(Ph_2PS)_2$ in THF. Such synthetic route involving protonolysis of [U]–NR₂ bonds with an acidic proton molecule would be similar to that employed for the preparation of $[Hf{=}C(Ph_2PNSiMe_3)_2Cl_2]^6$ and $[Sm{=}C(Ph_2PNSiMe_3)_2}(NCy_2)(THF)]$.⁷ This reaction afforded after 5 h at 60 °C a mixture of **2** and the mono-carbene derivative $[U{=}C(Ph_2PS)_2](NEt_2)_2]$ (**6**) in relative proportions of 73:27 (NMR experiments). Although this procedure cannot be considered as a convenient synthesis of **2**, efforts are currently being made to isolate **6** in a pure form.

Single crystals of $2' \cdot 1.5$ py $\cdot 0.5$ THF were formed by crystallization of 2 from a mixture of pyridine and THF. A view of 2' is presented in Fig. 1 together with selected bond distances and angles.§ The eight-coordinate uranium atom is in a slightly distorted square antiprismatic environment, the square bases defined by the N1–S2–N2–S4 and C1–S1–C26–S3 atoms (rms deviations 0.435 and 0.511 Å) forming a dihedral angle of 2.80(5)°. The line passing through the metal centre and perpendicular to the square bases is a two-fold axis of pseudo-symmetry. The U–C distances of 2.399(7) and 2.390(8) Å are intermediate between



Fig. 1 View of $[U{=C(Ph_2PS)_2}_2(py)_2]$ (2') with displacement ellipsoids drawn at the 40% probability level. The hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): U–S1 2.892(2), U–S2 2.940(2), U–C1 2.399(7), U–S3 2.876(2), U–S4 2.951(2), U–C26 2.390(8), U–N1 2.670(7), U–N2 2.683(6), S1–U–C1 66.44(18), S2–U–C1 66.49(19), S3–U–C26 67.24(19), S4–U–C26 65.79(19), N1–U–N2 83.5(2).

those of 2.323(3) and 2.47(2) Å (average) in the seven- and nine-coordinate complexes $[U{=C(Ph_2PS)_2}(BH_4)_2(THF)_2]$ and 1, respectively.² The average U–S distance of 2.91(3) Å can be compared with those of 2.88(2) and 3.08(4) in the above compounds. The U–S–P–C–P–S cores are planar (rms deviations 0.081 and 0.062 Å). The planarity at the carbene carbon atoms, also demonstrated by the sums of the P–C–P and U–C–P angles being equal to 360°, shows the donation of both lone pairs from the dianionic fragment to the metal centre.

That these complexes are useful precursors was indicated by the synthesis of **5** by reaction of **3** or **4** with two mol equivalents of TlCp in THF. After 6 h at 20 °C and usual work-up, the orange powder of **5** was isolated in 79% yield and pale orange crystals of **5**-toluene were deposited from a toluene solution. A view of **5** is shown in Fig. 2 together with selected bond distances and angles.§ The bis(cyclopentadienyl) complex adopts the familiar bent-sandwich configuration with the planar U–S–P–C–P–S core (rms deviation 0.086 Å) lying in the equatorial girdle of the Cp₂U fragment. The short U–C1 and mean U–S distances of 2.336(4) and 2.868(2) Å are identical to those measured in $[U{=C(Ph_2PS)_2}(BH_4)_2(THF)_2].^2$



Fig. 2 View of $[Cp_2U{=C(Ph_2PS)_2}]$ (5) with displacement ellipsoids drawn at the 50% probability level. The hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): U–S1 2.8656(11), U–S2 2.8694(12), U–C1 2.336(4), S1–U–C1 68.29(11), S2–U–C1 67.90(11).

In conclusion, we have demonstrated that either mono-, bis or even tris-carbene complexes of uranium can be conveniently prepared in good yields from UCl₄ either by substitution of the Cl groups with the methandiide compound $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ or by comproportionation reactions between UCl₄ and the tris- or biscarbene complexes. These syntheses are straightforward and the complexes, which are soluble in toluene, are easily separated from the LiCl by-product. These complexes are valuable precursors for the enlargement of the family of uranium nucleophilic carbene compounds, thus permitting further studies of their chemical properties and the nature of the U=C bond.

Notes and references

[‡] Synthesis and characterization data. All manipulations were carried out under argon. The ¹H and ³¹P NMR spectra were recorded at 23 °C in THF- d_8 on a Bruker DPX 200 spectrometer operating at 200.0 MHz for ¹H and 81.0 MHz for ³¹P; the ¹H NMR spectra are referenced internally using the residual proton solvent resonances relative to tetramethylsilane (δ 0), the ³¹P NMR chemical shifts are given relative to an 85% H₃PO₄ external reference.

 $\label{eq:constraint} \begin{array}{l} \label{eq:constraint} [\{Li(OEt_2)\}_2U\{=C(Ph_2PS)_2\}_3] \ (1): A flask was charged with UCl_4 (282.3 mg, 0.74 mmol) and a Et_2O solution (50 mL) of Li_2C(Ph_2PS)_2 prepared$ *in situ* $from H_2C(Ph_2PS)_2 (1000 mg, 2.23 mmol) and MeLi (2.79 mL of a 1.6 M solution in Et_2O, 4.46 mmol). The reaction mixture was stirred for 2 d at 20 °C. After evaporation of the solvent, 1 was extracted with toluene (50 mL) and isolated as a yellow powder after drying under vacuum (1086 mg, 84%). Complex 1 was characterized by its ¹H and ³¹P NMR spectra and its X-ray crystal structure.² \\ \end{array}$

 $[U{=C(Ph_2PS)_2}_2(THF)_2]$ (2): (a) A solution of Li₂C(Ph₂PS)₂ (120 mg, 0.26 mmol) in toluene (20 mL) was poured with stirring into a solution of UCl₄ (50.0 mg, 0.13 mmol) in THF (4 mL). After 5 min at 20 °C, the solvents were evaporated off, 2 was extracted with toluene (20 mL) and isolated as a dark orange powder after evaporation under vacuum (159 mg, 95%). Found: C, 55.16; H, 4.53; S, 9.94. $C_{58}H_{56}O_2P_4S_4U$ (M = 1275.25) requires C, 54.63; H, 4.43; S, 10.06%. ¹H NMR: δ 25.72 (s, 16H, o-Ph), 12.77 (s, 16H, *m*-Ph), 11.41 (s, 8H, *p*-Ph).³¹P {¹H} NMR: δ -324 (*w*_{1/2} = 290 Hz). (b) 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, 2 was extracted in toluene $(3 \times 20 \text{ mL})$ and isolated as a brown powder after evaporation to dryness (534 mg, 97%). (c) An NMR tube was charged with U(NEt₂)₄ (10.8 mg, 0.020 mmol) and H₂C(Ph₂PS)₂ (18.4 mg, 0.041 mmol) in THF (0.35 mL). After 5 h at 60 °C, the ¹H NMR spectrum showed the presence of 2 and $[U{=C(Ph_2PS)_2}(NEt_2)_2]$ (6) in the ratio 73:27. ¹H 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, CH₂).

[{Li(THF)₂}₂U{=C(Ph₂PS)₂}Cl₄](3): A solution of Li₂C(Ph₂PS)₂ (60 mg, 0.13 mmol) in toluene (20 mL) was poured with stirring into a solution of UCl₄ (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 **3** (143 mg, 98%). ¹H 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). ³¹P {¹H} NMR: the signal was not detected.

[U{=C(Ph₂PS)₂}Cl₂(THF)₂] (**4**): A flask was charged with **2** (100 mg, 0.078 mmol) and UCl₄ (29.78 mg, 0.078 mmol) in THF (15 mL). After 3 h at 20 °C, the solvent was evaporated off, leaving **4** as an orange powder (137 mg, 98%). Found: C, 43.94; H, 4.17; S, 6.95. C₃₃H₃₆Cl₂O₂P₂S₂U (M = 899.67) requires C, 44.05; H, 4.03; S, 7.13%. ¹H 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). ³¹P {¹H</sup> NMR: $\delta = 600.1$.

 $[Cp_2U{=C(Ph_2PS)_2}]$ (5): TICp (283.8 mg, 1.06 mmol) was added to a solution of 3 prepared as described before from UCl₄ (200 mg, 0.53 mmol)

in THF (10 mL) and Li₂C(Ph₂PS)₂ (30.9 mg, 0.53 mmol) in toluene (50 mL). After 6 h at 20 °C, the solvents were evaporated off and **5** was extracted with toluene (50 mL) and isolated as a pale orange powder after evaporation under vacuum (339 mg, 79%). Found: C, 51.17; H, 4.94; P, 7.25. C₃₅H₃₀P₂S₂U (M = 814.72) requires C, 51.60; H, 3.71; P, 7.60%. 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). ³¹P {¹H} NMR: δ -361.4.

§Crystal data for 2': $C_{69.5}H_{61.5}N_{3.5}O_{0.5}P_4S_4U$, M = 1443.87, monoclinic, space group $P2_1/c$, a = 13.8488(4), b = 28.6755(15), c = 17.9735(10) Å, $\hat{\beta} = 96.481(3)^{\circ}$, V = 7092.1(6) Å³, Z = 4. Refinement of 847 parameters on 13 350 independent reflections out of 157 915 measured reflections ($R_{\rm int} = 0.075$) led to $R_1 = 0.061$, w $R_2 = 0.162$, S = 1.047, $\Delta \rho_{\rm min} =$ -1.49, Δρ_{max} = 1.61 e Å⁻³. Crystal data for **5**: C₄₂H₃₈P₂S₂U, M = 906.81, monoclinic, space group $P2_1/c$, a = 13.0722(6), b = 16.8709(9), c = 10.072(6), b = 10.8709(9), c = 10.072(6), b = 10.072(6)16.7480(8) Å, $\beta = 90.816(3)^{\circ}$, V = 3693.2(3) Å³, Z = 4. Refinement of 425 parameters on 6980 independent reflections out of 108 095 measured reflections ($R_{int} = 0.043$) led to $R_1 = 0.032$, w $R_2 = 0.074$, S = 1.031, $\Delta \rho_{min} = -1.21$, $\Delta \rho_{max} = 0.91$ e Å⁻³. Data were collected at 150(2) K on a Nonius Kappa-CCD area-detector diffractometer and processed with HKL2000.8 Absorption effects were corrected with SCALEPACK.8 The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXTL.⁹ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions. The solvent molecules are badly resolved in 2' and some of them were given 0.5 occupancy factors in order to retain acceptable displacement parameters.

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