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The first uranyl–methine carbon bond; a complex with out-of-plane uranyl equatorial coordination†

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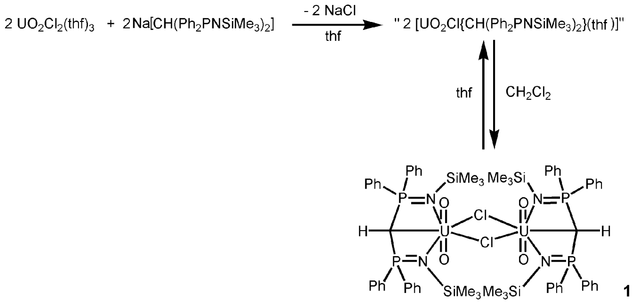
Treatment of [$UO_2Cl_2(thf)_3$] in thf with one equivalent of [Na{CH($Ph_2P = NSiMe_3)_2$}] yields an unusual uranyl chloro-bridged dimer containing a uranium(VI)–carbon bond as part of a tridentate bis(iminophosphorano)methanide chelate complex. The methine carbon is displaced significantly from the uranyl equatorial plane.

The chemistry of uranium in its lower oxidation states (U^{III} and U^{IV}) involves coordination by a wide variety of atoms arranged in a number of different coordination geometries.[1–3] In contrast U^{VI} chemistry is dominated by the uranyl ion UO_2^{2+} which accommodates hard donor ligands (F, Cl, O, or N) in an equatorial plane perpendicular to the O = U = O unit.[4] Here we report the formation of the first uranyl–methine carbon bond in a bis(iminophosphorano)methanide complex and comment on the deviation of the ligand from the equatorial plane.

Treatment of a bright yellow thf solution of [$UO_2Cl_2(thf)_3$][5] with one equivalent of [Na{CH($Ph_2PNSiMe_3)_2$}] instantly gives a deep red solution, which after concentration and extraction into CH_2Cl_2 yields analytically pure, diffraction quality, red crystals of [UO_2Cl{CH($Ph_2PNSiMe_3)_2$}]$_2$ **1**,‡ in good yield (Scheme 1). The compound is hydrolysed in water, soluble in thf and moderately soluble in CH_2Cl_2. An Ortep representation of compound **1** is shown in Fig. 1.[6]

The structure consists of two distorted pentagonal bipyramidal uranyl units each bridged by two chlorine atoms in a centrosymmetric dimer. Each uranyl group is bonded to a tridentate bis(iminophosphorano)methanide ligand through two nitrogen donor atoms and the central carbon atom. Uranyl oxo bond lengths for **1** are slightly longer (1.777(8) and 1.789(8) Å) than those in the seven coordinate chloro-bridged dimer [$UO_2Cl_2(thf)_2$]$_2$ (1.763(6) and 1.764(6) Å) whereas the bridging U–Cl bonds are slightly shorter (2.7880(19) and 2.8095(19) Å for **1** *c.f.* 2.83(2) and 2.80(2) Å for [$UO_2Cl_2(thf)_2$]$_2$).[7] A close contact between uranium and the methine carbon (2.691(8) Å) suggests a U^{VI}–C bond (the sum of the Van der Waals radii = 3.56 Å),[8] which is only slightly longer than the U–N bonds (2.514(7) and 2.458(7) Å). There are many examples of U(IV) complexes containing U–C bonds,[9–11] however, the only other crystallographically characterised complexes containing a uranyl–C bond are [$UO_2Cl_2(IMes)_2$] (IMes = 1,3-dimesitylimidazole-2-ylidene or 1,3-dimesityl-4,5-dichloroimidazole-2-ylidene) containing dative carbene–uranium bonds (2.626(7) and 2.609(4) Å, respectively),[12] comparable to that found in **1** (2.695(12)).



Scheme 1 Reaction scheme for the formation of **1**.

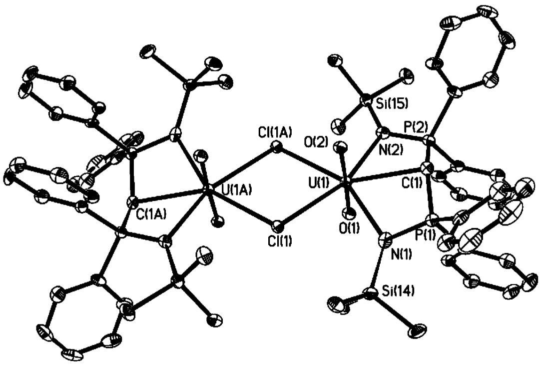


Fig. 1 Molecular structure and atom labeling scheme for [UO_2Cl{CH($Ph_2PNSiMe_3)_2$}]$_2$, (**1**) with H atoms omitted (50% probability ellipsoids). Selected bond lengths (Å): U(1)-O(2) 1.763(6), U(1)-O(2) 1.764(6), U(1)-C(1) 2.691(8), U(1)-Cl(1) 2.7880(19), U(1)-Cl(1A) 2.8095(19), U(1)-N(1) 2.514(7), U(1)-N(2) 2.458(7). Selected bond angles (deg): O(1)-U(1)-O(2) 177.3(2), O(1)-U(1)-N(1) 84.7(2), O(1)-U(1)-N(2) 86.0(2), O(2)-U(1)-C(1) 79.4(2), O(1)-U(1)-C(1) 103.1(3), P(1)-C(1)-P(2) 139.6(5).

In compound **1**, the bis(iminophosphorano)methanide forms a six membered ring with the uranium atom to give a distorted boat conformation. It was possible to locate the hydrogen atom attached to the methine carbon (see Fig. 2), although due to its proximity to U(1) its position is somewhat unreliable. However, the ligand atoms P(1)–C(1)–H–P(2) lie in the same plane, angle sum 358.9° around C(1).

It is possible for bonded and non-bonded metal carbon interactions in complexes of this type. For example, molecular orbital calculations on [NiBr{CH($Ph_2PN(C_6H_3{}^iPr_2))_2$}][13] and [$YCl_2${CH($Ph_2PNSiMe_3)_2$}]$_2$,[14] show a bonding orbital between the metal centre and a *p*-type orbital on the carbon atom. A number of Ln complexes [$LnCl_2${CH($Ph_2PNSiMe_3)_2$}]$_2$ exhibit Ln–C interactions (Ln = Sm, Er, Dy, Yb, Lu; 2.720–2.596 (5) Å),[14] with decreasing Ln–C bond length across the series as expected. In contrast, there is no metal–methine carbon bond in [$AlMe_2${CH($Ph_2PNSiMe_3)_2$}] (Al–C = 3.002(3) Å).[15] Both bonded (2.148(5) Å) and non-bonded

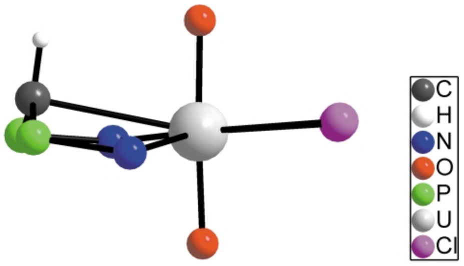


Fig. 2 Side view of a fragment of **1** showing the twist-boat conformation of the UN_2P_2C ring (peripheral atoms omitted for clarity).

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† Electronic supplementary information (ESI) available: displacement of atoms from least-squares plane; NMR, Raman and UV-Vis spectra. See http://www.rsc.org/suppdata/cc/b2/b206889c/

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(2.921(3) Å) carbon atoms are present in the two structural isomers of the chloro-bridged Cr^{II} dimer $[CrCl\{CH(Ph_2PNSiMe_3)_2\}]_2$.[16] In each case the ligand adopts a twist-boat conformation regardless of carbon coordination to the metal. Given these precedents and bond length data, we believe that C(1) is displaced out of the NPCPN ring plane and the filled *p*-orbital points towards the uranium center to form a σ-*p* type bond (Fig. 2). This is in contrast to the uranyl carbon bond formed in the $[UO_2Cl_2(IMes)_2]$[12] complexes where the bonding involves σ-*sp*² type carbon based orbitals.

Ligand atoms coordinated to uranyl lie in the equatorial position, *i.e.* in a plane at 90° to the uranyl oxo atoms. In **1** the uranyl moiety is nearly linear ($O{=}U{=}O$ = 177.3(2)°), with a slight tilt away from the bis(iminophosphorano)methanide ligand, but the ligand atoms deviate significantly from the equatorial plane (Fig. 2). For example, the methine carbon is displaced by 0.8877 (96) Å from a least squares plane defined by the atoms U(1), N(1), N(2), Cl(1) and Cl(1A) equating to a displacement of the methine carbon by ~ 18° from the defined equatorial plane projected from U(1).

In the Raman spectrum the symmetric $O{=}U{=}O$ stretch is observed at 838 cm^{-1}, intermediate between those of the chloro-bridged uranyl dimer $[UO_2Cl_2(thf)_2]_2$ (882, 840 cm^{-1})[7] and $[UO_2\{N(SiMe_3)_2\}_2(thf)_2]$ (819 cm^{-1}).[17] The IR spectrum reveals a similar situation with the asymmetric $O{=}U{=}O$ stretch at 924 cm^{-1}, in the range observed for $[UO_2Cl_2(thf)_2]_2$[7] (921 cm^{-1}) and $[UO_2\{N(SiMe_3)_2\}_2(thf)_2]$ (935 cm^{-1}).[17] It is not clear why the methine carbon coordinates in such an unusual manner to uranyl, but molecular orbital calculations on **1** are in progress. In NMR spectroscopy, the size of the coupling constants $^1J_{CX}$ (X = H, P) provide a good indication of the amount of the % *s*-character in the C–X bond; the larger the value the more the *s*-character. The coupling constant for **1** in CD_2Cl_2 $^1J_{CH}$ = 136.5 Hz is intermediate between that of the neutral ligand $CH_2(Ph_2PNSiMe_3)_2$ ($^1J_{CH}$ = 123.7 Hz) *sp*³ carbon and of the ligand precursor $[Na\{CH(Ph_2PNSiMe_3)_2\}]$ ($^1J_{CH}$ = 144.2) *sp*² carbon; consistent with an interaction between uranyl and the methine carbon atom of **1**. However, the $^1J_{CP}$ value is a less reliable tool. The ^{13}C NMR spectrum of **1** in thf-d_8 shows a PCHP coupling constant of $^1J_{CP}$ = 115.6 Hz. $[NiBr\{CH(Ph_2PN(C_6H_3{}^iPr_2)_2\}]$[13] ($^1J_{CP}$ = 108.5 Hz) has a strong Ni–C interaction whereas the methine carbon is non-coordinated in $[Na\{CH(Ph_2PNSiMe_3)_2\}]$ (J_{CP} = 131.0 Hz) and $[K\{CH(Ph_2PNSiMe_3)_2\}]$ (J_{CP} = 134.0 Hz).[18] In contrast, there are weak M–C interactions in $[MCl_2\{CH(Ph_2PNSiMe_3)_2\}]_2$; these exhibit unusually small coupling constants [M = Y ($^1J_{CP}$ = 89.1 Hz); Lu ($^1J_{CP}$ = 87.5 Hz)].[14]

The red colour of compound **1**, which is retained upon dissolution, is unusual for a uranyl complex but not unique and is a result of ligand to metal charge transfer.[17,19,20] Preliminary investigations into the electronic structure of **1** using UV/Visible spectroscopy show two unstructured strong absorption bands at 498 and 426 nm in thf, which are shifted to 515 and 434 nm in CH_2Cl_2; the higher energy band in the latter spectrum shows signs of poorly resolved vibronic fine structure. This change with solvent was investigated further by ^1H and ^{31}P NMR spectroscopy in CD_2Cl_2. Addition of small amounts of thf results in clean conversion to a new species formed consistent with coordinated thf (see †Electronic Supplementary Information); evidence which suggests that the chloro-bridged dimer **1** cleaves to give monomeric units in the presence of coordinating ligands (Scheme 1). The NMR spectral parameters of **1** in thf-d_8 (see Experimental Section) are similar to those observed in CD_2Cl_2, and the coupling constants for the methine carbon are essentially identical ($^1J_{CH}$ = 137.6, 136.5 Hz, respectively) suggesting that the bonding between uranyl and the methine carbon does not change when the dimer is cleaved. Further investigation of the chemistry of this unique system is currently underway.

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Notes and references

‡ **1**: a solution of $[UO_2Cl_2(thf)_2]_2$ (1.21 g, 2.50 mmol) in thf (50 cm^3) was treated with a toluene (50 cm^3) solution of $Na[CH(Ph_2P{=}NSiMe_3)_2]$ (5.00 mmol) and stirred at ambient temperature for 30 min. The resulting deep red solution was evaporated under vacuum and the red oily residue extracted with CH_2Cl_2 (3 × 30 cm^3). Concentration of the extract, under vacuum, to approximately 50 cm^3 and maintaining at 4 °C for 3 days gave bright red crystals of **1**. Yield 0.98 g, 70%. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 0.31 (s, 18H, $SiMe_3$), 2.52 (t, ^2J(H,P) = 11.1 Hz, ^1J(H,C) = 136.5 Hz, 1H; CH), 7.24 (brm, 8H, *o*-Ph), 7.51 (brm, 4H, *p*-Ph), 7.70 (brm, 8H, *m*-Ph); ^{31}P NMR (162 MHz, CD_2Cl_2, 85% H_3PO_4): δ 9.28. IR (Nujol): (cm^{-1}) = 1259(w), 1249(w), 1223(w), 1115(m), 1085(m), 1070(m), 1026(w), 1005(w), 996(w), 924(s), 842(mbr), 773(w), 736(m), 721(s). Raman (solid in glass capillary) (cm^{-1}) = 1410(w), 1186(w), 1160(w), 1117(m), 1087(w), 1028(m), 1000(s), 921(vw), 867(m), 838(s), 775(w), 702(w), 662(w), 621(m). Anal. calc. for $C_{62}H_{78}Cl_2N_4O_4P_4U_2$: C, 43.14; H, 4.56; Cl, 4.11; N, 3.25; P, 7.18; U, 27.58. Found: C, 43.93; H, 4.59; Cl, 4.65; N, 2.96; P, 6.49; U, 27.57%.

NMR data for **1** in thf-d_8. ^1H NMR (400 MHz, thf-d_8, 25 °C): δ = 0.20 (s, 18H, $SiMe_3$), 2.28 (t, 1H, CH, ^2J(H,P) = 10.6 Hz), 1.75 (m, CH_2-thf), 3.62 (m, CH_2-thf), 7.22 (m, 8H, *o*-Ph), 7.35 (m, 4H, *p*-Ph), 7.73 (m, 8H, *m*-Ph); ^{13}C NMR (100 MHz, thf-d_8, 25 °C): δ = 0.0 ($SiMe_3$), 19.5 (d,t, CH, ^1J(H,C) = 137.6 Hz, ^1J(C,P) = 115.8 Hz), 21.7 (CH_2-thf), 63.6 (CH_2O-thf), 124.1 (t, *o*-Ph, ^2J(C,P) = 12.0 Hz), 127.1 (s, *p*-Ph), 128.1 (m, *m*-Ph), 132.9 (d, *i*-Ph, ^1J(C,P) = 101.2 Hz); ^{31}P NMR (162 MHz, thf-d_8, 25 °C, 85% H_3PO_4): δ = 7.97.

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6 Crystal data: for **1**.3 CH_2Cl_2: $C_{65}H_{84}Cl_8N_4O_4P_4Si_4U_2$, M = 1938.80, a = 10.1019(17), b = 12.771(2), c = 16.299(3) Å, V = 1962.4(6) Å³, triclinic, space group *P-1*, Z = 1, T = 100(2) K, μ = 4.582 mm^{-1}, Reflections collected/unique = 23229/6907 [R(int) = 0.0433], R_1(I > 2σ(I)) = 0.0571, and wR_2(I > 2σ(I)) = 0.1577. The structure was solved by the direct methods. The asymmetric unit contains half the molecule, together with 1 complete and 0.5 CH_2Cl_2 molecules, the latter being disordered. The non-H atoms except C33 and C33B, were refined anisotropically. All but one H atoms were included in calculated positions. H1 was found by difference Fourier techniques and refined positionally with the isotropic thermal parameter fixed at 1.2 times that of C1. Restraints were applied to the geometry of the disordered CH_2Cl_2 molecule (with carbon C33), and this molecule was fixed for the final rounds of refinement. The large peaks in the final difference map were less than 1 Å away from the uranium atoms. CCDC 190095. See http://www.rsc.org/suppdata/cc/b2/b206889c/ for crystallographic data in CIF or other electronic format.

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