The First Authenticated Uranium(v)–Phosphine Complex, $UCl_2[N(CH_2CH_2PPr^i_2)_2]_3$

Simon J. Coles, Peter G. Edwards,* Michael B. Hursthouse and Paul W. Read

Department of Chemistry, University of Wales Cardiff, P.O. Box 912, Cardiff, UK CF1 3TB

The reaction of UCl_4 with the diphosphinoamido ligand, $(Pr^i_2PCH_2CH_2)_2N^-$, in the presence of oxygen gives rise to the first well characterised uranium(v)–tertiary phosphine complex.

In view of the fact that potentially tridentate bis(2-dialkylphosphinoethyl)phosphido and bis(2-dialkylphosphinoethyl)-amido ligands [$^-E(CH_2CH_2PR_2)_2$] (E = N, R = Et, Pr^i; E = P, R = Me) stabilise novel actinide[1] and transition metal[2] complexes and since actinide complexes with diphosphinoamido ligands are presently unknown, we have studied reactions of the potentially terdentate dialkylphosphinoamido ligand [$(Pr^i_2PCH_2CH_2)_2N^-$](PNP$_{Pr^i}$) with UCl_4 and report herein the synthesis and characterisation of a unique uranium(v) amido–tertiary phosphine complex.

Freshly prepared UCl_4 reacts with three mole equivalents of LiPNP$_{Pr^i}$ at −80 °C in THF generating an intense green/brown solution, from which traces of a dark brown paramagnetic crystalline material can be isolated, along with a dark green brown oil, which is miscible in all proportions with aliphatic hydrocarbons. The nature of this oil is currently under investigation. Microanalysis of the brown crystals confirms the stoichiometry $UCl_2[Pr^i_2PCH_2CH_2)_2N]_3$† and acidified silver nitrate confirms the presence of chloride. The magnetic susceptibility of the complex in solution is consistent with f^1 uranium(v)[3] (μ_{eff} = 1.61 BM). The formation of a uranium(v) species is surprising and is likely due to trace aerial oxidation.

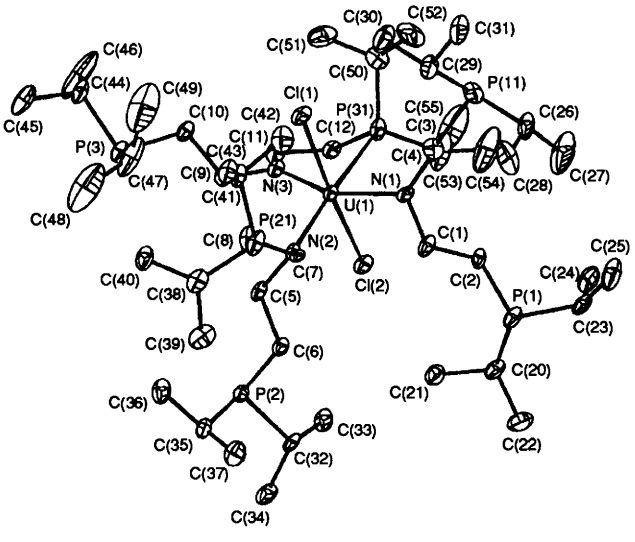

Fig. 1 The molecular structure of $UCl_2[N(CH_2CH_2PPr^i_2)_2]_3$ (30% probability ellipsoids). Selected bond lengths (Å): Cl(1)–U(1), 2.6250(3); Cl(2)–U(1), 2.6413(13); N(1)–U(1), 2.163(4); N(2)–U(1), 2.159(4); N(3)–U(1), 2.146(4); P(31)–U(1), 2.995(2). Selected bond angles (°): Cl(1)–U(1)–Cl(2), 172.83(4); Cl(1)–U(1)–P(31), 95.34(5); Cl(1)–U(1)–N(1), 89.23(10); Cl(1)–U(1)–N(2), 95.43(10); Cl(1)–U(1)–N(3), 89.21(10); Cl(2)–U(1)–N(1), 91.43(10); Cl(2)–U(1)–N(2), 91.56(10); Cl(2)–U(1)–N(3), 87.15(10); Cl(2)–U(1)–P(31), 77.54(4); N(1)–U(1)–N(2), 97.2(2); N(1)–U(1)–P(31), 89.22(12); N(2)–U(1)–N(3), 108.0(2); N(3)–U(1)–P(31), 65.89(12).

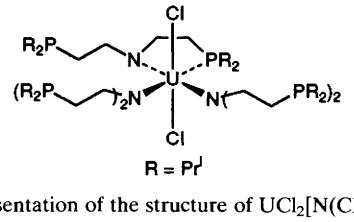

Fig. 2 A representation of the structure of $UCl_2[N(CH_2CH_2PPr^i_2)_2]_3$

This assumption is confirmed when a stoichiometric equivalent of dry oxygen is introduced to the UCl_4–THF solution prior to the addition of LiPNP$_{Pr^i}$. The title complex can then be isolated in moderate yield (36%).

The compound gives rise to temperature dependant NMR spectra. In the variable temperature $^{31}P[^1H]$ NMR spectrum, a signal is observed at δ 5 at the low temperature limit (−100 °C). This signal broadens upon warming and disappears altogether at temperatures above 25 °C, indicating that the complex is fluxional in solution due to exchange of uncoordinated with coordinated tertiary phosphine functions. In the ^1H NMR spectrum, broad resonances are observed at δ 5.8 and 2.1 and are assigned to the 2-propyl methyl protons and methylene protons respectively on the basis of signal intensity.

Since authenticated stable tertiary phosphine–actinide complexes were first reported only recently[4] and are still uncommon [thorium(IV), uranium(IV) and uranium(III) examples are known[5,6]], and the only prior report of uranium(v) tertiary phosphine complexes [*i.e.* $UCl_5(PPh_3)$ and UCl_5(dppe)][7] is unsubstantiated, we have undertaken an X-ray crystallographic study of the title compound. This study is also of interest since there is only one structurally characterised amido complex of uranium(v) ({[$(Me_3Si)_2N]_3U$=NSiMe$_3$}[8]).

The solid state structure‡ of UCl_2 [$(Pr^i_2PCH_2CH_2)_2N]_3$ shows the uranium to be six coordinate, the geometry best described as distorted octahedral (Fig. 1), with clearer representation is shown in Fig. 2. The complex has two *trans* chlorides, two monodentate diphosphinoamido ligands (bonding through the amido nitrogen only) and a bidentate ligand which has one coordinated and one uncoordinated tertiary phosphine group. All three amido nitrogens are planar within experimental error.§ The U–N bond length [average 2.156(4) Å] is shorter than that reported for other uranium(v) amido complexes, *c.f.* 2.295(10) Å in $[(Me_3Si)_2N]_3U(NSiMe_3)$.[8] The U–Cl bond length [average 2.633(1) Å] is longer than that reported in UCl_6^- [average 2.454(5) Å].[9] Since the uranium(v) centre is expected to be smaller than uranium(IV), and the six coordinate geometry in the title compound should allow closer metal ligand interactions, the uranium–phosphine bond [2.995(2) Å] is longer than expected, compared with the eight coordinate $U[P(CH_2CH_2PMe_2)_2]_4$ [average 2.993(5) Å[10]]. This may be explained by increased steric bulk of the tertiary phosphine functions in the title complex and its chelate nature.

Other reactions of UCl_4 and $ThCl_4$ with LiPNP$_{Pr^i}$ and with the less bulky LiPNP$_{Et}$ [$(Et_2PCH_2CH_2)_2NLi$] give rise to $ThCl_2[(Pr^i_2PCH_2CH_2)_2N]_2$, $ThCl_3[(Pr^i_2PCH_2CH_2)_2N]$, $UCl_2[(Pr^i_2PCH_2CH_2)_2N]_2$ and complexes of the form $(PNP_{Et})_nAnCl_{4-n}$. These compounds give rise to satisfactory elemental analysis and have been characterised spectroscopically; further studies are in progress.

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Footnotes

† Microanalysis performed by C. H. N. Analysis Ltd. Leicester. Calc. for $C_{48}H_{108}N_3P_6Cl_2U$: C, 47.17; H, 8.91; N, 3.44. Found: C, 47.45; H, 8.80; N 3.38%.

‡ *Crystal data* for $C_{48}H_{108}Cl_2N_3P_6U$: M_r = 1222.12, triclinic, a = 13.347(3), b = 14.768(4), c = 17.585(7) Å, α = 90.87(3), β = 107.308(14), γ = 108.85(2)°, V = 3108(2) Å^3, space group $P\bar{1}$ (no. 2), Z = 2, D_c = 1.306 g cm^{-3}, $F(000)$ = 1266, μ (Mo-Kα) = 27.74 cm^{-1}. Data were collected at 120 K, on a FAST TV Area detector diffractometer following previously described procedures.[11] 13529 data were recorded and merged to give 8765 unique (R_{int} = 0.0484). The structure was solved *via* heavy atom methods (SHELX-S)[12] and refined by full matrix least-squares on all F_o^2 data (SHELX-93).[13] An absorption correction was applied using DIFABS.[14] The final R, R_w indices [$I > 2\sigma(I)$] were 0.0407 and 0.0688 for 565 parameters (non-hydrogen atoms anisotropic hydrogen atoms in idealised positions, C–H = 0.96 Å, with U_{iso} tied to U_{eq} of the parent atoms).

Full details of the data collection, structure refinement, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Σ angles around amido nitrogen: N(1) 359.3°, N(2) 359.4°, N(3) 360.0°.

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