Diphosphinoamido Complexes of Thorium(IV) and Uranium-(IV) and -(V). Crystal Structures of $[\{ThCl_2[N(CH_2CH_2PPr^i_2)_2]_2\}_2]$ and $[\{UCl_2[N(CH_2CH_2PEt_2)_2]_2\}_2]$†

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The complexes $[MCl_x\{N(CH_2CH_2PR_2)_2\}_{4-x}]$ (M = Th or U; R = Et or Pr^i; x = 1–3) and $[UCl_2\{N(CH_2CH_2PPr^i_2)_2\}_3]$ have been isolated in moderate to good yields from the reaction of MCl_4 with $Li[N(CH_2CH_2PR_2)_2]$. The uranium(V) complex is shown to be formed by adventitious oxidation. The complexes isolated depend on the stoichiometry of the reaction, the bulk of the tertiary phosphine donors and the oxidation state of the metal (for uranium); they all have pendant donors and are labile in solution involving exchange of co-ordinated for unco-ordinated tertiary phosphine. The solid-state structure of $[ThCl_2\{N(CH_2CH_2PPr^i_2)_2\}_2]$ has been determined: triclinic, space group $P\bar{1}$, a = 11.47(1), b = 13.18(1), c = 15.08(4) Å, α = 103.98(4), β = 96.01(5), γ = 99.17(4)°. It is dimeric in the solid state with two bidentate PNP ligands, one bridging and one terminal chloride per thorium. The geometry of the thorium centres is shown to be distorted capped octahedral. The solid-state structure of $[UCl_2\{N(CH_2CH_2PEt_2)_2\}_2]$ was also determined: monoclinic, space group $P2_1/a$, a = 26.274(3), b = 10.782(4), c = 24.659(7) Å, β = 90.31(14). It is dimeric in the solid state, containing one tri- and one bi-dentate chelating PNP ligand, one bridging and one terminal chloride per uranium centre. The geometry of the uranium centres is shown to be distorted dodecahedral.

We have recently described the preparation of a homoleptic thorium dialkylphosphide with chelating diphosphinophosphide ligands[1] and its unique reactivity with CO.[2] In view of the ability of ligands of this type to stabilise unusual complexes with new properties, we have extended this study to analogous diphosphinoamides. Amido complexes of the actinides are more common than their corresponding phosphido analogues.[3] The majority are in oxidation state IV and examples of homoleptic species have been reported. Less common are uranium-(III) and -(V) amides.[4,5] Prior to our present study of actinide complexes with diphosphinoamide ligands,[6] there have been only two reports of crystallographically characterised uranium(V) amides, the mixed amido–imido complex $[U\{N(SiMe_3)\}\{N(SiMe_3)_2\}]$[5] and the cationic $[U(cp)(NEt_2)_3(thf)]^+$ (cp = η^5-C_5H_5, thf = tetrahydrofuran).[7] Tertiary phosphine complexes of thorium(IV) and uranium-(III)[8] and -(IV),[9,10] although still uncommon, are now well established, while uranium(V), $[UCl_5(PPh_3)]$ and $[UCl_5(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane],[11] are unsubstantiated. The successful application of diphosphinoamide ligands to a range of transition metals[12] and lanthanides[12b] has been demonstrated by Fryzuk and others although examples of actinide complexes with these ligands are presently unknown.

In this paper we report the reactions of potentially tridentate diphosphinoamide ligands of the type $[N(CH_2CH_2PR_2)_2]^-$ (R = Et or Pr^i) with thorium and uranium tetrahalides which result in the isolation of the first diphosphinoamidoactinide(IV) complexes and the first authentic uranium(V) phosphine complex.[6] The new compounds reported are represented in Scheme 1.

Results and Discussion

$[ThCl_2\{N(CH_2CH_2PEt_2)_2\}_2]$ **1**.—The reaction of $ThCl_4$ in thf with 2 equivalents of $Li[N(CH_2CH_2PEt_2)_2]$ generates colourless solutions from which white light petroleum-soluble needles can be isolated in good yield. Microanalysis confirms the stoichiometry $[ThCl_2\{N(CH_2CH_2PEt_2)_2\}_2]$ and the presence of chloride is confirmed upon addition of acidified silver nitrate. The room-temperature ^{31}P-$\{^1H\}$ NMR spectrum of **1** shows two broad resonances at δ 27.2 ($\nu_{\frac{1}{2}}$ = 50 Hz) and −25.2 (150 Hz) in a ratio of 3:1 respectively; at lower temperature the two resonances are better resolved but no other temperature-dependent behaviour was observed. The former is assigned to co-ordinated tertiary phosphine and has a co-ordination chemical shift difference of *ca.* 52 ppm which is larger than previously observed for thorium phosphine complexes.[9] The latter resonance is assigned to unco-ordinated tertiary phosphine. In a static picture, the complex appears to have three co-ordinated and one unco-ordinated phosphines and must have (at least) a dimeric structure. This conclusion is consistent with the solid-state structure of the uranium analogue (see below). At high temperature (100 °C) a single resonance is observed at δ 1.4. This suggests a rapid exchange of co-ordinated and unco-ordinated tertiary phosphine functions. The ^1H NMR spectrum contains four resonances at δ 3.60, 1.92, 1.54 and 1.14 which may be assigned to NCH_2CH_2P, NCH_2CH_2P, PCH_2CH_3 and PCH_2CH_3 protons on the basis of chemical shift and signal intensity. The peaks due to the chelate backbone are broadened and poorly resolved, appearing as an apparent quartet (δ 3.60, separation of outer lines 22 Hz) and an apparent triplet (δ 1.92, separation of outer lines 16 Hz). The ethyl-group methylene protons give rise to a doublet of quartets (δ 1.54, $^3J_{HH}$ = 7.9, $^2J_{PH}$ = 3.6 Hz) and the ethyl-group methyl protons to a doublet of triplets (δ 1.14, $^3J_{HH}$ = 7.9, $^3J_{PH}$ = 14.5 Hz). The equivalence of the ethyl functions again suggests that a rapid exchange of co-ordinated with unco-ordinated diethylphosphino functions is occurring in solution.

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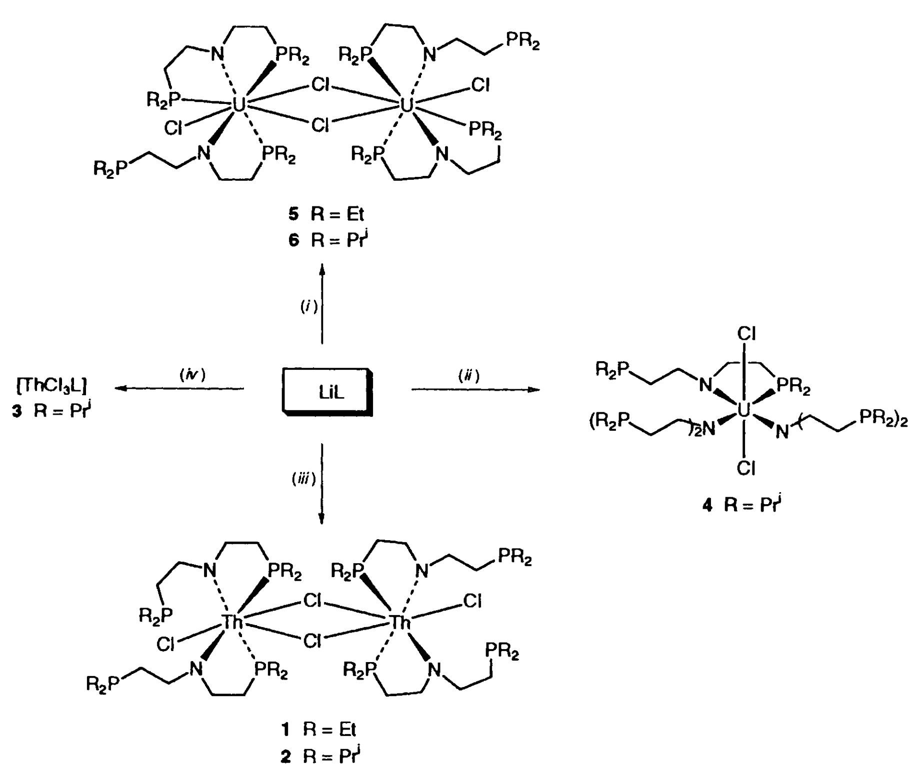
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI units employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, mmHg ≈ 133 Pa.



Scheme 1 L = $N(CH_2CH_2PR_2)_2^-$; (*i*) $\frac{1}{2}UCl_4$; (*ii*) $\frac{1}{3}UCl_4$, $\frac{1}{6}O_2$; (*iii*) $\frac{1}{2}ThCl_4$; (*iv*) $ThCl_4$

$[ThCl_2\{N(CH_2CH_2PPr^i{}_2)_2\}_2]$ **2**.—The reaction of $ThCl_4$ with 2 equivalents of $Li[N(CH_2CH_2PPr^i{}_2)_2]$ in thf generates clear solutions from which colourless light petroleum-soluble needles can be isolated in good yield. Microanalysis confirms the stoichiometry $[ThCl_2\{N(CH_2CH_2PPr^i{}_2)_2\}_2]$ and a positive chloride test is given with acidified silver nitrate. The $^{31}P-\{^1H\}$ NMR spectrum of **2** indicates that the complex is fluxional in solution. At room temperature it shows a resonance at δ 15.08. At low temperature (−80 °C) the spectrum shows two broad resonances at δ 29.0 and 21.0 ($\nu_{\frac{1}{2}}$ 312 and 447 Hz respectively) and a poorly resolved multiplet of at least three lines centred at δ −3.0 and with relative intensities of 1 : 1 : 2 respectively. Coalescence occurs at about −50 °C. This indicates that the fluxional process is linked to a process involving the exchange of co-ordinated for unco-ordinated tertiary phosphine. The low temperature spectrum indicates that either the complex contains two different phosphinoamide ligands, each with a pendant donor, or that there is a mixture of isomers in solution (*e.g. cis* and *trans* bis-chelates) which interconvert slowly on the NMR time-scale at low temperature. The room-temperature ^1H NMR spectrum shows three broad resonances (δ 3.36, 2.26 and 1.46) in a ratio of 1 : 1 : 3 respectively. These broaden further at low temperature and no fine structure was observed. The first two are assigned to methylene backbone protons and the last to 2-propyl methyl protons on the basis of signal intensity. The resonance at δ 3.36 can be assigned to methylene protons α to nitrogen by comparison with zirconium complexes of this ligand.[13] A resonance attributable to the 2-propyl methine protons was not observed.

The solid-state crystal structure of complex **2** is shown in Fig. 1. Atomic coordinates and selected bond lengths and angles are given in Tables 1 and 2 respectively. Complex **2** is dimeric in the solid state, the two thorium centres being related by a centre of symmetry and bridged by two chloride atoms. Each thorium is seven-co-ordinate, the geometry being best described[14] as C_{3v} capped octahedral distorted towards C_{2v} capped trigonal prismatic; the capping atom is P(2).* Both thorium centres have two bidentate phosphineamide ligands (each with one co-ordinated and one unco-ordinated phosphine function). The amido nitrogen atoms are planar within experimental error [Σ angles at N(1) 358.4(8), at N(2) 360.1(7)°]. The Th–P bond lengths [average 3.162(4) Å] correspond well with other literature values,[10] and are only slightly longer than the average U–P bond length in $[UCl_2\{N(CH_2CH_2PEt_2)_2\}_2]$ **5** [3.122(1) Å] (see below). We have recently shown that for isostructural actinide tetraphosphine complexes that the covalent radius of thorium is 0.08 Å larger than that of uranium.[15] This would suggest that in the seven-co-ordinate thorium complex **2** the two-co-ordinated 2-propylphosphine functions impart slightly

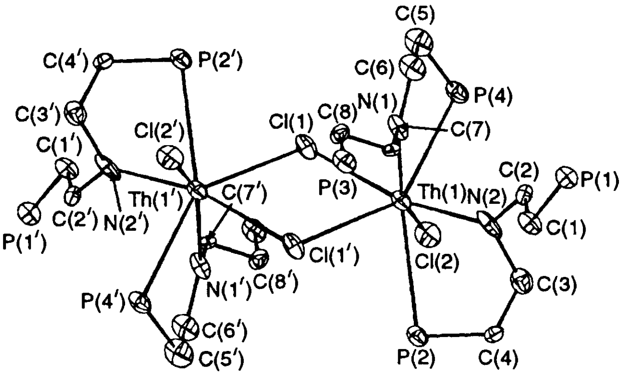


Fig. 1 Crystal structure of $[ThCl_2\{N(CH_2CH_2PPr^i{}_2)_2\}_2]$

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* The δ angles as defined by the planes P(2), Cl(2), Cl(1) intersecting P(2), Cl(1′), Cl(1) and N(2), Cl(2), Cl(1) intersecting N(2), N(1), Cl(1) and P(2), Cl(2), N(2) intersecting P(2), P(4), N(2) are 9.16, 17.48 and 28.93° respectively. For the idealised capped octahedron (C_{3v}) and capped trigonal prism (C_{2v}) the corresponding angles are 24.2, 24.2, 24.2 and 0, 0, 41.51° respectively.

Table 1 Atomic coordinates (× 10^4) for $[\mathrm{ThCl_2\{N(CH_2CH_2PPr^i{}_2)_2\}_2}]$ **2**

Atom	*x*	*y*	*z*
Th(1)	294.5(5)	−1703.5(4)	−786.0(4)
Cl(1)	599(3)	−136(2)	1040(2)
Cl(2)	−1065(3)	−2853(2)	123(2)
P(1)	2690(3)	−3488(2)	−3976(2)
P(2)	−2065(3)	−2484(2)	−2300(2)
P(3)	2578(3)	579(2)	−2971(2)
P(4)	2282(3)	−2386(2)	385(2)
N(1)	2186(8)	−998(6)	−910(6)
N(2)	388(8)	−3148(7)	−1976(7)
C(1)	1281(10)	−3340(8)	−3466(7)
C(2)	1390(10)	−3393(8)	−2471(7)
C(3)	−724(10)	−4059(8)	−2392(8)
C(4)	−1624(10)	−3691(8)	−3015(7)
C(5)	3490(11)	−1246(9)	428(8)
C(6)	3420(11)	−956(9)	−494(8)
C(7)	2149(10)	−702(8)	−1781(8)
C(8)	2572(11)	431(7)	−1798(7)
C(11)	2803(11)	−4926(8)	−4172(9)
C(12)	2247(13)	−3470(9)	−5181(8)
C(111)	3605(12)	−5067(9)	−3430(9)
C(112)	1559(11)	−5708(8)	−4298(9)
C(121)	3336(11)	−3441(10)	−5686(9)
C(122)	1655(12)	−2483(9)	−5224(9)
C(21)	−3522(13)	−2911(10)	−1967(10)
C(22)	−2367(11)	−1743(8)	−3164(9)
C(211)	−3626(11)	−3960(9)	−1647(9)
C(212)	−3798(13)	−2030(10)	−1199(10)
C(221)	−1307(11)	−1265(9)	−3484(8)
C(222)	−3400(12)	−2363(9)	−3980(8)
C(31)	2342(12)	1968(9)	−2853(9)
C(32)	4224(11)	711(9)	−3050(9)
C(311)	1037(12)	2028(10)	−2736(11)
C(312)	3217(12)	2805(9)	−1998(9)
C(321)	4614(10)	−361(8)	−3023(10)
C(322)	4476(12)	987(10)	−3939(10)
C(41)	2420(11)	−2523(8)	1570(8)
C(42)	2864(12)	−3517(9)	−297(10)
C(411)	2218(11)	−1524(9)	2261(8)
C(412)	1563(11)	−3511(8)	1663(8)
C(421)	3976(12)	−3777(10)	204(9)
C(422)	1851(13)	−4538(9)	−655(9)

less steric encumbrance than the three-co-ordinated diethylphosphine functions in the eight-co-ordinate complex **5** because of the lower co-ordination number. The only structural comparison that can be made between actinide complexes with chelating 2-propylphosphino functions is between **2** and $[\mathrm{UCl_2\{N(CH_2CH_2PPr^i{}_2)_2\}_3}]$ **4** since there are no other examples in the literature. In the six-co-ordinate uranium(V) complex **4** the U–P bond length is 2.995(2) Å.[6] It is commonly assumed that a 'rule-of-thumb' allowance of 0.05 Å may be made per oxidation number and co-ordination number difference in order to relate metrical data between complexes with similar ligands. (In structural chemistry folklore there is a 0.05 Å change in bond length per change in co-ordination number and a similar change per oxidation state.) On this basis and if an allowance is also made for the difference in radii between thorium and uranium, the U–P bond in **4** may be expected to be 0.18 Å shorter than the average Th–P bond length in **2** (*i.e.* 2.982 Å) which gives a value very close to that observed. The Th–N and terminal Th–Cl bond lengths [average 2.286(9) and 2.702(4) Å respectively] are similar to those reported for complex **5** (see below) allowing for this difference in radii.

$[\mathrm{ThCl_3\{N(CH_2CH_2PPr^i{}_2)_2\}}]$ **3**.—The stoichiometric reaction of $\mathrm{ThCl_4}$ with $\mathrm{Li[N(CH_2CH_2PPr^i{}_2)_2]}$ affords pale yellow solutions from which fine colourless toluene-soluble needles can be isolated in moderate yield. Accurate microanalytical data have not been obtained. The stoichiometry closest to the observed values is $[\mathrm{ThCl_3\{N(CH_2CH_2PPr^i{}_2)_2\}}]$ and the presence of chloride was confirmed by addition of acidified silver nitrate. The room-temperature $^{31}\mathrm{P}$-$\{^1\mathrm{H}\}$ NMR spectrum of **3** consists of two resonances at δ 10.87 and −4.09 in a ratio of 1 : 1 which are assigned to co-ordinated and unco-ordinated tertiary phosphine respectively. In the variable-temperature $^{31}\mathrm{P}$-$\{^1\mathrm{H}\}$ NMR spectra the two peaks coalesce at 40 °C. Above this a single resonance is observed at δ 4.65. Below 40 °C two triplets, due to co-ordinated phosphines, at δ 10.67 and 13.07 (J = 2 Hz) and a multiplet, due to unco-ordinated phosphines, at δ −4.09 (J = 2 Hz) in a ratio of 1 : 1 : 2 respectively are observed. For this to occur there must be at least two inequivalent phosphorus atoms co-ordinated to thorium and two unco-ordinated tertiary phosphines at the slow-exchange limit and consistent with an ABMN spin system suggesting that **3** is at least dimeric in solution. The spectrum can be satisfactorily simulated assuming this spin system and where δ_M and δ_N are virtually coincident. (Using Bruker 'PANIC' NMR simulation software with δ_A 13.1, δ_B 10.7, δ_M −4.2 and δ_N −4.8, a line broadening of 12 Hz and J_{AB} = 0, J_{BM} = 12, J_{BN} = 12 and J_{MN} = 0 Hz respectively.) The room-temperature $^1\mathrm{H}$ NMR spectrum of **3** shows two broad resonances at δ 3.35 and 1.37 in a ratio of 2 : 7 and are assigned to the methylene protons and 2-propyl methyl protons respectively. At the high-temperature limit (100 °C) four broad resonances appear at δ 3.98, 2.60, 2.20 and 1.83 in a ratio of 1 : 1 : 1 : 6 which are assigned to $\mathrm{NCH_2}$, $\mathrm{PCH_2}$, $\mathrm{PC}H\mathrm{(CH_3)_2}$ and $\mathrm{PCH(C}H_3)_2$ respectively on the basis of chemical shift and intensity.

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Th(1)–N(1)	2.266(9)	Th(1)–N(2)	2.305(10)
Th(1)–Cl(2)	2.702(4)	Th(1)–Cl(1′)	2.871(3)
Th(1)–Cl(1)	2.965(6)	Th(1)–P(4)	3.116(4)
Th(1)–P(2)	3.207(5)	Th(1′)–Cl(1)	2.871(3)
N(1)–Th(1)–N(2)	88.2(3)	N(1)–Th(1)–Cl(2)	144.9(2)
N(2)–Th(1)–Cl(2)	94.8(3)	N(1)–Th(1)–Cl(1′)	92.8(2)
N(2)–Th(1)–Cl(1′)	124.1(3)	Cl(2)–Th(1)–Cl(1′)	113.60(11)
N(1)–Th(1)–Cl(1)	87.8(2)	N(2)–Th(1)–Cl(1)	164.0(2)
Cl(2)–Th(1)–Cl(1)	79.8(2)	Cl(1′)–Th(1)–Cl(1)	71.59(13)
N(1)–Th(1)–P(4)	65.2(2)	N(2)–Th(1)–P(4)	87.4(3)
Cl(2)–Th(1)–P(4)	80.03(13)	Cl(1′)–Th(1)–P(4)	142.14(8)
Cl(1)–Th(1)–P(4)	76.90(13)	N(1)–Th(1)–P(2)	130.5(2)
N(2)–Th(1)–P(2)	66.2(3)	Cl(2)–Th(1)–P(2)	81.6(2)
Cl(1′)–Th(1)–P(2)	71.51(9)	Cl(1)–Th(1)–P(2)	127.00(11)
P(4)–Th(1)–P(2)	146.23(9)	Th(1′)–Cl(1)–Th(1)	108.41(13)

Symmetry transformation used to generate primed atoms: −*x*, −*y*, −*z*.

$[\mathrm{UCl_2\{N(CH_2CH_2PPr^i{}_2)_2\}_3}]$ **4**.—The reaction of freshly prepared $\mathrm{UCl_4}$ with 3 equivalents of $\mathrm{Li[N(CH_2CH_2PPr^i{}_2)_2]}$ generates intense green-brown solutions from which brown paramagnetic, light petroleum-soluble needles can be isolated in low yield. Microanalysis confirms the stoichiometry $[\mathrm{UCl_2\{N(CH_2CH_2PPr^i{}_2)_2\}_3}]$ and a positive chloride test is given with acidified silver nitrate. The solution magnetic susceptibility of **4** (μ_{eff} = 1.61 μ_B) is consistent with f^1 uranium(V)[16] and spin–orbit coupling presumably accounts for the observed magnetic moment being lower than the 'spin-only' value.

On investigating the cause of the oxidation of uranium-(IV) to -(V), the yield of complex **4** was greatly improved by using thf as solvent during the reaction of fresh UCl_4 with the lithium amide and adding a measured quantity of dry air to the UCl_4 solution *via* a syringe. It would, therefore, appear that adventitious oxidation of the UCl_4 occurs, generating a uranium(V) complex. It is not clear whether oxidation of uranium occurs prior to substitution or of an intermediate anionic 'ate' triamidouranium complex *e.g.* $[UCl_2\{N(CH_2CH_2PPr^i_2)_2\}_3]^-$. The formation of such anionic complexes is well known in transition-metal chemistry.

Complex **4** gives rise to temperature-dependent NMR spectra which clearly indicate that the tertiary phosphine co-ordinates to the uranium(V) nucleus in solution. In the low-temperature $^{31}P-\{^1H\}$ NMR spectrum (−100 °C) a signal is observed at δ −5 and is assigned to unco-ordinated tertiary phosphine. 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 unco-ordinated with co-ordinated tertiary phosphine functions. In the ^1H NMR spectrum broad resonances were observed at δ −5.8 and −2.1 and are assigned to the 2-propyl methyl and methylene protons respectively on the basis of signal intensity. A signal assignable to the 2-propyl methine proton was not observed.

The ESR spectrum (77 K) of complex **4** shows a very weak single line ($g = 2.0039$) with no hyperfine coupling to nitrogen or phosphorus. Other reported uranium(V) species have g values of ≈ 1.25.[17] The expected g value for uranium(V) is, in fact, negative *cf.* the calculated g value for $UCl_5 \cdot SOCl_2$ is −1.18,[18] $g = -1.14$ for Pa^{IV} [19] and $g = -0.60$ for Np^{IV}.[20] Caution must be exercised in comparing g values, as most previously reported values are for UCl_5 co-ordinated to other ligands including the unconfirmed $[UCl_5(PPh_3)]$. The quality of these values must, therefore, be questioned. No ESR signals for four- and eight-co-ordinate uranium(V) are generally observed,[21] although they are for regular octahedral uranium(V) complexes at low temperature. The weakness of the signal from **4** may be due to a distortion from octahedral geometry. Further studies at lower temperatures are planned.

The solid-state structure of complex **4** has been reported in a preliminary communication.[6] The complex has distorted-octahedral geometry (indicated in Scheme 1) with two chloro, three amido and one tertiary phosphine function co-ordinated to the uranium centre. Thus, two amide ligands each support two pendant phosphines and one amide ligand has one chelating and one pendant phosphine function.

Previous attempts to prepare uranium tertiary phosphine complexes in oxidation states greater than IV have failed, despite the use of chelating ditertiary phosphines (*e.g.* $Me_2PCH_2CH_2PMe_2$, dmpe) and uranium-(V) and -(VI) precursors.[22] The formation of **4** highlights the effectiveness of the chelating amido/phosphino ligand system in stabilising unusual complexes, possibly due to the good π-donating properties of the amido nitrogen combined with strong σ-donating phosphines rendering a highly electrophilic uranium(V) centre relatively stable. It is interesting that this chelate complex forms in thf as solvent, and there is no evidence of thf co-ordination in any isolated products, indicating that the tertiary phosphine competes favourably for co-ordination.

$[UCl_2\{N(CH_2CH_2PEt_2)_2\}_2]$ **5**.—The reaction of UCl_4 with 2 mole equivalents of $Li[N(CH_2CH_2PEt_2)_2]$ generates intense green solutions from which green paramagnetic, light petroleum-soluble prisms can be isolated in moderate yield. Microanalysis confirms the stoichiometry $[UCl_2\{N(CH_2CH_2PEt_2)_2\}_2]$ and the presence of chloride is confirmed by addition of acidified silver nitrate. The room-temperature $^{31}P-\{^1H\}$ NMR spectrum of **5** shows a single broad resonance at δ −26.9 ($\nu_{\frac{1}{2}} = 278$ Hz). This resonance is at a position normally associated with unco-ordinated tertiary phosphine and disappears on warming, indicating the exchange of co-ordinated for unco-ordinated tertiary phosphine. The room-temperature ^1H NMR spectrum consists of four resonances at δ 41.3, −7.05, −10.50 and −13.04. These integrate in a ratio of 1:1:4:1 respectively. The relative intensity of the peak at δ −10.50 implies a coincidence of resonances due to methyl and methylene protons and since there are then four resonances which can be attributed to pairs of methylene protons the ethyl methylene protons are presumably diastereotopic. The signal assigned to the methyl protons of the phosphorus alkyl functions indicates that they are equivalent (δ −10.5) under the conditions, hence rapid exchange of co-ordinated for unco-ordinated phosphine functions is again indicated.

The crystal structure of complex **5** is shown in Fig. 2. Atomic coordinates and bond lengths and angles are in Tables 3 and 4 respectively. It reveals the complex to be dimeric in the solid state with the two uranium centres related by a centre of symmetry and bridged by two chlorides. Each uranium centre is eight-co-ordinate. The co-ordination geometry around uranium is difficult to assess by visual inspection of the SNOOPI[23] plot of the structure, especially in this case where there are several ligand environments. An accurate description of the structure is only possible by inspection of appropriate shape parameters[14,24] which indicate that the co-ordination polyhedron is best described as D_{2d} dodecahedral distorted towards D_{4d} square antiprismatic, where Cl(1), P(5), P(6) and P(7) occupy the A sites and N(3), N(4), Cl(2) and Cl(4) occupy the B sites.* Both uranium centres have one tridentate (both tertiary phosphine functions co-ordinated) and one bidentate phosphinoamide ligand (one co-ordinated and one unco-ordinated phosphine function). Three of the amide functions are planar within experimental error, each amide acting as a four-electron donor [Σ angles at N(2) 359.5(2), at N(3) 359.9(2) and at N(4) 360.0(2)°]. The fourth amide [N(1)] function deviates from planarity (Σ bond angles 350.1°). The uranium–amide bond lengths [average 2.250(2) Å] are similar to the average terminal U–N bond length in $[\{U(NEt_2)_4\}_2]$.[25] The uranium–phosphine bond lengths [average 3.122(10) Å] also compare favourably with previously observed values {*e.g.* in $[U(CH_2Ph)_3Me(dmpe)]$ [9a] U–P 3.015(5) Å (average) and in $[U(OPh)_4(dmpe)_2]$ [10] U–P 3.104(6) Å (average)} and the terminal uranium–chloride bond lengths [2.670(1) Å] are similar to other reported literature

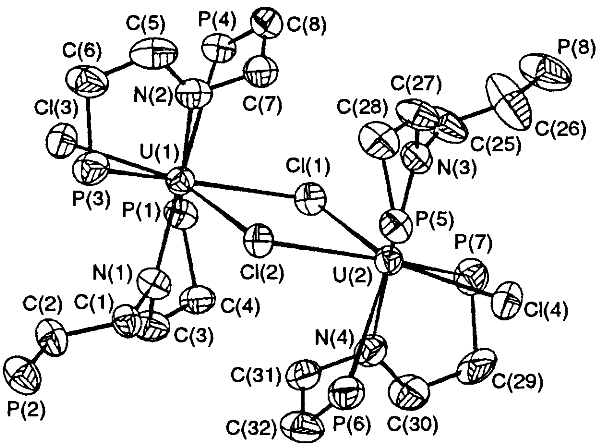

Fig. 2 Crystal structure of $[UCl_2\{N(CH_2CH_2PEt_2)_2\}_2]$

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* The φ angles, defined by the planes Cl(2) and Cl(4) intersecting Cl(1) and P(7), and N(3) and N(4) intersecting P(5) and P(6) are 12.88 and 2.91° respectively and the δ angles, defined by planes N(3), P(5), Cl(2) intersecting Cl(2), Cl(1), N(3) and N(4), P(6), Cl(2) intersecting Cl(2), Cl(1), N(4) and N(3), P(5), Cl(4) intersecting Cl(4), P(7), N(3) and N(4), P(6), Cl(4) intersecting Cl(4), P(7), N(4) are 18.56, 7.23, 30.6 and 2.85° respectively. Idealised angles for D_{2d} dodecahedral, $\varphi = 0$ and $\delta = 29.5, 29.5, 29.5, 29.5°$; D_{4d} square antiprismatic, $\varphi = 24.5°$ and $\delta = 0, 0, 52.4, 52.4°$.

Table 3 Atomic coordinates (× 10^4) for $[UCl_2\{N(CH_2CH_2PEt_2)_2\}_2]$ **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U(1)	2 708.8(1)	5 562.7(1)	1 629.6(1)	C(18)	4 511(1)	5 579(3)	2 300(1)
U(2)	2 327.5(1)	6 918.1(1)	3 375.8(1)	C(19)	4 306(1)	4 915(3)	1 010(1)
Cl(1)	1 902(1)	6 251(1)	2 341(1)	C(20)	4 653(2)	4 036(5)	823(2)
Cl(2)	3 139(1)	6 189(1)	2 673(1)	C(20′)	4 202(5)	4 703(17)	459(4)
Cl(3)	2 868(1)	4 951(1)	594(1)	C(21)	4 359(2)	9 943(3)	1 515(2)
Cl(4)	2 130(1)	7 563(1)	4 398(1)	C(22)	4 816(2)	10 550(4)	1 697(2)
P(1)	1 840(1)	6 955(1)	1 018(1)	C(23)	4 618(1)	8 947(4)	498(1)
P(2)	4 396(1)	8 445(1)	1 172(1)	C(24)	4 662(2)	7 889(4)	92(1)
P(3)	3 821(1)	4 624(1)	1 529(1)	C(25)	1 615(1)	4 647(3)	3 497(2)
P(4)	1 880(1)	3 469(1)	1 491(1)	C(26)	1 299(1)	4 279(4)	3 924(2)
P(5)	3 154(1)	5 524(1)	4 036(1)	C(27)	2 417(1)	3 847(3)	3 792(1)
P(6)	3 207(1)	8 919(1)	3 521(1)	C(28)	2 968(1)	4 007(3)	3 783(1)
P(7)	1 231(1)	7 934(1)	3 431(1)	C(29)	1 445(1)	9 523(3)	3 594(1)
P(8)	642(1)	3 913(2)	3 711(2)	C(30)	1 832(1)	9 892(3)	3 181(1)
P(8′)	601(1)	4 159(2)	3 813(1)	C(31)	2 562(1)	9 212(3)	2 660(1)
N(1)	2 877(1)	7 542(2)	1 442(1)	C(32)	3 026(1)	9 856(3)	2 946(2)
N(2)	2 895(1)	3 624(2)	1 928(1)	C(33)	3 907(1)	8 848(4)	3 469(2)
N(3)	2 142(1)	4 939(2)	3 569(1)	C(34)	4 183(2)	9 978(4)	3 359(2)
N(4)	2 189(1)	8 867(2)	3 069(1)	C(35)	3 104(2)	9 996(3)	4 088(2)
C(1)	3 408(1)	7 911(3)	1 528(1)	C(36)	3 414(4)	10 753(9)	4 330(4)
C(2)	3 724(1)	8 184(3)	1 006(1)	C(36′)	3 287(2)	9 892(6)	4 638(2)
C(3)	2 605(1)	8 621(3)	1 198(1)	C(37)	3 081(1)	5 316(3)	4 771(1)
C(4)	2 022(1)	8 456(3)	1 268(1)	C(38)	3 233(2)	6 378(3)	5 105(1)
C(5)	3 247(1)	2 612(3)	1 798(1)	C(39)	3 842(1)	5 559(4)	3 965(2)
C(6)	3 636(1)	3 038(3)	1 402(1)	C(40)	4 126(1)	4 451(4)	4 156(2)
C(7)	2 523(1)	3 297(3)	2 337(1)	C(41)	788(1)	7 649(4)	3 980(1)
C(8)	2 071(1)	2 657(3)	2 106(1)	C(42)	346(1)	8 640(4)	3 998(1)
C(9)	1 176(1)	3 428(3)	1 539(2)	C(43)	868(1)	8 168(3)	2 819(1)
C(10)	938(2)	2 100(3)	1 586(2)	C(44)	555(1)	7 036(4)	2 635(1)
C(11)	2 035(1)	2 288(3)	963(1)	C(45)	615(1)	2 289(2)	3 523(1)
C(12)	1 801(2)	2 618(4)	420(1)	C(46)	187(1)	2 231(7)	3 122(2)
C(13)	1 151(1)	6 918(3)	1 161(1)	C(46′)	492(3)	3 016(4)	3 030(1)
C(14)	852(1)	8 078(4)	996(2)	C(47)	450(1)	4 028(2)	4 570(1)
C(15)	1 861(1)	7 177(3)	305(1)	C(48)	−96(1)	3 667(7)	4 659(3)
C(16)	1 646(2)	6 145(3)	−63(1)	C(48′)	457(4)	2 709(3)	4 412(3)
C(17)	4 204(1)	4 413(3)	2 157(1)				

values {*e.g.* in $[UCl_6]^{2-}$ U–Cl 2.625(5) Å (average)}.[26] The U ··· U distance is indicative of no metal–metal interaction. It is interesting that in **5** there is a lengthening of the U–P bond *trans* to amide as compared with the U–P bond *trans* to chloride {U(1)–P(1) [*trans* N(2)] 3.115(1), U(1)–P(4) [*trans* to N(1)] 3.154(1), U(1)–P(3) [*trans* to Cl(1)] 3.104(1), U(2)–P(5) [*trans* to N(4)] 3.095(1), U(2)–P(6) [*trans* to N(3)] 3.180(1), U(2)–P(7) [*trans* to Cl(2)] 3.088(1) Å}. This relative lengthening is greater for the phosphines *trans* to bidentate amido nitrogen than for phosphines *trans* to the amido nitrogen in the tridentate $N(CH_2CH_2PPr^i_2)_2$ ligands. The U–N distances in the bidentate ligands are shorter than those in the tridentate ligands [U(1)–N(2) 2.268(2), U(2)–N(4) 2.262(2); *cf.* U(1)–N(1) 2.228(2), U(2)–N(3) 2.241(3) Å], chelate strain preventing the amido nitrogen atoms from attaining closer U–N contacts within the complex. This also indicates that the amido nitrogens exhibiting the shorter U–N distances have a greater *trans* influence. The amido nitrogen atoms are planar and appear to be π bonded to uranium (see above). Any influence on M–P bonding must be σ-bonding orbitals since if the phosphines are acting as effective π acceptors a shortening of the M–N bonds would increase the opportunity for M–P π bonding. This would shorten the M–P bond not lengthen it as is observed. This suggests that π acceptance of electron density by tertiary phosphine in this complex is not significant.

A similar inspection of the solid-state structure of complex **4**[6] reveals that the amido nitrogen *trans* to phosphorus has a shorter bond length than when *trans* to amido nitrogen {U(1)–N(2) [*trans* to P(31)] 2.159(3), U(1)–N(3) [*trans* to N(1)] 2.146(3) Å}. This is of less significance than above, although it would tend to indicate that PR_3 has a smaller *trans* influence than amido nitrogen, $^-NR_2$.

$[UCl_2\{N(CH_2CH_2PPr^i_2)_2\}_2]$ **6**.—The reaction of UCl_4 with 2 mole equivalents of $Li[N(CH_2CH_2PPr^i_2)_2]$ generates intense green-brown solutions from which green paramagnetic, light petroleum-soluble prisms can be isolated in moderate yield. Microanalysis confirms the stoichiometry $[UCl_2\{N(CH_2CH_2PPr^i_2)_2\}_2]$ and a positive chloride test is given with acidified silver nitrate. The magnetic susceptibility of **6** in solution (μ_{eff} = 2.83 μ_B) is consistent with f^2 uranium(IV).

Complex **6** has temperature-dependent NMR spectra. The $^{31}P-\{^1H\}$ NMR signals are not observed at temperatures exceeding 0 °C. However, at temperatures below this a single broad resonance is observed at δ −2.9. This resonance is at a maximum intensity at −40 °C. Below this temperature the resonance begins to broaden, and at −100 °C three broad, new resonances are observed at δ 4.6 ($\nu_{\frac{1}{2}}$ = 74), −2.4 (59) and −4.3 (33 Hz) in a ratio of 2:1:2 respectively. This is consistent with an interconversion process involving the exchange of co-ordinated tertiary phosphine for unco-ordinated pendant phosphine (δ 4.7) and *vice versa*. The ^1H NMR spectrum is more complex. At temperatures above 20 °C, it consists of at least five broad resonances (δ 4.41, −0.52, −2.10, −2.73 and −3.61). These begin to coalesce at −20 °C and, by −64 °C, only two broad resonances are observed (δ 4.40 and −2.87). This indicates that the complex is fluxional, although the nature of the fluxionality is unclear.

Experimental

All manipulations were performed using a Vacuum Atmospheres HE-43-2 or Halco Engineering 140 FF glove-box, or using standard Schlenk techniques under purified nitrogen. Unless otherwise stated all solvents were refluxed under

Table 4 Selected bond lengths (Å) and angles (°) for complex **5**

U(1)–N(1)	2.228(2)	U(1)–N(2)	2.268(2)
U(1)–Cl(3)	2.672(1)	U(1)–Cl(1)	2.857(1)
U(1)–Cl(2)	2.885(1)	U(1)–P(3)	3.104(1)
U(1)–P(1)	3.115(1)	U(1)–P(4)	3.154(1)
U(2)–N(3)	2.241(3)	U(2)–N(4)	2.262(2)
U(2)–Cl(4)	2.667(1)	U(2)–Cl(2)	2.865(1)
U(2)–Cl(1)	2.872(1)	U(2)–P(7)	3.088(1)
U(2)–P(5)	3.095(1)	U(2)–P(6)	3.180(1)

N(1)–U(1)–N(2)	155.13(9)	N(1)–U(1)–Cl(3)	90.33(6)
N(2)–U(1)–Cl(3)	92.71(6)	N(1)–U(1)–Cl(1)	91.55(6)
N(2)–U(1)–Cl(1)	101.56(7)	Cl(3)–U(1)–Cl(1)	140.45(3)
N(1)–U(1)–Cl(2)	83.37(6)	N(2)–U(1)–Cl(2)	81.01(6)
Cl(3)–U(1)–Cl(2)	147.95(3)	Cl(1)–U(1)–Cl(2)	71.34(2)
N(1)–U(1)–P(3)	96.21(6)	N(2)–U(1)–P(3)	61.54(7)
Cl(3)–U(1)–P(3)	72.02(3)	Cl(1)–U(1)–P(3)	146.70(3)
Cl(2)–U(1)–P(3)	77.46(3)	N(1)–U(1)–P(1)	65.35(6)
N(2)–U(1)–P(1)	139.25(7)	Cl(3)–U(1)–P(1)	76.92(3)
Cl(1)–U(1)–P(1)	68.17(2)	Cl(2)–U(1)–P(1)	127.01(2)
P(3)–U(1)–P(1)	143.72(3)	N(1)–U(1)–P(4)	143.15(6)
N(2)–U(1)–P(4)	61.54(7)	Cl(3)–U(1)–P(4)	80.26(3)
Cl(1)–U(1)–P(4)	74.84(2)	Cl(2)–U(1)–P(4)	122.08(2)
P(3)–U(1)–P(4)	114.07(3)	P(1)–U(1)–P(4)	77.81(3)
N(3)–U(2)–N(4)	157.03(10)	N(3)–U(2)–Cl(4)	90.23(6)
N(4)–U(2)–Cl(4)	92.38(6)	N(3)–U(2)–Cl(2)	91.76(7)
N(4)–U(2)–Cl(2)	99.91(7)	Cl(4)–U(2)–Cl(2)	142.37(3)
N(3)–U(2)–Cl(1)	82.30(6)	N(4)–U(2)–Cl(1)	82.78(6)
Cl(4)–U(2)–Cl(1)	145.88(3)	Cl(2)–U(2)–Cl(1)	71.43(2)
N(3)–U(2)–P(7)	97.13(7)	N(4)–U(2)–P(7)	62.37(7)
Cl(4)–U(2)–P(7)	71.30(3)	Cl(2)–U(2)–P(7)	145.32(2)
Cl(1)–U(2)–P(7)	76.65(3)	N(3)–U(2)–P(5)	65.11(7)
N(4)–U(2)–P(5)	137.56(7)	Cl(4)–U(2)–P(5)	76.68(3)
Cl(2)–U(2)–P(5)	70.25(2)	Cl(1)–U(2)–P(5)	127.88(2)
P(7)–U(2)–P(5)	143.28(3)	N(3)–U(2)–P(6)	141.37(7)
N(4)–U(2)–P(6)	61.52(7)	Cl(4)–U(2)–P(6)	82.03(3)
Cl(2)–U(2)–P(6)	73.25(3)	Cl(1)–U(2)–P(6)	123.31(3)
P(7)–U(2)–P(6)	115.60(3)	P(5)–U(2)–P(6)	76.29(3)

nitrogen over sodium–benzophenone and distilled immediately prior to use. Toluene was refluxed under nitrogen over sodium and distilled immediately prior to use. The light petroleum used had a boiling point of 40–60 °C. The compounds Li[N-$(CH_2CH_2PR_2)_2$] (R = Et or Pr^i) were prepared following previously published procedures.[27] Perdeuterio solvents were refluxed over sodium (8 h) and distilled therefrom under nitrogen. Commercially available $ThCl_4$ was dried by refluxing in thionyl chloride and then *in vacuo* (170 °C, 0.05 mmHg, 8 h); UCl_4 was prepared by a literature procedure[28] and dried by reflux in $SOCl_2$ followed by heating *in vacuo* (170 °C, 0.05 mmHg, 8 h). Microanalyses were performed by Butterworths Ltd., Teddington, or C.H.N. Analysis Ltd., Leicester. The ^{31}P NMR spectra were recorded on a Bruker WM360 spectrometer operating at 145 MHz (^{31}P) or a JEOL FX90Q at 36.23 MHz and referenced externally to 85% H_3PO_4 (δ 0), ^1H NMR at 360 or 90 MHz (^1H) referenced to residual protons (C_6D_6, δ 7.15; $C_6D_5CD_3$, δ 7.19) and ESR spectra on a Varian E3 spectrometer referenced to diphenylpicrylhydrazyl (*g* = 2.0036). Melting points were recorded in sealed glass capillaries and are uncorrected.

Preparations.—$[ThCl_2\{N(CH_2CH_2PEt_2)_2\}_2]$ **1**. To a stirred suspension of $ThCl_4$ (0.70 g, 1.87 mmol) in thf (70 cm^3) at −80 °C was added $Li[N(CH_2CH_2PEt_2)_2]$ (0.96 g, 3.74 mmol) in light petroleum (20 cm^3). The mixture was allowed to warm to room temperature and stirred for 8 h. The volatile materials were removed *in vacuo* and the residue was washed with cold (−80 °C) light petroleum (2 × 5 cm^3) and extracted with light petroleum (2 × 25 cm^3). The supernatant was evaporated to *ca.* 10 cm^3 and cooled (−20 °C) for 4 h. Complex **1** crystallised as a white microcrystalline material in moderate yield (0.85 g, 57%) and melts to an oil on warming (Found: C, 35.0; H, 6.8; N, 3.4. $C_{24}H_{56}Cl_2N_2P_4Th$ requires C, 35.7; H, 7.0; N, 3.5%). IR (Nujol, cm^{-1}): 1294w, 1268m, 1212m, 1170w, 1248w, 1092s (br), 1031s (br), 909s, 805m, 764m, 735w, 683w, 670w, 562w, 546w, 390w, 464m, 436m and 388m. NMR ($C_6D_5CD_3$ 20 °C): ^{31}P-{^1H} (36.23 MHz), δ 27.2 (br, $\nu_{\frac{1}{2}}$ 50), −25.2 (br, $\nu_{\frac{1}{2}}$ 150); ^1H, δ 3.60 (br q, $\nu_{\frac{1}{2}}$ 22, 1 H), 1.92 (br t, $\nu_{\frac{1}{2}}$ 16, 1 H), 1.54 (dq, $^3J_{HH}$ 7.9, $^2J_{PH}$ 3.6, 2 H) and 1.14 (dt, $^3J_{HH}$ 7.9, $^3J_{PH}$ 14.5 Hz, 3 H).

$[ThCl_2\{N(CH_2CH_2PPr^i_2)_2\}_2]$ **2**. To a stirred suspension of $ThCl_4$ (0.70 g, 1.87 mmol) in thf (20 cm^3) at −80 °C was added $Li[N(CH_2CH_2PPr^i_2)_2]$ (1.16 g, 3.82 mmol) in light petroleum (22 cm^3). The mixture was allowed to warm to room temperature and stirred for 8 h. The volatile materials were removed *in vacuo* and the residue was washed with cold (−80 °C) light petroleum (2 × 5 cm^3) and extracted with diethyl ether (2 × 50 cm^3). The supernatant was evaporated to *ca.* 10 cm^3 and cooled (−20 °C) for 4 h. Complex **2** crystallises as opaque prisms in good yield (1.10 g, 64%), m.p. 134–136 °C (Found: C, 41.4; H, 7.8; N, 3.0. $C_{32}H_{72}Cl_2N_2P_4Th$ requires C, 42.2; H, 8.0; N, 3.1%). IR (Nujol, cm^{-1}): 1330w, 1287m, 1185w, 1040m (br), 833w, 748m, 585w and 287m. NMR ($C_6D_5CD_3$, 20 °C): ^{31}P-{^1H} (36.23 MHz) δ 15.08 (s); ^1H, δ 3.36 (br, 2 H), 2.26 (br, 2 H) and 1.46 (s, 6 H).

$[ThCl_3\{N(CH_2CH_2PPr^i_2)_2\}]$ **3**. To a stirred suspension of $ThCl_4$ (0.70 g, 1.87 mmol) in thf (20 cm^3) at −80 °C was added $Li[N(CH_2CH_2PPr^i_2)_2]$ (0.58 g, 1.90 mmol) in light petroleum (11 cm^3). The mixture was allowed to warm to room temperature and stirred for 8 h. The volatile materials were removed *in vacuo* and the residue was washed with light petroleum (2 × 10 cm^3) and extracted with diethyl ether (2 × 50 cm^3). The supernatant was evaporated to *ca.* 20 cm^3 and cooled (−20 °C) for 4 h. Complex **3** crystallised as feathery white needles in good yield (0.69 g, 58%), m.p. 168–170 °C (Found: C, 34.9; H, 6.7; N, 2.5. $C_{16}H_{36}Cl_3NP_2Th$ requires C, 29.9; H, 5.6; N, 2.2%). IR (Nujol, cm^{-1}): 1325m, 1237m, 1220m, 1147m, 1076s (br), 1044s (br), 978w, 910w, 870s, 784s, 718s, 648m, 475m, 254m and 230m. NMR ($C_6D_5CD_3$, 20 °C): ^{31}P-{^1H} (36.23 MHz), δ 10.87 (s, 1 P) and −4.09 (s, 1 P); ^1H, δ 3.35 (br, 2 H) and 1.37 (br, 7 H).

$[UCl_2\{N(CH_2CH_2PPr^i_2)_2\}_3]$ **4**. To a stirred solution of UCl_4 in thf (0.14 mol dm^{-3} cm^3), 4 was added dry air (30 cm^3, 0.28 mmol O_2). The solution was stirred for 8 h when $Li[N(CH_2CH_2PPr^i_2)_2]$ (0.52 g, 1.66 mmol) in light petroleum (25 cm^3) was slowly added at −80 °C. The mixture was allowed to warm to room temperature and stirred for 8 h. The volatile materials were removed *in vacuo* and the resultant green solid was washed with cold (−80 °C) light petroleum (2 × 10 cm^3) and extracted with diethyl ether (2 × 50 cm^3). The black supernatant was evaporated to *ca.* 20 cm^3 and cooled (−20 °C) for 4 h. Complex **4** crystallised as small brown needles in moderate yield (0.37 g, 54%), m.p. 98–102 °C (Found: C, 47.8; H, 8.8; N, 3.4. $C_{48}H_{108}Cl_2N_3P_6U$ requires C, 47.2; H, 8.9; N, 3.4%). IR (Nujol, cm^{-1}): 1729w, 1296w, 1248w, 1146m, 1070m (br), 1031m (br), 962w, 870m, 791w, 613s, 562w, 468w, 259m, 244m and 236m. NMR ($C_6D_5CD_3$, 20 °C): ^{31}P-{^1H} (36.23 MHz), δ −5 (br, $\nu_{\frac{1}{2}}$ 130 Hz); ^1H, δ −5.8 (br, 7 H) and −2.1 (br, 2 H). ESR (C_6H_5Me, −196 °C): *g* 2.0039.

$[UCl_2\{N(CH_2CH_2PEt_2)_2\}_2]$ **5**.—To a stirred suspension of UCl_4 (0.40 g, 1.05 mmol) in thf (50 cm^3) at −80 °C was added $Li[N(CH_2CH_2PEt_2)_2]$ (0.54 g, 1.05 mmol) in light petroleum (20 cm^3). The mixture was allowed to warm to room temperature and stirred for 8 h. The volatile materials were removed *in vacuo*. The resultant green solid was washed with cold (−80 °C) light petroleum (2 × 10 cm^3) and extracted with light petroleum (2 × 50 cm^3). The green-brown supernatant was evaporated to *ca.* 10 cm^3 and cooled (−20 °C) for 4 h. Complex **5** crystallises as green prisms in good yield (0.85 g, 81%) (Found: C, 35.7; H, 7.2; N, 3.4. $C_{24}H_{56}Cl_2N_2P_4U$ requires C, 35.8; H, 7.0; N, 3.5%). IR (Nujol, cm^{-1}): 1294w, 1268m, 1212m, 1170w, 1148w, 1092s (br), 1031s (br), 909s, 805m, 764m, 735w, 683w, 670w, 562w, 546w, 390w, 464m, 436m and 388m. ^{31}P-{^{1}H} NMR δ (36.23 MHz, C_7D_8, 20 °C) −26.86 (br, $\nu_{\frac{1}{2}}$ 278 Hz). ^{1}H NMR (360 MHz, C_6D_6, 20 °C): δ 41.3 (s, 1 H), −7.05 (s, 1 H), −10.50 (s, 4 H) and −13.04 (s, 1 H).

$[UCl_2\{N(CH_2CH_2PPr^i{}_2)_2\}_2]$ **6**. To a stirred solution of UCl_4 in thf (0.14 mol dm^{-3}, 8 cm^3) at −80 °C was added $Li[N(CH_2CH_2PPr^i{}_2)_2]$ (0.52 g, 1.66 mmol) in light petroleum (25 cm^3). The mixture was allowed to warm to room temperature and stirred for 8 h. After removing volatile materials *in vacuo*, the resultant green solid was washed with cold (−80 °C) light petroleum (2 × 10 cm^3) and extracted with diethyl ether (2 × 50 cm^3). The black supernatant was evaporated to *ca.* 20 cm^3 and cooled (−20 °C) for 4 h. Complex **6** crystallises as green prisms in good yield (0.79 g, 78%) m.p. 104–107 °C (Found: C, 41.2; H, 8.1; N, 3.1. $C_{36}H_{72}Cl_2N_2P_4U$ requires C, 41.9; H, 7.9; N, 3.0%). IR (Nujol, cm^{-1}): 1749w, 1305m, 1250s, 1220w, 1147m, 1080s (br), 1039s (br), 972m, 918m, 870s, 794s, 718s, 644m, 610m, 566m, 475m, 378w, 257s and 239s. NMR ($C_6D_5CD_3$): ^{31}P-{^{1}H} (36.23 MHz, −20 °C), −2.9 (br, $\nu_{\frac{1}{2}}$ 87 Hz); ^{1}H (20 °C), δ 4.41 (s), −0.52 (s), −2.10 (s), −2.73 (s) and −3.61 (s).

X-Ray Crystallography.—Suitable crystals of complex **2** were grown from light petroleum and mounted in Dow Corning silicone grease at 150 K.

Crystal data. $C_{32}H_{72}Cl_2N_2P_4Th$, $M_r = 911.74$, triclinic, space group $P\bar{1}$, $a = 11.47(1)$, $b = 13.18(1)$, $c = 15.08(4)$ Å, $\alpha = 103.98(4)$, $\beta = 96.01(5)$, $\gamma = 99.17(4)°$, $U = 2160(6)$ Å^3 (by least-squares refinement at 293 K of diffractometer angles for 250 reflections within $\theta = 1.82$–$24.92°$), $Z = 2$, $D_c = 1.402$ g cm^{-3}, $F(000) = 924$, μ(Mo-Kα) = 0.3745 cm^{-1}. White, air-sensitive needles. Crystal dimensions 0.15 × 0.08 × 0.10 mm.

Data collection and processing.[29] Delft Instruments FAST TV Area detector diffractometer using Mo-Kα radiation ($\lambda = 0.710\,69$ Å); 7 286 unique reflections measured ($1.82 < \theta < 24.92°$; index ranges $-9 < h < 13$, $-15 < k < 15$, $-17 < l < 15$) ($R_{int} = 0.0824$). A DIFABS[30] absorption correction was made, maximum and minimum absorption correction factors 1.015 and 0.735.

Structure analysis and refinement. The structure was solved by direct methods (SHELXS)[31] and refined by full-matrix least squares (SHELXL 93)[32] using all unique $F_o{}^2$ data corrected for Lorentz and polarisation factors. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions with U_{iso} set at 1.2 times U_{eq} of the parent carbon. The weighting scheme used was $w = 1/\sigma^2(F_o)^2$, which gave satisfactory agreement analyses. Final R_1 $[= \Sigma(\Delta F)/\Sigma(F_o)]$ and wR_2 $[= \Sigma w(\Delta(F^2)^2/\Sigma w(F_o{}^2)^2]^{\frac{1}{2}}$ values were 0.0909 and 0.1171 for 386 parameters and all 7286 data (ρ_{min}, ρ_{max} −0.836, 0.845 e Å^{-3}). The corresponding R indices for data with $I > 2\sigma(I)$ were 0.0440 and 0.0851 respectively. Sources of scattering factor data are given in ref. 32. All calculations were performed on a 486DX2/66 personal computer.

Suitable crystals of complex **5** were grown from light petroleum and mounted in Lindemann capillaries under purified nitrogen.

Crystal data. $C_{48}H_{112}Cl_4N_4P_8U_2$, $M_r = 1611.04$, monoclinic, space group $P2_1/a$, $a = 26.274(3)$, $b = 10.782(4)$, $c = 24.659(7)$ Å, $\beta = 90.31(14)$, $U = 6985.5(2)$ Å^3 (by least-squares refinement at 293 K of diffractometer angles for 250 reflections within $\theta = 1.55$–$21.99°$), $Z = 4$, $D_c = 1.532$ g cm^{-3}, $F(000) = 3200$, μ(Mo-Kα) = 0.4805 cm^{-1}. Green, air-sensitive prisms. Crystal dimensions 0.10 × 0.10 × 0.15 mm.

Data collection and processing.[33] Delft Instruments CAD4 diffractometer using Mo-Kα radiation ($\lambda = 0.710\,69$ Å); 8507 unique reflections measured ($1.55 < \theta < 21.99°$; index range $-26 < h < 26$, $0 < k < 11$, $0 < l < 25$) ($R_{int} = 0.0484$). An empirical absorption correction (Ψ scan) was applied, maximum and minimum transmission coefficients 0.989 and 0.823.

Structure analysis and refinement. The structure was solved and refined as for complex **2**. Final R_1 and R_2 0.1183 and 0.0764 for 660 parameters and all 8507 data (ρ_{min}, ρ_{max} −0.676, 0.920 e Å^{-3}). The corresponding R indices for data with $I > 2\sigma(I)$ were 0.0392 and 0.0739 respectively. Sources of scattering factor data and computer used as for complex **2**.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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