

Synthesis, Crystal Structure and Some Derivatives of the Chlorotris(tetramethylphospholyl)uranium

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Reaction of UCl_4 with the potassium salt of the tetramethylphospholyl anion afforded the title compound, which has been transformed into the derivatives $[\text{U}(\eta\text{-C}_4\text{Me}_4\text{P})_3\text{X}]$ ($\text{X} = \text{H, Me, OPri}$); the trigonal crystal structure revealed that the three phospholyl ligands are pentahapto bonded to the uranium.

The fortuitous discovery of the tris(pentamethylcyclopentadienyl)samarium¹ recently revealed that, contrary to accepted ideas, a single metal atom could accommodate more than two $\eta\text{-C}_5\text{Me}_5$ ligands. On the basis of the sole geometrical parameters, it became clear that $\text{M}(\text{C}_5\text{Me}_5)_3$ complexes should exist for a series of elements, including the actinides Th^{III} and U^{III} ; however, preparation of such compounds is not straightforward and remains to be devised. As part of our studies of the influence of electronic and steric factors on the structure and stability of uranium compounds,² we decided to use the tetramethylphospholyl group ($\eta\text{-C}_4\text{Me}_4\text{P} = \text{tmp}$),³ which is a steric mimic of the ubiquitous C_5Me_5 ligand, while rendering the metal centre more electrophilic. We have found that the uranium(IV) compounds $[\text{U}(\text{tmp})_3\text{X}]$ ($\text{X} = \text{Cl, H, Me, OPri}$), which are the first tris(phospholyl) metal complexes, could be easily prepared; here we present their synthesis and characterization, with the X-ray crystal structure of the chloro derivative.

The chlorotris(tetramethylphospholyl)uranium $[\text{U}(\text{tmp})_3\text{Cl}]$ **1** was obtained in 90% yield, by treatment of UCl_4 (1008 mg) with 3 equiv. of tmpK (1420 mg) in toluene (30 ml) (Scheme 1); the mixture was stirred at 20 °C for 16 h, evaporated under vacuum and the red compound was extracted with toluene (2×15 ml) and crystallized from this solvent. The bis(phospholyl) complex $[\text{U}(\text{tmp})_2\text{Cl}_2]$ **2** was less easily isolated from the reaction of UCl_4 with only 1 equiv. of the phospholyl anion; after stirring for 1 h at 20 °C, the suspension was filtered and evaporated, and the brown compound **2** was extracted with pentane, from which it crystallized (33% yield). The uranium tetrachloride reacted with 2 equiv. of tmpK to give a 40:60 mixture of **1** and **2** and, in coordinating solvents like tetrahydrofuran, the syntheses were impeded by the concomitant reduction of UCl_4 .

Complex **1** was a precursor for a series of $[\text{U}(\text{tmp})_3\text{X}]$ derivatives. Its reaction with KBET_3H led to the rapid formation of $[\text{U}(\text{tmp})_3\text{H}]$ **3**, a new example of a stable U^{IV} hydride⁴ which, after the usual work-up, was isolated as yellow crystals from toluene (30% yield). The methyl and isopropoxide compounds $[\text{U}(\text{tmp})_3\text{Me}]$ and $[\text{U}(\text{tmp})_3\text{OPri}]$ were formed when **1** was treated in toluene with MeLi and

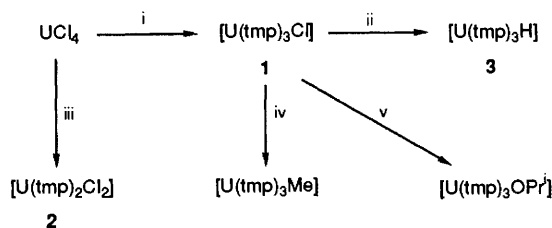
PriONa , respectively; these complexes were characterized only by their ^1H NMR spectra.[†]

The crystal structure of **1**‡ (Fig. 1) revealed that the uranium and chlorine atoms lie on the ternary axis of the molecule. The phospholyl ligands are pentahapto bonded to the uranium; the tmp rings, which are planar within $\pm 0.08(2)$ Å, are oriented so that the three centroids and the three phosphorus atoms lie in the same plane, the metal being at 0.22(6) Å from this plane. This slightly deformed trigonal planar arrangement of the $\text{U}(\text{tmp})_3$ fragment represents the best geometry to minimize the repulsions between the sterically demanding ligands. The U–P bond length is 2.927(4) Å and the U–C (ring) distances vary from 2.82(1) to 2.97(1) Å [mean 2.90(8) Å]. The corresponding average values determined in the less congested complex $[\text{U}(\text{tmp})_2(\text{BH}_4)_2]$ are U–P = 2.90(1) Å and U–C = 2.81(4) Å;³ the average U–C(C_5Me_5) bond distance, in a variety of bis(pentamethylcyclopentadienyl)uranium(IV) complexes,⁵ is typically equal to 2.75 Å. The carbon atoms of the methyl groups are in the plane of the tmp ring, except C(7), which lies out of this plane by 0.17(1) Å. The differences between the structural parameters of the $\text{U}(\text{tmp})_3$ and $\text{U}(\text{tmp})_2$ fragments, which reflect the increasing steric crowding, resemble those observed between the geometries of the $\text{Sm}(\text{C}_5\text{Me}_5)_3$ and $\text{Sm}(\text{C}_5\text{Me}_5)_2$ units.¹

The facile synthesis of **1**, whereas the isosteric complex $[\text{U}(\text{C}_5\text{Me}_5)_3\text{Cl}]$ could never be prepared,⁶ may be accounted for by the electronic effect of the phospholyl ligand. We have found a series of facts which clearly demonstrate that the tmp group is a less electron donating ligand than the pentamethylcyclopentadienyl. This can be illustrated, for example,

† The new complexes have been characterized by their elemental analyses (C, H, B, P, Cl) and their ^1H NMR spectra. δ (60 MHz, 30 °C, in $[\text{C}_6\text{H}_6]$ /toluene) **1**: 22.11 and -12.56 (18 H + 18 H); **2**: 42.93 and -16.27 (18 H + 18 H); **3**: 18.11 (18 H, Me), -26 (18 H, w_1 500 Hz, Me), 333.4 (1H, U–H); $[\text{U}(\text{tmp})_3\text{Me}]$: 18.41 and -20.16 (18 H + 18 H, C–Me), -233.1 (3 H, U–Me); $[\text{U}(\text{tmp})_3\text{OPri}]$: 120.28 (1 H, CHMe_2), 36.08 (6 H, CHMe_2), 1.15 and -4.20 (18 H + 18 H, Me); $[\text{U}(\text{C}_5\text{Me}_5)_2(\text{BH}_4)_2]$: 12.58 (30 H, Me), -62.58 (8H, q, J 80 Hz, BH_4). When not specified, the signals are singlets with $w_1 = 10\text{--}30$ Hz.

‡ Crystal data for **1**: $\text{C}_{24}\text{H}_{36}\text{P}_3\text{ClU}$, trigonal, space group $R\bar{3}$, $a = 16.056(6)$, $c = 16.839(6)$ Å, $V = 3759(3)$ Å³, $Z = 6$, $D_c = 1.831$ g cm⁻³, $\mu = 64.47$ cm⁻¹. Data were collected using an Enraf-Nonius CAD-4 diffractometer (Mo-K α radiation, $\lambda = 0.71073$ Å) in the range $2 < \theta < 40^\circ$. 630 reflections with $I > 3\sigma(I)$ were used after Lorentz polarisation, intensity decay ($\sim 56\%$ after 36 h, linearly corrected), and empirical absorption corrections. The structure was solved by the heavy-atom method and refined by full-matrix least-squares (F) with anisotropic thermal parameters. The hydrogen atoms were introduced in idealized positions and constrained to ride on their parent carbon atoms. Analytical scattering factors for neutral atoms were corrected for f' and f'' . The final R values were $R = 0.044$ and $R_w = 0.052$ ($w = 1$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1 Reagents and conditions: i, tmpK (3 equiv.), 16 h; ii, KBET_3H , 2 h; iii, tmpK (1 equiv.), 1 h; iv, MeLi , 2 h; v, PriONa , 2 h. All reactions in toluene.

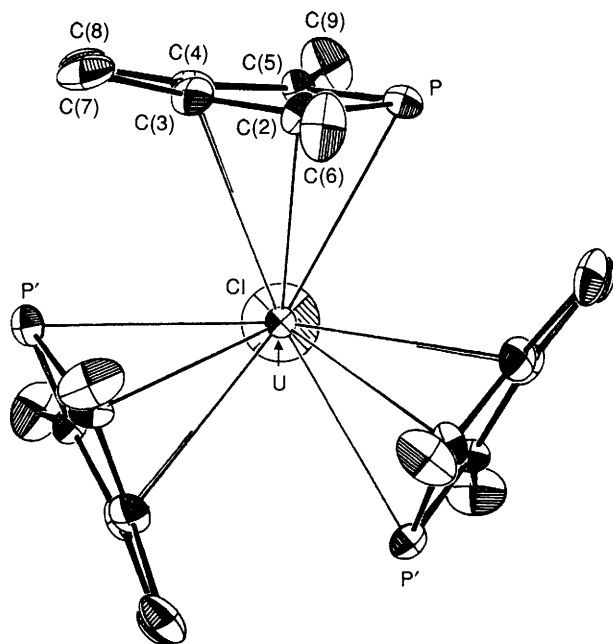


Fig. 1 The X-ray crystal structure of **1**. View along the U-Cl bond (ternary axis). Important distances (Å) and angles (°): U-Cl 2.67(1), U-P 2.927(4), U-C(2) 2.82(1), U-C(3) 2.95(1), U-C(4) 2.97(1), U-C(5) 2.88(1), U-ring centroid 2.61(1), P-C(2) 1.74(1), P-C(5) 1.73(1), C(2)-C(3) 1.35(2), C(3)-C(4) 1.44(2), C(4)-C(5) 1.32(2); ring centroid-U-Cl 94.8(7), ring centroid-U-ring centroid 119(1). P and P' atoms are related by the ternary axis.

by the distinct properties of the borohydride compounds $[\text{U}(\text{tmp})_2(\text{BH}_4)_2]^3$ and $[\text{U}(\text{C}_5\text{Me}_5)_2(\text{BH}_4)_2]$.[§] Each of these could be reversibly reduced into the corresponding anion, but

[§] $[\text{U}(\text{C}_5\text{Me}_5)_2(\text{BH}_4)_2]$ was prepared in 85% yield from the reaction of $\text{U}(\text{BH}_4)_4$ with 2 equiv. of $(\text{C}_5\text{Me}_5)\text{K}$ in toluene; the mixture was stirred for 2 h at 20 °C and after the usual work-up, the compound was isolated as red microcrystals from pentane.

the reduction of an equimolar mixture of the two complexes, with 0.5 equiv. of sodium amalgam, gave only the anion $[\text{U}(\text{tmp})_2(\text{BH}_4)_2]^-$, the cyclopentadienyl compound $[\text{U}(\text{C}_5\text{Me}_5)_2(\text{BH}_4)_2]$ remaining unaffected; electrochemical studies indicated that the reduction potentials were respectively -1.61 and -1.83 V (vs. ferrocene-ferricinium) for the phospholyl and the cyclopentadienyl complexes.

We have previously showed that the electron density of actinide complexes should not exceed an upper limit and that the use of electron donating ligands should favour the synthesis of sterically unsaturated compounds.² From the above results, we believe that the tris(pentamethylcyclopentadienyl)actinide complexes are difficult to prepare, not because they are sterically crowded, but because they are too electron rich.

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