Tertiary Phosphine Complexes of Trivalent Uranium: Preparation and Structure of $U(BH_4)_3(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$)

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$U(BH_4)_3(THF)_x$ (THF = tetrahydrofuran) reacts cleanly with excess of dmpe (dmpe = $Me_2PCH_2CH_2PMe_2$) producing $U(BH_4)_3(dmpe)_2$; an *X*-ray structural analysis of this molecule has been carried out revealing U–P(1) = 3.139(8) and U–P(2) = 3.051(9) Å.

Successful syntheses of stable co-ordination compounds of trivalent uranium are few in number. For instance, tetrahydroborate (BH_4^-) complexes of U^{III} are virtually unknown. Additionally, stable tertiary phosphine complexes of uranium in any valence state are rare. Anderson *et al.*[1] have reported the species $X_4U(dmpe)_2$ [X = Cl, Br, I, Me, and OPh, dmpe = $Me_2PCH_2CH_2PMe_2$; bis(dimethylphosphino)ethane] including the crystal structure of $(PhO)_4U(dmpe)_2$, while the only stable U^{III} phosphine complex known is $(\eta^5\text{-}C_5Me_5)_2U(dmpe)(H)$.[2]

Gilbert, Boocock, and Shore[3] have commented on the unusual stability of transition metal complexes containing both BH_4^- and phosphine ligands. Borohydrides also possess the potential for stabilizing lower oxidation states and forming high co-ordination number complexes. In this and the following article we report the preparation and structure of several trivalent uranium phosphine complexes containing BH_4^- ligands, the first examples combining these two types of ligands about an actinoid centre.

A tetrahydrofuran (THF) solution containing $U(BH_4)_3(THF)_x$ (*ca.* 0.9 mmol) was prepared as previously reported[4] and to this solution, dmpe (0.2 ml) in THF (30 ml) was added. The THF was removed by vacuum distillation, the dark olive-coloured paste was extracted into diethyl ether (100 ml), and the solution was filtered. Crystals suitable for *X*-ray analysis were obtained by reducing the volume of ether to 30—50 ml and cooling overnight at 0 °C. The crystals thus obtained are olive-coloured by reflected light and red by transmitted light.

Attempts at characterization of the mode of borohydride co-ordination *via* i.r. spectroscopy[5] were unsuccessful owing to the presence of a complex series of overlapping bands in the 2000—2500 cm^{-1} region (ν 2440, 2360, 2340, 2300, 2220, and 1125 cm^{-1}); however, the large number of bands observed suggests more than a single mode of co-ordination is present.

A perspective view of the structure is shown in Figure 1.† The molecule resides on a crystallographic two-fold axis of symmetry which passes through the uranium atom and atom B(1). The non-hydrogen atoms surrounding the central U^{III} ion produce a pentagonal bipyramidal co-ordination geometry. The dmpe chelate angles are P(1)–U–P(2) = P(1′)–U–P(2′) = 65.1(3)° while the interchelate angles are P(1)–U–P(1′) = 76.9(2)° and P(2)–U–P(2′) = 152.8(4)°; the equatorial borohydride group, B(2), acts as a bisector for this last angle, with B(2)–U–P(2) = B(2)–U–P(2′) = 76.4(2)°. The *trans*-diaxial angle is 166(1)°.

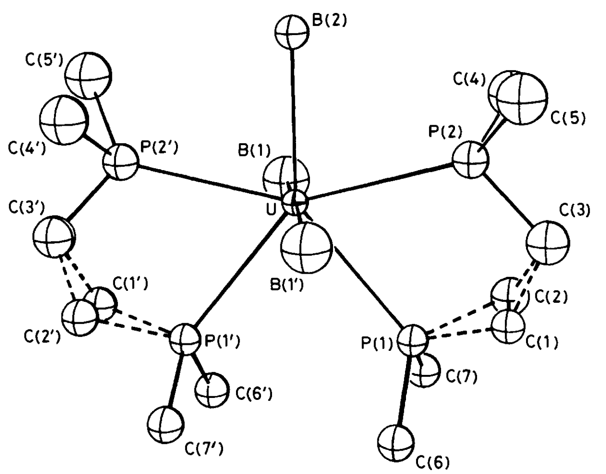

Figure 1. A perspective view of the structure of $U(BH_4)_3(dmpe)_2$. Components of the disordered dmpe ligands are represented by dashed lines.

Although hydrogen atoms of the three tetrahydroborate ligands were not located, two different modes of BH_4 attachment in $U(BH_4)_3(dmpe)_2$ may be distinguished on the basis of U · · · B distances.[6] Thus, the U · · · B(2) separation of 2.84(3) Å clearly indicates bidentate co-ordination and compares well with the corresponding $U(\mu\text{-}H)_2BH_2$ linkage of 2.86(2) Å in $U(BH_4)_4$.[7] The observed U · · · B(1) distance of 2.68(4) Å corresponds to a tridentate arrangement, based upon an ionic radius of 1.6 ± 0.1 Å assigned to the $(\mu\text{-}H)_3BH$ group by Edelstein.[6]

If it is assumed that the two metal-bound hydrogen atoms associated with the $(\mu\text{-}H)_2BH_2$ group lie directly in the equatorial belt of the molecule then the $M(\text{tridentate})_2(\text{bidentate})_3$ co-ordination geometry is best described as cuboctahedral or anticuboctahedral. In the absence of precise hydrogen atom positions it is impossible to distinguish between these.

The two crystallographically unique uranium–phosphorus distances in $U(BH_4)_3(dmpe)_2$ show the effect of different chemical environments, *i.e.*, the phosphorus atoms adjacent to the BH_4 ligand are associated with shorter U–P bond lengths than those opposite the BH_4 group [U–P(2) = 3.051(9) Å *vs.* U–P(1) = 3.139(9) Å]. Nevertheless, both of these values are consistent with the two previous uranium phosphine structures, *viz.* U–P(avg.) = 3.104(6) Å

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† *Crystal data:* $C_{12}H_{44}B_3P_2U$, $M = 520.2$, tetragonal, space group $I\bar{4}2d$, $T = -48(5)$ °C, $a = 14.509(4)$, $c = 24.426(10)$ Å, $U = 5141.7$ Å^3, $D_O = 1.35$ g cm^{-3}, $Z = 8$, $\mu(\text{Mo-}K_\alpha) = 61.0$ cm^{-1}. Intensity data were collected with an Enraf-Nonius CAD-4 diffractometer and the structure was solved by a combination of Patterson and difference-Fourier techniques. All non-hydrogen atoms were located and refined. The dmpe ligand exhibits conformational disorder arising from the presence of both λ and δ conformers within the crystal. The disordered components of one of the two affected carbon atoms were resolved and fixed at one-half occupancy. The final unweighted residual was 4.8% for 799 observed reflections having $I > 3\sigma(I)$ (60 parameters). A test refinement in which the signs of the $\Delta F''$ terms were reversed indicated the handedness initially chosen for the crystal examined to be correct.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

in $U(OPh)_4(dmpe)_2$[1] and U–P = 3.211(8) and 3.092(8) Å in (η^5-C_5Me_5)U(dmpe)(H).[2]

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