# Tetrahydroborate Complexes of Uranium with 2-(Diphenylphosphino)pyridine

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$U(BH_4)_3(THF)_x$, (THF = tetrahydrofuran) and ($\eta^5$-$C_5H_5$)$UCl_3$ react with 2-(diphenylphosphino)pyridine, ($Ph_2Ppy$), producing 1 : 2 and 1 : 1 adducts, respectively; an *X*-ray crystal structure of $U(BH_4)_3(Ph_2Ppy)_2 \cdot 1/2C_6H_6$ shows U–P = 3.162(1) and U–N = 2.659(4) Å.

Balch and coworkers have used the ligand 2-(diphenylphosphino)pyridine ($Ph_2Ppy$) to prepare heterobimetallic complexes of transition metals.[1] The same ligand has also been shown to bind to metals in a bidentate-chelate mode, as in $Ru(Ph_2Ppy)(CO)_2Cl_2$[2] and $[Pt(Ph_2Ppy)_2Cl][Rh(CO)_2Cl_2]$.[1] We report now the preparation of several uranium complexes of $Ph_2Ppy$ and the structure of an unusual bis-chelate complex of this ligand.

$U(BH_4)_3(Ph_2Ppy)_2$ was prepared by allowing a slight excess of $Ph_2Ppy$ to react with $U(BH_4)_3(THF)_x$[3] in THF (THF = tetrahydrofuran). No apparent reaction occurred until almost all the THF had been removed *in vacuo*. The purple crystalline product was precipitated by addition of diethyl ether and characterized by elemental analysis and *X*-ray analysis of single crystals grown from benzene. In contrast with $U(BH_4)_3(dmpe)_2$ [dmpe = bis(dimethylphosphino)ethane][4] the i.r. spectrum of $U(BH_4)_3(Ph_2Ppy)_2$ clearly indicates tridentate borohydride binding,[5] with strong bands at 2420, 2300, 2200, and 1120 $cm^{-1}$. The ($\eta^5$-$C_5H_5$)$UCl_3(Ph_2Ppy)$ complex was prepared similarly, by allowing ($\eta^5$-$C_5H_5$)$UCl_3$ to combine with excess of $Ph_2Ppy$ in THF, followed by precipitation with ether. The 1 : 1 adduct formulation was established by complete elemental analysis and $^1H$ n.m.r. data. At present it is not clear whether the reaction of ($\eta^5$-$C_5Me_5$)$UCl_3$ with $Ph_2Ppy$ produces an analogous product.

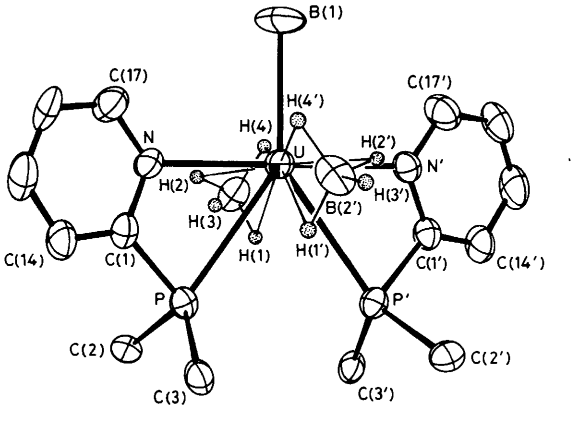

**Figure 1.** Overall geometry of the $U(BH_4)_3(Ph_2Ppy)_2$ molecule (ORTEP II diagram; 30% probability thermal ellipsoids).

The structure of $U(BH_3)_4(Ph_2Ppy)_2$ is shown in Figure 1.[†] The molecule exhibits crystallographically imposed $C_2$ symmetry, the axis of which lies along the U–B(1) direction. If each borohydride ligand is regarded as occupying one co-ordination site, then the formally 13-co-ordinate $U^{III}$ ion adopts an unusual co-ordination geometry closely approaching pentagonal bipyramidal. However, angles within the equatorial plane show large deviations from uniform pentagonal distribution, with B(1)–U–N = B(1)–U–N' = 90.1(1), N–U–P = N'–U–P' = 52.8(1), P–U–P' = 74.30(3), and N–U–N' = 179.8(2)°. These distortions arise from the presence of the tridentate equatorial $BH_4$ group, for which U · · · B(1) = 2.61(2)Å. The axial borohydride ligands are also tridentate, with U–B(2) = 2.656(8) Å and U–H–B(2) angles in the range 84(4)—93(3)°.

The single unique uranium–phosphorus bond length in $U(BH_4)_3(Ph_2Ppy)_2$ is 3.162(1) Å, a value that falls within the range of all previously determined U–P distances,[4] and is close

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[†] *Crystal Data*: $C_{34}H_{40}B_3N_2P_2U \cdot 1/2C_6H_6$, $M = 848.2$, monoclinic, space group $C2/c$ ($C^6_{2h}$; no. 15), $a = 19.482(2)$, $b = 12.176(2)$, $c = 18.529(3)$ Å, $\beta = 109.71(1)°$, $U = 4137.8$ Å$^3$, $D_c = 1.36$ g $cm^{-3}$, $Z = 4$, $\mu(Mo\text{-}K_\alpha) = 38.2$ $cm^{-1}$. Diffraction data were collected as noted previously.[4] Hydrogen atoms from one of the two unique borohydride ligands were located and refined: the remaining $BH_4$ group resides on a crystallographic two-fold axis of symmetry requiring disorder of the three metal-bound hydrogen atoms. Convergence was reached with $R$ 2.5% for 2396 observed data $[I > 3.0\sigma(I)]$.

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.

to the value of 3.139(8) Å obtained for a U–P linkage *trans*-related to a bidentate $BH_4$ group in $U(BH_4)_3(dmpe)_2$. The uranium–nitrogen distance is 2.659(4) Å.

In conclusion, we note that stable uranium complexes with ligands possessing both 'hard' and 'soft' donor sites may well provide a suitable entry into mixed transition metal–actinoid molecules.

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