Synthesis and *X*-Ray Crystal Structure of Bis(tetrahydroborato)bis[1,5-bis(diphenylphosphino)pentane]dicobalt(I), $Co_2(BH_4)_2(Ph_2P[CH_2]_5PPh_2)_2{\cdot}0.5C_6H_6$: a Novel Mode of Tetrahydroborate Co-ordination

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The title compound, obtained as one of several intermediates in a complex sequence of reactions involving Co^{II}, $NaBH_4$, and α,ω-bis(diphenylphosphino)alkanes, is isolated as a phosphine-bridged binuclear species in which each of two tetrahydroborato groups also bridges the two Co^I units *via* the previously unknown $M{-}H{-}BH_2{-}H{-}M$ type of linkage; an additional and unexpected feature of the *X*-ray crystal structure is that one hydrogen atom of each of the two central BH_2 groups also acts as a bridging ligand.

Tetrahydroborato complexes have received considerable attention recently largely because of the variety of possible co-ordination modes available to the BH_4^- grouping. Tridentate[1] and bidentate[1,2] BH_4^- complexes are now well characterized and, recently, unidentate co-ordination of BH_4^- has been confirmed in two Cu^I complexes using *X*-ray[3,4] and neutron diffraction[5] methods. Bridging of two metal ions by BH_4^- has not yet been observed with any certainty although bridged structures have been postulated[1,6] for certain BH_4^- complexes.

In a study[7] of the interaction of Co^{II} with $NaBH_4$ in the presence of the α,ω-bis(diphenylphosphino)alkanes $Ph_2P[CH_2]_nPPh_2$ (n = 1—6), we have isolated as one of the numerous products and product types an air-sensitive, solvated tetrahydroborato complex of empirical formula $Co(BH_4)(Ph_2P[CH_2]_5PPh_2){\cdot}0.25C_6H_6$.† This complex has been shown by *X*-ray diffraction‡ to be the binuclear species $Co_2(BH_4)_2(Ph_2P[CH_2]_5PPh_2)_2{\cdot}0.5C_6H_6$ (Figure 1, disordered lattice solvent not shown); suitable crystals for this study were obtained from benzene–hexane (1 : 1) at −15 °C under N_2.

Crystal data: $C_{58}H_{68}B_2Co_2P_4$; M = 1028.57; triclinic; space group $P\bar{1}$; a = 10.305(3), b = 14.990(3), c = 20.343(5) Å; α = 107.87(2), β = 90.72(2), γ = 105.88(2)°; U = 2861(3) Å^3; D_c = 1.240 g cm^{-3}; Z = 2; μ(Mo-K_α) = 7.527 cm^{-1}. Diffraction data [4290 reflections with $I > 2\sigma(I)$] were collected on a CAD-4 Enraf–Nonius diffractometer using Mo radiation. The structure was solved using conventional heavy-atom techniques with the Co atoms being located by Patterson synthesis.§ Successive least-squares refinements and difference-Fourier methods were used to locate the P, B, and C atoms in the co-ordination complex. Positional parameters and anisotropic thermal parameters for all non-hydrogen atoms in the complex were refined. Hydrogen atoms attached to C in the co-ordination complex were fixed at appropriate locations and not refined. Hydrogen atoms attached to boron were located using a difference-Fourier map; positional parameters and the isotropic thermal parameters for these hydrogen atoms were refined. The solvent molecule, benzene, was disordered. The largest peak in the final difference-Fourier map was 0.326 e/Å^3. In the BH_4^- region of the final difference-Fourier map, no chemically significant peaks were found and this indicates that the hydrogen atoms on the BH_4^- groups refined satisfactorily. The final R and R_w values are 0.052 and 0.049, respectively.

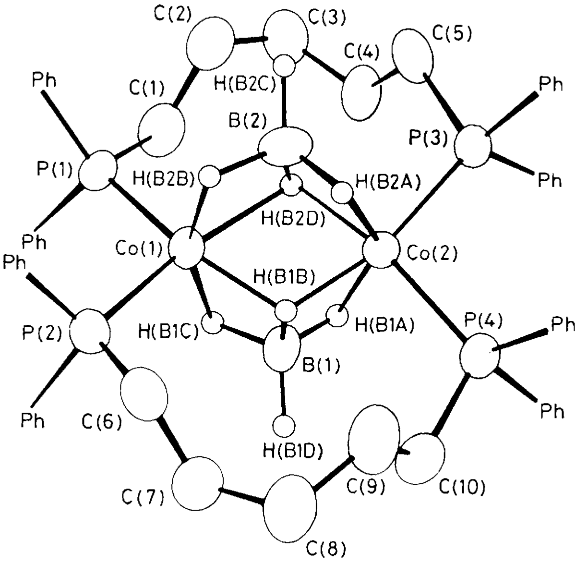

Figure 1. Molecular structure of $Co_2(BH_4)_2(Ph_2P[CH_2]_5PPh_2)_2$: structural details of the phenyl groups and the methylene hydrogen atoms are omitted for reasons of clarity. Principal bond lengths: Co(1)–Co(2), 2.869(1); Co(1)–P(1), 2.270(2); Co(1)–P(2), 2.267(2); Co(1)–B(1), 2.239(7); Co(1)–B(2), 2.215(7); Co(1)–H(B1B), 1.73(6); Co(1)–H(B1C), 1.85(5); Co(1)–H(B2B), 1.76(6); Co(1)–H(B2D), 1.88(5); B(1)–H(B1A), 1.08(6); B(1)–H(B1B), 1.29(6); B(1)–H(B1C), 1.20(5); B(1)–H(B1D), 1.18(6); B(1)–B(2), 3.422(9) Å. Bond angles P(1)–Co(1)–P(2), 105.83(6); B(1)–Co(1)–B(2), 100.4(2); H(B2B)–Co(1)–H(B2D), 71(2); H(B2B)–Co(1)–H(B1C), 156(3); H(B2B)–Co(1)–H(B1B), 91(3); H(B2D)–Co(1)–H(B1C), 90(2); H(B2D)–Co(1)–H(B1B), 66(2); H(B1C)–Co(1)–H(B1B), 67(3); H(B1A)–B(1)–H(B1B), 104(4); H(B1A)–B(1)–H(B1C), 109(4); H(B1A)–B(1)–H(B1D), 113(4); H(B1B)–B(1)–H(B1C), 105(4); H(B1B)–B(1)–H(B1D), 115(4); H(B1C)–B(1)–H(B1D), 108(4)°; dimensions about Co(2) and B(2) are similar except that the Co(2)–H(B2D) bond is apparently shorter than the Co(1)–H(B2D) bond (see text).

From Figure 1, it is clear that the framework of the molecule consists of two six co-ordinated Co^I atoms bridged by both phosphine and tetrahydroborate ligands. The mode of BH_4^- bridging co-ordination illustrated in Figure 1 is unprecedented in that it involves both $Co{-}H{-}BH_2{-}H{-}Co$

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† Prepared by treatment of $CoCl_2{\cdot}6H_2O$ with $Ph_2P[CH_2]_5PPh_2$ and $NaBH_4$ in a 1 : 3 : 2 molar ratio in benzene–ethanol under N_2. Full details will be given in a later publication[7] devoted to a variety of related syntheses.

‡ 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.

§ Enraf-Nonius CAD4-SDP programmes on PDP 8A and 11/34 computers at the University of Minnesota were used in all calculations.

linkages and direct bridging of the cobalt atoms by one hydrogen atom of each of the two central BH_2 units. A further point to note is that since there is no crystallographic centre of symmetry present in the molecular species, the successful refinement of the hydrogen atoms of both BH_4^- groups into nearly chemically equivalent positions adds weight to the structure refinement. The BH_4^- ligand is, therefore, both tridentate *and* chelating to two different cobalt atoms. The presence of three different kinds of hydrogen atom in the tetrahydroborate grouping is also apparent from the distinctive i.r. spectrum which shows $\nu(B\text{–}H_t)$ at 2415 cm^{-1} (strong, sharp) together with two absorptions at 2030 (sharp) and 1985 (broad) cm^{-1}. These two absorptions are due to the two kinds of co-ordinated $B\text{–}H_b$ vibrations[1] although a more detailed assignment cannot yet be made. The cobalt and boron atoms are nearly coplanar but the steric and electronic requirements of the bridging tetrahydroborate ligands apparently dictate that the P(1)P(2)Co(1) plane is skewed relative to the P(3)P(4)Co(2) plane (dihedral angle = 17.5°). The Co–H bond distances in the Co–H–B and Co–H–Co units are generally quite similar. However, the Co(1)- and Co(2)–H(B2D) distances of 1.88(5) and 1.64(5) Å respectively apparently differ from the corresponding Co(1)- and Co(2)–H(B1B) distances of 1.73(6) and 1.71(6) Å respectively. In our view, because of the errors associated with the location of the hydrogen atoms, there is no significance to the apparent asymmetry of the Co(1)- and Co(2)–H(B2D) bonds.

Full details of this and related complexes and a discussion of the critical dependence of the formation of this type of bridged structure upon the chain length of the bidentate phosphine will appear in a later publication.[7]

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