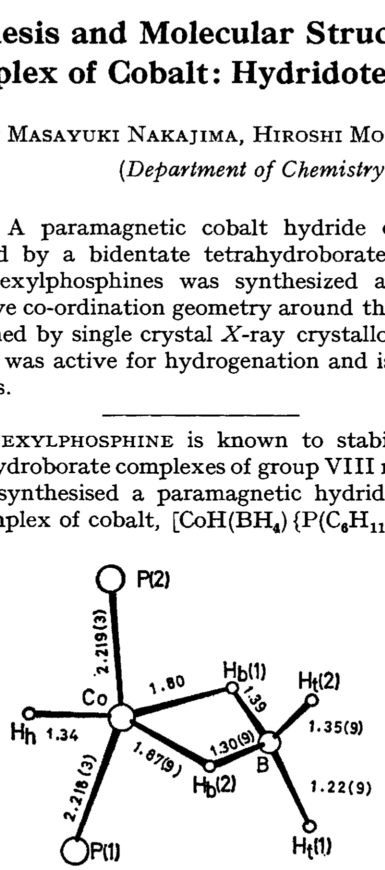
Synthesis and Molecular Structure of a Paramagnetic Hydridotetrahydroborato Complex of Cobalt: Hydridotetrahydroboratobis(tricyclohexylphosphine)cobalt

By MASAYUKI NAKAJIMA, HIROSHI MORIYAMA, AKIKO KOBAYASHI, TARO SAITO, and YUKIYOSHI SASAKI*
(*Department of Chemistry, The University of Tokyo, Hongo, Tokyo* 113, *Japan*)

Summary A paramagnetic cobalt hydride complex co-ordinated by a bidentate tetrahydroborate ligand and tricyclohexylphosphines was synthesized and the distorted five co-ordination geometry around the cobalt was determined by single crystal *X*-ray crystallography; the complex was active for hydrogenation and isomerization of olefins.

TRICYCLOHEXYLPHOSPHINE is known to stabilize hydride and tetrahydroborate complexes of group VIII metals.[1] We have now synthesised a paramagnetic hydridotetrahydroborato complex of cobalt, $[CoH(BH_4)\{P(C_6H_{11})_3\}_2]$.



FIGURE

The complex was prepared by treating a solution of cobalt dichloride hexahydrate and tricyclohexylphosphine in toluene–ethanol with sodium tetrahydroborate in an atmosphere of nitrogen and was then crystallised by the addition of methanol. The complex is an air-unstable brownish-yellow solid [m.p. 93° (decomp.)], and can be recrystallized from toluene–methanol in the presence of free tricyclohexylphosphine. Magnetic susceptibility was measured by the Gouy method and μ_{eff} was 2·15 B.M. The e.s.r. spectrum of a xylene solution in the presence of free tricyclohexylphosphine at 77 K showed a broad signal centred at about g 2·025. These magnetic data are typical of low-spin cobalt(II) complexes.[2] The i.r. spectrum showed ν(Co–H) 1797 cm^{-1}, ν[B–H(terminal)] at 2390 and 2368 cm^{-1}, and ν[B–H(bridge)] at 1958 and 1379 cm^{-1}. To confirm the assignments, a deuteriated complex $[CoD(BD_4)\{P(C_6H_{11})_3\}_2]$ was prepared and isotopic shifts [ν(D)/ν(H)] were examined. While the absorptions assigned to the Co–H stretching mode showed a shift (0·727),[3] all the absorptions assignable to B–H stretching vibrations showed larger shifts (0·751—0·740).[4]

To examine the co-ordination of the tetrahydroborato group and the existence of a hydridic hydrogen, we carried out an *X*-ray crystal structure analysis. *Crystal data* $[CoH(BH_4)\{P(C_6H_{11})_3\}_2]$, monoclinic, space group $P2_1/a$, a = 23·391(10), b = 12·614(4), c = 13·195(6) Å, β = 106·93(3)°, D_c = 1·13 g cm^{-3}, Z = 4. A crystal was sealed in a glass capillary under an atmosphere of nitrogen for the measurements. Independent reflections of $2\theta \leqslant 50°$ were collected on an automated diffractometer with monochromatized Mo-K_α radiation and 3707 reflections ($F_0 \geqslant 3\sigma$) were used for the structure determination. The structure was solved by the standard heavy-atom method. All the atoms including hydrogens were located and refined to a final R value of 0·062.

The inner co-ordination geometry is shown in the Figure. The co-ordination around the cobalt atom can be described as a distorted square pyramid, where the hydridic hydrogen H_h, one of the bridging hydrogen atoms of the tetrahydroborato group $H_b(1)$, and two phosphorus atoms of tricyclohexylphosphine ligands P(1) and P(2) form a plane and $H_b(2)$ is in an axial position. The P(1) and P(2) atoms bend from the ideal equatorial position to accommodate the BH_4 group so that the P(1)–Co–P(2) angle is 157·83°. The $H_b(2)$ atom bends from an ideal axial position to $H_b(1)$.

The bond length Co–H_h, 1·34(9) Å appears to be one of the shortest M–H bond lengths of transition-metal hydride complexes reported on the basis of single crystal *X*-ray diffraction studies,[5] although this conclusion must be considered tentative in view of the high standard deviation. The Co–B distance, 2·13(1) Å, is shorter than the corresponding transition metal-boron distances in copper and titanium BH_4 complexes.[6] This is in accord with the small single bond metallic radius of cobalt relative to those of copper and titanium. The positions of the four tetrahydroborato hydrogens around the boron atom are considerably distorted from the ideal C_{2v} symmetry.

The complex is an active selective catalyst for hydrogenation and isomerization of olefins under atmospheric pressure and at room temperature. For example, hex-1-ene [$4{\cdot}8 \times 10^{-2}$ mol in benzene (50 ml)] absorbed 200 ml of H_2 in 30 min at 30° under 1 atmosphere of H_2 using a catalytic amount of the complex ($2{\cdot}9 \times 10^{-4}$ mol). Initial rates of hydrogenation were in the order of 1-olefin > styrene > 2-olefin > isoprene, butadiene. Cyclohexene, 4-vinylcyclohex-1-ene, 2-methylpent-1-ene and *trans*-stilbene were not hydrogenated at all under similar conditions. Isomerisation caused the hydrogenation to slow down markedly.

(*Received*, *8th October* 1974; *Com.* 1262.)

[1] M. L. H. Green, H. Munakata, and T. Saito, *J. Chem. Soc.* (*A*), 1971, 469; L. Vaska, W. V. Miller, and B. R. Flynn, *Chem. Comm.*, 1971, 1615; D. G. Holah, A. N. Hughes, B. C. Hui, and K. Wright, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 835.

[2] J. R. Sanders, *J.C.S. Dalton*, 1972, 748; B. A. Goodman, and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

[3] A. Sacco, and M. Rossi, *Inorg. Chim. Acta*, 1968, **2**, 127.

[4] S. G. Lippard and D. A. Ucko, *Inorg. Chem.*, 1968, **7**, 1051; N. Davies, B. D. James, and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1969, 2601.

[5] B. A. Frenz, and J. A. Ibers, 'Transition Metal Hydrides,' ed. E. L. Muetterties, Marcel Dekker, New York, 1971, ch. 3, p. 41.

[6] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1967, **6**, 2223; K. M. Melmed, D. Coucouvanis, and S. J. Lippard, *Inorg. Chem.*, 1973, **12**, 232.