nido-Pentaboranyl Complexes of Cadmium

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The complexes [Cd(μ-B_5H_8)Cl(PPh_3)] and [Cd(μ-1-BrB_5H_7)Cl(PPh_3)] have been prepared by reaction of [$CdCl_2(PPh_3)_2$] with the potassium salts of the appropriate pentaborane anions. On the basis of boron-decoupled ^{1}H, proton-decoupled ^{11}B, and ^{31}P n.m.r. spectra the complexes have been shown to be non-fluxional, η^2 complexes of the ligands [B_5H_8]$^-$ and [1-BrB_5H_7]$^-$. The cadmium is formally a 16-electron species and the structure resembles that recently established by *X*-ray analysis for the 'isoelectronic' copper complex [Cu(μ-B_5H_8)(PPh_3)$_2$]. Attempts to prepare analogous complexes of zinc and mercury have been unsuccessful.

THE reactions of several derivatives of cadmium with boron hydrides and related compounds have been reported in recent years,[1-5] and cadmium complexes of [$B_{10}H_{12}$]$^{2-}$ and B_6H_{10} are now known. In this paper we report the first *nido*-pentaborane derivatives of cadmium, *viz*. [Cd(μ-B_5H_8)Cl(PPh_3)] and [Cd(μ-1-BrB_5H_7)Cl(PPh_3)].

RESULTS AND DISCUSSION

In typical preparations, [$CdCl_2(PPh_3)_2$] was mixed with an equimolar quantity of either K[B_5H_8] or K[1-BrB_5H_7] in tetrahydrofuran (thf)–dichloromethane at low temperature; potassium chloride was precipitated, 1 mol of triphenylphosphine was eliminated, and addition of pentane to the filtered solution led to the precipitation of the products as white powders. Treatment of both products with anhydrous HCl in diethyl ether regenerated the parent pentaborane or bromopentaborane in *ca*. 50% yield, indicating that the borane cluster remains intact in the metal derivative.

In the solid state both complexes are stable in air for several days, and under a nitrogen atmosphere at —15 °C they are stable for at least 6 months. The complexes [Cd(μ-B_5H_8)Cl(PPh_3)] and [Cd(μ-1-BrB_5H_7)Cl(PPh_3)] melt without decomposition at 83 and 98 °C respectively. They are soluble in polyethers and chlorinated hydrocarbons but insoluble in diethyl ether and hydrocarbon solvents. In solution at room temperature under nitrogen, decomposition is complete in 6 h; in the presence of air decomposition is more rapid.

The i.r. spectrum (Nujol mull) of [Cd(μ-B_5H_8)Cl(PPh_3)] shows strong terminal B–H stretching absorptions at 2 595, 2 575, 2 545, and 2 520 cm^{-1}. The corresponding absorptions in the bromopentaborane derivative occur 5—10 cm^{-1} lower at 2 590, 2 565, 2 540, and 2 510 cm^{-1}. B–H–B stretching absorptions in the 2 000—1 700 cm^{-1} region are overlaid by absorptions due to the triphenylphosphine ligand.

The 28.87-MHz ^{11}B n.m.r. spectrum of [Cd(μ-B_5H_8)Cl(PPh_3)] at room temperature in dichloromethane is shown in Figure 1(*a*) and is labelled according to the recent internationally agreed convention that chemical shifts to high field of the standard are given a negative sign. The high-field doublet of area 1 occurs at —51.5 p.p.m. relative to $OEt_2 \cdot BF_3$ (*J* 160 Hz) and is assigned to the unique apical boron atom B^1. The low-field group of area 4 consists of two overlapping doublets at —9.4 (*J* ~ 150) and —13.8 p.p.m. (*J* ~ 150 Hz) as shown by the proton decoupling [Figure 1(*b*)]. The corresponding resonances in the ^{11}B n.m.r. spectrum of the bromopentaborane derivative occur at —45.2 (singlet due to brominated apical boron), —9.6 (*J* ~ 145), and —14.2 p.p.m. (*J* ~ 150 Hz). These results establish

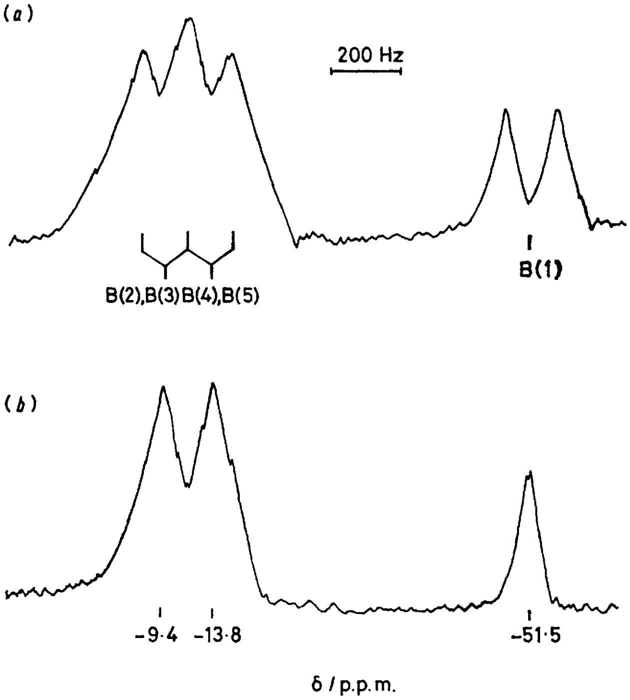

FIGURE 1 The 28.87-MHz ^{11}B n.m.r. spectrum of [Cd(μ-B_5H_8)Cl(PPh_3)]: (*a*) without proton decoupling, (*b*) ^{1}H-decoupled. Chemical shifts are relative to $OEt_2 \cdot BF_3$ with upfield shifts being given a negative sign

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[2] N. N. Greenwood and N. F. Travers, *J. Chem. Soc.* (*A*), 1967, 880.

[3] N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J.C.S. Dalton*, 1972, 989.

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the presence of two pairs of magnetically equivalent boron atoms in the base of the pentaborane ligand. This suggests that the CdCl(PPh_3) group is inserted into a bridging position in the base of the pentaborane pyramid between two adjacent basal boron atoms B(2) and B(3) and that this system is static on the n.m.r. time scale. The doublet to lowest field in the basal resonance is probably due to B(2) and B(3) since the chemical shift of these particular boron nuclei is furthest removed from the value of B(2)—B(5) in pentaborane(9). The ^{11}B n.m.r. spectrum of [Cd(μ-B_5H_8)Cl(PPh_3)] is virtually unchanged over the range −30 to +23 °C.

The copper complex [Cu(μ-B_5H_8)(PPh_3)$_2$] has been reported previously[6,7] and on the basis of ^1H n.m.r. evidence was assigned a static structure in solution with the Cu(PPh_3)$_2$ group in a bridging position between two adjacent basal boron atoms. The basal-boron resonance of this complex however is an unresolved hump which has been attributed to the influence of quadrupolar relaxation of the copper nuclei.[7] The n.m.r.-active isotopes of cadmium (^{111}Cd, $I = \frac{1}{2}$, 12.8% abundant; ^{113}Cd, $I = \frac{1}{2}$, 12.3% abundant) possess no nuclear quadrupole and in the present complexes the basal resonance is resolved into two overlapping doublets, consistent with a static structure.

This interpretation is supported by the ^{11}B-decoupled 90-MHz ^1H n.m.r. spectrum (Figure 2) of [Cd(μ-B_5H_8)Cl(PPh_3)]. In addition to the expected strong peak at τ 2.4 due to the aromatic protons on the phosphine ligand there are a pair of resonances of area 2 : 2 at τ 7.2 and 7.8 due to basal-terminal hydrogen atoms, a singlet of area 1 at τ 9.6 due to the apical hydrogen atom, and a pair of resonances of area 1 : 2 at τ 12.4 and 13.0 due to the bridging hydrogen atoms respectively *trans* and *cis* to the bridging CdCl(PPh_3) group. The structure is clearly static on this time scale.

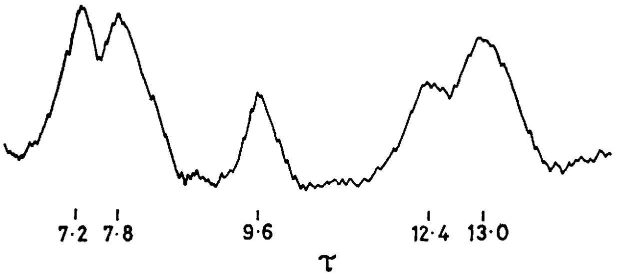

FIGURE 2 The 90-MHz ^1H-{^{11}B} n.m.r. spectrum of [Cd(μ-B_5H_8)Cl(PPh_3)] in the borane region. The pair of resonances (areas 2 : 2) at lowest field are assigned to basal-terminal hydrogen atoms on B(2),B(3), and B(4),B(5) respectively, the midfield resonance (area 1) is due to the apical hydrogen on B(1), and the high-field resonances (areas 1 : 2) are due to the bridging hydrogen atoms *trans* and *cis* respectively to the bridging cadmium atom

The proton-decoupled 36.42-MHz ^{31}P n.m.r. spectrum of [Cd(μ-B_5H_8)Cl(PPh_3)] in dichloromethane at ambient temperature shows only a single peak at −137.8 p.p.m. relative to P(OMe)$_3$ due to the single triphenylphosphine ligand. The corresponding resonance of the bromopentaborane complex occurs at −137.1 p.p.m. These spectra are independent of temperature over the range −20 to +23 °C. There is no evidence of cadmium–phosphorus coupling.

The species [Cd(μ-B_5H_8)Cl(PPh_3)] and [Cd(μ-1-BrB_5H_7)Cl(PPh_3)] are the first examples of cadmium complexes of the octahydropentaborate(1−) ion or its derivatives. On the basis of the foregoing evidence the structure of [Cd(μ-B_5H_8)Cl(PPh_3)] is considered to be similar to the 'isoelectronic' complex[8] [Cu(μ-B_5H_8)(PPh_3)$_2$] with the cadmium atom in approximately trigonal-planar co-ordination, being bound to a triphenylphosphine group, a chlorine atom, and to the B_5H_8 cage by a B–Cd–B three-centre two-electron bond (Figure 3). The Cd^{II} in these pentaborane complexes is formally a 16-electron species and the complexes are thus further examples of a growing class of 16-electron species containing a bridge-bonded B_5H_8 unit.[9] It is of interest to note that cadmium has 18 valence-shell electrons in the starting material [$CdCl_2$(PPh_3)$_2$] and that one triphenylphosphine group is eliminated during the reaction in addition to the Cl^- ion replaced by [B_5H_8]$^-$.

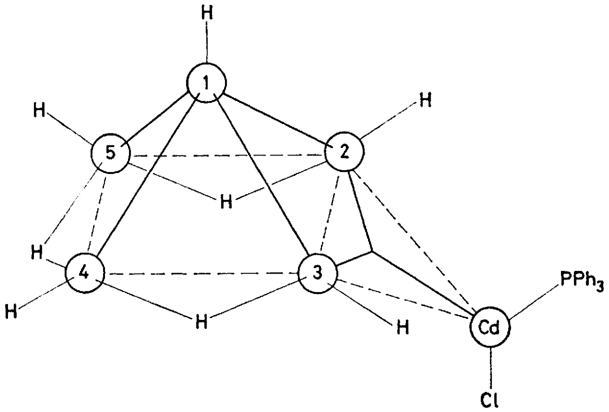

FIGURE 3 Proposed structure of [Cd(μ-B_5H_8)Cl(PPh_3)] showing the trigonal-planar 16-electron cadmium atom and the three-centre two-electron bond from B(2) and B(3) to cadmium

A number of phosphine complexes of zinc and mercury were used in attempts to prepare *nido*-pentaborane complexes of these metals but no products could be isolated in which the B_5H_8 group was present.

EXPERIMENTAL

Pentaborane(9) was procured by courtesy of Dr. R. E. Williams (Chemical Systems Inc., California). Potassium hydride (Alpha Products Ltd.) was freed from trace amounts of mineral oil by washing with dry pentane. The complex [$CdCl_2$(PPh_3)$_2$] was prepared according to the

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[6] V. T. Brice and S. G. Shore, *Chem. Comm.*, 1970, 1312.

[7] V. T. Brice and S. G. Shore, *J.C.S. Dalton*, 1975, 334.

[8] N. N. Greenwood, J. A. Howard, and W. S. McDonald, *J.C.S. Dalton*, 1977, 37.

[9] J. Staves, Ph.D. Thesis, University of Leeds, 1976; N. N. Greenwood and J. Staves, unpublished work.

literature.[10] All the solvents were dried immediately prior to use.

In a typical preparation of [Cd(μ-B_5H_8)Cl(PPh_3)], potassium hydride (0.285 g, 5.0 mmol, 70% active) was weighed in a glove-box into a reaction flask (100 cm^3) equipped with a Teflon-covered stirring bar and a tipper-tube side arm. The complex [$CdCl_2(PPh_3)_2$] (3.2 g, 4.5 mmol) was weighed into the tipper-tube, and the apparatus was assembled, removed to the vacuum line, and evacuated. The flask was frozen at −196 °C and pentaborane(9) (5.3 mmol) and thf (10 cm^3) were condensed in. Potassium octahydropentaborate was prepared according to the literature.[11] The flask and contents were frozen to −196 °C and dichloromethane (20 cm^3) was condensed in and the contents of the tipper-tube were added. The flask was warmed at −40 °C and the contents were stirred at this temperature for 8 h. The resulting precipitate was filtered off and the volume of the filtrate was reduced to 10 cm^3 at −40 °C *in vacuo*. Pentane (60 cm^3) was added at −78 °C to precipitate the product as a white powder. The product was filtered off under nitrogen, washed with cold diethyl ether, and dried *in vacuo*, yield *ca.* 60%. Analytical data are tabulated above (calculated values in parentheses).

Complex	Analytical data (wt. %) C	H	B	Br	Cl	P
[Cd(μ-B_5H_8)Cl(PPh_3)]	46.6	5.2	10.9		7.2	6.5
	(45.8)	(4.9)	(11.5)		(7.5)	(6.6)
[Cd(μ-1-BrB_5H_7)Cl(PPh_3)]	38.9	4.2	9.3	12.9	6.3	5.5
	(39.2)	(4.2)	(9.8)	(14.3)	(6.5)	(5.6)

Starting from K[1-BrB_5H_7], prepared as in the literature,[12] the complex [Cd(μ-1-BrB_5H_7)Cl(PPh_3)] was similarly prepared in 65% yield.

Regeneration of Pentaborane(9).—The complex [Cd(μ-B_5H_8)Cl(PPh_3)] (0.47 g, 1.0 mmol) was weighed into a reaction flask containing a Teflon-covered stirring bar. Diethyl ether (3 cm^3) and anhydrous HCl (3 cm^3) were condensed into the flask at −196 °C. The flask was warmed to −30 °C and the contents were stirred at this temperature for 4 h. Fractionation of the volatile contents of the flask through a series of cold traps yielded pentaborane(9) in 55% yield. Similar treatment of [Cd(μ-1-BrB_5H_7)Cl(PPh_3)] yielded 1-bromopentaborane(9) in 45% yield.

Infrared spectra of Nujol mulls were recorded on a Perkin-Elmer 457 grating spectrometer. The n.m.r. spectra were obtained on a Bruker HFX4 spectrometer modified for use in the Fourier-transform mode by Bruker Datasystem BNC 12. The deuterium lock was provided by the solvent. Chemical shifts are quoted using the convention that a resonance to high frequency (low field) of the standard is positive.

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[11] H. D. Johnson, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, 1970, **9**, 908.

[12] V. T. Brice and S. G. Shore, *Inorg. Chem.*, 1973, **12**, 309.