Complexes of (Diphosphine)halogenonickel(II) with the Anions of Pentaborane(9) and 1-Bromopentaborane(9)

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Diphosphine complexes of nickel(II) halides react readily at low temperature with $K[B_5H_8]$ and $K[1\text{-}BrB_5H_7]$ to give the corresponding complexes $[Ni(\mu\text{-}B_5H_8)X(dppe)]$ and $[Ni(\mu\text{-}1\text{-}BrB_5H_7)X(dppe)]$ [X = Cl, Br, or I, dppe = 1,2-bis(diphenylphosphino)ethane]. The complex $[Ni(\mu\text{-}B_5H_8)Br(dppp)]$ has also been prepared [dppp = 1,3-bis(diphenylphosphino)propane]. The complexes are monomeric and non-conducting in solution and their n.m.r. spectra (^1H, ^{11}B, and ^{31}P) are best interpreted in terms of a square-planar NiX(dppe) group inserted *via* a three-centre two-electron B–Ni–B bond into a bridging position between two basal boron atoms of the pentaborane cluster. The four basal boron atoms and three bridging hydrogen atoms are equivalent on the n.m.r. time scale, implying fluxional behaviour. In this, the nickel complexes differ from 'isoelectronic' (16-electron) copper(I) and cadmium(II) complexes of the type $[Cu(\mu\text{-}B_5H_8)(PPh_3)_2]$ and $[Cd(\mu\text{-}B_5H_8)Cl(PPh_3)]$ which are non-fluxional.

A NUMBER of copper(I) and cadmium(II) derivatives of pentaborane(9) have been prepared and characterised,[1-5] and this prompted us to investigate the reaction of B_5H_9 and its 1-bromo-derivative with selected complexes of nickel, palladium, and platinum.[6] The results for nickel are reported in this paper and those for palladium and

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[5] N. N. Greenwood and J. Staves, preceding paper.

[6] J. Staves, Ph.D. Thesis, University of Leeds, 1976; a preliminary account of some of these results was presented at the 3rd Internat. Meeting Boron Chem., Ettal, West Germany, July 1976 (see N. N. Greenwood, *J. Pure Appl. Chem.*, 1977, **49**, in the press).

platinum will be published later. The only other borane complexes with these metals involve the ligand $[\eta^3\text{-}B_3H_7]^{2-}$, the η^4 ligands $[B_{10}H_{12}]^{2-}$, $[n\text{-}B_{18}H_{20}]^{2-}$, and $[i\text{-}B_{18}H_{20}]^{2-}$,[7] and the more recently reported complexes with the hypothetical $[B_{11}H_{11}]^{4-}$ and $[B_{10}H_{10}]^{6-}$ ions and the *nido*-metalloboranes derived from $[B_{10}H_{10}]^{2-}$.[8]

RESULTS AND DISCUSSION

The reaction of equimolar quantities of *cis*-$[NiX_2(dppe)]$ with $K[1\text{-}YB_5H_7]$ [X = Cl, Br, or I; Y = H or Br; dppe = 1,2-bis(diphenylphosphino)ethane] in tetrahydrofuran (thf)–dichloromethane produced red or orange solids (dependent on X and Y) which were shown to have the general formula $[Ni(\mu\text{-}1\text{-}YB_5H_7)X(dppe)]$. The complex $[Ni(\mu\text{-}B_5H_8)Br(dppp)]$ was also prepared [dppp = 1,3-bis(diphenylphosphino)propane]. The complexes were isolated as non-volatile amorphous powders of varying stability in the atmosphere (see Table 1). For example, $[Ni(\mu\text{-}B_5H_8)Br(dppe)]$ and $[Ni(\mu\text{-}1\text{-}BrB_5H_7)Br(dppe)]$ are stable in air for at least 14 months, whereas when X = Cl or I decomposition in the air is extensive after 4 months. Under an inert atmosphere at −15 °C all of the dppe complexes can be stored for at least 12 months without significant decomposition but the dppp complex decomposes within 24 h.

TABLE 1

Some properties of the complexes

Complex	Colour	M.p. (θ_c/°C)	Stability in air (t/month)	Analysis (wt. %) [a]							
				C	H	B	P	Cl	Br	I	Ni
$[Ni(\mu\text{-}B_5H_8)Cl(dppe)]$	Orange	190	4	56.2	5.9	9.5	11.3	6.6			10.3
				(56.3)	(5.8)	(9.75)	(11.2)	(6.4)			(10.6)
$[Ni(\mu\text{-}1\text{-}BrB_5H_7)Cl(dppe)]$	Orange	210	3	48.9	5.0	8.3	9.8	6.0	11.7		9.1
				(49.3)	(4.95)	(8.5)	(9.8)	(5.6)	(12.6)		(9.3)
$[Ni(\mu\text{-}B_5H_8)Br(dppe)]$	Red	220	>14	51.0	5.7	9.0	10.3		12.8		10.0
				(52.1)	(5.4)	(9.0)	(10.35)		(13.4)		(9.8)
$[Ni(\mu\text{-}1\text{-}BrB_5H_7)Br(dppe)]$	Red	241	>14	46.1	4.7	7.6	9.1		23.5		8.7
				(46.1)	(4.6)	(8.0)	(9.15)		(23.6)		(8.7)
$[Ni(\mu\text{-}B_5H_8)I(dppe)]$	Brick-red	209	4	49.1	5.1	8.2	9.6			18.8	9.0
				(48.3)	(5.0)	(8.4)	(9.6)			(19.6)	(9.1)
$[Ni(\mu\text{-}1\text{-}BrB_5H_7)I(dppe)]$	Brick-red	220	2	41.9	4.6	7.2	8.6		11.6	17.1	8.0
				(43.1)	(4.3)	(7.45)	(8.5)		(11.0)	(17.5)	(8.1)
$[Ni(\mu\text{-}B_5H_8)Br(dppp)]$	Orange	190	0 [b]	52.1	5.7	8.4	9.7		12.9		
				(52.9)	(5.6)	(8.8)	(10.1)		(13.0)		(9.6)

[a] Calculated values are given in parentheses. [b] 24 h at −15 °C under nitrogen.

Molecular-weight determinations and conductivity measurements indicate that the complexes are monomeric and non-conducting in solution. They are soluble in chlorinated hydrocarbons and polyethers, but are insoluble in hydrocarbon solvents and diethyl ether. In solution at room temperature under an inert atmosphere, decomposition occurs within 24 h; in the presence of air decomposition is more rapid. The complexes are not attacked by cold water or ethanol, but are rapidly degraded by boiling water or by cold aqueous acid or alkali. Treatment of the complexes with anhydrous hydrogen chloride in dimethyl or diethyl ether yielded the parent pentaborane(9) or 1-bromopentaborane(9) in *ca.* 20% yield.

The i.r. spectrum (Nujol mull) of $[Ni(\mu\text{-}B_5H_8)Br(dppe)]$ is typical of this series of complexes. Strong terminal B–H stretching absorptions are apparent at 2 565, 2 560, 2 540, and 2 500 cm^{-1}, the spectra in this region being similar to that of $[Cu(\mu\text{-}B_5H_8)(PPh_3)_2]$ [2,3] and $[Cd(\mu\text{-}B_5H_8)Cl(PPh_3)]$.[5] In contrast the i.r. spectrum of $[Ni(\mu\text{-}B_5H_8)Br(dppe)]$ in chloroform solution displays a much broader peak at 2 500 cm^{-1}, and no fine structure is exhibited in this region.

The 28.87-MHz ^{11}B n.m.r. spectrum of $[Ni(\mu\text{-}B_5H_8)Br(dppe)]$ consists of two symmetrical doublets in the ratio of 4 : 1 at −12.6 (*J* 160 Hz) and −44.4 p.p.m. (*J* 155 Hz) relative to $OEt_2{\cdot}BF_3$. The high-field doublet at −44.4 p.p.m. is assigned to the unique apical boron atom B(1); on proton decoupling this doublet collapses to give a single peak. The low-field doublet of area 4 is assigned to the basal boron atoms B(2)—B(5) and this also collapses to give a single peak on proton decoupling. The ^{11}B n.m.r. spectrum of $[Ni(\mu\text{-}1\text{-}BrB_5H_7)Br(dppe)]$ consists of a symmetrical doublet of area 4 at −12.9 p.p.m. (*J* 158 Hz) and a single peak of area 1 at −38.1 p.p.m. On proton decoupling, the latter is little affected, but the low-field doublet collapses to give a single peak at −12.5 p.p.m. The ^{11}B n.m.r. spectra of the corresponding chloro- and iodo-derivatives were similar (see Table 2).

The high-field resonances and their behaviour on proton decoupling are as expected for the respective derivatives of pentaborane(9). The symmetrical low-field doublet due to the basal boron atoms indicates that each basal boron nucleus is spin–spin coupled to one proton (presumably the basal-terminal hydrogen atoms) and this suggests that the NiX(dppe) group is in a bridging position and is fluxional. Rapid exchange of the NiX-

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(dppe) group and the bridging hydrogen atoms in the base of the pentaborane cluster would render the basal boron atoms magnetically equivalent but would leave each free to couple with its static basal-terminal hydrogen atom. Alternatively, but less probably, one could assume that the bridging NiX(dppe) group was static and that the two sets of equivalent basal boron atoms B(2) and B(3) and B(4) and B(5) fortuitously have the same chemical shift. This seems unlikely in view of the known behaviour of analogous copper[2] and cadmium[5] complexes, where insertion of a metal into the bridging position has differing effects on the two sets of basal boron atoms.

TABLE 2

Selected i.r. and ^{11}B n.m.r. data

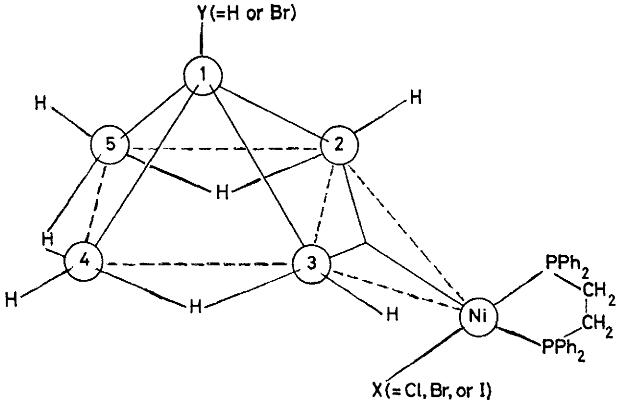
		^{11}B N.m.r.*			
		Basal borons		Apical boron	
Complex	Terminal B–H stretch (cm^{-1})	δ/p.p.m.	J/Hz	δ/p.p.m.	J/Hz
[Ni(μ-B$_5$H$_8$)Cl(dppe)]	2 565, 2 560 2 510, 2 495	−12.5 (d)	160	−44.1 (d)	150
[Ni(μ-1-BrB$_5$H$_7$)Cl(dppe)]	2 570, 2 555 2 530, 2 500	−12.6 (d)	155	−38.5 (s)	
[Ni(μ-B$_5$H$_8$)Br(dppe)]	2 565, 2 560 2 540, 2 500	−12.6 (d)	160	−44.4 (d)	155
[Ni(μ-1-BrB$_5$H$_7$)Br(dppe)]	2 580, 2 560 2 540, 2 510	−12.9 (d)	158	−38.1 (s)	
[Ni(μ-B$_5$H$_8$)I(dppe)]	2 560, 2 555 2 530, 2 500	−12.0 (d)	155	−45.0 (d)	155
[Ni(μ-1-BrB$_5$H$_7$)I(dppe)]	2 565, 2 545 2 530, 2 515	−13.0 (d)	150	−37.8 (s)	
[Ni(μ-B$_5$H$_8$)Br(dppp)]	2 575, 2 560 2 540, 2 505	−13.0 (d)	155	−45.6 (d)	150

* s = Singlet, d = doublet. All the n.m.r. spectra were run in CH$_2$Cl$_2$. Chemical shifts are quoted using the recent internationally agreed convention that resonances occurring to high frequency (low field) from the standard have a positive chemical shift.

On cooling from room temperature to −30 °C the resonance due to the basal boron atoms broadens but the apical boron resonance shows only slight loss of resolution. The broadening of the basal resonance of the complex [Cu(μ-B$_5$H$_8$)(PPh$_3$)$_2$] with decreasing temperature has been attributed to the influence of quadrupolar relaxation of the copper nuclei.[2] In the present case the less pronounced broadening may be substantially due to a slowing down of the rate of exchange of the NiX(dppe) group and the bridging protons.

The 90-MHz ^{1}H n.m.r. spectrum (^{11}B-decoupled) of [Ni(μ-1-BrB$_5$H$_7$)Br(dppe)] in dichloromethane shows, in addition to resonances of the phosphine ligand, two areas of resonance due to the borane hydrogen atoms at τ 7.5 and 12.5. The two resonances are of approximately equal intensity: the former is attributed to the four basal-terminal protons and the latter to the three bridging protons which are considered to be fluxional with the NiBr(dppe) group. The apparent equivalence of the basal-terminal protons amongst themselves on the one hand, and of the bridging protons amongst themselves on the other, favours a dynamic system which places them in an averaged magnetic environment.

The 36.42-MHz ^{31}P n.m.r. spectrum (^{1}H-decoupled) of [Ni(μ-B$_5$H$_8$)Br(dppe)] in dichloromethane at room temperature shows two resonances of equal intensity at −85 and −110 p.p.m respectively, relative to P(OMe)$_3$. This establishes the inequivalence of the two phosphorus atoms in the phosphine ligand and confirms the expected *cis* configuration of the ligand about the metal atom. The resonance at higher field (−110 p.p.m.) is broader than the low field resonance at −85 p.p.m. This broadening may be due to unresolved coupling between the basal boron atoms *via* the nickel, $^2J(^{31}$P–Ni–^{11}B). The value of this coupling may be only a few Hertz. The coupling is expected to be greater when the coupling path is *trans* rather than *cis* and therefore the broader resonance would be due to the phosphorus atom *trans* to the pentaborane moiety.



Proposed structure of [Ni(μ-1-YB$_5$H$_7$)X(dppe)] showing the square-planar 16-electron nickel atom and the three-centre two-electron bond from B(2) and B(3) to nickel

On the basis of the foregoing evidence it is suggested that these derivatives of Ni^{II} adopt square-planar geometry about the nickel atom as shown in the Figure. The colour of these materials is also consistent with them being square planar. Although no direct magnetic measurements were made, the well resolved n.m.r. spectra of the complexes argue for a diamagnetic state. The complexes *cis*-[Ni(μ-1-YB_5H_7)X(dppe)] and *cis*-[Ni(μ-B_5H_8)Br(dppp)] are examples of 16-electron species which contain a bridge-bonded as opposed to a σ-bonded B_5H_8 unit.[2-6]

EXPERIMENTAL

Pentaborane(9) was procured by courtesy of Dr. R. E. Williams (Chemical Systems Inc., California). 1-Bromopentaborane(9) [9] and the appropriate (diphosphine)dihalogenonickel(II) complexes [10] were prepared according to the literature. The ligands 1,2-bis(diphenylphosphino)ethane and 1,3-bis(diphenylphosphino)propane were obtained from B.D.H. Chemicals Ltd. Potassium hydride (Alpha Products Ltd.) was freed from trace amounts of mineral oil by washing with dry pentane. All the solvents were dried prior to use.

The preparation of [Ni(μ-B_5H_8)Br(dppe)] will serve to illustrate the procedure by which the nickel derivatives of pentaborane and bromopentaborane were prepared. In a typical experiment, 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 tipper-tube side arm and a Teflon-covered stirring bar. The complex [NiBr_2(dppe)] (3.0 g, 4.8 mmol) was weighed into the tipper-tube, and the apparatus was assembled, transferred to the vacuum line, and evacuated. The flask was frozen at -196 °C and thf (10 cm^3) and pentaborane(9) (5.0 mmol) were condensed in. Potassium octahydropentaborate was prepared as described in the literature.[11] The flask was refrozen at -196 °C, dichloromethane (20 cm^3) was condensed in, and the contents of the tipper-tube were added. The flask was warmed to -40 °C and the contents were stirred at this temperature for 6 h and then at -78 °C overnight. The solution was filtered under nitrogen and the volume of the filtrate was reduced to 10 cm^3 *in vacuo*. The solution was stirred vigorously at -78 °C whilst diethyl ether (60 cm^3) was condensed into the flask to precipitate the product. The product was filtered off under nitrogen, washed with diethyl ether, and dried *in vacuo*. In general, yields were 50—75%.

The 1-bromopentaborane(9) complexes were prepared from K[1-BrB_5H_7] [12] in similar yields. Analytical data for the new complexes are given in Table 1.

Other Conditions used.—The use of K[B_5H_8] in thf–dichloromethane appeared to give the optimum yield of product. However, [Ni(μ-B_5H_8)Br(dppe)] was also prepared (in 12% yield) by the reaction of [NiBr_2(dppe)] with an equimolar quantity of [PPh_4][B_5H_8] or [AsPh_4][B_5H_8] [13] under the conditions described above. Additionally, [Ni(μ-B_5H_8)Br(dppe)] was prepared by the reaction of [PPh_4][B_5H_8] with [NiBr_2(dppe)] in dichloromethane at -20 °C under a nitrogen atmosphere (yield 23%).

Regeneration of Pentaborane(9).—The complex [Ni(μ-B_5H_8)Br(dppe)] (0.3 g, 0.5 mmol) was placed in a reaction flask containing a Teflon-covered stirring bar. Diethyl ether (5 cm^3) and anhydrous hydrogen chloride were condensed into the flask at -196 °C. The contents of the flask were stirred at -10 °C for 24 h. Fractionation of the volatile contents of the flask through a series of cold traps yielded pentaborane(9) in 20% yield. Similar treatment of [Ni(μ-1-BrB_5H_7)Br(dppe)] regenerated 1-bromopentaborane(9) in 22% yield.

Physical Measurements.—Infrared spectra of Nujol mulls were recorded on a Perkin-Elmer 457 grating spectrophotometer. The n.m.r. spectra were obtained on a Bruker HFX4 spectrometer modified for use in the Fourier-transform mode by Bruker Datasystem BNC12. The deuterium lock was provided by the solvent. Chemical shifts are quoted using the convention that those to high frequency (low field) of the standard have a positive sign.

Molecular weights were determined in a sealed isopiestic apparatus at 20 °C. Chloroform solutions were used and a period of 24 h was allowed for equilibration. Typical results were [Ni(μ-B_5H_8)Br(dppe)] 563 (calc. 599), [Ni(μ-1-BrB_5H_7)Br(dppe)] 657 (calc. 679).

Electrical conductivity was measured at several concentrations at 25 °C using a Wayne–Kerr universal bridge B221. Chloroform, although not ideal for conductivity measurements, was found to be the most suitable solvent. A typical result for [Ni(μ-B_5H_8)Br(dppe)] at a concentration of 1×10^{-3} mol dm^{-3} was $\Lambda = 0.011$ S cm^2 mol^{-1}. Values for the non-electrolytes SnI_4 and benzoic acid under the same conditions were 0.02 and 0.015 S cm^2 mol^{-1} respectively.

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