Some Palladium(II) and Platinum(II) Derivatives of Pentaborane(9)

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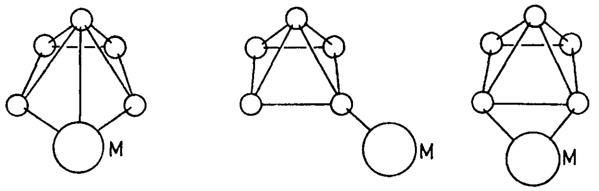
Metathesis of potassium *nido*-octahydropentaborate, $K[B_5H_8]$, with numerous *cis*-bis(phosphine) complexes of palladium(II) and platinum(II) halides affords *cis*-$[M(B_5H_8)(PR_3)_2X]$ in good yields (X = Cl, Br, I, or Me; PR_3 = PPh_3, PMe_2Ph, PMe_3, or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$). The platinum complexes are more stable than those of palladium and can be stored unchanged for long periods at room temperature. Similar reactions with appropriate starting materials lead to *cis*-$[Pt(B_5H_8)Cl(AsPh_3)_2]$, *cis*-$[\{Pt(B_5H_8)(PMe_2Ph)(\mu\text{-SMe})\}_2]$, and the less-stable *trans*-$[Pt(B_5H_8)I(PMe_2Ph)_2]$ and *trans*-$[Pt(B_5H_8)Me(PMe_2Ph)_2]$. In all cases the B_5H_8 ligand is η^2-bonded to the metal *via* two of the basal boron atoms B(2) and B(3). Hydrogen-1, ^{11}B, ^{31}P, and ^{195}Pt n.m.r. data for the *cis* complexes are discussed in terms of the detailed geometrical structure and the nature of the metal–borane bonding.

RECENT research has shown that pentaborane(9) and its simple derivatives can react with a variety of transition-metal complexes to form metalloboranes.[1-13] In some cases the reactions are accompanied by partial degradation of the borane moiety to produce complexes with four or fewer boron atoms in the metal–borane cluster,[1,2] but generally metal–pentaborane species result. In these, apart from an isolated example in which the metal atom inserts into the borane cage to form a metallahexaborane [structure (1), Figure 1],[3] the pentaborane moiety typically acts as a ligand which may be either σ or η^2 in character [structures (2) and (3), Figure 1]. In the complexes of iridium(I),[4,5] manganese(I),[6] rhenium(I),[6] and iron(II) [7] so far reported the metal–borane bonding is 2-σ, whereas for cadmium(II),[8] copper(I),[9-11] silver(I),[11] and nickel(II) [12] it is 2—3-η^2 (μ-bonded). In the copper, cadmium, and silver complexes the metal atom bridges two adjacent boron atoms in a structure which is static on the ^{11}B n.m.r. time scale, whereas for the nickel compounds the available evidence has been interpreted to suggest that the μ-bonded metal groups and the bridging hydrogen atoms undergo rapid interchange.[12] The possibility of forming analogous complexes of palladium and platinum is therefore clearly of interest, and here we report their preparation and properties. The platinum complexes are of particular interest because their n.m.r. properties (involving ^1H, ^{11}B, ^{31}P, and ^{195}Pt nuclei) give added insight into the nature of the metal–borane bond; previous gauges of relative chemical effects of borane ligands have generally been limited to comparisons of Brønsted acidities and of bond lengths obtained from diffraction experiments. A preliminary account of some of this work was presented at a recent conference.[14]



(1) (2) (3)

FIGURE 1 Structural types in metallopentaborane chemistry (hydrogen atoms omitted for clarity): (1) metallahexaborane; (2) 2-σ metallopentaborane; (3) 2—3-η^2 metallopentaborane

RESULTS AND DISCUSSION

The reaction of potassium *nido*-octahydropentaborate with *cis*-bis(phosphine) complexes of palladium(II) or platinum(II) dihalides in equimolar amounts at low temperature in tetrahydrofuran–dichloromethane resulted in the displacement of one halide ion by $[B_5H_8]^-$ in high yield according to equation (1). In general the

$$K[B_5H_8] + [MX_2L_2] \longrightarrow [M(B_5H_8)XL_2] + KX \quad (1)$$

resulting *cis*-halogeno(2—3-η^2-octahydropentaborato)-bis(phosphine)metal(II) complexes are beige or white solids, m.p. (decomp.) > 170 °C, soluble in chlorinated hydrocarbons and polyethers, but insoluble in acyclic monoethers and saturated hydrocarbons. The reaction occurred for a variety of phosphine ligands (Table 1), although under the conditions used reactions involving methyldiphenylphosphine, $PMePh_2$, as ligand resulted in decomposition rather than metalloborane formation. The generality of the reaction was further demonstrated by its applicability to *cis*-$[PtCl(Me)(PMe_2Ph)_2]$, *cis*-$[PtCl_2(AsPh_3)_2]$, and *cis*-$[\{PtCl(PMe_2Ph)(\mu\text{-SMe})\}_2]$ to give *cis*-$[Pt(B_5H_8)Me(PMe_2Ph)_2]$, *cis*-$[Pt(B_5H_8)Cl(AsPh_3)_2]$, and *cis*-$[\{Pt(B_5H_8)(PMe_2Ph)(\mu\text{-SMe})\}_2]$ respectively; it may also be noted that preliminary experiments have shown that the analogous *trans*-bis(phosphine) complexes may in some cases be prepared although they are much less stable than the *cis* complexes. Analytical data for the new complexes are in Table 1.

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[1] N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison, and S. S. Wreford, *J.C.S. Chem. Comm.*, 1974, 718.

[2] V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 1973, **95**, 5078.

[3] T. P. Fehlner, J. Ragaini, M. Mangion, and S. G. Shore, *J. Amer. Chem. Soc.*, 1976, **98**, 7085.

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[7] N. N. Greenwood, J. D. Kennedy, C. G. Savory, J. Staves, and K. R. Trigwell, *J.C.S. Dalton*, 1978, 237.

[8] N. N. Greenwood and J. Staves, *J.C.S. Dalton*, 1977, 1786.

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

[10] N. N. Greenwood, J. A. Howard, and W. S. McDonald, *J.C.S. Dalton*, 1976, 1977.

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

[12] N. N. Greenwood and J. Staves, *J.C.S. Dalton*, 1977, 1788.

[13] For a review on earlier work on metalloboranes, see N. N. Greenwood and I. M. Ward, *Chem. Soc. Rev.*, 1974, **3**, 231.

[14] N. N. Greenwood, Third International Meeting on Boron Chemistry, Ettal, Federal Republic of Germany, July 1976 (see N. N. Greenwood, *Pure Appl. Chem.*, 1977, **49**, 791).

In the solid state the complexes are indefinitely stable under dry nitrogen at −15 °C, but slowly decompose in solution at room temperature. The qualitative order of stability appears to be Pd < Pt and PMe_3 < PMe_2Ph < $AsPh_3$ ~ PPh_3 ~ $Ph_2PCH_2CH_2PPh_2$ (dppe). For example, a sample of $[Pt(B_5H_8)Cl(dppe)]$ was unchanged after storage in air in a simple stoppered tube for 6 months, but under similar conditions the palladium analogue showed extensive decomposition after only 1 month; in dichloromethane solution under nitrogen at room temperature the platinum complex was unchanged after 3 d whereas under the same conditions decomposition of the corresponding palladium complex was complete in 6 h. The solids were not immediately attacked by cold water or by ethanol, but treatment of representative complexes with hydrogen chloride in diethyl ether resulted in the generation of pentaborane(9) in 40—70% yield [equation (2)].

$$[M(B_5H_8)XL_2] + HCl \longrightarrow [MCl(X)L_2] + B_5H_9 \quad (2)$$

TABLE 1

Analytical data in wt. % (calculated values in parentheses)

Complex	C	H	B	Halogen	P or As
$[Pd(B_5H_8)Cl(dppe)]$	52.0 (51.9)	5.2 (5.4)	8.5 (9.0)	5.7 (5.9)	10.0 (10.3)
cis-$[Pd(B_5H_8)Cl(PPh_3)_2]$	59.1 (59.4)	5.3 (5.3)	7.4 (7.4)	4.8 (4.9)	8.2 (8.5)
cis-$[Pd(B_5H_8)Cl(PMe_2Ph)_2]$	39.5 (40.0)	6.4 (6.3)	11.0 (11.3)	7.0 (7.4)	12.8 (12.9)
$[Pt(B_5H_8)Cl(dppe)]$	45.0 (45.2)	4.7 (4.7)	8.1 (7.8)	5.0 (5.1)	8.7 (9.0)
cis-$[Pt(B_5H_8)Cl(PPh_3)_2]$	53.2 (52.9)	4.8 (4.7)	6.2 (6.6)	4.5 (4.3)	7.8 (7.6)
cis-$[Pt(B_5H_8)Cl(PMe_2Ph)_2]$ [a]	33.2 (33.8)	5.8 (5.3)	9.3 (9.5)	6.0 (6.2)	10.6 (10.9)
cis-$[Pt(B_5H_8)Cl(PMe_3)_2]$	16.4 (16.2)	5.6 (5.9)	11.8 (12.1)	7.5 (8.0)	13.7 (13.9)
$[Pt(B_5H_8)Br(dppe)]$	42.7 (42.5)	4.6 (4.4)	7.7 (7.4)	11.1 (10.9)	8.4 (8.4)
cis-$[Pt(B_5H_8)Br(PPh_3)_2]$	48.9 (50.2)	4.2 (4.4)	6.1 (6.3)	10.0 (9.3)	7.3 (7.2)
cis-$[Pt(B_5H_8)Br(PMe_2Ph)_2]$	31.6 (31.3)	5.3 (4.9)	8.8 (8.8)	13.6 (13.0)	10.6 (10.1)
$[Pt(B_5H_8)I(dppe)]$	39.2 (39.9)	4.0 (4.1)	6.8 (6.9)	16.7 (16.2)	7.7 (7.9)
cis-$[Pt(B_5H_8)I(PPh_3)_2]$	46.1 (47.6)	4.1 (4.2)	6.3 (5.95)	13.5 (14.0)	6.6 (6.8)
cis-$[Pt(B_5H_8)I(PMe_2Ph)_2]$	29.3 (29.1)	4.8 (4.6)	7.7 (8.2)	19.0 (19.2)	9.4 (9.4)
cis-$[Pt(B_5H_8)Me(PMe_2Ph)_2]$	38.0 (37.2)	6.3 (6.1)	9.1 (9.8)		11.3 (11.3)
cis-$[Pt(B_5H_8)Cl(AsPh_3)_2]$	46.3 (47.8)	4.7 (4.2)	6.3 (6.0)	4.3 (3.9)	15.9 (16.6)
trans-$[Pt(B_5H_8)I(PMe_2Ph)_2]$	28.6 (29.1)	5.1 (4.6)	8.0 (8.2)	18.8 (19.2)	9.5 (9.4)
trans-$[Pt(B_5H_8)Me(PMe_2Ph)_2]$	38.1 (37.2)	6.0 (6.1)	9.6 (9.8)		11.3 (11.3)
cis-$[\{Pt(B_5H_8)(PMe_2Ph)(\mu\text{-}SMe)\}_2]$	24.3 (24.4)	5.2 (5.0)	11.8 (12.2)	7.4 (7.25) [b]	7.1 (7.0)

[a] Pt, 33.7 (34.3%). [b] Refers to sulphur.

TABLE 2

Boron-11 and ^{31}P chemical shifts (δ/p.p.m.) and coupling constants (*J*/Hz) in dichloromethane solutions

	$\delta(^{11}B)$ [a]		$^1J(^{11}B-^1H)$ [b]	$\delta(^{31}P)$ [c]		$^1J(^{195}Pt-^{31}P)$ [d]		
Complex	basal	apical	(apical)	*cis* to B_5H_8	*trans* to B_5H_8	*cis* to B_5H_8	*trans* to B_5H_8	$^2J(^{31}P-^{31}P)$ [d]
$[Pd(B_5H_8)Cl(dppe)]$	−12.5 [e]	−47.6	160	−97.6	−84.5			*f*
cis-$[Pd(B_5H_8)Cl(PPh_3)_2]$	−13.0 [e]	−46.1	165	−117.0	−112.0			*f*
cis-$[Pd(B_5H_8)Cl(PMe_2Ph)_2]$	−13.2 [e]	−45.7	150	−145.0	−134.8			*f*
$[Pt(B_5H_8)Cl(dppe)]$	−12.1 [g]	−44.1	160	−97.3	−82.0	3 780	1 430	*ca.* 0
cis-$[Pt(B_5H_8)Cl(PPh_3)_2]$	−12.9 [g]	−46.4	160	−120.8	−109.1	3 993	2 325	20
cis-$[Pt(B_5H_8)Cl(PMe_2Ph)_2]$ [h]	−11.6 [g]	−45.1	160	−152.0	−137.0	3 714	2 341	15
cis-$[Pt(B_5H_8)Cl(PMe_3)_2]$	−15.5 [g]	−51.0	155	−161.0	−155.0	3 200	2 400	10
$[Pt(B_5H_8)Br(dppe)]$	−13.6 [g]	−46.1	160	−93.1	−86.3	3 672	2 412	*ca.* 0
cis-$[Pt(B_5H_8)Br(PPh_3)_2]$	−14.3 [g]	−48.3	155	−120.0	−112.0	3 860	2 328	15
cis-$[Pt(B_5H_8)Br(PMe_2Ph)_2]$	−15.0 [g]	−49.1	155	−148.0	−144.0	3 658	2 411	10
$[Pt(B_5H_8)I(dppe)]$	−12.6 [g]	−47.8	155	−92.7	−88.0	3 540	2 420	*ca.* 0
cis-$[Pt(B_5H_8)I(PPh_3)_2]$	−12.3 [g]	−49.0	160	−122.3	−118.0	3 695	2 351	10
cis-$[Pt(B_5H_8)I(PMe_2Ph)_2]$	−14.7 [g]	−50.0	155	−148.0	−145.0	3 565	2 405	15
cis-$[Pt(B_5H_8)Me(PMe_2Ph)_2]$	−14.3 [g]	−48.3	150	−144.0	−140.1	1 915	2 510	10
cis-$[Pt(B_5H_8)Cl(AsPh_3)_2]$	−13.8 [g]	−46.3	*ca.* 140					
trans-$[Pt(B_5H_8)I(PMe_2Ph)_2]$	−14.5 [g]	−47.1	150	−151.1		2 575		*f*
trans-$[Pt(B_5H_8)Me(PMe_2Ph)_2]$	−12.8 [g]	−48.8	160	−148.5		3 075		*f*
cis-$[\{Pt(B_5H_8)(PMe_2Ph)(\mu\text{-}SMe)\}_2]$	−15.1 [g]	−49.1	160	−145.9		3 086		

[a] To high frequency (low field) of $[BF_3(OEt_2)]$; ±0.3 p.p.m. [b] ±10 Hz. [c] To high frequency (low field) of $P(OMe)_3$; ±0.2 p.p.m.; in each case the resonance designated *trans* to B_5H_8 was significantly the broader (*e.g.* Figure 2). [d] ±5 Hz. [e] Broad doublets; apparent splitting *ca.* 140 Hz (see Figure 6). [f] Not measured. [g] Broad singlet (see Figure 6). [h] $\Xi(^{195}Pt)$ 21 400 780 ± 100 Hz.

Molecular-weight and conductivity data on representative complexes showed that they were monomeric non-ionic species in chloroform solution. The complexes with dppe as ligand must obviously retain *cis* stereochemistry about the metal atom and this also held for the other ligands as indicated by the $^{31}P-\{^1H\}$ n.m.r. spectra (Table 2). These typically showed two chemical environments for the phosphorus nuclei (see, for example, Figure 2) as required by the *cis* configuration, and the small magnitudes of the coupling constants $^2J(^{31}P-M-^{31}P)$ of <*ca.* 15 Hz also confirmed the *cis* stereochemistry.[15] In each case the resonance lines for the phosphorus nuclei in one environment were noticeably broader than those for the other. This selective broadening was

[15] A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 1826.

probably due either to incompletely resolved coupling with the ^{10}B and ^{11}B nuclei in the molecule or to a rapid quadrupole-induced relaxation of the ^{31}P nucleus resulting from such coupling. These effects will be larger when the coupling path is *trans* rather than *cis*, and therefore the broader resonance may reasonably be ascribed to the nucleus of the phosphorus atom *trans* to the pentaborane moiety. For the platinum complexes the main resonance lines in the ^{31}P spectra were flanked by additional lines (' satellites ') due to coupling $^1J(^{195}Pt-^{31}P)$ (natural abundance of ^{195}Pt, 33.7%) (*e.g.* Figure 2) and the behaviour of this coupling (see below) is also consistent with this ascription.

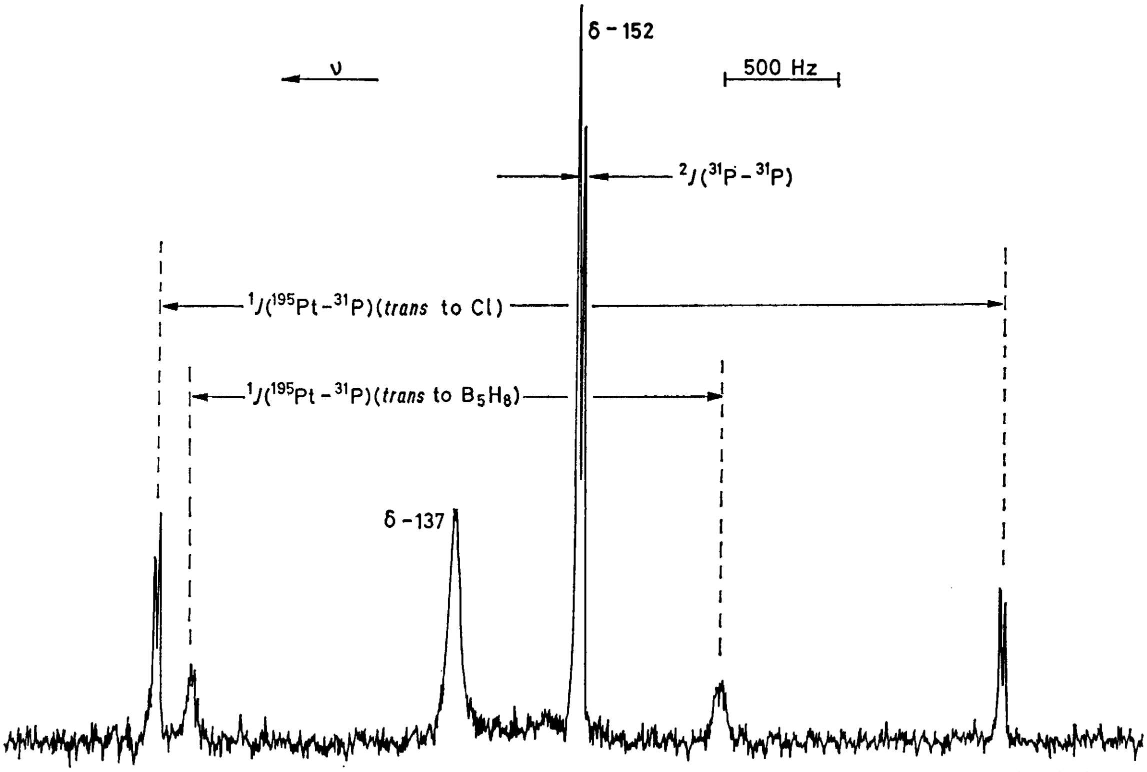

FIGURE 2 36.4-MHz $^{31}P-\{^1H(\text{broad band})\}$ n.m.r. spectrum of *cis*-$[Pt(B_5H_8)Cl(PMe_2Ph)_2]$ in CD_2Cl_2 solution

The solid-state i.r. spectra of these *cis* complexes (see, for example, Figure 3) were all similar and in general showed fine structure in the ν(B–H) region around 2 500 cm^{-1} which, however, was not apparent in the solution spectra. This behaviour is similar to that [16] of $[Cu(B_5H_8)(PPh_3)_2]$ which, both in the solid state [10] and in solution,[9] has the static structure (3) (Figure 1) in which the metal atom bridges the B(2) and B(3) atoms of the pentaborane cluster. These i.r. data suggest that the palladium and platinum complexes discussed here may also have this structure. That this is indeed so is evident from the $^1H-\{^{11}B\}$ n.m.r. spectra of the representative complex $[Pt(B_5H_8)Cl(PPh_3)_2]$ (Figure 4), in which the basal and apical proton-resonance assignments were confirmed by selective $^1H-\{^{11}B\}$ decoupling experiments: the 2 : 2 intensity ratio for the basal-terminal proton resonances and the *ca.* 2 : 1 ratio for the bridging protons clearly establish the static μ-2,3 bridging structure (3).

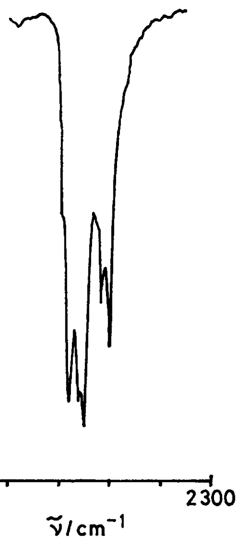

FIGURE 3 ν(B–H) region of the solid-state i.r. spectrum of *cis*-$[Pt(B_5H_8)Cl(dppe)]$ (KBr disc) exhibiting strong peaks at 2 580, 2 560, 2 550, 2 520, and 2 500 cm^{-1}. The spectrum of a solution in CH_2Cl_2 shows loss of fine structure to give two broader peaks with $\nu_{max.}$ at 2 560 and 2 520 cm^{-1}

The triplet form of the basal-terminal proton resonance at δ 3.4 p.p.m. may result from coupling with the ^{195}Pt nuclei $[|^2J(^{195}Pt-B-^1H)|$ *ca.* 75 Hz$]$; if this is so then the static solution structure is further confirmed and the triplet resonance may be assigned to the terminal protons

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[16] G. G. Outterson, jun., V. T. Brice, and S. G. Shore, *Inorg. Chem.*, 1976, **15**, 1456.

on the B(2) and B(3) atoms of the pentaborane skeleton. It is probable that this is the structure for all the palladium and platinum pentaborates reported here, but confirmation of this is hindered by the presence of overlapping *P*-alkyl resonances in the ^{1}H n.m.r. spectra.

The orientation of the pentaborate ligand with respect to the square-planar metal environment in these complexes cannot be determined from present evidence, but a structural analogy with the trigonal copper(I) complex, $[Cu(B_5H_8)(PPh_3)_2]$,[10] would predict that the B(2)–B(3) vector will be perpendicular to the square plane, and that the metal atom will lie in the same plane as the B(1)–B(2)–B(3) face (Figure 5). This implies two possible isomers, in which the 4 and 5 positions of the borane skeleton may be either *syn* [structure (4a)] or *anti* [structure (4b)] to the halogen atom X; examination of models based on reasonable estimates of interatomic distances and angles suggests that the steric requirements of the bulky phosphine groups would dictate the *syn* stereochemistry (4a).

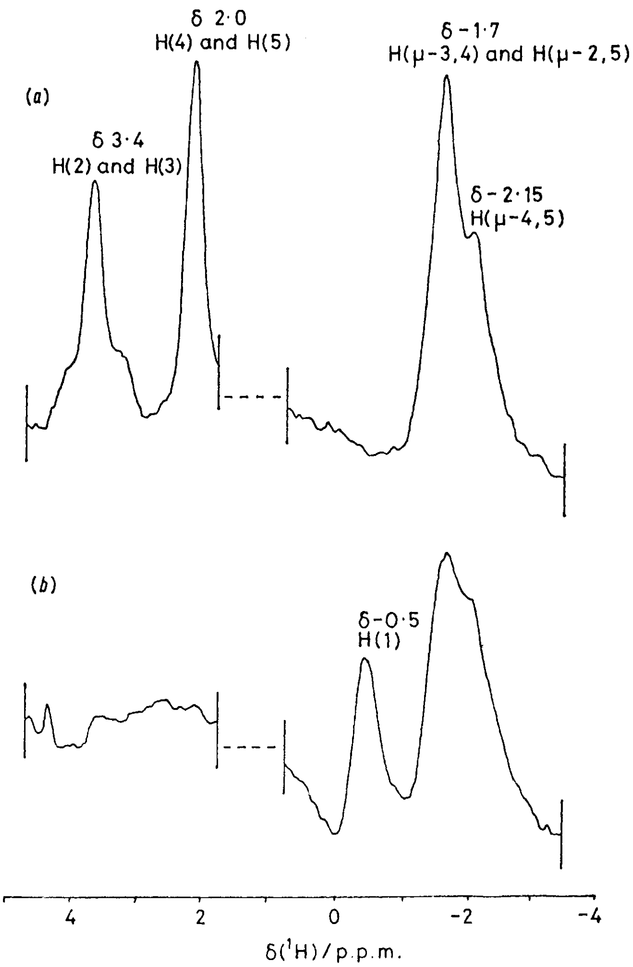
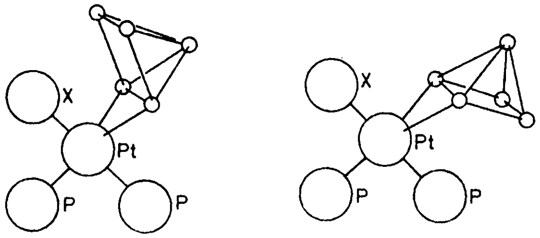


FIGURE 4 Borane region of the 100-MHz ^{1}H n.m.r. spectrum of *cis*-$[Pt(B_5H_8)Cl(PPh_3)_2]$ with simultaneous irradiation at the resonance frequency of the ^{11}B nuclei of the basal-boron atoms B(2)—B(5) (*a*) and the apical boron atom B(1) (*b*). (*a*) shows selective collapse of the multiplets due to the basal terminal protons, and sharpening of the (basal) bridging proton resonances; (*b*) shows selective sharpening of the apical proton resonance



(4a) (4b)

FIGURE 5 Possible isomers of *cis*-$[Pt(\mu\text{-}2,3\text{-}B_5H_8)(PPh_3)_2X]$ with hydrogen atoms and substituents on phosphorus omitted for clarity. Structure (4a) has the basal B(4) and B(5) atoms *syn* to the halogen atom X, and (4b) has the B(4) and B(5) atoms *anti* to the halogen atom

The ^{11}B n.m.r. behaviour of these platinum and palladium pentaborates merits comment; the data are summarized in Table 2, and the spectra of $[Pd(B_5H_8)Cl(PPh_3)_2]$ and $[Pt(B_5H_8)Cl(PPh_3)_2]$ as typical examples are given in Figure 6, together with that of the nickel analogue $[Ni(B_5H_8)Br(dppe)]$ [12] for comparison. In each case ^{11}B-{^{1}H} double-resonance experiments confirmed that the doublet structure where exhibited was due to coupling [$^1J(^{11}B-^1H)$] with adjacent protons, and the high-field and low-field resonances are reasonably ascribed to the apical [B(1)] and basal [B(2)–B(5)] boron atoms respectively. The basal-boron resonances in the platinum complexes remained unaffected in proton-decoupling experiments, and broadened considerably as the temperature was decreased. The basal-boron resonance for the palladium complexes also broadened with decreasing temperature: at −30 °C the doublet structure was lost and the spectra resembled those of the platinum complexes recorded at ambient temperatures (Figure 6). Similarly, the basal-boron resonances for the nickel complexes are known to be broader at lower temperatures,[12] and at −30 °C the spectra resemble those of the palladium complexes at ambient temperatures (Figure 6).

In the nickel complexes this behaviour was tentatively ascribed to a rapid interchange between the halogenobis(phosphine)nickel moiety and the bridging hydrogen atoms.[12] However, the static structure evident from the ^{1}H n.m.r. spectrum (Figure 4) clearly vitiates this rationalization in the case of the platinum analogues, and for the complexes reported here the observed broadening at lower temperatures may therefore result from the more efficient quadrupolar relaxation of the basal ^{11}B nuclei. This implies that the relaxation efficiency increases in the order Ni < Pd < Pt for an isostructural series, but why this should be so is not clear since it is unlikely that the differences in electric-field gradients (e.f.g.s) across the basal-boron nuclei as the metal atom is changed will be sufficiently large to account for the observed changes in behaviour. These may therefore arise from substantial increases in the molecular-reorientation correlation time in the order Ni < Pd < Pt, which could result either from an increasing solute–solvent (or solute–solute) interaction in the same order, or more probably from the effect of the molecular inertial moment which will also increase in the order Ni $<$ Pd $<$ Pt. At present, however, it is not possible to distinguish between these two mechanisms since a thorough assessment of the latter requires a knowledge of the individual components both of the e.f.g. tensors at the boron nuclei and of the molecular rotational-diffusion tensors.[17] Similar relaxation behaviour was observed for the B(2)–B(3)-bridged metalloborane $[Cu(B_5H_8)(PPh_3)_2]$ and ascribed there to the influence of the quadrupolar relaxation of the adjacent ^{63}Cu and ^{65}Cu nuclei (spin quantum number $I = \frac{3}{2}$);[9] however, this mechanism cannot apply to the complexes of Ni, Pd, and Pt discussed here.

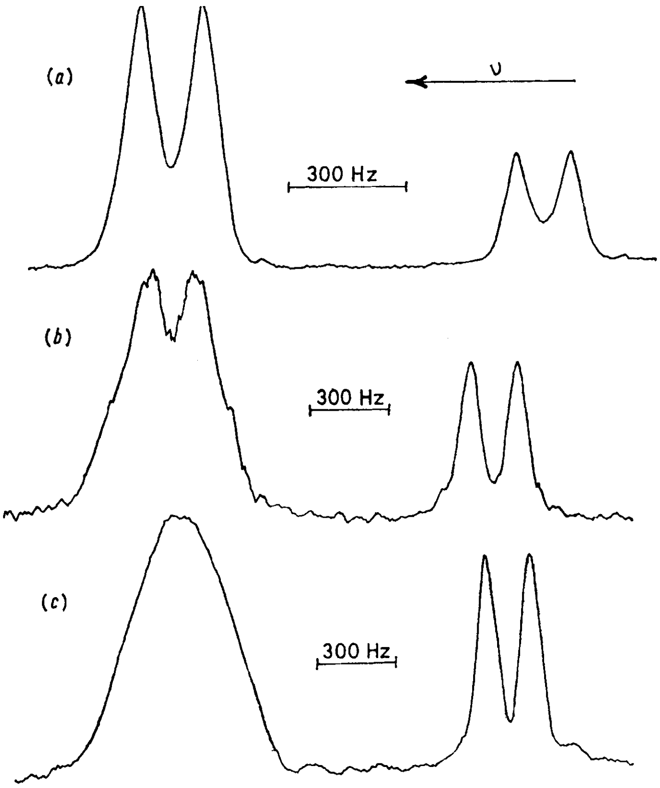


FIGURE 6 28.9-MHz Boron-11 n.m.r. spectra of (*a*) $[Ni(B_5H_8)Br(dppe)]$, (*b*) $[Pd(B_5H_8)Cl(PPh_3)_2]$, and (*c*) $[Pt(B_5H_8)Cl(PPh_3)_2]$. On cooling, the resonances at lower field broadened considerably as described in the text. The spectrum of the nickel complex is taken from the work described in ref. 12, and the horizontal scale is greater than that of the other two spectra

As mentioned above, the ^{31}P n.m.r. spectra of the platinum complexes show the effect of coupling to the ^{195}Pt nucleus: observed values of the coupling constant $^1J(^{195}Pt-^{31}P)$ are given in Table 2, and it can be seen that there is a significant difference in this coupling constant according to whether the phosphine is *cis* or *trans* to the pentaborane moiety (*i.e.* respectively *trans* and *cis* to the halogen atom). Platinum–phosphorus coupling constants are often interpreted in terms of a mean excitation-energy approximation[18,19] in which the magnitude of the coupling constant is proportional to, *inter alia*, the amount of *s* character in the Pt–P bond. In the square-planar sp^3d hybridization framework the two orthogonal pairs of bonding orbitals behave to a certain extent independently. Thus, to a first approximation, if the electronegativity of a group *trans* to a phosphorus atom is increased the amount of Pt *s* character in the Pt–P bond is increased at the expense of *p* and *d* character thereby resulting in a larger value of $^1J(^{195}Pt-^{31}P)$.[19] In Table 3 the values of $^1J(^{195}Pt-^{31}P)$ for *cis*-$[Pt(B_5H_8)Cl(PMe_2Ph)_2]$ are compared to those for other relevant *cis*-bis(dimethylphenylphosphine)platinum(II) complexes, and it can be seen that the effect of various ligands in increasing the magnitude of the *trans* Pt–P coupling constants is in the order Me $\leqslant$ B_5H_8 $<$ I $<$ Br $<$ Cl, indicating that the electronegativity of the $[\mu\text{-}2,3\text{-}B_5H_8]^-$ moiety, measured in terms of σ-electron demand, decreases in the sequence Cl $>$ Br $>$ I $>$ B_5H_8 $\geqslant$ Me. This conclusion may be compared to that of ref. 5, in which metal–phosphorus bond-length measurements show that the *trans* effect of a $[\sigma\text{-}2\text{-}B_5H_8]^-$ moiety is similar to that of a σ-bonded alkyl carbon atom. It is clear that n.m.r. measurements of this type offer a convenient and delicate probe into the nature of metal–borane bonding.

For the complexes with ligands containing *P*-methyl groups the ^1H n.m.r. spectra exhibited two doublets for the methyl protons, consistent with the *cis* stereochemistry. The complex $[Pt(B_5H_8)Cl(PMe_2Ph)_2]$ was sufficiently soluble in dichloromethane for the ^{195}Pt satellites $[^3J(^{195}Pt-^1H)$ +21.0 and +35.5 Hz] of these doublets [1.48, $^2J(^{31}P-^1H)$ −9.6; δ 1.53 p.p.m., $^2J(^{31}P-^1H)$ −10.8 Hz respectively] to be observable at adequate signal-to-noise ratios for satisfactory $^1H-\{^{31}P\}$ and $^1H-\{^{195}Pt\}$ selective double-resonance experiments to be performed.[20] The relative signs of various coupling constants involving ^{195}Pt, ^{31}P, and ^1H thus obtained were also as expected for the proposed stereochemistry,[21] and in addition the ^{195}Pt resonance frequency, $\Xi(^{195}Pt)$, was found to be 21 400 780 ± 100 Hz. The platinum resonance exhibited no apparent fine structure and was several hundred hertz broad, presumably due to the effect of the adjacent boron nuclear quadrupoles. It was at 28 p.p.m. to low frequency of the value measured for *cis*-$[PtCl(Me)(PMe_2Ph)_2]$ and at 90 p.p.m. to high frequency of that for *cis*-$[PtCl_2(PMe_2Ph)_2]$ (Table 3).[20] This indicates that there is no significant deviation from the square-planar bonding configuration at the platinum atom since it is known that incorporation of a ^{195}Pt nucleus into a constrained small-ring system produces fluctuations of several hundred p.p.m. in the ^{195}Pt chemical shift.[20] This may therefore imply an electronic structure in which the platinum bonding electrons are directed towards the

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[17] See, for example, A. Allerhand, A. O. Clause, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, 1972, **94**, 2445 and refs. therein.

[18] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[19] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.

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[21] J. D. Kennedy, W. McFarlane, and R. J. Puddephatt, *J.C.S. Dalton*, 1976, 745 and refs. therein.

centre of the B(2)–B(3) vector in a three-centre bond, rather than one involving three two-centre bonds in a diboraplatinacyclopropane system, although such conclusions are necessarily tentative at present.

The platinum and palladium complexes reported here are further examples of 16-electron transition-metal pentaborane species with a μ-2,3-bonded structure (2), which is characteristic of all the 16-electron species so far reported.[8-12] All the 18-electron transition-metal species have the σ-2-bonded structure (3),[4-7] and it is therefore tempting [7] to ascribe the bridging structure (2) to the mitigation of the electron deficiency of the metal atom in the 16-electron complexes. However, the limited comparison that can now be made between the n.m.r. evidence discussed above and the evidence available from bond-length measurements suggests that the electronic requirements of the two structures may in fact be quite similar. Stereochemical non-bonded interactions may therefore play a part in determining the structures to be adopted, and it may be relevant in this respect that the 18-electron σ-bonded species so far reported all have high metal co-ordination numbers.

TABLE 3

Phosphorus-31 and ^{195}Pt n.m.r. data for complexes *cis*-$[Pt(PMe_2Ph)_2X(Y)]$

		$^1J(^{195}Pt-^{31}P)$ [a]				
X	Y	*trans* to X	*trans* to Y	$\Xi(^{195}Pt)$ [b]	$\delta(^{195}Pt)$ [c]	Notes
Cl	Cl	3 548	3 548	21 402 710 ± 15	90	*d*
B_5H_8	Cl	2 341	3 714	21 400 780 ± 150	0	*e*
Me	Cl	1 730	4 250	21 400 185 ± 150	−28	*d*
Me	Me	1 820	1 820	21 398 645 ± 70	−100	*d*
B_5H_8	Me	2 510	1 915	*f*	*f*	*e*
B_5H_8	Br	2 411	3 658	*f*	*f*	*e*
B_5H_8	I	2 405	3 565	*f*	*f*	*e*
I	I	3 364	3 364	21 386 800 ± 150	−653	*d*

[a] ±5 Hz. The resonance frequency in Hz corrected to a field strength in which the $SiMe_4$ protons resonate at exactly 100 MHz. [c] In p.p.m. to high frequency (low field) of *cis*-$[Pt(B_5H_8)Cl(PMe_2Ph)_2]$. [d] From ref. 20. [e] This work. [f] Not measured.

EXPERIMENTAL

General.—All the operations were carried out under rigorously anaerobic conditions using standard vacuum-line, Schlenk, and glove-box techniques. Pentaborane(9) was obtained by courtesy of Dr. R. E. Williams (Chemical Systems Inc., California) and samples of some of the platinum starting complexes were kindly donated by Dr. R. J. Puddephatt. Other palladium and platinum starting materials were made by literature methods,[22-25] the bromides and the iodides by refluxing the appropriate chloride with sodium bromide or iodide in acetone–dichloromethane solution. Commercially obtained potassium hydride was freed from mineral oil by washing with pentane before use.

Preparation of Complexes.—The following preparation of *cis*-$[Pt(B_5H_8)Cl(PPh_3)_2]$ is typical. Pentaborane(9) (5.2 mmol) and tetrahydrofuran (thf) (10 cm^3) were condensed at −196 °C on to potassium hydride (70% active, 0.285 g, corresponding to 5.0 mmol KH) and stirred at −60 °C for 1 h to produce $K[B_5H_8]$.[26] Dichloromethane (20 cm^3) was then condensed in at −196 °C, *cis*-$[PtCl_2(PPh_3)_2]$ (3.6 g, 4.5 mmol) was added, and the mixture stirred at −40 °C for 6 h, then at −78 °C overnight. The cold solution was filtered rapidly and the volume of the filtrate reduced to *ca.* 15 cm^3 at −40 °C under reduced pressure. The solution was stirred vigorously at −78 °C whilst pentane (*ca.* 60 cm^3) was condensed in to precipitate the product $[Pt(B_5H_8)Cl(PPh_3)_2]$. This was filtered off at *ca.* −40 °C, washed with cold diethyl ether (3 × 5 cm^3), and dried for 12 h *in vacuo*, yielding a white *solid* (2.5 g, 3.0 mmol, 60% yield), m.p. (decomp.) *ca.* 170 °C. Analytical data for this and the other metallopentaboranes prepared are given in Table 1.

Regeneration of Pentaborane(9).—Diethyl ether (5 cm^3) and anhydrous hydrogen chloride (3 cm^3, *ca.* 100 mmol) were condensed on to *cis*-$[Pt(B_5H_8)Cl(PPh_3)_2]$ (0.4 g, 0.5 mmol) at −196 °C and the mixture was stirred at −30 °C for 6 h. Fractionation of the volatile components through a series of cold traps yielded pentaborane(9) in 70% yield. Similar treatment of a number of other palladium and platinum derivatives led to the recovery of pentaborane in yields of 50—60%.

Infrared Spectra.—These were recorded on a Perkin-Elmer 457 grating spectrometer, and calibrated using a polystyrene film; errors in the quoted band maxima are ±5 cm^{-1}. The spectra of complexes in the solid state were recorded from KBr discs or from Nujol mulls between KBr plates. Solution spectra were recorded for 0.01 mol dm^{-3} solutions in dichloromethane using a path length of 0.02 dm and a cell with KBr windows.

N.M.R. Spectra.—90-MHz Hydrogen-1, 36.4-MHz $^{31}P-\{^1H\}$, and 28.9-MHz ^{11}B and $^{11}B-\{^1H\}$ spectra were recorded on a Bruker HFX4 spectrometer modified for Fourier transform with a Bruker BNC12 Datasystem, and using saturated solutions in $CDCl_3$, CD_2Cl_2, or C_6D_6 at ambient temperature; 60-MHz $^1H-\{^{31}P\}$ and $^1H-\{^{195}Pt\}$ experiments were carried out as described elsewhere,[20,21] on a modified JEOL C-60H instrument with the kind permission of Dr. W. McFarlane. The 100-MHz $^1H-\{^{11}B\}$ spectra of $[Pt(B_5H_8)Cl(PPh_3)_2]$ were obtained for a solution in CD_2Cl_2 using a JEOL FX-100 instrument with the co-operation of Dr. P. Beynon. The results are discussed in the text and/or are given in Table 2. Chemical shifts are quoted to high frequency (low field) of the reference standards which are tetramethylsilane for ^1H, $P(OMe)_3$ for ^{31}P, and $[BF_3(OEt_2)]$ for ^{11}B. A reference standard for ^{195}Pt chemical shifts has not yet been agreed upon, and so the resonance positions are quoted as frequencies Ξ which have been corrected to a field strength at which the protons in $SiMe_4$ resonate at exactly 100 MHz.

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Conductivity Measurements.—The conductances of solutions of the metalloboranes were measured using a conventional cell immersed in a constant-temperature bath and a Wayne–Kerr Universal Bridge B221. Λ for [Pt(B_5H_8)Cl(dppe)$_2$] at a concentration of 10^{-3} mol dm^{-3} in chloroform was found to be 0.015 S cm^2 mol^{-1}, and the corresponding value for *cis*-[Pt(B_5H_8)Cl(PPh_3)$_2$] was 0.021 S cm^2 mol^{-1}. At the same dilution in chloroform Λ for the two non-electrolytes benzoic acid and tin(IV) iodide was found to be 0.015 and 0.02 S cm^2 mol^{-1} respectively.

Molecular-weight Determinations.—These were carried out using an isopiestic apparatus of standard design. Chloroform solutions of [Pt(B_5H_8)Cl(dppe)$_2$] and *cis*-[Pt(B_5H_8)Cl(PPh_3)$_2$] gave values of 651 (calc. 691) and 791 (calc. 817) respectively.

We thank the S.R.C. for the award of a maintenance grant (to J. S.).

[7/1639 *Received*, 15*th September*, 1977]