Synthesis, Molecular Structure, and Nuclear Magnetic Resonance Investigation of the Platinanonaborane and Diplatinadecaborane Cluster Compounds, $[4,4-(PMe_2Ph)_2-arachno-4-PtB_8H_{12}]$ and $[6,6,9,9-(PMe_2-Ph)_4-arachno-6,9-Pt_2B_8H_{10}]$ [†]

By Simon K. Boocock, Norman N. Greenwood,* Michael J. Hails, John D. Kennedy, and Walter S. McDonald, Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT

The reaction of *cis*-[PtCl₂(PMe₂Ph)₂] with an excess of $[B_9H_{14}]^-$ gives 4.4-bis(dimethylphenylphosphine)arachno-4-platinanonaborane, $[4,4-(PMe_2Ph)_2-4-PtB_8H_{12}]$, (I), in high yield. The pale yellow crystals are monoclinic, space group C2/c, with a = 1.9771(8), b = 1.3025(4), c = 1.9773(4) nm, $\beta = 110.99(3)^\circ$, Z = 8, and the molecular structure is that of a nine-vertex arachno-platinanonaborane in which the B₈ unit shows trihaptobonding to the metal centre. The compound is also formed in lower yield from several other polyhedral borane derivatives. The 14-vertex bis(dimethylphenylphosphine)bis- μ -(2--4- η -nido-hexaboranyl)-diplatinum(Pt-Pt), [Pt₂(B₈H₉)₂(PMe₂Ph)₂], is also formed in moderate yield from the [B₉H₁₄]⁻ reaction, and this offers the most convenient route yet established for its preparation. Treatment of (I) with KH followed by *cis*-[PtCl₂(PMe₂Ph)₂] gives the very stable diplatinum compound 6,6,9,9-tetrakis(dimethylphenylphosphine)-*arachno*-6,9-diplatinadecaborane, [6,6,9,9-(PMe₂Ph)₄-6,9-Pt₂B₈H₁₀], (II). The colourless crystals are monoclinic, space group C2/c, with a = 1.3762(3), b = 1.5105(4), c = 1.9210(3) nm, $\beta = 92.59(2)^\circ$, and Z = 4; the molecular structure is that of an *arachno*-diplatina-decaborane anion [B₁₀H₁₄]²⁻. The ¹H, ¹¹B, ³¹P, and ¹⁹⁵Pt n.m.r. behaviour of both title compounds has been investigated in detail using both single and double resonance techniques, and a number of important structural correlations emerge.

In recent years there have been a number of synthetic and structural studies in the series of arachno-ten-vertex platinum-containing cluster compounds exemplified by $[6,6,9-(PR_3)_3-6-PtB_9H_{11}],^1$ [6,6-(PMe₃)₂-6,5,9-PtC₂B₇-has been particular interest in and some dissension concerning the interpretation of these various species in terms of formal cluster electron counts. This prompts us to communicate here definitive results on a further member of this series, the interesting new diplatinadecaborane $[6,6,9,9-(PMe_2Ph)_4-6,9-Pt_2B_8H_{10}]$, (II), and also on the precursor in its synthesis, the platinanonaborane [4,4-(PMe₂Ph)₂-4-PtB₈H₁₂], (I), a compound of known type ¹ but for which no structural data have been reported; the location of, and the nature of, the 'pseudobridging ' (or ' endo-terminal ') arachno-hydrogen atoms in this latter compound are of particular theoretical interest.

This work forms part of a wider programme to investigate and interrelate structure, bonding, and important physicochemical characteristics, such as the n.m.r. behaviour, of both mono- and poly-metallaboranes using platinum as a model metal.⁶⁻¹³ Accordingly we report the results of single-crystal X-ray diffraction analyses and detailed 'multinuclear' n.m.r. investigations of compounds (I) and (II) together with methods for their syntheses in good yields.

In this paper we use the conventional I.U.P.A.C. recommended ¹⁴ numbering systems [structures (1)---(4)] for the constituent atoms of the eleven-, ten-, nine-, and eight-vertex clusters discussed. This has the disadvantage that successive addition of atoms as additional

^{† 4,4-}Bis(dimethylphenylphosphine)-*arachno*-4-platinanonaborane and 6,6,9,9-tetrakis(dimethylphenylphosphine)-*arachno*-6,9-diplatinadecaborane.



vertices to a particular cluster will in general change the numbering of other atoms in the cluster. This may temporarily confuse the reader, but the relationships will be apparent from comparisons among (la)-(4a) and (1b)—(4b).

RESULTS AND DISCUSSION

1416

I. Preparation .-- Compounds of the general formula $[L_2PtB_8H_{12}]$, where L is a tertiary phosphine ligand, have been known for some time,¹ and were initially obtained as the products of alcoholic degradation of $[6,6-L_2-9-L'-6-PtB_9H_{13}]$ [equation (1)]. We have now $[L_{2}PtB_{9}H_{13}L'] + 3ROH \longrightarrow$

$$[L_2PtB_8H_{12}] + L' + B(OR)_3 + 2H_2 \quad (1)$$

found that [(PMe₂Ph)₂(PtB₈H₁₂)] occurs in small but significant amounts in the product mixtures of many reactions, e.g. equations (2)-(4),^{15,16} but that excellent yields may be obtained by the reaction of cis-[PtCl₂-(PMe₂Ph)₂] with a two-fold excess of the arachno- $[B_9H_{14}]^-$ anion [equation (5)]. This reaction contrasts

$$\begin{aligned} \operatorname{cis-[PtCl_2(PMe_2Ph)_2]} + 6,6' - (B_{10}H_{13})_2 O &\longrightarrow \\ & \operatorname{products} \quad (2) \\ \operatorname{cis-[PtCl_2(PMe_2Ph)_2]} + B_9 H_{13}(SMe_2) + \text{base} &\longrightarrow \end{aligned}$$

cis-[PtCl₂(PMe₂Ph)₂] + B₁₀H₁₂(SMe₂)₂ + base ---products (4)

$$cis-[PtCl_2(PMe_2Ph)_2] + 2[NMe_4][B_9H_{14}] \xrightarrow{1} [(PMe_2Ph)_2(PtB_8H_{12})] (85\% \text{ yield}) \quad (5)$$

to the other preparations of metallaboranes from $[B_9H_{14}]^-$ that have so far been reported, in which the cluster of nine boron atoms is generally retained in the products. Thus, reaction with [MnBr(CO)₅] resulted in ten-vertex nido-metalladecaboranes 17 although low yields of the arachno-compound [(CO)₃(MnB₈H₁₃)] were also produced; ¹⁸ this latter compound however has a completely different structure to those reported here. in that the manganese atom is bonded via three Mn-H-B bridge bonds to the 1, 3, and 8 positions [structure (4)] on the neutral B₈H₁₃ ligand.¹⁹

The reaction of $[PtCl_2(PMe_2Ph)_2]$ with $[B_9H_{14}]^-$ also yields a number of other products. Most of these are as vet unidentified, but one is the known¹² 14-vertex binuclear species $[(PMe_2Ph)_4(Pt_2B_{12}H_{18})]$; this is, in fact, obtained in reasonable yield (ca. 15%) and this route now provides the most efficient preparative method yet discovered for this interesting compound.

The mechanisms for the formation of these platinum compounds are at present unknown, but the need for an excess of $[B_9H_{14}]^-$ may imply a comproportionation to give also a decaborane species. In any event, $[B_9H_{14}]^$ is easily made 20 by the base degradation of the readily available *nido*-decaborane, $B_{10}H_{14}$ (we describe a convenient new variant of its synthesis in the Experimental section) and so reaction (5) offers a convenient high-yield synthesis of the very pale yellow crystalline compound $[(PMe_2Ph)_2(PtB_8H_{12})]$. On the basis of their spectroscopic properties compounds of this type have been

generally thought 1 to have the nine-vertex arachno-4-platina-nonaborane structure: the results of singlecrystal X-ray diffraction analysis reported below confirm this and provide more precise details of this structural type.

The compound may be regarded as being formally derived from the parent *arachno*-octaborane, B_8H_{14} ,²¹ by the replacement of the pair of endo-terminal/pseudobridging hydrogen atoms in the 3,4 and 4,5 positions [structure (4)] by the neutral Pt(PMe₂Ph)₂ moiety (see Discussion, part IV, below). This suggests that the endo-terminal hydrogen atoms in the 6,7 and 7,8 positions [structure (3)] in $[(PMe_2Ph)_2(PtB_8H_{12})]$ itself may also be similarly replaceable. This is indeed found to be the case: addition of potassium hydride to [(PMe2Ph)2- $(PtB_{8}H_{12})$] results in the evolution of hydrogen, and subsequent addition of cis-[PtCl₂(PMe₂Ph)₂] produces the novel diplatinadecaborane $[(PMe_2Ph)_4(Pt_2B_8H_{10})]$ as an air-stable solid in an isolable pure yield of 55% [equations (6) and (7)]. Interestingly, this is also found as a

$$[(PMe_{2}Ph)_{2}(PtB_{8}H_{12})] + 2KH \longrightarrow [(PMe_{2}Ph)_{2}(PtB_{8}H_{10})]^{2-} + 2K^{+} + 2H_{2} \quad (6)$$

$$[(PMe_{2}Ph)_{2}(PtB_{8}H_{10})]^{2-} + [PtCl_{2}(PMe_{2}Ph)_{2}] \longrightarrow [(PMe_{2}Ph)_{4}(Pt_{2}B_{8}H_{10})] + 2Cl^{-} \quad (7)$$

major product from the treatment of [(PMe₂Ph)₂- (PtB_8H_{12}) with alcoholic base. The pure compound is colourless and readily yielded single crystals suitable for X-ray diffraction analysis; it appears to be a particularly stable species.

II. Crystal and Molecular Structures.-The atomic co-ordinates for 4,4-bis(dimethylphenylphosphine)arachno-4-platinanonaborane, (I), are given in Table 1; selected interatomic distances are in Table 2, and angles between selected interatomic vectors in Table 3. An

Table	1
-------	---

Atomic co-ordinates for (I) with estimated standard deviations in parentheses

	x	у	z
$\mathbf{B}(1)$	0.058 3(7)	$0.093\ 7(11)$	-0.0439(6)
$\mathbf{B}(2)$	$0.118\ 7(8)$	$0.028\ 7(10)$	-0.0783(7)
$\mathbf{B}(3)$	0.079 8(8)	0.1494(11)	-0.1165(6)
Pt(4)	0.107 50(2)	$0.166\ 73(3)$	$0.065\ 08(2)$
$\mathbf{B}(\mathbf{\hat{5}})$	$0.135 \ 4(8)$	$0.024 \ 0(9)$	0.017 0(7)
$\mathbf{B}(6)$	0.2091(8)	0.031 9(12)	-0.0198(7)
$\mathbf{B}(7)$	0.1724(9)	$0.125\ 3(12)$	-0.0974(8)
$\mathbf{B}(8)$	0.1405(10)	$0.256\ 2(12)$	-0.0881(8)
$\mathbf{B}(9)$	0.070 8(8)	$0.231\ 1(11)$	$-0.046 \ 3(7)$
$\mathbf{P}(\mathbf{l})$	0.13972(16)	$0.089\ 16(23)$	0.177 03(14)
$\mathbf{P}(2)$	$0.088 \ 46(16)$	0.326 88(24)	0.104 45(15)
C(1)	0.224 1(6)	$0.132 \ 0(7)$	0.246 5(5)
C(2)	$0.232 \ 1(6)$	$0.135\ 1(8)$	0.320 1(6)
C(3)	$0.297 \ 9(7)$	$0.166\ 2(10)$	$0.371\ 3(6)$
C(4)	0.355 1(7)	0.190 8(8)	$0.349 \ 4(7)$
C(5)	0.347 7(7)	0.189 2(9)	0.276 1(8)
C(6)	0.280 3(6)	0.157 5(9)	0.224 9(6)
C(7)	0.068 4(6)	$0.105\ 2(11)$	0.216 6(6)
C(8)	0.152 6(8)	-0.050 3(9)	0.182 3(6)
C(9)	0.149 1(7)	0.368 0(9)	0.195 5(7)
C(10)	0.097 5(7)	0.440 1(9)	$0.051\ 7(7)$
C(11)	-0.0034(6)	$0.341\ 2(9)$	0.105 3(5)
C(12)	-0.055 0(7)	$0.262 \ 2(10)$	$0.072 \ 0(6)$
C(13)	$-0.126\ 2(7)$	$0.268 \ 8(12)$	$0.072 \ 3(7)$
C(14)	-0.1440(8)	$0.354 \ 9(13)$	$0.106\ 3(8)$
C(15)	-0.092 7(9)	$0.431 \ 8(12)$	$0.138\ 1(8)$
C(16)	-0.022 7(8)	0.425 2(10)	0.138 2(7)

Interatomic distances (pm) for (I) with estimated standard deviations in parentheses

(i) From th	e platinum atom		
Pt(4)-P(1)	230.6(3)	Pt(4)-P(2)	230.4(3)
Pt(4)-B(1)	223.4(12)		
Pt(4)-B(5)	224.5(14)	Pt(4)-B(9)	222.2(13)
(ii) Boron-	boron		
B(1) - B(2)	179(2)	B(1) - B(3)	179(2)
$\mathbf{B}(1) - \mathbf{B}(5)$	181(2)	$\mathbf{B}(1) - \mathbf{B}(9)$	181(2)
B(2) - B(3)	179(2)	., .,	
B(2) - B(5)	179(2)	B(3) - B(9)	181(2)
B(2) - B(6)	175(2)	B(3) - B(8)	179(2)
B(2) - B(7)	177(2)	B(3)-B(7)	176(2)
B(5) - B(6)	185(2)	B(8) - B(9)	187(3)
B(6) - B(7)	189(2)	B(7) - B(8)	185(2)
(iii) Phosp	horus-carbon		
P(1) - C(1)	182.8(9)	P(2)-C(9)	184.8(12)
P(1) - C(7)	185.4(14)	P(2) - C(10)	185.1(13)
P(1) - C(8)	183.2(12)	P(2) - C(11)	183.1(13)
(iv) Other			
C = C(Ph)	136 6	mean	140.1
	143.3(18)	C-C(Ph)	
		()	

TABLE 3

Angles (°) between interatomic vectors for (I) with estimated standard deviations in parentheses

(i) At the platir	um atom		
P(1) = Pt(4) = P(9)	95 4(1)		
P(1) - Pt(4) - B(1)	127.9(4)	P(2) - Pt(4) - B(1)	130.1(3)
P(1) - Pt(4) - B(5)	91,1(3)	P(2) - Pt(4) - B(9)	87.6(4)
P(1) - Pt(4) - B(9)	175.5(4)	$\mathbf{P}(2) - \mathbf{Pt}(4) - \mathbf{B}(5)$	170.9(4)
B(1) - Pt(4) - B(5)	47.7(4)	$\mathbf{B}(1) - \mathbf{Pt}(4) - \mathbf{B}(9)$	47.9(5)
$\mathbf{B}(5) - \mathbf{Pt}(4) - \mathbf{B}(9)$	86.3(5)		.,
(ii) Platinum-b	oron-boror	1	
Pt(4)-B(1)-B(2)	116.8(6)	Pt(4)-B(1)-B(3)	117.1(7)
Pt(4) - B(1) - B(5)	66.5(7)	Pt(4) - B(1) - B(9)	65.7(6)
Pt(4) - B(5) - B(1)	65.8(7)	Pt(4) - B(9) - B(1)	66.4(6)
Pt(4) - B(5) - B(2)	115.9(7)	Pt(4) - B(9) - B(3)	116.9(7)
Pt(4)-B(5)-B(6)	117.9(7)	Pt(4)-B(9)-B(8)	118.2(7)
(iii) Boron-bor	on-boron		
(a) range 57.0)64.9	mean 60.0	
(b) range 102	.8-116.4	mean 104.0	
does not in	clude B(6)	-B(7)-B(8) 124.0(10)	
(iv) Platinum-p	hosphorus-	carbon	

(vv) i lacinam	phoophorad		
Pt(4) - P(1) - C(1)	116.9(4)	Pt(4) - P(2) - C(9)	117.6(4)
Pt(4) - P(1) - C(7)	111.4(4)	Pt(4) - P(2) - C(10)	118.1(5)
Pt(4) - P(1) - C(8)	118.3(4)	Pt(4)-P(2)-C(11)	112.2(4)

ORTEP drawing of all located atoms is given in Figure 1. The PtB₈ unit is seen to form an open-faced nine-vertex, cluster, the six-atom open face and other gross features being similar to those found for nine-vertex arachnononaborane' species such as $B_9H_{13}(NCMe)^{22}$ and $[B_9-H_{14}]^{-,23}$ as distinct from the structures with open faces containing four or five atoms which would be expected for nido-nine-vertex species generated by formal removal of an apical or equatorial vertex from the ten-vertex bicapped square-antiprismatic structure represented ²⁴ by $[B_{10}H_{10}]^{2-}$. This confirms the arachno-nature of the cluster and the general structural predictions made ¹ when this compound type was first reported.

The atomic co-ordinates of the diplatina compound 6,6,9,9-tetrakis(dimethylphenylphosphine)-arachno-6,9-

diplatinadecaborane, (II), are given in Table 4, selected interatomic distances in Table 5, and selected angles between interatomic vectors in Table 6. An ORTEP drawing to show all atoms of the $Pt_2B_8H_{10}$ cluster is given in Figure 2. The gross structure of the metalla-



FIGURE 1 ORTEP drawing of the structure of (I). The projection has been chosen to emphasise the structural similarity of the PtB_8 unit to the *arachno*-nonaborane cluster

borane unit can be seen to be an open-faced ten-vertex cluster with a six-atom open face, as found in ten-vertex decaborane species with either a *nido*-electron count, as in $B_{10}H_{14}$,²⁵ or an *arachno*-count, as in $[B_{10}H_{14}]^{2-}$ and $B_{10}H_{12}L_{2}$.^{26,27} In [(PMe₂Ph)₄(Pt₂B₈H₁₀)], however, the



FIGURE 2 ORTEP drawing of the molecular structure of (11). Only the borane hydrogen atoms have been included. The projection has been chosen to emphasise the structural similarity of the Pt_2B_8 unit to the *arachno*-decarboranyl fragment. The molecule has crystallographic symmetry C_2

location of the bridging hydrogen atoms, the magnitudes of the B-B distances, and the n.m.r. properties, as variously discussed below, all indicate an *arachno*formulation for this compound. It is therefore an analogue of *arachno*- $[B_{10}H_{14}]^{2-}$ in which the BH₂⁻ groups in the 6 and 9 positions [structure (2)] have been replaced by the isoelectronic ⁵ (but not exactly isolobal, see below) neutral Pt(PMe₂Ph)₂ moieties. This equivalence of BH₂⁻ and Pt(PR₃)₂ appears to be quite general in cluster chemistry, and has ramifications for

J.C.S. Dalton

Atomic co-ordinates for (II) with estimated standard deviations in parentheses

	x	v	z
B(1)	-0.0610(4)	0.441.7(3)	0.234.6(3)
B(2)	0.030.2(4)	0.402.4(3)	0 180 7(3)
D(2) D+(6)	0.030 2(4)	0.4024(3)	0.159 57(1)
$\mathbf{P}(0)$	0.105 0(4)	0.25501(1)	0.100 07(1)
	0.1259(4)	0.3490(3)	0.2309(3)
B(8)	0.084 0(4)	0.3519(3)	$0.323\ 5(3)$
P(1)	$0.165\ 71(9)$	0.158 91(8)	$0.164\ 74(6)$
P(2)	-0.06179(8)	0.183 00(8)	0.081 36(6)
C(1)	0.206 8(3)	0.1124(3)	$0.084 \ 2(2)$
C(2)	0.262 8(4)	$0.035\ 3(4)$	0.083 7(3)
C(3)	0.297 7(4)	0.005 2(5)	$0.022\ 2(3)$
C(4)	0.279.9(4)	0.049 2(4)	-0.0385(4)
Č(5)	0.225.3(5)	0 124 6(4)	-0.038.8(3)
C(6)	0.1884(4)	0.156.1(4)	0.022 1(3)
C(7)	0.137 0(5)	0.063 3(4)	0.0221(3) 0.9170(4)
	0.157 0(5)	$0.0033(\pm)$	0.2170(4)
	0.2817(4)		0.2001(3)
C(9)	-0.0446(5)	0.064 2(4)	0.0714(3)
C(10)	-0.1928(4)	0.1839(5)	0.092 8(4)
C(11)	-0.0537(4)	0.226 8(4)	-0.0065(3)
C(12)	-0.0817(5)	0.177 3(5)	-0.065 4(3)
C(13)	$-0.075\ 2(5)$	0.2151(6)	-0.1311(3)
C(14)	-0.042 1(5)	0.297 8(7)	-0.1392(4)
C(15)		0.346 9(5)	-0.081.6(4)
C(16)	-0.0187(4)	0.311.6(4)	-0.015.8(3)
HUN	-0.097.6(31)	0.496.4(31)	0 228 3(22)
H(9)	-0.057 0(01) 0.056 3(31)	0.446.8(34)	0 138 1(94)
$\mathbf{U}(7)$	0.000 0(01)	0.269 7(29)	0.100 1(24)
	0.2021(30)	0.3027(32)	0.220 7(20)
	0.141 7(30)	0.309 8(31)	0.303 7(20)
H(78)	0.1110(33)	0.2943(37)	0.280 9(24)
H(2)	0.285 0(43)	-0.0046(43)	0.128 1(32)
H(3)	0.321 9(50)	-0.0467(49)	0.024 5(34)
H(4)	0.315 6(46)	0.025 9(42)	$-0.083 \ 2(33)$
H(5)	0.205 6(38)	$0.144 \ 9(37)$	$-0.076\ 8(30)$
H(6)	$0.160\ 0(31)$	$0.197 \ 3(33)$	$0.023 \ 4(22)$
H(71)	$0.095 \ 0(61)$	$0.009 \ 4(55)$	$0.193 \ 8(45)$
H(72)	$0.194\ 7(49)$	$0.020 \ 8(45)$	$0.226\ 7(32)$
H(73)	0.127 3(53)	0.071 9(50)	$0.258\ 8(39)$
H(81)	0.3231(39)	0.144 1(36)	$0.207\ 2(25)$
H(82)	0.268.9(36)	0.199 8(39)	0.253.5(31)
H(83)	0.313.9(39)	0.234.5(33)	0 188 6(28)
H(01)	-0.088.9(30)	0.033 5(27)	0.038 5/20
11(91)	-0.060 2(30)	0.033 3(27)	0.030 5(20)
П (92)	-0.001 5(41)	0.0313(41)	0.110 0(31)
H(93)	0.018 0(38)	0.0310(31)	0.071 1(24)
H(101)	-0.2209(33)	0.152 5(33)	0.051 9(27)
H(102)	-0.220 1(53)	0.142 0(50)	0.144 3(38)
H(103)	-0.2160(78)	0.221 4(70)	0.105 7(62)
H(12)	-0.1084(49)	$0.112 \ 3(48)$	-0.0596(33)
H(13)	-0.1041(49)	0.171 1(44)	-0.177 8(38)
H(14)	$-0.050 \ 3(61)$	$0.320 \ 4(57)$	-0.1903(46)
H(15)	$0.003 \ 1(47)$	0.404 3(44)	$-0.085\ 2(33)$
H(16)	-0.0061(37)	0.350 6(36)	$0.023\ 3(29)$

example in the structural interpretations of the so-called ' slipped ' closo-metallacarboranes, 28.29 although apparent exceptions are known to occur in small species with particular symmetries, such as in the closo-1,6,8-platinadicarbanonaboranes.30

Comparison of horizontal rows within each of Tables 2, 3, 5, and 6 shows that there is little deviation from idealised C_s symmetry for the PtB₈ cluster in [(PMe₂Ph)₂- (PtB_8H_{12})] and C_{2v} symmetry for the Pt_2B_8 cluster in $[(PMe_2Ph)_4(Pt_2B_8H_{10})]$. The largest deviations from these idealized symmetries occur in the bonds to B(6)and B(8) in the monoplatinum compound. Whether these result from cage electronic effects arising from the different Pt(4)-P(1) and Pt(4)-P(2) bond rotamers or from packing forces is not clear, but in any event the deviations are small.

In each of the two compounds therefore the B_8H_n units can be regarded as ligands which bind to the Interatomic distances (pm) for (II) with estimated standard deviations in parentheses *

(i) From the	platinum atom		
Pt(6) - P(1)	230.5(1)	Pt(6) - P(2)	230.3(1)
Pt(6) - B(2)	220.3(5)	() ()	
Pt(6) - B(5) *	224.1(5)	Pt(6) - B(7)	224.5(5)
(11) Boron-bo	oron		
B(1) - B(2)	176.6(8)	B(1)-B(4) *	176.6(8)
B(1) - B(3) *	175.3(8)		
B(1) - B(5) *	177.6(7)	B(1)-B(10) *	179.5(8)
B(2)-B(5) *	174.5(8)	B(2)-B(7)	178.6(8)
B(7) - B(8)	189.4(8)		
	1		
(iii) Boronn	yarogen		
B(1) - H(1)	97(5)		
B(2) - H(2)	113(5)		
B(7) - H(7)	108(5)	B(8) - H(8)	112(5)
B(7)-H(78)	130(5)	B(8) - H(78)	126(5)
(iv) Phosphor	rus-carbon		
P(1) = C(1)	191 9(5)	P(9) = C(11)	199 1(5)
P(1) = C(7)	181.2(5)	P(2) = C(0)	182.1(0)
P(1) = C(8)	191.5(6)	P(2) = C(10)	182.1(0)
I (I) C(0)	181.5(0)	1 (2) C(10)	102.1(0)
(v) Other			
C-C(Ph)	134-140(1); mean	CC(Ph) 13	7.6
C-H '	70-124(10); mea:	n C—ÌI Ó 9	6

* Due to the C_2 symmetry B(3) is B(1'), B(4) is B(2'), B(5) is B(8'), and B(10) is B(7').

TABLE 6

Angles (°) between interatomic vectors, with estimated standard deviations in parentheses, for (II)

(i) At the platinur	n atom		
P(1) - Pt(6) - P(2)	97.7(1)		
P(1) - Pt(6) - B(2)	133.5(1)	P(2) - Pt(6) - B(2)	125.2(1)
P(1) - Pt(6) - B(5) *	168.0(1)	P(2) - Pt(6) - B(7)	172.4(1)
P(1) - Pt(6) - B(7)	89.6(1)	P(2) - Pt(6) - B(5) *	88.2(1)
B(2) - Pt(6) - B(5) *	46.2(2)	B(2) - Pt(6) - B(7)	47.3(2)
B(5) - Pt(6) - B(7) *	84.9(2)		
	0 = 10 (-)		
(ii) Platinum-boro	on–boron		
Pt(6) - B(2) - B(1)	119.5(3)	Pt(6)-B(2)-B(3) *	119.5(3)
Pt(6) - B(2) - B(5) *	68.0(3)	Pt(6) - B(2) - B(7)	67.5(3)
Pt(6) - B(5) - B(1) *	117.1(3)	Pt(6) - B(7) - B(3) *	116.1(3)
Pt(6) - B(5) - B(2) *	65.8(3)	Pt(6)-B(7)-B(2)	65.1(3)
Pt(6) - B(5) - B(10) *	113.5(3)	Pt(6) - B(7) - B(8)	114.7(3)
1 ((0) 2(0) 2(-0)	(-)		
(iii) Boron-boron-	-boron		
B(2)-B(1)-B(3) *	60.2(4)	B(3)-B(1)-B(4) *	60.2(4)
B(2)-B(1)-B(4) *	106.3(4)		. ,
B(2)-B(1)-B(5) *	59.0(3)	B(4)-B(1)-B(10) *	60.2(3)
B(2)-B(1)-B(10) *	109.5(3)	B(4) - B(1) - B(5) *	110.6(3)
B(3) - B(1) - B(5) *	110.7(3)	B(3) - B(1) - B(10) *	111.1(3)
B(5)-B(1)-B(10) *	64.0(3)		
B(1)-B(2)-B(3) *	59.5(4)		
B(1) - B(2) - B(5) *	60.8(4)	B(3)-B(2)-B(7) *	60.7(3)
B(1) - B(2) - B(7)	111.0(4)	B(3) - B(2) - B(5) *	111.5(4)
$\vec{B}(5) - \vec{B}(2) - \vec{B}(7) *$	118.1(3)		()
B(1)-B(5)-B(2) *	60.2(4)	B(1)-B(10)-B(4) *	59.1(3)
B(1) - B(5) - B(10) *	58.5(3)	B(1) - B(10) - B(5) *	57.5(3)
B(2) - B(5) - B(10) *	106.1(3)	B(4) - B(10) - B(5) *	104.6(3)
= (-, -)	()		. ,
(<i>iv</i>) Platinum-pho	sphorus-carbo	n	
Pt(6) - P(1) - C(1)	118.3(1)	Pt(6) - P(2) - C(11)	110.7(2)
Pt(6) - P(1) - C(7)	111.8(2)	Pt(6) - P(2) - C(9)	119.0(2)
Pt(6) - P(1) - C(8)	119.5(2)	Pt(6) - P(2) - C(10)	119.5(2)
	· ·		
(v) Selected bor	on-boron-hydi	ogen and boron-h	ydrogen-
horon			

boron

B(7)-H(78)-B(8) B(3)-B(7)-H(78) *	$96(3) \\ 97(2)$	B(3)-B(8)-H(78) * 100(2)	
* Due to the C_2 :	symmetry,	Pt(9) is Pt(6'), B(3) is B(1'), B(4))

(0) is B(2'), B(5) is B(8'), and B(10) is B(7').

platinum atoms as symmetrical η^3 -B₃ donors, as found ³ for the similar arachno-ligand in [6,6-(PPh3)2-arachno-6,9-PtSB₈H₁₀], but in contrast to the asymmetric bonding ³¹ of the η^3 -B₃H₇ ligand in [(PMe₂Ph)₂(PtB₃- H_7]. It also contrasts with the 'twist' asymmetry observed ^{13,16} for the η^4 -borane-metal bonding in the 11vertex [7,7-(PMe₂Ph)₂-nido-7-PtB₁₀H₁₂] and related compounds, but in these the asymmetry arises from crystal packing forces and a low activation energy for ligand pseudorotation about an axis within the platinum bonding plane which is also manifested in intramolecular fluxionality. There is also a twist distortion from ideal symmetry about the platinum atoms in the compounds reported here, presumably also arising from crystal packing forces, but this is small (ca. 7° for the monoplatinum and 8.5° for the diplatinum compound), and additionally there is no evidence for rotational fluxionality. The bonding at platinum is therefore rigidly five-co-ordinate to the P(1)P(2)B(1)B(5)B(9) atoms (monoplatinum compound) and the P(1)P(2)B(2)B(5)-B(7) atoms (diplatinum compound). Within this coordination sphere the formal platinum(II) tetragonal bonding plane for the monoplatinum compound is defined by P(1)P(2)B(5) and B(9) but excludes B(1)[deviation 79 pm from the plane defined by Pt(4)P(1)-P(2)], and for the diplatinum compound similarly the tetragonally co-ordinated atoms are P(1)P(2)B(5) and B(7) but B(2) is excluded. The orientation of this formal tetragonal plane is of particular interest, as it differs from that hitherto more generally observed, for example in $[(PMe_2Ph)_2(PtB_3H_7)]^{31}$ and in $[5,9-Me_2 6,6-(PEt_3)_2-6,5,9-NiC_2B_7H_9]$ ² For these, the η^3 -binding of the metal atom within the cluster is asymmetric in that the formal tetragonal dsp^2 metal bonding plane intersects a B-B vector within the η^3 system and contains only one other cluster atom. This results in a σ , η^2 bidentate cluster binding mode, presumably involving one two-electron two-centre bond and one twoelectron three-centre bond. In [(PMe₂Ph)₂(PtB₈H₁₂)], by contrast {and analogous considerations apply to $[(PMe_2Ph)_4(Pt_2B_8H_{10})]$, the geometry indicates that the tetragonally disposed platinum dsp^2 valence electrons form two direct two-electron two-centre σ bonds with the B(5) and B(9) atoms. However, it is also apparent that a strong Pt(4)-B(1) interaction is present, which may therefore indicate a $(dsp^2 + d)$ -type of platinum electronic involvement with the cluster, as discussed below in section IV. Consistent with this, there is evidence for some square-pyramidal distortion in that the platinum atom is somewhat above the mean P(1)P(2)B(5)B(9) (monoplatinum compound) and P(1)-P(2)B(5)B(7) (diplatinum compound) planes (deviations ca. 3 pm and 8 pm respectively). Within this platinum co-ordination sphere the bonds

within this platinum co-ordination sphere the bonds to phosphorus of *ca.* 230.5 pm lie in the centre of ranges typical for this general type of compound (*e.g.* refs. 30—32 and other refs. cited therein), as do the platinumboron distances of *ca.* 223 pm.^{3,30-32} There is no significant difference in the Pt-B distances when the monoplatinum and diplatinum compounds are compared, nor is there between the direct Pt-B contacts within the same compound; there is only a small difference between these and those in the thiaborane analogue $[6,6-(PPh_3)_2-6,9-PtSB_{10}H_{10}]^3$ in which the Pt(6)-B(2) distance is somewhat shorter [218.4(1.6) pm]. This geometry contrasts with that of the only other trihaptoboron-donor molecule for which data are so far available: this is the σ, η^2 compound [(PMe_2Ph)_2(PtB_3H_7)] mentioned above which has a Pt-B σ -bond length of 238(4) pm, with the distances to the boron atoms in the η^2 bond being 213(2) and 218(4) pm.³¹

The closed deltahedral boron-boron distances of 175-180 pm within the clusters are within ranges normal³³ for polyhedral boron clusters. Of those in the open face the B(6)-B(7)/B(7)-B(8) distance of ca. 186.5 pm in [(PMe₂Ph)₂(PtB₈H₁₂)] is similar to that ²² in the nine-vertex arachno-compound B₉H₁₃(NCMe), which is probably similarly structured in this part of the molecule (see below), and also to that of the related arachno- $[B_9H_{14}]^-$ anion.^{23,34} This distance contracts somewhat upon the replacement of the 6- and 8-endo-terminal hydrogen atoms by an η^3 -co-ordination to the metal centre; the resulting B(2)-B(5) distance [structure (2)] and its equivalents in the two compounds average ca. 179 pm, which is significantly less than those of 186(5)and 192(5) pm measured ³¹ for $[(PMe_{2}Ph)_{2}(PtB_{3}H_{7})]$. The contraction of the B-B bond distance on the replacement of a B-H-B bridge by a bond to a metal centre is also found when the η^4 complex $[7,7-(PMe_2Ph)_2-nido-7-$ PtB₁₀H₁₂] is made from B₁₀H₁₄ by replacement of the 5,6 and 9,10 bridging hydrogen atoms with the neutral Pt(PMe₂Ph)₂ moiety.¹⁶ In the eight-boron clusters described in the present work it is interesting that the contraction is greater for $[(PMe_2Ph)_2(PtB_8H_{12})]$ than for the diplatinum compound which may represent a competition in electron demand between the B(3)B(4)-B(5) and the B(6)B(7)B(8) η^3 -bonding sites of the arachno-octaborane nucleus [structure (4)].

The B(5)-B(10)/B(7)-B(8) distances in the ten-vertex system of $[(PMe_2Ph)_4(Pt_2B_8H_{10})]$ require particular comment: the distance of 189.4(8) pm is similar to the corresponding ones in the typical arachno-species $6,9-(SMe_2)_2B_{10}H_{12}$ [191(2) pm],³⁵ $6,9-(MeCN)_2B_{10}H_{12}$ [188.1(8) pm],²⁷ $[5,9-Me_2-6,6-(PEt_3)_2-6,5,9-NiC_2B_7H_9]$ [187(1) pm],² and $[6,6-(PPh_3)_2-6,9-PtSB_8H_{10}]$ [184.4(2.8) pm].³ It is much shorter than the corresponding distances in typical nido-ten-vertex structures such as $B_{10}H_{14}$ [197.3(4) pm] ²⁵ and $[5-(thf)-6,6,6-(CO)_3-6-MnB_9-H_{12}]$ (thf = tetrahydrofuran) [203.7(7) pm] ¹⁸ which is additional evidence consistent with the arachno-description of $[(PMe_2Ph)_4(PtB_8H_{10})]$.

This conclusion is further reinforced by the location of the hydrogen atoms in the 5,10 and 7,8 bridging positions in $[(PMe_2Ph)_4(Pt_2B_8H_{10})]$. Data were sufficiently good for these to be reasonably well defined, with a mean B-H_{bridge} distance of *ca.* 128 pm (Table 5). Bridging atoms in these positions are characteristic of ten-vertex *arachno*-structures,^{2,3,25,27,35} and their incidence is also required for a correct ³⁶ arachno-ten-vertex cluster electron count on the assumption that the neutral $Pt(PMe_2Ph)_2$ unit is a BH_2^- subrogator. In accord with this the distance of *ca*. 128 pm is similar to the equivalent distances of *ca*. 125 pm measured by X-ray diffraction analysis for $[B_{10}H_{14}]^2$, $L_2B_{10}H_{12}$, *etc.*^{25,27,35} In addition to these bridging hydrogens, all the other cluster (terminal) hydrogen atoms for this compound were defined with a mean B-H distance of 107 pm (Table 5).

The X-ray diffraction analysis of the structure of the monoplatinum compound $[(PMe_2Ph)_2(PtB_8H_{12})]$ on the other hand was limited by decomposition of the crystals in the X-ray beam over the periods required to collect sufficiently accurate data for the location of the hydrogen atoms in the molecule. However, selective ${}^{1}H{}^{{11}}B$ n.m.r. spectroscopy (section III below) showed that there was a terminal hydrogen atom associated with each boron atom, that there were bridging hydrogen atoms associated principally with the 5,6 and 8,9 positions, and that there were two endo-terminal (pseudo-bridging) hydrogen atoms associated principally with B(6) and B(8). Peaks corresponding to all these atoms were apparent in the final difference maps, but the limited accuracy of the data precluded precise location of the interesting endo-terminal atoms.

III. Nuclear Magnetic Resonance Studies.—We have investigated the n.m.r. behaviour of these compounds in some detail. There are few ways of experimentally assessing the electronic distribution within metallaborane clusters, and it is important to assign n.m.r. parameters for known structures so that theories which attempt to describe these parameters and thence the electronic structures may be developed and tested. Such assignments also enable empirical correlations to be established to aid the structural determination of new species. Within this context, the n.m.r. behaviour of $[4,4-(PMe_2-Ph)_2-4-PtB_8H_{12}]$ and of $[6,6,9,9-(PMe_2Ph)_4-6,9-Pt_2B_8-H_{10}]$ have a number of interesting and important features.

The ¹¹B and ¹H n.m.r. parameters for the metallaborane cluster of the diplatinum compound [(PMe2- $Ph_{4}(Pt_{2}B_{8}H_{10})$] are summarised in Table 7. For this compound, 'satellites' arising from coupling to ¹⁹⁵Pt (natural abundance 34%) are apparent for two of the ¹¹B resonances, and the ¹¹B spectra (Figure 3) are readily assigned ¹¹ on the basis of relative intensity and of the values of the coupling constants ${}^{n}I({}^{195}Pt-{}^{11}B)$ for the 2,4 and the 5,7,8,10 positions which are within the range expected ^{3,11} for n = 1. These assignments indicate high shielding for the 1,3 nuclei and low shielding for the 2,4 nuclei as observed in arachno-species such as $[B_{10}]$ $H_{14}]^{2-} [\delta^{(11B)} (1,3) ca. -42; (2,4) ca. -7 p.p.m.]^{38,39}$ and $6,9-(SEt_2)_2B_{10}H_{12}$ [δ ⁽¹¹B) (1,3) -38.7; (2,4) -2.9 p.p.m.]³⁹ and in contrast to the shieldings in nido- $B_{10}H_{14} [\delta^{(11B)} (1,3) +11.3; (2,4) -35.8 \text{ p.p.m.}]^{40}$ and other established related nido-ten-vertex structures. This is consistent with the arachno-description of the cluster established by the X-ray diffraction experiments above.

J.C.S. Dalton

The ¹¹B resonance positions for $[(PMe_2Ph)_2(PtB_8H_{12})]$ are also readily assigned (Table 8); of the two high-field resonances of relative intensity two, that at highest field is reasonably ascribed to the 1,3 position by comparison with the diplatinum compound and with the parent B_8H_{14} ,²¹ and the other positions follow on the basis of relative intensity and incidence of observable couplings ${}^1J({}^{195}\text{Pt}{}^{-11}\text{B})$; the separate 2 and 9 resonances were differentiated by ' partial relaxation '.^{41,42}



FIGURE 3 32 MHz ¹¹B and ¹¹B-{¹H(broad band)} n.m.r. spectra of (I) [traces (a) and (b)] and (II) [traces (c) and (d)]. Traces (a) and (c) are normal spectra; (b) and (d) have {¹H(broad band)} decoupling. Trace (a) has a $2 \times$ increased print-out gain compared to trace (b)

As also observed for the eleven-vertex $[7,7-(PMe_2Ph)_2-nido-7-PtB_{10}H_{12}]$,¹¹ the net effect of substitution of platinum on to the octaborane cluster is one of deshielding. The apical positions directly bonded to the metal atom {B(2) and B(4) for $[(PMe_2Ph)_4(Pt_2B_8H_{10})]$; B(1) for $[(PMe_2Ph)_2(PtB_8H_{12})]$ } are little affected and the largest deshielding contribution occurs at the platinum-substituted 5,7 and 8,10 positions (diplatinum compound, Table 7) or 5,9 position (monoplatinum compound, Table 8). Interestingly, there is also a large deshielding effect at the apical β positions [B(1,3) in the diplatinum compound, B(2,3) in the monoplatinum compound], an effect again noted ¹¹ for the similar 4 and 6 positions in the eleven-vertex [(PMe_2Ph)_2(PtB_{10}H_{12})].

TABLE 7

Proton and boron-11 n.m.r. data for the borane cluster in (II); saturated solution in CD₂Cl₂ at 21 °C unless otherwise indicated

		maicated		
Assignment	2,4	5,7,8,10	1,3	bridge
$\delta^{(11B)/p.p.m.a}$	+28.1	+ 0.7 *	-19.3	
Relative intensity	2	4	2	
SCS(¹¹ B)/p.p.m. ^e	-3.2	-21.4	-18.9	
Approx. $\hat{T}_1(^{11}B)/ms$	1.95	1.23	4.90	
$\delta(^{1}H)/p.p.m.^{d}$	+4.76	+2.94 •	+1.57	-1.83
$\delta(^{1}\mathrm{H})(\hat{\mathrm{C}}_{a}\hat{\mathrm{D}}_{a})/\mathrm{p.p.m.}^{d,f}$	+6.14	+3.85	[ca. +3.5]	-1.28
Relative intensity	2	4	2	2
ASIS(¹ H)/p.p.m. ^k	-1.38	0.91	$[-1.9]^{g}$	-0.55
$^{n}/(195 \text{Pt}-11 \text{B})/\text{Hz}$	$300 \pm 40(^{1}J)$	$280 \pm 60(1/)$	(2 I) i	
n/(195 Pt-1 H)/Hz	$15 \pm 3(2)$	$< ca. 15(^{2}J)^{\frac{3}{2}}$	$50 \pm 5(^{3}/)$	$35 \pm 5(^{2}J)$
Relative sign	opposite	opposite	not measured	k
J(11B-1H)Hz	120 ± 10	$110^{-}\pm 20$	$135~\pm~10$	< ca. 70

¹ $J(^{11}B^{-1}H)/HZ$ 120 ± 10 110 ± 20 135 ± 10 < *cd.* 70 ^a±0.5 p.p.m. to high frequency (low field) of BF₃(OEt₂). ^b Possible odd-number multiplet in ¹¹B-{¹H} spectrum, splitting *ca.* 55 Hz. ^cSCS = Substituent chemical shift = ($\delta(B_8H_{14}) - \delta[[(PMe_2Ph)_4(Pt_2B_8H_{10})]$) and is the increase in shielding $\Delta\sigma$ over that measured (ref. 21) for unsubstituted B_8H_{14} . ^d±0.02 p.p.m. to high frequency (low field) of SiMe₄. ^ePartially resolved fine structure apparent in ¹H-{¹¹B} spectra probably arising principally from ³ $J(^{31}P^{-1}H)$ interactions. ^fSaturated solution in C₆D₆ at 21 °C. ^g Uncertain. ^kASIS = Aromatic solvent induced shielding (T. Onak, W. Inman, H. Rosendo, E. W. Distefano, and J. Nurse, *J. Am. Chem. Soc.*, 1977, **99**, 6488) = [$\delta($ in CD₂Cl₂) $- \delta($ in CC₆D₆)] in this case and is the increase in *shielding* $\Delta\sigma$ on dissolution in the aromatic solvent. ^{i 2}J not resolved, *i.e.* ^{i 2}J| < *ca.* 90 Hz. ^j The apparent small size of this compared to that for [(PMe₂Ph)₂-(PtB₈H₁₂)] (Table 8) indicates that ³ $J(^{106}Pt^{-1}H)$ of opposite sign may also be present. ^{k +}H-{¹¹B} experiments showed differential(5,7,8,10)]; however, these results were not as definitive as for the 2,4 nuclei which suggests that a negative coupling ² $J[^{106}Pt^{-11}B(5,7,8,10)]$; however, these results were not as definitive as for the 2,4 nuclei which suggests that a negative coupling ² $J[^{106}Pt^{-11}B(5,7,8,10)]$; however, these results were not as definitive as for the 2,4 nuclei which suggests that a negative coupling ² $J[^{106}Pt^{-11}B(5,7,8,10)]$; however, these results were not as definitive as for the 2,4 nuclei which suggests that a negative coupling ² $J[^{106}Pt^{-11}B(5,7,8,10)]$; however, these results were not as definitive as for the 2,4 nuclei which suggests that a negative coupling ² $J[^{106}Pt^{-11}B(5,7,8,10)]$; however, these results were not as definitive as for the 2,4 nuclei which suggests that a negative

TABLE 8

Proton and boron-11 n.m.r. data for the borane cluster in (I); saturated solution in CDCl₃ at 21 °C unless otherwise indicated

						bridge	pseudo-bridge
Assignment	1	7	5,9	6,8	2,3	5,6 and 8,9	6 and 8
S(¹¹ B)/p.p.m. ^a	+21.6	+18.8	-+ 1.7 b	-23.0	-31.6		
Relative intensity	1	1	2	2	2		
SCS(¹¹ B)/p.p.m. ^c	+3.3	+6.1	-19.0	+2.3	-6.6		
Approx. $\hat{T}_1(^{11}B)/ms$	3.2	1.6	1.9	2.0	5.6		
S(¹ H)/p.p.m. ^d	+3.97	+4.20	+2.97 •	+2.12	+0.92	-3.05	+0.25
$(^{1}H)(\hat{C}_{g}\hat{D}_{g})/p.p.m.^{d,f}$	+4.97	+4.97	$+3.53$ $^{\circ}$	+2.88	+2.08	-2.66	+0.81
Relative intensity	1	1	2	2	2	2	2
ASIS(¹ H)/p.p.m. ^g	1.00	-0.77	-0.56	-0.76	-1.16	-0.39	-0.56
/(195Pt-11B)/Hz	$330 \pm 50(1)$	h	$260 \pm 50(1/)$	h	h		
/(¹⁹⁵ Pt- ¹ H)/Hz	<ca. 20<="" td=""><td>i</td><td>$30 \pm 5(^{2}J)$</td><td>i</td><td>$62 \pm 2(3/)$</td><td>$43 \pm 2(^{2}J)$</td><td>i</td></ca.>	i	$30 \pm 5(^{2}J)$	i	$62 \pm 2(3/)$	$43 \pm 2(^{2}J)$	i
Relative sign	not measured ^j	i	opposite	i	k	k	i
$J(^{11}B-^{1}H)/Hz$	$135~\pm~5$	$140~\pm~20$	140 ± 5	$135~\pm~5$	$145~\pm~5$	< 70	< 70

^a See footnote *a* to Table 7. ^b Possible fine structure in ¹¹B spectrum due to ${}^{1}f({}^{11}B-{}^{11}H_{bridge})$ of *ca*. 50 Hz. ^c SCS = $(\delta(B_{8}H_{14}) - \delta\{[(PMe_{2}Ph)_{2}(PtB_{8}H_{12})]\})$, see footnote *c* to Table 7. ^d See footnote *d* to Table 7. ^e Some fine structure splitting *ca*. 10 Hz apparent, presumably arising from ${}^{3}f({}^{31}P-{}^{1}H)$ and ${}^{3}f({}^{11}H-{}^{1}H)$ interactions. ^f See footnote *f* to Table 7. ^e ASIS = $[\delta(\text{in CDCl}_{3}) - \delta(\text{in C}_{6}D_{6})]$, see footnote *h* to Table 7. ^h Couplings not resolved, *i.e.* ${}^{2}f$ and ${}^{3}f < ca$. 90 Hz. ⁱ Smaller couplings "f < ca. 15 Hz would not be resolved. ^j Partially obscured by ${}^{1}H(7)$. ^k No differential satellite sharpening in ${}^{1}H-{}^{(11}B)$ experiments.

For both compounds, the magnitudes of any phosphorus couplings ${}^{2}J({}^{31}P-Pt-{}^{11}B)$ or ${}^{3}J({}^{31}P-Pt-B-{}^{11}B)$ to the cluster boron atoms are expected to be of the order of up to a few tens of Hz, 10,43 , * but none was definitely resolvable although line-narrowing experiments on ${}^{11}B-{}^{11}H(broad band)$ } spectra indicated some fine structure in the 5,7,8,10 ${}^{11}B$ lines for the diplatinum compound $[(PMe_2Ph)_4(Pt_2B_8H_{10})]$ which may arise from this (Table 7); in any event in this compound the 5,7,8,10 ${}^{11}B$ and ${}^{10}B$ nuclei and the four ${}^{31}P$ nuclei will constitute at simplest an $\{[A]_2[X]_2\}_2$ spin system which will result in a complex spectrum that will be complicated further by the other boron nuclei in the molecule. Similar considerations apply to the interpretation of the

non-Lorenzian shapes also apparent particularly for the 5,9 resonance in the monoplatinum compound $[(PMe_2 Ph)_2(PtB_8H_{12})]$.

For both compounds, the ¹H n.m.r. resonances of the borane cluster hydrogen atoms were readily observed in ¹H-{¹¹B} experiments (e.g. Figure 4), and selective decoupling experiments ^{11,42,44,45} assigned their positions and confirmed that each boron atom has a terminal hydrogen atom associated with it (Tables 7 and 8). It was also confirmed for each compound that there are additionally two equivalent bridging hydrogen atoms principally associated with the 5,7,8,10 boron atoms (Pt₂B₈H₁₀ compound) and 5,6,8,9 atoms (PtB₈H₁₂ compound), again consistent with the solid-state structure and, for [(PMe₂Ph)₄(Pt₂B₈H₁₀)] in particular, the *arachno*-description of the cluster bonding. For the monoplatinum compound, the selective decoupling

ě

^{*} By comparison with the various couplings involving ¹³C in organometallic compounds such as cis-[PtMe₂(PMe₂Ph)₂] (ref. 43*a*) and [Pt(CH₂=CH₂)(PPh₃)₂] (ref. 43*b*).

J.C.S. Dalton

with the 6,9 boron resonances only.¹⁶ The *endo*-terminal hydrogens are discussed below in section IV.

The most striking aspect of the measurement and assignment of the proton shieldings of the other (*i.e. exo*) terminal hydrogen atoms for both compounds is the manner in which they parallel the shieldings of the boron atoms to which they are attached (Figure 5). It is notable that the parallel holds also for the boron atoms adjacent to the heavy metal. The line of slope $\delta(^{11}B)/\delta(^{1}H) = 16$ is of the same gradient as that observed ⁴² for a similar plot for the bis(*nido*)-compound 6,6'-(B₁₀-



FIGURE 5 Plot of $\delta({}^{1}\text{H})$ against $\delta({}^{11}\text{B})$ for the *cxo*-terminal B-H groups in $B_{8}H_{14}$ (\bigcirc), (I) (\square), and (II) (\triangle). Values for the two platinum compounds are from this work (CDCl₃ and CD₅-Cl₂ solutions respectively), and values for $B_{8}H_{14}$ (CS₂ and C₅H₁₂ solutions) are from ref. 21. The line drawn represents the quotient $\delta({}^{11}\text{B})/\delta({}^{11}\text{H}) = 16$

 H_{13} O and indicates that this relationship may be quite general.

' Satellites ' due to coupling with ¹⁹⁵Pt were detectable for many of the cluster protons in $[(PMe_{o}Ph)_{o}(PtB_{o}H_{10})]$ and for all of the cluster protons in [(PMe₂Ph)₄(Pt₂- B_8H_{10}]. For those in terminal positions on boron atoms directly bonded to platinum, selective ¹H-{¹¹B} experiments were used to increase the effective finestructure resolution in both the ¹H and ¹¹B spectra.⁴² and to compare ¹¹ the signs of the corresponding couplings ${}^{1}J({}^{195}Pt-{}^{11}B)$ and ${}^{2}J({}^{195}Pt-{}^{1}H)$ (Figure 6 and Tables 7 and 8). In general the values obtained are qualitatively similar to those reported 11 for the PtB₁₀H₁₂ cluster in the eleven-vertex compound [7,7-(PMe₂Ph)₂-7-PtB₁₀- H_{12}]. Firstly, the geminal couplings ${}^{2}J({}^{195}Pt-B-{}^{1}H)$ (bridge or terminal) are smaller (<ca. 35 Hz), and the terminal coupling is opposite in sign (where measurable) to the corresponding ${}^{1}J({}^{195}Pt-{}^{11}B)$. Secondly, the geometrically similar longer-range vicinal 'transbutterfly ' couplings ${}^{3}J[{}^{195}Pt-{}^{1}H(2,3)]$ (PtB₈H₁₂ compound), ${}^{3}J[{}^{195}Pt^{-1}H(1,3)]$ (Pt₂B₈H₁₀ compound), and $J[195Pt^{-1}H(4,6)]$ (PtB₁₀H₁₂ compound) [structure (5)] are somewhat larger and are associated with only small couplings ${}^{2}I({}^{195}Pt-{}^{11}B)$. We are currently assessing the generality of this and similar emerging patterns of behaviour.

Other selected ¹H, ³¹P, and ¹⁹⁵Pt n.m.r. parameters



FIGURE 4 100 MHz ¹H-{¹¹B} n.m.r. spectra (CDCl₃ solution) of the boron hydride region of (1): (a), normal spectrum; (b)– (g), with the subtraction of equivalent spectra with no {¹¹B} decoupling. Spectra (a) and (b) have complete {¹¹B(broad</sup> band)} decoupling, and (c) to (g) have selective {¹¹B(broad</sup> band)} decoupling, and (c) to (g) have selective {¹¹B(broad</sup> decoupling with ν (¹¹B) corresponding to δ (¹¹B) = (c) +21.6, (d) +18.8, (e) -1.7, (f) -23.0, and (g) -31.6 p.p.m. Peaks I are impurities and the structure centred at δ (¹¹H) = ca. +1.7 p.p.m. in (b) results from the perturbation of the P-methyl ¹¹H resonances upon {¹¹B} irradiation. Note the selective sharpening of the endo-terminal resonance at δ (¹¹H) = +0.25 p.p.m. upon irradiation at ν [¹¹B(6,8)] [trace (f)] but not upon irradiation at ν [¹¹B(7)] [trace (d)]

experiments also indicated that the endo-terminal/ pseudo-bridging hydrogen atoms [which resonate at $\delta(^{1}\text{H}) = +0.25$ p.p.m. (CDCl₃ solution) (Table 8)] are associated principally with the 6,8 boron atoms; indeed selective irradiation at v[¹¹B(7)] produced no selective sharpening of this proton resonance (Figure 4). This selectivity is similar to that found for the endo-terminal protons in the arachno-decaboranyl compound 6,9-(SMe₂)₂B₁₀H₁₂, $\delta(^{1}\text{H}) = -0.37$ p.p.m. (CDCl₃ solution), which have no bridging character, and are associated

1422



FIGURE 6 100 MHz ¹H-{¹¹B} spectra of the 2,4 proton resonance of (II) (CD₂Cl₂ solution) with selective irradiation at (a) $\{\nu[^{11}B(2,4)] + \frac{1}{2} \cdot 1_{J}(^{195}Pt-^{11}B)\}, (b) \{\nu[^{11}B(2,4)] - \frac{1}{2} \cdot 1_{J}(^{195}Pt-^{11}B)\},$ and (c) $\nu[^{11}B(2,4)]$. These experiments show the presence of ${}^{2}J(^{195}Pt-B-1H) = ca.$ 15 Hz and show that its sign is opposite to that of ${}^{1}J(^{195}Pt-^{11}B)$

observed for $[(PMe_2Ph)_2(PtB_8H_{12})]$ and $[(PMe_2Ph)_4-(Pt_2B_8H_{10})]$ are listed in Table 9 and warrant some comment. In both compounds the phosphine ligands



are on prochiral metal centres and the ¹H spectra of the P-methyl groups consist of two central resonances arising from the consequent inequivalence of the methyl

1423

groups, 13, 46 flanked by satellite lines arising from coupling to ¹⁹⁵Pt; the two slightly different values of ${}^{3}I({}^{195}\text{Pt} P-C^{-1}H$) are as expected.⁴⁶ In the absence of $\{^{31}P\}$ decoupling each resonance resembles the X part of an $[AX_n]_2$ spin system ⁴⁷ (A = ³¹P, X = ¹H) although the actual spin system which dictates the lineshape will involve the boron nuclei and aromatic protons and be more complex than this. However, the 'N lines' [of separation $N = {}^{2}J({}^{31}P-{}^{1}H) + {}^{4}J({}^{31}P-{}^{1}H)$ in this case] are common to all these systems and can readily be discerned; the shape 48 of the additional intensity suggests a coupling $|{}^{2}J({}^{31}P-Pt-{}^{31}P)|$ somewhat greater than |N|, *i.e.* up to a few tens of Hz, consistent with the cis stereochemistry at platinum. Selective ${}^{1}H-{}^{31}P$ and ¹H-{¹⁹⁵Pt} experiments ^{49,50} on the ¹⁹⁵Pt satellites of these P-methyl resonances confirmed that ${}^{3}J({}^{195}Pt^{-1}H)$ is positive and N negative relative to ${}^{1}J({}^{195}Pt^{-1}H)$ being taken⁵¹ as positive, as again is general⁵² in cis-bis-(phosphine)platinum(II) compounds. As expected from the complex spin system, the P-methyl resonances were also affected in ¹H-{¹¹B} experiments, but this is not discussed here.

The ³¹P-{¹H(broad band)} n.m.r. spectrum for each compound (Table 9) consists of a central resonance together with satellites due to ¹⁹⁵Pt with ¹ $J(^{195}Pt-^{31}P)$ ca. 2 700 Hz, this value being unexceptional for cis-bis-(dimethylphenylphosphine)platinum(II) compounds with a bidentate borane(2-) ligand.^{10,11,16} At ambient temperatures the resonances are broad due to the effect of adjacent ¹⁰B and ¹¹B nuclei, but at lower temperatures these effects become less significant ¹⁰ and the lines sharpen.

For the diplatinum compound $[(PMe_2Ph)_4(Pt_2B_8H_{10})]$ this reveals structure arising from small longer-range couplings ${}^{5}J({}^{31}P-Pt-B-B-Pt-{}^{31}P)$ and ${}^{4}J({}^{195}Pt-B-B-Pt-{}^{31}P)$ (Figure 7). It is apposite to point out here that the origin of this fine structure differs from that observed ${}^{9.16}$ for compounds such as $[4-(2'-B_{10}H_{13})-7,7-(PMe_2Ph)_2-7-PtB_{10}H_{11}]$ which have two chemically inequivalent phosphorus nuclei for which the chemical shifts are accidentally almost degenerate, but for which the different coupling constants ${}^{1}J({}^{195}Pt-{}^{31}P)$ give rise to two [AB] sub-spectra at $[v({}^{31}P)_{mean} \pm \frac{1}{2} {}^{1}J({}^{195}Pt-{}^{31}P)_{mean}]$

TABLE	9
-------	---

, F	······································			
Compound	(II) <i>a</i>		(I) ^b	
$\delta(^{31}P)/p.p.m.^{c}$	$-7.7 + 0.5^{4,e}$		-6.7 ± 0.5 ^d	
$\Xi(195 \text{Pt})/\text{Hz}$	$21\ 383\ 640\ +\ 200\ f$		$21~376~790~\pm~150~^{f}$	
$1 \dot{f} (195 \text{Pt} - 31 \text{P}) / \text{Hz}$	$+2.757$ \pm 2 d		$+2$ 724 \pm 2 a	
4 / (195 Pt-31 P)/Hz	-20.8 ± 1.0 d			
$[{}^{5}/({}^{31}P-{}^{31}P)_{cis} + {}^{5}/({}^{31}P-{}^{31}P)_{trans}]/Hz^{\sigma}$	20.0 ± 1.0 d			
³ /(¹⁹⁵ Pt- ¹⁹⁵ Pt)/Hz	17 ± 8			
$\delta(^{1}H)(MeP)/p.p.m.^{h,i}$	+1.72 (A)	+1.57 (B)	+1.75 (A)	+1.67 (B)
$\delta(^{1}H)(MeP)(\hat{C}_{6}D_{6})/p.p.m.^{h,i}$	+1.44 (A)	+1.34 (B)	+1.26 (A)	+1.17 (B)
$ASIS(^{1}H)/p.p.m.^{h,j}$	+0.28 (A)	+0.23 (B)	+0.49 (A)	+0.50 (B)
$\frac{3}{(195 \text{Pt} - 1 \text{H})}/\text{Hz}^{h}$	$+27.5 \pm 0.5$ (A)	$+23.9\pm0.5$ (B)	$+27.3 \pm 0.5$ (A)	$+25.6 \pm 0.5$ (B)
$\left[\frac{2}{(31P-1H)} + \frac{4}{(31P-1H)}\right]/Hz^{h}$	-8.0 ± 0.5 (A)	-8.0 + 0.5 (B)	-8.5 ± 0.5 (A)	-8.3 + 0.5 (B)

^{a,b} Saturated solutions in CD₂Cl₂ and CDCl₃ at 21 °C respectively unless otherwise indicated. ^c To high frequency of 85% H₃PO₄. ^d At -60 °C. ^e $w_4 = 40$ Hz (21 °C); 4.5 Hz (-80 °C). ^f Resonances very broad (cf. ref. 11). ^e ⁵ J_{eti} and ⁶ J_{trent} probably of same sign and of similar magnitude. ^h (A) and (B) distinguish two inequivalent *P*-methyl groups. ⁱ To high frequency of SiMe₄; ± 0.03 p.p.m. ^f See footnote *h* to Table 7.

1424

with splittings arising from the coupling ${}^{3}J({}^{31}P-{}^{31}P)_{cis}$. In the diplatinadecaborane reported here, by contrast, the observed satellite patterns can be considered as arising in the first instance from an A[X]₂[X']₂ spin system (where A = ¹⁹⁵Pt, X = ³¹P) [structure (6)] so that the spectrum (Figure 7) has both 'inner' and 'outer' pairs of satellites at $[\nu({}^{31}P) \pm \frac{1}{2} {}^{4}J({}^{195}Pt^{-31}P)]$ and $[\nu({}^{31}P) \pm \frac{1}{2} {}^{1}J({}^{195}Pt^{-31}P)]$ respectively. Each pair of inner and outer satellites constitutes an $[AX]_2$ sub-spectrum ⁵³ (where A and X are here regarded as the two ³¹P resonance positions for a particular ¹⁹⁵Pt spin state) for which the constituent line positions depend upon the three phosphorus-phosphorus couplings ${}^{2}J({}^{31}P-Pt-{}^{31}P), {}^{5}J-$ (${}^{31}P-Pt-B-B-Pt-{}^{-31}P)_{cis}$, and ${}^{5}J({}^{31}P-Pt-B-B-Pt-{}^{-31}P)_{trans}$.



FIGURE 7 40 MHz ³¹P-{¹H(broad band)} spectra of the central resonance and ¹⁰⁹Pt satellites of (II) at -80 °C in CD₂Cl₂ solution. The spectrum is centrosymmetric; lines at A—F arise from species containing one ¹⁰⁶Pt nucleus, lines at G—I from species with two ¹⁰⁶Pt nuclei: A—C = D—F = [⁵J(³¹P-³¹P)_{cit} + ⁵J(³¹P-³¹P)_{rons}]; B—B' = A—C' = C—A' = ¹J-(¹⁰⁶Pt-³¹P); E—E' = D—F' = F—D' = ⁴J(¹⁰⁶Pt-³¹P); and G-G' = [¹J(¹⁰⁶Pt-³¹P) + ⁴J(¹⁰⁵Pt-³¹P)]. Lines at H and I are symmetrically disposed about points L, where L—L' = L = [¹J(¹⁰⁶Pt-³¹P) - ⁴J(¹⁰⁶Pt-³¹P)]; the separation H—I approximates to ³J(¹⁰⁶Pt-¹⁰⁵Pt)

Since ${}^{1}J({}^{195}\text{Pt}-{}^{31}\text{P}) \gg {}^{4}J({}^{195}\text{Pt}-{}^{31}\text{P})$ these sub-spectra have negligible second-order character, and the positions of the N lines 53 [where now the separation $N = {}^{5}J({}^{31}\text{P}-{}^{31}\text{P})_{cis} + {}^{5}J({}^{31}\text{P}-{}^{31}\text{P})_{trans}$] for both inner and outer satellite systems are readily apparent (Figure 7, lines A, C, D, and F). The rest of the intensity of this spin system is symmetrically disposed about the centre of each N-line pair (*i.e.* at B and E, Figure 7), and the shape of this intensity shows that $|{}^{5}J({}^{31}\text{P}-{}^{31}\text{P})_{cis} - {}^{5}J({}^{31}\text{P}-{}^{31}\text{P})_{trans}| \ll |{}^{2}J({}^{31}\text{P}-{}^{19}\text{P}+{}^{-31}\text{P})|$, which implies together with the magnitude of N, that the two longerrange phosphorus-phosphorus couplings have similar magnitudes and signs.

In addition to these transitions, there are also lines arising from the *ca.* 11% of molecules which have *both* metal positions [structure (6)] occupied by ¹⁹⁵Pt in natural abundance. In the absence of any residual boron coupling, these will give rise to an $[AX_2]_2$ spin system ⁵⁴ (A = ¹⁹⁵Pt, X = ³¹P) for which the ³¹P N lines are at v(³¹P) $\pm \frac{1}{2}N$, where N is now $[{}^{1}J({}^{195}\text{Pt}-{}^{31}\text{P}) + {}^{4}J$ -

J.C.S. Dalton

 $(^{195}\text{Pt}^{-31}\text{P})]$, and since ${}^{4}J(^{195}\text{Pt}^{-31}\text{P})$ is small these are near the 'outer ' satellite patterns arising from molecules with only one ${}^{195}\text{Pt}$ nucleus. The positions of these lines are also readily apparent (G,G', Figure 7) and show that $|N| < |{}^{1}J({}^{195}\text{Pt}^{-31}\text{P})|$ and therefore that ${}^{4}J({}^{195}\text{Pt}^{-}$ B-B-Pt- ${}^{31}\text{P})$ is negative on the reasonable assumption 51 that ${}^{1}J({}^{195}\text{Pt}^{-31}\text{P})$ is positive. The additional intensity (at H, I, Figure 7) from this spin system is symmetrically disposed about each position L (Figure 7), where $L = [{}^{1}J({}^{195}\text{Pt}^{-31}\text{P}) - {}^{4}J({}^{195}\text{Pt}^{-31}\text{P})]$, with the constituent line positions depending upon ${}^{3}J({}^{195}\text{Pt}^{-1}$



¹⁹⁵Pt) as well as upon the other couplings mentioned above. The spectral resolution obtainable was insufficient for their precise analysis, possibly because of incomplete ' thermal decoupling ' of the boron nuclei ^{10,55} together with more efficient CSA (chemical-shift anisotropy) relaxation ⁵⁶ of the ¹⁹⁵Pt at low temperatures, but it is probable that the separation H-I approximates to ${}^{3}J({}^{195}Pt^{-195}Pt)$ and this indicates a value of *ca.* 17 Hz for this coupling.

These results are summarized in Table 9. The observation of the longer-range *trans*-cluster couplings is of interest. Although long-range ³¹P-³¹P, ¹⁹⁵Pt-³¹P, and ¹⁹⁵Pt-¹⁹⁵Pt couplings are well documented,⁵⁷ this is the first time that such long-range couplings *via* several atoms in a polyhedral cluster have been observed. A discussion of the mechanism of their propagation through the cluster must however await more extensive data.

IV. Structure and Bonding Correlations.-The compounds $[4,4-(PMe_2Ph)_2-4-PtB_8H_{12}]$, (I), and [6,6,9,9- $(PMe_2Ph)_4-6,9-Pt_2B_8H_{10}]$, (II), can be regarded as covalent platinum(II) complexes of the (hypothetical) arachno- $[B_8H_{12}]^{2-}$ and arachno- $[B_8H_{10}]^{4-}$ anions respectively. These are conjugate bases of the tetrabasic acid, arachno-B8H14. A consensus of experimental 21,58 and theoretical 59 considerations indicates that this parent compound is non-fluxional with the static structure (7)and that the electronic structure has its basis in structures such as (8) in which the effect of the vacant orbitals on the 4 and 7 boron atoms is mitigated somewhat by partial 'pseudo-bridging' character of the 3, 5, 6, and 8 endo-hydrogens (as indicated) together with some additional donation 59 from the electrons in the B(1)-B(2) bond. In structures (7) and (8) each B atom has an exo(radial) hydrogen atom in addition to the ones shown. The pseudo-bridging hydrogen atoms are of particular interest, since they resemble the unique pseudobridging hydrogen atom ⁶⁰ in arachno-pentaborane, B₅H₁₁. However, in B_5H_1 , dynamic tautomerism of the pseudobridging hydrogen atom on B(1) probably occurs $[(9) \iff (10)$, equation (8)]⁶⁰ and the precise nature of the interaction has obvious differences to that in B₈H₁₄.



The determination of the location of the B_8H_{14} pseudobridging/endo-terminal hydrogen atoms is therefore of interest, but B_8H_{14} itself does not yield crystals suitable for diffraction analysis,^{21,58} although X-ray data for the arachno-nonaborane derivative B_9H_{13} (NCMe),²² which also has a similar type of hydrogen,⁶¹ indicates



that in this case they are in fact *endo*-terminal with no bridging character. It is however important to examine further examples, particularly in the area of eight-boron clusters, and in the present work the n.m.r. properties of the *endo*-terminal hydrogen atoms in $[(PMe_2Ph)_2-(PtB_8H_{12})]$ (Table 8) are similar to those in B_8H_{14} ,²¹ and to those in compounds $B_9H_{13}L$,⁶¹ which implies that this pseudo-bridging character is also retained in the platinum compound [schematic structure (11)]. Unfortunately, our samples of $[(PMe_2Ph)_2(PtB_8H_{12})]$ decomposed in the X-ray beam in the times required for the collection of data of sufficient quality to locate these atoms accurately, but an indication of their nature arises from the results

of selective ¹H-{¹¹B} double resonance n.m.r. spectroscopy. The endo-hydrogen proton resonance at $\delta =$ +0.25 p.p.m. (CDCl₃ solution, Table 8) is selectively sharpened by simultaneous irradiation at v[¹¹B(6,8)] but remains unaffected upon irradiation with similar power levels at v[¹¹B(7)] (Figure 6). The selectivity is comparable to that found ¹⁶ for the endo-6,9 terminal protons in arachno-6,9-(SMe₂)₂B₁₀H₁₂ which have no bridging character. This indicates that in the platinum compound any coupling ¹J[¹¹B(7)⁻¹H(6_{endo} or 8_{endo})] is negligible and consequently that there is little direct *s*electron overlap between B(7) and the two hydrogen atoms. It also indicates that the low values of the coupling ¹J[¹¹B(6,8)⁻¹H(6,8)_{endo}] and the analogous couplings ^{21.61} in B₈H₁₄ and B₉H₁₃L may therefore



represent a tendency for the diversion of B(6,8) p character into this *endo*-terminal bond and/or a general loss of electron density into the cluster proper. These arguments tend therefore to favour a structure for B₈H₁₄ such as in (8), but with minimal hydrogen-atom bridges to the 4 and 7 boron atoms, so that the structure may have substantial contributions from canonical forms having vacant orbitals in these positions.

These considerations have implications in the interpretation of the bonding at platinum in the structures of $[(PMe_2Ph)_2(PtB_8H_{12})]$ and $[(PMe_2Ph)_4(Pt_2B_8H_{10})]$. In these, taking the $Pt_2B_8H_{10}$ complex as the example, the Pt(6)P(1)P(2)B(5)B(7) system is essentially planar which would be expected if pairs of endo-terminal hydrogen atoms with no bridging character were replaced by two direct two-electron two-centre bonds from boron to square-planar platinum(II) [structure (12)]. This structure has many similarities but important differences to that expected on the basis of the supposed 59 electronic structure of the typical arachno-decaborane $[B_{10}H_{14}]^{2-1}$ [(13); exo-hydrogens omitted]. In this, formal subrogation of the 6,9 BH2⁻ groups by neutral Pt(PMe2-Ph), moieties would be expected to yield platinum borane bonds with substantial three-centre character, *i.e.* the platinum(II) square plane of, for example, Pt(6)would intersect the midpoints of the B(2)-B(7) and B(2)-B(5) interatomic vectors, contrary to observation.

The difference arises from the nature of the donation of the extra electron pairs to the cluster bonding. In $[B_{10}H_{14}]^{2-}$ and related species this is provided by the bonding electron-pairs in the tangential *endo*-terminal B(6)-H(6) and B(9)-H(9) bonds. In $[(PMe_2Ph)_2-(PtB_8H_{12})]$ and $[(PMe_2Ph)_4(Pt_2B_8H_{10})]$, however, the Pt-P bonding pairs are *exo*-polyhedral, and the additional cluster electron pairs are therefore supplied by overlap



of the tangential occupied platinum (formal) d_{z^*} orbitals with the tangential unoccupied B(1) [structure (11)] or B(2) and B(4) [structure (12)] orbitals, as indicated by the hatched arrows in (11) and (12), and producing a strong bond {e.g. Pt(6)-B(2) ca. 220 pm in [(PMe_2Ph)_4-(Pt_2B_8H_{10})]}.



The nature of the η^3 interaction in these eight-boron complexes has important differences to that observed for the metallatetraborane³¹ [(PMe₂Ph)₂(PtB₃H₇)] and related species,⁶² to which parallels with η^3 -hydrocarbon ligand interaction have been drawn.³¹ Thus, [(PMe₂-Ph)₂(PtB₃H₇)] has a $\eta^3 \sigma,\mu$ -' borallyl' structure in the

J.C.S. Dalton

solid state, (14), but exhibits ¹⁶ a mean structure in solution which may be due to the rapid equilibration represented by equation (9) or (less likely) to valence tautomerism when free of crystal packing constraints. In the solid state the platinum(II) square plane of the metallatetraborane accurately contains ³¹ Pt(1)P(1)P(2)B(4) and the *midpoint* of B(2)-B(3) [structure (14)], and thus clearly involves both a two-electron two-centre and a two-electron three-centre bond, in contrast to the eightboron species reported here.

In addition, in the metallatetraborane the B-B bonds are much longer,³¹ and ${}^{1}J[{}^{195}Pt{}^{-11}B(3)]$ has the exceptionally large value of 565 \pm 10 Hz 16 which also suggests a different type of interaction to that observed for the B₈ species.

EXPERIMENTAL

General.-Reactions were carried out in an atmosphere of dry nitrogen although, except where indicated, no rigorous attention was paid to maintaining anaerobic conditions during the subsequent work-up. Solvents were generally distilled from drying agents under nitrogen before use. The products obtained were reasonably air-stable in the solid state. nido-Decaborane was obtained commercially and purified by sublimation before use; cis-[PtCl₂(PMe₂Ph)₂] was prepared by standard literature methods; 63 6,6'- $(B_{10}H_{13})_2O$ was prepared from arachno-6,9- $(SMe_2)_2B_{10}H_{12}$ and H₂SO₄; ⁶⁴ KH was obtained commercially and freed of mineral oil by washing with pentane before use. Thinlayer chromatography (t.l.c.) was carried out on plates made in the laboratory as required from silica gel [Kieselgel 60G (Merck)] and column chromatograms typically used ca. 100 g of silica gel [Kieselgel 60 (Merck); 0.063-0.200 mm mesh] in a column of dimensions ca. $20 \text{ cm} \times 10 \text{ cm}^2$. General chromatographic techniques were as described in previous reports from these laboratories.65,66 Infrared spectra were recorded using KBr discs on a Perkin-Elmer 457 grating instrument, and v_{max} are quoted ± 5 cm⁻¹. Melting points were determined in open capillary tubes.

Preparation of [NMe4][B9H14].-The method is an adaptation of that used by Pretzer and Rudolph 67 to generate the anions $[SB_8H_9]^-$ and $[SB_{10}H_{11}]^-$. Potassium hydroxide (0.56 g, 10 mmol) was added to a solution of $nido-B_{10}H_{14}$ (1.22 g, 10 mmol) in CH₃OH (20 cm³) and stirred at ca. 20 °C for 0.5 h, producing a yellow homogeneous solution with mild effervescence. The solution was allowed to stand overnight, and the liquid components then removed under reduced pressure at $20 < \theta < 40$ °C. Water (15 cm³) was added, the mixture filtered, and a solution of [NMe₄]Cl (6 g, 54 mmol) in water (10 cm³) added. The product separated as a colourless flocculent precipitate which was filtered off, washed repeatedly with water, and dried in vacuo to yield a white powder, $[NMe_4][B_9H_{14}]$ (1.52 g. 8.2 mmol, 82%), identified as such by comparison of n.m.r. and i.r. properties with those 68 in the literature.

Preparation of $[4,4-(PMe_2Ph)_2-arachno-4-PtB_8H_{12}]$ from $[NMe_4][B_9H_{14}]$ and $cis-[PtCl_2(PMe_2Ph)_2]$.—The complex $cis-[PtCl_2(PMe_2Ph)_2]$ (0.30 g, 0.55 mmol) was dissolved in a solution of $[NMe_4][B_9H_{14}]$ (0.20 g, 1.1 mmol) in CH_2Cl_2 (100 cm³) and allowed to stand overnight. T.l.c. analysis of the very pale yellow solution using $CH_2Cl_2-C_6H_{12}$ (80 : 20) as eluant showed a major product (R_1 0.35) and a minor

product $(R_f 0.42)$ as the principal products. The volume was reduced to ca. 20 cm³ under reduced pressure and the resulting mixture was filtered through silica gel [Kieselgel 60 (Merck); mesh 0.063-0.200 mm; ca. 5 g], at which point some gas was evolved. The silica gel was repeatedly washed with hot CH₂Cl₂ until the extracts were colourless and did not exhibit the presence of the major component $(R_{\rm f} 0.35)$ by t.l.c. analysis. The volume of the combined CH₂Cl₂ solutions was reduced to ca. 10 cm³, cyclohexane (ca. 10 cm³) added, and the crude product mixture separated by column chromatography using $CH_2Cl_2-C_6H_{12}$ (50:50; ca. 1 dm³) as eluant. The minor yellow product (0.025 g, 0.03 mmol) was identified as bis(dimethylphenylphosphine) bis- μ -(2-4- η -nido-hexaboranyl)-diplatinum(Pt-Pt), $[Pt_2(\eta^3 - B_6H_9)_2(PMe_2Ph)_2],$ by comparison with an authentic 12 sample. The major component was recrystallised from CH_2Cl_2 (ca. 5 cm³) by slow evaporation under

nitrogen, and an additional minor crop was obtained by addition of n-pentane to the mother-liquor followed by cooling to *ca.* -20 °C. This *product*, almost colourless when pure, m.p. (decomp.) 142—144 °C, was identified as 4,4-bis(dimethylphenylphosphine)-*arachno*-4-platinanonaborane, [4,4-(PMe₂Ph)₂-4-PtB₈H₁₂] (total isolated yield 0.275 g, 0.48 mmol, 85%), by comparison with the sample isolated and identified as described below [Found: C, 33.5; H, 6.00; B, 14.8; P, 10.9; Pt (by difference) 34.8. C₁₆H₃₄-B₈P₂Pt requires C, 33.7; H, 6.00; B, 15.2; P, 10.9; Pt, 34.2%], v_{max}. 2 515 cm⁻¹ (v_{BH}).

Isolation of [4,4-(PMe₂Ph)₂-arachno-4-PtB₈H₁₂], (I), from the Reaction of 6,6'-(B₁₀H₁₃)₂O with cis-[PtCl₂(PMe₂Ph)₂].-A solution of cis-[PtCl₂(PMe₂Ph)₂] (0.21 g, 0.38 mmol) and 6.6'-(B₁₀H₁₃)₂O (0.10 g, 0.38 mmol) in CH₂Cl₂-Et₂O (1:1, ca. 20 cm³) was stirred at ca. 20 °C for 72 h, filtered through silica gel [Kieselgel 60 (Merck), 0.063-0.200 mm mesh; ca. 5 g] and washed through with CH₂Cl₂-light petroleum (b.p. 60-80 °C) (50:50, ca. 100 cm³). The more volatile components were then removed from the combined filtrates under reduced pressure at $20 < \theta < 60$ °C and the product mixture separated using repeated preparative t.l.c. with CH₂Cl₂-light petroleum (b.p. 60-80 °C) (50:50) as eluant, vielding bis(dimethylphenylphosphine)bis-µ-(2-4-n-nidohexaboranyl)-diplatinum(Pt-Pt), $[Pt_{2}(\eta^{3}-B_{6}H_{9})_{2}(PMe_{2}-$ Ph)₂], ¹² as one of the products (10 mg, 0.013 mmol, 3.6%), together with somewhat larger quantities of 4,4-bis(dimethylphenylphosphine)-arachno-4-platinanonaborane, (\mathbf{I}) $[R_{\rm f} 0.35 \text{ in CH}_2Cl_2-\text{light petroleum (b.p. 60-80 °C) (50:50)}]$ (ca. 25 mg, 0.044 mmol, 10.5%), which was tentatively identified as such by n.m.r. spectroscopy (Tables 8 and 9). Recrystallisation from hot benzene yielded very pale yellow crystals, m.p. (decomp.) 142-144 °C, of which one was suitable for the X-ray diffraction experiments (see below and Tables 1-3, Figure 1) that confirmed the structure.

Preparation of $[6,6,9,9-(PMe_2Ph)_4$ -arachno- $6,9-Pt_2B_8-H_{10}]$, (II).—Potassium hydride (70% active, 0.040 g, corresponding to 0.69 mmol KH) was added to a solution of $[4,4-(PMe_2Ph)_2-4-PtB_8H_{12}]$ (0.15 g, 0.26 mmol) in CH_2Cl_2- thf (66: 34, 30 cm³). Mild heating was maintained by use of a hot-air blower and slow effervescence and some darkening of the solution occurred. The complex cis-[PtCl_2-(PMe_2Ph)_2] (0.143 g, 0.26 mmol) was then added, and the mixture stirred overnight at ca. 20 °C, during which time a precipitate developed. T.l.c. analysis of the solution showed one major component (R_f 0.35, 100% CH_2Cl_2 as eluant) together with a small quantity of the starting metallanonaborane (R_f 0.85). The mixture was filtered and the

precipitate washed with CH2Cl2 until the run-off was colourless. The combined liquids were evaporated to dryness under reduced pressure at $20 < heta_{
m c} < 50$ °C, and the residue separated by column chromatography using CH₂Cl₂ (ca. 1 dm³) as eluant. The major product was recrystallised from CH₂Cl₂ (ca. 5 cm³) by slow evaporation, and an additional minor crop was obtained from the mother-liquor by the addition of n-pentane. The colourless crystalline product, m.p. (decomp.) 194-196 °C, was identified as 6,6,9,9 $tetrak is (dimethyl phenyl phosphine) \hbox{-} arachno-6, 9 \hbox{-} diplatina$ decaborane, (II) (0.148 g, 0.14 mmol, 55%), by singlecrystal X-ray diffraction analysis and n.m.r. spectroscopy as described below and in the text [Found: C, 36.4; H, 5.1; B, 8.0; P, 11.6; Pt (by difference) 38.9. C₃₂H₅₄B₈P₄Pt₂ requires C, 37.0; H, 5.25; B, 8.3; P, 11.9; Pt 37.6%], v_{max}. 2 500 cm⁻¹ (v_{BH}).

X-Ray Diffraction Analysis.—(I). $C_{16}H_{34}B_8P_2Pt$, M = 570.0, Monoclinic, $a = 1.977 \ 1(8)$, $b = 1.302 \ 5(4)$, $c = 1.977 \ 3(4) \ nm$, $\beta = 110.99(3)^{\circ}$, $U = 4.754(3) \ nm^3$, Z = 8, $D_c = 1.593 \ Mg \ m^{-3}$, F(000) = 2.224, space group C2/c, Mo- K_{α} radiation, graphite monochromatized, $\lambda = 71.069 \ pm$, $\mu(Mo-K_{\alpha}) = 6.097 \ m^{-1}$.

(II). $C_{32}H_{54}B_8P_4Pt_2$, $M = 1\ 039.3$, Monoclinic, $a = 1.376\ 2(3)$, $b = 1.510\ 5(4)$, $c = 1.921\ 0(3)\ nm$, $\beta = 92.59(2)^\circ$, $U = 3.989(2)\ nm^3$, Z = 4, $D_c = 1.731\ Mg\ m^{-3}$, $F(000) = 2\ 008$, space group C2/c, μ (Mo- K_{α}) = 7\ 260\ m^{-1}.

Structure Determination .- Measurements were made on a Syntex P2, diffractometer. Cell dimensions and their standard deviations for each compound were obtained by least-squares treatment of the setting angles of 15 reflections having $35 < 2\theta < 40^{\circ}$. Intensities for all independent reflections with $4 < 2\theta < 50^\circ$ for (I) and with $4 < 2\theta < 45^\circ$ for (II) were measured in the ω -2 θ scan mode, with scans running from 1° below α_1 to 1° above α_2 . For (II), variable scan speeds (according to a pre-scan intensity) of 1-29° min⁻¹ were used. When these scan speeds were used for (I) however, there was substantial decomposition of the crystal during data collection and a much faster data collection with scan speeds of 4-29° min⁻¹ was used, when a control reflection showed negligible decline in intensity. In this way 4 331 reflections for (I) and 2 621 for (II) were measured. After correction for Lorentz, polarisation, and transmission factors $[A^* = 1.7 - 3.4 \text{ for (I)}, 2.9 - 6.7 \text{ for }$ (II)] those reflections having $I > 3\sigma(I)$ were retained for the structure analyses [3 194 for (I) and 2 410 for (II)]. The structures were solved from Patterson and electrondensity syntheses and full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms converged at R = 0.042, R' = 0.046 for (I) and R =0.030, R' = 0.057 for (II). For (II), a difference synthesis then readily gave the hydrogen positions as peaks of 0.43- $0.92 \text{ e} \text{ Å}^{-3}$ (430-920 e nm⁻³). These were included in the refinement, initially as fixed contributions (R = 0.024) and then refined with anisotropic temperature factors, giving a final R of 0.020 and R' = 0.029. For (I), with lower accuracy because of the more rapid data collection, satisfactory hydrogen positions were not obtainable from a difference map, and the structure analysis was terminated at the stage mentioned above. Atomic scattering factors were calculated using the analytical approximation and coefficients given in ref. 69. Least-squares weights were obtained from the modified variances $\sigma^2(I) = \sigma_e^2(I) +$ $(QI)^2$, with Q = 0 for (I) and Q = 0.02 for (II). The final atomic co-ordinates and their estimated standard deviations are given in Tables 1 and 4. Vibration parameters and a

J.C.S. Dalton

list of observed and calculated structure factors are in Supplementary Publication No. SUP 23035 (44 pp.).*

Nuclear Magnetic Resonance Spectroscopy.-100-MHz ¹H, ¹H-{¹¹B}, and ¹H-{³¹P}, 32-MHz ¹¹B and ¹¹B-{¹H}, and 40-MHz ³¹P-{¹H} experiments were carried out on a JEOL FX-100 pulse (Fourier-transform) spectrometer equipped for double resonance. Solutions and conditions were as specified in Tables 7-9 and in the text. Chemical shifts δ are given in p.p.m. to low frequency (' high field ') of SiMe₄ for ¹H, of $BF_3(OEt_2)$ for ¹¹B, and of 85% H_3PO_4 (Ξ 40 480 730 Hz) for ³¹P. Boron-11 longitudinal relaxation times $T_1(^{11}\text{B})$ were measured using the $\pi - \tau - \pi/2$ pulse sequence together with the null method; this was calibrated against the semilogarithmic plot method over the range of T_1 values measured using suitable model compounds.^{11,42} The π and $\pi/2$ pulses measured for the samples used were found to be 32 and 16 μ s respectively. The $\{X\}$ irradiation power levels used in selective ${}^{1}H{}^{-}\{X\}$ experiments had previously 11,42 been optimised by trial and error on known compounds for each particular type of decoupling experiment; however, the conditions were not particularly critical. ¹H-{¹⁹⁵Pt} experiments were carried out at 60 MHz observing frequency in the continuous wave observation mode on a modified JEOL C60-H instrument as described elsewhere.49

We thank the S.R.C. for equipment grants, and for a maintenance grant (to M. J. H.), the University of Leeds for a student demonstratorship (to S. K. B.), Mr. A. Hedley for micro-analyses, and Dr. W. McFarlane for collaboration in the ¹H-{¹⁹⁵Pt} n.m.r. experiments.

[0/1673 Received, 3rd November, 1980]

* For details see Notices to Authors No. 7, J. Chem. Soc., Dalton Trans., 1980, Index issue.

REFERENCES

1428

- ¹ A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, J.
- Am. Chem. Soc., 1970, 92, 2571.
 ² M. Green, J. A. K. Howard, K. L. Spencer, and F. G. A. Stone, J. Chem. Soc., Chem. Commun., 1974, 153; J. Chem. Soc., Dalton
- Trans., 1975, 2274. ³ D. A. Thompson, T. K. Hilty, and R. W. Rudolph, J. Am.
- Chem Soc., 1977, 99, 6774. ⁴ G. A. Kukina, I. A. Zakharova, M. A. Porai-Koshic, B. Stíbr, V. G. Sergienko, K. Baše, and J. Dolansky, *Izv. Akad.* Nauk SSSR, Ser. Khim., 1978, 1229.
- ⁵ K. Baše, A. Petřina, B. Stíbr, V. Petríček, K. Malý, and A. Linek, Chem. Ind. (London), 1979, 212.
- ⁶ N. N. Greenwood, *Pure Appl. Chem.*, 1977, **49**, 791. ⁷ N. N. Greenwood, J. D. Kennedy, and J. Staves, *J. Chem.* Soc., Dalton Trans., 1978, 1146.
- J. D. Kennedy, in Proceedings of the 19th International Conference on Coordination Chemistry, Praha, September 1978,
- vol. 1, p. 79. S. K. Boocock, N. N. Greenwood, M. J. Hails, J. D. Kennedy, W. S. McDonald, and J. Staves, 4th International Meeting on Boron Chemistry (IMEBORON IV), Salt Lake City, July 1979,
- paper no. 05. ¹⁰ J. D. Kennedy and J. Staves, Z. Naturforsch., Teil B, 1979,
- 84, 808.
 ¹¹ J. D. Kennedy and B. Wrackmeyer, J. Magn. Reson., 1980, **38**, 5Ž9.
- ¹² N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S.
 McDonald, J. Chem. Soc., Chem. Commun., 1980, 37.
 ¹³ S. K. Boocock, N. N. Greenwood, and J. D. Kennedy, J.
- Chem. Soc., Chem. Commun., 1980, 307.
- R. M. Adams, Pure Appl. Chem., 1972, 30, 683.
 N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, unpublished work.
- ¹⁶ R. Ahmad, Y. M. Cheek, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, unpublished work.

- ¹⁷ J. W. Lott, D. F. Gaines, H. Shenav, and R. Schaeffer, J. Am. Chem. Soc., 1973, 95, 3042.
 ¹⁸ J. W. Lott and D. F. Gaines, Inorg. Chem., 1974, 13, 2261.
 ¹⁹ J. C. Calabrese, M. B. Fischer, D. F. Gaines, and J. W. Lott,
- J. Am. Chem. Soc., 1974, 96, 6318.
- ²⁰ L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, J. Am. Chem. Soc., 1963, **85**, 2674. ²¹ D. C. Moody and R. Schaeffer, *Inorg. Chem.*, 1976, **15**,
- 233.
- ²² F. E. Wang, P. G. Simpson, and W. N. Lipscomb, J. Chem. Phys., 1961, **35**, 1335.
- ²³ N. N. Greenwood, H. J. Gysling, J. A. McGinnety, and J. D. Owen, *Chem. Commun.*, 1970, 505.
 ²⁴ R. D. Dobrott and W. N. Lipscomb, J. Chem. Phys., 1962,
- **37**, 1977.
- ²⁵ A. Tippe and W. Hamilton, Inorg. Chem., 1969, 8, 464.
- ²⁶ D. S. Kendall and W. N. Lipscomb, Inorg. Chem., 1973, 12, 546.
- ²⁷ J. Riddy and W. N. Lipscomb, J. Chem. Phys., 1959, **31**, 610; ²⁷ J. Riddy and W. N. Lipscomb, J. Chem. Phys., 1959, 31, 610;
 J. Am. Chem. Soc., 1959, 81, 754.
 ²⁸ D. M. P. Mingos, M. I. Forsyth, and A. J. Welch, J. Chem. Soc., Chem. Commun., 1977, 605.
 ²⁹ H. M. Colquhoun, T. J. Greenhough, and M. G. H. Wallbridge, J. Chem. Soc., Chem. Commun., 1977, 737; 1978, 322.
 ³⁰ M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, J. Chem. Soc., Chem. Commun., 1974, 794.
 ³¹ L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, J. Am. Chem. Soc. 1972 94 5665

- Am. Chem. Soc., 1972, 94, 5665.
- A. J. Welch, J. Chem. Soc., Dalton Trans., 1975, 2270.
 N. N. Greenwood, 'Boron,' Pergamon Press, Oxford, 1973,
- pp. 665–991 and refs. therein. ³⁴ N. N. Greenwood, J. A. McGinnety, and J. D. Owen, J. Chem. Soc., Dalton Trans.; 1972, 986.
- 35 D. E. Sands and A. Zalkin, Acta Crystallogr., 1962, 15, 410.
- ³⁶ K. Wade, Adv. Inorg. Chem. Radiochem., 1976, 18, 1.
 ³⁷ L. J. Todd, A. R. Siedle, F. Sato, A. R. Garber, F. R. Scholer, and G. D. Mercer, Inorg. Chem., 1975, 14, 1249.
 ³⁸ E. L. Muetterties, Inorg. Chem., 1963, 2, 647.
 ³⁹ D. E. Hyatt, F. R. Scholer, and L. J. Todd, Inorg. Chem., 1967, 4, 620.
- 1967, **6**, 630.
- ⁴⁰ A. O. Clouse, D. C. Moody, R. R. Rietz, T. Roseberry, and R. Schaeffer, J. Am. Chem. Soc., 1973, 95, 2496.
 ⁴¹ A. Allerhand, A. O. Clouse, R. R. Rietz, T. Roseberry, and
- R. Schaeffer, J. Am. Chem. Soc., 1972, 94, 2445.
- ⁴² J. D. Kennedy and N. N. Greenwood, Inorg. Chim. Acta, 1980, **35**, 93.
- 43 (a) A. J. Cheney, B. E. Mann, and B. L. Shaw, Chem.
- Commun., 1971, 431; (b) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, J. Am. Chem. Soc., 1972, 94, 5087, 44 V. T. Aftandalian, H. C. Miller, G. W. Parshall, and E. L.
- ⁴⁵ S. K. Boocock, N. N. Greenwood, J. D. Kennedy, and D. Taylorson, J. Chem. Soc., Chem. Commun., 1979, 16.
 ⁴⁶ P. Haake and P. C. Turley, J. Am. Chem. Soc., 1967, 89,
- 4611.
- ⁴⁷ R. K. Harris, *Can. J. Chem.*, 1964, **42**, 2275.
 ⁴⁸ E. G. Finer and R. K. Harris, *Mol. Phys.*, 1967, **12**, 457.
 ⁴⁹ J. D. Kennedy, W. McFarlane, R. J. Puddephatt, and P. J. Thompson, J. Chem. Soc., Dalton Trans., 1976, 874.
- ⁵⁰ J. D. Kennedy, W. McFarlane, and R. J. Puddephatt, J. Chem. Soc., Dalton Trans., 1976, 745. ⁵¹ W. McFarlane, J. Chem. Soc. A, 1967, 1922. ⁵² J. D. Kennedy, I. J. Colquhoun, W. McFarlane, and R. J.
- Puddephatt, J. Organomet. Chem., 1979, 172, 479, and refs. therein.
- 53 J. Emsley, J. Feeney, and L. Sutcliffe, 'High Resolution NMR Spectroscopy,' Pergamon Press, Oxford, 1966, vol. 1, pp. 392—399.
- ⁵⁴ R. K. Harris, J. R. Wolpin, R. E. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsenges. Phys. Chem.*, 1972, **76**, 44.
 ⁵⁵ D. W. Lowman, P. D. Ellis, and J. D. Odom, J. Magn. Reson.,

- 1972, 8, 289.
 ⁵⁶ J.-Y. Lallemand, J. Soulié, and J.-C. Chottard, J. Chem. Soc., Chem. Commun., 1980, 436.
 ⁵⁷ L. Ernst, Org. Magn. Reson., 1977, 9, 35; J. Chem. Soc., Chem. Commun., 1977, 375.
 ⁵⁸ D. Debeen and P. Schooffer. Lucag. Chem. 1968, 7 402.
- ⁵⁸ J. Dobson and R. Schaeffer, *Inorg. Chem.*, 1968, 7, 402.
 ⁵⁹ W. N. Lipscomb, *Pure Appl. Chem.*, 1977, 49, 701.
 ⁶⁰ R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *J. Am. Chem.* Soc., 1970, **92**, 3514. ⁶¹ R. Schaeffer and E. Walter, *Inorg. Chem.*, 1973, **12**, 2209.

⁶² N. N. Greenwood, J. D. Kennedy, and D. Reed, J. Chem. Soc., Dalton Trans., 1980, 196.

Soc., Dalton Trans., 1980, 196.
⁶³ See, for example, Inorg. Synth., 1970, 12, 27.
⁶⁴ J. Plešek, S. Heřmánek, and B. Stíbr, Collect. Czech. Chem. Commun., 1967, 32, 1095.
⁶⁵ N. N. Greenwood, J. D. Kennedy, T. R. Spalding, and D. Taylorson, J. Chem. Soc., Dalton Trans., 1979, 840.
⁶⁶ S. K. Boocock, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, and J. Staves, J. Chem. Soc., Dalton Trans., 1980, 790.

⁶⁷ W. R. Pretzer and R. W. Rudolph, J. Am. Chem. Soc., 1976,

⁶⁹ W. R. Fletzel and R. W. Rudolph, J. Inst. Chem. 1977, 11,
⁶⁹ R. Schaeffer and L. G. Sneddon, *Inorg. Chem.*, 1972, 11,
⁶¹ R. Schaeffer and L. G. Sneddon, *S. E. Stafiej*, and E. A. Takacs, *Inorg. Chem.*, 1970, 9, 1844; V. T. Brice, H. D. Johnson, D. L. Denton, and S. G. Shore, *Inorg. Chem.*, 1972, 11, 1135.
⁶⁹ International Tables for X-Ray Crystallography,' Kynoch

Press, Birmingham, 1974, vol. 4.