Polyhedral platinaborane chemistry. Some structural and NMR studies on the four-vertex *arachno*-1-platinatetraborane system

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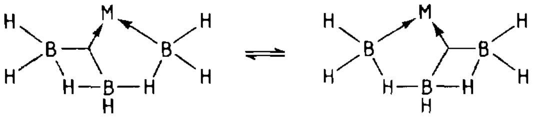
Abstract

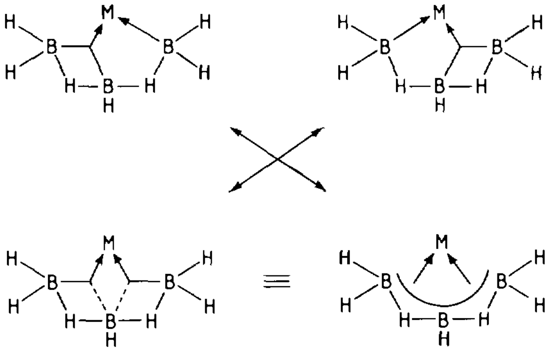
The structure of the four-vertex platinaborane [1,1-$(PPh_3)_2$-*arachno*-1-PtB_3H_7] (**4**) has been determined from single-crystal X-ray diffraction data and compared to the disordered asymmetric structure of the compound [1,1-$(PMe_2Ph)_2$-*arachno*-1-PtB_3H_7] (**1**) and to the palladium analogue [1,-(1,1′-bdppf)-1-PdB_3H_7] (**3**) (bdppf = bis(diphenylphosphino)ferrocene). Compound **4** crystallizes in the triclinic space group $P\bar{1}$, with $a = 1065.2(2)$, $b = 1800.6(3)$, $c = 989.0(2)$ pm, $\alpha = 99.14(2)$, $\beta = 108.23(1)$, $\gamma = 88.06(1)°$, $Z = 2$ and $V = 1.7785(5)$ nm^3; $R = 0.045$ ($R_w = 0.091$). The B(2)Pt(1)B(4) plane of the borane ligand is slightly tilted (7.7(4)°) with respect to the platinum–bis(phosphorus) plane and resembles the arrangement found in the dimethylphenylphosphine compound **1** and the palladium analogue **3**. NMR properties of compound **4** have been measured and those of compound **1** remeasured and reassessed. In both compounds **1** and **4** the nucleus of the platinum atom is more strongly coupled to that of the central boron atom ($^1J(^{195}Pt-^{11}B)$ *c.* 600 Hz) compared to those of the outer boron atoms ($^1J(^{195}Pt-^{11}B)$ *c.* 230 Hz). This is in contrast to the coupling pattern found for $^1J(^{195}Pt-^{13}C)$ in π-allyl η^3-C_3H_5-type compounds, suggesting that the central boron atom may be bound to the platinum atom via a bond with substantial 2-electron 2-centre s character.

Introduction

Since the work of Muetterties and co-workers some 20 years ago on the synthesis and characterization of the so-called 'borallyl' *arachno*-1-platinatetraboranes such as [$(PMe_2Ph)_2PtB_3H_7$] (**1**) [1, 2], there has been occasional sporadic interest in other examples of this type of system, for example the iridium compound [$(CO)(PPh_3)_2HIrB_3H_7$] (**2**) [3]. The original work on platinum compounds [1, 2] resulted in an X-ray structure for [$(PMe_2Ph)_2PtB_3H_7$] (**1**) [2] that revealed the *arachno*-1-platinatetraborane cluster nature of the species, and thereby indicated a geometric parallel between the disposition of the atoms in the {PtB_3} cluster and the disposition of the atoms in the {MC_3} clusters of metal π-allyl species. This original structural solution was severely beset with disorder problems, but indicated that the borane ligand adopted an unsymmetrical orientation with respect to the platinum atom. This, taken together with (i) the different Pt(1)–B(2) and Pt(1)–B(4) distances of 238 and 213 pm, respectively, in the solid-state structure, and (ii) a supposed inequivalence of the phosphine ligands inferred from the results of ^1H NMR spectroscopy, was interpreted as being indicative either of (i) a σ–π-type bonding of the borane cluster to the platinum atom (Scheme 1), or alternatively of (ii) a π-allyl type bonding (Scheme 2) in which the tilt of the B(2)–Pt(1)–B(4) plane with respect to the P–Pt–P plane would be representative of an asymmetric ground state of the molecule.



Scheme 1.



Scheme 2.

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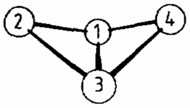
Some aspects of this interpretation, however, would not seem to be consistent with a more complete investigation of the NMR properties of the compound (see below), by the results of structural studies of $[(CO)(PPh_3)_2HIrB_3H_7]$ (**2**) [3] and, more recently, by an account of some structural and NMR work [4] on an *arachno*-2-palladatetraborane analogue [1-(1,1′-bdppf)-1-PdB_3H_7] (bdppf = bis(diphenylphosphino)-ferrocene) (**3**), which displays a somewhat more symmetrical arrangement. Some interest therefore still focuses on the nature of the boron-to-metal bonding in these systems and on any parallels that there might be with hydrocarbon π-allyl ligands: in particular, there is interest as to whether there is a true parallel between the borane and the hydrocarbon π-allyl coordination modes, and thereby whether a 'borally' descriptor is truly merited. Our initial objective in the present work therefore was to obtain a more exact solid-state structure* on a platinum derivative in order to effect a geometrical comparison with the palladium compound **3** and our iridium analogue $[(CO)(PPh_3)_2HIrB_3H_7]$ (**2**) [3]. A second objective was to effect an NMR study in order to look for useful comparisons that also may throw light on any bonding differences or similarities.

Some aspects of this work have been mentioned previously in review articles [5, 6]. The four-vertex *arachno* numbering system is as in structure **I**.



I

Results and discussion

Preparative and structural studies

The platinaborane [1,1-$(PPh_3)_2$-*arachno*-1-PtB_3H_7] (**4**) was prepared in a manner that differed somewhat from that used by Muetterties and co-workers [1, 2] who obtained the compound from the reaction of [*arachno*-B_3H_8]$^-$ with [*trans*-$PtClH(PMe_2Ph)_2$] in 1,2-dimethoxyethane. In the present work we obtained our product from the reaction of [*trans*-$PtClH(PPh_3)_2$] with [*nido*-B_5H_8]- in tetrahydrofuran at *c*. 210 K. The reaction apparently proceeds via a yellow intermediate compound which decomposes at room temperature to give compound **4**. A similar reaction between [*nido*-B_5H_8]- and *cis*-[$PtCl_2(PPh_3)_2$] has previously been found to give *cis*-[$Cl(PPh_3)_2Pt$(μ-2,3-*nido*-B_5H_8)] [7] and in the present work the intermediate may well be the hydride analogue of this, viz. *cis*-[$H(PPh_3)_2Pt$(μ-2,3-*nido*-B_5H_8)]. However, in our hands so far, compound **4** has been the only isolatable and characterizable metallaborane product from this reaction. Crystals suitable for X-ray diffraction analysis were obtained via the diffusion of pentane into a solution of the compound in dichloromethane.

In the X-ray diffraction analysis all non-hydrogen atoms were located from the diffraction data but the reliable location of the borane hydrogen atoms was not possible. Figure 1 shows an ORTEP diagram of the molecule of compound **4**, and Table 1 contains a listing of selected interatomic distances and angles, together with interplanar angles of interest, for compounds **1** and **3** as well as **4**. The comparative dispositions of the MB_3 clusters versus the PMP planes in **1**, **3** and **4**, and in the iridatetraborane $[(CO)(PPh_3)_2HIrB_3H_7]$ (**2**), are illustrated in Fig. 2.

The $\{MB_3H_7\}$ cluster structure of compound **4** is very similar to that of the recently reported [4] palladium compound **3**, with all equivalent metal–boron and interboron distances between the two compounds being the same within experimental error. The $\{B_3H_7\}$ and phosphine ligands show similar relative orientations, with the vector between the B(2)–B(4) atoms in **4** slightly twisted at an angle of 7.7(4)° with respect to the P(1)–Pt(1)–P(2) plane, compared to 11.7° in **1** and 6.5° in **3**.

The interatomic distances and angles in **3** and **4** are also quite similar in many respects to the values obtained for **1** and for $[(CO)(PPh_3)_2HIrB_3H_7]$ (**2**) [3]. Comparing the more accurately determined structures of **3** and **4** with the iridatetraborane **2**, the most noticeable difference is that among the dihedral angles between the P(1)M(1)P(2) and B(2)B(3)B(4) planes, which are *c*. 119 and 121° in the platinum and palladium compounds and only 101° in the iridium compound (see also Fig. 2). The former values are on the higher limits of the range of those generally found in π-allyl–metal compounds (108–120°) [8]. The latter value is associated

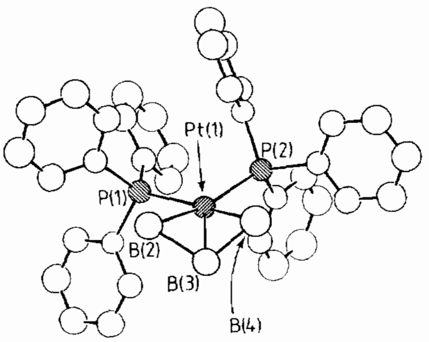


Fig. 1. ORTEP drawing of the crystallographically determined molecular structure of [1,1-$(PPh_3)_2$-*arachno*-1-PtB_3H_7] (**4**) with hydrogen atoms omitted.

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*During the preparation of this manuscript structural work on two other platinatetraboranes, [$\{Ph_2P(CH_2)_nPPh_2\}PtB_3H_7$], where $n = 2$ or 4, has been reported; cluster hydrogen atoms in these species were also not located (see ref. 29).

TABLE 1. Selected distances (pm) and angles between interatomic vectors (°) for [1,1-$(PPh_3)_2$-*arachno*-1-PtB_3H_7] (**4**), together with those of [1-(1,1′-bdppf)-1-PdB_3H_7] (**3**) and [1,1-$(PMe_2Ph)_2$-*arachno*-1-PtB_3H_7] (**1**) for comparison, with e.s.d.s in parentheses

	4	**3**	**1**
Distances			
M(1)–P(1)	234.1(3)	236.6(1)	230.19(4)
M(1)–P(2)	231.3(3)	236.4(1)	231.1(4)
M(1)–B(2)	218.8(17)	218.2(3)	238(4)
M(1)–B(3)	214.9(16)	215.4(3)	218(4)
M(1)–B(4)	222.3(20)	219.0(3)	213(3)
B(2)–B(3)	175.0(30)	179.2(5)	186(5)
B(3)–B(4)	189.0(30)	178.7(5)	192(4)
C(11)–P(1)	182.4(6)		
C(21)–P(1)	184.7(7)		
C(31)–P(1)	182.4(7)		
C(41)–P(2)	183.6(7)		
C(51)–P(2)	181.5(7)		
C(61)–P(2)	182.1(7)		
Angles			
P(1)–M(1)–P(2)	100.4(1)	104.2(1)	96.2(1)
B(2)–M(1)–P(1)	84.8(5)	82.6(1)	82.6(9)
B(2)–M(1)–P(2)	164.5(5)	166.6(1)	164.8(9)
B(3)–M(1)–P(1)	123.6(5)	121.5(1)	117.9(9)
B(3)–M(1)–P(2)	133.6(5)	130.8(1)	141.7(9)
B(4)–M(1)–P(1)	171.4(5)	168.1(1)	170.4(9)
B(4)–M(1)–P(2)	87.4(5)	87.4(1)	93.3(9)
B(2)–M(1)–B(3)	48.2(6)	48.7(1)	47.8(12)
B(2)–M(1)–B(4)	86.7(7)	85.5(1)	88.3(13)
B(3)–M(1)–B(4)	50.2(7)	48.7(1)	52.9(12)
B(2)–B(3)–B(4)	113.2(12)	112.0(3)	112.9(23)
Planes			
P(1)M(1)P(2)/B(2)B(4)	7.7(4)	6.5(1)	11.7(8)
P(1)M(1)P(2)/B(2)B(3)B(4)	121.4(13)	119.1(2)	117(2)
M(1)B(2)B(3)/M(1)B(3)B(4)	129.7(10)	129.4(2)	129(2)

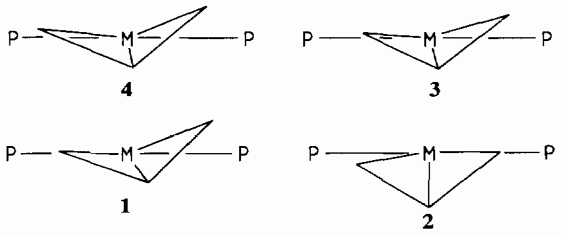

Fig. 2. Views of the $\{MB_3\}$ butterfly cluster structures of compounds **1**, **2**, **3** and **4**, viewed in the PMP plane and along the P–M–P bisector. Compounds **1**, **3** and **4** are structurally closely related, but differ from the iridium compound **2** which is claimed to have a different electronic structure [3]. The difference is also manifested in the different NMR characteristics (e.g. Fig. 4).

with a noticeably shorter distance to the central B(3) atom in the iridium compound (Ir(1)–B(3) *c.* 220 pm and Ir(1)–B(2/4) *c.* 230 pm) and this has been taken to be a result of extra electronic contributions to the central atom from a d^4 iridium(V) centre [3]. It may be noted that the Pd(1)–B(3) and Pt(1)–B(3) distances of **3** and **4** are, by contrast, only slightly shorter than the Pd(1)–B(2,4) and Pt(1)–B(2,4) distances, a feature which is also a characteristic of metal–carbon distances in many $\{MC_3H_5\}$ π-allyl complexes.

Terminal borane hydrogen atoms were not located in compound **4**, but the H(axial)–B(2/4)–H(endo) angles in the palladium compound **3** at *c.* 120 and 124(2)° could perhaps be taken to be more in line with a 120° angle required for sp^2 hybridized boron atoms rather than 109° expected for sp^3 hybridization (see, however, NMR considerations below). In this context those in the iridaborane **2** appear to be intermediate at *c.* 115(4)°, but in both species **2** and **3** the e.s.d.s are large so that little useful information can realistically be ascertained from these particular angles.

NMR considerations

We thought that additional insight into the bonding patterns in these compounds might derive from a consideration of their NMR properties. Details of the NMR properties of **1** and **4** are listed in Table 2. In the consideration of these there are a number of factors which must be taken into account in order to distinguish between a σ–π 'borallyl'-type of bonding and other possibilities.

As stated previously [1, 2] an unsymmetrical bonding arrangement would in principle involve inequivalent phosphine NMR resonances. In the original work on compound **1** this type of inequivalence was inferred from the measured ^1H NMR spectrum, which showed two distinct resonances ($\Delta\sigma$ *c.* 0.2 ppm) arising from the phosphine methyl hydrogen atoms, although no inequivalence was noted for the ^{31}P resonances. The ^1H inequivalence, however, will arise from the proximity of the methyl groups to the prochiral metal centre, and in fact in this system inequivalent phosphine ligands would require four not two methyl hydrogen atom resonance positions. Additionally two ^{31}P resonance positions would be predicted, but each of the PMe_2Ph (compound **1**), PPh_3 (compound **4**) and the PEt_3 [1] complexes features only one ^{31}P resonance position. An inequivalence could, in principle, arise from an equilibrium process (Scheme 1), but we have found there is no evidence of any 'freezing out' of two species at temperatures down to 203 K for **1** and 223 K for **4**. Further possible dynamic processes could include a rocking of the $\{B_3H_7\}$ ligand about an approximate Pt(1)–B(3) axis, or a rotation of the ligand as is found in π-allyl complexes [11]. The observed tilting of the B(2)–B(4) vector with respect to the metal phosphine plane, of 3.9(2)→6.5(1)→7.7(4)→11.7(8)° in the compound sequence **2**→**3**→**4**→**1**, suggests that the rocking librations may well occur in solution, with these reported solid-state structures representing 'snapshots' of the process, but we have found no evidence for the freezing of such a fluxionality in the NMR spectra of these

TABLE 2. Multinuclear NMR data for [1,1-$(PMe_2Ph)_2$-*arachno*-1-PtB_3H_7] (**1**) and [1,1-$(PPh_3)_2$-*arachno*-1-PtB_3H_7] (**4**)

Assignment	[$(PMe_2Ph)_2PtB_3H_7$] (**1**)[a]			[$(PPh_3)_2PtB_3H_7$] (**4**)	
	$\delta(^{11}B)$[b]	$J(B–H)$	$^{1}J(^{195}Pt–^{11}B)$[c]	$\delta(^{11}B)$	$^{1}J(^{195}Pt–^{11}B)$
B(2,4)	+1.6[d]	115[e]	230±30	+2.8	Not resolved
B(3)	+18.6[f]	130	+560±10	+18.3	600±20
	$\delta(^{1}H)$[g]	$\delta(^{1}H)$[b]	$J(^{195}Pt–^{1}H)$[c]	$\delta(^{1}H)$[b]	$J(^{195}Pt–^{1}H)$
H(3)	+3.96	+2.97[h]	−58±5	+3.23(3H)	
H(2,4)	+4.53	+3.67	−70±10	+2.38(2H)	76.5
H(2,4)	+3.60	+2.66	<15(−ve)		
H(bridge)	−2.10	−2.97[h, i]	+61±3	−2.64(2H)	80
$H(Me_2P)$[j]	+1.29	+1.57	23.5±0.5[k]		
	+1.34	+1.62	26.4±0.5[k]		

[a] $\delta(^{31}P)(CD_2Cl_2$, 294 K) −5.9 ppm, $w_{1/2} \sim 80$ Hz, $J(^{195}Pt–^{31}P)$ 2625±5 Hz; (CD_2Cl_2, 203 K) −6.0 ppm, $w_{1/2}$ 12±2 Hz, $J(^{195}Pt–^{31}P)$ 2610±2 Hz. [b] CD_2Cl_2 solution at *c.* 298 K. [c] Signs by $^{1}H\{^{11}B\}$ experiments relative to 560 Hz coupling (δ +18.6) taken as positive; no differential sharpening observed in $^{1}H–\{^{11}B\}$ experiments at $\nu(^{11}B) \pm 115$ Hz when ν corresponds to $\delta(^{11}B)$ +1.6. [d] $T_1 \sim 0.9$ ms. [e] Both couplings approximately equal. [f] $T_1 \sim 1.7$ ms. [g] C_6D_6 solution at *c.* 298 K. [h] Probable coupling $^{2}J(^{1}H–B–^{1}H)$ 6.5 Hz. [i] Splitting $N = (^{2}J + ^{4}J)(^{31}P–^{1}H) = 11 \pm 2$ Hz. [j] Splitting $N = (^{2}J + ^{4}J)$ $(^{31}P–^{1}H)$ 8.5 Hz. [k] $^{1}H–\{^{195}Pt\}$ experiments (technique as in ref. 9) gave $\Xi(^{195}Pt)$ 21 380 990±300 Hz; i.e. $\delta(^{195}Pt)$ −1917±15 relative to [$PtCl_2(SMe_2)_2$] which has $\Xi(^{195}Pt)$ 21 420 980 Hz (see also ref. 10).

compounds at low temperature, which suggests a very low-energy process. Conversely there was no evidence for a full rotational fluxionality at higher temperatures. In this context the reported temperature dependence [2] of the ^{1}H NMR spectrum of compound **1** is almost certainly due to thermal decoupling [12] of H(B) atoms.

Thus the tilting away from a presumed symmetrical ground-state structure is reasonably ascribed to crystal packing forces [4], although at present there is no experimental evidence to discount the possibility that these observed asymmetric solid-state structures do in fact approximate to asymmetric ground states of the molecules, with an extremely facile rocking between the enantiomers in solution. In this respect it may be noted that a number of other borane clusters, that contain a platinum atom similarly bound to three boron atoms, and in which an analogous mode of metal–borane bonding is proposed [13–18], show similar orientations of the metal-bound B_3 triangle. Thus in [$(PMe_2Ph)_2$-*arachno*-PtB_8H_{12}] [13] the twist angle is 7.1(4)° and the tilt angle 117.9(7)°, in [9,9-$(PMe_2Ph)_2$-*arachno*-9,6-$PtCB_8H_{11}$] [18] the angles are 7.3(1) and 118.3(4)°, and in [9,9-$(PMe_2Ph)_2$-*arachno*-9,6-$PtNB_8H_{10}$] [18] they are 7.1(3) and 107.4(5)°. Other related compounds [14–17], however, show a variety of orientations thereby not excluding the possibility that the few {MB_3H_7} structures so far observed could all be coincidentally similar, and that other variations may occur with different metal centres.

NMR-derived coupling constant information is also of relevance. It may be noted that the coupling constants $^{1}J(^{195}Pt–^{11}B)$ to the central (B(3)) and wingtip (B(2) and B(4)) boron atoms are quite different, with the $^{1}J(^{195}Pt(1)–^{11}B(3))$ values of *c.* 600 Hz being amongst the largest of which we are aware [6] for an intracluster platinum–boron link. Thus they are much larger than the more usual [6] intracluster values of *c.* 230 Hz to B(2) and B(4) in compound **1**, and also larger than the similarly typical values of *c.* 250 Hz in other platinaboranes such as [$(PMe_2Ph)_2PtB_8H_{12}$] [13] mentioned above, and in other platinaheteroboranes in which the platinum atom is similarly bound to three boron atoms [14, 17–19]. This suggests a strong two-centre bonding interaction between the platinum and the central B(3) atoms that involves high boron s character, a conclusion reinforced by the only other comparable high value of *c.* 595 Hz observed for the intersubcluster Pt(7)–B(2′) linkage in [$(PMe_2Ph)_2Pt$-η^1,η^2-*anti*-$B_{18}H_{20}$] (Fig. 3) [6, 20] in which the boron atom is reasonably thought to be bound to the platinum atom by a two-electron two-centre σ-bond with substantial apical boron *exo*-terminal s character. By contrast comparable organoplatinum {PtC_3} π-allyl compounds typically feature low values for coupling constants $^{1}J(^{195}Pt–^{13}C)$ to the central carbon atom, particularly as compared to the wingtip atoms, as illustrated in Table 3. This is in accord with the π-bonded nature of the hydrocarbon ligand which will involve little C(3) s character in the platinum–carbon interaction.

There is also some interest in a comparison of the ^{11}B NMR chemical shifts of the above range of com-

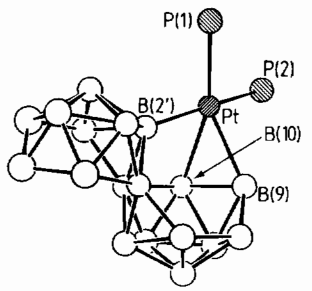

Fig. 3. Molecular structure of $[(PMe_2Ph)_2Pt\text{-}\eta^1,\eta^2\text{-}anti\text{-}B_{18}H_{20}]$. The platinum–B(2) linkage *trans* to P(2) is relatively short at 212(1) pm and is believed to have high platinum and boron s character with a correspondingly large coupling constant $^1J(^{195}Pt–^{11}B)$ of 595 Hz associated with it (compare compounds **1** and **4**). By contrast the couplings to $^{11}B(9)$ and $^{11}B(10)$ *trans* to P(1) are *c.* 250 Hz, more typical [6] of intracluster three-centre linkages. The couplings $^1J(^{195}Pt–^{31}P)$ to P(1) and P(2) are markedly different at 3335 and 1430 Hz, respectively, reflecting the relative σ-demand of the three-centre bond to B(9)B(10) and the two-centre bond to B(2).

TABLE 3. Coupling constant data $^1J(^{195}Pt–^{13}C)$ and $^1J(^{195}Pt–^{11}B)$ for various π-allyl compounds and compounds **1** and **4**

Compound	C(2)	C(3)	C(4)	Reference
$[trans\text{-}Pt(C_3H_5)_2]$	225.8	61.0	225.8	21
$[Pt(1\text{-}MeC_3H_4)(Pet_3)_2]^+$	74	6	86.3	22
$[Pt(2\text{-}MeC_3H_4)(C_8H_{12})]^+$	154	47	154	23
$[Pt(2\text{-}MeC_3H_4)(C_8H_8)]^+$	142	43	142	23
	B(2)	B(3)	B(4)	
Compound **1**	230	560	230	this work
Compound **4**	^{a}	600	^{a}	this work

^{a}Not resolved.

pounds, both among each other, and also against the borane analogues $[1\text{-}(CO)\text{-}arachno\text{-}B_4H_8]$ [22] and $[1\text{-}(PF_3)\text{-}1\text{-}arachno\text{-}B_4H_8]$ [24] in which the position of the metal moiety of compounds **1**, **3** and **4** is occupied by an LBH moiety (L = CO or PF_3). These comparisons are illustrated in Fig. 4.

The chemical shifts for the central boron atoms B(3) in compounds **1**, **3** and **4** show a large difference of *c.* 20 ppm to low field when compared to the LB_4H_8 analogues, with that for the wingtip boron atoms being little changed. Here there is a notable contrast with the iridium compound **2**, in which the wingtip boron atoms now exhibit an upfield shift of *c.* 30 ppm with the resonance for the central boron atom now being little changed. This suggests that the cluster bonding in this iridium compound is substantially different to that in the platinum and palladium compounds, but it is not clear to what extent this may or may not support the iridium(V) d^4 'capped octahedral' bonding description of compound **2** that has been proposed elsewhere [3].

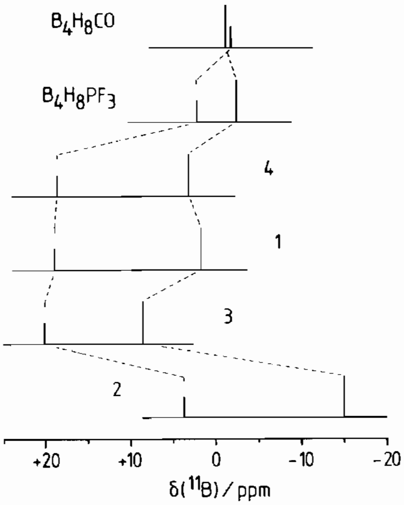

Fig. 4. Stick diagrams of the chemical shifts and relative intensities in the ^{11}B NMR spectra of the *arachno* four-vertex compounds $[1\text{-}(PF_3)B_4H_8]$, $[1\text{-}(CO)B_4H_8]$, $[(PPh_3)_2PtB_3H_7]$ (**4**), $[(PMe_2Ph)_2PtB_3H_7]$ (**1**), $[(bdppf)PdB_3H_7]$ (**3**) and $[(CO)(PPh_3)_2HIrB_3H_7]$ (**2**). In addition to the $^{11}B(3)$ and $^{11}B(2,4)$ resonances shown here the two tetraboranes $[(PF_3)B_4H_8]$ and $[(CO)B_4H_8]$ have very high field $^{11}B(1)$ resonances at *c.* −58 ppm [24].

Incidental observations

An interesting observation incidental to this work that is convenient to report here concerns the nature of any intermediates that must arise in the originally reported [1, 2] reactions between the $[arachno\text{-}B_3H_8]^-$ anion and $[PtHCl(PMe_2Ph)_2]$ or $[PtCl_2(PMe_2Ph)_2]$ in the presence of base to generate $[(PMe_2Ph)_2PtB_3H_7]$ (**1**). Such intermediates could be of general formulation $\{(PMe_2Ph)_2ClPtB_3H_8\}$ or $\{(PMe_2Ph)_2HPtB_3H_8\}$, and the reaction coordinate would thereby presumably proceed successively through these $\{arachno\text{-}2\text{-}PtB_3H_8\}$, and then $\{arachno\text{-}1\text{-}PtB_3H_7\}$, structural types [25] as H_2 or HCl, respectively, are eliminated. There is some interest as to whether any such intermediates are observable or isolatable, and with this in mind we have examined the reaction between $[B_3H_8]^-$ and $[PtCl_2(PMe_2Ph)_2]$ in the absence of base. NMR spectroscopy on the reaction products shows the presence of a new platinaborane species, the observed parameters (Table 4) perhaps being more suggestive of a $\{PtB_3H_7\}$ intermediate such as $\{(PMe_2Ph)_2HClPtB_3H_7\}$ rather than a $\{PtB_3H_8\}$ one such as $\{(PMe_2Ph)_2ClPtB_3H_8\}$ (compare ^{11}B NMR data for the iridium compound **2**). This intermediate is, we think, sufficiently stable to be isolatable, but in our hands so far we have not been able to obtain it sufficiently free of $[PtCl_2(PMe_2Ph)_2]$, $[PtHCl(PMe_2Ph)_2]$ or $[(PMe_2Ph)_2PtB_3H_7]$ for rigorous characterization.

TABLE 4. NMR data (CD_2Cl_2 solution) for the proposed $\{PtB_3H_7\}$ intermediate in the synthesis of $[(PMe_2Ph)_2PtB_3H_7]$ (**1**)

$\delta(^{11}B)$ (294 K) (ppm)	$+13.3$ [1B $^1J(^{195}Pt–^{11}B)$ 540 ± 40 Hz] *c.* -0.1 [2B, possibly inequivalent; any $^1J(^{195}Pt–^{11}B)$ unresolved]
$\delta(^{31}P)$ (203 K) (ppm)	-8.1 [$^1J(^{195}Pt–^{31}P)$ 2495 ± 3 Hz] -7.7 [$^1J(^{195}Pt–^{31}P)$ 2693 ± 3 Hz]
$^2J(^{31}P–^{31}P)$ (Hz)	18 ± 1 at 203 K
$\delta(^1H)$ (PMe_2) (294 K) (ppm)	$+1.87$ [$^3J(^{195}Pt–^1H)$ 25 Hz] $+1.71$ [$^3J(^{195}Pt–^1H)$ 30 Hz]

Conclusions

The main conclusions that may be drawn from this work are as follows. (i) The structure obtained by Muetterties and co-workers [1, 2] is asymmetric because of crystallographic considerations and probably not because of an intrinsically asymmetric σ–π metal–borane bonding mode. This is also supported by conclusions made [4] by considering the palladium compound **3**. (ii) The large coupling $^1J(^{195}Pt(1)–^{11}B(3))$ is indicative of high boron s character and suggests that the bonding in these complexes is significantly different to that in the organometallic $\{MC_3\}$ π-allyl complexes. One principal difference is that the intercarbon linkages in the quasi-planar allyl $\{C_3H_5\}^-$ anion involve predominantly sp^2 hybrids, and in these terms bonding to the central metal atom will thereby have predominant carbon p character, whereas in the quasi-isoelectronic $\{B_3H_7\}^{2-}$ ligand system the B–H–B bridging hydrogen atoms induce more boron sp^3 hybrid character and there is correspondingly a substantially greater boron s interaction with the metal centre.

Experimental

General

Reactions were carried out under a dry nitrogen atmosphere although separatory procedures were carried out in air. [*cis*-$PtHCl(PPh_3)_2$] was prepared by standard methods [26] and samples of $[(PMe_2Ph)_2PtB_3H_7]$ (**1**) were prepared essentially according to the original method [1, 2].

NMR spectroscopy

^1H (*c.* 100 mHz), ^{31}P (*c.* 40 MHz), and ^{11}B (*c.* 32 MHz) NMR data were obtained using a JEOL FX100 instrument. $^{31}P\{^1H(\text{broadband noise})\}$ spectra were recorded at lower temperatures to maximize line sharpening arising from the 'thermal decoupling' of the effects of boron nuclear spins [12]. Chemical shifts are given in parts per million (ppm) to high frequency (low field) of $SiMe_4$ (Ξ 100 MHz) for ^1H, of $BF_3 \cdot OEt_2$ (Ξ 32 083 971 Hz) for ^{11}B, and of 85% H_3PO_4 (Ξ 40.480 730 MHz) for ^{31}P, Ξ being defined as in ref. 27. Electron-mediated coupling constants J are given in Hz.

Synthesis of [1,1-$(PPh_3)_2$-arachno-1-PtB_3H_7] (4)

Tetrahydrofuran (*c.* 10 ml) and *nido*-B_5H_9 (75 μmol) were condensed into a flask containing KH (60 mg, 50% active, corresponding to 75 μmol) at 208 K and allowed to react with stirring until gas evolution stopped. CH_2Cl_2 (*c.* 10 ml) was then condensed in, and [*cis*-$PtHCl(PPh_3)_2$] (0.57 g, 75 μmol) was added via a tipper tube. Stirring was continued. The solution rapidly turned a yellow colour, and after 1 h it was a light orange colour. On warming to room temperature rapid gas evolution occurred and the solution darkened. Preparative thin-layer chromatography (silica gel, Fluka type GF-254, 50/50 CH_2Cl_2/pentane) yielded a very pale yellow crystalline substance, [1,1-$(PPh_3)_2$-*arachno*-1-PtB_3H_7] (**4**), as the only metallaborane product (0.11 g, 140 μmol, 19%).

X-ray crystallography

Data collection

Measurements on a crystal of compound **4** were made on a Syntex $P2_1$ diffractometer. Cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles of 15 reflections with $35 < 2\theta < 40°$. All independent reflections with $4 < 2\theta < 45°$ were measured in the ω–2θ scan mode, with scans running from 1° below α_1 to above α_2 and scan speeds ranging from 1–29° min^{-1}, depending on a pre-scan intensity. The data were corrected for Lorentz, polarization and transmission factors and the 4635 reflections having $I > 2\sigma(I)$ were employed in the structure determination.

Structure determination

Computations were carried out using SHELX 76 [28] programs. Solution of the structure by heavy atom methods was followed by full-matrix least-squares refinement using weights determined from counting statistics. Introduction of absorption corrections at the isotropic stage of the refinement reduced R from 0.12

TABLE 5. Non-hydrogen fractional atomic coordinates for [1,1-$(PPh_3)_2$-*arachno*-1-PtB_3H_7] (**4**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Pt(1)	0.41303(4)	0.22537(2)	0.66765(4)
P(1)	0.28442(31)	0.31258(17)	0.53359(34)
P(2)	0.25954(29)	0.12893(17)	0.61810(32)
B(2)	0.5807(17)	0.2952(9)	0.6771(18)
B(3)	0.5990(17)	0.2533(11)	0.8323(18)
B(4)	0.5610(18)	0.1508(11)	0.7907(20)
C(11)	0.2739(7)	0.4020(3)	0.6456(6)
C(12)	0.3397(7)	0.4128(3)	0.7935(6)
C(13)	0.3260(7)	0.4801(3)	0.8790(6)
C(14)	0.2466(7)	0.5366(3)	0.8166(6)
C(15)	0.1808(7)	0.5258(3)	0.6687(6)
C(16)	0.1945(7)	0.4585(3)	0.5832(6)
C(21)	0.1069(6)	0.2974(4)	0.4328(7)
C(22)	0.0217(6)	0.2930(4)	0.5135(7)
C(23)	−0.1136(6)	0.2813(4)	0.4444(7)
C(24)	−0.1636(6)	0.2741(4)	0.2946(7)
C(25)	−0.0784(6)	0.2785(4)	0.2139(7)
C(26)	0.0569(6)	0.2901(4)	0.2830(7)
C(31)	0.3533(7)	0.3349(4)	0.3973(7)
C(32)	0.3672(7)	0.2754(4)	0.2941(7)
C(33)	0.4220(7)	0.2884(4)	0.1888(7)
C(34)	0.4629(7)	0.3609(4)	0.1868(7)
C(35)	0.4490(7)	0.4204(4)	0.2900(7)
C(36)	0.3942(7)	0.4073(4)	0.3952(7)
C(41)	0.3076(7)	0.0373(3)	0.6759(7)
C(42)	0.3211(7)	0.0307(3)	0.8184(7)
C(43)	0.3558(7)	−0.0380(3)	0.8671(7)
C(44)	0.3770(7)	−0.1001(3)	0.7734(7)
C(45)	0.3635(7)	−0.0935(3)	0.6309(7)
C(46)	0.3288(7)	−0.0248(3)	0.5821(7)
C(51)	0.1308(6)	0.1495(3)	0.7022(7)
C(52)	0.1510(6)	0.2124(3)	0.8094(7)
C(53)	0.0594(6)	0.2295(3)	0.8839(7)
C(54)	−0.0524(6)	0.1836(3)	0.8511(7)
C(55)	−0.0727(6)	0.1207(3)	0.7439(7)
C(56)	0.0189(6)	0.1036(3)	0.6694(7)
C(61)	0.1903(7)	0.1034(4)	0.4234(6)
C(62)	0.0562(7)	0.1014(4)	0.3446(6)
C(63)	0.0167(7)	0.0849(4)	0.1945(6)
C(64)	0.1111(7)	0.0703(4)	0.1232(6)
C(65)	0.2452(7)	0.0723(4)	0.2020(6)
C(66)	0.2848(7)	0.0888(4)	0.3521(6)

to 0.056. The platinum and phosphorus atoms were then allowed anisotropic vibrations and the phenyl hydrogen atoms were introduced in idealized positions, the phenyl groups being refined as rigid groups with C–C 120° and C–H 108 pm. This led to convergence at $R=0.045$, $R'=0.091$. A difference map showed some indication of the borane hydrogen atoms, but these were not sufficiently clearly resolved to permit their inclusion in the refinement. Atomic coordinates are listed in Table 5. Selected distances and angles between interatomic vectors are in Table 1 above.

Crystal data

$C_{36}H_{37}B_3P_2Pt$, $M=759.16$, triclinic, space group $P\bar{1}$, $a=1065.2(2)$, $b=1800.6(3)$, $c=989.0(2)$ pm, $\alpha=99.14(2)$, $\beta=108.23(1)$, $\gamma=88.06(1)°$, $Z=2$, $U=1.7785(5)$ nm^3, $Z=2$, $D_c=1.418$ Mg M^{-3}, $F(000)=752$. Mo Kα radiation, $\lambda=71.069$ pm, μ(Mo Kα)$=40.95$ cm^{-1}. $R_f=0.045$ ($R_w=0.091$).

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