

POLYHEDRAL PLATINADICARBABORANE CHEMISTRY.
THE MOLECULAR STRUCTURE AND SOME NMR PROPERTIES
OF [9,9-(PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁]

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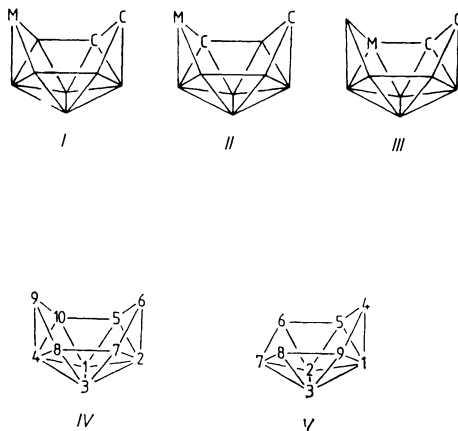
Received April 26, 1990

Accepted August 30, 1990

The reaction of [Pt(PPh₃)₄] with [*arachno*-4,5-C₂B₇H₁₃] in benzene solution at room temperature yields the *arachno* ten-vertex platinadicarbaborane [9,9-(PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁] as white air-stable needles (80%). Crystals are monoclinic, space group *P*2₁/*n*, with *a* = 1 433.9(3), *b* = 1 495.9(3), *c* = 1 852.5(4) pm, *β* = 105.89(2)⁰, and *Z* = 4. From 5 193 observed [*I* < 2σ(*I*)] data, the final *R*(*R*_w) were 0.0376(0.0374) (406 variables). The structure is based on an *arachno* {B₁₀H₁₄²⁻} -type ten-vertex {PtC₂B₇} skeleton with the Pt and two C atoms respectively in the 9,5 and 6 positions in the open face. The assigned ¹¹B and ¹H NMR chemical shifts have been measured and are briefly compared to those of the [*arachno*-4,5-C₂B₇H₁₃] substrate.

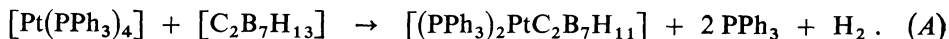
About ten years ago we started to develop an interest in the incorporation of the bis(tertiary phosphine)platinum residue in polyhedral boron-containing substrates¹⁻⁶. In 1980 one of our groups reported the synthesis and preliminary NMR investigation of the ten-vertex platinadicarbaborane [9,9-(PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁] (*I*) (ref.⁷), prepared from [Pt(PPh₃)₄] and [*arachno*-4,5-C₂B₇H₁₃] (at the time this last nine-vertex dicarbaborane substrate was believed to be [*nido*-4,5,-C₂B₇H₁₁]⁸⁻¹¹, but it is now known^{12,13} to have the *arachno* formulation). We now report further details of the preparation of the platinadicarbaborane, together with a more detailed NMR study, and we also now report its molecular structure as determined by single-crystal X-ray diffraction analysis. As far as we are aware there are only two other structurally characterized ten-vertex metalladicarbaboranes of this general cluster shape. One is the *arachno*-type species [6,6-(PEt₃)₂-5,9-Me₂-*arachno*-6,5,9-NiC₂B₇H₉] (*II*) (ref.¹⁴), prepared from the reaction of [4,6-Me₂-*arachno*-4,6-C₂B₇H₁₁] (rather than a 4,5-species as used in this present report) with bis(phosphine)nickel(0) species. The second is the *nido*-type species [10-(η⁵-C₅H₅)-*nido*-10,5,6,-CoC₂B₇H₁₁] (*III*) (ref.¹⁵), formed by polyhedral contraction¹⁶ from the eleven-vertex species [1-(η⁵-C₅H₅)-1,2,4-CoC₂B₈H₁₀]. Although

this last compound is formally *closo*, it probably has¹⁷ an open *isonido*-type structure. The numbering schemes for the ten-vertex *nido*/*arachno* and nine-vertex *arachno* systems encountered in this work are in structures (IV) and (V) respectively.

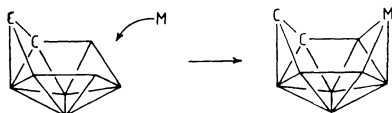


RESULTS AND DISCUSSION

The reaction between equimolar quantities of $[\text{Pt}(\text{PPh}_3)_4]$ and $[\text{arachno-4,5-C}_2\text{B}_7\text{H}_{13}]$ (refs¹¹⁻¹³) in benzene solution at room temperature for six hours, followed either by crystallisation from boiling ethanol or by vapour diffusion of hexane into a solution in dichloromethane, resulted in the formation of $[\text{9,9-(PPh}_3)_2\text{-arachno-9,5,6-PtC}_2\text{B}_7\text{H}_{11}]$ as a colourless air-stable crystalline solid, isolated in 80% yield. As an alternative method of purification, preparative thin-layer chromatography can be used (silica gel, benzene, R_F 0.43). The compound was characterized by single-crystal X-ray diffraction analysis and NMR spectroscopy as described below. A simple stoichiometry of formation may be written down as in Eq. (A):



The general mechanism presumably proceeds by a straightforward addition of the metal centre as in Scheme 1 with a concomitant loss of dihydrogen and displacement of two phosphine ligands from the labile $[\text{Pt}(\text{PPh}_3)_4]$ coordination sphere.



SCHEME 1

The molecular structure was determined by a single-crystal X-ray diffraction analysis on one of the crystals obtained from the hexane-dichloromethane purification. The crystals were of good aspect and the data set obtained was a good quality one that enabled the location and free refinement of all the cluster hydrogen atoms. Selected interatomic distances and angles are in Tables I and II respectively, and fractional atomic coordinates are in Table III below. The compound is seen to be [9,9-(PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁] (Fig. 1) in accord with the conclusions

TABLE I

Selected interatomic distances (pm) for [9,9-(PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁] with estimated standard deviations (e.s.d.'s) in parentheses

To platinum			
P(1)—Pt(9)	231·9(4)	P(2)—Pt(9)	232·5(4)
B(4)—Pt(9)	221·3(10)	B(8)—Pt(9)	223·9(11)
B(10)—Pt(9)	223·0(9)		
Boron-boron and carbon-boron			
B(2)—B(1)	175·1(14)	B(3)—B(2)	174·3(15)
B(3)—B(1)	175·1(15)		
B(4)—B(1)	171·9(14)	B(4)—B(3)	178·5(15)
C(5)—B(1)	173·2(14)	B(7)—B(3)	176·3(15)
B(10)—B(1)	175·5(14)	B(8)—B(3)	178·3(14)
C(6)—B(2)	171·7(14)		
C(5)—B(2)	171·0(15)	B(7)—B(2)	175·6(15)
C(6)—C(5)	159·1(13)	B(7)—C(6)	181·0(16)
B(10)—C(5)	159·9(12)	B(8)—B(7)	186·9(16)
B(10)—B(4)	178·2(14)	B(8)—B(4)	179·8(14)
Phosphorus-carbon			
C(111)—P(1)	182·4(6)	C(211)—P(2)	184·0(5)
C(121)—P(1)	183·4(6)	C(221)—P(2)	183·7(6)
C(131)—P(1)	185·1(6)	C(231)—P(2)	183·2(6)
Boron-hydrogen and carbon-hydrogen			
H(1)—B(1)	106(7)	H(3)—B(3)	107(8)
H(2)—B(2)	124(7)	H(4)—B(4)	108(7)
H(5)—C(5)	87(8)	H(7)—B(7)	100(7)
H(6)(<i>exo</i>)—C(6)	106(9)	H(6)(<i>endo</i>)—C(6)	104(7)
H(10)—B(10)	109(5)	H(8)—B(8)	109(7)
H(7,8)(μ)—B(7)	115(7)	H(7,8)(μ)—B(8)	109(7)

made from NMR spectroscopy (see also below) in our original preliminary communication⁷.

Thus the structure is based on that of the [*arachno*-B₁₀H₁₄]²⁻ parent skeleton¹⁸, with: *a*) the two {BH₂} units at the (6)- and (9)-positions being replaced by {CH₂} and {Pt(PPh₃)₂} respectively, and *b*) the {BH} unit at the (5)-position being replaced by {CH}, but with *c*) the (5,10)-bridging hydrogen atom missing in order to maintain diamagnetism and an *arachno*-type cluster electron formalism.

TABLE II

Selected interatomic angles (°) for [9,9-(PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁] with e.s.d.'s in parentheses

At platinum

P(2)—Pt(9)—P(1)	100.0(2)		
B(10)—Pt(9)—P(1)	82.5(3)	B(8)—Pt(9)—P(2)	93.3(3)
B(4)—Pt(9)—P(1)	123.8(3)	B(4)—Pt(9)—P(2)	132.0(2)
B(8)—Pt(9)—P(1)	164.5(2)	B(10)—Pt(9)—P(2)	175.6(2)
B(10)—Pt(9)—B(4)	47.3(3)	B(8)—Pt(9)—B(4)	47.6(3)
B(10)—Pt(9)—B(8)	83.8(4)		

About the open face

C(5)—B(10)—Pt(9)	115.7(6)	B(7)—B(8)—Pt(9)	109.9(6)
B(10)—C(5)—C(6)	117.0(7)	B(8)—B(7)—C(6)	111.1(7)
B(7)—C(6)—C(5)	107.3(7)		

Involving bridging and terminal hydrogen

H(7,8)—B(8)—Pt(9)	91(4)	H(7,8)—B(7)—C(6)	100(4)
H(7,8)—B(8)—B(7)	35(4)	H(7,8)—B(7)—B(8)	33(3)
H(7,8)—B(8)—H(8)	111(5)	H(7,8)—B(7)—H(7)	108(5)
H(6)(<i>exo</i>)—C(6)—B(2)	116(5)	H(6)(<i>endo</i>)—C(6)—B(2)	142(4)
H(6)(<i>exo</i>)—C(6)—C(5)	128(5)	H(6)(<i>endo</i>)—C(6)—C(5)	115(4)
H(6)(<i>exo</i>)—C(6)—B(7)	115(5)	H(6)(<i>endo</i>)—C(6)—B(7)	89(4)
H(6)(<i>exo</i>)—C(6)—H(6)	95(6)		
(<i>endo</i>)			
B(8)—H(7,8)—B(7)	113(6)		

At phosphorus

C(111)—P(1)—Pt(9)	108.5(3)	C(211)—P(2)—Pt(9)	119.2(3)
C(121)—P(1)—Pt(9)	113.0(3)	C(221)—P(2)—Pt(9)	111.6(3)
C(131)—P(1)—Pt(9)	123.7(3)	C(231)—P(2)—Pt(9)	112.5(3)
C(121)—P(1)—C(111)	108.1(3)	C(221)—P(2)—C(211)	102.9(3)
C(131)—P(1)—C(111)	104.1(3)	C(231)—P(2)—C(211)	100.3(3)
C(131)—P(1)—C(121)	98.2(3)	C(231)—P(2)—C(221)	109.4(3)

The juxtapositioning of the $\{\text{CH}_2\}$ and $\{\text{CH}\}$ groupings on the open hexagonal face of the ten-vertex skeleton is unusual⁷, and in this context it is interesting that the distance C(6)—B(7) is long at 181.0(16) pm, possibly reflecting some weakening arising from diversion of bonding electron density into the C(5)—C(6) linkage, which at 159.1(13) pm approaches the sp^3 — sp^3 intercarbon single-bond distance of 154 pm (compare also ref.¹⁹). In *nido*-5,6-dicarbadeborane skeletons this intercarbon distance is even shorter, at less than 146 pm (refs^{15,20}). It would be of interest to have a theoretical treatment of these two cluster types.

TABLE III

Non-hydrogen- and cluster hydrogen-atom co-ordinates ($\cdot 10^4$) for [9,9-(PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁] with e.s.d.'s in parentheses

Atom	x	y	z	Atom	x	y	z
Pt(9)	1982.8(2)	2187.9(2)	10609.6(1)	C(224)	2632(3)	574(3)	7908(2)
P(1)	2018(1)	3347(1)	9786(1)	C(225)	1926(3)	475(3)	8292(2)
P(2)	3223(1)	1297(1)	10419(1)	C(226)	2133(3)	713(3)	9048(2)
C(111)	816(2)	3453(3)	9130(3)	C(231)	4423(3)	1795(3)	10806(3)
C(112)	245(2)	4218(3)	9078(3)	C(232)	4474(3)	2601(3)	11194(3)
C(113)	-703(2)	4223(3)	8613(3)	C(233)	5373(3)	3000(3)	11513(3)
C(114)	-1079(2)	3462(3)	8200(3)	C(234)	6291(3)	2592(3)	11443(3)
C(115)	-508(2)	2697(3)	8252(3)	C(235)	6167(3)	1786(3)	11055(3)
C(116)	439(2)	2693(3)	8717(3)	C(236)	5269(3)	1388(3)	10737(3)
C(121)	2340(3)	4425(2)	10260(3)	B(1)	122(6)	2533(6)	11408(5)
C(122)	2370(3)	5205(2)	9854(3)	B(2)	-548(6)	1615(7)	10957(5)
C(123)	2724(3)	5995(2)	10229(3)	B(3)	518(7)	1443(7)	11670(5)
C(124)	3049(3)	6005(2)	11011(3)	B(4)	1335(6)	2300(6)	11561(5)
C(125)	3019(3)	5226(2)	11417(3)	C(5)	-318(5)	2492(5)	10440(5)
C(126)	2665(3)	4436(2)	11042(3)	C(6)	-329(6)	1517(6)	10095(5)
C(131)	2852(3)	3385(4)	9181(3)	B(7)	263(8)	777(6)	10854(6)
C(132)	3813(3)	3611(4)	9530(3)	B(8)	1523(7)	1162(6)	11322(5)
C(133)	4482(3)	3672(4)	9109(3)	B(10)	719(5)	2952(5)	10769(5)
C(134)	4190(3)	3507(4)	8339(3)	H(1)	-311	2936(44)	11658(41)
C(135)	3228(3)	3281(4)	7989(3)	H(2)	-1411(50)	1442(46)	10890(39)
C(136)	2559(3)	3220(4)	8410(3)	H(3)	564(56)	1206(54)	12221(47)
C(211)	3426(4)	183(2)	10856(2)	H(4)	1893(47)	2535(44)	12045(38)
C(212)	3871(4)	141(2)	11625(2)	H(5)	-854(57)	2794(46)	10284(43)
C(213)	3991(4)	-682(2)	11993(2)	H(6a)	217(48)	1387(43)	9841(37)
C(214)	3666(4)	-1463(2)	11592(2)	H(6b)	-886(63)	1213(57)	9666(49)
C(215)	3220(4)	-1421(2)	10822(2)	H(7)	81(49)	130(47)	10801(39)
C(216)	3100(4)	-599(2)	10454(2)	H(8)	2050(51)	683(48)	11644(41)
C(221)	3045(3)	1050(3)	9419(2)	H(10)	726(38)	3677(36)	10756(31)
C(222)	3751(3)	1149(3)	9035(2)	H(78)	1051(51)	846(44)	10825(38)
C(223)	3544(3)	911(3)	8279(2)				

The asymmetry of the *arachno* ten-vertex cluster of the platinum compound that arises from the 5,6-C₂ configuration is not manifested to any significant extent in the geometry of bonding to the Pt(9) centre. Thus the platinum-phosphorus distances are mutually very similar, as are the distances from platinum to the B(8) and B(10) atoms. The phosphorus NMR parameters (see Table IV below) are also mutually very similar. Additionally, there is little twist in the metal-to-borane bonding (Fig. 2; compare also ref.²¹, and pp. 259–260 in ref.²²). This contrasts to the twisted nickel species [6,6-(PEt₃)₂-5,9-Me₂-*arachno*-6,5,9-NiC₂B₇H₉] (ref.¹⁴) in which the asymmetry-inducing carbon atom is at the position now directly linked to the metal atom (see also Fig. 2), again possibly reflecting a greater localisation of electron density in bonding to the more electronegative carbon atom. In terms of the [*arachno*-B₁₀H₁₄]²⁻ analogy discussed above, the Pt(PPh₃)₂ moiety can be regarded in the first instance as a two-orbital two-electron contributor to the cluster bonding proper, just like {BH₂}⁻, and so has substantial *dsp*² platinum(II) square

TABLE IV

Measured NMR data for [9,9-(PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁] in C²H₂Cl₂ at 294–297 K

Assignment	$\delta(^1\text{B})$	$\delta(^1\text{H})^b$	Observed ^1H - ^1H -COSY correlations ^c			
BH(4)	+15.6 ^d	+3.52	1 w	3 w	μw	
BH(10)	+2.5 ^e	+2.83 ^f	1 s	5 w	6(a)?	
BH(2)	+0.7	+2.65	5 w	6(a)w	6(b)s	
BH(8)	-2.4 ^g	+2.04 ^h	3 w	μs_2		
BH(7)	-5.2	+2.56	3 w	μs_2		
BH(1)	-15.1	+1.46 ⁱ	4 w	10 s	3 w	
BH(3)	-42.0	+0.05 ^j	4 w	8 w	7 w	1 w
H(7,8)(μ)	—	-1.66	4 w	8 w ₂	7 s ₂	6(a)w
CH(5)	—	+1.65	10 w	2 w	6(a)?	6(b):
CH(6a) ^k	—	+1.55	10 w	2 w	5? μw	6(b)s
CH(6b) ^l	—	+1.03	2 s	5?	6(a)s ₂	

^a Additional data: $\delta(^{31}\text{P}) + 29.8$ ppm (sharper), $^1J(^{195}\text{Pt}-^{31}\text{P})$ 3 003 Hz, and $\delta(^{31}\text{P}) + 29.4$ ppm (broader), $^1J(^{195}\text{Pt}-^{31}\text{P})$ 2 641 Hz; $^2J(^{31}\text{P}-^{31}\text{P})$ 13.2 Hz; C²H₂Cl₂ solution at 203 K. ^b ¹H resonances related to directly bound ¹¹B positions by ¹H-¹¹B(selective) experiments; additional ¹H signals from aromatic groups closely grouped at $\delta(^1\text{H})$ c. +7.25. ^c Measured under conditions of ¹¹B(broadband noise) decoupling; s stronger, w weaker, ? uncertain; numerical subscripts refer to *n* in $^nJ(^1\text{H}-^1\text{H})$ when *n* ≠ 3. ^d $^1J(^{195}\text{Pt}-^{11}\text{B})$ c. 315 Hz. ^e $^1J(^{195}\text{Pt}-^{11}\text{B})$ c. 330 Hz. ^f Doublet structure, ³¹P splitting c. 19 Hz. ^g Partially resolved $^1J(^{195}\text{Pt}-^{11}\text{B})$ c. 300 Hz. ^h Doublet structure, ³¹P splitting c. 12 Hz. ⁱ $^3J(^{195}\text{Pt}-^1\text{H})$ 63 Hz. ^j $^3J(^{195}\text{Pt}-^1\text{H})$ 69 Hz. ^{k,l} 6(a) and 6(b) tentatively assigned *exo* and *endo* respectively on the basis of a higher ¹H shielding for *endo* vs *exo*, and a stronger coupling (i.e. [¹H-¹H]-COSY correlation) to ¹H(7,8)(*E*) expected for a *transoid* $^3J(^1\text{H}-^1\text{H})$ coupling path to ¹H(6)(*exo*).

planar character. However, there is undoubtedly additional platinum-to-boron bonding interaction as adequately discussed elsewhere²¹⁻²⁵.

The measured NMR parameters for [9,9-(PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁] are in Table IV. The cluster ¹H resonances were assigned to their directly bound ¹¹B positions by ¹H-¹¹B(selective)} spectroscopy, and thence [¹H-¹H]-COSY-¹¹B (broadband noise)} spectroscopy, together with the incidence of satellites in the ¹¹B spectrum arising from ¹J(¹⁹⁵Pt-¹¹B), permitted the assignment of the ¹¹B and ¹H resonances to their individual cluster positions. The NMR properties are entirely consistent with the molecular structure (Fig. 1 above), confirming that the crystal was representative of the bulk sample. The general *arachno* ten-vertex features, for example δ[¹¹B(1)] and δ[¹¹B(3)] to higher field, and the incidence and positions of the (7,8)-bridging and {CH₂}-group ¹H resonances, are readily apparent, and there is also a general parallel between the ¹¹B and ¹H nuclear shieldings (Fig. 3, uppermost diagram), with the 16 : 1 δ(¹¹B) : δ(¹H) slope being similar to those observed in other ten-vertex *arachno*-type systems^{21,23,24,27,28}.

It is of interest to compare the ¹¹B NMR shielding properties of the platinadiborane with those of [4,5-C₂B₇H₁₃] from which it is electronically and structurally notionally derived by the replacement of the H(6)(*endo*) and H(7,8)(μ)

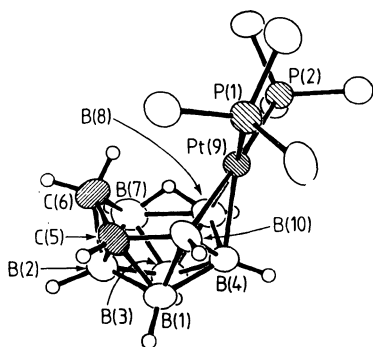


FIG. 1

ORTEP-type drawing of the crystallographically determined molecular structure of [9,9-(PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁]; the P-phenyl group atoms, except for the *ipso* carbon ones, are omitted for clarity

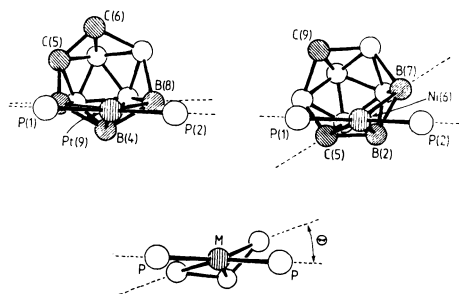
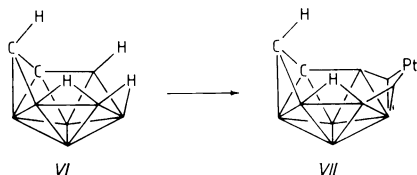


FIG. 2

Drawings to show the P(1)P(2)Pt(9)B(8)B(4).B(10) ligand sphere of [9,9-(PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁] (upper left) and of the corresponding atoms in the nickeladiborane [6,6-(PEt₃)₂-5,9-Me₂-*arachno*-6,5,9-NC₂B₇H₉] (upper right, data from ref.¹⁴), both viewed along the approximate bisector of the P-M-P interatomic angle. The twist angle θ , as defined in the lower diagram, is 8.5(2)° for the platinum compound and 35.2(2)° for the nickel species

hydrogen atoms (structure VI, Scheme 2) (compare ref.²⁷) by multicentre bonding to platinum (for example as in VII, but see discussion above (near Fig. 2) and in refs^{21,24}).

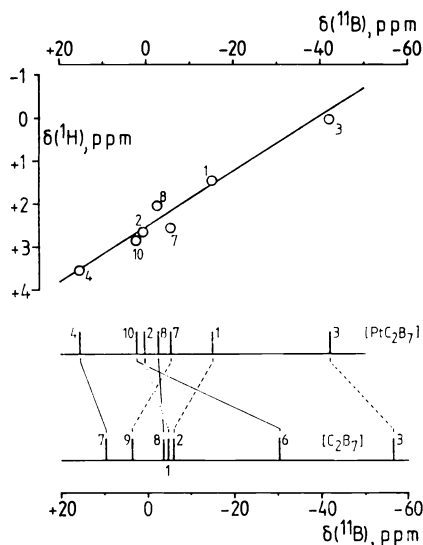


SCHEME 2

The lower two diagrams in Fig. 3 relate equivalent positions in stick representations of the ^{11}B NMR spectra of the two species. The shielding patterns are in general very similar, indicating the similarity of bonding in the two species. The one exception to this generalisation is the $^{11}\text{B}(6)$ position in $[4,5\text{-C}_2\text{B}_7\text{H}_{13}]$, which moves downfield by over 20 ppm upon platinadiborane formation to a position similar to that of $^{11}\text{B}(8)$. The resulting similarity of the $\delta[^{11}\text{B}(8)]$ and $\delta[^{11}\text{B}(10)]$ values in the platinadiborane reflects the similarity of the Pt(9)–B(8) and Pt(9)–B(10) linkages that is also apparent from the similarity of the two couplings $^1J(^{195}\text{Pt}\text{-}^{31}\text{P})$ to the *transoid* phosphine ligands (Table IV). The high shielding of $^{11}\text{B}(6)$ in the $[4,5\text{-C}_2\text{B}_7\text{H}_{13}]$ substrate may arise from a high electronic symmetry about this

FIG. 3

NMR data (ppm) for $[9,9\text{-}(\text{PPh}_3)_2\text{-arachno-}9,5,6\text{-PtC}_2\text{B}_7\text{H}_{11}]$. The uppermost diagram is a plot of $\delta(^1\text{H})$ vs $\delta(^{11}\text{B})$ for the BH(*exo*) units. The line drawn has slope $\delta(^{11}\text{B})$: $\delta(^1\text{H})$ 16 : 1, intercept +2.55 in $\delta(^1\text{H})$ (compare similar correlation slopes in other *arachno*-platinaboranes, e.g. refs^{21,23,24,26}). The bottom two diagrams are stick representations of the ^{11}B chemical shifts of the platinadiborane (upper trace) and of the *arachno* nine-vertex dicarborene substrate $[4,5\text{-C}_2\text{B}_7\text{H}_{13}]$ (lower trace, data from ref.¹³); lines join equivalent positions in the two species: ——— adjacent α to platinum, - - - - β to platinum, and $\cdots\cdots\cdots$ γ to platinum. Note that numbering conventions [structures IV and V above] dictate that the numbering of particular atoms changes on interconversion between nine-vertex and ten-vertex *arachno* structures



nucleus, perhaps arising from a reasonably symmetrical sp^3 hybridisation. This is to some extent supported by the observation¹³ of two mutually similar couplings $^1J(^{11}\text{B}-^1\text{H})$ of c. 120 Hz each to the *endo* and *exo* protons in the $\{\text{BH}_2(6)\}$ grouping.

EXPERIMENTAL

Preparation of [9,9-((PPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁)]

A solution of [*arachno*-4,5-C₂B₇H₁₃] (200 mg; 1.77 mmol; prepared as in refs¹¹⁻¹³) in benzene (40 cm³) was added to a solution of [Pt(PPh₃)₄] (2.250 mg; 1.88 mmol) in benzene (50 cm³) under nitrogen. The solution was left standing for 1 h at room temperature in an inert atmosphere, and then carefully overlaid with hexane (60 cm³). The white crystals that separated after c. 2 h were filtered off and recrystallised from minimum boiling EtOH (c. 70 cm³) to give [9,9-(PPPh₃)₂-*arachno*-9,5,6-PtC₂B₇H₁₁] (950 mg; 1.14 mmol; 64%) as a white crystalline solid. A second crop was obtained (236 mg; 0.28 mmol; 16%: total yield 1.186 mg; 80%) by evaporating the mother liquors *in vacuo* and recrystallising the solid residue by diffusion of hexane vapour into a solution in dichloromethane. An analytical product [m.p. 216–218°C (dec.)] was obtained in a similar manner. For C₃₈H₄₁B₇P₂Pt (829.1) calculated: 54.95% C, 4.97% H, 9.12% B, 7.45% P, 23.49% Pt; found: 55.12% C, 5.02% H, 8.97% B, 7.28% P, 23.25% Pt.

Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy reported here was performed at 9.4 Tesla (400 MHz ¹H) on commercially available Bruker AM400 instrumentation, with the techniques of ¹H-¹¹B(selective)}⁶ and [¹H-¹H]-COSY-¹¹B} spectroscopy²⁸, and also general techniques, being essentially as described and exemplified in more detail in other recent papers from our laboratories (refs^{27,29-31}). Chemical shifts δ are given to high frequency (low field) of Ξ 100 (SiMe₄) for ¹H (quoted ± 0.05 ppm), Ξ 40.480730 (nominally 85% H₃PO₄) for ³¹P (quoted ± 0.5 ppm) and Ξ 32.083 071 MHz (nominally F₃BOEt₂ in C²HCl₃) for ¹¹B (quoted ± 0.5 ppm), Ξ being defined as in ref.³². Spectra were calibrated in δ by using ²H or residual ¹H solvent resonances as internal secondary standards. Because of the large molecular size arising from the bulky PPh₃ ligands, the ¹¹B lines were broad so that [¹¹B-¹¹B]-COSY spectroscopy, and a reasonable estimation of ¹J(¹¹B-¹H), were not feasible.

Single Crystal X-Ray Analysis

All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the $\omega - 2\theta$ scan mode using a standard procedure described elsewhere³³. The data set was corrected for absorption empirically once the structure had been determined³⁴.

The structure was determined via standard heavy-atom methods and refined by full-matrix least-squares using the SHELX program system³⁵. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl hydrogen atoms were included in calculated positions and assigned to an overall isotropic parameter. The borane hydrogen atoms were freely refined with individual isotropic parameters. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement in order to obtain satisfactory agreement analyses. Final atomic co-ordinates are given in Table III.

Crystal data for compound. C₃₈H₄₁B₇P₂Pt, $M = 830.4$, monoclinic, $a = 1.433.9(3)$, $b = 1.495.5(3)$, $c = 1.852.5(4)$ pm, $\beta = 105.89(2)^\circ$, $V = 3.8218(13)$ nm³, $Z = 4$, space group

$P2_1/n$ (= non-standard setting of $P2_1/c$, No. 14), $D_c = 1.44 \text{ Mgm}^{-3}$, $\mu = 36.14 \text{ cm}^{-1}$, $F(000) = 1647.94$.

Data collection. ω Scan widths $1.0^\circ + \alpha$ -doublet splitting, scans speeds $2.0\text{--}29.3^\circ \text{ min}^{-1}$. $4.0 < 2\theta < 50.0^\circ$. 7170 Data collected, 5193 with $I < 2.0\sigma(I)$ considered observed, $T = 290 \text{ K}$,

Structure refinement. Number of parameters = 406, $g = 0.0006$, $R = 0.0376$, $R_w = 0.0374$.

We thank the Royal Society and Borax Research Limited for support, and the S.E.R.C. (United Kingdom) for equipment grants. We thank Dr J. B. Farmer and Professor N. N. Greenwood for their interest, and Mr Filip and (the late) Mr Skalický for elemental analyses.

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Translated by the author (B.Š.).