Metallaborane Chemistry. Part 9.[1] Oxidative–insertion Reactions of Zerovalent Nickel and Platinum Complexes with 1,7-Dicarba-*closo*-octaborane, 4,5-Dicarba-*closo*-nonaborane, 1,6-Dicarba-*closo*-decaborane, and their *C*-Methyl Derivatives

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The complexes [Pt(PEt$_3$)$_3$], [Pt(*trans*-stilbene)(PR'$_3$)$_2$] (R' = Et or Me), [M(cod)(PMe$_3$)$_2$] (M = Pt or Ni; cod = cyclo-octa-1,5-diene), and [Ni(cod)(PEt$_3$)$_2$] react with *closo*-1,7-R$_2$-1,7-C$_2$B$_6$H$_6$ (R = H or Me), *closo*-4,5-R$_2$-4,5-C$_2$B$_7$H$_7$, and *closo*-1,6-C$_2$B$_8$H$_{10}$ to give the carbametallaboranes *closo*-[4,5-R$_2$-6,6-(PR'$_3$)-4,5,6-C$_2$MB$_6$H$_6$] (M = Pt, R = H, R' = Me; M = Pt, R = Me, R' = Me or Et; M = Ni, R = Me, R' = Me or Et), *nido*-[4,5-R$_2$-7,7-(PR'$_3$)-4,5,7-C$_2$PtB$_6$H$_6$] (R = H, R' = Me, and R = Me, R' = Et), *nido*-[2,8-R$_2$-10,10-(PR'$_3$)-2,8,10-C$_2$MB$_7$H$_7$] (M = Pt, R' = Et, R = H or Me; M = Ni, R = H, R' = Et, and R = Me, R' = Me), and *nido*-[μ-(6,10)-{Pt(PMe$_3$)$_2$}-10,10-(PMe$_3$)$_2$-7,9,10-C$_2$PtB$_8$H$_{10}$], respectively. The latter compound, on reaction with activated charcoal, afforded the compound *nido*-[10,10-(PMe$_3$)$_2$-7,9,10-C$_2$PtB$_8$H$_{10}$]. The ^{1}H, ^{11}B, and ^{31}P n.m.r. spectra of the new compounds are reported, and their mechanism of formation and molecular structures discussed.

SINCE our original discovery[2] that low-valent transition-metal complexes were capable of direct insertion into *closo*-carbaborane cages, we have described the results of reactions of nickel(0), palladium(0), and platinum(0) d^{10} species with *closo*-C$_2$B$_9$,[3] *closo*-C$_2$CoB$_8$,[3] and *closo*-CB$_{10}$[4] cage systems. These reactions were found to be stereospecific, giving only one product in high yield. In contrast, the cage-reduction, cation-insertion approach to carbametallaborane synthesis developed by Hawthorne and his co-workers[5] leads often to several products when applied to the medium-sized carbaboranes, *closo*-1,7-C$_2$B$_6$H$_8$, *closo*-4,5-C$_2$B$_7$H$_9$, and *closo*-1,6-C$_2$B$_8$H$_{10}$. It was of interest, therefore, to extend our direct oxidative–insertion method to the medium-size carbaboranes, and thus delineate the synthetic scope of the direct metal-insertion route to carbametallaboranes. Preliminary reports on some aspects of this work have already appeared.[6-8]

RESULTS AND DISCUSSION

Reaction of the zerovalent platinum complex [Pt(*trans*-stilbene)(PMe$_3$)$_2$][3] with the carbaborane *closo*-1,7-C$_2$B$_6$H$_8$ in light petroleum at 20 °C gave an air-stable yellow crystalline compound (1) as the major product, and a darker orange material (2) in much lower yield. Elemental analysis (Table 1) suggested that these compounds were isomers, of composition [Pt(PMe$_3$)$_2$(C$_2$B$_6$H$_8$)]. The ^{31}P n.m.r. spectrum of (1) (Table 2) showed a single resonance at δ 4.5 with ^{195}Pt satellites [J(PtP) 3 267 Hz]. The ^{11}B n.m.r. (^{1}H-decoupled) spectrum (Figure 1) shows only two signals (δ 16.1 and 19.7) of relative intensity 2 : 1, that at lower field showing a coupling to ^{195}Pt of 176 Hz. Moreover, in the ^{1}H n.m.r. spectrum only one resonance attributable to the cage C–H groups was observed. Thus the spectroscopic evidence suggested a structure of high symmetry and this was confirmed by a single-crystal *X*-ray structure determination[9] which revealed the complex as [6,6-(PMe$_3$)$_2$-4,5,6-C$_2$PtB$_6$H$_8$] having a *closo*-cage structure of approximate C_{2v} symmetry derived from a tricapped trigonal prism. The platinum atom was shown to be symmetrically bound to four boron atoms, while the two cage carbon atoms occupied the other two capping positions. Figure 2 illustrates the basic features of the metallacarbaborane cage.

A similar reaction of [Pt(*trans*-stilbene)(PEt$_3$)$_2$][10] with *closo*-1,7-Me$_2$-1,7-C$_2$B$_6$H$_6$ afforded two isomeric products (3) and (4), formulated as [Pt(PEt$_3$)$_2$(Me$_2$C$_2$B$_6$H$_6$)] from

TABLE 1

Analytical[a] and melting-point data for the complexes

	Complex	M.p. (θ_c/°C)	Yield (%)	Analysis (%)			
				C	H	B	P
(1)	*closo*-[6,6-(PMe$_3$)$_2$-4,5,6-C$_2$PtB$_6$H$_8$]	173	62	21.8 (21.6)	5.8 (5.9)	14.4 (14.6)	13.8 (13.9)
(2)	*nido*-[7,7-(PMe$_3$)$_2$-4,5,7-C$_2$PtB$_6$H$_8$]	206	3	21.5 (21.6)	5.8 (5.9)	14.3 (14.6)	13.9 (13.9)
(3)	*closo*-[4,5-Me$_2$-6,6-(PEt$_3$)$_2$-4,5,6-C$_2$PtB$_6$H$_6$]	71	45	34.2 (34.5)	7.7 (7.6)		
(4)	*nido*-[4,5-Me$_2$-7,7-(PEt$_3$)$_2$-4,5,7-C$_2$PtB$_6$H$_6$]	136	13	35.1 (34.5)	8.1 (7.6)	11.5 (11.7)	11.4 (11.1)
(5)	*closo*-[4,5-Me$_2$-6,6-(PMe$_3$)$_2$-4,5,6-C$_2$PtB$_6$H$_6$]	119	53	25.5 (25.4)	6.5 (6.4)	13.0 (13.7)	13.6 (13.1)
(6)	*closo*-[4,5-Me$_2$-6,6-(PEt$_3$)$_2$-4,5,6-C$_2$NiB$_6$H$_6$]	82	65	45.6 (45.7)	9.9 (10.1)		
(7)	*closo*-[4,5-Me$_2$-6,6-(PMe$_3$)$_2$-4,5,6-C$_2$NiB$_6$H$_6$]	120	45	35.3 (35.8)	9.2 (9.0)		
(8)	*nido*-[10,10-(PEt$_3$)$_2$-2,8,10-C$_2$PtB$_7$H$_9$]	153	70	31.7 (31.1)	7.5 (7.3)	13.9 (14.0)	11.4 (11.5)
(9)	*nido*-[2,8-Me$_2$-10,10-(PEt$_3$)$_2$-2,8,10-C$_2$PtB$_7$H$_7$]	138	65	34.3 (33.8)	7.9 (7.6)		
(10)	*nido*-[10,10-(PEt$_3$)$_2$-2,8,10-C$_2$NiB$_7$H$_9$][b]	168	75	42.2 (41.6)	10.3 (9.7)		
(11)	*nido*-[2,8-Me$_2$-10,10-(PMe$_3$)$_2$-2,8,10-C$_2$NiB$_7$H$_7$]	138	66	34.6 (34.5)	9.3 (9.0)		
(12)	*nido*-[μ-(6,10)-{Pt(PMe$_3$)$_2$}-10,10-(PMe$_3$)$_2$-7,9,10-C$_2$PtB$_8$H$_{10}$]	156 (decomp.)	78	21.0 (20.6)	5.9 (5.7)		
(13)	*nido*-[10,10-(PMe$_3$)$_2$-7,9,10-C$_2$PtB$_8$H$_{10}$]	283	55	20.2 (20.5)	6.0 (6.0)		

[a] Calculated values in parentheses. [b] Found: Ni, 14.0; calc. 14.5%.

TABLE 2

Phosphorus-31, hydrogen-1, and platinum-195 n.m.r. data [a]

Complex	^{31}P [b]		^{1}H [c]							^{195}Pt [d]
	δ_P	^1J(PtP)	cage C-*H*	cage C-*Me*	P-Me(-CH$_2$)	*J*(PH)	^3J(PtH)	CH$_2$*Me*	^3J(PH)	δ_{Pt}
(1) *closo*-[6,6-(PMe$_3$)$_2$-4,5,6-C$_2$PtB$_6$H$_8$]	4.5 [e]	3 267	7.26		8.44 [f]	8.2	26.0			382
(2) *nido*-[7,7-(PMe$_3$)$_2$-4,5,7-C$_2$PtB$_6$H$_8$]	28.4 [g]	2 711	6.75		8.49	8.9	23.2			716
	29.5 [g]	3 650	6.97		8.30	10.0	34.2			
(3) *closo*-[4,5-Me$_2$-6,6-(PEt$_3$)$_2$-4,5,6-C$_2$PtB$_6$H$_6$]				7.91	8.01 [h]	*ca.* 7.5	45	8.92	15	
(4) *nido*-[4,5-Me$_2$-7,7-(PEt$_3$)$_2$-4,5,7-C$_2$PtB$_6$H$_6$]				8.1	*ca.* 7.85			*ca.* 9.0		
				ca. 9.0						
(5) *closo*-[4,5-Me$_2$-6,6-(PMe$_3$)$_2$-4,5,6-C$_2$PtB$_6$H$_6$]	4.6 [i]	3 343		7.89	8.43 [f]	8.1	24.4			417
(6) *closo*-[4,5-Me$_2$-6,6-(PEt$_3$)$_2$-4,5,6-C$_2$NiB$_6$H$_6$]				7.84 [j]	8.30 [h]	*ca.* 7		8.93	14	
(7) *closo*-[4,5-Me$_2$-6,6-(PMe$_3$)$_2$-4,5,6-C$_2$NiB$_6$H$_6$]				7.83	8.68	7				
(8) *nido*-[10,10-(PEt$_3$)$_2$-2,8,10-C$_2$PtB$_7$H$_9$]	−14.0 [k]	2 957	6.58 [l]		8.06 [h]	8	22	9.01	16	747
(9) *nido*-[2,8-Me$_2$-10,10-(PEt$_3$)$_2$-2,8,10-C$_2$PtB$_7$H$_7$]				8.03	8.02 [h]	*ca.* 7.5	22	8.98	16	
(10) *nido*-[10,10-(PEt$_3$)$_2$-2,8,10-C$_2$NiB$_7$H$_9$]			6.45		8.18 [h]	*ca.* 7.5		8.97	15	
(11) *nido*-[2,8-Me$_2$-10,10-(PMe$_3$)$_2$-2,8,10-C$_2$NiB$_7$H$_7$]				8.00	8.60 [m]					
(12) *nido*-[μ-(6,10)-{Pt(PMe$_3$)$_2$}-10,10-(PMe$_3$)$_2$-7,9,10-C$_2$PtB$_8$H$_{10}$] [n,o]	C 21.2 [g]	1 948			8.39	6.8	19.3			519
	A 22.4 [g,p]	4 695			8.19	10.3	50.6			
	B 47.3 [g,q]	3 712			8.32	9.4	27.0			1 231
	D 56.2 [g]	1 530			8.63	8.0	11.8			
(13) *nido*-[10,10-(PMe$_3$)$_2$-7,9,10-C$_2$PtB$_8$H$_{10}$]	14.5 [r]	2 781	*ca.* 7.5		8.23	11	28			
	23.9	3 053			8.30	10	26			

[a] Spectra measured in CH$_2$Cl$_2$ or CD$_2$Cl$_2$ at 30 °C unless otherwise specified. Coupling constants (magnitude only) are in Hz. [b] Phosphorus-31 data from ^{1}H{^{31}P} INDOR measurements, unless otherwise specified. Chemical shifts δ_P are in p.p.m. to low frequency of 85% H$_3$PO$_4$ (external). [c] Hydrogen 1 chemical shifts in τ. [d] Platinum-195 data from ^{1}H{^{195}Pt} INDOR measurements. Chemical shifts (δ_{Pt}) are in p.p.m. to high frequency of 21.4 MHz (SiMe$_4$ = 100 MHz). [e] ^2J(PP) 13.7 Hz. [f] [AX$_9$]$_2$ spectrum type. Coupling constant given is $|^2J(PH) + {}^4J(PH)|$. Detailed analysis gives ^4J(PH) *ca.* 0.2 Hz, and of opposite sign to ^2J(PH). [g] ^{1}H Signal corresponding to this ligand is entered on the same line. [h] *J*(HH) 7—8 Hz. [i] *J*(PP) 16.7 Hz. [j] Recorded at 60 MHz (CDCl$_3$). [k] Also measured directly by 40.48 MHz Fourier-transform n.m.r. (CH$_2$Cl$_2$, −75 °C); δ −14.6, *J*(PtP) 2 964 Hz. [l] *J*(PtH) 32 Hz. [m] Broad ligand signal probably caused by rapid exchange with free phosphine liberated by slight decomposition of the complex. [n] See Expermental section for a detailkd explanation. [o] Cage C–H ^{1}H resonance not observed. [p] ^2J(PtP) 100; ^2J(PP) 28 Hz. [q] ^2J(PtP) 68; ^2J(PP) 28 Hz. [r] *J*(PP) 25 Hz.

elemental analysis. The major product, (3), exhibited the same general properties as (1) and the marked simplicity of the ^{1}H, ^{31}P, and ^{11}B n.m.r. spectra lead us to propose compound (3) to be *closo*-[4,5-Me$_2$-6,6-(PEt$_3$)$_2$-4,5,6-C$_2$PtB$_6$H$_6$] with a structure analogous to that of (1).

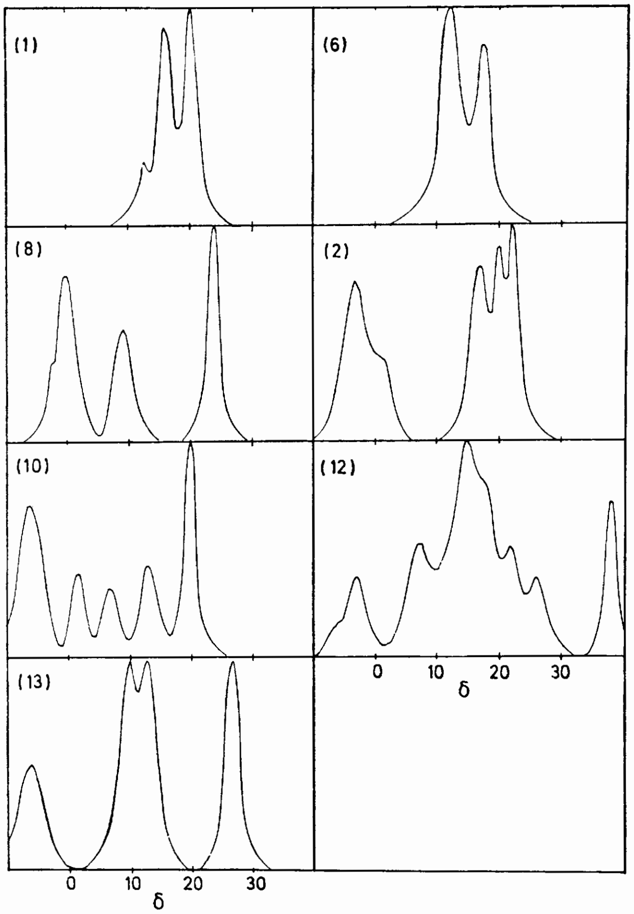


FIGURE 1 Boron-11 n.m.r. (^{1}H-decoupled) spectra of the complexes (1), (2), (6), (8), (10), (12), and (13)

In contrast, the two minor products of these reactions, complexes (2) and (4), respectively, gave n.m.r. spectra of some complexity, indicative of low molecular symmetry. Thus for (2) the ^{1}H and ^{31}P n.m.r. spectra (Table 2) suggest inequivalent cage C–H groups and inequivalent trimethylphosphine ligands respectively, while the ^{11}B n.m.r. spectrum (Figure 1) showed five resolved signals. It was not possible to propose a structure for this compound on the basis of the n.m.r. spectroscopic studies alone, and unfortunately crystals of (2) suitable for data collection could not be found. Hence an *X*-ray crystal structure determination [11] was carried out on the analogue (4), derived from the dimethylcarbaborane Me$_2$C$_2$B$_6$H$_6$. This analysis showed the compound to be, as expected, an asymmetric carbametallaborane but with a cage so severely distorted from tricapped trigonal prismatic geometry that the prefix *closo* is inappropriate. The carbametallaborane cage of (4), which may be formulated as *nido*-[4,5-Me$_2$-7,7-(PEt$_3$)$_2$-4,5,7-C$_2$PtB$_6$H$_6$], is depicted in Figure 2. Although it is not possible, by comparison of the available spectroscopic data, to say with certainty that (2) has a similar structure to (4), we feel nevertheless that (2) is most probably *nido*-[7,7-(PMe$_3$)$_2$-4,5,7-C$_2$PtB$_6$H$_8$].

The asymmetric compounds (2) and (4) are of lower oxidative and thermal stability than their respective symmetric isomers (1) and (3). Indeed, from the reaction of [Pt(*trans*-stilbene)(PMe$_3$)$_2$] with 1,7-Me$_2$-1,7-C$_2$B$_6$H$_6$ only the symmetrical isomer (5) was isolated and characterized, though there was evidence for the formation of another orange crystalline compound, presumably an isomer of (5) corresponding to (2) and (4). Comparison of the spectroscopic data for (5) with that for (1) and (3) (Table 2) reveals a close similarity, on which basis we proposed that (5) should be formulated as *closo*-[4,5-Me$_2$-6,6-(PMe$_3$)$_2$-4,5,6-C$_2$PtB$_6$H$_6$]. An *X*-ray crystallographic study [9] on two crystalline forms of (5) verified the proposed geometry.

Reactions of [Ni(cod)(PEt$_3$)$_2$] [12] and [Ni(cod)(PMe$_3$)$_2$] with *closo*-1,7-Me$_2$-1,7-C$_2$B$_6$H$_6$ afforded, respectively, the light red crystalline complexes (6) and (7), shown by elemental analysis (Table 1) to have the stoicheiometry [$Ni(PR'_3)_2(Me_2C_2B_6H_6)$]. No other products were isolated. Hydrogen-1 n.m.r. spectra were uncomplicated, showing resonances for only one type of phosphine and one cage methyl group in each case. Also the ^{11}B n.m.r. spectrum of (6) (Figure 1) consisted of two signals (δ 11.7 and 17.5) in the ratio 4 : 2. Furthermore, the i.r. spectra of (6) and (7) bore a marked resemblance to those of (3) and (5) respectively. It is suggested, therefore, that the nickel complexes should be formulated as *closo*-[4,5-Me_2-6,6-$(PR'_3)_2$-4,5,6-$C_2NiB_6H_6$] [(6), R' = Et; (7), R' = Me]having a symmetrical (C_{2v}) tricapped trigonal prismatic structure similar to that established for (1) and (5). It is interesting that no evidence was found for the existence of a nickel analogue of the unsymmetrical platinum complexes (2) and (4).

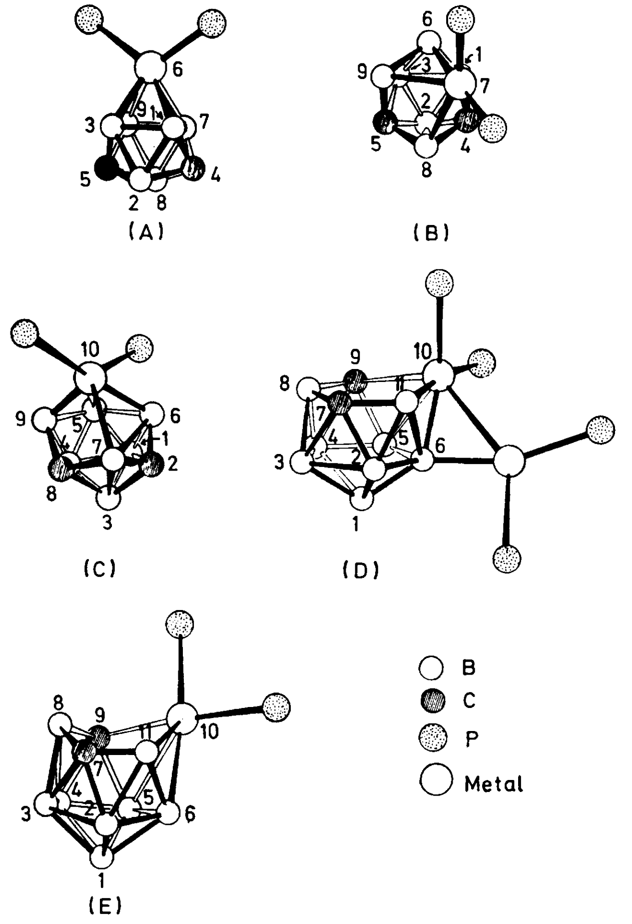


FIGURE 2 Cage-atom arrangements for: (A) *closo*-complexes {(1), [6,6-$(PMe_3)_2$-4,5,6-$C_2PtB_6H_8$]; (3), [4,5-Me_2-6,6-$(PEt_3)_2$-4,5,6-$C_2PtB_6H_6$]; (5), [4,5-Me_2-6,6-$(PMe_3)_2$-4,5,6-$C_2PtB_6H_8$]; (6), [4,5-Me_2-6,6-$(PEt_3)_2$-4,5,6-$C_2NiB_6H_6$]; and (7), [4,5-Me_2-6,6-$(PMe_3)_2$-4,5,6-$C_2NiB_6H_6$]}: (B) *nido*-complexes {(2), [7,7-$(PMe_3)_2$-4,5,7-$C_2PtB_6H_8$]; and (4), [4,5-Me_2-7,7-$(PEt_3)_2$-4,5,7-$C_2PtB_6H_6$]}: (C) *nido*-complexes {(8), [10,10-$(PEt_3)_2$-2,8,10-$C_2PtB_7H_9$]; (9), [2,8-Me_2-10,10-$(PEt_3)_2$-2,8,10-$C_2PtB_7H_7$]; (10), [10,10-$(PEt_3)_2$-2,8,10-$C_2NiB_7H_9$]; and (11), [2,8-Me_2-10,10-$(PMe_3)_2$-2,8,10-$C_2NiB_7H_7$]}: (D) {(12), *nido*-[μ-(6,10)-{$Pt(PMe_3)_2$}-10,10-$(PMe_3)_2$-7,9,10-$C_2PtB_8H_{10}$]}: and (E) {(13), [*nido*-10,10-$(PMe_3)_2$-7,9,10-$C_2PtB_8H_{10}$]}

Extending the investigation to the next member of the carbaborane series, we found that *closo*-4,5-$C_2B_7H_9$ reacted smoothly and rapidly with tris(triethylphosphine)platinum[3] in light petroleum at room temperature to give, in good yield, an almost colourless crystalline product (8), shown by elemental analysis (Table 1) to have the empirical formula [$Pt(PEt_3)_2(C_2B_7H_9)$]. Hydrogen-1 n.m.r. of (8) at 30 °C showed evidence of only one cage C–H environment (τ 6.58) and one type of phosphine ligand, the latter being confirmed by the ^{31}P n.m.r. spectrum which showed a singlet at δ −14.0 with ^{195}Pt satellites [J(PPt) 2 957 Hz]. The apparent relatively high symmetry of the complex was supported by the room-temperature ^{11}B n.m.r. spectrum (Figure 1), which could be explained in terms of a 2 : 2 : 2 : 1 or a 2 : 2 : 1 : 1 : 1 ratio of boron atom types, suggesting a molecular plane of symmetry.

A similar complex [$Pt(PEt_3)_2(Me_2C_2B_7H_7)$] (9) was prepared from the reaction of [Pt(*trans*-stilbene)$(PEt_3)_2$] with *closo*-4,5-Me_2-4,5-$C_2B_7H_7$, and crystals of this material were considered to be more suitable for an *X*-ray diffraction study because of the unambiguous marking of the cage carbon atoms by their substituent methyl groups. This analysis[13] showed the complex to be *nido*-[2,8-Me_2-10,10-$(PEt_3)_2$-2,8,10-$C_2PtB_7H_7$] with an open structure which, like that of (4), deviates markedly from the anticipated geometry. The lack of any molecular symmetry is compatible with the n.m.r. data only if it is assumed that a rapid dynamic process[6] occurs in solution. Welch[13] has discussed the distortion of the polyhedron from the expected bicapped square antiprism.

Nickel analogues of the platinum complexes (8) and (9) were readily prepared in good yield by the reactions of [Ni(cod)$(PEt_3)_2$] and [Ni(cod)$(PMe_3)_2$] with *closo*-4,5-$C_2B_7H_9$ and *closo*-4,5-Me_2-4,5-$C_2B_7H_7$ which gave, respectively, [$Ni(PEt_3)_2(C_2B_7H_9)$] (10) and [$Ni(PMe_3)_2$-$(Me_2C_2B_7H_7)$] (11). These yellow crystalline complexes were much less oxidatively stable than their platinum counterparts, and decomposed in minutes in solution when exposed to the atmosphere. The boron-11 n.m.r. spectrum of (10) (Figure 1) showed a 2 : 2 : 1 : 1 : 1 distribution of boron atoms and the ^1H n.m.r. spectrum, which had resonances for only one type of cage C–H protons and one type of phosphine ligand (Table 2), was also consistent with the molecule having a plane of symmetry. Comparison of the n.m.r. and i.r. data of (10) with the corresponding data for (8), together with the observed similarity of their general physical properties such as solubility and crystal habit, led to the conclusion that (8) and (10) have the same basic structure, which is presumably closely related to that of (9).

We next considered the insertion of a zerovalent platinum species into a ten-atom carbaborane cage. Addition of a solution of *closo*-1,6-$C_2B_8H_{10}$ to a 2 : 1 mixture of trimethylphosphine and bis(cyclo-octa-1,5-diene)platinum(0)[14] in light petroleum at room temperature gave a yellow flocculent precipitate, which on recrystallization from dichloromethane and light petroleum gave small yellow crystals of stoicheiometry $[Pt_2(PMe_3)_4(C_2B_8H_{10})]$ (12). From ^1H and ^{31}P n.m.r. spectra (Table 2) it was apparent that the molecule contained four inequivalent trimethylphosphine ligands, while the ^{11}B n.m.r. spectrum (Figure 1) indicated no symmetry at all in the cage.

That the preliminary experimental evidence established (12) as a dimetalla-compound was, at the time, not surprising. Hawthorne and co-workers [5,15] have reported numerous examples of multiple insertion of metal cations into carbaboranes and in this case we expected an initially produced eleven-atom dicarbaplatinaundecaborane to be particularly susceptible to further nucleophilic attack by a metal species, both because of the supposedly greater stability of the icosahedral framework, and because we had already observed the oxidative-insertion of a platinum(0) species into an eleven-atom dicarbacobaltaborane.[3] However, as a result of a single crystal *X*-ray diffraction study, the complex (12) was shown by Welch [7] to have the unprecedented structure depicted in Figure 2, and is thus formulated as *nido*-$[\mu\text{-}(6,10)\{Pt(PMe_3)_2\}\text{-}10,10\text{-}(PMe_3)_2\text{-}7,9,10\text{-}C_2PtB_8H_{10}]$.

An interesting question which has not so far been settled by further refinement of the crystal structure is the location of the hydrogen atom originally bound to B(6). In the hope of elucidating this point a more detailed n.m.r, study of ^1H, ^{31}P, and ^{195}Pt nuclei was undertaken by continuous-wave, pulsed Fourier-transform, and homo- and hetero-nuclear INDOR techniques. While this provided much information detailed in Table 2, and in the Experimental section, it did not locate the hydrogen atom. Although this might be taken as evidence suggesting a hydrogen position on the open face remote from the platinum atoms, the low resolution of the spectra due to coupling with ^{10}B and ^{11}B nuclei meant that a coupling between the missing hydrogen and one of the nuclei studied might have escaped detection.

It had previously been observed [3] that when the unstable dicarbadimetallaborane *closo*-$[(cod)NiC_2B_8H_{10}Co(\eta\text{-}C_5H_5)]$ was passed through a short column of activated charcoal, the [Ni(cod)] moiety was detached from the cage. When a dichloromethane solution of complex (12) was passed through a column of activated charcoal, the *exo*-polyhedral $[Pt(PMe_3)_2]$ group was removed and the very stable complex $[Pt(PMe_3)_2(C_2B_8H_{10})]$ (13) was formed. The boron-11 n.m.r. spectrum of (13) (Figure 1) was very different from that of its precursor, suggesting perhaps a fundamental rearrangement of the cage hetero-atoms to give a more symmetrical polyhedron. However, a single-crystal *X*-ray diffraction study [8] revealed a structure for (13) which was surprisingly similar to that of (12) (Figure 2). In particular, the polyhedral platinum and carbon atoms retained their relative positions in a cage which differed from that of the precursor (12), mainly in the non-planarity of the open-five-membered face [C(7), Pt, B(9), C(10), B(11)]. Thus (13) may be formulated as *nido*-$[10,10\text{-}(PMe_3)_2\text{-}7,9,10\text{-}C_2PtB_8H_{10}]$.

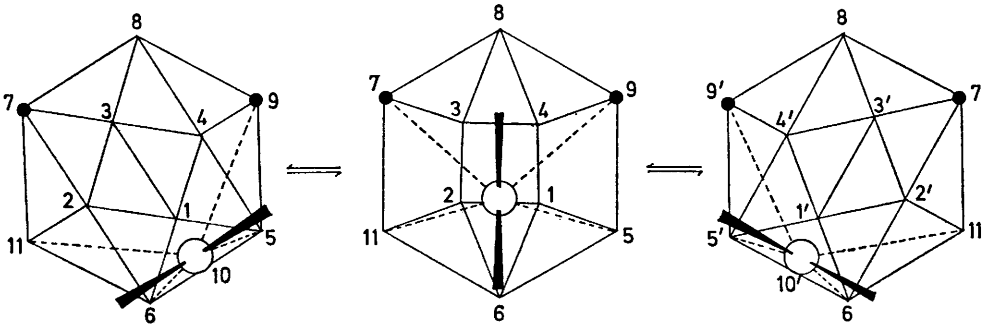
The Skeletal Electron Pair Theory (SEPT) [16] relating cage structures to the number of skeletal electron pairs has been remarkably successful in general for predicting the structures of the carbametallaboranes. Hawthorne and his co-workers [5] have developed in some depth the chemistry of the intermediate carbaboranes with transition metals, principally cobalt, nickel, and iron, and there are no authenticated examples of large deviations from the expected geometries other than distortions which can reasonably be ascribed to the larger radius of the hetero-atom. In this respect the pronounced deviations of several of the compounds discussed above from anticipated *closo*-geometry appears anomalous. Thus (4) deviates from a *pseudo*-tricapped trigonal prismatic structure as a result of an increase in the B(8)–B(9) separation to the point where there can be no significant bonding between these atoms. Similarly (9) differs from the expected bicapped square antiprism by a lengthening of the Pt–C(8) distance. In both these examples the open face is four-sided as shown in Figure 2. In contrast, (13) suffers a lengthening of the contact between Pt and B(8) and C(7) giving rise to a buckled five-sided face more reminiscent of an eleven-atom *nido*-icosahedral fragment than of the octadecahedral cage of, *e.g.*, 2,3-dimethyl-2,3-dicarba-*closo*-undecaborane.[17]

This apparently anomalous behaviour could have its origins in the well established preference of platinum(II) for a 16- rather than an 18-electron configuration, the remaining vacant metal orbital being of too high energy to interact effectively with a fifth ligand orbital. The SEPT approach [16] to polyhedral bonding requires that a cage atom have three orbitals of suitable energy and orientation to become fully incorporated in a *closo*-skeleton. Presumably platinum(II), and perhaps also nickel(II), are able to provide only two orbitals of low energy, and the very weak interaction of the other cage atoms with the third platinum orbital manifests itself in the very long connectivities across the ' open ' faces. Thus the $[Pt(PR_3)_2]$ fragment should perhaps be compared with a CH_2 rather than a BH cage fragment for the purposes of electron-pair counting. An extended Hückel account of the related phenomena observed in icosahedral carbametallaboranes has been published, in which it has been shown that the unequal bonding capabilities of the metal d_{xz} and d_{yz} orbitals play a major role in undermining the simple electron-counting rules.[18]

The diplatinum complex (12), with an almost planar pentagonal face, has a cage structure related to the 11-atom, 26-electron derivatives of icosahedral geometry such as *nido*-$[7,9\text{-}C_2B_9H_{12}]^-$.[19] A closer analogy is with the Lewis-base adducts of *closo*-2,3-$C_2B_9H_{11}$,[20] or with the pyridine adduct of *closo*-$[1\text{-}(\eta\text{-}C_5H_5)\text{-}2,4,1\text{-}C_2CoB_8H_{10}]$ [21] and related compounds. In these examples the Lewis base attacks a boron atom, effectively donating two extra electrons to the skeletal bonding. The cage distorts to give a *nido* structure and the hydrogen atom, originally resident on the boron under attack, is thought to migrate to the open face. In (12) the *exo*-polyhedral

$[Pt(PMe_3)_2]$ group bridging Pt(8) and B(4) assumes the role of the Lewis base in providing electrons to the cage, so stabilizing the *nido* configuration.

An interesting feature of the complexes derived from the nine-atom carbaboranes is the relatively simple ^{11}B n.m.r. spectra which imply a molecular plane of symmetry, in contrast to the observed C_1 symmetry of (9) in the solid state. We have rationalized this previously[6] in terms of a rapid degenerate intramolecular rearrangement leading to the time-averaged equivalence of the phosphine ligands and of the cage carbon atoms, and giving rise to five types of boron atom in the ratio 2 : 2 : 1 : 1 : 1. Low-temperature n.m.r. studies failed to ' freeze ' the motion, although at -130 °C in a $CHClF_2$–CH_2Cl_2 solvent mixture the ^{11}B n.m.r. spectrum of (8) showed only one very broad, featureless peak close to δ 0.0. However, whether this loss of resolution was due to the slowing of the fluxional process, or whether it was due to some other factor, is not certain. Indeed, the ^{31}P n.m.r. spectrum of (8) at -75 °C in dichloromethane is sharper than the spectrum taken at 30 °C.



SCHEME Possible polytopal rearrangement of the $[PtC_2B_8]$ core atoms of complex (13), viewed from above the open face

Another example of an unexpectedly simple ^{11}B n.m.r. spectrum is provided by complex (13) (Figure 1) with resonances of equal area at δ -8.5, 10.3, 12.7, and 26.8, and apart from a general broadening of the peaks this pattern is unchanged down to -60 °C. However, in contrast to the $[MC_2B_7]$ system, compound (13) exhibits two resonances in the ^{31}P n.m.r. spectrum at room temperature. Unfortunately it is not clear from the ^1H n.m.r. spectrum whether the broad signal at τ 7.5 (Table 2) represents one or both of the protons bound to the polyhedral carbon atoms. On the evidence available it is suggested that the $[PtC_2B_8]$ cage is undergoing a rapid polyhedral rearrangement, possibly by the mechanism shown in the Scheme. Note that in the transition state the co-ordination plane of the platinum is aligned with the mirror plane at the cage making the phosphine ligands inequivalent. This is comparable with the ground state geometry of *closo*-$[2,2\text{-}(PMe_2Ph)_2\text{-}1,7\text{-}Me_2\text{-}1,7,2\text{-}C_2PtB_9H_9]$ where the PtP_2 plane coincides with the polyhedral mirror plane.[3] The process depicted in the Scheme, which corresponds to the ' rotation of pentagonal faces '[22] in an icosahedron, does not in fact make equivalent pairs of all the boron atoms in the cage, and it is still necessary to postulate the accidental coincidence of the ^{11}B signals due to B(6) and B(8).

Given the ease with which (13) and the derivatives of the $[MC_2B_7]$ system undergo degenerate intramolecular rearrangement, it is surprising that none of the compounds described in this paper was observed to undergo an irreversible polyhedral rearrangement.[23] Although we have not made an extensive investigation into this aspect of their chemistry, it was observed that the platinum compounds, with the exception of (12) which decomposed at 156 °C, could be recovered unchanged (from i.r. evidence) after being held for several minutes at their melting points. One interpretation of this observation is that the products are obtained under thermodynamic control.

The method of carbametallaborane synthesis developed by Hawthorne and his collaborators[5] and termed ' polyhedral expansion '[24] has been shown to be a complicated reaction [equation (1), M = Co and Fe]. In general the reaction processes may give rise to the following types of product: $[(\eta\text{-}C_5H_5)M(C_2B_nH_{n+2})]$, $[\{(\eta\text{-}C_5H_5)M\}_2\text{-}(C_2B_nH_{n+2})]$, $[(\eta\text{-}C_5H_5)M(C_2B_nH_{n+1})(C_2B_nH_{n+1})]$, $[(\eta\text{-}C_5H_5)\text{-}M(C_2B_{n-1}H_{n+1})]$, $[\{\eta\text{-}C_5H_5)M\}_2(C_2B_{n+1}H_{n+3})]$, and $[(\eta\text{-}C_5H_5)\text{-}M(C_2B_{n+1}H_{n+3})]$. Furthermore, variations in reaction times and temperatures affect the yields and nature of the products. In contrast, the reactions reported in this paper proceed without complicating side-reactions and with high stereospecificity, affording only one product in the case of *closo*-4,5-$C_2B_7H_9$ and *closo*-1,6-$C_2B_8H_{10}$, and two in the reactions of *closo*-1,7-$C_2B_6H_8$. Moreover, the yields quoted in Table 1 represent the amount of product recovered after recrystallization and are not a good indication of the true yield of the reaction. For instance the reaction of $[Pt(PEt_3)_3]$ and *closo*-4,5-$C_2B_7H_9$ is believed to afford (8) in essentially quantitative yield. The milder reaction conditions and shorter reaction times are undoubtedly important factors in

$$C_2B_nH_{n+2} \xrightarrow[\text{catalyst}]{\text{Na}} [C_2B_nH_{n+2}]^{2-}$$

$$\xrightarrow[(ii)\ [O]]{(i)\ M^{2+},Na[C_5H_5]} \text{products} \qquad (1)$$

favouring the simplicity of the oxidative–insertion reaction.

The other interesting point of comparison with the findings of Hawthorne and co-workers [5,24] is the relative positions of metal and carbon atoms in the products. Polyhedral expansion *via* intermediate *nido*-carbaborane anions leads to products which almost invariably have the metal atom adjacent to at least one carbon atom. This arises because the position of the carbon atoms in the product is almost certainly determined by their position in the intermediate anion, and carbon atoms are believed to prefer low connectivity sites on the open faces of *nido*- and *arachno*-carbaboranes.[25]

In our first paper [3] we discussed the possibility of insertion occurring *via* an initial nucleophilic attack on a single boron atom leading to a *nido*-intermediate with a σ-bonded *exo*-metal group. A subsequent rearrangement was postulated to place the metal atom above the open face as part of the polyhedral framework. This mechanism was conceived by analogy with the reported reactions of main-group nucleophiles with 2,3-$C_2B_9H_{11}$, where stable *nido*-adducts were isolated.[20] On the other hand, Mingos and Welch,[26] using calculations based on the extended Hückel approximation, have recently shown that the insertion pattern and approximate isomer ratios in the C_2PtB_6 case may be rationalized in terms of interaction of the lowest unoccupied molecular orbital of a 1,7-$C_2B_6H_8$ dodecahedron and an angular $Pt(PR_3)_2$ fragment, which leads these authors to propose a concerted insertion process.

While the reactions here reported provided little direct evidence as to the mechanism, it was noted that the formation of (13) from (12) was not reversible. That is, the reaction of (13) with 1 equiv. of $[Pt(cod)(PMe_3)_2]$ under conditions similar to those employed originally in the synthesis of (12) from *closo*-1,6-$C_2B_8H_{10}$, failed to give any of this dicarbadimetallaborane. The implication is that (13) is not an intermediate in the formation of (12), which is surprising, particularly as the basic cage structures are so similar. It may be inferred, therefore, that it is the *exo*-platinum atom which first adds to the cage giving a *nido*-intermediate as discussed above, and that a second $[Pt(PMe_3)_2]$ group then rapidly attacks the open face and is incorporated in the polyhedral framework. However, why, in this case, secondary metal attack should proceed more rapidly than the internal *exo–endo* rearrangement is not clear. Alternatively, all the reactions here reported may proceed *via* a dimetalla-intermediate, but only in the $C_2B_8H_{10}$ case is this sufficiently stable to be observed.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded at 100 MHz on a Varian Associates HA 100 spectrometer. The technique of $^1H\{^{31}P\}$ and $^1H\{^{195}Pt\}$ INDOR measurements has been described elsewhere.[27] Boron-11 and ^{31}P n.m.r. spectra were measured at 32.1 and 40.48 MHz, respectively, using a JEOL PFT 100 Fourier-transform spectrometer, with a facility for the broad-band decoupling of protons.

Melting points were measured in sealed, evacuated tubes. All reactions were performed in a dry, oxygen-free nitrogen atmosphere using solvents dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction of b.p. 40—60 °C. The carbaboranes were prepared by literature methods,[28] as were the zerovalent metal complexes, $[Pt(PEt_3)_3]$,[3] $[Pt(trans\text{-stilbene})(PR'_3)_2]$ (R′ = Et [10] and Me [3]), $[Ni(cod)(PR'_3)_2]$,[12] and $[Pt(cod)_2]$.[14]

Syntheses.—(a) *6,6-Bis(trimethylphosphine)-4,5-dicarba-6-platina-*closo*-nonaborane and 7,7-bis(trimethylphosphine)-4,5-dicarba-7-platina-*nido*-nonaborane.* The complex *trans*-stilbenebis(trimethylphosphine)platinum (1.45 g, 2.75 mmol) was suspended in light petroleum (10 cm^3) and *closo*-1,7-$C_2B_6H_8$ added as a neat liquid (0.4 cm^3, *ca.* 3 mmol). The platinum complex dissolved rapidly and a bright yellow precipitate formed. After 10 min the mixture was transferred to a short (30 × 2.5 cm) column of Florisil. Three bands were eluted with light petroleum–dichloromethane (compositions 75 : 25, 65 : 35, and 45 : 55, respectively). The first fraction was identified as *trans*-stilbene contaminated with a small quantity of yellow material. A second fraction yielded, on evaporation of the solvent, a yellow substance which was recrystallized from light petroleum–dichloromethane to give yellow *crystals* of *closo*-$[6,6\text{-}(PMe_3)_2\text{-}4,5,6\text{-}C_2PtB_6H_8]$ (1); $\nu_{max.}$ (Nujol) at 2 585 (sh), 2 575s, 2 525s, 2 510s, 1 440m, 1 420m, 1 308w, 1 292m, 1 288 (sh), 1 150w, 1 105m, 1 057m, 1 039s, 967 (sh), 958vs, 935s, 866m, 825w, 746s, and 684m cm^{-1}.

Some decomposition was observed as the third band was eluted from the column. This fraction, on recrystallization, yielded yellow *crystals* of *nido*-$[7,7\text{-}(PMe_3)_2\text{-}4,5,7\text{-}C_2PtB_6H_8]$ (2); $\nu_{max.}$ (Nujol) at 2 585s, 2 535s, 2 505s, 1 422m, 1 303w, 1 296s, 1 290 (sh), 1 165w, 1 130m (br), 1 020w, 975s, 955vs, 893w, 864w, 808w, 750 (sh), 745m, 696w, 686w, and 562w cm^{-1}.

(b) *4,5-Dimethyl-6,6-bis(triethylphosphine)-4,5-dicarba-6-platina-*closo*-nonaborane and 4,5-dimethyl-7,7-bis(triethylphosphine)-4,5-dicarba-7-platina-*nido*-nonaborane.* *trans*-Stilbenebis(triethylphosphine)platinum (0.9 g, 1.5 mmol) was dissolved in light petroleum (10 cm^3) and *closo*-1,7-Me_2-1,7-$C_2B_6H_6$ (0.24 cm^3, *ca.* 1.5 mmol) was added from a microsyringe. Almost immediately a bright yellow colour developed and within a few minutes pale yellow crystals were deposited. After 16 h the mother-liquor was decanted and several well formed orange crystals were separated manually from the mass of pale yellow material. The orange compound was recrystallized from diethyl ether–light petroleum at −10 °C giving large orange *crystals* of *nido*-$[4,5\text{-}Me_2\text{-}7,7\text{-}(PEt_3)_2\text{-}4,5,7\text{-}C_2PtB_6H_6]$ (4); $\nu_{max.}$ (Nujol) at 2 565 (sh), 2 555s, 2 540 (sh, 2 510s, 1 263m, 1 255 (sh), 1 243m, 1 155w (br), 1 105w, 1 041s, 1 019s, 1 010 (sh), 978m, 943s, 840w, 808w, 774s, 727m, 723 (sh), 685m, and 635m cm^{-1}. The pale yellow solids were combined with the mother liquor and recrystallized, affording initially large colourless plates of *trans*-stilbene. After concentration of the remaining solution and cooling to −10 °C for 3 d, large yellow *crystals* of *closo*-$[4,5\text{-}Me_2\text{-}6,6\text{-}(PEt_3)_2\text{-}4,5,6\text{-}C_2PtB_6H_6]$ (3), were isolated; $\nu_{max.}$ (Nujol) at 2 565s, 2 525s, 2 495 (sh), 1 433m, 1 420m, 1 306w, 1 290w, 1 258m, 1 240 (sh), 1 120w, 1 041s, 1 038 (sh), 1 017w, 1 006w, 986m, 951m, 938w, 903w, 864s, 839w, 770s, 746w, 733s, 728 (sh), 717m, 678w, 639m, 618w, 446m, and 422m cm^{-1}.

(c) *4,5-Dimethyl-6,6-bis(trimethylphosphine)-4,5-dicarba-6-platina-*closo*-nonaborane.* Similarly the reaction of $[Pt(trans\text{-stilbene})(PMe_3)_2]$ with *closo*-1,7-Me_2-1,7-$C_2B_6H_6$ gave yellow *crystals* of *closo*-[$4,5\text{-Me}_2\text{-}6,6\text{-}(\text{PMe}_3)_2\text{-}4,5,6\text{-C}_2\text{PtB}_6\text{H}_6$], (5); $\nu_{\text{max.}}$ (Nujol) at 2 565 (sh), 2 550 (sh), 2 545s, 2 510s, 1 418w, 1 304w, 1 288m, 984 (sh), 968 (sh), 949s, 885w, 877 (sh), 858m, 743m, and 684w cm^{-1}. Orange needles, in low yield, were also isolated from this reaction but they decomposed rapidly, and were not characterized.

(d) 4,5-*Dimethyl*-6,6-*bis*(*trimethylphosphine*)-4,5-*dicarba*-6-*nickela*-closo-*nonaborane*. Bis(cyclo-octa-1,5-diene)nickel (0.55 g, 2 mmol) was suspended in light petroleum–toluene (7 cm^3, 4 : 3) and trimethylphosphine (0.31 g, 4 mmol) was distilled into the Schlenk tube. The resulting yellow solution was added to a light petroleum solution (5 cm^3) of *closo*-$1,7\text{-Me}_2\text{-}1,7\text{-C}_2\text{B}_6\text{H}_6$ (0.35 cm^3, *ca.* 2.2 mmol). An orange colour developed immediately. After 6 h at 20 °C the mixture was cooled to −78 °C for 16 h before the supernatant liquid was decanted from the mass of crystals. Recrystallization from light petroleum at −78 °C gave orange *crystals* of *closo*-[$4,5\text{-Me}_2\text{-}6,6\text{-}(\text{PMe}_3)_2\text{-}4,5,6\text{-C}_2\text{NiB}_6\text{H}_6$], (7); $\nu_{\text{max.}}$ (Nujol) at 2 580 (sh), 2 570s, 2 560s, 2 510s, 2 490 (sh), 1 425w, 1 308 (sh), 1 303w, 1 289m, 1 285 (sh), 986 (sh), 967 (sh), 952s, 876 (sh), 865m, 858 (sh), 853 (sh), 736m, 680m, and 466w cm^{-1}.

(e) 4,5-*Dimethyl*-6,6-*bis*(*triethylphosphine*)-4,5-*dicarba*-6-*nickela*-closo-*nonaborane*. Similarly, the reaction of [$\text{Ni(cod)(PEt}_3)_2$] with *closo*-$1,7\text{-Me}_2\text{-}1,7\text{-C}_2\text{B}_6\text{H}_6$ afforded orange *crystals* of *closo*-[$4,5\text{-Me}_2\text{-}6,6\text{-}(\text{PEt}_3)_2\text{-}4,5,6\text{-C}_2\text{NiB}_6\text{H}_6$], (6); $\nu_{\text{max.}}$ (Nujol) at 2 590 (sh), 1 580s, 2 560s, 2 535 (sh), 2 530s, 2 515 (sh), 2 505 (sh), 1 321vw, 1 290vw, 1 256w, 1 039s, 1 015vw, 1 005 (sh), 999w, 987w, 945vw, 874w, 861m, 836vw, 766s, 723s, 714 (sh), 673vw, 630w, 462w, and 418w cm^{-1}.

(f) 10,10-*Bis*(*triethylphosphine*)-2,8-*dicarba*-10-*platina*-nido-*decaborane*(9). Tris(triethylphosphine)platinum (0.5 g, 0.9 mmol) dissolved in light petroleum (1 cm^3) was added to a solution of *closo*-$4,5\text{-C}_2\text{B}_7\text{H}_9$ (0.1 g, 0.9 mmol) in light petroleum (10 cm^3). Immediately fine off-white needles began to precipitate from the solution. Recrystallization from dichloromethane–light petroleum afforded very pale yellow *prisms* of *nido*-[$10,10\text{-}(\text{PEt}_3)_2\text{-}2,8,10\text{-C}_2\text{PtB}_7\text{H}_9$], (8); $\nu_{\text{max.}}$ (Nujol) at 2 565 (sh), 2 555s, 2 540 (sh), 2 510 (sh), 2 495 (sh), 1 428 (sh), 1 418w, 1 253w, 1 120w, 1 088m, 1 036s, 1 025 (sh), 1 001w, 941m, 929 (sh), 856vw, 844vw, 826vw, 763s, 741w, 720m, 709 (sh), and 631w cm^{-1}.

(g) Similarly prepared from [$\text{Pt(PEt}_3)_3$] and *closo*-$4,5\text{-Me}_2\text{-}4,5\text{-C}_2\text{B}_7\text{H}_7$ were the very pale yellow *crystals* of 2,8-*dimethyl*-10,10-*bis*(*triethylphosphine*)-2,8-*dicarba*-10-*platina*-nido-*decaborane*(9); $\nu_{\text{max.}}$ (Nujol) at 2 565s, 2 505s, 2 480s, 1 418m, 1 260w, 1 252 (sh), 1 240 (sh), 1 039m, 1 028 (sh), 1 009w, 1 000w, 987 (sh), 978w, 944w, 935w, 921w, 894w, 870w, 847w, 823w, 768s, 756 (sh), and 722s cm^{-1}.

(h) 2,8-*Dimethyl*-10,10-*bis*(*trimethylphosphine*)-2,8-*dicarba*-10-*nickela*-nido-*decaborane*. A light petroleum solution containing bis(cyclo-octa-1,5-diene)nickel (0.275 g, 1 mmol) and trimethylphosphine (0.152 g, 2 mmol) in a volume of 4 cm^3 was added to a similar volume of light petroleum containing *closo*-$4,5\text{-Me}_2\text{-}4,5\text{-C}_2\text{B}_7\text{H}_7$ (0.16 g, *ca.* 1.2 mmol) at 0 °C. The mixture was allowed to warm to room temperature and then set aside for 6 h. On cooling to −78 °C for 16 h a yellow solid was deposited. Recrystallization from light petroleum–toluene (2 : 1) afforded yellow *crystals* of *nido*-[$2,8\text{-Me}_2\text{-}10,10\text{-}(\text{PMe}_3)_2\text{-}2,8,10\text{-C}_2\text{NiB}_7\text{H}_7$], (11); $\nu_{\text{max.}}$ (Nujol) at 2 575 (sh), 2 565 (sh), 2 550s, 2 515 (sh), 2 505s, 2 495s, 2 490 (sh), 1 308w, 1 291m, 1 288m, 1 120w (br), 990 (sh), 970 (sh), 954s, 908m, 879w, 857w, 745 (sh), 732m, 724 (sh), and 679w cm^{-1}.

(i) 10,10-*Bis*(*triethylphosphine*)-2,8-*dicarba*-10-*nickela*-nido-*decaborane*. Solid *closo*-$4,5\text{-C}_2\text{B}_7\text{H}_9$ (0.16 g, 1.5 mmol) was added to a light petroleum solution of [Ni(cod)_2] (0.56 g, 2 mmol) and triethylphosphine (0.6 cm^3, *ca.* 4 mmol). Within 1 min yellow crystals began forming. The mixture was cooled to 0 °C for several hours before the supernatant liquid was decanted off and the crystals washed with light petroleum and dried *in vacuo*. The fine yellow *needles* of *nido*-[$10,10\text{-}(\text{PEt}_3)_2\text{-}2,8,10\text{-C}_2\text{NiB}_7\text{H}_9$] (10), thus prepared were not recrystallised; $\nu_{\text{max.}}$ (Nujol) at 2 575 (sh), 2 560vs, 2 525 (sh), 2 490s, 1 430m, 1 257m, 1 121w, 1 095m, 1 041s, 1 015 (sh), 1 003m, 958m, 930w, 899w, 887w, 853w, 842w, 768s, 718s, 675w, 633m, and 600w cm^{-1}.

(j) μ-(6,10)-*Bis*(*trimethylphosphine*)*platinum*-10,10-*bis*(*trimethylphosphine*)-7,9-*dicarba*-10-*platina*-nido-*undecaborane*. Trimethylphosphine (0.33 g, 4.3 mmol) was distilled into a tube containing [Pt(cod)_2] (0.82 g, 2 mmol) and light petroleum (40 cm^3). On warming to room temperature, the suspended [Pt(cod)_2] dissolved and a white precipitate formed. A solution of *closo*-$1,6\text{-C}_2\text{B}_8\text{H}_{10}$ (0.15 g, 1.4 mmol) in light petroleum (20 cm^3) was added. Immediately a flocculent yellow precipitate formed. After 15 min the mixture was filtered and the yellow solid washed with light petroleum and dried. Recrystallization from light petroleum–dichloromethane afforded small yellow *crystals* of *nido*-[$\mu\text{-}(6,10)\text{-}\{\text{Pt(PMe}_3)_2\}\text{-}10,10\text{-}(\text{PMe}_3)_2\text{-}7,9,10\text{-C}_2\text{PtB}_8\text{H}_{10}$], (12); $\nu_{\text{max.}}$ (Nujol) at 2 515vs, 2 455 (sh), 1 422m, 1 308m, 1 289s, 1 090w, 1 039w, 1 011w, 975 (sh), 955vs, 865m, 860 (sh), 829w, 740 (sh), 736s, 689m, 680m, and 658 (sh) cm^{-1}. The crystals thus prepared were unsuitable for *X*-ray data collection, but when (12) was prepared from [Pt(*trans*-stilbene)$(\text{PMe}_3)_2$] and recrystallized from light petroleum–dichloromethane suitable crystals were formed which contained both *trans*-stilbene and dichloromethane in the crystal lattice.[29] The results of the n.m.r. experiments on (12) are summarized in Table 2. INDOR spectra ($^1\text{H}\{^{195}\text{Pt}\}$) have shown that two nuclei referred to as P(A) (δ_P 22.4) and P(C) (δ_P 21.2) are bonded to the same platinum (δ_Pt −519), and that two other nuclei P(B) (δ_P 47.3) and P(D) (δ_P 56.2) are bonded to the other platinum (δ_Pt −1 231). Furthermore, P(A) and P(B) are coupled [^3J(PP) 28 Hz], and both these nuclei gave sharp lines in the ^{31}P Fourier-transform n.m.r. spectrum, in contrast to P(C) and P(D) which have exceptionally broad linewidths (>200 and 170 Hz, respectively). This indicates that P(A) and P(B) are mutually *trans* across the Pt–Pt bond whereas P(C) and P(D) must be *trans* to boron.

(k) 10,10-*Bis*(*trimethylphosphine*)-7,9-*dicarba*-10-*platina*-nido-*undecaborane*(10). A solution of (12) (0.3 g, 0.33 mmol) in dichloromethane was applied to a column of activated charcoal (20 × 1 cm). Elution with dichloromethane gave a pale yellow solution which, on evaporation, afforded yellow *crystals* of *nido*-[$10,10\text{-}(\text{PMe}_3)_2\text{-}7,9,10\text{-C}_2\text{PtB}_8\text{H}_{10}$] (13); $\nu_{\text{max.}}$ (Nujol) at 2 535vs, 2 505vs, 1 421m, 1 311m, 1 295s, 1 168w, 1 130w, 1 114w, 1 094w, 1 030w, 960vs, 888w, 859m, 834w, 772w, 746m, 726w, and 687m cm^{-1}.

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