Metallaborane Chemistry. Part VI.[1] Molecular and Crystal Structures of the *closo*-Carbaplatinaoctaboranes 6,8-Dimethyl-1,1-bis(trimethylphosphine)- and 1,1-Bis(trimethylphosphine)-6,8-dicarba-1-platinaoctaborane

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The molecular structures of the title compounds have been determined by single-crystal *X*-ray diffraction. The *C*-methylated metallacarbaborane exhibits two crystalline modifications, an $A2/a$ (α) and a $P2_1/c$ (β) form. The latter crystallises in a cell of dimensions a = 11.892(4), b = 9.280(4), and c = 18.724(8) Å, β = 106.17(3)°, and its structure was determined by the heavy-atom method and refined to R 0.044 for 2 487 independent observed reflections. Both compounds exhibit C_2 molecular symmetry and have *closo*-polyhedral cages with geometries approximating to those of tricapped trigonal prisms, whose low connectivity 'cap' positions are occupied by the three heteroatoms. Some experimental data are given for (I)-α and (II): the gross features of their molecular geometries were determined but their structures were not refined.

THIS series of papers has been concerned with the chemical and structural aspects of the oxidative-addition reactions of zerovalent nickel-group complexes with carbaboranes. *closo*-Metallacarbaboranes with skeletal 1,2,4-MC_2B_9,[2,3] 1,2,7,8-CoC_2PtB_8,[2,4] and 1,2-MCB_{10} (ref. 4) arrangements and the *nido*-species 2,7,9-C_2PtB_7,[5] and 2,7,10-CM'CB_7 (ref. 1) (where M = Ni, Pd, or Pt; M' = Ni or Pt) have been described.

This paper describes the results of *X*-ray diffraction studies on single crystals of the title compounds, being the major products of the reaction between [Pt(*trans*-stilbene)$(PMe_3)_2$] [2] and *closo*-1,6-R_2-1,6-$C_2B_6H_6$ (refs. 6—8) (R = Me or H). The findings of a similar study on the minor product of the corresponding reaction by use of [Pt(*trans*-stilbene)$(PEt_3)_2$] and the *C*-methylated carbaborane will appear in a following paper. Preliminary details of these structures have already been published.[9]

EXPERIMENTAL

Following reaction between the platinum(0) species and carbaborane the major of two isomeric products was separated by fractional crystallisation, and recrystallised from light petrol (b.p. 40—60 °C) at −5 °C. Microscopic examination revealed that whilst the greater part of the bright-yellow transparent sample crystallised as irregular blocks (β form) a few crystals were prismatic needles (α form).

(I): β *Form*.—A single crystal in the shape of a triangulated prism, 0.05 × 0.045 × 0.04 cm, was mounted on a quartz fibre with an epoxy-resin adhesive, and set in the optical centre of the cradle of a Syntex $P2_1$ four-circle diffractometer. Following an established procedure [10] units cell dimensions and errors, and sets of diffracted intensities were recorded. In the present experiment the following details applied: 15 reflections, $14° < 2\theta < 24°$, were centred and used to calculate the unit cell parameters, their associated standard deviations and orientation matrix; reflection data were limited by the criteria $0 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 9$, $\overline{18} \leqslant l \leqslant 18$, and $2.9° \leqslant 2\theta \leqslant 60.0°$; Mo-$K_\alpha$ radiation ($\lambda_{\alpha1}$ = 0.709 26, $\lambda_{\alpha2}$ = 0.713 54 Å) and a 96-step θ—2θ scan were used throughout; peaks were integrated from 1.0° below $K_{\alpha1}$ to 1.0° above $K_{\alpha2}$, and were scanned at rates (which varied from 0.075 2 to 0.976 5° s^{-1}) calculated from an initial 2 s peak-count in which 15.0 and 850.0 were used as minimum and maximum threshold values. All intensities were thereafter scaled to a 1.0° min^{-1} basis. Three check reflections were each measured once every batch of 43, but subsequent analysis [11] of their net intensities as a function of time revealed that no significant crystal decomposition or machine variance had taken place during data collection. Of the 4 027 reflections measured, 2 487 were deemed significantly intense $\{I \geqslant 2.5\sigma(I)\}$ and were used to solve and refine the structure. The intensities of equivalent $0kl$ and $0k\bar{l}$ reflections were merged. An absorption correction was applied, resulting in correction factors (A^*) ranging from 4.62 (9 0 18) to 14.69 (8 5 $\bar{1}$).

Crystal Data.—$C_{10}H_{24}PtP_2B_6$, M = 472.25, Monoclinic, a = 11.892(4), b = 9.280(4), c = 18.724(8) Å, β = 106.17(3)°, U = 1 984(1) Å^3, D_m = 1.60 (flotation), Z = 4, D_c = 1.580, $F(000)$ = 888. μ(Mo-K_α) = 76.2 cm^{-1}. Space group $P2_1/c$.

Data were further corrected for Lorentz and polarisation effects. The structure was solved, with some difficulty arising from pseudo-symmetry (see later), *via* a three-dimensional Patterson synthesis (Pt and P atoms), full-matrix least-squares refinement, and successive difference electron-density maps (C, B, and cage H atoms). Weights were applied according to $w = (xy)^{-1}$ with $x = b/\sin\theta$ if $\sin\theta < b$, $x = 1$ if $\sin\theta \geqslant b$, and $y = F_o/a$ if $F_o > a$, $y = 1$ if $F_o \leqslant a$, in which a and b took values 100.0 and 0.3, respectively.

Since the matrix caused the isotropic thermal parameter of H(2) to refine non-positive definite, the position of this atom (determined from a peak listing) was held invariant, and structure-factor calculations assume a U of 0.05 Å^2. No attempt was made to locate methyl hydrogen atoms. In the final stages of refinement all non-hydrogen atoms were allowed anisotropic thermal motion. R converged to 0.044 (R' 0.050). In the final cycle the mean shift-to-error ratio for refined parameters was <0.009, and a final ΔF synthesis showed a maximum of *ca.* 0.6 eÅ^{-3} in the locality of C(12').

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[11] A. G. Modinos, DRSYN, a Fortran program for data analysis.

Atomic scattering factors for neutral atoms were taken from ref. 12 for platinum and boron, ref. 13 for phosphorus

TABLE 1

(I)-β: Final positions [a] of the non-hydrogen atoms

Atom	x	y	z
Pt(1)	0.25330(4) [b]	−0.01142(4)	0.00408(2)
B(2)	0.2598(10)	0.1923(12)	−0.0534(6)
B(3)	0.1067(11)	0.0987(16)	−0.0792(7)
B(2′)	0.1657$_5$(12)	−0.0542(16)	−0.1152(7)
B(3′)	0.3231(14)	0.0411(16)	−0.0910(8)
C(6)	0.1443(11)	0.2331(14)	−0.1189(7)
B(7)	0.1121(12)	0.0935(17)	−0.1755(7)
C(6′)	0.2364(10)	0.0143(15)	−0.1704(6)
B(7′)	0.2524(13)	0.1868$_5$(18)	−0.1509(7)
C(61)	0.0818$_5$(15)	0.3798(17)	−0.1324(9)
C(61′)	0.2660(15)	−0.0618(21)	−0.2348$_5$(8)
P(1)	0.3148(3)	−0.2463(3)	0.0317(2)
C(11)	0.1936(15)	−0.3645(17)	0.0343(12)
C(12)	0.4209(14)	−0.2892(20)	0.1187(10)
C(13)	0.3807(19)	−0.3304(20)	−0.0356(12)
P(1′)	0.2495(3)	0.0898(4)	0.1163(2)
C(11′)	0.3836(14)	0.1923(22)	0.1577(9)
C(12′)	0.2303(17)	−0.0270(21)	0.1907(8)
C(13′)	0.132 5$_5$(14)	0.2220(17)	0.1095(10)

[a] Expressed as fractions of the respective unit cell edges. [b] Estimated standard deviations are presented in parentheses throughout this paper.

TABLE 2

(I)-β: Final anisotropic thermal parameters [a] (Å^2, × 10^3) of the non-hydrogen atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	47.5(3)	39.8(2)	36.6(2)	−2.0(3)	14.2(1)	−0.6(2)
B(2)	42(7)	33(6)	34(6)	−6(5)	4(5)	−6(4)
B(3)	32(7)	70(9)	44(7)	13(6)	6(5)	−5(6)
B(2′)	42(7)	59(8)	51(7)	−20(6)	17(5)	−16(6)
B(3′)	52(9)	62(9)	48(7)	5(6)	17(6)	−5(6)
C(6)	41(7)	62(8)	51(7)	7(5)	8(5)	6(5)
B(7)	44(8)	66(9)	45(7)	−7(6)	11(6)	0(6)
C(6′)	44(7)	75(8)	45(6)	8(6)	15(4)	−5(6)
B(7′)	52(9)	82(10)	30(7)	2(7)	7(5)	20(6)
C(61)	89(12)	57(9)	90(11)	25(8)	20(9)	20(7)
C(61′)	90(11)	117(13)	47(8)	9(10)	31(7)	−15(8)
P(1)	52(2)	43(2)	73(2)	3(1)	29(2)	11(1)
C(11)	71(11)	60(9)	136(15)	−17(7)	35(10)	1(9)
C(12)	65(10)	95(12)	98(12)	6(8)	5(8)	47(10)
C(13)	114(16)	75(11)	119(14)	33(10)	65(12)	2(10)
P(1′)	57(2)	59(2)	43(2)	−5(1)	17(1)	−6(1)
C(11′)	57(9)	126(15)	76(10)	−21(9)	22(7)	−49(10)
C(12′)	113(13)	116(14)	47(8)	−13(11)	39(8)	8(8)
C(13′)	74(11)	66(9)	100(12)	0(7)	48(9)	−19(8)

[a] Defined as $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

TABLE 3

(I)-β: Positional [a] and thermal [b] parameters of the hydrogen atoms

Atom	x	y	z	U_j(Å^2, × 10^2)
H(2) [c]	0.300	0.259	−0.032$_5$	5
H(3)	0.036(11)	0.105(13)	−0.055(7)	6(3)
H(2′)	0.134(9)	−0.164(11)	−0.124(5)	3(3)
H(3′)	0.403(10)	0.003(11)	−0.080(5)	3(3)
H(7)	0.025(11)	0.089(13)	−0.227(6)	5(3)
H(7′)	0.294(12)	0.269(15)	−0.180(8)	7(4)

[a] See footnote, Table 1. [b] Isotropic thermal parameter in the form $\exp[-8\pi^2 U_j(\sin^2\theta)/\lambda^2]$. [c] This atom not refined. See text.

and carbon, and ref. 14 for hydrogen, those of platinum and phosphorus being corrected [15] for both components of anomalous dispersion. Final atomic parameters are listed in Table 1—3. Appendix * A contains a comparison of F_o and F_c.

Complex (II)

This compound is prepared from 1,6-$C_2B_6H_8$ in an entirely analogous reaction to that producing (I). On recrystallisation from diethyl ether at −5 °C the major product is deposited, as bright yellow plates, in a single crystalline form.

Intensity data for compounds (II) and (I)-α have been recorded and the gross features of their molecular geometries determined. In neither case, however, do we feel that the advantages gained by rigorously treating the data and fully refining the structures would warrant the man-hours and computer time required.

Experimental data for compounds (I)-α and (II) are presented in Table 4, and Appendices B and C compare their observed structure factor amplitudes with those calculated at the termination of refinement.

Programs used in the structure solutions and refinements were as reported previously.[3]

TABLE 4

(I)-α and (II): Experimental data

	(I)-α	(II)
Formula	$C_{10}H_{24}PtP_2B_6$	$C_8H_{20}PtP_2B_6$
M	472.25	444.19
System	Monoclinic	Monoclinic
Space group	$A2/a$	$A2$
a/Å	12.002(5)	5.716(2)
b/Å	10.415(7)	9.785(4)
c/Å	16.559(7)	15.329(8)
β/°	102.47(3)	94.24(3)
U/Å^3	2 021(1)	885.2(6)
D_m (flotation)	1.54	1.73
Z	4	2
D_c	1.552	1.725
F(000)	888	412
μ(Mo-$K_{\bar\alpha}$)/cm^{-1}	74.4	87.9
$2\theta_{max.}$	50.0	50.0
Independent reflections	1 562	698
Significant reflections	1 077	698
(criterion)	[$I \geqslant 4.0\sigma(I)$]	[$I \geqslant 2.5\sigma(I)$]
Refinement mode	Pt, P anisotropic; C, B isotropic	Pt, P anisotropic; C[a], B[a] isotropic
R	0.070	0.079

[a] For (II) cage atoms were distinguished on the basis of internuclear separations.

DESCRIPTION AND DISCUSSION OF THE STRUCTURES

Both species crystallise as well-separated, neutral, monomer molecules, perspective views of which are given in Figures 1 and 2. Both have C_2 symmetry, which in the case of (I)-α and (II) is crystallographically imposed. The molecular diad axis bisects the P–Pt–P angle and the B(7)–B(7′) linkage.

In Table 5, the list of internuclear separations (uncorrected for thermal motion) for pairs of bonds related by the effective C_2 axis of (I)-β are taken together, and are compared with the corresponding distances in (I)-α and (II). Inter-bond angle data for (I)-β are presented in

* All Appendices may be recovered from Supplementary Publication No. SUP 21568 (25 pp., 1 microfiche). See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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[13] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
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Table 6, whilst those for the other species are deposited (Appendices D and E), as are all the molecular parameters of (I)-β involving hydrogen atoms (Appendix F).

Compound (I)-β.—The carbaplatinaborane fragment may be geometrically described as a distorted tricapped (Pt and 2 × C) trigonal prism of boron atoms. Assuming that the metal atom adopts a d^8 configuration, thus

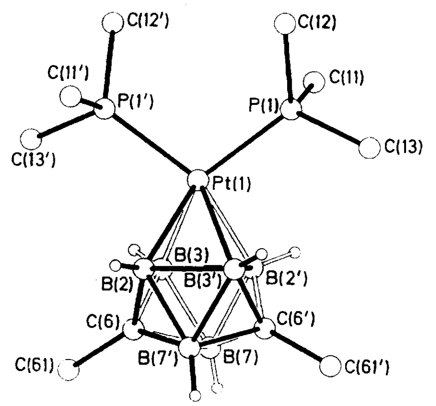

FIGURE 1 Perspective view of compound (I). Hydrogen atoms are numbered according to the boron to which they are attached

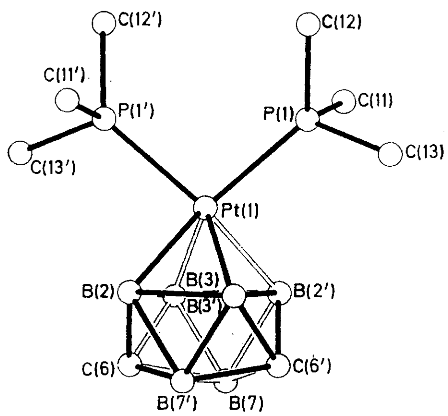

FIGURE 2 Perspective view of compound (II)

utilizing two electrons in cage-binding, this overall geometry would have been predicted by empirical electron-counting rules.[16]

Equations of, individual atomic deviations from, and dihedral angles between, the best planes through the three capped B_4 units are recorded in Appendix G. The approximate symmetry of the B_6 prism alone is reduced from D_{3h} to C_{2v} by the highly significant difference between the mean B(2)–B(3) and B(2')–B(3') distances [$1.97_5(4)$ Å] and that of all other B–B bonds [1.81(2) Å]. Since B(7)–B(7') is only 1.82(2) Å, the two triangular faces of the prism, B(2,3' and 7') and B(3,2' and 7), are not parallel: planes defined by these sets of atoms subtend a dihedral angle of *ca.* 6.0°.

The low-connectivity carbon atoms 6 and 6' cap their respective B_4 faces symmetrically, as evidenced by the

TABLE 5

Interatomic distances (Å)

	(I)-β [a]	(I)-α	(II)
Pt(1)–B(2)	2.19(1) 2.22(1)	2.19(3)	2.17(6)
Pt(1)–B(3)	2.24(1) 2.22(2)	2.22(3)	2.16(6)
B(2)–B(3)	1.95(2) 2.00(2)	1.98(5)	2.24(8)
B(2)–B(3')	1.82(2) 1.80(2)	1.85(4)	2.01(8)
B(2)–B(7')	1.80(2) 1.78(2)	1.81(4)	1.89(7)
B(2)–C(6)	1.61(1) 1.63(2)	1.58(4)	1.80(8)
B(3)–B(7)	1.82(2) 1.81(2)	1.87(4)	1.84(8)
B(3)–C(6)	1.58(2) 1.57(2)	1.60(4)	1.72(7)
C(6)–B(7)	1.65(2) 1.64(2)	1.69(4)	1.81(7)
C(6)–B(7')	1.62(2) 1.63(2)	1.65(4)	1.81(7)
B(7)–B(7')	1.82(2)	1.96(5)	2.13(7)
Pt(1)–P(1)	2.311(3) $2.314(3_5)$	2.307(7)	2.45(1)
P(1)–C(11)	1.82(2) 1.83(2)	1.78(5)	1.76(5)
P(1)–C(12)	1.81(2) 1.83(2)	1.80(4)	1.92(7)
P(1)–C(13)	1.83(2) 1.83(2)	1.87(3)	1.80(7)
C(6)–C(61)	1.54(2) 1.52(2)	1.59(4)	—

[a] For compound (I)-β the upper value pertains to the bond described and the second to its near-C_2 symmetry-related equivalent.

high degree of internal consistency of C–B bond lengths [range 1.57(2)—1.65(2), mean 1.62(3) Å] and C–C–B angles [range 125(1)—127(1), mean 126(1)°].

The platinum atom provides the third cap of the polyhedron, co-ordinating four boron atoms at 2.19(1) to 2.24(1), mean 2.22(2) Å. Although strictly not significantly different from the mean metal–boron distances we have observed in skeletal 1,2,4-PtC_2B_9,[2,3] 1,2-$PdCB_{10}$,[4] and 2,7,9-C_2PtB_7 species,[5] this value nevertheless represents a mean M–B shortening of *ca.* 0.034 Å on reducing the polyhedral metal connectivity from five * to four in d^8 metallacarbaboranes.

Previously only two *closo*-9-atom metallacarbaboranes have been structurally authenticated and in both cases the metals involved [Mn^{I} [17] and Co^{III} [18]] were located in the prism, being five-co-ordinate with respect to the polyhedron. Although several authors [19-23] have

* Although the metal atom in 9,9-$(Et_3P)_2$-2,7-Me_2-2,7,9-$C_2PtB_7H_7$ [5] is formally four-co-ordinate with respect to the cage, it occupies a classically five-co-ordinate site.

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suggested small- or medium-order metallaborane and metallacarbaborane structures in which a transition metal caps a closed four-atom polyhedral face, the present work constitutes the first crystallographically proven example of this mode of bonding.

TABLE 6

(I)-β Interbond angles (°)

(*a*) Within the polyhedron			
B(2)–Pt(1)–B(3)	52.4(5)	B(2′)–Pt(1)–B(3′)	53.7(5)
B(3)–Pt(1)–B(2′)	47.5(5)	B(3′)–Pt(1)–B(2)	48.9(5)
Pt(1)–B(2)–B(3)	65.1(5)	Pt(1)–B(2′)–B(3′)	63.1(5)
B(3)–B(2)–C(6)	51.5(7)	B(3′)–B(2′)–C(6′)	50.1(7)
C(6)–B(2)–B(7′)	56.3(8)	C(6′)–B(2′)–B(7)	$56.9_5(8)$
B(7′)–B(2)–B(3′)	59.8(8)	B(7)–B(2′)–B(3)	61.3(8)
B(3′)–B(2)–Pt(1)	66.4(6)	B(3)–B(2′)–Pt(1)	66.7(6)
Pt(1)–B(3)–B(2)	62.5(5)	Pt(1)–B(3′)–B(2′)	63.3(6)
B(2)–B(3)–C(6)	53.0(7)	B(2′)–B(3′)–C(6′)	52.6(8)
C(6)–B(3)–B(7)	57.5(8)	C(6′)–B(3′)–B(7′)	57.6(8)
B(7)–B(3)–B(2′)	58.8(8)	B(7′)–B(3′)–B(2)	59.6(8)
B(2′)–B(3)–Pt(1)	65.8(6)	B(2)–B(3′)–Pt(1)	64.7(6)
B(2)–C(6)–B(3)	75.5(8)	B(2′)–C(6′)–B(3′)	77.4(9)
B(3)–C(6)–B(7)	68.7(9)	B(3′)–C(6′)–B(7′)	68.3(8)
B(7)–C(6)–B(7′)	67.7(9)	B(7′)–C(6′)–B(7)	67.7(9)
B(7′)–C(6)–B(2)	67.9(8)	B(7)–C(6′)–B(2′)	66.0(9)
B(3)–B(7)–B(2′)	59.8(8)	B(3′)–B(7′)–B(2)	60.7(7)
B(2′)–B(7)–C(6′)	57.0(8)	B(2)–B(7′)–C(6)	55.8(7)
C(6′)–B(7)–B(7′)	56.5(8)	C(6)–B(7′)–B(7)	56.9(8)
B(7′)–B(7)–C(6)	55.4(8)	B(7)–B(7′)–C(6′)	55.9(8)
C(6)–B(7)–B(3)	53.8(8)	C(6′)–B(7′)–B(3′)	54.1(7)
(*b*) Exo-polyhedral atoms			
C(61)–C(6)–B(2)	127(1)	C(61′)–C(6′)–B(2′)	127(1)
C(61)–C(6)–B(3)	126(1)	C(61′)–C(6′)–B(3′)	126(1)
C(61)–C(6)–B(7)	125(1)	C(61′)–C(6′)–B(7′)	125(1)
C(61)–C(6)–B(7′)	125(1)	C(61′)–C(6′)–B(7)	126(1)
P(1)–Pt(1)–P(1′)	105.3(1)		
P(1)–Pt(1)[a]–B(2′)	95.0(4)	P(1′)–Pt(1)–B(2)	96.2(3)
P(1)–Pt(1)–B(3′)	102.8(4)	P(1′)–Pt(1)–B(3)	103.8(4)
Pt(1)–P(1)–C(11)	111.8(4)	Pt(1)–P(1′)–C(11′)	111.1(6)
Pt(1)–P(1)–C(12)	120.5(6)	Pt(1)–P(1′)–C(12′)	119.3(6)
Pt(1)–P(1)–C(13)	114.6(6)	Pt(1)–P(1′)–C(13′)	114.5(5)
C(11)–P(1)–C(12)	101.7(8)	C(11′)–P(1′)–C(12′)	105.3(8)
C(11)–P(1)–C(13)	104.7(9)	C(11′)–P(1′)–C(13′)	103.7(8)
C(12)–P(1)–C(13)	101.6(9)	C(12′)–P(1′)–C(13′)	101.3(9)

[a] Only *cis*-P-Pt-B angles are given.

Attempts to rationalise the formation and stereochemistry of the C_2B_6 carbaplatinaboranes are of value since little attention has yet been focused on the interaction of medium-order carbaboranes and metal nucleophiles.

Cumulative-charge M.O. studies [8] on $1,6-C_2B_6H_8$ and $1,6-Me_2-1,6-C_2B_6H_6$ have shown that the lowest-lying unfilled M.O. resides mainly on boron atom (5) [≡ (7), since the molecules possess C_2 symmetry]. Thus nucleophilic attack should occur at this centre, displacing the incumbent hydrogen, H(5). The most likely fate of this atom is one of association with an open polyhedral face on which the metal atom subsequently collapses, reclosing the (expanded) polyhedron and generating a metallacarbaborane. Concomitantly the face hydrogen returns to its original boron atom.

The exact factors determining which deltahedra combine to produce the intermediates' open face are far from clear. One influence may derive from the fact that collapse of the metal atom on the open face increases the connectivity numbers of all the atoms in it by one. Thus, in polyhedra containing only four and five connecting atoms, four- or five-membered faces (derived from two and three deltahedra respectively), comprising at least two previously four-connectivity atoms not involved in connectivity breaking and that originally attacked, might be favoured. An example is illustrated in Figure 3.

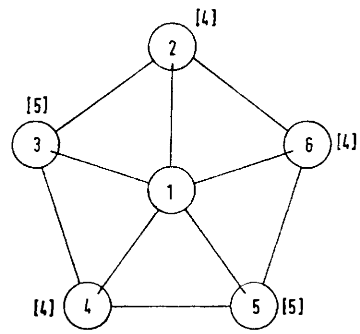
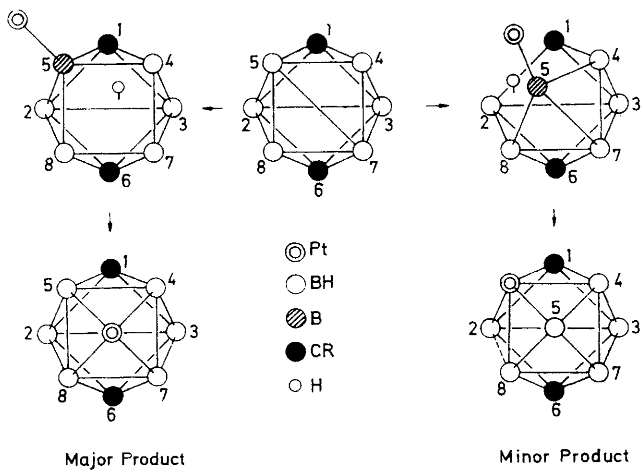


FIGURE 3 Five deltahedra about an atom (1), the point of nucleophilic metal attack on a carbaborane. Atomic connectivity numbers are shown in square brackets. Favoured reaction intermediates may include those with 1 654, 1 234, 1 2654, and 1 4326 open faces



SCHEME Possible mechanisms in the reaction between $1,6-R_2-1,6-C_2B_6H_6$ and zerovalent platinum(0) species

Applied to the reaction of the $1,6-C_2B_6H_6$ carbaboranes with the Pt^0 nucleophile, these principles suggest the possible formation of $1,6,8-PtC_2B_6$ (major reaction product, see Scheme), $1,2,8-PtC_2B_6$ * (unobserved), and $1,2,8-CPtCB_6$ (minor reaction product, see Scheme),

* These polyhedra may have relatively high potential energies since they possess a carbon atom in a high [20,25] connectivity site which cannot be relieved by polyhedral distortion of the type suggested [5] for the $2,3,10-CPtCB_7$ skeleton.

[24] M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 571.
[25] R. E. Williams, *Progr. Boron. Chem.*, 1970, **2**, 37.

and 1,7,9-$CPtCB_6$ (unobserved) skeletons (all numbered as *closo*-tricapped trigonal prisms). Further, when applied to 1,6-C_2B_7 they correctly preduct 2,3,10-$CPtCB_7$ [5,24] although also imply that 1,2,10-PtC_2B_7 * (unobserved) (both numbered as *closo*-bicapped square antiprisms) might form.

Finally, it might be possible to rationalise the apparent preference of the phosphorus atoms in compounds (I) and (II) to lie *trans* to the B(2)–B(3) [B(2')–B(3')] linkages † since, at least for 1,6-Me_2-1,6-$C_2B_6H_6$,[8] the B(4)–B(5) [B(7)–B(8)] bonds [at 1.806(7) Å] are more than 12σ longer than B(5)–B(8) [B(4)–B(7)] [1.696(9) Å]. The former would accordingly be more susceptible to attack by dsp^2-type platinum orbitals as the metal swings into position, leading to a complex in which the metal might be considered to exhibit essentially square-planar co-ordination.

(I)-β: *The Non-cage Atoms*.—Platinum–phosphorus bonds are identical to within 1σ, reflecting the symmetrical nature of the metal-to-cage bonding. The P–Pt–P angle (105.3°), the largest we have yet observed in bis(phosphine) d^8 metallacarbaboranes, may most accurately represent the preferred value, since the metal binds only a four-atom polyhedral face which is, further, free from accompanying methyl groups. P–C and C–C separations show good internal consistencies and require no special comment. Similarly the boron– (refined) hydrogen bond lengths are unexceptional, averaging *ca.* 0.1 Å less than the accepted internuclear distance, consistent with many other determinations *via* X-ray diffraction.[26]

(I)-β: *Molecular and Crystal Packing*.—In spite of not locating methyl hydrogen atoms, we have investigated the intra- and inter-molecular interligand packing by assuming a 2.0 Å van der Waals radius for methyl groups. Shorter-than-preferred contacts have been tabulated (Appendix H). The plane defined by the metal and phosphorus atoms lies perpendicular to the B(2,3,2',3') plane (Appendix G) but is twisted towards boron atoms 3 and 3' *ca.* 12.3° (= Δ) from a plane through Pt, C(6), and C(6'), whereas solution spectra imply at least time-averaged C_{2v} symmetry.[27] Although we have suggested [3] that a similar order of twist in 1,1-$(PhMe_2P)_2$-2,4-Me_2-1,2,4-$PtC_2B_9H_9$ might be due to efficient intramolecular packing, only one such contact [C(13') ··· H(13), 3.17(12) Å] is notionally ' short ' in the present compound. Further, since the Δ value (20.9°) for the less-crowded molecule (II) is greater, we conclude that intermolecular packing effects may be the more important for small- to medium-order metallacarbaboranes.

The crystal packing is represented by Figure 4, the ($h0l$) projection of the unit-cell contents. The shortest intermolecular contact is C(71) ··· C(11^{I}) (I at x, $1 + y$, z). An interesting feature of the crystal packing is that the semi-special position of the metal atom (*ca.* 0.25,0,0), the $a:c$ ratio, and the magnitude of β, combine to produce a near body-centred orthorhombic array of heavy atoms, with lattice parameters $a' \approx 0.5a$, $b' \approx b$, $c' \approx c\sin\beta$ and $U' \approx 0.5U$. The influence of this array on the Laue symmetry of the primitive cell is clearly visible from Weissenberg X-ray photographs.

Comparison of the Molecular Parameters of (I) *and* (II).—Although the comparative inaccuracy of the structural

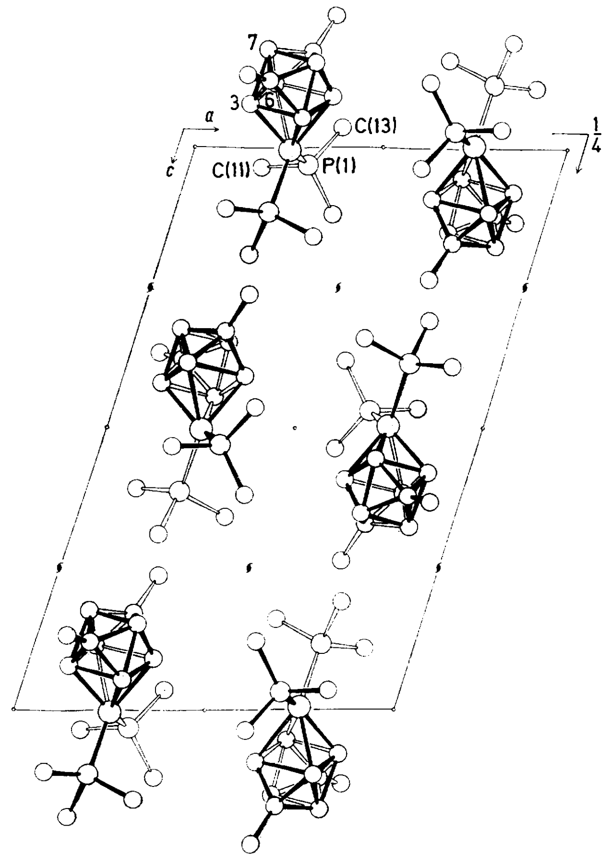


FIGURE 4 Compound (I)-β: unit cell contents seen in ($h0l$) projection

determination of (II) precludes a statistically meaningful comparison of corresponding bond lengths, we note somewhat shorter Pt–B (accompanied by longer Pt–P) distances for compound (II). This trend is readily understandable in terms of nucleophilic attack and a greater $B \overset{\rightarrow}{-} C$ inductive effect for the non-methylated cage.

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[5/1333 *Received, 7th July* 1975]

* Same footnote as on page 228.
† The stereochemistry is defined with respect to the cage carbon atoms.

[26] M. R. Churchill, *Inorg. Chem.*, 1973, **12**, 1213.
[27] J. L. Spencer, personal communication.