Metallaborane Chemistry. Part IV.[1] Molecular and Crystal Structures of a Ten-atom, Twentytwo-electron *nido*-Metallacarbaborane: 2,7-Dimethyl-9,9-bis(triethylphosphine)-2,7-dicarba-9-platina-*nido*-decaborane(7) †

By **Alan J. Welch,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The molecular structure of the title compound has been elucidated by single-crystal *X*-ray diffraction and refined to *R* 0.036 for 3 185 independent observed reflections. The compound crystallises in a monoclinic cell of dimensions a = 17.23(1), b = 18.86(1), c = 10.093(6) Å, and β = 126.96(4)°, space group $P2_1/a$. The polyhedral geometry approximates to that of a bicapped (B and C) square antiprism, with the metal atom in a CBBPt prism face, adjacent to the boron cap. The platinum–carbon distance [2.83(1_5) Å] is non-bonding and thus the molecule has a *nido*-structure with an open $\overline{\mathrm{BCBPt}}$ face. Distortions from the expected *closo*-structure are ascribed to the preferred planar co-ordination of $\mathrm{Pt^{II}}$ and low polyhedral connectivity of carbon.

THE direct addition of a nucleophilic $\mathrm{Ni^0}$, $\mathrm{Pd^0}$, or $\mathrm{Pt^0}$ species to *closo*-carbaboranes has recently led[1-5] to the isolation of a variety of novel d^8 metallacarbaboranes *via* relatively smooth polyhedral expansion reactions.

In a typical example of this technique $[\mathrm{Pt(PEt_3)_2}$-(*trans*-stilbene)] was treated with 1,6-$\mathrm{Me_2}$-1,6-$\mathrm{C_2B_7H_7}$ to produce a high yield of a complex $[\mathrm{Pt(Me_2C_2B_7H_7)(PEt_3)_2}]$ as the only isolable product. Since spectral data[4] did not unambiguously define its structure the reaction product has been subjected to a single-crystal *X*-ray study.[4]

EXPERIMENTAL

Crystals (m.p. *ca.* 153 °C, *in vacuo*) from methylene chloride–light petroleum were pale yellow transparent hexagonal prisms, elongated along [101]. Of several single crystals mounted on thin glass fibres with epoxy resin

---

† We have chosen to regard the polyhedron as a heteroborane, and since the preliminary communication[4] have slightly modified the numbering of atoms in the open face.

[1] Part III, W. E. Carroll, M. Green, F. G. A. Stone, and A. J. Welch, preceding paper.

[2] J. L. Spencer, M. Green, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1178.

[3] M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1975, 179.

[4] M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 571.

[5] M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 794.

adhesive, one of dimensions *ca.* $0.025 \times 0.011 \times 0.010$ cm was selected for analysis. Oscillation and equi-inclination Weissenberg *X*-ray photography showed the Laue symmetry to be $2/m$. The crystal was then transferred to a Syntex $P2_1$ four-circle diffractometer, and the precise unit-cell constants and asymmetric set of diffracted intensities were recorded as reported previously.[6] 15 reflections, $11° < 2\theta < 24°$, were taken from a 15 min rotation photograph recorded with generator settings of *ca.* 50 kV and 20 mA: these were centred and used to derive the unit-cell vectors, their associated standard deviations, and orientation matrix. Graphite-monochromated Mo-K_α radiation ($\lambda_{\alpha1} = 0.709\ 26$; $\lambda_{\alpha2} = 0.713\ 54$ Å) and a 96-step θ—2θ scan procedure were used to collect one asymmetric unit of intensity data in the range $2.9° \leqslant 2\theta \leqslant 50.0°$. Scan rates were determined from initial 2 s peak counts and varied from 0.0337 (for counts $\leqslant$150) to 0.4883° s^{-1} (for counts $\geqslant$1 500): regular remeasurement of the beams diffracted by the (612), (343), and (080) planes showed that no significant crystal decomposition or machine variance had occurred over the *ca.* 123 h exposure. All net intensities were scaled to a 1.0° min^{-1} basis. Analysis by a local program [7] showed that of 4 364 measured reflections, 3 185 had $I \geqslant 2.5\sigma(I)$ and were considered observed. The observed intensities were corrected for absorption by the Gaussian integration approximation.

Crystal Data.[*]—$C_{16}H_{43}B_7P_2Pt$, $M = 568.23$, Monoclinic, $a = 17.23(1)$, $b = 18.86(1)$, $c = 10.093(6)$ Å, $\beta = 126.96(4)°$, $U = 2\ 621(3)$ Å^3, $D_m = 1.42$ (by flotation), $Z = 4$, $D_c = 1.440$, $F(000) = 1\ 128$. μ(Mo-K_α) = 57.5 cm^{-1}. Space group $P2_1/a$.

Data were corrected for Lorentz and polarisation effects, and from a three-dimensional Patterson map co-ordinates of the platinum and phosphorus atoms were easily deduced. These were refined to *R ca.* 0.19 by three cycles of isotropic full-matrix least-squares. A difference electron-density synthesis, computed after the final cycle, revealed all the remaining non-hydrogen atom positions. The metal and phosphorus atoms were then assigned anisotropic thermal parameters and subsequent refinement converged *R* to *ca.* 0.062.

Although the seven cage hydrogen atoms were located from an accompanying difference Fourier, methylene protons were introduced in calculated positions with r(C–H) 1.10 Å, U_H 0.08 Å^2 and were not thereafter refined. With the Hughes-type [8] weighting scheme (F^* set at 105.0 on an absolute scale) introduced, all non-hydrogen atoms were then allowed anisotropic temperature factors. The variables were divided between two approximately equally dimensioned blocks and refined to final residuals of *R* 0.036, *R'* 0.043. The mean shift-to-error ratio was <0.001, and the most prominent feature on a final difference synthesis was a peak of *ca.* 0.7 eÅ^{-3} near the metal atom.

Scattering factors for neutral atoms were obtained from refs. 9 (platinum and boron), 10 (phosphorus and carbon), and 11 (hydrogen), those of platinum and phosphorus being corrected [12] for both parts of the anomalous dispersion. Programs used in the structure determination were as reported previously.[1] Tables 1—3 list the derived atomic parameters, and Figure 1 shows a view of the molecule.

TABLE 1

Final positional parameters (fractional co-ordinates) of the non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x	y	z
B(1)	0.4090(9)	0.0948(8)	0.913(2)
C(2)	0.3209(8)	$0.0454_5(6)$	0.882(2)
B(3)	0.338(1)	0.0362(8)	0.741(2)
B(4)	0.3779(9)	0.1174(8)	0.718(2)
B(5)	0.3616(7)	0.1809(7)	0.831(1)
B(6)	0.3131(8)	0.1270(7)	0.914(1)
C(7)	0.2605(8)	0.0895(6)	0.586(1)
B(8)	0.2768(9)	0.1738(8)	0.610(2)
Pt(9)	0.195 99(3)	0.189 21(2)	0.710 39(5)
B(10)	0.2244(9)	0.0699(6)	0.705(2)
C(21)	0.335(1)	−0.0158(7)	0.991(2)
C(71)	0.215(1)	0.0587(8)	0.414(2)
P(1)	0.0975	$0.1733_5(2)$	$0.7937_5(4)$
P(2)	0.1254(2)	0.2866(2)	0.5352(4)
C(110)	0.111(1)	0.2455(9)	0.935(2)
C(120)	0.1180(9)	0.0923(8)	0.904(2)
C(130)	−0.0343(8)	0.1705(9)	0.630(2)
C(111)	0.210(1)	0.259(1)	1.084(2)
C(121)	0.050(1)	0.071(1)	0.946(2)
C(131)	−0.068(1)	0.111(1)	0.505(2)
C(210)	0.218(1)	0.3549(7)	0.596(2)
C(220)	0.033(1)	0.3385(7)	0.526(2)
C(230)	0.067(1)	0.2681(8)	0.314(2)
C(211)	0.265(1)	0.3818(8)	0.770(2)
C(221)	−0.004(1)	0.4077(7)	0.428(2)
C(231)	−0.004(1)	0.2063(9)	0.245(2)

TABLE 2

Anisotropic thermal parameters [*] (Å^2, $\times 10^3$) of the non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
B(1)	44(7)	92(11)	76(9)	14(7)	29(7)	9(8)
C(2)	64(7)	58(7)	84(8)	19(6)	42(7)	5(6)
B(3)	69(9)	62(9)	90(11)	22(7)	38(8)	−8(8)
B(4)	57(8)	80(10)	70(9)	13(7)	39(7)	−2(7)
B(5)	36(6)	67(8)	61(7)	1(6)	29(5)	−16(6)
B(6)	39(6)	73(9)	50(7)	3(6)	24(5)	8(6)
C(7)	65(7)	59(7)	59(7)	8(5)	37(6)	−5(5)
B(8)	61(8)	86(11)	81(9)	11(7)	57(7)	15(8)
Pt(9)	40(1)	45(1)	52(1)	1.2(2)	31.1(7)	2.0(2)
B(10)	63(8)	33(6)	79(8)	−3(5)	41(7)	−6(6)
C(21)	111(11)	71(9)	105(11)	35(8)	65(9)	42(8)
C(71)	102(10)	112(12)	67(8)	19(9)	38(8)	−28(8)
P(1)	48(2)	73(2)	75(2)	−3(1)	45(2)	4(2)
P(2)	56(2)	66(2)	68(2)	10(1)	47(2)	12(1)
C(110)	113(12)	139(14)	134(14)	6(11)	108(12)	−14(11)
C(120)	74(9)	115(12)	118(11)	−0.08(8)	69(9)	35(9)
C(130)	45(7)	129(13)	134(13)	6(7)	57(8)	32(10)
C(111)	86(11)	196(19)	102(12)	−18(22)	60(10)	−53(12)
C(121)	97(11)	185(18)	119(13)	−19(12)	72(10)	52(12)
C(131)	83(11)	165(17)	91(11)	−56(11)	31(9)	−32(11)
C(210)	88(9)	66(9)	118(11)	9(7)	68(9)	33(8)
C(220)	100(10)	81(9)	120(12)	21(8)	79(10)	20(8)
C(230)	91(10)	113(12)	71(8)	36(9)	54(8)	32(8)
C(211)	105(11)	96(11)	75(9)	−25(9)	33(9)	−12(8)
C(221)	119(12)	70(9)	111(11)	42(8)	60(10)	30(8)
C(231)	111(12)	122(14)	70(9)	−22(10)	33(9)	−11(9)

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

---

[*] The previously reported unit-cell data (ref. 4) were calculated from 2θ values of only the six strongest reflections.

[6] A. G. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

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

[8] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[10] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[11] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[12] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21360 (15 pp., 1 microfiche).*

TABLE 3

Positional (fractional co-ordinates) and isotropic thermal * parameters (Å^2, × 10^2) of the hydrogen atoms, with estimated standard deviations in parentheses

Atom	x	y	z	U_j
H(1)	0.470(7)	0.083(5)	1.01(1)	8(3)
H(3)	0.341(6)	−0.016(5)	0.71(1)	6(3)
H(4)	0.434(8)	0.111(6)	0.70(1)	9(4)
H(5)	0.407(6)	0.236(5)	0.90(1)	6(3)
H(6)	0.323(5)	0.130(4)	1.026(9)	4(2)
H(8)	0.269(5)	0.209(4)	0.515(9)	4(2)
H(10)	0.162(6)	0.042(5)	0.65(1)	6(3)
H(111)	0.082	0.291	0.864	8
H(112)	0.067	0.233	0.967	8
H(121)	0.116	0.051	0.833	8
H(122)	0.187	0.093	1.010	8
H(131)	−0.068	0.167	0.684	8
H(132)	−0.055	0.219	0.569	8
H(211)	0.269	0.333	0.586	8
H(212)	0.186	0.395	0.512	8
H(221)	−0.026	0.306	0.481	8
H(222)	0.059	0.349	0.647	8
H(231)	0.033	0.313	0.247	8
H(232)	0.121	0.259	0.301	8

* Defined as $q_j = \exp\{-8\pi^2 U_j(\sin^2\theta)/\lambda^2\}$.

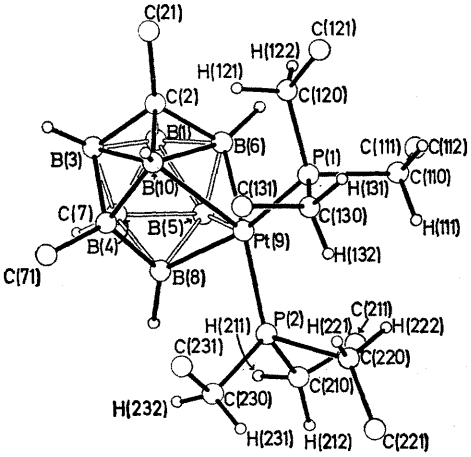

FIGURE 1 Perspective view of a single molecule. Hydrogen atoms H(1) and H(5) are obscured by C(2) and Pt(9) respectively

RESULTS AND DISCUSSION

The Metallacarbaborane Cage.—The polyhedron is best described in geometrical terms as a very distorted bicapped Archimedian square antiprism. Whilst the upper prism face, B(1)B(3)B(10)B(6), is capped approximately symmetrically by C(2), the lower face, defined by C(7)B(4)B(5), and Pt(9), and capped by B(8), deviates dramatically from ideal geometry. Although the other three tropical bond lengths are quite normal, the Pt(9) ··· C(7) distance 2.83(1_5) Å must be considered non-bonding. The open face, B(8)C(7)B(10)Pt(9) thus produced necessitates the classification of this molecule as a *nido*-species, and is unprecedented amongst structural studies of borane[13] and metallacarbaborane[14,15] ten-atom polyhedra.

The B(1)B(3)B(10)B(6) and C(7), B(4), B(5), Pt(9) units are planar to within 0.05 and 0.04 Å respectively and are nearly parallel (dihedral angle 5.2°).

Boron–carbon distances range from 1.59(2) to 1.69(3) Å and are typical of those measured, by *X*-ray,[4,14–22] electron diffraction,[23,24] and microwave studies,[25–27] in polyhedra containing carbon bound to four other cage atoms.

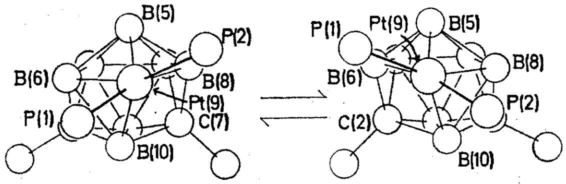

FIGURE 2 Suggested interconversion of geometrical isomers, viewed normal to the metalla-co-ordinated B_4 unit

The boron–boron lengths are also as expected, except for B(6)–B(10) which is unusually long [2.02(2) Å]. The implied weakness of this bond is consistent with our interpretation of the room-temperature n.m.r. data[4] which suggest molecular C_s symmetry. It is suggested that, in solution at normal temperatures, continuous interchange exists between one geometrical isomer and its mirror image (Figure 2) at a greater frequency than is resolvable on the spectrometer. The interchange essentially involves the simultaneous breaking of the B(6)–B(10) bond, formation of a B(8)–B(10) bond, and

---

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[13] R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **37**, 1779.

[14] D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 1972, **11**, 377.

[15] E. L. Hoel, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, 1974, **13**, 1388.

[16] T. F. Koetzle and W. N. Lipscomb, *Inorg. Chem.*, 1970, **9**, 2279.

[17] H. Hart and W. N. Lipscomb, *Inorg. Chem.*, 1968, **7**, 1070.

[18] T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *Inorg. Chem.*, 1968, **7**, 1076.

[19] J. C. Huffman and W. E. Streib, *J.C.S. Chem. Comm.*, 1972, 665.

[20] F. J. Hollander, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1973, **12**, 2262.

[21] G. Evrard, J. A. Ricci, jun., I. Bernal, W. J. Evans, D. F. Dustin, and M. F. Hawthorne, *J.C.S. Chem. Comm.*, 1974, 234.

[22] K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, 1974, **13**, 1393.

[23] V. S. Mastryukov, O. V. Dorofeeva, L. V. Vilkov, A. F. Zhigach, V. T. Laptev, and A. B. Petrunin, *J.C.S. Chem. Comm.*, 1973, 276.

[24] E. A. McNeill, K. L. Gallaher, F. R. Scholer, and S. H. Bauer, *Inorg. Chem.*, 1973, **12**, 2108.

[25] R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, 1965, **43**, 2166.

[26] R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, 1970, **53**, 1899.

[27] G. L. McKown and R. A. Beaudet, *Inorg. Chem.*, 1971, **10**, 1350.

rotation of the PEt_3 moieties *ca.* 70° about the bisector of the P–Pt–P angle.[28]

Co-ordination of the Metal Atom.—The platinum is co-ordinated to four (endopolyhedral) boron atoms, at 2.16(1)—2.34(1) Å, and two (exopolyhedral) phosphorus atoms [2.322(3) and 2.322(5) Å]. Although the four boron atoms are not required by the polyhedron to be coplanar (and, indeed, are not so), we have calculated the dihedral angle between the B_4 and PtP_2 units to be 81.3°. Figure 2, a view perpendicular to the best plane through the B_4 moiety, shows that P(1) and P(2) lie *trans* to points on the B(5)–B(8) and B(6)–B(10) bonds respectively. These points are displaced towards B(8) and B(6), the more so for the former. Thus, if the co-ordination geometry about the platinum atom is regarded as essentially square-planar, and assuming the metal–phosphorus bonds are of the same strength, we would expect the Pt–B lengths to vary in the sequence B(8) < B(6) ⩽ B(10) < B(5). The respective separations determined were 2.18(2), 2.16(1), 2.31(1), and 2.34(1) Å.

TABLE 4

Interatomic distances (Å), with estimated standard deviations in parentheses

(*a*) Within the polyhedron

B(1)–C(2)	$1.64_5(2)$	B(4)–C(7)	1.70(2)
B(1)–B(3)	1.78(2)	B(4)–B(8)	1.75(2)
B(1)–B(4)	$1.74_5(2_5)$	B(5)–B(6)	1.81(2)
B(1)–B(5)	1.78(2)	B(5)–B(8)	1.79(2)
B(1)–B(6)	1.77(2)	B(5)–Pt(9)	2.34(1)
C(2)–B(3)	1.62(3)	B(6)–Pt(9)	1.26(1)
C(2)–B(6)	1.59(2)	B(6)–B(10)	2.02(2)
C(2)–B(10)	1.61(1)	C(7)–B(8)	1.69(3)
B(3)–B(4)	1.75(2)	B(8)–Pt(9)	2.18(2)
B(3)–C(7)	1.65(2)	B(10)–C(7)	1.69(3)
B(3)–B(10)	$1.87(2_5)$	B(10)–Pt(9)	2.31(1)
B(4)–B(5)	1.79(2)		

(*b*) Other bonds

Pt(9)–P(1)	2.322(5)	C(220)–C(221)	1.53(2)
Pt(9)–P(2)	2.322(3)	C(230)–C(231)	1.52(2)
P(1)–C(110)	1.87(2)	B(1)–H(1)	0.93(8)
P(1)–C(120)	1.80(2)	B(3)–H(3)	1.0(1)
P(1)–C(130)	1.84(1)	B(4)–H(4)	1.1(2)
P(2)–C(210)	$1.84(1_5)$	B(5)–H(5)	1.23(8)
P(2)–C(220)	1.83(2)	B(6)–H(6)	1.0(1)
P(2)–C(230)	$1.85(1_5)$	B(8)–H(8)	$1.10(9_5)$
C(110)–C(111)	$1.46_5(2)$	B(10)–H(10)	1.02(9)
C(120)–C(121)	1.52(3)	C(2)–C(21)	1.51(2)
C(130)–C(131)	$1.52(2_5)$	C(7)–C(71)	$1.52_5(2)$
C(210)–C(211)	1.51(2)		

In recent structural studies [1,29] we have emphasised the square-planar description of the d^8 metal co-ordination and noted the increasing length of the metal-cage carbon bonds, doubtless aided by the carbon atoms' preference for only four cage connectivities.[30,31] Metal–carbon lengths of 2.422(7) and 2.452(8) Å (Pt–carbaborane) and 2.600(6) Å (Pd–carbaborane) have been recorded. For the present compound the equivalent interaction, Pt(9) to C(7), is non-bonding at $2.83(1_5)$ Å. We thus conclude that the decrease in molecular potential-energy due to the acquisition of the approximately square-planar d^8 metal co-ordination, and to the relatively low cage connectivity of C(7), is sufficient to warrant the breaking of the Pt(9)–C(7) bond in the otherwise *closo*-polyhedron.

The exo-Polyhedral Atoms.—Tables 4(*b*) and 5(*b*) demonstrate no unusual molecular parameters involving the *exo*-polyhedral atoms save those of C(110). P(1)–C(110) is long [1.87(2) Å], and C(110)–C(111) short

TABLE 5

Inter-bond angles

(*a*) Within the polyhedron

C(2)–B(1)–B(3)	56(1)	B(1)–B(6)–C(2)	$58.3_5(9)$
B(3)–B(1)–B(4)	59.6(9)	C(2)–B(6)–B(10)	51.5(6)
B(4)–B(1)–B(5)	$60.8_5(9)$	B(10)–B(6)–Pt(9)	67.1(4)
B(5)–B(1)–B(6)	61.2(9)	Pt(9)–B(6)–B(5)	$71.6(5_5)$
B(6)–B(1)–C(2)	55.5(9)	B(5)–B(6)–B(1)	59.8(9)
B(1)–C(2)–B(3)	66(1)	B(3)–C(7)–B(4)	69.9(8)
B(3)–C(2)–B(10)	71(1)	B(4)–C(7)–B(8)	$63.9(7_5)$
B(10)–C(2)–B(6)	78(7)	B(8)–C(7)–B(10)	102(1)
B(6)–C(2)–B(1)	66.1(9)	B(10)–C(7)–B(3)	68(1)
B(1)–B(3)–C(2)	58(1)	B(4)–B(8)–B(5)	60.5(8)
C(2)–B(3)–B(10)	54.5(9)	B(5)–B(8)–Pt(9)	$71.4(8_5)$
B(10)–B(3)–C(7)	57.0(9)	Pt(9)–B(8)–C(7)	96(1)
C(7)–B(3)–B(4)	$59.9(7_5)$	C(7)–B(8)–B(4)	$60.7_5(8)$
B(4)–B(3)–B(1)	59.2(9)		
B(1)–B(4)–B(3)	61.2(9)	B(5)–Pt(9)–B(6)	47.1(6)
B(3)–B(4)–C(7)	57.2(7)	B(6)–Pt(9)–B(10)	53.5(4)
C(7)–B(4)–B(8)	55.4(7)	B(10)–Pt(9)–B(8)	69.8(6)
B(8)–B(4)–B(5)	60.9(8)	B(8)–Pt(9)–B(5)	46.6(5)
B(5)–B(4)–B(1)	60.6(9)		
B(1)–B(5)–B(4)	58.6(9)	C(2)–B(10)–B(3)	55.0(9)
B(4)–B(5)–B(8)	$58.6_5(8)$	B(3)–B(10)–C(7)	55.1(9)
B(8)–B(5)–Pt(9)	62.0(7)	C(7)–B(10)–Pt(9)	$88.7_5(6_5)$
Pt(9)–B(5)–B(6)	61.3(5)	Pt(9)–B(10)–B(6)	59.5(5)
B(6)–B(5)–B(1)	59.0(9)	B(6)–B(10)–C(2)	50.6(6)

(*b*) Other angles

C(21)–C(2)–B(1)	$124.9(9_5)$	Pt(9)–P(1)–C(110)	113.6(7)
C(21)–C(2)–B(3)	122(1)	Pt(9)–P(1)–C(120)	114.8(7)
C(21)–C(2)–B(10)	129(1)	Pt(9)–P(1)–C(130)	116.9(7)
C(21)–C(2)–B(6)	126(1)	Pt(9)–P(2)–C(210)	110.3(4)
		Pt(9)–P(2)–C(220)	$120.2_5(6)$
C(71)–C(7)–B(3)	115(1)	Pt(9)–P(2)–C(230)	115.2(5)
C(71)–C(7)–B(4)	125(1)		
C(71)–C(7)–C(8)	118(1)	C(110)–P(1)–C(120)	$104{\cdot}4_5(9)$
C(71)–C(7)–B(10)	124(1)	C(110)–P(1)–C(130)	103.3(8)
		C(120)–P(1)–C(130)	102.1(7)
P(1)–Pt(9)–B(5)	137.0(4)	C(210)–P(2)–C(220)	101.2(7)
P(1)–Pt(9)–B(6)	$93.1_5(5)$	C(210)–P(2)–C(230)	105.6(8)
P(1)–Pt(9)–B(10)	95.5(5)	C(220)–P(2)–C(230)	102.6(7)
P(1)–Pt(9)–B(8)	164.1(4)	P(1)–C(110)–C(111)	117(2)
P(2)–Pt(9)–B(5)	$111.4(3_5)$	P(1)–C(120)–C(121)	107(1)
P(2)–Pt(9)–B(6)	156.0(4)	P(1)–C(130)–C(131)	114(1)
P(2)–Pt(9)–B(10)	140.6(4)	P(2)–C(210)–C(211)	112(1)
P(2)–Pt(9)–B(8)	86.5(4)	P(2)–C(220)–C(221)	120(2)
P(1)–Pt(9)–P(2)	102.5(1)	P(2)–C(230)–C(231)	113(1)

(*c*) Summary of angles (°) involving cage H atoms

	No., *N*	Range	Mean *
H–B–Pt	4	110(5)—123(5)	116(5)
H–B–B	22	112(6)—138(4)	125(7)
H–B–C	8	107(4)—125(5)	117(6)

* Estimated standard deviation of the mean from the expression $\sigma^2 = \{\sum_{i=1}^{N}(\chi_i - \bar{\chi})^2\}/(N - 1)$, where χ_i is the i^{th} and $\bar{\chi}$ the mean of N similar types.

---

[28] J. L. Spencer, personal communication.

[29] A. J. Welch, *J.C.S. Dalton*, 1975, 1473.

[30] R. E. Williams, *Progr. Boron Chem.*, 1970, **2**, 37.

[31] W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1973, **95**, 4565.

[1.46$_5$(2) Å]; an indication of the inability of our model to describe this atom satisfactorily may lie in the fact that it has the largest mean U_{ii} of all the methylene carbon atoms.

The B–H bonds are, as expected,[32] generally *ca.* 0.1 Å shorter than the predicted [33] internuclear separation.

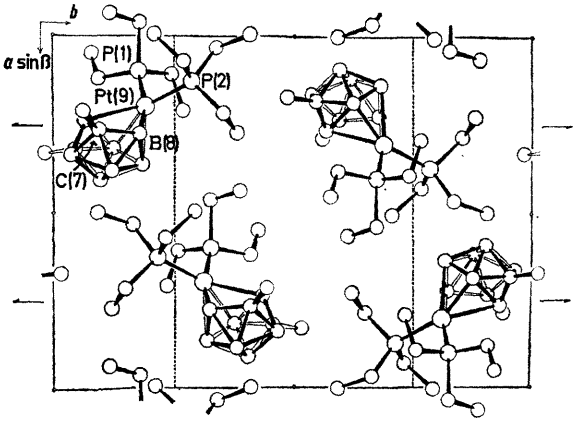

FIGURE 3 Packing diagram, as seen along the *c* axis, looking towards the origin. Hydrogen atoms are omitted for clarity

Figure 3 is a view of the contents of one unit cell, looking along the *c* axis, towards the origin, and Table 6 lists the unique non-bonded interligand contacts shorter than the appropriate van der Waals sum [33] (the contact radius for methyl groups has been estimated at 2.0 Å). The absence of unusually short contacts implies that packing forces play only a minimal rôle in determining the stereochemistry adopted.

TABLE 6

Non-bonded contacts (Å)

(*a*) Intramolecular		
H(6) · · · H(122)	x, y, z	2.4
H(9) · · · H(232)	x, y, z	2.3
H(10) · · · H(121)	x, y, z	2.4
H(111) · · · H(222)	x, y, z	2.3
H(132) · · · H(221)	x, y, z	2.1
(*b*) Intermolecular		
H(131) · · · H(211$^{\mathrm{I}}$)		2.3
C(121) · · · C(71$^{\mathrm{II}}$)		2.78(2)
C(221) · · · C(221$^{\mathrm{III}}$)		3.68(3)
H(5) · · · C(231$^{\mathrm{IV}}$)		3.0(1)

Roman numeral superscripts define the following equivalent positions relative to the reference molecule at x, y, z:

I $x - \frac{1}{2}, \frac{1}{2} - y, z$
II $x, y, 1 + z$
III $-x, 1 - y, 1 - z$
IV $\frac{1}{2} + x, \frac{1}{2} - y, 1 + z$

I thank Dr. J. L. Spencer for supplying the crystalline sample, and Professor F. G. A. Stone and Dr. P. Woodward for helpful discussions.

[4/2677 *Received, 23rd December,* 1974]

---

[32] M. R. Churchill, *Inorg. Chem.*, 1973, **12**, 1213.

[33] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.