Metallaborane Chemistry. Part II.[1] Molecular and Crystal Structure of 1,1-Bis(dimethylphenylphosphine)-2,4-dimethyl-2,4-dicarba-1-platina-*closo*-dodecaborane

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

The structure of the title compound has been determined by single-crystal *X*-ray diffraction methods and refined to *R* 0.033 for 4073 independent observed reflections collected on a diffractometer. Crystals are triclinic, space group $P\bar{1}$, with $a = 9.324(3)$, $b = 10.285(4)$, and $c = 14.208(8)$ Å, $\alpha = 100.40(4)$, $\beta = 94.32(4)$, and $\gamma = 98.95(3)$°. The carbaborane fragment has a distorted icosahedral geometry with the carbon atoms at positions 2 and 4 (relative to the metal at 1). The platinum atom is *ca.* 1.81 Å above a (non-planar) C_2B_3 face which in turn is nearly perpendicular to the PtP_2 plane. Pt–P Distances are 2.249(2) and 2.303(2) Å. All the hydrogen atoms in the molecule have been located and positionally refined.

HEREIN is reported a full structural analysis of $[Pt(Me_2C_2B_9H_9)(PMe_2Ph)_2]$, one of several compounds prepared[1-5] by the direct reaction of a heteroborane cage with a nucleophilic Ni^0, Pd^0, or Pt^0 species. Preliminary crystallographic details have appeared elsewhere.[1,4]

EXPERIMENTAL

A sample of the compound was recrystallised from methylene chloride–methanol to constant m.p. (*ca.* 187 °C *in vacuo*). Individual crystals grow as pale yellow, transparent, irregular blocks which may be freed from cohesive

---

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

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

[3] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1974, 153.

[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.

crystallites by rolling gently between the fingers. That chosen for analysis was multifaceted and very nearly spherical (' diameter ' *ca.* 0.02 cm). It was mounted on a glass fibre with an epoxy resin glue, set on a Syntex $P2_1$ four-circle diffractometer, and the unit-cell constants, their standard deviations, and one asymmetric set of diffracted intensities recorded *via* a procedure already described.[6]

Details pertinent to the present experiment were as follows: 15 reflections ($14.5 < 2\theta < 24.5$) were chosen from a 10 min rotation photograph, and an accurately defined cell was obtained from these alone; graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) and a 96-step θ—2θ scan procedure were used; the scan rate was determined from a preliminary 2 s peak-count and varied from 0.0337 (for counts $\leqslant 1\,500$) to 0.9765 ° s^{-1} (for counts $\geqslant 5\,000$); the 2θ range for data collection was $2.9 < 2\theta < 50.0°$; 3 check reflections monitored periodically showed no significant crystal decomposition or machine variance during data collection; preliminary data treatment was carried out by use of local programs.[7] Of 4 269 intensities recorded, 4 073 having $I \geqslant 2.5\sigma(I)$ were used to solve and refine the structure, 188 having $I < 2.5\sigma(I)$ being discarded. For 8, having measured counts in excess of 50 000 s^{-1} at the peak maximum, the linear correction for counter coincidence effects (applied to all intensity steps with counts $> 5\,000$ s^{-1}) is considered invalid, and the offending data were automatically deleted from the observed set. Unfortunately, these were not re-recorded at reduced voltage and remain absent; no absorption correction was considered necessary since the maximum difference in absorption factors was calculated to be $< 2\%$.

Crystal Data.—$C_{20}H_{37}B_9P_2Pt$, $M = 631.844$, Triclinic, $a = 9.324(3)$, $b = 10.285(4)$, $c = 14.208(8)$ Å, $\alpha = 100.40(4)$, $\beta = 94.32(4)$, $\gamma = 98.95(3)°$, $U = 1\,316(1)$ Å^3, $D_m = 1.58$ (by flotation), $Z = 2$, $D_c = 1.593$, $F(000) = 620$. Mo-K_α radiation, $\lambda = 0.71069$ Å; $\mu(\text{Mo-}K_\alpha) = 57.3$ cm^{-1}.

The 4 073 observed data were corrected for Lorentz and polarisation effects and a three-dimensional Patterson map computed. Examination revealed one maximum distinctly larger than all others: this was taken as the Pt · · · Pt vector. Consideration of peaks within 5 Å of the origin revealed only one set of two that might be Pt · · · P vectors, implying the centric space group.

Since inspection failed to locate a P · · · P (intramolecular) vector and a P–Pt–P angle near 90° was expected, there existed four reasonable possibilities for the orientation of the PtP_2 moiety, and thus the location of the metal atom alone was used to calculate the first set of phases. Full-matrix least-squares refinement (2 cycles) with an arbitrary isotropic variable of 0.04 Å^2 gave a first *R* of *ca.* 0.23. A difference electron-density synthesis, computed after the second cycle, revealed all the non-hydrogen atoms. Inclusion of these atoms and the assignment of anisotropic temperature factors to Pt and P converged *R* to 0.044 after four cycles. Examination of the variation of Δ^2F over ranges of $|F_o|$ and sin θ suggested a Hughes-type [8] weighting scheme of the form $w^{\frac{1}{2}} = 1$ for $F_o \leqslant F^*$ and $w^{\frac{1}{2}} = F^*/F_o$ for $F_o > F^*$, with F^* set at 190.0 (absolute scale).

In allowing all the (non-hydrogen) atoms to refine anisotropically the variable parameters were divided into four similarly dimensioned blocks. Three cycles converged to *R* 0.036, and from an accompanying difference synthesis all hydrogen atoms were located. For subsequent F_c calculations these were assigned an isotropic temperature factor set at 110% that of the attached ' heavy ' atom at its isotropic convergence, but the hydrogen thermal parameters were not subsequently refined.

TABLE 1

Final atomic positions (fractional co-ordinate $\times 10^4$; for Pt $\times 10^5$) of the non-hydrogen atoms, with estimated standard deviations in parentheses

	x	*y*	*z*
Pt(1)	19 946(3)	46 199(3)	2 4057(2)
P(1)	1 543(2)	6 682(2)	2 315(1)
P(2)	4 503(2)	5 166(2)	2 649(2)
C(2)	796(9)	3 155(7)	3 403(6)
B(3)	1 852(9)	2 486(9)	2 652(7)
C(4)	1 238(8)	2 365(8)	1 436(6)
B(5)	16(10)	3 394(9)	1 453(7)
B(6)	−281(9)	3 927(9)	2 761(7)
B(7)	437(11)	1 483(10)	3 119(9)
B(8)	751(11)	1 012(10)	1 885(9)
B(9)	−517(11)	1 611(10)	1 178(8)
B(10)	−1 495(10)	2 597(10)	1 948(8)
B(11)	−993(10)	2 404(10)	3 142(8)
B(12)	−1 053(11)	1 038(10)	2 186(9)
C(21)	1 324(10)	3 741(10)	4 462(7)
C(41)	2 274(11)	2 204(10)	642(7)
C(110)	1 177(10)	7 631(8)	3 465(7)
C(120)	−100(9)	6 718(9)	1 545(7)
C(130)	2 908(8)	7 772(7)	1 856(6)
C(131)	3 780(9)	8 914(8)	2 439(7)
C(132)	4 835(10)	9 690(9)	2 049(7)
C(133)	5 081(10)	9 358(10)	1 103(8)
C(134)	4 200(11)	8 252(10)	518(7)
C(135)	3 131(10)	7 471(9)	895(7)
C(210)	5 379(10)	5 199(10)	1 555(7)
C(220)	5 453(9)	4 037(9)	3 207(8)
C(230)	5 305(8)	6 743(8)	3 462(6)
C(231)	6 524(9)	7 571(9)	3 275(7)
C(232)	7 137(11)	8 715(10)	3 969(9)
C(233)	6 530(12)	8 998(10)	4 807(8)
C(234)	5 351(12)	8 184(10)	5 005(7)
C(235)	4 700(10)	7 044(9)	4 321(6)

Incorporating the hydrogen-atom positions into a fifth block, mixed isotropic–anisotropic refinement of the whole molecule * converged at *R* 0.033 and *R′* 0.040 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. In the final cycle the mean shift-to-error of refined parameters was 0.003 and in a final difference synthesis the largest peak was *ca.* 0.45 e Å^{-3}.

Atomic scattering factors for neutral atoms were taken from ref. 9 for platinum and boron, ref. 10 for phosphorus and carbon, and ref. 11 for hydrogen. Those of platinum and phosphorus were corrected for both components of anomalous dispersion.[12] Tables 1—3 list the final atomic parameters. Details of molecular planes, parameters involving hydrogen atoms, and observed and calculated

---

* Whilst the hydrogens attached to boron atoms seem reasonably well defined, some rather unexpected molecular parameters are calculated from the positions of those bound to C(21), C(41), C(135), and C(232). Since the offending hydrogens are not involved in close interligand packing (see later, Table 7) they were removed from F_c calculations at one stage in the refinement, only to reappear on a difference synthesis in the same positions. Partly for this reason and also because neither the C–H, H–C–H, nor H–C–C parameters of any one carbon atom do not differ significantly from the expected value, it is felt the ' suspect ' hydrogens should be included in the final model.

[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.

structure factor amplitudes are listed in Supplementary Publication No. SUP 21267 (24 pp., 1 microfiche).*

All calculations were performed on the University of London CDC 7600 computer with the '*X*-Ray '72' crystallographic computing system,[13] except where otherwise stated.

TABLE 2

Final anisotropic thermal parameters * (Å^2 × 10^3; Pt and P, × 10^4) of the non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	208(1)	192(1)	293(1)	35(1)	32(1)	−1(1)
P(1)	268(10)	228(10)	325(11)	50(7)	37(8)	37(8)
P(2)	212(9)	261(10)	405(12)	40(7)	43(8)	19(8)
C(2)	41(5)	22(4)	39(5)	4(3)	−4(3)	1(3)
B(3)	22(4)	30(5)	43(5)	−1(3)	−5(4)	9(4)
C(4)	22(4)	26(4)	47(5)	3(3)	−3(3)	−12(3)
B(5)	29(5)	30(5)	37(5)	5(4)	0(4)	−7(4)
B(6)	27(5)	28(5)	39(5)	3(3)	5(4)	4(4)
B(7)	42(6)	26(5)	70(7)	3(4)	5(5)	15(5)
B(8)	32(5)	29(5)	72(7)	3(4)	2(5)	−3(5)
B(9)	32(5)	32(5)	63(7)	1(4)	−3(5)	−7(4)
B(10)	26(5)	35(5)	58(6)	4(4)	−3(4)	2(4)
B(11)	30(5)	39(6)	61(7)	−1(4)	10(4)	15(5)
B(12)	32(5)	34(6)	86(9)	−2(4)	0(5)	9(5)
C(21)	47(5)	59(6)	38(5)	10(4)	3(4)	13(4)
C(41)	60(6)	50(6)	47(6)	10(5)	15(5)	−26(4)
C(110)	50(5)	26(4)	51(5)	13(4)	19(4)	−2(4)
C(120)	31(5)	42(5)	62(6)	11(4)	−1(4)	16(4)
C(130)	23(4)	29(4)	39(4)	9(3)	4(3)	8(3)
C(131)	38(5)	30(4)	48(5)	2(3)	1(4)	3(4)
C(132)	45(5)	35(5)	67(7)	−4(4)	1(5)	13(4)
C(133)	42(5)	53(6)	68(7)	−1(4)	6(5)	32(5)
C(134)	58(6)	63(7)	48(6)	−1(5)	14(5)	19(5)
C(135)	40(5)	44(5)	45(5)	−2(4)	3(4)	4(4)
C(210)	37(5)	63(6)	53(6)	3(4)	15(5)	−6(5)
C(220)	26(5)	36(5)	96(8)	11(4)	−1(5)	15(5)
C(230)	30(4)	26(4)	42(5)	4(3)	−7(3)	4(3)
C(231)	30(5)	41(5)	66(6)	−2(4)	1(4)	3(4)
C(232)	43(6)	40(6)	96(9)	−8(4)	−12(5)	6(5)
C(233)	68(7)	41(6)	64(7)	6(5)	−22(5)	−9(5)
C(234)	77(7)	45(6)	47(6)	16(5)	−7(5)	−6(4)
C(235)	46(5)	38(5)	40(5)	9(4)	−2(4)	5(4)

* The anisotropic thermal parameter is defined as $\exp\{-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)\}$.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The compound exists in the solid state as discrete, neutral, monomer molecules with no crystallographically imposed symmetry. Interatomic distances (not corrected for thermal motion) and interbond angles appear in Tables 4—6 with, in each case, the estimated standard deviation in parentheses. Figure 1 is a perspective ORTEP [14] plot of a single molecule showing the atomic numbering scheme adopted [hydrogen atoms not shown take the same number as the atom (C or B) to which they are bound].

The Platinacarbaborane Fragment.—The analysis confirms that the metal atom co-ordinates three boron and two carbon atoms to complete a 2,4-dicarba-1-platina-*closo*-icosahedron.

Least-squares planes data show that the platinum

TABLE 3

Final positional (fractional co-ordinates, × 10^3) and thermal * parameters (Å^2 × 10^3) of the hydrogen atoms

Hydrogen	x	y	z	U_j
H(3)	300(8)	229(8)	285(6)	35
H(5)	−15(8)	391(8)	86(6)	37
H(6)	−75(8)	489(8)	300(5)	34
H(7)	70(9)	85(9)	368(6)	51
H(8)	116(9)	16(8)	161(6)	48
H(9)	−80(9)	108(9)	38(6)	49
H(10)	−267(9)	277(8)	177(6)	45
H(11)	−176(9)	242(8)	366(6)	46
H(12)	−185(10)	20(9)	212(6)	54
H(21)	66(10)	314(9)	491(7)	56
H(22)	218(10)	377(9)	456(7)	56
H(23)	107(10)	488(9)	455(6)	56
H(41)	266(10)	305(10)	27(7)	59
H(42)	187(10)	172(10)	10(7)	59
H(43)	337(10)	207(9)	95(7)	59
H(111)	37(9)	709(9)	373(6)	47
H(112)	81(9)	843(9)	336(6)	47
H(113)	243(9)	787(8)	395(6)	47
H(121)	−9(9)	635(9)	82(6)	50
H(122)	−93(9)	620(9)	188(6)	50
H(123)	−29(9)	757(9)	155(6)	50
H(131)	367(9)	912(8)	311(6)	46
H(132)	545(10)	1 039(9)	248(7)	57
H(133)	590(10)	997(7)	79(7)	62
H(134)	407(10)	804(10)	−26(7)	64
H(135)	274(9)	686(9)	72(6)	51
H(211)	533(10)	589(10)	140(7)	58
H(212)	642(10)	523(9)	174(7)	58
H(213)	495(10)	454(10)	116(7)	58
H(221)	648(10)	436(9)	328(7)	58
H(222)	530(10)	322(9)	283(7)	58
H(223)	492(10)	390(9)	383(7)	58
H(231)	687(10)	751(9)	272(6)	53
H(232)	782(11)	918(10)	372(7)	70
H(233)	697(11)	971(10)	532(7)	69
H(234)	497(10)	833(10)	562(7)	65
H(235)	329(9)	653(9)	452(6)	48

* Isotropic thermal parameters, given by the expression $\exp\{-8\pi^2U_j(\sin^2\theta)/\lambda^2\}$, were estimated at 110% of the converged isotropic parameter of the atom bound to the hydrogen atom, and were thereafter held invariant in the final refinement (see text).

TABLE 4

Bond lengths (Å)

(*a*) Within the polyhedron

Pt(1)–C(2)	2.452(8)	B(5)–B(6)	1.89(1)
Pt(1)–B(3)	2.270(9)	B(5)–B(9)	1.79(1)
Pt(1)–C(4)	2.442(7)	B(5)–B(10)	1.77(1)
Pt(1)–B(5)	2.261(8)	B(6)–B(10)	1.80(1)
Pt(1)–B(6)	2.255(9)	B(6)–B(11)	1.79(1)
C(2)–B(3)	1.64(1)	B(7)–B(8)	1.80(2)
C(2)–B(6)	1.69(1)	B(7)–B(11)	1.75(2)
C(2)–B(7)	1.67(1)	B(7)–B(12)	1.79(2)
C(2)–B(11)	1.71(1)	B(8)–B(9)	1.75(2)
B(3)–C(4)	1.76(1)	B(8)–B(12)	1.77(2)
B(3)–B(7)	1.79(1)	B(9)–B(10)	1.76(2)
B(3)–B(8)	1.81(1)	B(9)–B(12)	1.72(2)
C(4)–B(5)	1.67(1)	B(10)–B(11)	1.78(2)
C(4)–B(8)	1.65(1)	B(10)–B(12)	1.80(2)
C(4)–B(9)	1.68(1)	B(11)–B(12)	1.76(2)

(*b*) Exo-polyhedral bonds

Pt(1)–P(1)	2.249(2)	C(130)–C(131)	1.40(1)
Pt(1)–P(2)	2.303(2)	C(131)–C(132)	1.38(1)
C(2)–C(21)	1.53(1)	C(132)–C(133)	1.37(2)
C(4)–C(41)	1.54(1)	C(133)–C(134)	1.38(1)
P(1)–C(110)	1.829(9)	C(134)–C(135)	1.38(1)
P(1)–C(120)	1.820(9)	C(135)–C(130)	1.38(1)
P(1)–C(130)	1.802(8)	C(230)–C(231)	1.38(1)
P(2)–C(210)	1.809(10)	C(231)–C(232)	1.40(1)
P(2)–C(220)	1.816(11)	C(232)–C(233)	1.36(2)
P(2)–C(230)	1.828(7)	C(233)–C(234)	1.35(2)
		C(234)–C(235)	1.40(1)
		C(235)–C(230)	1.39(1)

---

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

[13] Technical Report TR 192 of the Computer Science Centre, University of Maryland, June 1972.

[14] C. K. Johnson, ORTEP, Report ORNL 3794, Oak Ridge National Laboratory, 1965.

atom is 1.814 Å above the C_2B_3 face (which is non-planar, with the carbon atoms bent back into the cage and away from the metal). Although individual members of the Pt–B and Pt–C bond types do not mutually differ significantly, the geometry of the C_2B_3 face is not regular with the B(3)–C distances differing by *ca.* 9σ. The point of projection of the metal atom onto the C_2B_3 face is 0.134 Å from its centre. This may

TABLE 5

Inter-bond angles (°)

(*a*) Within the polyhedron			
C(2)–Pt(1)–B(3)	40.4(3)	C(2)–B(7)–B(3)	56.5(5)
B(3)–Pt(1)–C(4)	43.6(3)	B(3)–B(7)–B(8)	60.9(6)
C(4)–Pt(1)–B(5)	41.3(3)	B(8)–B(7)–B(12)	59.2(6)
B(5)–Pt(1)–B(6)	49.6(3)	B(12)–B(7)–B(11)	59.6(6)
B(6)–Pt(1)–C(2)	41.7(3)	B(11)–B(7)–C(2)	60.0(5)
Pt(1)–C(2)–B(3)	63.8(4)	B(3)–B(8)–C(4)	60.8(5)
B(3)–C(2)–B(7)	65.5(6)	C(4)–B(8)–B(9)	59.3(5)
B(7)–C(2)–B(11)	62.4(6)	B(9)–B(8)–B(12)	58.7(7)
B(11)–C(2)–B(6)	63.8(6)	B(12)–B(8)–B(7)	60.4(6)
B(6)–C(2)–Pt(1)	62.9(4)	B(7)–B(8)–B(3)	59.5(5)
Pt(1)–B(3)–C(2)	75.8(5)	C(4)–B(9)–B(5)	57.5(5)
C(2)–B(3)–B(7)	58.0(5)	B(5)–B(9)–B(10)	60.1(5)
B(7)–B(3)–B(8)	59.6(6)	B(10)–B(9)–B(12)	62.2(7)
B(8)–B(3)–C(4)	55.0(5)	B(12)–B(9)–B(8)	61.2(7)
C(4)–B(3)–Pt(1)	73.4(4)	B(8)–B(9)–C(4)	57.4(5)
Pt(1)–C(4)–B(3)	63.0(4)	B(5)–B(10)–B(6)	64.0(5)
B(3)–C(4)–B(8)	64.2(6)	B(6)–B(10)–B(11)	60.2(5)
B(8)–C(4)–B(9)	63.3(6)	B(11)–B(10)–B(12)	59.0(6)
B(9)–C(4)–B(5)	64.4(5)	B(12)–B(10)–B(9)	57.9(6)
B(5)–C(4)–Pt(1)	63.5(4)	B(9)–B(10)–B(5)	60.7(6)
Pt(1)–B(5)–C(4)	75.1(4)	C(2)–B(11)–B(6)	57.5(5)
C(4)–B(5)–B(9)	58.2(5)	B(6)–B(11)–B(10)	60.6(6)
B(9)–B(5)–B(10)	59.2(6)	B(10)–B(11)–B(12)	61.1(6)
B(10)–B(5)–B(6)	58.7(5)	B(12)–B(11)–B(7)	61.3(6)
B(6)–B(5)–Pt(1)	65.0(3)	B(7)–B(11)–C(2)	57.6(5)
Pt(1)–B(6)–C(2)	75.4(4)	B(7)–B(12)–B(8)	60.5(6)
C(2)–B(6)–B(11)	58.7(5)	B(8)–B(12)–B(9)	60.1(7)
B(11)–B(6)–B(10)	59.3(6)	B(9)–B(12)–B(10)	59.9(6)
B(10)–B(6)–B(5)	57.3(5)	B(10)–B(12)–B(11)	60.0(6)
B(5)–B(6)–Pt(1)	65.4(4)	B(11)–B(12)–B(7)	59.1(6)
(*b*) Other angles			
P(1)–Pt(1)–P(2)	97.30(7)	C(110)–P(1)–C(130)	106.3(4)
P(1)–Pt(1)–C(2)	125.2(2)	C(120)–P(1)–C(130)	102.0(4)
P(1)–Pt(1)–B(3)	164.5(3)		
P(1)–Pt(1)–C(4)	135.8(2)	C(210)–P(2)–Pt(1)	114.4(3)
P(1)–Pt(1)–B(5)	98.7(3)	C(220)–P(2)–Pt(1)	116.5(3)
P(1)–Pt(1)–B(6)	92.8(2)	C(230)–P(2)–Pt(1)	117.8(3)
P(2)–Pt(1)–C(2)	117.4(2)	C(210)–P(2)–C(220)	101.8(5)
P(2)–Pt(1)–B(3)	96.3(2)	C(210)–P(2)–C(230)	105.3(4)
P(2)–Pt(1)–C(4)	110.6(2)	C(220)–P(2)–C(230)	98.7(4)
P(2)–Pt(1)–B(5)	147.0(3)		
P(2)–Pt(1)–C(6)	157.1(3)	P(1)–C(130)–C(131)	122.9(6)
C(21)–C(2)–Pt(1)	109.1(5)	P(1)–C(130)–C(135)	119.4(5)
C(21)–C(2)–B(3)	122.6(7)	C(131)–C(130)–C(135)	117.8(7)
C(21)–C(2)–B(7)	115.2(8)	C(130)–C(131)–C(132)	120·1(8)
C(21)–C(2)–B(11)	116.7(7)	C(131)–C(132)–C(133)	121.5(8)
C(21)–C(2)–B(6)	120.8(7)	C(132)–C(133)–C(134)	118.8(9)
		C(133)–C(134)–C(135)	120.2(9)
C(41)–C(4)–Pt(1)	107.3(5)	C(134)–C(135)–C(130)	121.5(7)
C(41)–C(4)–B(3)	121.7(7)		
C(41)–C(4)–B(8)	115.1(7)	P(2)–C(230)–C(231)	122.5(7)
C(41)–C(4)–B(9)	118.7(7)	P(2)–C(230)–C(235)	117.2(6)
C(41)–C(4)–B(5)	122.3(8)	C(231)–C(230)–C(235)	120.1(7)
		C(230)–C(231)–C(232)	118.9(9)
C(110)–P(1)–Pt(1)	113.3(3)	C(231)–C(232)–C(233)	120.3(9)
C(120)–P(1)–Pt(1)	115.1(3)	C(232)–C(233)–C(234)	121.4(9)
C(130)–P(1)–Pt(1)	117.1(3)	C(233)–C(234)–C(235)	119.8(10)
C(110)–P(1)–C(120)	101.3(4)	C(234)–C(235)–C(230)	119.5(8)

TABLE 6

Bond length and angle summary

Type	No. (*N*)	Range	Mean *
(*a*) Bonds (Å)			
Pt–B	3	2.255(9)—2.270(9)	2.262(8)
Pt–C	2	2.442(7), 2.452(8)	
Pt–P	2	2.249(2), 2.303(2)	
B–B	17	1.71(1)—1.89(1)	1.78(4)
B–C	8	1.64(1)—1.76(1)	1.68(4)
C(cage)–C	2	1.53(1), 1.54(1)	
P–C	6	1.802(8)—1.829(9)	1.817(11)
C(Ph)–C(Ph)	12	1.35(2)—1.40(1)	1.38(2)
B–H	9	1.04(9)—1.16(9)	1.11(5)
C–H	28	0.68(8)—1.27(8)	0.98(13)
(*b*) Angles (°)			
P–Pt–P	1	97.30(7)	
B–Pt–B	1	46.6(3)	
B–Pt–C	4	40.4(3)—43.6(3)	42(1)
Pt–B–B	2	65.0(3), 65.4(4)	
Pt–B–C	4	73.4(4)—75.8(5)	75(1)
B–B–C	12	55.0(5)—60.8(5)	58(2)
B–B–B	27	57.3(5)—64.0(6)	60(1)
H–B–Pt	3	106(4)—109(4)	107(2)
H–B–B	34	111(4)—131(5)	122(4)
H–B–C	8	113(4)—130(4)	121(5)
Pt–C–B	4	62.9(4)—63.8(4)	63.3(4)
B–C–B	6	62.4(5)—65.5(6)	64(1)
Pt–C–C	2	107.3(5), 109.1(5)	
B–C–C	8	115.1(6)—122.6(7)	119(3)
H–C–C(cage)	6	103(4)—122(5)	112(6)
H–C–H	18	90(8)—120(8)	109(8)
H–C–P	12	102(5)—116(5)	109(4)
Pt–P–C	6	113(3)—117.8(3)	116(2)
C–P–C	6	98.7(4)—106.3(4)	103(3)
P–C–C	4	117.2(6)—122.9(6)	121(3)
C–C–C	12	117.8(7)—121.5(8)	120(1)
H–C–C(phenyl)	20	106(8)—132(8)	120(7)

* The σ of the mean of several similar types is given by the expression $\sigma^2 = \{\sum_{i=1}^{i=n} (\chi_i - \bar{\chi})^2\}/(N - 1)$, where χ_i is the *i*th and $\bar{\chi}$ the mean of *N* similar types.

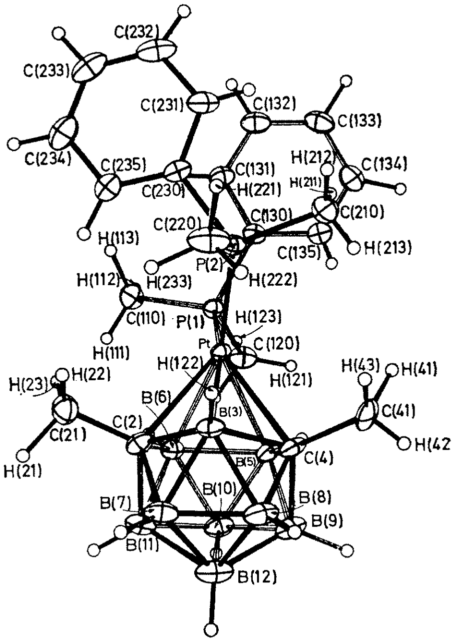

FIGURE 1 ORTEP plot of a single molecule; enclosing 30% electron probability, except for hydrogen atoms which have an artificial radius of 0.1 Å for clarity

be compared with the corresponding distance of *ca.* 0.15 Å in the bis-(3)-1,7-dicarbollylnickelate(II) dianion,[15] the only other 2,4-dicarba-1-(d^8)-metalla-dodecaborane reported as structurally characterised.

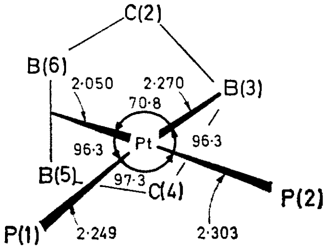

FIGURE 2 Co-ordination about platinum; $\Sigma\hat{P}t = 360.7°$

Tables 4 and 5 demonstrate that the overall distortion of the twelve-atom polyhedron from ideal icosahedral geometry is due almost entirely to the greater covalent radius of the metal atom. Pentagonal-prismatic faces not containing this atom are appreciably less distorted (with the exception of the C_2B_3 face). Further, the dihedral angle between planes (1) and (2) (1.1°) lies well below the range (2.2—6.4°) for other near-parallel face sets where one face contains the platinum.

The boron–boron distances [1.72(2)—1.89(1), mean 1.78(4) Å], boron–carbon distances [1.64(1)—1.76(1), mean 1.68(4) Å], and their associated angles are all as expected for icosahedral carbaboranes.

The Metal Co-ordination.—The plane containing the PtP_2 moiety intersects the C_2B_3 face nearly perpendicularly and almost symmetrically. Thus the co-ordination about the platinum atom is best described in terms of an approximately square planar geometry with the mutually *cis*-phosphorus atoms P(1) and P(2) lying *trans* to B(3) and the midpoint of the B(5)–B(6) bond respectively (Figure 2). The existence of an appreciable *trans*-influence is apparent, with the metal hybrids overlapping less strongly with the single atomic orbital of B(3) than with the two of the B(5),B(6) unit. This geometry allows the cage carbon atoms to bond only weakly to the platinum, and to tend towards their preferred cage co-ordination number of four.[16,17] [The Pt–C are longer than the Pt–B bonds by *ca.* 0.19 Å, though the covalent radius of (tetrahedral) carbon is 0.11 Å less than that of (tetrahedral) boron.[18]]

The Pt–B bond lengths [2.270(9), 2.261(8), and 2.255(9) Å] agree well with those found in [Pt(H)-($B_9H_{10}S$)(PEt_3)$_2$] (2.20—2.25 Å),[19] [Pt(B_3H_7)(PMe_2Ph)$_2$] (2.13—2.38 Å),[20] [Pt(B_6H_{10})$_2$$Cl_2$] (two of 2.27 Å),[21] and in several compounds [4,5,22] we have studied. Although the Pt–P lengths differ by *ca.* 27σ neither lies outside the range usually observed (see *e.g.* Table 7 of ref. 20).

The Phosphine Ligands.—An effective C_2 axis bisecting the P–Pt–P angle relates the two dimethylphenylphosphine ligands and, as might be predicted from intramolecular steric considerations, the phenyl groups are directed away from both the metalla-carbaborane unit and its associated methyl groups.

The length of all pairs of bonds related by the axis agree within statistical error, with the exception of the P–C(Ph) bonds (Δ *ca.* 3.25σ). The C–C bond lengths and all the angles of the phosphine ligands are as expected. In agreement with previous results,[23] inter-bond angles at the phosphorus atom are greater if one bond involved is the co-ordinate bond. The C(130)–C(135) and C(230)–C(235) rings are planar, with the phenyl hydrogen atoms showing maximum deviations of −0.263 [H(134)] and 0.125 Å [H(231)] out of the respective planes.

For the molecule as a whole, mean bond lengths involving hydrogen atoms [B–H 1.11(5), C–H 0.98(13) Å] are predictably [24] shorter than the accepted [18] internuclear separations of *ca.* 1.2 and *ca.* 1.1 Å.

Non-bonding Contacts and Crystal Packing.—Figure 3 is a molecular packing diagram viewed along *a*. Table 7 lists the short contacts between non-bonded centroids of electron density around the hydrogen atoms (true internuclear H · · · H contacts could be up to 0.2 Å less).[24]

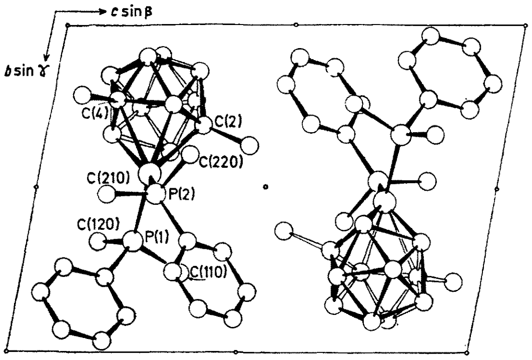

FIGURE 3 The unit-cell contents looking down the *a* axis. Hydrogen atoms are omitted for clarity

TABLE 7

Interligand H · · · H contacts <2.4 Å

H(3) · · · H(222)	2.21(12)	H(113) · · · H(235)	2.31(13)
H(3) · · · H(223)	2.40(11)	H(21) · · · H(111^{I})	2.25(13)
H(6) · · · H(111)	2.35(10)	H(5) · · · H(121^{II})	2.39(12)
H(6) · · · H(122)	2.26(13)	H(10) · · · H(134^{II})	2.37(12)

Roman numeral superscripts denote the following equivalent positions, relative to the reference molecule at x, y, z: I $\bar{x}, 1 - y, 1 - z$; II $x, 1 - y, \bar{z}$.

Of particular interest are the first four (intramolecular)

---

[15] R. M. Wing, *J. Amer. Chem. Soc.*, 1970, **92**, 1187.

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

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

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

[19] A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 2571.

[20] L. J. Guggenberger, A. R. Kane, and E. L. Mutterties, *J. Amer. Chem. Soc.*, 1972, **94**, 5665.

[21] J. P. Brennan, R. Schaeffer, A. Davidson, and S. S. Wreford, *J.C.S. Chem. Comm.*, 1973, 345.

[22] A. J. Welch, unpublished work.

[23] U. A. Gregory, J. A. Jarvis, B. T. Kilbourne, and P. G. Owston, *J. Chem. Soc.* (*A*), 1970, 2770.

[24] See *e.g.*, M. R. Churchill, *Inorg. Chem.*, 1973, **12**, 1213, and refs. therein.

contacts, which may be responsible for the slight twist (10.1_5°) of the PtP_2 plane towards C(4) and B(6) exhibited by the molecule in the solid state. (The ^1H n.m.r. spectrum implies a molecular plane of symmetry containing the PtP_2 moiety.[1])

I thank Dr. J. L. Spencer for supplying the crystalline sample, Dr. A. Quick (Imperial College, London) for the ORTEP plot, and Dr. P. Woodward and Professor F. G. A. Stone for helpful discussion.

[4/2063 *Received, 7th October, 1974*]