

Metallaborane Chemistry. Part VII.¹ The *nido*-Carbaplatinanonaborane. Molecular and Crystal Structure of *nido*-3,8-Dimethyl-2,2-bis(triethylphosphine)-3,8-dicarbaplatinanonaborane(6) †

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The molecular structure of the title compound has been determined by analysis of single-crystal X-ray diffraction data recorded on a diffractometer. Two independent molecules crystallise in the asymmetric unit of an orthorhombic cell of dimensions $a = 18.868(8)$, $b = 17.143(7)$, and $c = 31.07(2)$ Å; space group $Pbca$. Least-squares refinement, by use of 4 542 independent observed reflections, has converged to R 0.069 (all atoms save methyl hydrogens included).

Geometrically the nine-atom metallacage is based on a tricapped trigonal prism in which the metal lies in a prism face, adjacent to boron and carbon caps. The other low-connectivity position hosts the second cage carbon atom which binds a B₄ unit possessing a non-bonding B(7) ··· B(9) mean separation of 2.435 Å. This produces an open Pt(2)B(7)C(8)B(9) face and classifies the species as a *nido*-polyhedron.

THE general reaction between the *closo*-carbaborane 1,6-R¹₂-1,6-C₂B₆H₆ (R¹ = H or Me)²⁻⁴ and zerovalent metal species [M(*trans*-stilbene)L₂] (M = Pd or Pt; L = PR₃) affords two isomeric products. A previous paper¹ reports structural analyses of three members of the family of major derivative. Herein is described the elucidation of the structure of the minor product in the particular case where R¹ = Me, M = Pt, and R² = Et.⁵ A preliminary account has already appeared.⁶

EXPERIMENTAL

Crystals of the compound were grown from diethyl ether-light petroleum (b.p. 40–60 °C) at –5 °C as bright yellow, transparent blocks, stable in air for several weeks; m.p. 135–136 °C *in vacuo*. A single crystal, 0.035 × 0.035 × 0.025 cm, selected for analysis was mounted on a thin glass fibre with an epoxy-resin adhesive. Preliminary X-ray diffraction photographs showed *mmm* Laue symmetry, and allowed approximate calculation of the axial lengths. The specimen was thereafter transferred to a Syntex P2₁ four-circle autodiffractometer and the unit cell and intensity data accurately recorded in a manner already documented.⁷

For the present investigation the following details applied: 15 reflections ($21.0 > 2\theta > 10.0^\circ$) were taken from a 10 min rotation photograph recorded at random orientation, centred in θ , ω , and χ , and used to generate direct-cell vectors and intervector cosines; a unit cell was chosen, and the intensities of several $0kl$, $h0l$, and $hk0$ zonal reflections quickly recorded. Systematic absences suggested the existence of three axial glide planes, and thus the unit cell was redefined to correspond to the standard setting of space group $Pbca$; employing graphite-monochromated Mo- K_α radiation ($\lambda = 0.71069$ Å) and a θ - 2θ scan in 96 steps, one independent set of diffracted intensities was recorded; $h \leq 18$, $k \leq 17$, $l \leq 31$, and $2.9 \leq 2\theta \leq 50.0^\circ$; $K_{\alpha 1}$ to above $1.0^\circ K_{\alpha 2}$, at rates varying from 0.0813 to 0.9765 ° s⁻¹ (according to initial 2 s peak counts) all net intensities were adjusted to a common 1.0° min⁻¹ basis; the $6\bar{1}2$, 612 , and $61\bar{2}$ reflections were monitored once every 28

† The numbering scheme adopted differs from that used in the preliminary account of this work.

‡ Terminal hydrogen atoms (BH) were positional according to the H–B–B, H–B–C, and H–B–M angles observed in 1,1-(PhMe₂P)₂-2,4-Me₂-1,2,4-PtC₂B₉H₉ (ref. 9) and 1,1-(BuⁿNC)₂-2-Me₂N-1,2-PdCB₁₀H₁₀ (ref. 10).

¹ Part VI, A. J. Welch, *J.C.S. Dalton*, 1976, 225.

² R. E. Williams and F. J. Gerhart, *J. Amer. Chem. Soc.*, 1965, **87**, 3513.

³ F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1966, **88**, 609.

reflections but subsequently showed⁸ insignificant intensity variation over the *ca.* 145 h X-ray exposure period; of the 7 918 reflections measured, 4 542 were retained [$I \geq 2.5 \sigma(I)$] and were used for the solution and refinement of the structure; correction for X-ray absorption was accomplished using a Gaussian integration approximation and resulted in correction factors, A^* , ranging from 9.73 (7,17,1) to 33.53 (5,2,1).

Crystal Data.—C₁₆H₄₂B₆P₂Pt, $M = 556.47$, Orthorhombic, $a = 18.868(8)$, $b = 17.143(7)$, $c = 31.07(2)$ Å, $U = 10\ 050(4)$ Å³, $D_m = 1.47$ (by flotation), $Z = 16$, $D_c = 1.471$, $F(000) = 4\ 416$. Mo- K_α X-radiation, $\lambda = 0.71069$ Å; $\mu(\text{Mo-}K_\alpha) = 60.0$ cm⁻¹. Space group $Pbca$.

Data were further corrected for Lorentz and polarisation effects, and the positions (in one asymmetric unit) of the metal and phosphorus atoms deduced from a three-dimensional Patterson synthesis. Three cycles of full-matrix least-squares refinement of the positional and (isotropic) temperature variables resulted in R 0.190, and from an accompanying electron-density difference synthesis all non-hydrogen atoms were located. Blocked refinement of all parameters (one molecule per block; Pt, P anisotropic, C, B isotropic) subsequently converged to R 0.072. F_o moduli were then weighted such that $w = (xy)^{-1}$ with $x = b/\sin\theta$, $\sin\theta < b$; $x = 1$, $\sin\theta \geq b$; $y = F_o/a, F_o > a$; $y = 1$, $F_o \leq a$, with a and b set at 160.0 and 0.25 respectively.

The relatively long crystallographic d spacings in the present compound have produced a study of comparatively poor resolution. For this reason no attempt was made to locate hydrogen atoms *via* a difference-Fourier synthesis. Cage and methylene hydrogens were, in fact, introduced into calculated ‡ positions (assuming B–H 1.10, C–H 1.00 Å, and U_H 0.05 Å²), and were subsequently held invariant. No allowance was made for the contribution from methyl hydrogen atoms.

Several cycles of mixed refinement (ethyl carbon atoms isotropic) converged to R 0.069, R' 0.088; the mean shift-to-error ratio in the final cycle was better than 0.001. A final

⁴ H. V. Hart and W. N. Lipscombe, *J. Amer. Chem. Soc.*, 1976, **89**, 4220; *Inorg. Chem.*, 1968, **7**, 1070.

⁵ J. Browning, M. Green, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 97.

⁶ M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 794.

⁷ A. G. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

⁸ A. G. Modinos, 'DRSYN,' Fortran program for data analysis.

⁹ A. J. Welch, *J.C.S. Dalton*, 1975, 1473.

¹⁰ W. E. Carroll, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1975, 2263.

TABLE 1

Positional parameters (fractional co-ordinate $\times 10^4$; for Pt $\times 10^5$) of the $C_4PtP_2B_6$ moiety

| Atom | x | y | z |
|--------------|-------------|------------|-----------|
| Molecule (A) | | | |
| B(1A) | 1 903(19) * | 619(25) | 4 916(15) |
| Pt(2A) | 20 980(4) | 20 297(5) | 47 665(3) |
| C(3A) | 1 256(15) | 1 170(13) | 4 853(9) |
| B(4A) | 1 201(19) | 679(22) | 5 329(13) |
| B(5A) | 2 102(22) | 596(19) | 5 475(11) |
| B(6A) | 2 607(18) | 1 105(20) | 5 124(13) |
| B(7A) | 1 120(21) | 1 724(16) | 5 248(11) |
| C(8A) | 1 529(16) | 1 306(15) | 5 653(10) |
| B(9A) | 2 290(20) | 1 606(25) | 5 524(13) |
| C(31A) | 662(19) | 1 077(20) | 4 513(10) |
| C(81A) | 1 280(21) | 1 353(24) | 6 123(13) |
| P(21A) | 3 228(3) | 2 417(4) | 4 601(2) |
| P(22A) | 1 476(3) | 3 045(4) | 4 443(2) |
| Molecule (B) | | | |
| B(1B) | -888(15) | 375(18) | 2 276(7) |
| Pt(2B) | 4 620(4) | 3 094(4) | 23 019(3) |
| C(3B) | -500(12) | -221(14) | 2 548(8) |
| B(4B) | -1 021(13) | 274(17) | 2 827(9) |
| B(5B) | -972(17) | 1 232(22) | 2 651(12) |
| B(6B) | -344(12) | 1 211(14) | 2 227(9) |
| B(7B) | -122(14) | 31(16) | 2 963(9) |
| C(8B) | -477(12) | 888(16) | 3 073(8) |
| B(9B) | -36(14) | 1 417(19) | 2 729(10) |
| C(31B) | -643(16) | -1 111(16) | 2 457(12) |
| C(81B) | -583(16) | 1 154(23) | 3 555(11) |
| P(21B) | 1 095(3) | 1 058(3) | 1 829(2) |
| P(22B) | 1 305(3) | -666(3) | 2 438(2) |

* Estimated standard deviations in parentheses throughout this paper.

TABLE 2

Final positional (fractional co-ordinate $\times 10^4$) and isotropic thermal* ($\text{\AA}^2 \times 10^3$) parameters of the ethyl-carbon atoms

| Atom | x | y | z | U_j |
|--------------|-----------|------------|-----------|---------|
| Molecule (A) | | | | |
| C(210A) | 3 723(18) | 1 661(19) | 4 304(10) | 83(8) |
| C(211A) | 3 294(20) | 1 300(21) | 3 921(12) | 96(10) |
| C(212A) | 3 371(16) | 3 283(18) | 4 261(9) | 76(8) |
| C(213A) | 4 173(18) | 3 538(20) | 4 164(11) | 88(9) |
| C(214A) | 3 775(16) | 2 646(17) | 5 071(9) | 70(7) |
| C(215A) | 3 543(17) | 3 337(19) | 5 323(10) | 81(8) |
| C(220A) | 506(15) | 2 992(16) | 4 459(9) | 68(7) |
| C(221A) | 79(20) | 3 726(22) | 4 356(12) | 100(10) |
| C(222A) | 1 634(16) | 4 009(17) | 4 711(9) | 73(7) |
| C(223A) | 1 431(18) | 3 993(20) | 5 205(11) | 89(9) |
| C(224A) | 1 637(18) | 3 270(20) | 3 872(11) | 86(9) |
| C(225A) | 1 524(27) | 2 608(30) | 3 595(16) | 137(16) |
| Molecule (B) | | | | |
| C(210B) | 608(14) | 1 244(16) | 1 322(9) | 67(7) |
| C(211B) | 318(17) | 472(18) | 1 125(10) | 81(9) |
| C(212B) | 1 972(14) | 713(15) | 1 623(8) | 59(6) |
| C(213B) | 2 387(16) | 1 304(18) | 1 361(10) | 77(8) |
| C(214B) | 1 284(12) | 2 023(14) | 2 030(7) | 52(5) |
| C(215B) | 1 790(17) | 2 025(18) | 2 430(10) | 79(8) |
| C(220B) | 1 027(13) | -1 483(15) | 2 777(8) | 61(6) |
| C(221B) | 1 638(16) | -1 991(18) | 2 977(10) | 78(8) |
| C(222B) | 2 084(13) | -225(15) | 2 717(8) | 63(6) |
| C(223B) | 1 861(16) | 83(17) | 3 180(10) | 75(8) |
| C(224B) | 1 713(16) | -1 169(18) | 1 977(10) | 77(8) |
| C(225B) | 1 197(22) | -1 525(23) | 1 678(12) | 106(11) |

* The isotropic thermal parameter is defined as $\exp\{-8\pi^2 U_j / (\sin^2 \theta / \lambda^2)\}$.

ΔF map revealed a maximum of ca. 0.8 e\AA^{-3} near Pt(2B). Scattering factors for neutral atoms were those of ref. 11

† Anisotropic thermal parameters, hydrogen atom positions, details of molecular planes, intra- and inter-molecular interligand contacts (less than van der Waals distances), and observed and calculated structure factors are listed in Supplementary Publication No. SUP 21986 (27 pp., 1 microfiche). For details see Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue.

for platinum and boron, ref. 12 for phosphorus and carbon, and ref. 13 for hydrogen, with those of platinum and phosphorus corrected for anomalous dispersion using $\Delta f'$ and $\Delta f''$ values from ref. 14. Tables 1 and 2 contain the derived atomic (Pt, P, C, B) positional and isotropic thermal parameters.† All computer programs used were from the 'X-ray' system.¹⁵

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The species crystallises as discrete, neutral, monomer molecules with no imposed symmetry. There are two crystallographically independent molecules in the asymmetric fraction of the unit cell [molecules (A) and (B)].

Figure 1 provides a perspective view of a single molecule and demonstrates the atomic numbering scheme adopted. Tables 3 and 4 list the derived internuclear separations (uncorrected for thermal effects) and inter-bond angles.

The metallacage may be geometrically described as a highly distorted tricapped trigonal prism, comprising trigonal faces B(1), B(4), and B(5) and Pt(2), B(7), and B(9), capped by C(3), C(8), and B(6). Pt(2) lies adjacent to C(3) and B(6). The molecule therefore contrasts with the major product of its formative reaction, in which a

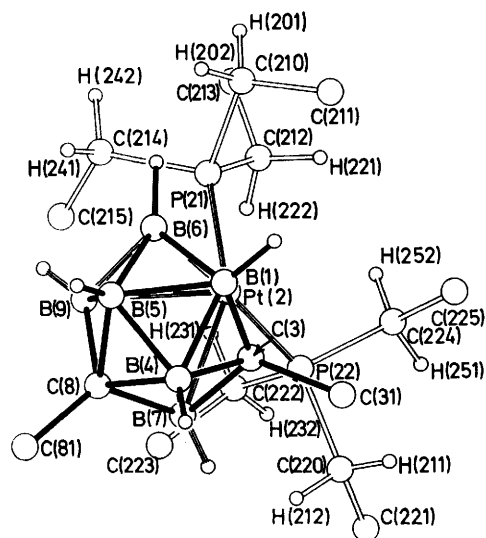


FIGURE 1 Perspective view of a single molecule. Hydrogen atoms of the cage take the same number as the boron to which they are bound

B_6 trigonal prism is capped by a platinum and two carbon atoms.^{1,6} It further contrasts with $[\text{Mn}(\text{B}_6\text{C}_2\text{H}_8)(\text{CO})_3]^-$, the only other tricapped trigonal prismatic metalladiborane to be structurally authenticated.¹⁶ In this the metal atom lies in a prism face, adjacent to both

¹¹ D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

¹² D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

¹³ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

¹⁴ 'International Tables for X-Ray Crystallography', vol. III, Kynoch Press, Birmingham, 1962.

¹⁵ Technical Report TR 192, Computer Science Centre, University of Maryland, June 1972.

¹⁶ F. J. Hollander, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1973, **12**, 2262.

cage carbons. The manganacarbaborane is prepared^{17,18} by treatment of $[\text{B}_7\text{C}_2\text{H}_{11}]^{2-}$ with either $[\text{Mn}(\text{CO})_5\text{Br}]$ or $[\text{Mn}_2(\text{CO})_{10}]$, and the reaction presumably proceeds *via* formation of the *nido*-carbaborane anion $[\text{B}_6\text{C}_2\text{H}_8]^{2-}$ in which both carbon atoms are located in the open face. None of the possible mechanisms previously described¹ for the reaction between 1,6- R^1_2 -1,6- $\text{C}_2\text{B}_6\text{H}_6$ and zero-valent Pt^0 nucleophiles proceeds *via* an analogous intermediate, thus re-emphasising the novelty of this synthetic approach.

TABLE 3
Interatomic distances (Å)

| Bond | Molecule (A) | Molecule (B) | |
|----------------------------|--------------|-----------------|----------|
| (a) Within the polyhedron | | | |
| B(1)-Pt(2) | 2.49(4) | 2.55(3) | |
| B(1)-C(3) | 1.56(5) | 1.51(4) | |
| B(1)-B(4) | 1.85(6) | 1.74(4) | |
| B(1)-B(5) | 1.78(6) | 1.88(5) | |
| B(1)-B(6) | 1.70(5) | 1.77(4) | |
| Pt(2)-C(3) | 2.18(3) | 2.17(2) | |
| Pt(2)-B(7) | 2.43(4) | 2.38(3) | |
| Pt(2)-B(9) | 2.49(4) | 2.50(3) | |
| Pt(2)-B(6) | 2.16(4) | 2.18(2) | |
| C(3)-B(7) | 1.57(4) | 1.54(4) | |
| C(3)-B(4) | 1.71(5) | 1.56(4) | |
| B(4)-B(7) | 1.82(5) | 1.80(4) | |
| B(4)-C(8) | 1.60(5) | 1.66(4) | |
| B(4)-B(5) | 1.77(6) | 1.73(5) | |
| B(5)-C(8) | 1.72(5) | 1.72(4) | |
| B(5)-B(9) | 1.77(5) | 1.81(4) | |
| B(5)-B(6) | 1.69(5) | 1.77(4) | |
| B(6)-B(9) | 1.62(5) | 1.70(4) | |
| B(7)-C(8) | 1.64(5) | 1.65(4) | |
| C(8)-B(9) | 1.58(5) | 1.63(4) | |
| (b) <i>exo</i> -Polyhedral | | | |
| C(3)-C(31) | 1.55(4) | 1.58(4) | |
| C(8)-C(81) | 1.53(5) | 1.58(4) | |
| Pt(2)-P(21) | 2.293(6) | 2.287(6) | |
| Pt(2)-P(22) | 2.328(7) | 2.346(6) | |
| P(21)-C(210) | 1.84(3) | 1.85(3) | |
| P(21)-C(212) | 1.84(3) | 1.87(3) | |
| P(21)-C(214) | 1.83(3) | 1.80(2) | |
| C(210)-C(211) | 1.57(5) | 1.56(4) | |
| C(212)-C(213) | 1.54(5) | 1.52(4) | |
| C(214)-C(215) | 1.49(4) | 1.57(4) | |
| P(22)-C(220) | 1.83(3) | 1.83(3) | |
| P(22)-C(222) | 1.87(3) | 1.87(3) | |
| P(22)-C(224) | 1.84(3) | 1.84(3) | |
| C(220)-C(221) | 1.53(5) | 1.57(4) | |
| C(222)-C(223) | 1.58(5) | 1.59(4) | |
| C(224)-C(225) | 1.44(6) | 1.48(5) | |
| (c) Summary | | | |
| Bond | N | Range/Å | Mean/Å |
| B-B | 16 | 1.62(5)—1.88(5) | 1.76(7)* |
| C-B | 14 | 1.51(4)—1.72(5) | 1.62(6) |
| P-C | 12 | 1.80(2)—1.87(3) | 1.84(2) |
| C-C | 16 | 1.44(6)—1.59(4) | 1.55(4) |

* The estimated standard deviation of the mean of N independent observations is given by the expression $\sigma^2 = \frac{1}{N} \sum_{i=1}^N (\chi_i - \bar{\chi})^2 / (N - 1)$ where χ_i is the i th and $\bar{\chi}$ the mean value.

The observed deviations of the cage in 2,2-(Et_3P)₂-3,8- Me_2 -2,3,8- $\text{PtC}_2\text{B}_6\text{H}_6$ from a more symmetrical geometry demonstrated, for example, by B_9Cl_9 ,¹⁹ may be regarded as originating from two sources. First, bond-length and -angle variations arise simply because

¹⁷ M. F. Hawthorne and A. D. Pitts, *J. Amer. Chem. Soc.*, 1976, **99**, 7115.

¹⁸ A. D. George and M. F. Hawthorne, *Inorg. Chem.*, 1969, **8**, 1801.

TABLE 4
Interbond angles (°)

| Atoms | Molecule (A) | Molecule (B) |
|------------------------|--------------|--------------|
| (a) Polyhedral surface | | |
| Pt(2)-B(1)-C(3) | 60(2) | 60(1) |
| C(3)-B(1)-B(4) | 59(2) | 57(2) |
| B(4)-B(1)-B(5) | 58(2) | 57(2) |
| B(5)-B(1)-B(6) | 58(2) | 58(2) |
| B(6)-B(1)-Pt(2) | 59(2) | 57(1) |
| B(1)-Pt(2)-C(3) | 38(1) | 36(1) |
| C(3)-Pt(2)-B(7) | 39(1) | 39(1) |
| B(7)-Pt(2)-B(9) | 58(1) | 61(1) |
| B(9)-Pt(2)-B(6) | 40(1) | 42(1) |
| B(6)-Pt(2)-B(1) | 42(1) | 43(1) |
| B(1)-C(3)-Pt(2) | 82(2) | 86(2) |
| Pt(2)-C(3)-B(7) | 79(2) | 78(1) |
| B(7)-C(3)-B(4) | 67(2) | 71(2) |
| B(4)-C(3)-B(1) | 69(2) | 69(2) |
| B(1)-B(4)-C(3) | 52(2) | 54(2) |
| C(3)-B(4)-B(7) | 53(2) | 54(1) |
| B(7)-B(4)-C(8) | 57(2) | 57(1) |
| C(8)-B(4)-B(5) | 61(2) | 61(2) |
| B(5)-B(4)-B(1) | 59(2) | 66(2) |
| B(1)-B(5)-B(4) | 63(2) | 57(2) |
| B(4)-B(5)-C(8) | 55(2) | 57(2) |
| C(8)-B(5)-B(9) | 54(2) | 55(2) |
| B(9)-B(5)-B(6) | 56(2) | 57(2) |
| B(6)-B(5)-B(1) | 59(2) | 58(2) |
| B(1)-B(6)-Pt(2) | 79(2) | 80(1) |
| Pt(2)-B(6)-B(9) | 81(2) | 79(1) |
| B(9)-B(6)-B(5) | 65(2) | 63(2) |
| B(5)-B(6)-B(1) | 63(2) | 64(2) |
| Pt(2)-B(7)-C(3) | 62(2) | 63(1) |
| C(3)-B(7)-B(4) | 60(2) | 55(2) |
| B(4)-B(7)-C(8) | 55(2) | 57(1) |
| C(8)-B(7)-Pt(2) | 102(2) | 101(1) |
| B(4)-C(8)-B(5) | 64(2) | 62(2) |
| B(5)-C(8)-B(9) | 65(2) | 65(2) |
| B(9)-C(8)-B(7) | 95(2) | 99(2) |
| B(7)-C(8)-B(4) | 68(2) | 66(2) |
| Pt(2)-B(9)-B(6) | 59(2) | 59(1) |
| B(6)-B(9)-B(5) | 60(2) | 60(2) |
| B(5)-B(9)-C(8) | 61(2) | 60(2) |
| C(8)-B(9)-Pt(2) | 102(2) | 97(2) |
| (b) Other angles | | |
| C(31)-C(3)-B(1) | 126(3) | 118(2) |
| C(31)-C(3)-Pt(2) | 121(2) | 119(2) |
| C(31)-C(3)-B(7) | 118(3) | 120(2) |
| C(31)-C(3)-B(4) | 120(2) | 121(2) |
| C(81)-C(8)-B(4) | 121(3) | 123(2) |
| C(81)-C(8)-B(5) | 122(3) | 124(2) |
| C(81)-C(8)-B(9) | 120(3) | 122(2) |
| C(81)-C(8)-B(7) | 124(3) | 120(2) |
| P(21)-Pt(2)-P(22) | 98.9(2) | 99.3(2) |
| Pt(2)-P(21)-C(210) | 112(1) | 113(1) |
| Pt(2)-P(21)-C(212) | 120(1) | 120(1) |
| Pt(2)-P(21)-C(214) | 114(1) | 113(1) |
| C(210)-P(21)-C(212) | 102(1) | 102(1) |
| C(210)-P(21)-C(214) | 105(1) | 104(1) |
| C(212)-P(21)-C(214) | 102(1) | 104(1) |
| P(21)-C(210)-C(211) | 113(2) | 111(2) |
| P(21)-C(212)-C(213) | 119(2) | 115(2) |
| P(21)-C(214)-C(215) | 115(2) | 113(2) |
| Pt(2)-P(22)-C(210) | 117(1) | 117(1) |
| Pt(2)-P(22)-C(212) | 113(1) | 109(1) |
| Pt(2)-P(22)-C(224) | 119(1) | 119(1) |
| C(220)-P(22)-C(222) | 101(1) | 105(1) |
| C(220)-P(22)-C(224) | 102(1) | 102(1) |
| C(222)-P(22)-C(224) | 103(1) | 103(1) |
| P(22)-C(220)-C(221) | 119(2) | 116(2) |
| P(22)-C(222)-C(223) | 112(2) | 110(2) |
| P(22)-C(224)-C(225) | 113(3) | 114(2) |

of the presence of the three heteroatoms. Thus Pt(2)-B(7) and Pt(2)-B(9) are, on average, *ca.* 0.66 Å longer

¹⁹ M. B. Hursthouse, A. Kane, and A. G. Massey, *Nature*, 1970, **228**, 659.

than B-B distances in the B(1), B(4), B(5) prism faces, with C-B separations *ca.* 0.09 Å shorter than the B(6)-B values. Distortions of similar magnitudes have been consistently observed^{1,9,10,20,21} in platina- and pallada-carborane structures.

Secondly, a different and more severe polyhedral distortion derives from the magnitude of the B(7)-B(9) prism edge (mean 2.435 Å over the two molecules). The omission of this linkage as a formal connectivity necessitates describing the structure as a *nido*-species, although it cannot be overemphasised that, both in terms of the skeletal electron-pair theory* and of overall architecture, the molecule is strictly *closo*, albeit highly distorted.

In that a connectivity is broken producing an open PtBCB face, the present molecular structure bears direct comparison with the essentially bicapped square-antiprismatic *nido*-2,7-Me₂-9,9-(Et₃P)₂-2,7,9-C₂PtB₇H₇,^{20,22} The four-atom open faces of these two structures are compared in Figure 2 which also shows the additional linkage (dashed line) to complete the total geometry. For the present title compound this is B···B, and for the second compound Pt···C. In spite of this fundamental difference, a common rationalisation of the molecular distortions, and of the orientation adopted by the

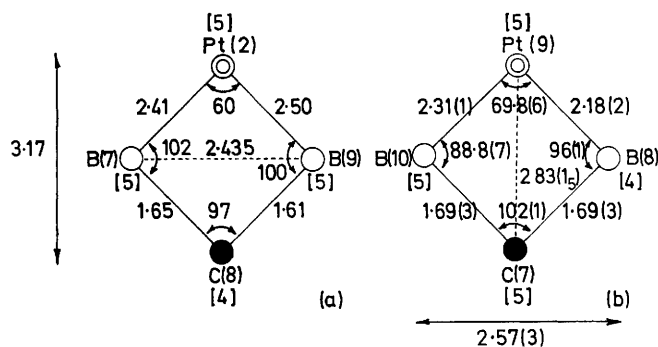


FIGURE 2 Summary of the PtBCB open faces of (a) the title compound (mean molecular parameters quoted), and (b) *nido*-2,7-Me₂-9,9-(Et₃P)₂-2,7,9-C₂PtB₇H₇, with formal atom connectivity numbers in square brackets; distances (Å), angles (°)

ML₂ (M = Pt or Pd; L = PR₃ or CNR) moiety in these and similar species is available as a result of extended-Hückel molecular orbital calculations.^{24,25}

No unusual features exist in the molecular parameters

* For (L₂Pt)(MeC)₂(HB)₆, assuming a formal +2 metal oxidation state, there are 2 + (2 × 3) + (6 × 2) = 20 skeletal electrons or (N + 1) electron pairs where N, the number of polyhedral vertices, is 9. One would accordingly predict²³ a *closo*-triccapped trigonal prismatic geometry.

²⁰ A. J. Welch, *J.C.S. Dalton*, 1975, 2270.

²¹ A. J. Welch, unpublished work.

²² M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 571.

calculated for the four independent triethylphosphine ligands.

Figure 3 represents a projection of half the unit cell contents (for the sake of clarity) on the *ac* plane.

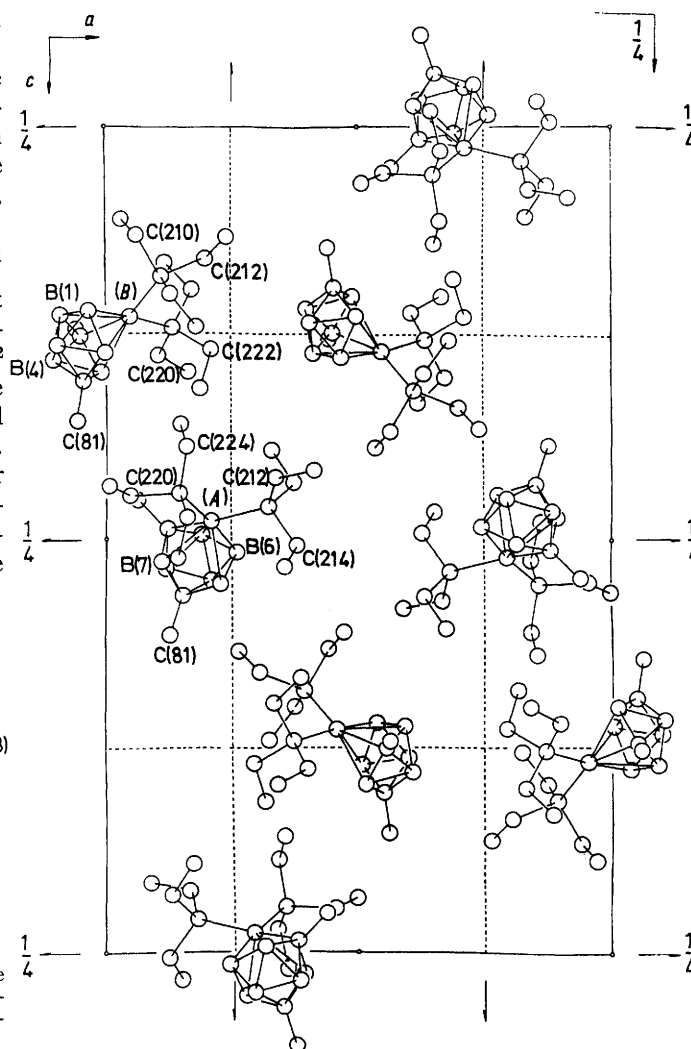


FIGURE 3 Packing diagram in *ac* projection. For the sake of clarity only half the molecules in the unit cell, and no hydrogen atoms, are shown

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²³ R. E. Williams, *Inorg. Chem.*, 1971, 10, 210; K. Wade, *J.C.S. Chem. Comm.*, 1971, 792; *Chem. in Britain*, 1975, 11, 177; R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, 1972, 11, 1973.

²⁴ D. M. P. Mingos, *J.C.S. Dalton*, 1977, 602.

²⁵ M. Forsythe, D. M. P. Mingos, and A. J. Welch, unpublished work.