

Formation of *closo*- and *nido*-Metallocarboranes from *closo*-C₂B₇ and -C₂B₇ Carboranes; Molecular Structures of *closo*-1,1-(Me₂PhP)₂-2,4-Me₂-1,2,4-PtC₂B₇H₉ and *nido*-10,10-(Et₃P)₂-2,8-Me₂-10,2,8-PtC₂B₇H₇

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Summary Reaction of *closo*-1,6-Me₂-1,6-C₂B₇H₇ with [Pt-(Et₃P)₃] affords *nido*-10,10-(Et₃P)₂-2,8-Me₂-10,2,8-PtC₂B₇H₇, a stereochemically non-rigid molecule; the structural identity of *closo*-1,1-(Me₂PhP)₂-2,4-Me₂-1,2,4-PtC₂B₇H₉ and the *nido*-metallocarborane are established by X-ray crystallography.

We have reported¹ a new synthesis of metallocarboranes involving direct insertion of *d*¹⁰ transition metals into the 11-atom *closo*-carborane C₂B₉H₉Me₂. However, the structure of the insertion products was based on spectroscopy, and on an alternative synthesis. An unambiguous structural characterisation was therefore necessary.

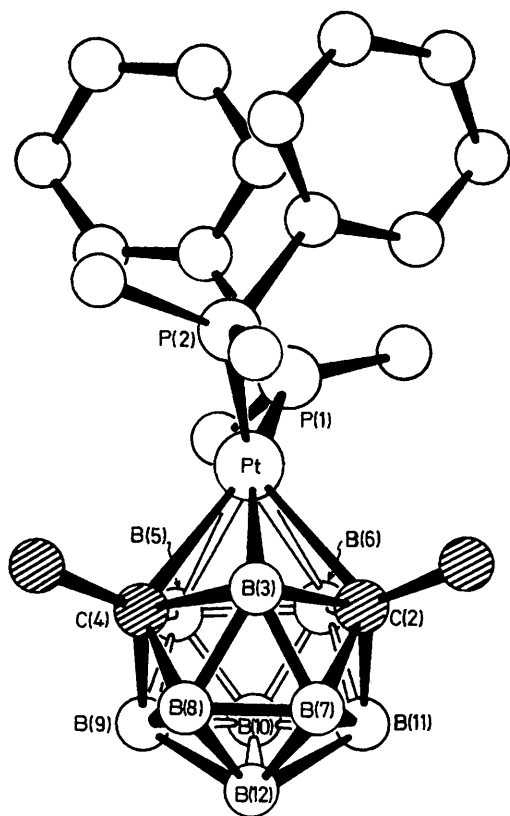


FIGURE 1. Structure of [Me₂C₂B₇H₉]Pt[PPhMe₂]₂.

A single crystal X-ray diffraction study of 1,1-(Me₂PhP)₂-2,4-Me₂-1,2,4-PtC₂B₇H₉, the product of the reaction of [Pt(Me₂PhP)₄] with 2,3-Me₂-2,3-C₂B₉H₉, established the molecular structure shown (Figure 1). *Crystal data*: centrosymmetric triclinic with *a* = 9.324(3), *b* = 10.285(4), *c* = 14.208(8) Å, α = 100.40(4), β = 94.32(4), γ = 98.95(3)°; *R* = 0.042 for 4330 reflections (Syntex P₂₁ four-circle diffractometer). This result confirms that the metal

co-ordinates three boron and two carbon atoms to complete a *closo*-2,4-dicarbaisahedron. The platinum atom is situated *ca.* 1.75 Å above the C₂B₃ face which exhibits distortions from an ideal geometry similar to those already recorded² for other 1-metallo-2,4-dicarbaboranes. Although the PtP₂ unit subtends an almost perpendicular dihedral angle (89.6°) with the B(3)B(5)B(6) plane, the former is twisted towards B(6) and C(4) *ca.* 10.2° with respect to the PtB(3)B(12)B(10) plane.

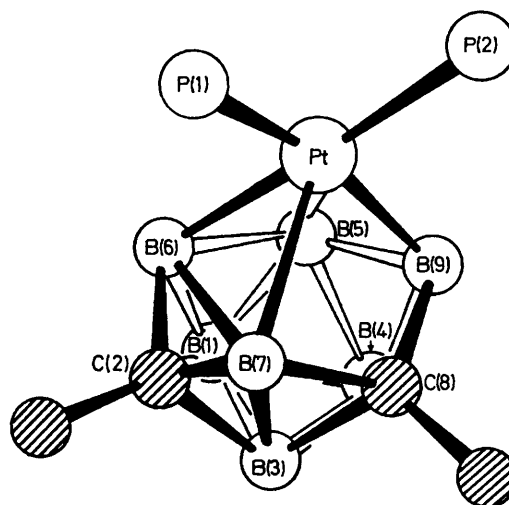


FIGURE 2. Structure of [Me₂C₂B₇H₇]Pt[PEt₃]₂. Phosphino ethyl groups are omitted for clarity.

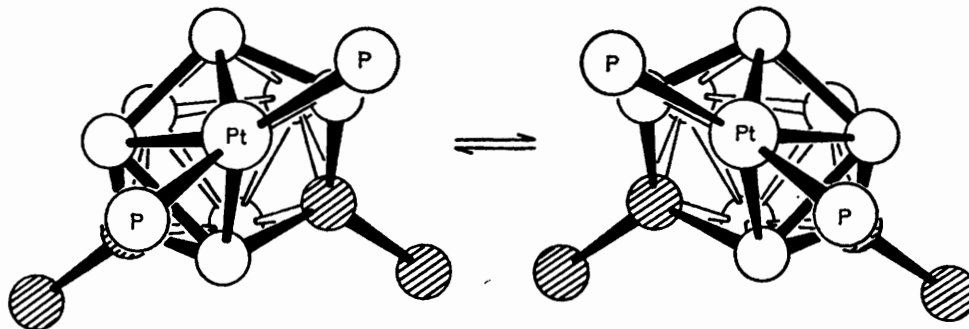
With structural confirmation of the nature of this polyhedral expansion reaction it was clearly important to examine the reaction of a Pt⁰ species with a 9-atom carborane. Treatment (room temperature) of [Pt(Et₃P)₃] with 1,6-Me₂-1,6-C₂B₇H₇³ in light petroleum affords (I) as the only isolable product (>90%) [m.p. 135°; ¹H n.m.r. resonances (CH₂Cl₂) at τ 8.02 (m, PCH₂Me), 8.03 (s, cage Me), and 8.98 (m, PCH₂Me)]. The corresponding reaction with 1,6-C₂B₇H₉³ gave pale yellow needles of (II) [m.p. 153°; ¹H n.m.r. resonances (CDCl₃) at τ 6.46 (m, 2H, cage CH), 8.04 (m, 12H, PCH₂Me), and 9.00 (m, 18H, PCH₂Me)]; ¹⁹⁵Pt resonance (INDOR) +747 p.p.m. (w.r.t. 21.4 MHz), ³¹P resonance (INDOR) -14.03 p.p.m. (w.r.t. external H₃PO₄), |*J*(PPt)| 2957 Hz; ¹¹B resonances (CH₂Cl₂; 80.5 MHz w.r.t. BF₃-Et₂O) at δ -1.6 (m, 3B), +10.5 (m, 2B), and +28.4 [d, 2B, *J*(BH) 140 Hz]. The n.m.r. data imply a molecular plane of symmetry for (I) and (II) in solution, and do not define a unique structure.

A single crystal X-ray diffraction study of (I) revealed the molecular structure shown (Figure 2). *Crystal data*: monoclinic, space group P₂₁/a, *a* = 16.955(10), *b* = 18.879(18), *c* = 10.066(16) Å, β = 125.66(8)°, *R* = 0.107 for 2810 significant reflections.

The platinum co-ordinates boron atoms 5, 6, 7, and 9 to produce a *nido*-10-atom polyhedron whose geometry best approximates to a bicapped [B(9) and C(2)] square antiprism. The length of the diagonals of the open face [defined by atoms Pt, B(7), C(8) and B(9)] do not constitute bonding interactions [Pt...C(2), 2.83(4) Å; B(7)...B(9), 2.52(7) Å]. It is interesting to note that in the geometry adopted both cage carbon atoms occupy relatively low co-ordination positions. Other important molecular parameters are: bond lengths to platinum; P(1), 2.29(1);

long Pt-B bonds, the B(6)-Pt-B(7) bond angle being the largest of the narrow B-Pt-B angles, and that B(6)-B(7) is the longest bond between the metallo-co-ordinated boron atoms.

It would be expected⁴ that both the 1,2,4-PtC₂B₉ and 10,2,8-PtC₂B₉ complexes should have a *closo*-structure. In the case of the 10-atom PtC₂B₉ species (22 electron) a bicapped square antiprismatic structure would be predicted, contrary to the structural result. Moreover, (I) and (II) show no evidence of thermal rearrangement up to 300°



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P(2), 2.34(1); B(5), 2.36(3); B(6), 2.29(5); B(7), 2.43(6); B(9), 2.07(4) Å; other bonds; B(9)-B(5), 1.74(8); B(5)-B(6), 1.98(6); B(6)-B(7), 2.09(9) Å; angles at platinum: P(1)P(2), 102.7(4); B(9)B(5), 41(2); B(5)B(6), 50(2); B(6)B(7), 52(2); and B(7)B(9), 67(2)°.

Such molecular asymmetry can only be correlated with the n.m.r. data in terms of a rapid interchange in solution at normal temperatures between the structure determined, and its mirror image (Scheme). This interpretation is consistent with the Pt-B(6) bond being the shortest of the

thus excluding the possibility that these are kinetically controlled products. It is interesting that the related π -C₆H₆CoC₂B₇H₉ and [Co(C₂B₇H₉)₂]⁻ species do in fact have the expected *closo*-structures.⁵

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