Double Insertion of a Platinum Nucleophile into a *closo*-Carbaborane: Molecular Structures of 4,4-(Et$_3$P)$_2$-1,7-Me$_2$-1,4,7-CPtCB$_5$H$_5$ and 1,1-(Et$_3$P)$_2$-6,6-(Et$_3$P)$_2$-4,5-Me$_2$-1,4,5,6-PtC$_2$PtB$_5$H$_5$[1]

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The carbaboranes *closo*-2,4-R$_2$-2,4-C$_2$B$_5$H$_5$ (R = H or Me) react with [Pt$_2$(μ-cod)(PEt$_3$)$_4$] (cod = cyclo-octa-1,5-diene) to afford the carbaplatinaboranes 4,4-(Et$_3$P)$_2$-1,7-R$_2$-1,4,7-CPtCB$_5$H$_5$ and 1,1-(Et$_3$P)$_2$-6,6-(Et$_3$P)$_2$-4,5-Me$_2$-1,4,5,6-PtC$_2$PtB$_5$H$_5$; the molecular structures of the two methyl derivatives have been established by X-ray diffraction.
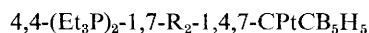
The direct insertion of low-valent Ni-, Pd-, Pt-, Co-, and Fe-ligand fragments into *closo*-carbaboranes is now an important synthetic route to carbametallaboranes.[2] The more recently studied Co and Fe species may yet prove susceptible to additional metal insertions but, with one exception,[3] it has not so far been possible to prepare by this method carbametallaboranes of the nickel sub-group in which two metal atoms lie in the polyhedral surface.[4] The single exception is a red diplatina-complex (Et$_3$P)$_4$Pt$_2$C$_2$B$_5$H$_7$ formed in the reaction between 2,4-C$_2$B$_5$H$_7$ and [Pt(styrene)(PEt$_3$)$_2$]. However, the X-ray diffraction study[3] was of limited precision because of space group ambiguity and/or partial disorder. Moreover, the ^{31}P {^{1}H, ^{11}B} n.m.r. spectrum, subsequently obtained (see below), was at variance with the positions of the cage-carbon atoms deduced earlier. Accordingly, the reactions of 2,4-C$_2$B$_5$H$_7$ and its C-methyl derivative with a Pt^0 species were reinvestigated using the reagent [Pt$_2$(μ-cod)(PEt$_3$)$_4$] (cod = cyclo-octa-1,5-diene).[5]

The diplatinum compound in hexane and the carbaboranes *closo*-2,4-R$_2$-2,4-C$_2$B$_5$H$_5$ (R = H or Me) were mixed at −196 °C and for both reactions the reactants were slowly warmed to room temperature. The orange (R = H) or deep

4,4-(Et$_3$P)$_2$-1,7-R$_2$-1,4,7-CPtCB$_5$H$_5$

(1) R = H
(2) R = Me

(Et$_3$P)$_4$Pt$_2$(C$_2$B$_5$H$_5$R$_2$)

(3) R = H
(4) R = Me

red (R = Me) solutions obtained were evaporated, and the respective residues recrystallised from diethyl ether (R = H) or hexane (R = Me) at −20 °C, thereby affording the compounds 4,4-(Et$_3$P)$_2$-1,7-R$_2$-1,4,7-CPtCB$_5$H$_5$ [(1) R = H (22%): (2) R = Me (35%)] and (Et$_3$P)$_4$Pt$_2$(C$_2$B$_5$H$_5$R$_2$) [(3) R = H (35%); (4) R = Me (55%)], characterised by microanalysis and spectroscopic properties.†
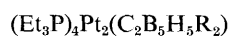
The i.r. and ^{11}B n.m.r. spectra of compounds (1) and (2) suggest that they are structural analogues. The architecture of (2) has been established by a diffraction study.

Crystal data: C$_{16}$H$_{41}$B$_5$P$_2$Pt, M = 544·59, monoclinic, space group P2$_1$/n, a = 18·021(12), b = 16·413(5), c = 18·731(12) Å,
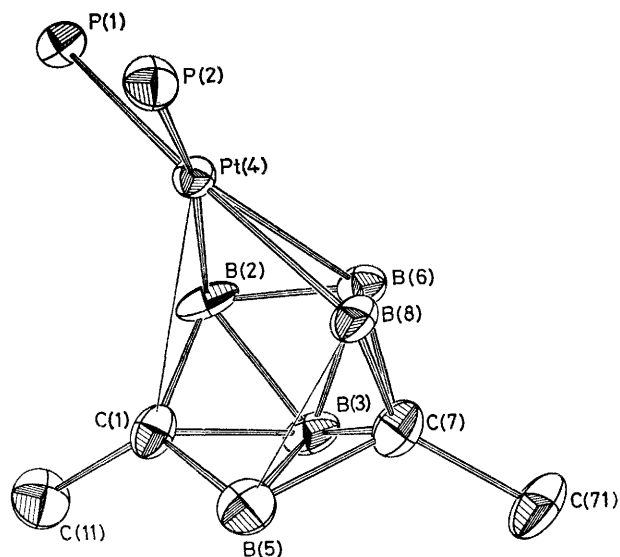

Figure 1. The molecular structure of 4,4-(Et$_3$P)$_2$-1,7-Me$_2$-1,4,7-CPtCB$_5$H$_5$ (2) with ethyl groups omitted for clarity. Important molecular parameters (average of two independent molecules) include Pt(4)–C(1) 2·742, Pt(4)–B(2) 2·200, Pt(4)–B(6) 2·337, Pt(4)–B(8) 2·100, Pt(4) · · · B(5) 3·105, B(5)–B(8) 2·138, C(1) · · · B(8) 2·896, Pt(4)–P(1) 2·327, Pt(4)–P(2) 2·278 Å; ∠ P(1)–Pt(4)–P(2) 105·5°.

Figure 2. The stereochemistry of 1,1-(Et$_3$P)$_2$-6,6-(Et$_3$P)$_2$-4,5-Me$_2$-1,4,5,6-PtC$_2$PtB$_5$H$_5$ (4) with ethyl functions omitted. Important dimensions; Pt(1)–Pt(6) 3·029 8(10), Pt(1)–B(3) 2·219(19), Pt(1)–B(2) 2·25(3), Pt(1)–C(4) 2·20(2), Pt(1)–B(7) 2·94(2), Pt(6)–B(3) 2·213(18), Pt(6)–B(9) 2·20(2), Pt(6)–B(7) 2·25(3), B(2)–B(3) 2·20(3), Pt(1)–P(11) 2·244(6), Pt(1)–P(12) 2·383(6), Pt(6)–P(61) 2·322(6), Pt(6)–P(62) 2·329(6) Å; ∠ P(11)–Pt(1)–P(12) 102·9(2), P(61)–Pt(6)–P(62) 101·1(2)°.

β = 116·36(4)°, U = 4 964(4) Å^3, Z = 8, D_c = 1·457 g cm^{-3}, F(000) = 2 160 electrons, μ(Mo-K_α) = 55·4 cm^{-1}.‡

Intensity data were recorded at 23 °C on a Nicolet $P3$ diffractometer (graphite-monochromated Mo-K_α X-radiation, $\bar\lambda$ = 0·710 69 Å), with 5 683 out of 7 520 reflections (θ_{max} = 50°) having $F \geqslant 2·0\sigma(F)$, and these were used to solve (Patterson and Fourier techniques) and refine (full matrix least-squares) the structure to a current R of 0·055. Dimensions within each of the two independent molecules per asymmetric unit are identical within the limits of the experiment, and average values (no e.s.d's) are hereafter discussed.

According to simple empirical counting rules,[6] the polyhedron of (2) should have the geometry of a dodecahedron, [D_{2d}-(2222)-Δ^{12}-*closo*], but clearly (Figure 1) the cage is seriously distorted, featuring an open four-atom [Pt(4)B(8)-B(5)C(1)] face. It should be noted that a dodecahedron could be envisaged by closing either of the diagonals of this face [Pt(4) . . . B(5) 3·105, B(8) . . . C(1) 2·896 Å], and our polyhedral numbering scheme[1] reflects only an arbitrary choice of the former. In addition, the formal connectivities B(5)–B(8), 2·138, and C(1)–Pt(4), 2·742 Å, are appreciably longer than expected. Polyhedral distortions producing 'open' frameworks in carbaplatinaboranes which are formally electronically *closo* (n + 1 skeletal pairs) are not uncommon.[7] Although the extent of the mis-shaping of (2) is without precedent, the molecule nevertheless represents the first crystallographically authenticated 8-vertex carbametallaborane with nine skeletal electron pairs.

The earlier X-ray diffraction study[3] on (3) led to the structure being interpreted as 1,1-(Et$_3$P)$_2$-7,7-(Et$_3$P)$_2$-1,4,6,7-PtC$_2$PtB$_5$H$_7$, *i.e.* a tricapped trigonal prism (TTP) in which the metal atoms are connected by a parallel prism linkage.§ However, the [31]P-
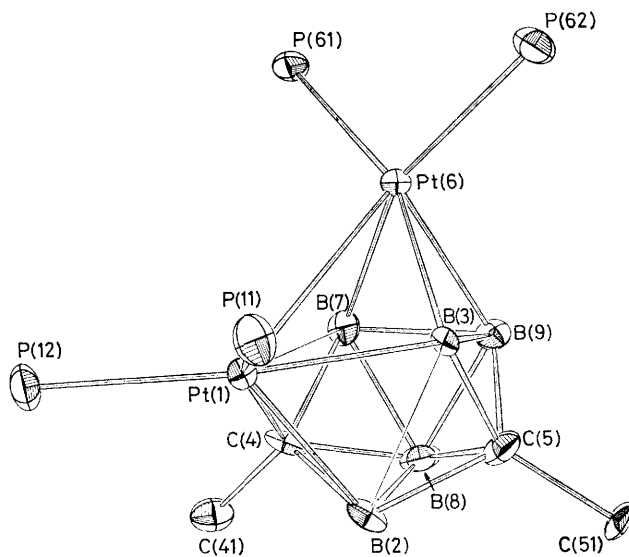
{^{1}H, ^{11}B } n.m.r. spectrum,† with four inequivalent resonances, does not accord with this geometry. In view of the difficulties with the X-ray diffraction work on (3) the molecular structure of the C-methyl derivative (4) was established by this technique.

Crystal data: C$_{28}$H$_{71}$B$_5$P$_4$Pt$_2$, M = 975·99, orthorhombic, space group *Pbca*, a = 17·267(2), b = 20·161(4), c = 23·086(3) Å, U = 8 036(5) Å^3, Z = 8, D_c = 1·613 g cm^{-3}, F(000) = 3 840 electrons, μ(Mo-K_α) = 68·4 cm^{-1}. Diffracted intensities were measured (Mo-K_α radiation) at 23 °C to θ_{max} = 25° on an Enraf–Nonius CAD4 diffractometer, with 4 820 out of 7 060 reflections [$F \geqslant 2·0\sigma(F)$] being used to solve and refine the structure, as described above, to a present R index of 0·102.‡

The molecule (Figure 2) has a cage which can be described as a TTP, but here the metal–metal vector is a capping, not a prism, linkage. This connection is rather long [3·029 8(10) Å], but lies roughly perpendicular to the two sets of P$_2$Pt planes, and if the latter are taken as local *xy* planes then the Pt–Pt bond results from the destabilising overlap of two filled d$_{z^2}$ orbitals.¶
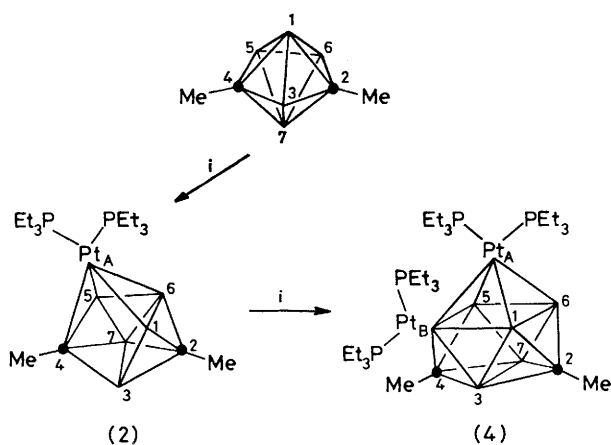
In addition, the cage of (4) has two other connectivities substantially longer than expected [Pt(1)–B(7) 2·94(2) and B(2)–B(3) 2·20(3) Å]. According to convention,[1] compound (4) may be systematically numbered as 1,1-(Et$_3$P)$_2$-6,6-(Et$_3$P)$_2$-4,5-Me$_2$-1,4,5,6-PtC$_2$PtB$_5$H$_5$.

It was observed that recrystallisation of (2) always led to the production of the free *closo*-carbaborane and the dinuclear complex (4). This suggests that the formation of (2) is reversible, and that the liberated Pt(PEt$_3$)$_2$ fragment reacts with (2) to give (4). Following the simplest pathway (Scheme 1), the second insertion, (2) → (4), occurs directly into the open face of (2), merely requiring rupture of the already stretched Pt(4)–C(1) connection of the monoplatinum species. Furthermore, the weak B–B interaction independently observed in (2)

Scheme 1. ● C atom; i, $Pt(PEt_3)_2$. For clarity a constant atomic numbering scheme is maintained. In **(2)** above, the connectivities Pt_A–4 and 1–3 correspond to the links Pt(4)–C(1) and B(5)–B(8), respectively, of Figure 1. In **(4)** above, the connectivity 1–3 corresponds to B(2)–B(3) of Figure 2.

and **(4)** is maintained in the same position. In this way the first inserting metal atom ultimately occupies the capping site in **(4)**.

The precise stereochemistry of **(3)** remains in some doubt. If the basic framework reported previously[3] is correct the n.m.r. data dictate a 1,3,4,7-PtC_2PtB_5 architecture, but it is difficult to envisage how this would be formed. On the other hand, its i.r. spectrum is very similar to that of **(4)** and, certainly, the n.m.r. results are not inconsistent with a 1,4,5,6-PtC_2PtB_5 formulation.

References

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