Reaction of Bis(triethylphosphine)platinum and Pentakis(t-butyl isocyanide)-ruthenium with Dicarba-*nido*-hexaboranes(8): Molecular Structures of $[\textit{nido}\text{-}\mu_{4,5}\text{-}\{\textit{trans}\text{-}(Et_3P)_2Pt(H)\}\text{-}\mu_{5,6}\text{-}H\text{-}2,3\text{-}C_2B_4H_6]$, $[\textit{closo}\text{-}1,1\text{-}(Et_3P)_2\text{-}2,3\text{-}Me_2\text{-}1,2,3\text{-}PtC_2B_4H_4]$, and $[RuH(Bu^tNC)_5]^+$ $[\textit{nido}\text{-}2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_4H_5]^-$

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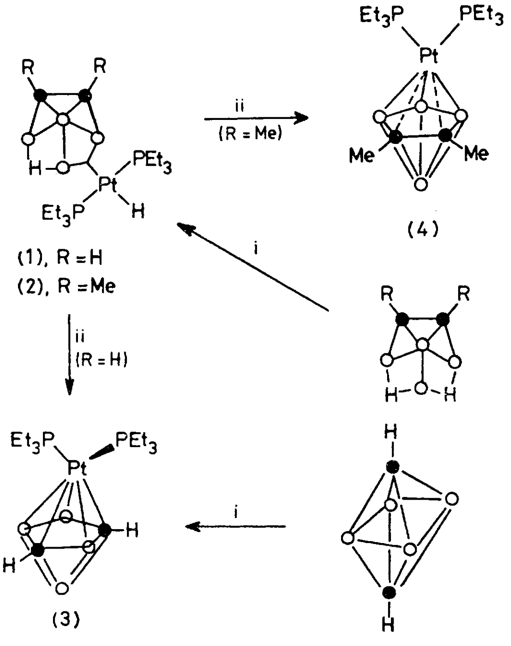
Summary Reaction of $[Pt(PEt_3)_2]$ with *nido*-2,3-$C_2B_4H_8$ or *nido*-2,3-Me_2-2,3-$C_2B_4H_6$ affords, respectively, $[\textit{nido}\text{-}\mu_{4,5}\text{-}\{\textit{trans}\text{-}(Et_3P)_2Pt(H)\}\text{-}\mu_{5,6}\text{-}H\text{-}2,3\text{-}C_2B_4H_6]$ and $[\textit{nido}\text{-}\mu_{4,5}\text{-}\{\textit{trans}\text{-}(Et_3P)_2Pt(H)\}\text{-}\mu_{5,6}\text{-}H\text{-}2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_4H_4]$, which on pyrolysis yield *closo*-platinacarbaboranes with non-adjacent and adjacent carbon atoms respectively; in contrast $[Ru(Bu^tNC)_5]$ reacts with *nido*-2,3-Me_2-2,3-$C_2B_4H_6$ to give $[RuH(Bu^tNC)_5]^+[\textit{nido}\text{-}2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_4H_5]^-$.

FOLLOWING the discovery[1] that d^{10} metal species can insert directly into 7 to 11 atom *closo*-carbaboranes we have explored the feasibility of obtaining metallacarbaboranes by a two-step oxidative-insertion by a transition metal species into a B–H bond of 2,3-dicarba-*nido*-hexaborane(8), followed by cage formation *via* elimination of H_2. Previous studies with *nido*-2,3-$C_2B_4H_8$ and *nido*-2,3-Me_2-2,3-$C_2B_4H_6$ have focused on the reaction of metal halides with the carbaborane mono-anion[2] or the high temperature reaction of the neutral carbaborane with $Fe(CO)_5$, Me_3Ga, or Me_3In[3] affording *closo*-derivatives.



Scheme. i, $[Pt(PEt_3)_2]$; ii, Heat; ●, C; ○, BH.

A hexane solution of bis(triethylphosphine)platinum‡ reacts at room temperature with *nido*-2,3-$C_2B_4H_8$ or *nido*-2,3-Me_2-2,3-$C_2B_4H_6$ to form, respectively, the crystalline 1:1 adducts (**1**) [colourless crystals, 48% yield, m.p. 40 °C, ν_{Pt-H} 2 055s and ν_{B-H} 2 570sh, 2 545s, 2 500s, and 2 450s cm^{-1}; n.m.r.: ^{11}B, (rel. extn. $BF_3{\cdot}Et_2O$) δ −0·46(2), 9·21(1), and 52·28(1) p.p.m.; ^{31}P (rel. extn. H_3PO_4) δ −15·50 p.p.m., *J*(Pt–P) 2647·7, *J*(H–P) 9·8 Hz] and (**2**) [pale yellow crystals, 52%, m.p. *ca.* 25 °C, ν_{Pt-H} 2 040s and ν_{B-H} 2 555sh, 2 540s, 2 510sh, and 2 440s cm^{-1}; n.m.r.: ^{11}B, δ 1·52(2), 10·88(1), and 45·6(1) p.p.m.; ^{31}P, δ −15·98 p.p.m.,

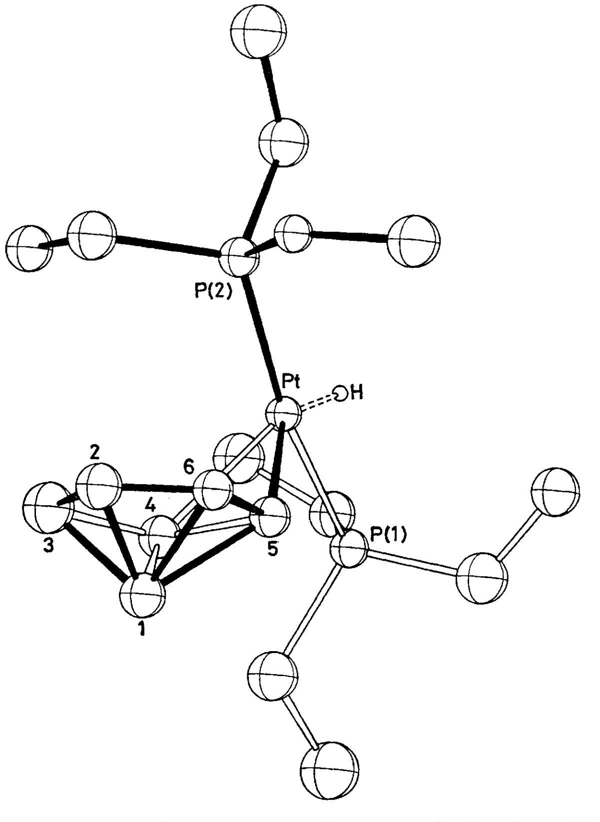


FIGURE 1. Molecular structure and cage numbering for $[\textit{nido}\text{-}\mu_{4,5}\text{-}\{\textit{trans}\text{-}(Et_3P)_2Pt(H)\}\text{-}\mu_{5,6}\text{-}H\text{-}2,3\text{-}C_2B_4H_6]$. Molecular parameters include Pt–P(1), 2·296(2); Pt–P(2), 2·285(2); Pt–B(4), 2·305(12); B(4)–B(5), 1·728(14); B/C(3)–B(4), 1·685(13); and C(2)–B/C(3), 1·478(12) Å; ∠P–Pt–P, 167·15(11)°.

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‡ Reaction of $[Pt(1,5\text{-}C_8H_{12})_2]$ with 2 equiv. of Et_3P in hexane affords yellow crystals of $[Pt(PEt_3)_2]$ [^{31}P n.m.r. δ −20·1 p.p.m., *J*(Pt–P) 3372 Hz], which reacts with H_2 to give *trans*-$[PtH_2(PEt_3)_2]$ and with 1 equiv. of Et_3P to give $[Pt(PEt_3)_3]$ [^{31}P n.m.r. δ −42·1 p.p.m., *J*(Pt–P) 4313 Hz].

J(Pt–P) 2667·8 Hz]. Although, these observations indicated that in both cases an oxidative-insertion into a bridged B–H bond had occurred affording isostructural molecules, the data did not elucidate the mode of bonding between the *trans*-PtHP$_2$ fragment and the carbaborane cage. This was established by a single crystal *X*-ray diffraction study of (**1**).

Crystal data: (**1**), $C_{14}H_{38}PtB_4P_2$, M 506·8, monoclinic, a = 10·970(4), b = 11·587(3), c = 9·459(3) Å, β = 114·47(2)°, U = 1094·3(6) Å^3, Z = 2, D_c = 1·538, μ(Mo-$K_{\bar{\alpha}}$) = 68·8 cm^{-1}, space group $P2_1$ or $P2_1/m$. The structure has been solved by conventional methods using 5106 independent reflections measured to θ = 37·5° (Mo-K_α radiation, Syntex $P2_1$ diffractometer, T *ca.* 215 K).§

Although Figure 1 shows the non-hydrogen skeleton of an asymmetric ordered molecule, the structure was solved on the assumption of space group $P2_1/m$ with atoms Pt, P(1), and P(2) and cage positions (1) and (2) on the crystallographic mirror plane. This treatment involved, however, partial disordering of the P(1) ethyl groups, and has led to a current R index of 0·06.

The carbaborane cage has the geometry of a *nido* pentagonal pyramid. Position (2) hosts one carbon atom with the other disordered over the symmetry related sites (3) and (6). The B(4)–B(5) link is bridged by the *trans*-PtH(PEt$_3$)$_2$ fragment, the acute dihedral angle between the PtB(4)B(5) and the C(2,3)B(4,5,6) planes being *ca.* 52·8°. The orientation of the platinum with respect to the η^2-bonded cage is thus related to that found in a number of comparable systems.[4]

At the present time terminal hydrogens have been located on all six cage atoms, while H(Pt) may reasonably be assumed to lie in, and bisect, the angle P–Pt–P. The remaining hydrogen atom presumably bridges the other facial B–B link, *i.e.* B(5)–B(6) for carbons at (2) and (3).

Pyrolysis of (**1**) (100 °C, 3 days) and (**2**) (100 °C, 2 h) in sealed tubes gave, respectively (Scheme), the yellow crystalline complexes (**3**) [45%, m.p. 78—80 °C; n.m.r.: ^{11}B, δ −1·75(3) and 7·38(1) p.p.m.; ^{31}P, δ −2·53, J(Pt–P) 3399·6 Hz] and (**4**) [80%, m.p. 128—130 °C; n.m.r.: ^{11}B, δ −50·32(1) and 6·32(3) p.p.m., ^{31}P, δ −20·23, J(Pt–P) 2487·8 Hz]. A single crystal *X*-ray study of (**4**) established the structure shown (Figure 2), where the adjacent carbon arrangement present in the *nido*-precursor (**2**) is still present.

Crystal data: (**4**), $C_{16}H_{40}PtB_4P_2$, M 532·8, monoclinic, a = 15·691(6), b = 10·118(6), c = 15·949(6) Å, β = 115·76(3)°, U = 2280·5(18) Å^3, Z = 4, D_c = 1·552, μ(Mo-$K_{\bar{\alpha}}$) = 66·1 cm^{-1}, space group $P2_1/a$. Refinement has converged at R = 0·067 using 7237 independent observed data collected to θ = 32·5° at *ca.* 215 K.§

The geometry of the metallacarbaborane polyhedron is that of a highly distorted and 'slipped' pentagonal bipyramid, symmetrical (within the limits of the experiment) about the plane defined by Pt, B(5), and B(7). The orientation and direction of slip of the PtP$_2$ fragment with respect to the bonded B$_3$C$_2$ face is similar to that in the related icosahedral complex [3,3-(Et$_3$P)$_2$-1,2,3-C$_2$PtB$_9$H$_{11}$].[5] Although the magnitude of the slip distortion in (**4**) is more difficult to estimate in the absence of a suitable reference plane, we take it to be considerably greater than in the analogous icosahedron for the following reasons: (i) Pt–C distances are, on average, *ca.* 0·28 Å longer in the present complex, (ii) Pt–B links are consistently shorter, Pt–B(4,6) by *ca.* 0·03 Å and Pt–B(5) by *ca.* 0·14 Å, and (iii) the 'folding' distortion, shown to be associated with slipping, and defined here as the acute dihedral angle between metalla-bonded BCCB and BBB sequences, is appreciably greater for the 7-atom polyhedron (21·4°; *cf.* 9·1° for the 12-atom case).

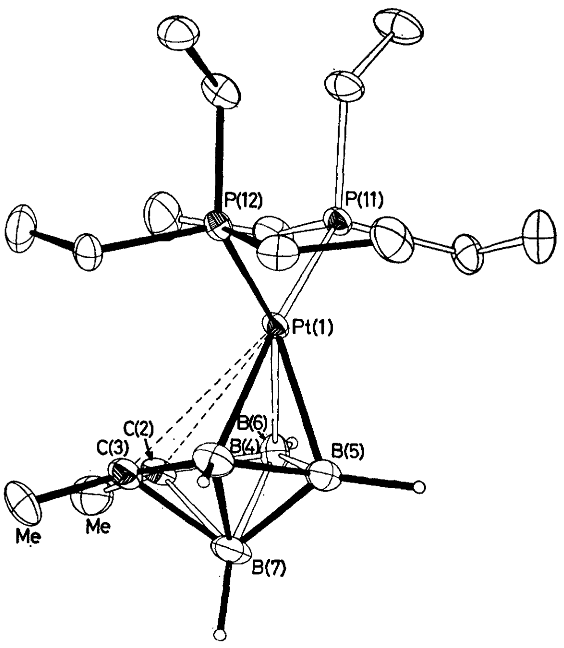

FIGURE 2. Molecular structure of [*closo*-1,1-(Et$_3$P)$_2$-2,3-Me$_2$-1,2,3-PtC$_2$B$_4$H$_4$]. Important molecular parameters are Pt–P(11), 2·2737(16); Pt–P(12), 2·2854(21); Pt · · · · C(2), 2·858(7); Pt · · · · C(3), 2·851(6); Pt–B(4), 2·257(8); Pt–B(5), 2·129(10); Pt–B(6), 2·244(8); and C(2)–C(3), 1·427(10) Å; ∠P–Pt–P, 105·75(6)°.

Comparison of the ^{11}B n.m.r. data for (**3**) and (**4**) established that the two molecules are not isostructural, and that in (**3**) the carbon atoms are unexpectedly[6] non-adjacent. This is supported by preliminary *X*-ray studies,[7] and also by the observation that (**3**) can be obtained (60 °C, 24 h) directly from reaction of [Pt(PEt$_3$)$_2$] with *closo*-1,6-C$_2$B$_4$H$_6$. It is interesting that pyrolysis of (**1**) at temperatures lower than 100 °C led only to incomplete conversion, there being no evidence for products containing adjacent carbon atoms. Conversely, pyrolysis of (**2**) for longer periods of time did not lead to products with non-adjacent cage carbons.

In contrast with the platinum systems, the reaction (room temperature, 1 h) of [Ru(Bu^{t}NC)$_5$][8] with *nido*-2,3-Me$_2$-2,3-C$_2$B$_4$H$_6$ affords the ionic 1:1 adduct (**5**) [ν_{Ru-H} 1 840s cm^{-1}, ^{1}H n.m.r. (C$_6$D$_6$) τ 18·73], which is formulated as [RuH(Bu^{t}NC)$_5$]$^+$[*nido*-2,3-Me$_2$-2,3-C$_2$B$_4$H$_5$]$^-$ arising by an oxidative insertion into a BH bond.

Crystal data: (**5**), [$C_{25}H_{46}RuN_5$]$^+$[$C_4H_{11}B_4$]$^-$, M 620·1, monoclinic, a = 16·309(13), b = 21·441(23), c = 12·190(9) Å β = 96·24(6)°, U = 4237(6) Å^3, Z = 4, D_c = 0·972, μ(Mo-$K_{\bar{\alpha}}$) = 3·85 cm^{-1}, space group $P2_1/a$.§

§ The atomic co-ordinates of all three structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The cation has idealized C_{4v} symmetry.¶ Equatorial Ru–C distances span the range 1·95(4) to 1·99(5) Å, whilst the unique axial Ru–C separation (*trans* to H) is somewhat longer at 2·07(6) Å. *cis*-Angles at the metal {86(2)—95(2)°} define an octahedral co-ordination within experimental error. All Ru–C–N and C–N–C sequences do not significantly deviate from linearity {angles range from 167(7) to 178(4) and 169(6) to 172(6)°, respectively}.

In the anion the cage atoms define a pentagonal pyramid in which the carbon atoms (unambiguously assigned *via* their terminal methyl groups) occupy adjacent facial sites. The basal B_3C_2 unit is planar to within 0·05 Å.

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¶ Crystals of (5) were of relatively poor quality for a diffraction study, and to date we have been unsuccessful in obtaining physically meaningful refinement of the methyl carbon atoms of the isocyanide groups. Although 3626 diffraction data were measured to $\theta = 30°$ (Mo-K_α radiation, *T ca.* 298 K) initial solution and refinement was concentrated on those 2337 reflections for which $(\sin\theta)/\lambda \leqslant 0{\cdot}5$. *R* currently stands at 0·18 for the $[Ru(CNC)]_5[C_4B_4]$ skeleton (Ru anisotropic).

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[6] Gas phase reaction of $Fe(CO)_5$ with *nido*-2,3-$C_2B_4H_8$ at 215 °C affords $[(\pi\text{-}2,3\text{-}C_2B_4H_6)Fe(CO)_3]$ and $[(\pi\text{-}2,3\text{-}C_2B_3H_7)Fe(CO)_3]$, and of MMe_3 (M = Ga, 215 °C; M = In, 100 °C) with *nido*-2,3-$C_2B_4H_8$ gives $[1\text{-MeM-}2,3\text{-}C_2B_4H_6]$ (ref. 3).

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