Metallaborane Chemistry. Part 10.[1] Insertion of Zerovalent Platinum Species into Bridging Boron–Hydrogen–Boron Bonds of 2,3-Dicarba-*nido*-hexaborane(8), 2,3-Dimethyl-2,3-dicarba-*nido*-hexaborane(8), and Monocarba-*nido*-hexaborane(9); Molecular and Crystal Structure of [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2Pt(H)$}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$]†

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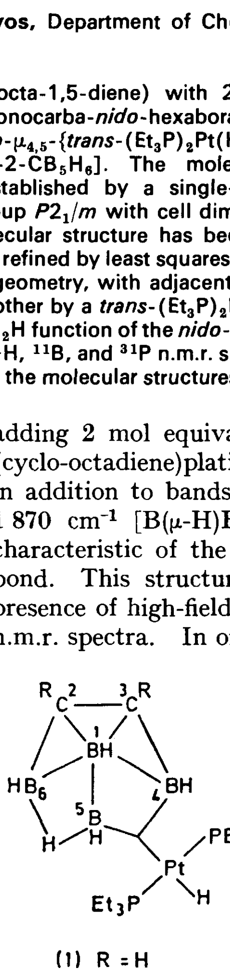
Reaction of $[Pt_2(\mu\text{-cod})(PEt_3)_4]$ (cod = cyclo-octa-1,5-diene) with 2,3-dicarba-*nido*-hexaborane(8), 2,3-dimethyl-2,3-dicarba-*nido*-hexaborane(8), and monocarba-*nido*-hexaborane(9) affords respectively, [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2Pt(H)$}-$\mu_{5,6}$-H-2,3-CB_5H_6], [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2Pt(H)$}-$\mu_{5,6}$-H-2,3-Me_2-2,3-$C_2B_4H_4$], and [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2Pt(H)$}-($\mu_{3,4}$-H)($\mu_{5,6}$-H)-2-CB_5H_6]. The molecular structure of [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2Pt(H)$}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$] has been established by a single-crystal *X*-ray diffraction study. Four molecules crystallise in the monoclinic space group $P2_1/m$ with cell dimensions $a = 10.970(4)$, $b = 11.587(3)$, $c = 9.459(3)$ Å, and $\beta = 114.47(2)$°. The molecular structure has been elucidated by the analysis of 5 106 diffractometer-measured reflection intensities, and refined by least squares to R 0.043. The cage core atoms of the molecule maintain a *nido* pentagonal-pyramidal geometry, with adjacent facial carbon atoms. Both pentagonal B–B links are bridged, one by hydrogen and the other by a *trans*-$(Et_3P)_2Pt(H)$ fragment, the latter demonstrating insertion by the metal nucleophile into a bridging B_2H function of the *nido*-carbaboranes. All cage hydrogen atoms have been located and positionally refined. The ^1H, ^{11}B, and ^{31}P n.m.r. spectra of the new compounds have been recorded, and the results are discussed in terms of the molecular structures of the carbaplatinaboranes.

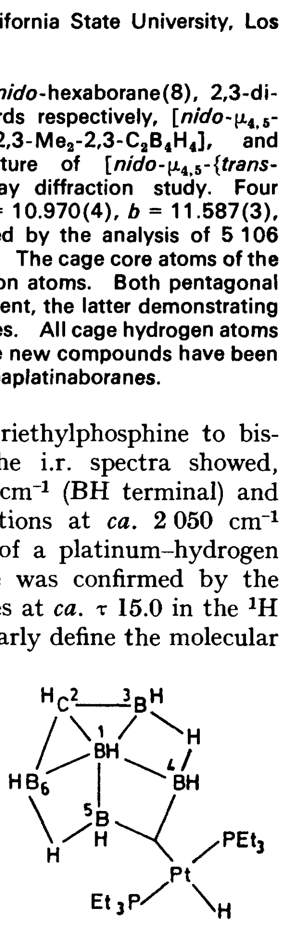
IN previous papers [1] we have described the formation of carbametallaboranes by the formal direct insertion of nucleophilic d^{10} nickel(0), palladium(0), or platinum(0) species into *closo*-carbaboranes. With the development [2] of a versatile synthetic route to highly nucleophilic platinum(0) species, we have explored the feasibility of preparing carbaplatinaboranes by an initial oxidative insertion of the d^{10} transition-metal species into a bridging BHB bond of the six-atom pentagonal-pyramidal compounds dicarba-*nido*-hexaborane(8), 2,3-dimethyl-2,3-dicarba-*nido*-hexaborane(8), and monocarba-*nido*-hexaborane(9). This process would be followed by a subsequent pyrolytic ring-closure step with loss of molecular hydrogen. It is interesting to note that at elevated temperatures (215 °C) pentacarbonyliron reacts [3] with *nido*-2,3-$C_2B_4H_8$ with loss of H_2 to form two products, one of which is formed by cage degradation. We expected, and this has been confirmed by our experiments, that reactions would occur at much lower temperatures with the platinum species, resulting in regioselective formation of products. This paper details the formation and structural characterisation of the hydridoplatinum complexes, the subsequent formation of the *closo*-carbaplatinaboranes being described in a subsequent paper. The salient features of this investigation have been mentioned in a preliminary communication.[4]

RESULTS AND DISCUSSION

The crystalline compounds (1), (2), and (3) are formed in high yield by treating the *nido*-carbaboranes 2,3-$C_2B_4H_8$, 2,3-Me_2-2,3-$C_2B_4H_6$, and 2-CB_5H_9 in hexane at room temperature with $[Pt_2(\mu\text{-cod})(PEt_3)_4]$ ‡ (cod = cyclo-octa-1,5-diene), the latter being prepared by adding 2 mol equivalents of triethylphosphine to bis(cyclo-octadiene)platinum.[2] The i.r. spectra showed, in addition to bands at 2 500 cm^{-1} (BH terminal) and 1 870 cm^{-1} [B(μ-H)B], absorptions at *ca.* 2 050 cm^{-1} characteristic of the presence of a platinum–hydrogen bond. This structural feature was confirmed by the presence of high-field resonances at *ca.* τ 15.0 in the ^1H n.m.r. spectra. In order to clearly define the molecular structures in the solid state of these complexes, which analysed respectively for $[PtH(PEt_3)_2(C_2B_4H_7)]$, $[PtH(PEt_3)_2(C_2B_4H_5Me_2)]$, and $[PtH(PEt_3)_2(CB_5H_8)]$, a single-crystal *X*-ray diffraction study was carried out on compound (1), for which a suitable crystal was available.



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



(3)

A perspective view of a single molecule is given in Figure 1, which also shows the atomic numbering scheme adopted (terminal cage H atoms carry the same number as the atom to which they are bound). Note that this Figure shows an ordered molecule for clarity. In the crystal H_b is disordered across the mirror plane

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† 4,5-μ-Hydridobis(triethylphosphine)platinum-2,3-dicarba-*nido*-hexaborane(8).

‡ Under high vacuum, $[Pt_2(\mu\text{-cod})(PEt_3)_4]$ slowly loses cod to form a white, sparingly soluble, microcrystalline solid formulated as $[\{Pt(PEt_3)_2\}_n]$. The compound $[Pt_2(\mu\text{-cod})(PEt_3)_4]$ reacts readily with H_2 (1 atm, 25 °C) and 1 mol equivalent of PEt_3 to form, respectively, *trans*-$[PtH_2(PEt_3)_2]$ and $[Pt(PEt_3)_3]$.

passing through B(1), C(2), and Pt, as are atoms C(11), C(111), C(12A), and C(12B). There is no way of knowing if the arrangement of the ethyl groups at P(1) has any influence on the relative positioning of H_b, and we simply present one of the two possibilities. Since, however, there is no precedent in heteroborane chemistry for a hydrogen atom bridging a C–B link, the compound may confidently be formulated as [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2$Pt(H)}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$]. Hence in an ordered molecule the second facial carbon atom is at position (3) [structural formula (1) with the H_b across the B(5)–B(6) edge].

For the sake of completeness the hydrogen atom terminally bound to Pt is shown (Figure 1) in an idealised position (bisecting the P–Pt–P angle, with Pt–H 1.40 Å). However, we emphasise that this atom could not be located and did not contribute (albeit in a minor role) to structure-factor calculations. Internuclear distances (uncorrected for thermal effects) and selected interbond angles are presented in Tables 1 and 2, respectively (all angles involving hydrogen atoms other than H_b being deposited as Appendix A *).

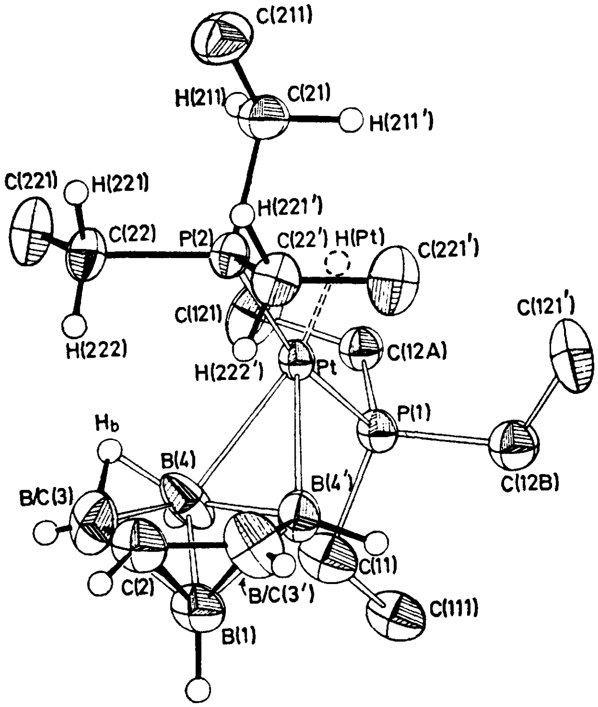

FIGURE 1 The molecule [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2$Pt(H)}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$] with the numbering used in the crystallographic study. Non-H atom thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have an artificial radius of 0.1 Å for clarity

Atoms B(1)C(2)B/C(3)B(4) and their mirror images (where appropriate) define a (*nido*) pentagonal pyramid whose distortions from C_{5v} geometry are simple consequences of the differing radii of boron and carbon atoms in polyhedra based on a pentagonal bipyramid.[5]

The cage architecture is consistent with that predicted by the Polyhedral Skeletal Electron Pair Theory[6] if the bridging metal atom is formally considered as Pt^{II}, one valence electron being available for cage bonding.

Of the three unique apical † distances, B(1)–B(4) [1.763(14) Å] is naturally the longest, whilst B(1)–B/C(3) and B(1)–C(2) are equivalent at 1.727(14) and 1.732(13) Å, respectively. It has already been emphasised[5] that the effect of carbon-atom substitution is much more pronounced with respect to the equatorial links in such polyhedra and, indeed, the distances C(2)–B/C(3), B/C(3)–B(4), and B(4)–B(4') increase steadily, *viz.* 1.463(11), 1.658(10), and 1.713(11) Å respectively, as their degree of carbon character is reduced. Whilst it is probable that B/C(3)–B(4) is slightly lengthened by virtue of its hydrogen bridge, the observed value is in close agreement with that recorded [1.65(3) Å, unbridged] for the carbametallaborane [(η-C_5H_5)Co($MeC_2B_3H_4$)Co(η-C_5H_5)], the only comparable

TABLE 1

Internuclear distances (Å) for the compound [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2$Pt(H)}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$]

Cage atoms			
B(1)–C(2)	1.732(13) [a]	B(1)–H(1)	1.08(17)
B(1)–B/C(3)	1.727(14)	C(2)–H(2)	0.97(16)
B(1)–B(4)	1.763(14)	B/C(3)–H(3)	0.65(11)
C(2)–B/C(3)	1.463(11)	B(4)–H(4)	1.11(9)
B/C(3)–B(4)	1.658(10)	B/C(3)–H_b	1.20(23)
B(4)–B(4') [b]	1.713(11)	B(4)–H_b	1.21(18)
B(4)–Pt	2.303(11)		
Pt–PEt_3 fragments			
Pt–P(1)	2.295 6(17)	Pt–P(2)	2.286 0(19)
P(1)–C(11)	1.847(16)	P(2)–C(21)	1.839(14)
C(11)–C(111)	1.549(17)	C(21)–C(211)	1.553(14)
P(1)–C(12A)	1.868(12)	C(21)–H(211)	1.13(9)
C(12A)–C(121)	1.461(14)	P(2)–C(22)	1.836(6)
P(1)–C(12B)	1.771(14)	C(22)–C(221)	1.514(10)
C(12B)–C(121')	1.530(20)	C(22)–H(221)	1.07(9)
		C(22)–H(222)	0.99(12)

[a] Estimated standard deviations in parentheses throughout this paper. [b] Primed atoms are the result of reflection in the crystallographic mirror at *y* 0.25.

TABLE 2

Important interbond angles (°) for the compound [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2$Pt(H)}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$] *

C(2)–B(1)–B/C(3)	50.0(4)	P(1)–Pt–P(2)	167.20(8)
B/C(3)–B(1)–B(4)	56.7(5)	Pt–P(1)–C(11)	116.7(3)
B(4)–B(1)–B(4')	58.1(5)	Pt–P(1)–C(12A)	111.7(3)
B(1)–C(2)–B/C(3)	64.8(5)	Pt–P(1)–C(12B)	114.5(4)
B(1)–B/C(3)–C(2)	65.2(6)	C(11)–P(1)–C(12A)	101.8(6)
B(1)–B/C(3)–B(4)	62.7(6)	C(11)–P(1)–C(12B)	106.1(7)
H_b–B/C(3)–B(4)	47(8)	C(12A)–P(1)–C(12B)	104.6(6)
B(1)–B(4)–B/C(3)	60.5(6)	P(1)–C(11)–C(111)	116.2(11)
B(1)–B(4)–B(4')	60.9(5)	P(1)–C(12A)–C(121)	114.3(8)
Pt–B(4)–B(4')	68.2(5)	P(1)–C(12B)–C(121')	116.2(9)
H_b–B(4)–B/C(3)	46(11)	Pt–P(2)–C(21)	111.1(3)
B/C(3)–H_b–B(4)	87(15)	Pt–P(2)–C(22)	116.0(2)
B(4)–Pt–B(4')	43.7(3)	C(21)–P(2)–C(22)	104.2(3)
B(4)–Pt–P(1)	91.9(2)	C(22)–P(2)–C(22')	104.0(3)
B(4)–Pt–P(2)	100.0(2)	P(2)–C(21)–C(211)	115.8(9)
		P(2)–C(22)–C(221)	112.8(4)

* Angles involving terminal hydrogen atoms are deposited (Appendix A).

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* All Appendices may be recovered from Supplementary Publication No. SUP 22561 (25 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

† In a pentagonal-pyramidal or bipyramidal geometry, *apical* interatomic distances are measured from the five-connected (with respect to the cage) to the four-connected core atoms, whilst *equatorial* links are those between the four-connected centres.

system in the literature.[7] The B(4)–B(4′) link also carries a bridging function (the metal fragment) but apparently does not appreciably lengthen, falling centrally in the known [5] range (1.686—1.736 Å) of unbridged equatorial B–B distances.

The five atoms C(2)B/C(3)B(4)B(4′)B/C(3′) are rigorously planar (the plane being defined by the equation $10.916x - 4.758z = 4.480$ Å, where x and z are the atomic co-ordinates) the maximum out-of-plane distortion being only *ca.* 0.002 Å [C(2)]. With respect to this plane the equatorial hydrogen atoms, H(2), H(3), and H(4), are depressed towards B(1) by *ca.* 19, 14, and 23°, respectively. It should be noted that although the lengths of X–H bonds, as determined by *X*-ray crystallography, are subject to systematic error [8] and, indeed, in the present compound cage atom–H terminal bonds vary in apparent length between 0.65(11) and 1.11(9) Å, this error is always *along* the X–H vector. It follows therefore that directional quantities defined by this vector may be regarded with a reasonable degree of confidence. The observed hydrogen-atom depression in (1), mentioned above, has previously been observed in a similar sense in the metalla-bridged borane anion $[nido\text{-}\mu_{2,3}\text{-}\{(OC)_3Fe\}\text{-}\mu_{4,5}\text{-}H_3B\text{-}(\mu\text{-}H)_3\text{-}B_7H_7]^-$ (ref. 9), and in the carbaborane *nido*-$(\mu\text{-}H)_2\text{-}2,3\text{-}C_2B_4H_6$,[10,11] and its C-methylated analogue.[10] For the carbaboranes, the depression angles range from 7.1 to 18.0° with a weighted mean of 12(3)°, and it is generally true that the greatest angles are found at the carbons. However, these atoms are the only ones not involved in hydrogen bridges, and thus it is clearly impossible with current data to apportion the relative effects of bridging and of heteroatom substitution on this angle.

The two bridging atoms, H_b and Pt, define ' bridge planes,' [B/C(3), H_b, B(4)] and [B(4), Pt, B(4′)], which are elevated by *ca.* 55 and 52.7° respectively, from the plane of the open face of the molecule. The angles quoted (x°) are the *acute* dihedral angles. To collapse the bridging atom onto the open face of the cage such that it lies *inside* the pentagon requires its rotation through $(180 - x)$° about the lines B/C(3) · · · B(4) and B(4) · · · B(4′) respectively. Even though H_b represents only a ' half ' hydrogen atom in the crystallographic analysis, we are confident of its refined position since the relevant bridge plane elevation angle, H_b–B distances, and H_b–B–B angles that it makes are all very reasonable.

Metal atoms bridging the five-atom faces of pentagonal-pyramidal boranes in a similar (η^2) manner are found with the $Fe(CO)_3$-bridged molecule [9] previously discussed, and for $[nido\text{-}B_6H_{10}\text{-}\mu(Cl_2Pt)\text{-}nido\text{-}B_6H_{10}]$.[12] A four-atom face is bridged in the compound $[nido\text{-}\mu\text{-}\{(Ph_3P)_2Cu\}\text{-}(\mu\text{-}H)_3\text{-}B_5H_5]$,[13] whilst in $[nido\text{-}\mu\text{-}(Me_2Al)\text{-}C_2B_9H_{12}]$ the cage has a *nido*-icosahedral geometry.[14] In the iron and platinum systems insufficient data are available to calculate the bridge elevation angles, but we note that the Pt–B distance [2.27(2) Å][12] closely agrees with our value of 2.303(11) Å.

For the fully documented molecules, bridge elevation angles are 50.0 (Cu) and 45.9° (Al). The general similarity of the latter angle with those of the copper and our platinum compounds lends support to the suggestion [14] that the (aluminium) bridged boron atoms do not additionally carry terminal hydrogens, since if they did unfavourable Al · · · H contacts would result by virtue of the substituent elevation angle of an icosahedral polyhedron being *ca.* 26°. The ' substituent elevation angle ' is simply the negative of the substituent depression angle already introduced.

Short intra- and inter-molecular non-bonded distances have been listed in Table 3. Whilst it is likely that the intramolecular crowding may explain the asymmetric B(4)–Pt–P angles [wider to P(2) by *ca.* 8°], the crystalline array is generally free from severe intermolecular forces. Figure 2 provides a view of the crystal packing, as seen along the *b* axis, looking towards the origin.

TABLE 3

Non-bonded contacts (Å) close to or more than 1 σ less than the van der Waals sum * for the compound $[nido\text{-}\mu_{4,5}\text{-}\{trans\text{-}(Et_3P)_2Pt(H)\}\text{-}\mu_{5,6}\text{-}H\text{-}2,3\text{-}C_2B_4H_6]$

Intramolecular		Intermolecular	
$H_b \cdots H(222)$	2.28(20)	$H(1) \cdots C(211^{I})$	3.09(13)
$H_b \cdots C(221)$	3.02(22)	$H(211) \cdots C(221^{II})$	2.87(10)
$H(4) \cdots C(11)$	2.54(8)	$C(121) \cdots C(211^{II})$	2.760(10)
		$C(121) \cdots C(121^{III})$	3.852(12)

Roman numeral superscripts denote the following equivalent positions, relative to the reference molecule at x, y, z. I $1 + x, \frac{1}{2} - y, z$; II $-x, 1 - y, -z$; III $1 - x, 1 - y, 1 - z$

* Radii taken as H 1.20 Å, Me 2.0 Å.

The ^{11}B, ^{1}H, and ^{31}P n.m.r. spectra of compounds (1)—(3) show many similarities. The ^{11}B spectra (^{1}H-decoupled) all exhibit a resonance at high field (*ca.* -50 p.p.m.), which is assigned to the apex boron in the cage, and two resonances at lower field due to the basal boron atoms. The ^{1}H-undecoupled ^{11}B spectra show the apex boron as a doublet, arising from coupling to the single terminal proton, whilst the basal boron resonances are broadened, but not resolved, due to coupling with the terminal and bridging protons.

All of the ^{1}H spectra (^{11}B-decoupled) show a high-field resonance assigned to Pt*H* at *ca.* τ 15. In addition, signals at *ca.* τ 12, 10, and 5.5 were observed which are assigned respectively to H(bridge), H(apex), and H(basal) boron–hydrogen environments. The ^{1}H spectrum of (1) showed broad singlets at τ 3.64 and 3.76 which are attributed to the cage CH protons, these being replaced in the corresponding spectrum of (2) by singlets at τ 7.60 and 7.70 due to cage CMe groups in two different environments. It is interesting that only the low-field cage CMe signal showed ^{195}Pt satellites suggesting that this signal can be assigned to the methyl substituents nearest to the $PtH(PEt_3)_2$ group. In the case of the unsubstituted system, partial ^{195}Pt coupling was observed with both cage C*H* signals.

These spectral data are all indicative of cage structures in solution identical to that established in the solid state for compound (1). However, examination of the n.m.r. spectra associated with the $PtH(PEt_3)_2$ group revealed an unexpected feature. In all three compounds the PEt protons appear in the ^{1}H spectrum as complex multiplets at *ca.* τ 8.5 and 9.1. The ^{31}P n.m.r. spectra (^{1}H decoupled, room temperature) of (1), (2), and (3) showed singlet resonances with ^{195}Pt satellites at −15.5, −16.0, and −14.5 p.p.m., respectively. On selectively decoupling the protons of the ethyl groups of (1) and (3), the ^{31}P resonance appeared as a doublet (9.8 and 10.0 Hz, respectively) due to the coupling with the Pt*H* proton. Considering first the two compounds (1) and (2), the observations of only *one* ^{31}P environment is surprising in view of the structure established in the solid state for (1). There are two possible explanations for this observation: accidental coincidence of ^{31}P chemical shifts, or alternatively, dynamic behaviour associated with apparent rotation about an axis through the platinum and the BPtB three-centre bond. Examination of the ^{31}P spectrum of (1) and (2) at −90 °C in [$^{2}H_8$]toluene as solvent revealed sharp singlets (with ^{195}Pt satellites) at −15.6 and −15.9 p.p.m., respectively, with no evidence of broadening.

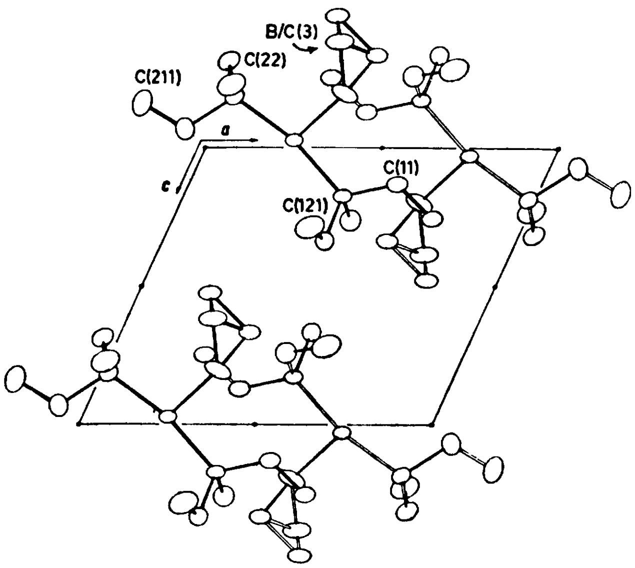

FIGURE 2 Packing diagram for the compound [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2Pt(H)$}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$]. For the sake of clarity hydrogen atoms are omitted

In regard to compound (3), if we assume the phosphine ligands are disposed above and below the CB_4 basal plane, as in the solid-state structure of (1), there are two possible molecular geometries. The $PtH(PEt_3)_2$ group can be either *trans* or *cis* to the basal carbon. Examination of the ^{1}H (^{11}B-decoupled) spectrum of (3) shows the cage C*H* as a resonance at τ 4.12 with no evidence of ^{195}Pt satellites, thus leading us to tentatively favour the illustrated structure with the carbon remote from the platinum. Regarding the question of the rotation or non-rotation of the $PtH(PEt_3)_2$ group relative to the cage, as in the case of compounds (1) and (2), it is not possible to distinguish between the two alternative explanations, *i.e.* coincidence or rotation, and therefore this aspect of the behaviour of these molecules in the liquid phase remains unresolved.

The generation of anionic species such as $[C_2B_4H_7]^-$ and reaction with [FeI$(CO)_2$(η-C_5H_5)] has formed the basis of the synthesis [3,15] of [*nido*-$\mu_{4,5}$-{(η-C_5H_5)Fe$(CO)_2$}-$\mu_{5,6}$-H-2, 3-$C_2B_4H_6$], and it is likely that in formation of compounds (1)—(3) the initial step in the reaction with the nucleophilic platinum species involves proton abstraction to form an ionic intermediate, for example, $[PtH(PEt_3)_2]^+[C_2B_4H_7]^-$, which then undergoes rapid charge collapse to form the isolated product.

EXPERIMENTAL

N.m.r. spectra were recorded on JEOL PS-100 and PFT-100 spectrometers (^{1}H, ^{11}B, ^{31}P), a Varian Associates HA-100 spectrometer (^{1}H, ^{11}B-decoupled), and a Brüker WP-60 spectrometer (^{13}C, ^{11}B-decoupled). The external references for 32.08-MHz ^{11}B and 40.48-MHz ^{31}P spectra were $OEt_2{\cdot}BF_3$ and 85% H_3PO_4, respectively. The ^{11}B shifts are to high frequency (low field) of $OEt_2{\cdot}BF_3$, and the ^{31}P shifts to low frequency of H_3PO_4. All spectra were recorded in deuteriobenzene solution with ^{1}H decoupling unless otherwise stated. Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer. Molecular weights were measured from mass spectra on an A.E.I. MS902 instrument operating at 70 eV.*

All reactions were performed in a dry, oxygen-free, nitrogen atmosphere. The carbaboranes *nido*-2,3-$C_2B_4H_8$ and *nido*-2,3-Me_2-2,3-$C_2B_4H_6$ were prepared from B_5H_9 and acetylene or but-2-yne, respectively.[16] The compound *nido*-2-CB_5H_9 was prepared by pyrolysis of 1-MeB_5H_9 in a flow system at 600 °C.[17] The carbaboranes were purified before use by either trap-to-trap distillation or cold-column distillation.

Preparation of [Pt_2(μ-cod)$(PEt_3)_4$].—A solution of triethylphosphine (2 mmol) in hexane (4.5 cm^3) was added dropwise to a stirred slurry of bis(cyclo-octa-1,5-diene)-platinum (0.4 g, 1 mmol) in hexane (5 cm^3). After 1 h at room temperature the volatile material was removed *in vacuo*, and the residue extracted with hexane (25 cm^3). Reduction of the volume of the solvent and cooling (−20 °C) afforded pale yellow *crystals* of [Pt_2(μ-cod)$(PEt_3)_4$] (0.36 g, 75%) (Found: C, 39.5; H, 7.5. $C_{32}H_{72}P_4Pt_2$ requires C, 39.5; H, 7.5%), $\nu_{max.}$ (Nujol) at 1 418(sh), 1 407w, 1 240m, 1 212m, 1 138w, 1 105w, 1 035s, 1 023(sh), 995m, 945w, 932m, 853w, 821m, 772(sh), 763s, 732m, 710s, 693w, 665w, 635(sh), 622s, 555s, 520w, and 410br cm^{-1}. N.m.r. spectra: ^{1}H, τ 6.82(br), 7.14 (br), 7.88 (br, cod), 8.36 (m), and 9.00 (m, PEt); ^{13}C, 9.0 (CH_3), 22.3 (CH_2), 38.4 [CH_2, cod, ^{2}J(PtC) 28, ^{3}J(PtC) 87, ^{3}J(PC) 6], and 52.7 p.p.m. [CH, cod, ^{1}J(PtC) 227, ^{2}J(PC) 13 Hz]; ^{31}P, −20.1 p.p.m. [J(PtP) 3 372 Hz].

Reaction of [Pt_2(μ-cod)$(PEt_3)_4$] *with* (*a*) *Dicarba*-nido-*hexaborane* (8).—The compound *nido*-2,3-$C_2B_4H_8$ (1.2 mmol) was condensed (−196 °C) into a tube fitted with a Westef stopcock containing a solution of [Pt_2(μ-cod)$(PEt_3)_4$] (0.43 g, 0.44 mmol) in hexane (10 cm^3). The tube and contents were allowed to warm to room temperature, the solution rapidly becoming colourless. After 1 h the volatile material was removed *in vacuo* leaving a colourless oil, which was extracted with hexane (3 cm^3), filtered, and cooled (−78 °C) affording colourless *crystals* of (1), [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2$-Pt(H)}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$] (0.24 g, 48%), m.p. 40 °C (Found: C, 32.1; H, 7.6. $C_{14}H_{38}B_4P_2Pt$ requires C, 33.1; H, 7.5%), $\nu_{max.}$ (Nujol) at 2 570(sh), 2 545s, 2 500s, 2 450s,

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 atm = 101 325 Pa.

2 055s, 1 413m, 1 335w, 1 295m, 1 265m, 1 250(sh), 1 115w, 1 105m, 1 080m, 1 055m, 1 044s, 1 010m, 982m, 935m, 875m, 850m, 833m, 815m, 765s, 758(sh), 745s, 732s, and 715m cm^{-1}. N.m.r. spectra: ^{1}H (^{11}B-decoupled), τ 3.64 [s(br), 1 H, cage CH], 3.76 [s(br), 1 H, cage CH], 5.50 [s(br), 1 H, basal BH, *J*(PtH) 84], 5.84 [s(br), 2 H, basal BH, *J*(PtH) 80], 8.39 (m, 4 H, PCH_2CH_3), 9.13 (m, 6 H, PCH_2CH_3), 10.26 [s(br), 1 H, apex BH], 12.04 [s(br), 1 H, BHB, *J*(PtH) 40], and 14.42 [t, 1 H, HPt, *J*(PH) 30, *J*(PtH) 960 Hz]; ^{11}B, 0.46 (br, 2 B, basal B), −9.2 (br, 1 B, basal B), and −52.3 p.p.m. [br, 1 B, apex B, *J*(BH) 168.5 Hz (from ^{1}H-undecoupled spectrum)]; ^{31}P, −15.5 p.p.m. [s, *J*(PtP) 2 648, *J*(PH) 9.8 Hz (from ^{1}H partially decoupled spectrum)]; ^{13}C (^{11}B-decoupled), 8.5 (PCH_2CH_3), 19.0 (PCH_2CH_3), 114.9 (cage CH), and 118.3 p.p.m. (cage CH).

(*b*) *2,3-Dimethyl-2,3-dicarba*-nido-*hexaborane*(8). Similarly, reaction of *nido*-2,3-Me_2-2,3-$C_2B_4H_6$ (1.2 mmol) with [Pt_2(μ-cod)$(PEt_3)_4$] (0.43 g, 0.44 mmol) in hexane (15 cm^3) gave from hexane (−78 °C) colourless *crystals* of (2) [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2$Pt(H)}-$\mu_{5,6}$-H-2,3-Me_2-2,3-$C_2B_4H_4$] (0.28 g, 52%), m.p. *ca.* 25 °C (Found: C, 34.9; H, 8.1%; *M* 533. $C_{16}H_{42}B_4P_2Pt$ requires C, 35.7; H, 7.9%; *M* 535), $\nu_{max.}$ (Nujol) at 2 555(sh), 2 540s, 2 510(sh), 2 440s, 2 040s, 1 415m, 1 260(br), 1 055(sh), 1 040s, 1 020m, 982m, 940w, 895w, 773s, 745m, 732m, 700w, 638m, and 610w cm^{-1}. N.m.r. spectra: ^{1}H (^{11}B-decoupled), τ 5.96 [s(br), 1 H, basal BH, *J*(PtH) 72], 6.24 [s(br), 2 H, basal BH], 7.60 [s, 3 H, cage CMe, *J*(PtH) 8], 7.70 (s, 3 H, cage CMe), 8.36 (m, 4 H, PCH_2CH_3), 9.08 (m, 6 H, PCH_2CH_3), 10.22 [s(br), 1 H, apex BH], 12.40 [s(br), 1 H, BHB, *J*(PtH) 42], and 14.38 [t, 1 H, PtH, *J*(PH) 32, *J*(PtH) 948 Hz]; ^{11}B, −1.52 (s, 2 B, basal B), −10.9 (s, 1 B, basal B), and −45.6 p.p.m. [s, 1 B, apex B, *J*(BH) 159 Hz (from ^{1}H-undecoupled spectrum)]; ^{31}P, −16.0 p.p.m. [s, *J*(PtP) 2 668 Hz]; ^{13}C (^{11}B-decoupled), 8.6 (PCH_2CH_3) and 19.1 p.p.m. (PCH_2CH_3).

(*c*) *Monocarba*-nido-*hexaborane*(9). A slurry of [Pt_2(μ-cod)$(PEt_3)_4$] (0.3 g, 0.2 mmol) in diethyl ether (10 cm^3) contained in a tube fitted with a high-pressure Westef stopcock was cooled (−196 °C) and monocarba-*nido*-hexaborane(9) (1 mmol) was condensed into the vessel. After 2 h at room temperature the solution became orange and a dark solid was deposited. The solution was removed with a syringe from the tube. This solution was evaporated *in vacuo*. The resulting orange solid was extracted with hexane (20 cm^3) and the volume of the solvent reduced. Cooling (−20 °C) gave pale yellow feathery *crystals* of (3) [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2$Pt(H)}-($\mu_{3,4}$-H)($\mu_{5,6}$-H)-2-CB_5H_6] (0.08 g, 23%), m.p. 61—63 °C (Found: C, 29.9; H, 7.6%; *M* 502. $C_{13}H_{39}B_5P_2Pt$ requires C, 30.9; H, 7.4%; *M* 507), $\nu_{max.}$ (Nujol) at 2 560s, 2 530(sh), 2 070m, 1 890(br), 1 410m, 1 250m, 1 235w, 1 150w, 1 100m, 1 035s, 1 005m, 930w, 865w, 845m, 765s, 725s, 710w, 630m, 465w, and 415w cm^{-1}. N.m.r. spectra: ^{1}H, τ 4.12 (s, 1 H, cage CH), 4.86 [s(br), 2 H, basal BH], 5.34 [s(br), 2 H, basal BH, *J*(PtH) 84], 8.53 (m, 4 H, PCH_2CH_3), 9.20 (m, 6 H, PCH_2CH_3), 10.38 [s(br), 1 H, apex BH], 12.44 [s(br), 2 H, BHB], and 15.24 [t, 1 H, HPt, *J*(PH) 29, *J*(PtH) 1 036 Hz]; ^{11}B, 14.9 (s, 2 B, basal B), −5.6 (s, 2 B, basal B), and −50.5 p.p.m. [s, 1 B, apex BH, *J*(BH) 156 Hz (from ^{1}H-undecoupled spectrum)]; ^{31}P, −14.5 p.p.m. [s, *J*(PtP) 2 627, *J*(PH) 10 Hz (from ^{1}H partially decoupled spectrum)]; ^{13}C (^{11}B-decoupled), 7.6 (PCH_2CH_3), 18.8 (PCH_2CH_3), and 102.0 p.p.m. (cage CH).

Determination of Molecular Structure of Compound (1).—A single crystal, *ca.* 0.3 × 0.25 × 0.1 mm, was mounted on a quartz fibre with an epoxy-resin adhesive, and examined photographically (oscillation, and zero- and first-level Weissenberg about *b*, using Cu-K_α radiation) for space group and approximate unit-cell dimensions. Thereafter it was transferred to a Syntex $P2_1$ four-circle diffractometer equipped with a ϕ-axis low-temperature device (N_2 stream), and slowly cooled to *ca.* 215 K. Setting and data collection followed an established procedure [18] with the following pertinent details: 15 reflections, $20 < 2\theta < 28°$ (Mo-K_α), taken from a 30-min rotation photograph and accurately centred in 2θ, ω, and χ, were used to generate the real space vectors and intervector cosines from which the unit cell was chosen by inspection. The orientation matrix, cell dimensions, and associated errors were calculated by a least-squares fit. For data collection, graphite-monochromated Mo-K_α *X*-radiation ($\lambda_{\alpha1}$ 0.709 26, $\lambda_{\alpha2}$ 0.713 54 Å) and a θ—2θ scan in 96 steps were used. Peaks were scanned from 1.0° below $K_{\alpha1}$ to 1.0° above $K_{\alpha2}$ at speeds between 0.042 5 and 0.488 3° s^{-1}, the precise rate being dependent on an initial 2-s peak count in which 150.0 and 1 500.0 were used as threshold counts. The intensities of 5 688 independent reflections ($0 + k - l$ and $+h + k \pm l$) were measured in two shells [$2.9 \leqslant 2\theta \leqslant 45.0°$ and $45.1 \leqslant 2\theta \leqslant 75.0°$] over a total period of *ca.* 161 h *X*-ray exposure. Throughout this time three check reflections ($17\bar{2}$, $\bar{2}4\bar{3}$, and $5\bar{1}\bar{1}$) were re-monitored once every 50 reflections, but subsequent analysis [19] of their net intensities as individual functions of time revealed no significant crystal decomposition or movement, or source variance. 5 106 Reflections had $I \geqslant 1.0\sigma(I)$ and were retained for structure solution. External crystal faces were identified as {$10\bar{1}$}, {010}, and {001} and their inversion equivalents and the data corrected for *X*-ray absorption *via* a Gaussian integration approximation.

Crystal data. $C_{14}H_{38}B_4P_2Pt$, $M = 506.8$, Monoclinic, $a = 10.970(4)$, $b = 11.587(3)$, $c = 9.459(3)$ Å, $\beta = 114.47(2)°$, $U = 1\,094.3(6)$ Å^3, $D_c = 1\,538$ g cm^{-3}, $Z = 2$, $F(000) = 500$, μ(Mo-K_α) = 68.8 cm^{-1}, space group $P2_1$ or $P2_1/m$ from the systematic absence $0k0$, $k = 2n + 1$.

Data were further corrected for Lorentz and polarisation effects, and the approximate *x* and *z* co-ordinates of the metal deduced from inspection of a three-dimensional Patterson synthesis. Initially the molecular structure was solved in the non-centrosymmetric space group $P2_1$, P, C(alkyl), and cage atoms (the latter all treated as boron) being located from a difference electron-density map computed after two cycles of isotropic full-matrix least-squares refinement of the platinum atom. Since, however, an effective mirror plane of symmetry, perpendicular to the *b* crystallographic axis, was found to bisect the atomic array, the centrosymmetric $P2_1/m$ was adopted ($Z = 2$ requires precise C_s symmetry) and all subsequent discussion refers to this space group.

The metal and phosphorus atoms (all of which lie in the crystallographic mirror plane) were allowed anisotropic thermal motion, and the molecular structure refined through several cycles of least squares. The refined temperature factors of several of the carbon atoms of the ethyl groups of P(1) were unacceptably high [$U_{C(11)}$ 0.19, $U_{C(12)}$ 0.16, $U_{C(111)}$ 0.10 Å^2; *cf.* $U_{C(121)}$ 0.05 Å^2] suggesting that a partial disordering of this fragment might be appropriate. Hence the description defined by Table 4 was adopted, C(12) being divided into two components A and B, and the C(11)C(111) group being moved slightly off the mirror plane at $y = 0.25$. It should be noted that, although this arrangement could be accommodated without disorder by reverting back to $P2_1$, parallel refinements in both space groups gave a considerably better fit for the molecule as a whole in $P2_1/m$.

Reflection intensities were weighted such that $w^{-1} = x \cdot y$ with $x = F_o/a$ if $F_o > a$, $x = 1$ if $F_o \leqslant a$, and $y = b/\sin\theta$ if $\sin\theta < b$, $y = 1$ if $\sin\theta \geqslant b$ in which a and b took values of 35.0 and 0.45, respectively. An attempt to distinguish the carbon atoms of the cage on the basis of refined temperature factors was not made since two of the atoms in the open face of the ligand are directly linked to platinum (and would therefore be expected to have comparatively low U values). Examination of internuclear distances within the cage, however, quickly revealed that position (2) hosts one carbon atom with the other equally disordered between the symmetry-related sites (3) and (6).

TABLE 4

Final positional parameters (fractional co-ordinate, $\times 10^5$ Pt, P; $\times 10^4$ B, C; $\times 10^3$ H) for [*nido*-$\mu_{4,5}$-{*trans*-$(Et_3P)_2Pt(H)$}-$\mu_{5,6}$-H-2,3-$C_2B_4H_6$]

Atom	x	y	z
B(1)	3 647(11)	2 500	−3 354(10)
C(2)	2 022(11)	2 500	−4 773(9)
B/C(3) [a]	2 429(11)	3 555(10)	−3 846(8)
B(4)	3 242(10)	3 239(7)	−1 977(8)
Pt	24 242(3)	25 000	−2 810(3)
P(1)	45 170(19)	25 000	17 293(19)
C(11) [b]	5 901(13)	3 069(15)	1 302(13)
C(111) [b]	7 336(13)	2 835(21)	2 543(21)
C(12A) [b]	4 593(11)	3 461(10)	3 349(13)
C(12B) [b]	5 055(14)	1 135(13)	2 612(16)
C(121)	3 996(10)	4 599(7)	2 850(10)
P(2)	1 819(19)	25 000	−18 467(21)
C(21)	−815(10)	2 500	−692(13)
C(211)	−2 359(11)	2 500	−1 632(17)
C(22)	−446(6)	3 749(6)	−3 142(7)
C(221)	−68(9)	4 889(6)	−2 289(10)
H(1)	457(14)	250	−351(16)
H(2)	183(14)	250	−587(16)
H(3)	246(10)	407(9)	−411(12)
H(4)	400(9)	382(9)	−114(11)
H_b [b]	227(18)	382(17)	−271(22)
H(211)	−39(9)	326(8)	12(11)
H(221)	−150(9)	359(8)	−360(11)
H(22)	0(9)	362(9)	−385(11)

[a] Treated as boron in the refinement. [b] Population parameter 0.5.

The position of the methylenic H atoms of the P(2) ligand, and the terminal hydrogens on all six polyhedral atoms, were taken from a ΔF synthesis computed with those 1 174 data for which $(\sin\theta)/\lambda \leqslant 0.5$. This map also yielded co-ordinates of the ' half hydrogen ' atom bridging the (3)—(4) [≡(5)—(6)] positions of the cage. No attempt was made to locate methyl hydrogens or the methylene hydrogens of the P(1) ligand. In spite of the $\sin\theta$ cut-off, the region around platinum was too irregular to allow H(Pt) to be located, and Figure 1 shows its presumed position.

All non-hydrogen atoms except C(12A) and C(12B) were allowed anisotropic thermal parameters. Hydrogen atoms were positionally refined (U_H fixed at 0.04 Å^2). In the final stages, data were included in the refinement if $I \geqslant 3.0\sigma(I)$ (4 550 reflections) or $3.0 \geqslant I/\sigma(I) \geqslant 1.0$ and $|F_c| \geqslant F_o$ (379 reflections), the data: variable ratio being thus better than 35 : 1.

Final agreement factors of R 0.043 (R' 0.054) were obtained. The ultimate difference Fourier (0.44 Å resolution, all data) showed residues between −1.7 and +1.9 e Å^{-3} around the metal atom, which we attribute primarily to inaccuracies in the absorption correction. In view of this we returned to the pre-corrected data set, but there found even poorer results for comparable refinement (R 0.054, ΔF residues between −3.2 and +3.0 e Å^{-3}). Furthermore, an independent re-measurement of the external faces of the crystal gave indices and dimensions as before. We therefore feel that the applied absorption correction represents at least a partial improvement.

Atomic scattering factors for neutral atoms were taken from refs. 20 (Pt and B), 21 (P and C), and 22 (H), with all non-hydrogen sets corrected [23] for both components of anomalous dispersion. Table 4 lists the final atomic co-ordinates. Appendices A, B, and C contain, respectively, interbond angles involving terminal hydrogen atoms, thermal parameters, and a comparison of $10|F_o|$ and $10F_c$. The structure was solved and initially refined with the Syntex XTL system,[24] final refinement employing the ' X-Ray '72 ' crystallographic package [25] implemented on the University of London CDC 7600 computer. Figures 1 and 2 were drawn with Johnson's ORTEP-11.[26]

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