Metallaborane Chemistry. Part I. Oxidative-insertion Reactions of Dicarbaundecaborane and Metalladicarbaundecaborane Species with Zerovalent Nickel, Palladium, and Platinum Complexes

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Reaction of $[Pt(PEt_3)_3]$, $[Pt(PMe_3)_2($*trans*-stilbene$)]$, $[Pt(PMe_2Ph)_4]$, $[Ni(1,5\text{-}C_8H_{12})_2]$, $[Ni(PEt_3)_2(1,5\text{-}C_8H_{12})]$, and $[Pd(CNBu^t)_2]$ with *closo*-$2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_9H_9$ affords the *closo*-metallacarbaboranes $1,1\text{-}L_2\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}MC_2B_9H_9$ (M = Pt, L = PEt_3, PMe_3, or PMe_2Ph; M = Ni, L_2 = $1,5\text{-}C_8H_{12}$ or L = PEt_3; M = Pd, L = Bu^tNC). A single-crystal *X*-ray diffraction study of the metallacarbaborane obtained from $[Pt(PMe_2Ph)_4]$ confirms the structural identity of the complex. Treatment of $1\text{-}(\eta\text{-}C_5H_5)\text{-}1,2,4\text{-}CoC_2B_8H_{10}$ with $[Pt(PEt_3)_2($*trans*-stilbene$)]$ leads to a related insertion reaction to form $1\text{-}(\eta\text{-}C_5H_5)\text{-}8,8\text{-}(Et_3P)_2\text{-}1,2,7,8\text{-}CoC_2PtB_8H_{10}$. An analogous reaction occurs with $[Ni(1,5\text{-}C_8H_{12})_2]$ to form a less-stable $CoC_2NiB_8H_{10}$ species.

IN order to place a metal atom in the polyhedral framework of a closed heteroborane structure, either one of the existing cage atoms must be removed and replaced by a suitable metal species or the cage must be opened by reduction and the metal species inserted into the newly created site. By this approach Hawthorne and his co-workers[1-3] prepared a remarkable series of metallacarbaboranes, and other workers have pursued parallel lines with various heteroborane systems.[4-6]

Of these two synthetic approaches, degradation or expansion, the latter has proved the most productive both in range of compounds obtained and in the generality of its application.[3] This procedure may be represented by equation (1). The first step is reduction

$$C_2B_nH_{n+2} \xrightarrow{+2e^-} [C_2B_nH_{n+2}]^{2-} \xrightarrow{(i),(ii)} (\eta\text{-}C_5H_5)MC_2B_nH_{n+2} \qquad (1)$$

(i), M^{II}, $Na(C_5H_5)$; (ii), [O]

of the carbaborane by an alkali metal giving an anion, a process involving the placement of two electrons in an unfilled molecular orbital. Rudolph and Pretzer[7] suggested that this gives rise to molecular distortion of the second-order Jahn–Teller type leading to an open *nido*-structure. In the second stage of the reaction a metal cation is inserted into the newly created cage site.

Our experience with the highly nucleophilic zerovalent derivatives of nickel, palladium, and platinum prompted us to consider the possibility that such species might insert directly into the *closo*-carbaborane, possibly in a concerted process. Such a reaction would involve a net transfer of electrons from the metal to the cage, and would represent an interesting new aspect of oxidative-addition chemistry.[8] Initial experiments were directed towards the reactions of the 11-atom carbaborane $2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_9H_9$, a compound known to be susceptible to mild nucleophilic attack.[4b,9]

RESULTS

Reaction of tris(triethylphosphine)platinum[10] with $2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_9H_9$ in light petroleum at −30 °C gave a high yield of the pale yellow complex (I), formulated as $[(Et_3P)_2Pt(Me_2C_2B_9H_9)]$ on the basis of elemental analysis and i.r. and n.m.r. spectroscopy. We considered a $1,2,4\text{-}PtC_2B_9$ icosahedral structure to be most likely in view of the geometry of cage opening proposed for reactions of $2,3\text{-}C_2B_9H_{11}$ derivatives with Lewis bases[4b,9] and carbanions.[11] Furthermore, an alternative synthesis of (I) from *cis*-$[PtCl_2(PEt_3)_2]$ and $[$*nido*-$7,9\text{-}Me_2\text{-}7,9\text{-}C_2B_9H_9]^{2-}$ strongly supported a $1,2,4\text{-}PtC_2B_9$ structure.

However, the surprising insolubility of (I) and the inherent complexity of the ^1H n.m.r. spectrum of the $Pt(PEt_3)_2$ system precluded a detailed investigation of the structure based on n.m.r. spectroscopy, and two further complexes were prepared to overcome this difficulty. Thus the reaction of (*trans*-stilbene)bis(trimethylphosphine)platinum and tetrakis(dimethylphenylphosphine)platinum with $2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_9H_9$ gave respectively $1,1\text{-}(Me_3P)_2\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}PtC_2B_9H_9$, (II), and $1,1\text{-}(PhMe_2P)_2\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}PtC_2B_9H_9$, (III). The mass spectrum of (II) showed a parent-ion envelope centred at *m/e* 507, and an isotopic distribution within 10% of that calculated from the natural elemental abundances. Measured in methylene chloride, the 100 MHz ^1H n.m.r. spectrum of (II) showed two distinct doublets ($P\text{–}CH_3$) with ^{195}Pt satellites centred at τ 8·23 and 8·27 indicating inequivalent phosphines. A broad singlet at τ 8·33 due to the cage methyl groups was partially obscured by the phosphine-ligand spectrum. However, this signal was readily observed at 60 MHz in pyridine as solvent. In both solvents satellites arising from coupling between the ^{195}Pt nuclei and the cage methyl groups were observed [$J(^{195}Pt\text{–}^1H)$ 15 Hz]. The ^1H n.m.r. spectrum of (III) showed only two doublet resonances for the four phosphine methyl groups implying that the PtP_2 plane is coincident with a molecular plane of symmetry, which also relates the two cage methyl groups (Figure 1).

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[1] M. F. Hawthorne, *Accounts Chem. Res.*, 1968, **1**, 281.

[2] M. F. Hawthorne and G. B. Dunks, *Science*, 1972, **178**, 462.

[3] M. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1973, **95**, 4565.

[4] (*a*) V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 1973, **95**, 2830; (*b*) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *ibid.*, p. 3046; (*c*) L. G. Sneddon, D. C. Beer, and R. N. Grimes, *ibid.*, p. 6623.

[5] (*a*) R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *J. Amer. Chem. Soc.*, 1970, **92**, 3351; (*b*) V. Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolph, *ibid.*, 1973, **95**, 4560.

[6] L. J. Todd, I. C. Paul, J. L. Little, P. S. Welcker, and C. R. Peterson, *J. Amer. Chem. Soc.*, 1968, **90**, 4489.

[7] R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, 1972, **11**, 1974.

[8] J. L. Spencer, M. Green, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1178.

[9] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1968, **90**, 869.

[10] D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 3543.

[11] D. A. Owen and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1969, **91**, 6002.

In order to confirm these structural conclusions a single-crystal *X*-ray diffraction study of (III) was undertaken.

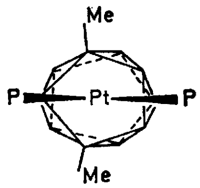

FIGURE 1 View of complex (III) down the plane defined by PtP_2

The results of the analysis (currently $R = 0{\cdot}042$) are summarised in the Table, and a general view of the molecule is shown in Figure 2. The analysis confirmed that the metal co-ordinates three boron and two carbon atoms to complete a *closo*-2,4-dicarba-icosahedron. The platinum atom is situated *ca.* 1·81 Å above the C_2B_3 face which exhibits distortions from an ideal geometry similar to those already recorded [12] for 1-metalla-2,4-dicarbaboranes. Although the PtP_2 moiety 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) by *ca.* 10·2° with respect to the PtB(3)B(12)B(10) plane.

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for the complex 1,1-$(PhMe_2P)_2$-2,4-Me_2-1,2,4-$PtC_2B_9H_9$

Bond lengths			
Pt–P(1)	2·52(2)	B–B range	1·75—1·91
Pt–P(2)	2·30(3)	B–B mean	1·80 (17 observations)
Pt–B(3)	2·27(2)	B–C range	1·65—1·76
Pt–B(5)	2·26(6)	B–C mean	1·69 (8 observations)
Pt–B(6)	2·26(3)		
Pt–C(2)	2·45(5)		
Pt–C(4)	2·44(5)		
Bond angles			
P(1)–Pt–P(2)	97·4(1)	B–B–B range	57·1—64·2
B(6)–Pt–C(2)	41·5(4)	B–B–B mean	60·0 (27 observations)
C(2)–Pt–B(3)	40·6(4)	B–B–C range	55·1—60·5
B(3)–Pt–C(4)	43·7(3)	B–B–C mean	57·9 (12 observations)
C(4)–Pt–B(5)	41·5(4)	B–C–B range	62·8—65·7
B(5)–Pt–B(6)	50·1(4)	B–C–B mean	64·2 (6 observations)

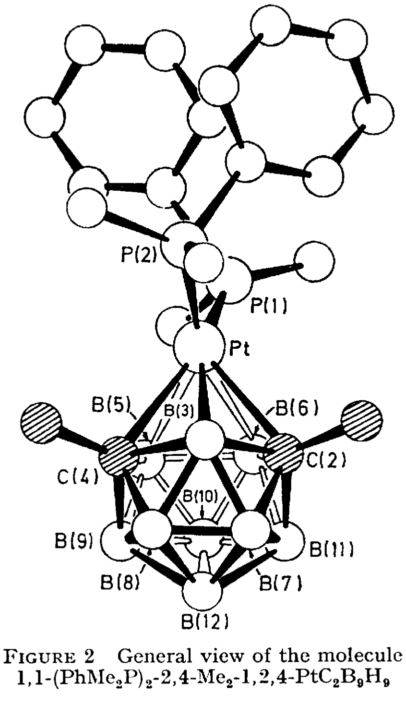

FIGURE 2 General view of the molecule 1,1-$(PhMe_2P)_2$-2,4-Me_2-1,2,4-$PtC_2B_9H_9$

With structural confirmation of the nature of the reaction of Pt^0 species with 2,3-Me_2-2,3-$C_2B_9H_9$, related reactions of other d^{10} systems were investigated. Thus, bis(η-cyclo-octa-1,5-diene)nickel, (η-cyclo-octa-1,5-diene)-bis(triethylphosphine)nickel,[13] and bis(t-butyl isocyanide)-palladium gave, respectively, the complexes 1-(1,5-C_8H_{12})-2,4-Me_2-1,2,4-$NiC_2B_9H_9$, (IV), 2,4-Me_2-1,1-$(Et_3P)_2$-1,2,4-$NiC_2B_9H_9$, (V), and 2,4-Me_2-1,1-$(Bu^tNC)_2$-1,2,4-$PdC_2B_9H_9$, (VI). Bis(η-cyclo-octa-1,5-diene)nickel was the least reactive of the d^{10} complexes studied, as might be expected of a co-ordinatively saturated 18-electron species. Both the nickel complexes (IV) and (V) were isolated as brown, diamagnetic, crystalline compounds, only a little less soluble than the platinum derivatives. Complex (IV) gave a mass spectrum with a parent envelope centred at *m*/*e* 327 with partial cut-off at *m*/*e* 330, corresponding to $^{60}Ni^{12}C_{12}{}^{11}B_9{}^1H_{27}$. Other major ions were derived from the parent by loss of either C_8H_{12} or $Me_2C_2B_9H_9$. The ^1H n.m.r. spectrum showed an unresolved multiplet centred at τ 4·36 (4H) ascribed to the olefinic protons of co-ordinated cyclo-octa-1,5-diene, a broad multiplet at τ 7·4 (8H) due to the aliphatic protons of C_8H_{12}, and a singlet at τ 7·20 (6H) assigned to the two cage methyl groups. The equivalence of the latter implies a molecular plane of symmetry, and this was corroborated by the 80·2 MHz ^{11}B n.m.r. spectrum which consisted of five doublets of relative intensity 1 : 2 : 2 : 1 : 3 at δ 2·7, 6·0, 9·9, 11·3, and 14·7 p.p.m. relative to F_3B,OEt_2. Although complex (V) was too insoluble for detailed n.m.r. spectroscopy, the i.r. spectrum was almost indistinguishable from that of its platinum analogue (I). The palladium derivative, (VI), proved much less stable than any of the other complexes so far discussed. As a yellow crystalline solid it decomposed above 130 °C *in vacuo*, while a diethyl ether solution decomposed over several hours at room temperature in air. The 80·2 MHz ^{11}B n.m.r. spectrum was poorly resolved, and only four doublets of relative intensity 1 : 4 : 3 : 1 could be distinguished. At 100 MHz the ^1H spectrum showed singlets at τ 7·85 (Me), 9·02, (Bu^tN), and 9·07 (Bu^tN).

In a recent series of papers the analogy between the chemistry of the carbaboranes and that of the (η-C_5H_5)Co metallacarbaboranes [14-16] has been developed. In particular, the reported reaction of *closo*-1-(η-C_5H_5)-1,2,4-$CoC_2B_8H_{10}$, a metallacarbaborane analogue of 2,3-$C_2B_9H_{11}$, with bases to yield *nido*-adducts [16,17] suggested that the parallel chemistry might extend to the reaction with zerovalent metal complexes. Treatment of (*trans*-stilbene)-bis(triethylphosphine)platinum with 1-(η-C_5H_5)-1,2,4-$CoC_2B_8H_{10}$ in toluene at 20 °C gave, on cooling, red crystals of (VII), which analysed as a toluene solvate of $(Et_3P)_2PtC_2B_8H_{10}Co(C_5H_5)$. The mass spectrum showed a group of ions centred at *m*/*e* 675, corresponding to the

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[12] R. M. Wing, *J. Amer. Chem. Soc.*, 1970, **92**, 1187.

[13] C. S. Cundy, Ph.D. Thesis, Bristol University, 1969.

[14] W. J. Evans and M. F. Hawthorne, *J.C.S. Chem. Comm.*, 1972, 611.

[15] C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1972, **94**, 8391.

[16] C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1973, **95**, 7633.

[17] M. R. Churchill and K. Gold, *J.C.S. Chem. Comm.*, 1972, 901; *Inorg. Chem.*, 1973, **12**, 1157.

parent envelope, and ions arising from the loss of 2H and 4H. In the ^{1}H n.m.r. spectrum a sharp singlet at τ 5·02 (5H) was assigned to the cyclopentadienyl protons, a broad singlet at 5·81 (1H) to one of the cage CH groups, and multiplets at 8·11 (12H) and 8·89 (18H) to the phosphine methylene and methyl protons, respectively. The position of the other cage CH resonance is not known, but it may be responsible for the shoulder at τ 8·35 on the high-field side of the methylene multiplet. The asymmetry of the complex was confirmed by the 80·5 MHz ^{11}B n.m.r. spectrum which showed seven signals at δ $-17·5$ (1), $-9·0$ (1), $+0·6$ (1), $+8·6$ (2), $+14·4$ (1), $+19·7$ (1), and $+30·0$ (1) p.p.m.

In a similar reaction bis(η-cyclo-octa-1,5-diene)nickel and 1-(η-C_5H_5)-1,2,4-$CoC_2B_8H_{10}$ gave the dark brown complex (VIII), which proved to be much less stable than (VII) and was not fully characterised. By analogy with the platinum complex, (VIII) was formulated as $(C_8H_{12})NiC_2B_8H_{10}Co(C_5H_5)$, in agreement with the ^{1}H n.m.r. spectrum which showed resonances at τ 4·79 (m), 4·89 (s) (9H, olefinic hydrogens and C_5H_5), 6·32 (1H, br.s, cage CH), and 7·6 (8H, br.m, CH_2). In solution (VIII) decomposed in air at room temperature, and when passed down a short column of charcoal the (C_8H_{12})Ni moiety was eliminated reforming 1-(η-C_5H_5)-1,2,4-$CoC_2B_8H_{10}$.

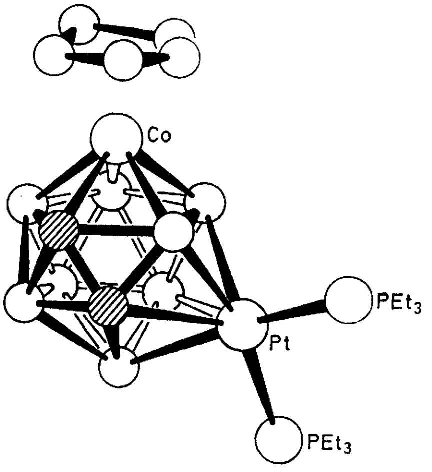


FIGURE 3 General view of the molecule 1-(η-C_5H_5)-8,8-$(Et_3P)_2$-1,2,7,8-$CoC_2PtB_8H_{10}$

These data clearly do not define the structures of either (VII) or (VIII), and therefore a single-crystal *X*-ray diffraction study of (VII) was undertaken. This is still at a preliminary stage (current $R = 0·081$): however, the analysis defines the geometry of the complex as that shown in Figure 3; *i.e.* complex (VII) is 1-(η-C_5H_5)-8,8-$(Et_3P)_2$-1,2,7,8-$CoC_2PtB_8H_{10}$.

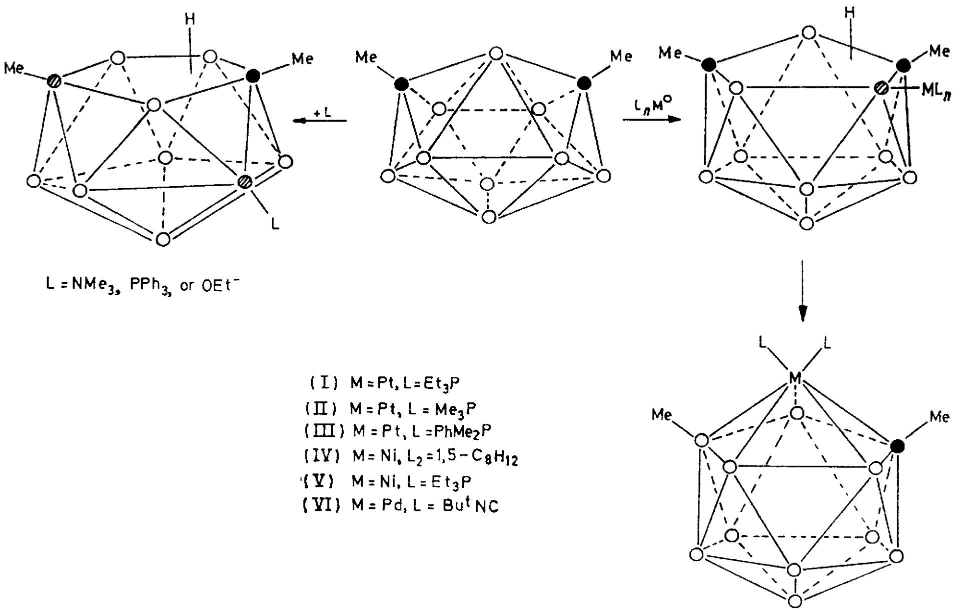
DISCUSSION

Although it is well established that 2,3-$C_2B_9H_{11}$ and its C-substituted derivatives are unusual amongst the carbaboranes in their susceptibility to attack by a wide range of Lewis bases under mild conditions, and that the adducts thus formed have a *nido*-structure closely related to that of the [7,9-$C_2B_9H_{12}]^-$ anion, the exact mechanism of this reaction does not appear to be fully understood. Rudolph and his co-workers[5] have discussed some of the possible modes of nucleophilic attack, and suggest that, although the boron atom in the unique 1 position is the most positive, reaction at the next most-positive borons 4, 5, 6, and 7 may well be favoured because it is on these atoms that the lowest unfilled molecular orbital is mainly localised. These workers studied in detail the 70·6 MHz ^{11}B n.m.r. spectra of NMe_3, PPh_3, and OEt^- (L) adducts of $C_2B_9H_{11}$ and $Me_2C_2B_9H_9$ for which they proposed a 3-L-7,9-$C_2B_9H_{11}$ structure; *i.e.* the molecule is asymmetric and the substituent is not located on the open pentagonal face. The suggested mechanism (Scheme 1) involves attack at one of the four equivalent boron atoms, with subsequent movement of the unique boron atom 1 towards the nucleophile with concerted intramolecular transfer of the displaced H atom to the open face.[5b]

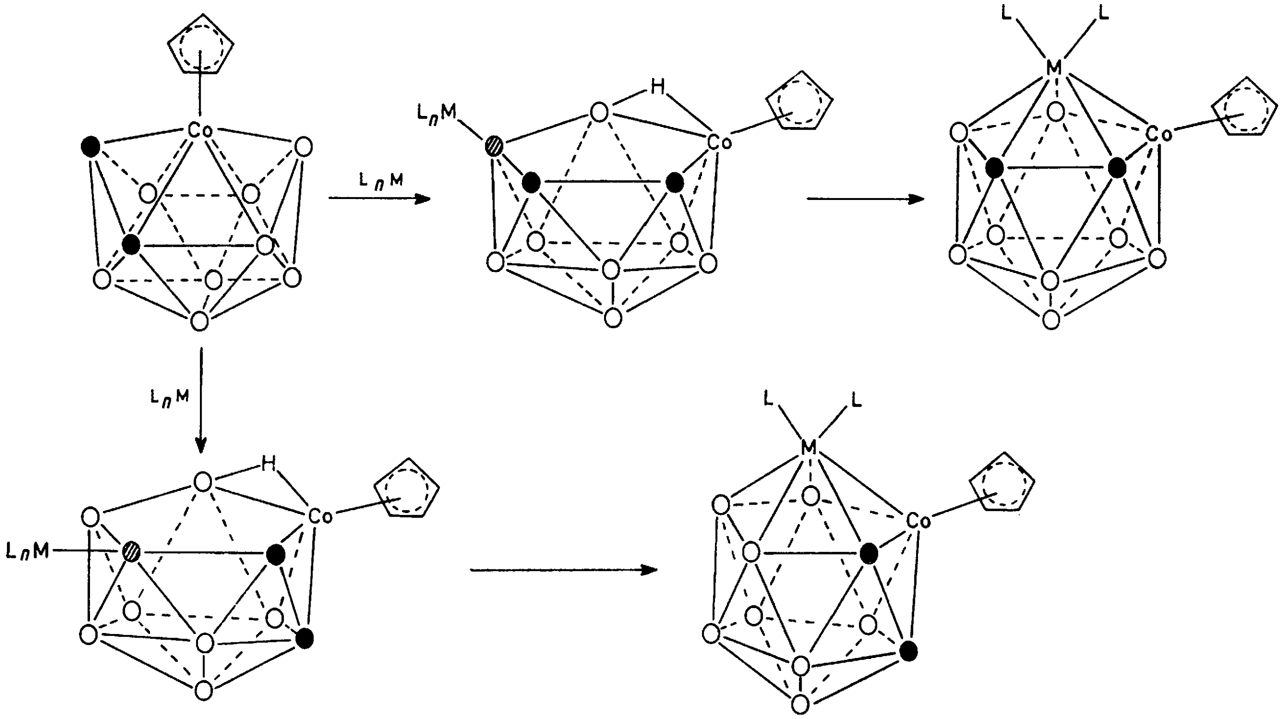
In contrast, it has been found[9] that carbanions react with 2,3-$C_2B_9H_{11}$ to give [10-L-7,9-$C_2B_9H_{11}]^-$ anions, in which the substituted boron atom is on the open face. This may be rationalised in terms of attack at one of the four equivalent borons, followed by cage opening in which the unique boron atom moves away from the substituent. At the present time the reasons for this differing behaviour, in which the reaction path followed is dependent on the nature of the nucleophile, are far from clear.

The situation with regard to reaction with co-ordinatively unsaturated transition-metal species is potentially more complex in that the metal complex has both donor (base) and acceptor (acid) capabilities, which normally are complementary. We believe, however, that it is the high nucleophilicity of the metal species which is necessary for reaction to occur with the carbaborane, and that there is a direct parallel with the reactions of other bases discussed above. Thus, reaction of a d^{10} metal species could conceivably occur at the 7 position with concomitant cage opening such that the boron associated with the metal atom lies in the 10(11) position on the open face of the intermediate *nido*-species. The metal atom is then in a position to swing over on to the open face, and with vacant orbitals of suitable energy is able to interact with the face atoms thus forming an icosahedral metallacarbaborane.

If these ideas are extended to formation of the bimetallic species (VII) and (VIII) then the CoC_2B_8 polyhedron could in principle open on nucleophilic attack in two ways. The first path (Scheme 2) is thought to occur in the reaction of pyridine with 1-(η-C_5H_5)-1,2,4-$CoC_2B_8H_{10}$ when a complex is formed in which the cobalt is bonded to one carbon and three boron atoms.[16] The second path involves motion of the cobalt atom from the CB_4 bonding face to a position where it is bonded to two carbon and two boron atoms, and is thought to occur in the EtOH–$FeCl_3$ degradation of the 1,2,4-CoC_2B_8 system.[15] However, examination of the structure of (VII) shows that if this species is formed in a kinetically controlled reaction, in which the platinum atom swings into position on an open face as the final step, then neither of these two reaction paths



SCHEME 1 ● = C, ○ = BH, and ▨ = B



SCHEME 2 L = Et$_3$P, M = Pt; ● = CH, ○ = BH, and ▨ = B

for nucleophilic attack can lead to the observed stereochemistry for (VII).

If these arguments are correct then either a subsequent thermodynamically controlled step, involving an intramolecular polyhedral diamond–square–diamond-rearrangement occurs, or nucleophilic attack by the Pt^0 species on the *closo*-1,2,4-CoC$_2$B$_8$ polyhedron proceeds very differently from other nucleophiles. We hope to investigate this question further.

EXPERIMENTAL

^{1}H N.m.r. spectra, unless otherwise specified, were recorded on a Varian Associates HA 100 spectrometer at 100 MHz. ^{11}B N.m.r. spectra were measured by Mr. B. Aufderheide of Carnegie–Mellon University and by Dr. R. R. Reitz on Professor F. A. L. Anet's instrument at U.C.L.A. The reference for the 80·2 MHz spectra was B(OMe)$_3$, but all ^{11}B chemical shifts are quoted with respect to F$_3$B,OEt$_2$ {δ(F$_3$B,OEt$_2$) = δ[B(OMe)$_3$] − 17·4 p.p.m.}. I.r. spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer, and mass spectra on an A.E.I. MS902 spectrometer at an ionising voltage of 70 eV.* M.p.s were measured *in vacuo*. All reactions were carried out in a dry oxygen-free nitrogen atmosphere. Solvents were dried and distilled under nitrogen prior to use.

Of the zerovalent metal complexes only (*trans*-stilbene)bis(trimethylphosphine)platinum has not been previously reported. Tris(triethylphosphine)platinum [10] was made by a modification of the method of Malatesta and Cariello.[18] The complexes [Pt(PMe$_2$Ph)$_4$],[19] [Ni(1,5-C$_8$H$_{12}$)$_2$],[20] [Pd(CNBu^t)$_2$],[21] and (*trans*-stilbene)bis(triethylphosphine)platinum [22] were made by the literature methods. The carbaborane 2,3-Me$_2$-2,3-C$_2$B$_9$H$_9$ was made from 1,2-Me$_2$-1,2-C$_2$B$_{10}$H$_{10}$ by the method of Hawthorne.[9] A sample of 1-(η-C$_5$H$_5$)-1,2,4-CoC$_2$B$_8$H$_{10}$ [15] was kindly supplied by Professor M. F. Hawthorne and Dr. C. J. Jones.

Preparations.—(trans-*Stilbene*)*bis*(*trimethylphosphine*)*platinum*. A rapidly stirred suspension of finely powdered *cis*-[PtCl$_2$(PMe$_3$)$_2$] (2·1 g, 5 mmol) and *trans*-stilbene (0·9 g, 5 mmol) in dry benzene (25 cm^3) was cooled (5 °C), and a benzene solution of Na[AlH$_2$(OCH$_2$CH$_2$OMe)$_2$] (3 cm^3 of 70% solution, 10 mmol) was added dropwise. The reaction mixture was stirred (0·5 h) until all the dichloride had dissolved and hydrogen evolution had ceased. The solvent was removed *in vacuo*, and the residue extracted with hot light petroleum (b.p. 40—60 °C). Filtration gave a clear brown solution which on cooling deposited crystals of the crude product. This was briefly exposed (15 min) to the air to oxidise the main impurity, and recrystallised from hot light petroleum (b.p. 40—60 °C) to give very pale yellow *crystals* of (*trans*-stilbene)bis(trimethylphosphine)platinum (1·6 g, 60%), m.p. 145—147 °C (Found: C, 45·5; H, 5·7. Calc. for C$_{20}$H$_{30}$P$_2$Pt: C, 45·5; H, 5·7%). $\nu_{max.}$ (Nujol) at 3 050vw, 3 010w, 1 598s, 1 575w, 1 490m, 1 421w, 1 300vw, 1 286s, 1 248w, 1 219w, 1 182w, 1 076w, 1 036w, 967s, 952vs, 860w, 852 (sh), 770m, 761s, 734m, 709s, 705s, and 680 cm^{-1}.

2,4-*Dimethyl*-1,1-*bis*(*triethylphosphine*)-1-*platina*-2,4-*dicarbadodecaborane*, (I). A solution of 2,3-Me$_2$-2,3-C$_2$B$_9$H$_9$ (0·64 g, 4 mmol) in light petroleum (10 cm^3) was added slowly to a cold (−30 °C) solution of tris(triethylphosphine)platinum (1·15 g, 2·1 mmol) in light petroleum (20 cm^3). Immediately a bright orange precipitate formed which faded to a pale yellow colour as the mixture was allowed to warm to room temperature. The yellow powder was collected by filtration and washed repeatedly with diethyl ether. Recrystallisation from methylene chloride gave pale yellow *crystals* of (I) (1·0 g, 81%), m.p. 235 °C (Found: C, 32·2; H, 7·9; B, 16·4; P, 10·4. Calc. for C$_{16}$H$_{45}$B$_9$P$_2$Pt: C, 32·4; H, 7·7; B, 16·4; P, 10·5%). $\nu_{max.}$ (Nujol) at 2 560 (sh), 2 550vs, 2 543 (sh), 1 253w, 1 175w, 1 081w, 1 050 (sh), 1 034s, 1 012m, 1 001m, 952w, 765s, 730m, and 720m cm^{-1}. The complex was too insoluble for n.m.r. studies.

A solution of [Me$_3$HN][7,9-Me$_2$-7,9-C$_2$B$_9$H$_{10}$] (0·2 g, 1 mmol) in tetrahydrofuran (50 cm^3) was treated with n-butyl-lithium (2 mmol) and heated under reflux for 1·5 h. After the solution had cooled to room temperature, *cis*-[PtCl$_2$(PEt$_3$)$_2$] (0·50 g, 1 mmol) was added with stirring. An orange colour developed but faded as pale yellow *crystals* of (I) (0·18 g, 31%) were deposited. These were identified by their m.p. and comparison of the i.r. spectrum with a sample of the complex prepared by polyhedral expansion.

2,4-*Dimethyl*-1,1-*bis*(*trimethylphosphine*)-1-*platina*-2,4-*dicarbadodecaborane*, (II). A solution of 2,3-Me$_2$-2,3-C$_2$B$_9$H$_9$ (0·20 g, 1·25 mmol) in light petroleum (10 cm^3) was added to a light petroleum solution of (*trans*-stilbene)bis(trimethylphosphine)platinum (0·53 g, 1·0 mmol) at room temperature. A bright orange precipitate formed immediately but after minutes this had faded to a very pale yellow. After 20 min the reaction mixture was filtered in air, and the crude product recrystallised (0 °C) from methylene chloride–light petroleum to give pale yellow *needles* of (II) (0·48 g, 94%), m.p. 231 °C (Found: C, 22·6; H, 6·5. Calc. for C$_{10}$H$_{33}$B$_9$P$_2$Pt: C, 23·7; H, 6·6%). $\nu_{max.}$ (Nujol) at 2 545vs, 2 515vs, 2 487s, 1 420s, 1 314w, 1 296s, 1 175w, 1 085w, 1 013w, 968s, 952vs, 860m, 759 (sh), 748m, 695m, and 687m cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 8·21 [d, 9H, MeP, ^2J(PH) −10·4, J(^{195}Pt–^{1}H) 41·7], 8·27 [d, 9H, MeP, ^2J(PH) −9·4, J(^{195}Pt–^{1}H) 29·9], and 8·33 [br.s with ^{195}Pt satellites, 6H, CMe, J(^{195}Pt–^{1}H) 15 Hz]. The mass spectrum showed peaks at *m/e* 507 (P^+), 347 [Pt(PMe$_3$)$_2$]$^+$, 332, 330, 270 [Pt{P(C$_3$H$_8$)}]$^+$, and 160 [Me$_2$C$_2$B$_9$H$_9$]$^+$.

1,1-*Bis*(*dimethylphenylphosphine*)-2,4-*dimethyl*-1-*platina*-2,4-*dicarbadodecaborane*, (III). In a similar reaction treatment of tetrakis(dimethylphenylphosphine)platinum (1·0 g, 1·3 mmol) with 2,3-Me$_2$-2,3-C$_2$B$_9$H$_9$ (0·56 g, 3·5 mmol) gave, after recrystallisation from methanol–methylene chloride, large yellow *crystals* of (III) (0·51 g, 63%), m.p. 187 °C (Found: C, 38·3; H, 6·0. Calc. for C$_{20}$H$_{37}$B$_9$P$_2$Pt: C, 38·0; H, 5·9%). $\nu_{max.}$ (Nujol) at 3 080vw, 2 580s, 2 565s, 2 550s, 2 527s, 2 515s, 2 480s, 1 589vw, 1 575vw, 1 438m, 1 422w, 1 410m, 1 298m, 1 285m, 1 175w, 1 108m, 1 076w, 1 007m, 949s, 923vs, 912m, 907s, 867w, 848m, 744s, 713m, and 699s cm^{-1}. The ^{1}H n.m.r. spectrum (60 MHz in CDCl$_3$) showed resonances at τ 2·5 (m, 10H, C$_5$H$_5$), 8·25 [d with ^{195}Pt satellites, ^2J(PH) −10·2, J(^{195}Pt–^{1}H) 41·0], 8·27 [s, with ^{195}Pt satellites, J(^{195}Pt–^{1}H) 14·0], and 8·34 [d with ^{195}Pt satellites, ^2J(PH) −9·0, J(^{195}Pt–^{1}H) 27·0 Hz].

1-(η-*Cyclo-octa*-1,5-*diene*)-2,4-*dimethyl*-1-*nickela*-2,4-*dicarbadodecaborane*, (IV).—Bis(η-cyclo-octa-1,5-diene)nickel (0·38 g, 1·4 mmol) was suspended in toluene (20 cm^3) at −78 °C, and a solution of 2,3-Me$_2$-2,3-C$_2$B$_9$H$_9$ (0·24 g, 1·5 mmol) in toluene (6 cm^3) added dropwise. The reaction mixture was stirred at −78 °C for 3 h and then at 20 °C for 6 h, the solution developing a rich burgundy colour. The solvent was removed *in vacuo* and the residue recrystallised (−10 °C) from toluene–light petroleum to give dark brown *crystals* of (IV) (0·25 g, 54%), m.p. 207—210 °C (decomp.) (Found: C, 44·0; H, 8·2; B, 29·6. Calc. for C$_{12}$H$_{27}$B$_9$Ni: C, 44·0; H, 8·3; B, 29·7%). $\nu_{max.}$ (Nujol) at 2 550vs, 2 520 (sh), 1 433m, 1 345w, 1 314w, 1 173m, 1 163 (sh), 1 091vw, 1 073w, 1 017 (sh), 1 008s, 985w, 954w, 942w, 928w, 895w, 871m, 820w, 779w, 750w, 724w, and 716w cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 4·36 (m, 4H, CH=CH), 7·4 (br.m, 8H, CH$_2$), and 7·80 (s, 6H, CMe). The ^{11}B n.m.r. spectrum (CH$_2$Cl$_2$) showed resonances at 2·7 [d, 1B, J(BH) 150], 6·0 [d, 2B, J(BH) 150], 9·9 [d, 2B, J(BH) 160], 11·3 [d, 1B, J(BH) *ca.* 170], and 14·7 p.p.m. [d, 3B, J(BH) 160 Hz]. The mass spectrum showed peaks at *m/e* 327 (P^+, with partial cut-off at *m/e*

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* 1 eV ≈ 1·6 × 10^{-19} J.

[18] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

[19] H. C. Clark and K. Itoh, *Inorg. Chem.*, 1971, **10**, 1707.

[20] B. Bogdanović, M. Kröner, and G. Wilke, *Annalen*, 1966, **699**, 1.

[21] E. O. Fischer and H. Werner, *Chem. Ber.*, 1962, **95**, 703.

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

$330 = {}^{60}Ni^{12}C_{12}{}^{11}B_9{}^{1}H_{27}$), 222 $[P - C_8H_{12}]^+$, and 168 $[P - C_4B_9H_{15}]^+$.

2,4-*Dimethyl*-1,1-*bis*(*triethylphosphine*)-1-*nickela*-2,4-*dicarbadodecaborane*, (V). Triethylphosphine (0·74 cm³, 5 mmol) was added to a suspension of bis(η-cyclo-octa-1,5-diene)nickel (0·66 g, 2·4 mmol) in toluene (20 cm³). The solution was cooled (−78 °C) and a solution of 2,3-Me_2-2,3-$C_2B_9H_9$ (0·40 g, 2·5 mmol) in toluene (2·5 cm³) added. The reaction mixture was then allowed to warm to room temperature, the colour changing from yellow through green to brown with crystals being deposited. The product was collected and recrystallised with some difficulty from methylene chloride to give fine brown *crystals* of (V) (0·70 g, 64%), m.p. 225—227 °C (Found: C, 42·1; H, 9·8; B, 21·2; P, 13·7. Calc. for $C_{16}H_{45}B_9P_2Ni$: C, 42·2; H, 10·0; B, 21·4; P, 13·6%). $\nu_{max.}$ (Nujol) at 2 553vs, 1 251vw, 1 173vw, 1 032m, 1 010w, 998w, 954w, 891vw, 755s, 712w, and 702w cm⁻¹.

2,4-*Dimethyl*-1,1-*bis*(*t-butyl isocyanide*)-1-*pallada*-2,4-*dicarbadodecaborane*, (VI). A solution of 2,3-Me_2-2,3-$C_2B_9H_9$ (0·32 g, 2 mmol) in toluene (8 cm³) was added dropwise with stirring to a cooled (−78 °C) solution of bis(t-butyl isocyanide)palladium (2 mmol) in toluene (20 cm³). After 3 h at −78 °C the stirred reaction mixture was allowed to warm to room temperature. The resulting yellow solution was decanted from a brown gum, and the solvent removed *in vacuo*. The residue was recrystallised (−5 °C, 3 times) from diethyl ether–light petroleum to give yellow *crystals* of (VI) (0·12 g, 14%), m.p. *ca.* 150 °C (decomp.) (Found: C, 38·6; H, 7·6; B, 22·2; N, 6·4. Calc. for $C_{14}H_{33}B_9N_2Pd$: C, 38·8; H, 7·7; B, 22·5; N, 6·5%). $\nu_{max.}$ (Nujol) at 2 545vs, 2 207vs, 2 190vs, 1 233w, 1 205s, 1 082vw, 1 004w, 940vw, 878w, 851w, and 719w cm⁻¹. The ¹H n.m.r. spectrum (C_6D_6) showed resonances at τ 7·86 (s, 6H, CMe), 9·03 (s, 9H, Bu^tN), and 9·08 (s, 9H, Bu^tN). The ¹¹B n.m.r. spectrum (80·2 MHz) showed resonances at 6·1 (d, 1B), 11·5 (d, 4B), 18·3 (d, 3B), and 20·8 p.p.m. (d, 1B).

1-(η-*Cyclopentadienyl*)-8,8-*bis*(*triethylphosphine*)-1-*cobalta*-2,7-*dicarba*-8-*platinadodecaborane*, (VII). A solution of (*trans*-stilbene)bis(triethylphosphine)platinum (0·21 g, 0·34 mmol) in toluene (6 cm³) was added dropwise to a stirred solution (20 °C) of 1-(η-C_5H_5)-1,2,4-$CoC_2B_8H_{10}$ (0·085 g, 0·36 mmol) in toluene (2 cm³). After several minutes the intense blue colour of the original metallacarbaborane changed to a deep orange-red colour. Light petroleum (10 cm³) was added and the solution cooled (−15 °C) depositing red crystals of the solvated complex (VII). Recrystallisation from methylene chloride–light petroleum afforded unsolvated *crystals* of (VII) (0·2 g, 90%), m.p. 174 °C (Found: C, 32·8; H, 6·5; B, 12·1; P, 8·6. Calc. for $C_{19}H_{45}B_8CoP_2Pt$: C, 33·8; H, 6·7; B, 12·8; P, 9·2%), $\nu_{max.}$ (Nujol) (toluene solvate) at 2 580s, 2 540s, 2 510vs, 2 480vs, 2 445s, 1 305w, 1 260w, 1 120 (sh), 1 075 (sh), 1 040vs, 970m, 925w, 845w, 822s, 770 (sh), 762s, 734vs, and 718 (sh) cm⁻¹.

Crystal-structure Determination.—Complex (III) crystallises in the centrosymmetric triclinic space group with cell constants $a = 9{\cdot}324(3)$, $b = 10{\cdot}285(4)$, $c = 14{\cdot}208(8)$ Å, $\alpha = 100{\cdot}40(4)$, $\beta = 94{\cdot}32(4)$, and $\gamma = 98{\cdot}95(3)$°. Based on a volume of 1 316(1) Å³, the assumption of two molecules per unit cell leads to a calculated density of 1·59 g cm⁻³ (obs. 1·58 g cm⁻³). Lattice parameters and intensity data were determined on a Syntex $P2_1$ computer-controlled four-circle diffractometer with a molybdenum target ($\lambda_{\bar{\alpha}} = 0{\cdot}71069$ Å). Out of 4 530 intensities measured to a 2θ limit of 50°, 4 330 were considered significant $[I \geqslant 2{\cdot}5\sigma(I)]$ and were used to solve and refine the structure by a combination of Patterson, Fourier, and least-squares techniques. Currently $R = 0{\cdot}042$ with the platinum and phosphorus atoms only assigned anisotropic thermal parameters.

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