Metallaborane Chemistry. Part V.[1] Reactions of Zerovalent Nickel and Platinum Complexes with *arachno*-5,9-C_2B_7 Carbaboranes; Crystal and Molecular Structure of a Carbadibora-allyl Nickel Complex

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Reaction of cyclo-octa-1,5-dienebis(triethylphosphine)nickel with 5,9-Me_2-5,9-$C_2B_7H_{11}$ leads to evolution of hydrogen and formation of $[Ni(C_2B_7H_9Me_2)(PEt_3)_2]$. Analogous reactions between $C_2B_7H_{11}Me_2$ and $[Ni(PMe_3)_2(cod)]$, $[Pt(PEt_3)_2(stilbene)]$, $[Pt(PMe_3)_2(stilbene)]$, or $[Pt(PPh_3)_2(stilbene)]$ give, respectively, $[Ni(C_2B_7H_9Me_2)(PMe_3)_2]$, $[Pt(C_2B_7H_9Me_2)(PEt_3)_2]$, $[Pt(C_2B_7H_9Me_2)(PMe_3)_2]$, and $[Pt(C_2B_7H_9Me_2)(PPh_3)_2]$. The parent *arachno*-5,9-$C_2B_7H_{13}$ carbaborane also reacts with $[Pt(PEt_3)_2(stilbene)]$ to give $[Pt(C_2B_7H_{11})(PEt_3)_2]$. A single crystal *X*-ray diffraction study on the nickel compound $[6,6\text{-}(Et_3P)_2\text{-}5,9\text{-}Me_2\text{-}6,5,9\text{-}NiC_2B_7H_9]$ establishes that the metal atom is joined to a B_2C-system in a 1,2,3-η bonding mode. This crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions $a = 9.144(2)$, $b = 18.954(5)$, $c = 15.021(3)$ Å, $\beta = 90.51(4)°$ and the structure refined to $R = 0.068$ using 3 445 diffracted intensities.

In previous papers [2-4] in this series a synthetic approach to metallacarbaboranes was described involving the direct oxidative insertion of a zerovalent Ni, Pd, or Pt species into a *closo*-carbaborane. As an extension of these studies we have examined related reactions of the *arachno*-5,9-R_2-5,9-$C_2B_7H_{11}$ ($R = Me$ or H) species.[5] However, although metallacarbaboranes are formed from d^{10} nickel and platinum complexes, the reaction is mechanistically unrelated to the processes previously

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[1] A. J. Welch, *J.C.S. Dalton*, previous paper.

[2] M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1975, 179.

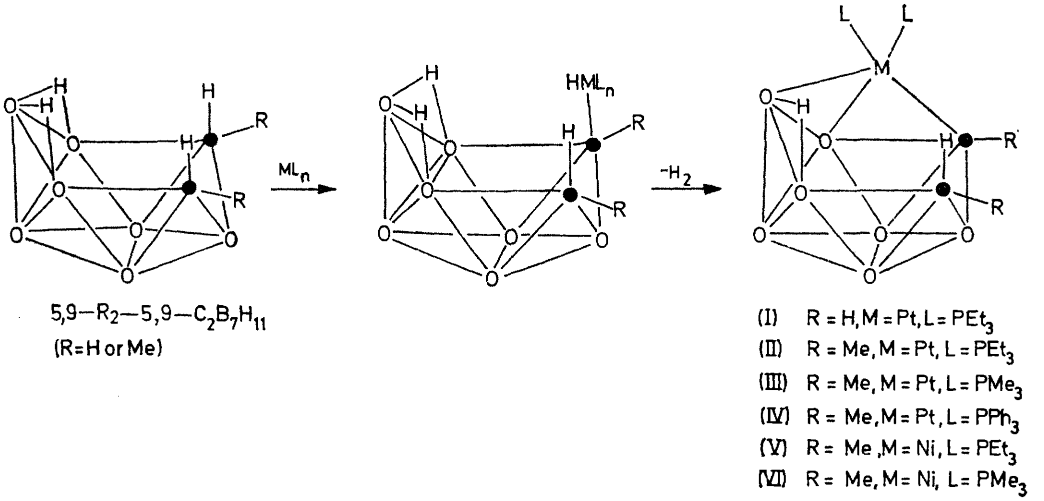
[3] M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 571, 794.

[4] E. W. Carroll, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1975, 2263.

[5] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1974, 153.

studied, and involves an initial oxidative insertion into a carbon–hydrogen bond of the *arachno*-carbaborane. The new compounds described have been characterised by elemental analysis, i.r. and n.m.r. spectroscopy, and in one case by a single-crystal *X*-ray diffraction study.

Addition of *arachno*-5,9-$C_2B_7H_{13}$ [6] to a solution of *trans*-stilbenebis(triethylphosphine)platinum [7] in toluene led to a change in colour from yellow to colourless, and the slow ($\frac{1}{2}$ h) evolution of one molar equivalent of hydrogen gas. *trans*-Stilbene was recovered from the reaction mixture as well as the white crystalline complex (I) $[Pt(PEt_3)_2(C_2B_7H_{11})]$ which showed typical B–H stretching frequencies in the i.r. spectrum (ν_{B-H}, 2 450—2 600 cm^{-1}). Similar reactions between *trans*-stilbenebis(triethylphosphine)platinum, *trans*-stilbenebis(trimethylphosphine)platinum,[2] or *trans*-stilbenebis(triphenylphosphine)platinum and *arachno*-5,9-Me_2-5,9-$C_2B_7H_{11}$ afford, respectively, the crystalline complexes (II), (III), and (IV) (see Scheme). Reaction of cycloocta-1,5-dienebis(triethylphosphine)nickel [8] and the corresponding trimethylphosphinenickel complex with *arachno*-5,9-Me_2-5,9-$C_2B_7H_{11}$ gave the red crystalline nickel complexes (V) and (VI), respectively. The mass spectra, although difficult to interpret in detail, were not inconsistent with the formulation of the complexes as mononuclear species. The ^{11}B n.m.r. spectra were very similar, and that of (I) showed seven distinct resonances, which except for that at 18.2 p.p.m. (rel. $Et_2O{\cdot}BF_3$) appeared as doublets due to $^1H-^{11}B$ coupling. This excluded a symmetrical structure in which the $(Et_3P)_2Pt$ system spanned the two 5,9-carbon atoms. Although the ^1H n.m.r. spectra showed interesting features which are discussed below, the spectroscopic data did not define unequivocally the molecular structure of the complexes. Therefore, an *X*-ray crystallographic investigation was undertaken, the nickel complex forming suitable crystals.



(I) R = H, M = Pt, L = PEt_3
(II) R = Me, M = Pt, L = PEt_3
(III) R = Me, M = Pt, L = PMe_3
(IV) R = Me, M = Pt, L = PPh_3
(V) R = Me, M = Ni, L = PEt_3
(VI) R = Me, M = Ni, L = PMe_3

SCHEME 1 ○ = BH, ● = C.

The molecular structure of (V) omitting hydrogen atoms, is shown in Figure 1. Figure 2 shows the relationship between the free ligand [9] *arachno*-5,9-Me_2-5,9-$C_2B_7H_{11}$ and the complex (V), and Figure 3 shows the contents of the unit cell projected down the *a* axis. Table 1 gives the bond lengths and angles within the molecule. There are no intermolecular contacts less than 2.52 Å, points of closest approach occurring between the hydrogen on B(2) and one of the hydrogens on C(51) (Figure 1). Tables 2 and 3 give the positional parameters and the anisotropic thermal parameters, respectively.

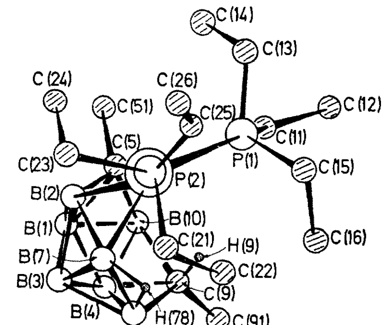


FIGURE 1 General view of the molecule $[6,6\text{-}(Et_3P)_2\text{-}5,9\text{-}Me_2\text{-}6,5,9\text{-}NiC_2B_7H_9]$

The geometry of (V) is that of a *nido*-nickelacarbaborane * isoelectronic and approximately isostructural with decaborane. The open six-atom face is defined by Ni, C(5), B(10), C(9), B(8), and B(7), with the P_2Ni system co-ordinated to C(5), B(2), and B(7). As can be

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* The atoms are numbered according to I.U.P.A.C. rules as a hetero-decaborane rather than as a metal–ligand complex.

[6] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1966, **88**, 607; 1968, **90**, 869.

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

[8] C. S. Cundy, *J. Organometallic Chem.*, 1974, **69**, 305; Ph.D. Thesis, Bristol, 1969.

[9] D. Voet and W. N. Lipscomb, *Inorg. Chem.*, 1967, **6**, 113.

seen by comparison of the relevant bond lengths (Table 4), the formation of (V) involves little change in the geometry of the parent C_2B_7 cage.[9]

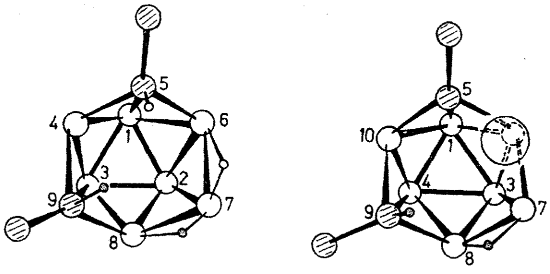

FIGURE 2 The molecules *arachno*-5,9-Me_2-5,9-$C_2B_7H_{13}$* and [6,6-$(Et_3P)_2$-5,9-Me_2-6,5,9-$NiC_2B_7H_9$]

* Molecule redrawn from atomic co-ordinates given in ref. 9.

The Ni, P(1), P(2) plane makes an angle of 35.2° with the Ni, C(5), B(7) plane, and of 23.6° with the plane through the midpoint of B(2)–B(7), the Ni atom, and atom C(5). Thus the geometry around the nickel is not strictly square planar. This is further emphasised by the observation that the atoms C(5), B(2), and B(7) lie at −0.57, −0.47, and +1.02 Å, respectively, from the NiP_2 plane. The P(1)–Ni–P(2) bond angle of 102.2(1)° is larger than the square-planar value of 90°, and this presumably reflects intramolecular steric effects.

It is not possible to draw any firm conclusions from the nickel to phosphorus bond lengths, because of a general lack of comparative data, however, the bond lengths Ni–P(1) 2.252(2) Å [*trans* to the midpoint of B(2)–B(7)] and Ni–P(2) 2.212(2) Å [*trans* to C(5)] are at the upper end of the range of values observed with a variety of complexes,[10] indicating fairly strong Ni–C_2B_7 bonding.

TABLE 1

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for the complex *nido*-[6,6-$(Et_3P)_2$-5,9-Me_2-6,5,9-$NiC_2B_7H_9$]

Bond lengths

Phosphine ligands			
Ni–P(1)	2.252(2)	Ni–P(2)	2.213(2)
P(1)–C(11)	1.825(9)	P(2)–C(21)	1.902(11)
C(11)–C(12)	1.51(1)	C(21)–C(22)	1.48(2)
P(1)–C(13)	1.872(8)	P(2)–C(23)	1.823(12)
C(13)–C(14)	1.45(1)	C(23)–C(24)	1.48(2)
P(1)–C(15)	1.814(9)	P(2)–C(25)	1.816(10)
C(15)–C(16)	1.60(1)	C(25)–C(26)	1.60(1)
Ni–Ni(2)	0.77(2)	Ni(2)–P(2)	2.039(15)
Ni(2)–P(1)	2.161(17)		
Cage atoms			
Ni–C(5)	2.045(7)	B(1)–B(10)	1.78(1)
Ni–B(7)	2.137(10)	B(1)–B(4)	1.71(1)
Ni–B(2)	2.071(10)	B(1)–B(3)	1.73(1)
C(5)–C(51)	1.53(1)	B(3)–B(4)	1.79(1)
C(5)–B(10)	1.57(1)	B(3)–B(7)	1.71(1)
C(5)–B(2)	1.62(1)	B(3)–B(8)	1.79(2)
C(5)–B(1)	1.70(1)	B(4)–B(8)	1.79(1)
B(2)–B(7)	1.75(1)	B(4)–B(10)	1.73(1)
B(2)–B(1)	1.73(1)	B(4)–C(9)	1.63(1)
B(2)–B(3)	1.80(1)	B(8)–C(9)	1.68(1)
B(10)–C(9)	1.74(1)	B(8)–B(7)	1.87(1)
C(9)–C(91)	1.56(1)	B(7)–H(78) [a]	1.29
C(9)–H(9) [a]	1.17	B(8)–H(78) [a]	1.35

TABLE 1 (*Continued*)

Bond angles

Phosphine ligands			
P(1)–Ni–P(2)	102.2(1)	P(1)–Ni(2)–P(2)	111.5(7)
P(1)–C(11)–C(12)	117.9(6)	P(2)–C(21)–C(22)	115.3(8)
P(1)–C(13)–C(14)	114.5(7)	P(2)–C(23)–C(24)	114.0(9)
P(1)–C(15)–C(16)	111.1(6)	P(2)–C(25)–C(26)	117.4(7)
C(11)–P(1)–C(13)	103.8(4)	C(21)–P(2)–C(23)	104.0(6)
C(11)–P(1)–C(15)	103.0(4)	C(21)–P(2)–C(25)	101.8(5)
C(13)–P(1)–C(15)	101.0(4)	C(23)–P(2)–C(25)	102.7(5)
Ni–P(1)–C(11)	116.2(3)	Ni–P(2)–C(21)	121.9(3)
Ni–P(1)–C(13)	119.1(3)	Ni–P(2)–C(23)	107.2(4)
Ni–P(1)–C(15)	111.8(3)	Ni–P(2)–C(25)	117.0(3)
Cage atoms			
B(2)–Ni–B(7)	49.0(4)	C(5)–Ni–P(1)	97.7(2)
B(2)–Ni–P(1)	143.7(3)	C(5)–Ni–P(2)	154.4(2)
B(2)–Ni–P(2)	111.3(3)	C(5)–Ni–B(2)	46.3(3)
B(7)–Ni–P(1)	150.6(3)	C(5)–Ni–B(7)	84.6(3)
B(7)–Ni–P(2)	85.9(3)		
Ni–C(5)–C(51)	114.3(5)	Ni–B(2)–B(7)	67.4(5)
Ni–C(5)–B(2)	67.1(4)	Ni–B(2)–C(5)	66.0(4)
Ni–C(5)–B(10)	114.7(5)	Ni–B(2)–B(1)	119.3(6)
Ni–C(5)–B(1)	122.2(5)	Ni–B(2)–B(3)	115.5(6)
B(10)–C(5)–C(51)	117.9(7)	B(7)–B(2)–B(1)	109.3(7)
B(10)–C(5)–B(1)	65.8(6)	B(7)–B(2)–B(3)	57.8(5)
B(10)–C(5)–B(2)	115.1(6)	B(7)–B(2)–C(5)	113.5(7)
B(2)–C(5)–C(51)	117.2(6)	B(1)–B(2)–B(3)	58.8(6)
B(1)–C(5)–C(51)	113.6(6)	B(1)–B(2)–C(5)	61.1(5)
B(2)–C(5)–B(1)	62.7(6)	B(3)–B(2)–C(5)	106.8(7)
B(2)–B(1)–C(5)	56.2(5)	B(1)–B(4)–B(10)	62.4(6)
B(2)–B(1)–B(10)	100.0(7)	B(1)–B(4)–C(9)	114.8(7)
B(2)–B(1)–B(4)	109.5(7)	B(1)–B(4)–B(8)	109.1(7)
B(2)–B(1)–B(3)	62.6(6)	B(1)–B(4)–B(3)	59.5(6)
C(5)–B(1)–B(10)	53.5(5)	B(10)–B(4)–C(9)	62.3(6)
C(5)–B(1)–B(4)	103.4(7)	B(10)–B(4)–B(8)	105.6(7)
C(5)–B(1)–B(3)	106.0(7)	B(10)–B(4)–B(3)	106.5(7)
B(10)–B(1)–B(4)	59.6(6)	C(9)–B(4)–B(8)	58.4(6)
B(10)–B(1)–B(3)	106.8(7)	C(9)–B(4)–B(3)	109.0(7)
B(2)–B(1)–B(3)	62.6(6)	B(8)–B(4)–B(3)	59.9(6)
C(5)–B(10)–B(1)	60.8(6)	Ni–B(7)–B(2)	63.5(4)
C(5)–B(10)–B(4)	108.2(7)	Ni–B(7)–B(8)	106.9(6)
C(5)–B(10)–C(9)	115.1(7)	Ni–B(7)–B(3)	116.1(6)
B(1)–B(10)–B(4)	58.1(6)	B(2)–B(7)–B(3)	62.6(6)
B(1)–B(10)–C(9)	106.0(7)	B(2)–B(7)–B(8)	105.3(7)
B(4)–B(10)–C(9)	56.0(6)	B(3)–B(7)–B(8)	59.5(6)
B(4)–B(8)–B(3)	60.0(6)	B(10)–C(9)–B(4)	61.7(6)
B(4)–B(8)–B(7)	105.0(7)	B(10)–C(9)–B(8)	110.3(7)
B(4)–B(8)–C(9)	56.1(6)	B(10)–C(9)–C(91)	119.8(7)
B(3)–B(8)–B(7)	55.9(6)	B(4)–C(9)–B(8)	65.4(6)
B(3)–B(8)–C(9)	107.1(7)	B(4)–C(9)–C(91)	114.0(7)
B(7)–B(8)–C(9)	113.5(6)	B(8)–C(9)–C(91)	121.3(7)
B(2)–B(3)–B(7)	59.6(6)	B(7)–B(3)–B(4)	112.0(7)
B(2)–B(3)–B(8)	106.8(7)	B(7)–B(3)–B(1)	110.7(7)
B(2)–B(3)–B(4)	103.0(7)	B(8)–B(3)–B(4)	60.1(6)
B(2)–B(3)–B(1)	58.6(6)	B(8)–B(3)–B(1)	107.9(7)
B(7)–B(3)–B(8)	64.6(6)	B(4)–B(3)–B(1)	57.9(6)

[a] E.s.d.s for B–H and C–H bond lengths are not physically meaningful since the hydrogen atom positional parameters were not refined (see text).

The Ni–C(5) bond length of 2.045(7) Å compares well with the Ni–C bond lengths [2.01—2.09 Å][11] observed in various π-allylic complexes, and is longer than the

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[10] V. Scatturin and A. Turco, *J. Inorg. Nuclear Chem.*, 1958, **8**, 447, [$NiBr_2(PEt_3)_2$], Ni–P 2.26 Å; G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 1963, 3625, [$NiCl_2(PPh_3)_2$], Ni–P 2.28 Å; G. Burnett, B. Büssemeier, P. Heimbach, P. W. Jolly, C. Krüger, I. Tkatchenko, and G. Wilke, *Tetrahedron Letters*, 1972, 1457, [$NiPCy_3(C_{10}H_{16})$], Ni–P 2.19 Å; P. W. Jolly, K. Jones, C. Krüger, and Y. K. Tsay, *J. Organometallic Chem.*, 1971, **33**, 109, [$Ni_2(Pcy_3)_4N_2$], Ni–P 2.15 and 2.19 Å.

[11] P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' vol. I, p. 357—360, Academic Press, 1974.

bond length (1.94, 1.95 Å)[12] reported for complexes containing a Ni–C σ-bond.

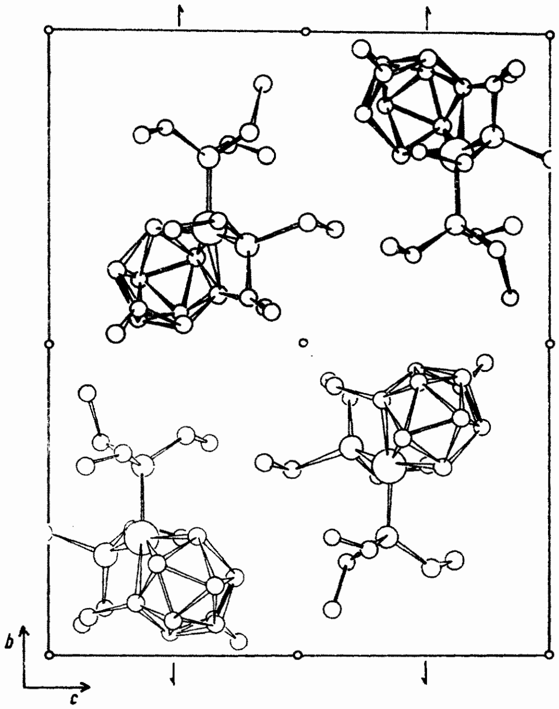

FIGURE 3 Molecular packing diagram looking along the *a* axis towards the origin. Hydrogen atoms are omitted

TABLE 2

Positional parameters of $[(Et_3P)_2Ni(C_2B_7H_9Me_2)]$ [a]

Atom	*x*	*y*	*z*
Ni [b]	0.9573(2)	0.1855(1)	0.1856(1)
Ni(2) [b]	1.0187(20)	0.2029(8)	0.2139(10)
P(1)	1.1687(2)	0.1645(1)	0.1146(1)
P(2)	0.9466(2)	0.3021(1)	0.1846(1)
C(5)	0.8712(7)	0.0862(4)	0.1754(4)
C(51)	0.8402(10)	0.0621(5)	0.0796(5)
C(9)	1.0246(10)	0.0670(4)	0.3354(5)
C(91)	1.1347(12)	0.0215(6)	0.3905(6)
C(11)	1.2301(9)	0.0729(4)	0.1125(5)
C(12)	1.3802(10)	0.0577(5)	0.0760(7)
C(13)	1.1881(10)	0.1939(5)	−0.0036(5)
C(14)	1.0677(13)	0.1738(6)	−0.0616(6)
C(15)	1.3213(9)	0.2100(5)	0.1669(6)
C(16)	1.3488(11)	0.1821(6)	0.2660(7)
C(21)	0.9897(13)	0.3567(5)	0.2878(8)
C(22)	1.1392(17)	0.3475(7)	0.3250(9)
C(23)	0.7591(13)	0.3264(5)	0.1560(10)
C(24)	0.7107(14)	0.3018(8)	0.0671(11)
C(25)	1.0520(10)	0.3474(4)	0.1001(6)
C(26)	1.0152(14)	0.4286(5)	0.0822(8)
B(1)	0.7501(12)	0.0539(6)	0.2508(7)
B(2)	0.7577(10)	0.1416(5)	0.2189(6)
B(3)	0.7383(11)	0.1171(6)	0.3339(6)
B(4)	0.8546(12)	0.0417(5)	0.3442(6)
B(7)	0.8338(11)	0.1915(5)	0.3055(6)
B(8)	0.9147(13)	0.1257(6)	0.3846(6)
B(10)	0.9384(11)	0.0309(5)	0.2420(6)
H(78) [c]	0.9651	−0.02	0.2081
H(9) [c]	1.0788	0.1140	0.2970

[a] Expressed as fractional co-ordinates of the unit cell edges. The estimated standard deviations are shown in parentheses. Hydrogen atom parameters are deposited with the structure factor data. [b] Refined population parameters Ni = 0.906 and Ni(2) = 0.094. [c] The isotropic thermal parameters are 6.33×10^{-2} Å².

TABLE 3

Thermal parameters of the $Ni(PC_2)_2(C_4B_7)$ moiety ($Å^2 \times 10^3$) [a]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	31(1)	33(1)	37(1)	0.8(0.5)	5(0.5)	1(0.5)
Ni(2)	57(10)	47(8)	49(9)	12(7)	29(7)	1(6)
P(1)	38(1)	50(1)	46(1)	6(1)	12(1)	−1(1)
P(2)	57(15)	36(13)	77(16)	9(10)	15(1)	5(1)
C(5)	42(4)	53(4)	47(4)	−11(4)	3(3)	−5(3)
C(51)	75(6)	82(5)	55(5)	−16(5)	−6(4)	−15(4)
C(9)	72(6)	67(5)	58(5)	−4(5)	−17(5)	17(4)
C(91)	90(8)	128(9)	86(7)	25(7)	−24(6)	41(6)
C(11)	64(6)	70(6)	59(5)	16(4)	5(4)	−18(4)
C(12)	60(6)	87(7)	110(8)	16(5)	8(5)	−40(6)
C(13)	67(6)	115(8)	41(4)	−12(6)	18(4)	−3(5)
C(14)	114(9)	133(10)	63(6)	22(8)	13(6)	−29(6)
C(15)	41(5)	69(6)	114(7)	3(4)	17(5)	2(5)
C(16)	65(7)	117(9)	109(8)	4(7)	−18(6)	−32(7)
C(21)	117(9)	43(5)	134(10)	1(6)	40(8)	−31(6)
C(22)	139(13)	139(12)	145(12)	11(10)	−30(10)	−69(10)
C(23)	67(8)	71(7)	201(13)	30(6)	22(9)	75(8)
C(24)	85(10)	155(14)	222(16)	−9(9)	−56(10)	115(13)
C(25)	86(7)	37(4)	105(7)	4(5)	34(6)	21(5)
C(26)	129(10)	44(5)	169(11)	11(6)	58(9)	33(6)
B(1)	61(6)	83(7)	66(6)	−17(6)	7(5)	12(6)
B(2)	52(6)	59(6)	56(6)	−2(5)	7(5)	7(4)
B(3)	54(6)	89(7)	63(6)	−11(6)	28(5)	11(6)
B(4)	74(7)	60(6)	60(6)	−18(5)	−3(5)	18(5)
B(7)	61(6)	59(6)	71(6)	8(5)	30(5)	−1(5)
B(8)	82(8)	98(8)	44(5)	−21(7)	5(5)	2(5)
B(10)	69(7)	47(5)	67(6)	−5(5)	7(5)	−3(4)

[a] The anisotropic temperature factor is defined as $q_j = \exp\{-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)\}$. E.s.d.s in parentheses.

TABLE 4

Comparison of selected bond lengths (Å) in $[6,6\text{-}(Et_3P)_2\text{-}5,9\text{-}Me_2\text{-}6,5,9\text{-}NiC_2B_7H_9]$ (V) and in *arachno*-5,9-Me_2-5,9-$C_2B_7H_{11}$.

Complex (V)		*arachno*-5,9-Me_2-5,9-$C_2B_7H_{11}$ [a]	
C(5)–B(2)	1.62(1)	C(5)–B(6)	1.714(4)
B(7)–B(2)	1.75(1)	B(6)–B(7)	1.826(5)
B(2)–B(1)	$1.73_5(1)$	B(6)–B(1)	1.778(6)
C(5)–B(1)	1.71(1)	B(1)–C(5)	1.671(5)
B(1)–B(3)	1.73(1)	B(1)–B(2)	1.779(5)
B(3)–B(7)	1.71(1)	B(7)–B(2)	1.719(6)
B(3)–B(4)	1.79(1)	B(2)–B(3)	1.777(6)
B(1)–B(4)	1.70(1)	B(3)–B(1)	1.710(5)
B(2)–B(3)	1.80(1)	B(6)–B(2)	1.817(5)

[a] Data from ref. 9.

These structural features suggest that these compounds, which formally have incorporated the $[C_2B_7]^{2-}$ ligand, may be regarded as 1,2,3-η-B_2C bonded complexes of Ni^{II} and Pt^{II} and are, therefore, analogous to the cationic species $[M(\eta^3\text{-}C_3H_5)L_2]^+$ (M = Ni or Pt),[13] and also to the neutral complex $[Pt(B_3H_7)(PEt_3)_2]$,[14] which is considered to contain a 1,2,3-η-B_3 bonded framework analogous to a π-allylic system. A similar analogy has been drawn in the 'slipped' sandwich complexes of $[C_2B_9H_{11}]^{2-}$ where three facial boron atoms play the role of allylic carbon atoms.[15] It is interesting to note that

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[12] B. L. Bennett and C. Krüger, *J. Organometallic Chem.*, 1972, **42**, 169; see also P. W. Jolly and G. Wilke, p. 165.

[13] B. F. G. Johnson, J. Lewis, and D. A. White, *J. Amer. Chem. Soc.*, 1969, **91**, 5186.

[14] L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 5665.

[15] R. M. Wing, *J. Amer. Chem. Soc.*, 1967, **89**, 5599; 1968, **90**, 4828.

the bonding mode of the $[C_2B_7]^{2-}$ ligand present in the complexes described herein is different from that exhibited by the isoelectronic cobalt complex $[Co(C_2B_7H_{11})(\eta^5\text{-}C_5H_5)]$.[16,17]

With the establishment of the structure of (V) it was then possible to interpret the ^1H n.m.r. spectra of the carbadibora-allyl complexes. The ^1H n.m.r. spectrum of the platinum complex (IV) provided the only view of the τ 8—10 region unobscured by ligand resonances. Three distinct signals were observed: (i) at τ 8.40 a partially resolved doublet of doublets with platinum-195 satellites, (ii) a broad doublet at τ 8.66, and (iii) a very broad peak centred at τ 9.38. Powerful irradiation of (iii) reduced the doublet (ii) at τ 8.66 to a singlet suggesting that these signals were due to H(9) and Me(91) respectively. Similarly, irradiation at a frequency corresponding to the centre of the ^{31}P spectrum reduced the central lines of (i) to a singlet, but not the ^{195}Pt satellites. Thus the signal (i) is due to Me(51). The ^1H n.m.r. spectrum of (V) showed a resonance centred at τ 9.83, which is assigned to H(9); the Me(51) and Me(91) resonances were partially obscured by the ethyl resonance of the triethylphosphine ligands. None of the spectra showed features which could conclusively be ascribed to the bridging hydrogen whose presence was identified in the crystal-structure determination.

DISCUSSION

A plausible mechanism (Scheme) for formation of complexes (I)—(VI) is an initial oxidative-addition reaction between the d^{10} metal species and one of the relatively protonic axial carbon–hydrogen bonds of the carbaborane. This is supported by the observation that the ^1H n.m.r. spectrum of a reacting solution (toluene) of $[Pt(PEt_3)_2(stilbene)]$ and $5,9\text{-}Me_2\text{-}5,9\text{-}C_2B_7H_{11}$ showed the development of a doublet signal at τ 16.24 [J(HP) 22.0 Hz] assignable to a platinum hydride; on further reaction this signal disappeared. During reaction the appearance of a band in the i.r. spectrum at 1 963 cm^{-1}, which also subsequently disappeared, provided further evidence for the intermediacy of a species containing a Pt–H system.

EXPERIMENTAL

^1H n.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 MHz; chemical shifts are relative to Me_4Si (τ 10.00). The ^{11}B n.m.r. spectrum was measured at 80.5 MHz by Dr. R. R. Reitz on Professor F. A. L. Anet's instrument at U.C.L.A.; the chemical shifts are relative to $Et_2O \cdot BF_3$. The i.r. spectra were recorded on a Perkin–Elmer 457 grating spectrophotometer, and mass spectra on an A.E.I. MS 902 spectrometer at an ionizing voltage of 70 eV.* Melting points were measured *in vacuo*. All reactions were performed in a dry oxygen-free nitrogen atmosphere. Solvents were dried and distilled under nitrogen prior to use. Light petroleum refers to the fraction b.p. 40—60 °C.

Preparation of *nido*-$[6,6\text{-}(Et_3P)_2\text{-}6,5,9\text{-}PtC_2B_7H_{11}]$, (I).—*trans*-Stilbenebis(triethylphosphine)platinum (0.58 g, 0.94 mmol) and dry toluene (3 cm^3) were placed in a Schlenk tube connected to a gas burette and the system sealed and allowed to equilibrate. A solution of *arachno*-$5,9\text{-}C_2B_7H_{13}$ (1.5 mmol) in toluene (7.2 cm^3) was introduced through a rubber syringe cap. The pale yellow solution became colourless, and a gas (0.94 mmol), assumed to be hydrogen, was evolved slowly over ½ h. The solvent was evaporated at reduced pressure and the white crystalline mass was extracted several times with light petroleum to remove *trans*-stilbene (0.15 g, 83%), which was identified by i.r. spectroscopy. Recrystallisation of the residue from methylene chloride–light petroleum gave white *crystals* of (I) (0.49 g, 90%), m.p. 199 °C (Found: C, 31.2; H, 7.7; B, 13.8; P, 11.4. $C_{14}H_{41}B_7P_2Pt$ requires C, 31.0; H, 7.6; B, 14.0; P, 11.4%), $\nu_{max.}$ (Nujol) 2 555sh, 2 535vs, 2 510sh, 2 475sh, 1 415m, 1 254m, 1 243sh, 1 126w, 1 090m, 1 058m, 1 049s, 1 040sh, 1 010w, 981m, 933m, 906w, 898w, 870w, 807w, 764s, 723s, and 633m cm^{-1}. The mass spectrum showed an unusual pattern of ions centred at *m/e* 542 apparently due to the overlapping isotopic patterns of [*P*] and [*P* − 2 H] ions. Other major ions arose from the fragmentation of $[Pt(PEt_3)_2]$ by successive loss of fragments with mass 28 (C_2H_4). Apart from the parent ion, boron-containing ions were of low intensity. The ^{11}B n.m.r. spectrum (CH_2Cl_2) showed seven distinct resonances at −10.4, 5.5, 8.4, 11.8, 18.2, 26.6, and 40.0 p.p.m. All the resonances had a doublet structure except that at 18.2 p.p.m. which was unresolved.

A similar procedure was followed in the synthesis of the following complexes. Reaction of *arachno*-$5,9\text{-}Me_2\text{-}5,9\text{-}C_2B_7H_{11}$ (0.25 g, 1.8 mmol) with *trans*-stilbenebis(triethylphosphine)platinum (1.0 g, 1.6 mmol) gave off-white *crystals* of (II) *nido*-$[6,6\text{-}(Et_3P)_2\text{-}5,9\text{-}Me_2\text{-}6,5,9\text{-}PtC_2B_7H_9]$ (0.65 g, 71%), m.p. 167 °C (Found: C, 33.7; H, 8.1. $C_{16}H_{45}B_7P_2Pt$ requires C, 33.7; H, 8.0%), ^1H n.m.r. resonances ($CDCl_3$) at τ 7.94 (complex m, 15 H, C*Me*, PC*H*$_2$Me) and 8.89 (complex m, 21 H, CH*Me*, PCH$_2$*Me*), 10.0 (br, 1 H, C*H*Me) and 11.80 (br, 1 H, possibly B*H*B). Similarly, *arachno*-$5,9\text{-}Me_2\text{-}5,9\text{-}C_2B_7H_{11}$ (0.15 g, 1.1 mmol) and *trans*-stilbenebis(trimethylphosphine)platinum (0.53 g, 1.0 mmol) gave white *crystals* of (III) *nido*-$[6,6\text{-}(Me_3P)_2\text{-}5,9\text{-}Me_2\text{-}6,5,9\text{-}PtC_2B_7H_9]$ (0.2 g, 40%), m.p. 248 °C (Found: C, 25.0; H, 7.0. $C_{10}H_{33}B_7P_2Pt$ requires C, 24.7; H, 6.8%), ^1H n.m.r. resonances (CH_2Cl_2) at τ 8.12 (m, 3 H, C*Me*), 8.89 (d, 3 H, CH*Me*, *J*(HH) 6.0 Hz) and 10.10 (m, 1 H, C*H*Me); 8.25 [d, with ^{195}Pt satellites, 9 H, P*Me*$_3$, *J*(HP) 9.8 Hz, *J*(HPt) 31.0 Hz], 8.38 [d, with ^{195}Pt satellites, 9 H, P*Me*$_3$, *J*(HP) 8.6 Hz, *J*(HPt) 24.1 Hz]; *arachno*-$5,9\text{-}Me_2\text{-}5,9\text{-}C_2B_7H_{11}$ (0.03 g, 0.21 mmol) and *trans*-stilbenebis(triphenylphosphine)platinum (0.15 g, 0.17 mmol) gave white *crystals* of (IV) *nido*-$[6,6\text{-}(Ph_3P)_2\text{-}5,9\text{-}Me_2\text{-}6,5,9\text{-}PtC_2B_7H_9]$ (0.09 g, 61%), m.p. 270 °C (Found: C, 54.9; H, 5.5. $C_{40}H_{45}B_7P_2Pt$ requires C, 56.0; H, 5.3%), ^1H n.m.r. resonances (CH_2Cl_2) at τ 2.56 (m, 30 H, *Ph*P), 8.40 [dd, with ^{195}Pt satellites, 3 H, *Me*(5), $J(HP^1) \simeq (HP^2) \simeq 4$ Hz, *J*(HPt) 16 Hz], 8.66 [d, 3 H, *Me*(9), *J*(HH) 6.0 Hz], and 9.38 [broad, 1 H, H(9)].

Preparation of (V), *nido*-$[6,6\text{-}(Et_3P)_2\text{-}5,9\text{-}Me_2\text{-}6,5,9\text{-}NiC_2B_7H_9]$.—Triethylphosphine (0.6 cm^3, 0.48 g, 4.0 mmol) was

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* 1 eV ≈ 1.6×10^{-19} J.

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[17] K. P. Callahan, F. Y. Lo, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, 1974, **13**, 2842.

[18] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

added to a suspension of [Ni(cod)$_2$] (0.60 g, 2.1 mmol) in light petroleum (10 cm^3). The solid dissolved to give a clear yellow solution, to which *arachno*-5,9-Me$_2$-5,9-C$_2$B$_7$H$_{11}$ (0.3 g, 2.1 mmol) was added. As the carbaborane dissolved the solution darkened but there was no apparent evolution of gas until the temperature was raised to 40 °C when a reaction occurred and deep red crystals were deposited. After 20 min, when gas evolution had ceased, the solvent was decanted from the crystals which were collected. Recrystallisation from toluene gave deep red *needles* of (V) *nido*-[6,6-(Et$_3$P)$_2$-5,9-Me$_2$-6,5,9-NiC$_2$B$_7$H$_9$] (0.69 g, 80%), m.p. 161—163 °C (decomp.) (Found: C, 44.0; H, 10.6. C$_{16}$H$_{45}$B$_7$NiP$_2$ requires C, 44.3; H, 10.5%), $\nu_{max.}$ (Nujol) 2 565s, 2 540s, 2 498s, 1 258m, 1 153w, 1 125w, 1 040s, 1 029m, 1 001m, 930w, 909w, 887w, 766s, 760sh, 714s, 668w, and 629m cm^{-1}. The ^{1}H n.m.r. spectrum (CH$_2$Cl$_2$) showed resonances at τ 8.25 (m, 15 H, 5-C*Me*, P*CH*$_2$CH$_3$), 8.87 (m, 21 H, 9-C*Me*, PCH$_2$*CH*$_3$), and 9.83 (broad, 1 H, C*H*Me). When benzene is used as solvent and reference the cage methyl resonance shifts to lower field relative to the phosphine ethyl protons, and a doublet of doublets [$J(\text{HP}_{cis}) \simeq J(\text{HP}_{trans}) \simeq 4.5$ Hz] ascribed to Me(5) is observed at τ 8.13.

A similar reaction of [Ni(cod)(PMe$_3$)$_2$] {prepared *in situ* from [Ni(cod)$_2$] (0.42 g, 1.5 mmol) and PMe$_3$ (0.35 g, 4.6 mmol)} with *arachno*-5,9-Me$_2$-5,9-C$_2$B$_7$H$_{11}$ (0.24 g, 2 mmol) in toluene gave red *crystals* of (VI) *nido*-[6,6-(Me$_3$P)$_2$-5,9-Me$_2$-6,5,9-NiC$_2$B$_7$H$_9$] (0.41 g, 78%), m.p. 184 °C (decomp.) (Found: C, 34.2; H, 9.5. C$_{10}$H$_{33}$B$_7$NiP$_2$ requires C, 34.4; H, 9.5%). The ^{1}H n.m.r. spectrum (CH$_2$Cl$_2$) showed resonances at τ 8.4 (m, C*Me*), 8.51 [d, 9 H, PMe$_3$, *J*(HP) 7.0 Hz], 8.59 [d, 9 H, P*Me*$_3$, *J*(HP) 7.0 Hz], 8.84 [d, 3 H, C*H*Me, *J*(HH) 6.0 Hz], and 10.04 [broad, 1 H, H(9)].

Crystal Structure Determination.—The complex (V) was recrystallised from toluene and formed deep red prisms. A single crystal, 0.50 × 0.37 × 0.15 mm, was mounted on a Syntex $P2_1$ four-circle diffractometer, and the unit cell and intensity data recorded in a manner already described.[18] 3 445 of the total 4 400 reflections recorded, $2.9° \leqslant 2\theta \leqslant 50°$, using graphite monochromated *X*-radiation were deemed 'observed' according to the criterion; $I \geqslant 2.5\,\sigma(I)$.

Crystal Data.—C$_{16}$H$_{45}$B$_7$NiP$_2$, $M = 433.3$, monoclinic space group $P2_1/n$, $a = 9.144(2)$, $b = 18.954(5)$, $c = 15.021(3)$ Å, $\beta = 90.51(4)°$, $U = 2\,603(1)$ Å^3, $D_m = 1.10$, $Z = 4$, $D_c = 1.11$ g cm^3, $\mu(\text{Mo-}K_{\bar{\alpha}}) = 8.7$ cm^{-1}, $\lambda = 0.710\,69$ Å.

The structure was solved by conventional heavy-atom methods, using absorption corrected data and was refined by least-squares techniques. Hydrogen atoms were incorporated in the structure-factor calculations at positions estimated from the electron-density maps, but neither their positional nor their thermal parameters were refined. Hydrogen atom parameters are deposited with the structure factors as a Supplementary publication (No. SUP 21475, 15 pp.) *. In the final stage of refinement, using block matrix refinement (246 variables), all non-hydrogen atoms were given anisotropic thermal parameters. Atomic scattering factors used were those given elsewhere,[19] with those for nickel corrected for the effects of anomalous dispersion [$\Delta f^1 = 0.35$, $\Delta f^2 = 1.1$ (Mo-$K_{\bar{\alpha}}$)].

The weighting scheme was $w = 1/\sigma^2$, where $\sigma(F)$ is that derived from counting statistics, and a satisfactory weight analysis was obtained.

An electron-density difference map at this stage showed no significant peaks, except for one peak located at approximately 0.7 Å from the nickel atom. Chemical and other evidence rule out the possibility of an extra atom at this position and it seemed likely that the cause was molecular disorder. The structure was, therefore, refined again to include a fractional nickel atom [Ni(2)] at this position, with a variable population parameter. This refinement converged at R 0.068 (R' 0.080) for 3 192 independent non-zero reflections with population parameters of 0.906 for the original nickel atom and 0.094 for the disordered site. There were no peaks greater than 0.4 nor less than −0.4 Å^3 in the residual electron density map. It was not considered feasible to attempt to locate all the other disordered positions for the rest of the cage atoms, because the densities sought would be within the same range as those of the general background.

The computational work was carried out at the University of London Computing Centre, and the Atlas Laboratory using the *X*-ray system of programs.[20] Observed and calculated structure factors are listed in the Supplementary Publication.

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* See Notice to Authors No. 7, *J.C.S. Dalton*, 1974, Index issue for details of Scheme.

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[20] Technical Report TR-192 of the Computer Science Center, University of Maryland, June 1972.