Metallaborane Chemistry. Part III.[1] Oxidative-insertion Reactions of Eleven-atom Monocarbon Carbaborane Species with Zerovalent Nickel, Palladium, and Platinum Complexes; the Molecular and Crystal Structure of 1,1-Bis(t-butyl isocyanide)-2-(trimethylamine)-2-carba-1-pallada-closo-decaborane(10)

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Reaction of $[Ni(cod)(Bu^tNC)_2]$, $[Pd(Bu^tNC)_2]$, and $[Pt(trans$-stilbene$)(PEt_3)_2]$ with $[Me_4N]^+$ $[closo$-$CB_{10}H_{11}]^-$ and $closo$-2-NMe_3-2-$CB_{10}H_{10}$ affords the $closo$-metallacarbaboranes $[Me_4N]^+[1,1$-L_2-1,2-$MCB_{10}H_{11}]^-$ and $[1,1$-L_2-2-NMe_3-1,2-$MCB_{10}H_{10}]$ (M = Ni or Pd, L = Bu^tNC; M = Pt, L = PEt_3). The molecular structure of the palladium complex has been determined from a single-crystal X-ray diffraction study and refined to R = 0.042 for 3 319 independent observed reflections. Crystals are monoclinic, space group $P2_1/n$, with cell dimensions of a = 10.947(3), b = 15.194(4), c = 15.804(4) Å, β = 103.45(2)°. The 12-atom polyhedron has a very distorted icosahedral geometry, marked by an extremely weak metal–carbon interaction with Pd–C(cage) at 2.600(6) Å. The metal to carbaborane bonding is described in terms of approximately square planar co-ordination.

In the first paper[2] in this series we described a new route to metallacarbaboranes involving the direct oxidative insertion of Ni, Pd, and Pt d^{10} species into $closo$-C_2B_9 and $closo$-CoC_2B_8 carbaboranes. The extension of this synthetic approach to the corresponding reactions of $closo$-C_2B_7[3] and $closo$-C_2B_6[4] species has been described in preliminary publications. In this paper are detailed experiments concerned with the related reaction of zerovalent Ni, Pd, and Pt species with the 11-atom carbaboranes[5,6] $[closo$-$CB_{10}H_{11}]^-$ and $closo$-2-NMe_3-2-$CB_{10}H_{10}$.

Reactions of $[Me_4N]^+[CB_{10}H_{11}]^-$ with $[Ni(cod)(Bu^t$-$NC)_2]$, $[Pd(Bu^tNC)_2]$, or $[Pt(trans$-stilbene$)(PEt_3)_2]$ at room temperature in acetone affords the metallamonocarbon carbaboranes (I), (II), and (III). The orange (I), yellow (II), and pale yellow (III) products were isolated as microcrystalline solids which had reasonable air stability in the solid state. Although the compounds (I) and (III) had very low solubilities in organic solvents, ^{1}H n.m.r. spectra could be observed in $[^2H_6]$dimethyl sulphoxide as solvent, and showed resonances assignable to terminal ligands and the tetramethylammonium

[1] Part II, A. J. Welch, J.C.S. Dalton, 1975, 1473.

[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.

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

[5] D. E. Hyatt, J. R. Scholer, L. J. Todd, and J. L. Weiner, Inorg. Chem., 1967, 6, 2229.

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cation. No signals were observed for the cage groups. The i.r. spectra showed terminal B–H stretching bands and complexes (I) and (II) also showed bands due to the co-ordinated isocyanide ligand.

In order to obtain more soluble derivatives the corresponding reactions of the zwitterionic species closo-2-Me$_3$N-2-CB$_{10}$H$_{10}$ were investigated. Thus, reaction of [Ni(cod)(Bu^{t}NC)$_2$] in acetone–toluene yielded the orange crystalline complex (IV). The i.r. spectrum showed two terminal isocyanide bands at 2 175 and 2 150 cm^{-1} consistent with a relative cis-configuration for the isocyanide ligands co-ordinated onto nickel. The ^{1}H n.m.r. spectrum, measured in [^{2}H$_6$]acetone, showed two sharp singlets at τ 6.54 (N-Me) and 8.48 (Bu^{t}NC) in a relative ratio of 1 : 2 in agreement with the illustrated structure. Similar reactions of closo-2-Me$_3$N-2-CB$_{10}$H$_{10}$ with [Pd(Bu^{t}NC)$_2$] and [Pt(trans-stilbene)(PEt$_3$)$_2$] gave respectively the yellow crystalline complexes (V) and (VI). As expected the spectroscopic properties of (IV) and (V) were similar. Compound (VI) showed in the i.r. spectrum B–H stretching frequencies at 2 530 and 2 498 cm^{-1}, and the ^{1}H n.m.r. spectrum had a sharp singlet at τ 6.66 (NMe) and two multiplets centred at τ 8.04 and 8.90 assignable to the phosphine ligands. The equi-
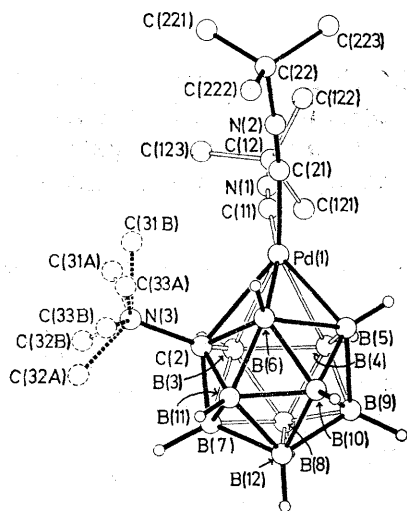

FIGURE 1 Perspective view of the molecule showing the atomic numbering scheme

valence of the two phosphine ligands was confirmed by the ^{31}P F.T. n.m.r. spectrum, which showed a single sharp peak at 2.29 p.p.m. (relative to H$_3$PO$_4$) with ^{195}Pt satellites (J_{PtP} 3 103 Hz). Although the 32 MHz ^{11}B F.T. n.m.r. spectra of complexes (IV), (V), and (VI) were obtained they did not allow an unambiguous structural assignment to be made. Since the palladium complex (V) formed suitable single crystals an X-ray diffraction study was undertaken.

A perspective view of a single molecule, showing the atomic numbering scheme adopted, is given in Figure 1 (cage hydrogen atoms take the same number as the boron to which they are attached). Tables 1—3 list the

interatomic distances (uncorrected for thermal effects) and inter-bond angles determined.

The 12-Atom Cage.—This fraction of the molecule exhibits approximate mirror symmetry (also possessed by the amino-group) about a plane containing Pd(1), B(9), B(12), and C(2) [N(3), C(32A), and C(31B)], consistent with that implied by the spectroscopic data.

TABLE 1

Bond length data

(A) Bonds within the polyhedron

Bond		Bond	
Pd(1)–C(2)	2.600(6)	B(5)–B(6)	1.86$_5$(1)
Pd(1)–B(3)	2.261(6)	B(5)–B(10)	1.74(1)
Pd(1)–B(4)	2.223(7)	B(5)–B(9)	1.75(1)
Pd(1)–B(5)	2.259(8)	B(6)–B(11)	1.85(1)
Pd(1)–B(6)	2.238(7)	B(6)–B(10)	1.80(1)
C(2)–B(3)	1.666(8)	B(7)–B(8)	1.78(1)
C(2)–B(7)	1.663(9)	B(7)–B(12)	1.75(1)
C(2)–B(11)	1.66(1)	B(8)–B(9)	1.77(1)
C(2)–B(6)	1.711(8)	B(8)–B(12)	1.81(1)
B(3)–B(4)	1.881(9)	B(9)–B(10)	1.76(1)
B(3)–B(8)	1.79(1)	B(9)–B(12)	1.75(1)
B(3)–B(7)	1.86(1)	B(10)–B(12)	1.78(1)
B(4)–B(5)	1.753(9)	B(11)–B(7)	1.74(1)
B(4)–B(9)	1.78(1)	B(11)–B(12)	1.75(1)
B(4)–B(8)	1.75(1)	B(11)–B(10)	1.78(1)

(B) All other bonds

C(2)–N(3)	1.550(7)	N(3)–C(32B)	1.44(2)
B(3)–H(3)	1.13(5)	N(3)–C(33B)	1.57(2)
B(4)–H(4)	1.02(6)		
B(5)–H(5)	1.05(5)	Pd(1)–C(11)	2.022(7)
B(6)–H(6)	1.10(4)	C(11)–N(1)	1.150(9)
B(7)–H(7)	1.20(7)	N(1)–C(12)	1.47(1)
B(8)–H(8)	1.08(6)	C(12)–C(121)	1.44(2)
B(9)–H(9)	1.17(6)	C(12)–C(122)	1.44(2)
B(10)–H(10)	1.06(7)	C(12)–C(123)	1.51(2)
B(11)–H(11)	1.10(6)		
B(12)–H(12)	1.09(6)	Pd(1)–C(21)	2.027(6)
		C(21)–N(2)	1.146(8)
N(3)–C(31A)	1.53(2)	N(2)–C(22)	1.463(8)
N(3)–C(32A)	1.57(1)	C(22)–C(221)	1.55(1)
N(3)–C(33A)	1.44$_5$(1$_5$)	C(22)–C(222)	1.55(1)
N(3)–C(31B)	1.58(2)	C(33)–C(223)	1.53(1)

Closed, non-ionic, single carbon metallacarbaboranes with a +2 oxidation-state metal atom must possess an electron-donating function exo to the cage to conform to the empirical ' (n + 1)-electron pair ' rule.[7] Thus, the present compound is strictly formulated as the zwitterion [NMe$_3$]$^+$[PdCB$_{10}$]$^-$ and, as such, should have an architecture based on that of a closed icosahedron.

The major structural deformations observed arise from the presence of the two heteroatoms. Compared with the mean B–B length of 1.79(4) Å, C–B averages 1.67$_5$(2) and Pd–B 2.24$_5$(2) Å, whilst Pd–C is 2.600(6) Å. The non-ideal geometry is further reflected in comparison of the magnitudes of the differing types of angles subtended by the polyhedral atoms, especially those at the metal [mean value 45(5)°] and the Pd–B–C pair [81.4(3) and 81.2(3)°].

The B–B and B–C bond lengths show reasonable internal consistencies and require no special comment.

Co-ordination at the Metal Atom.—The palladium atom co-ordinates the pentagonal $\overline{BBBBC}$ face to complete

[7] K. Wade, Chem. Comm., 1971, 792.

the *closo*-polyhedron. The co-ordinated atoms, however, are not co-planar since the carbon bends back into the cage, away from the metal atom. The B_4 unit retains its planarity (Table 4) and a projection of the $(C)_2Pd$-(BBBBC) moiety perpendicular to this plane is given in Figure 2.

however, there is no significant *trans*-effect. Although the present analysis shows that in the crystal the palladium co-ordinates the four boron atoms asymmetrically,

TABLE 2

Inter-bond angle data

Atoms	Angle (°)	Atoms	Angle (°)
(A) Angles within the polyhedron			
C(2)–Pd(1)–B(3)	39.3(2)	C(2)–B(7)–B(3)	52.7(3_5)
B(3)–Pd(1)–B(4)	49.6(2)	B(3)–B(7)–B(8)	59.3(4)
B(4)–Pd(1)–B(5)	46.0(3)	B(8)–B(7)–B(12)	61.6(5)
B(5)–Pd(1)–B(6)	49.0(3)	B(12)–B(7)–B(11)	60.1(4_5)
B(6)–Pd(1)–C(2)	40.6(2)	B(11)–B(7)–C(2)	58.2(4)
Pd(1)–C(2)–C(3)	59.3(3)	B(3)–B(8)–B(4)	64.3(4)
B(3)–C(2)–B(7)	66.6$_5$(4)	B(4)–B(8)–B(9)	60.8(4_5)
B(7)–C(2)–B(11)	63.2(4)	B(9)–B(8)–B(12)	58.5(4)
B(11)–C(2)–B(6)	66.8(4)	B(12)–B(8)–B(7)	58.5(5)
B(6)–C(2)–Pd(1)	58.3(3)	B(7)–B(8)–B(3)	61.7(4)
Pd(1)–B(3)–C(2)	81.4(3)	B(4)–B(9)–B(5)	59.5(4)
C(2)–B(3)–B(7)	56.6(4)	B(5)–B(9)–B(10)	59.5(4)
B(7)–B(3)–B(8)	58.9(4)	B(10)–B(9)–B(12)	61.0$_5$(4)
B(8)–B(3)–B(4)	56.9(4)	B(12)–B(9)–B(8)	61.8(4_5)
B(4)–B(3)–Pd(1)	64.2(3)	B(8)–B(9)–B(4)	59.0(4)
Pd(1)–B(4)–B(3)	66.2(3)	B(5)–B(10)–B(6)	63.4(4_5)
B(3)–B(4)–B(8)	58.8(4)	B(6)–B(10)–B(11)	62.3(4)
B(8)–B(3)–B(9)	60.2(4)	B(11)–B(10)–B(12)	58.9(4)
B(9)–B(4)–B(5)	59.5(4)	B(12)–B(10)–B(9)	59.2(4_5)
B(5)–B(4)–Pd(1)	68.1(3_5)	B(9)–B(10)–B(5)	60.1(5)
Pd(1)–B(5)–B(4)	65.9(4)	C(2)–B(11)–B(6)	58.0(4)
B(4)–B(5)–B(9)	61.0(4)	B(6)–B(11)–B(10)	59.5$_5$(4)
B(9)–B(5)–B(10)	60.4(5)	B(10)–B(11)–B(12)	60.6(4)
B(10)–B(5)–B(6)	59.9(4)	B(12)–B(11)–B(7)	60.3(4_5)
B(6)–B(5)–Pd(1)	64.9(3)	B(7)–B(11)–C(2)	58.64(4)
Pd(1)–B(6)–C(2)	81.2(3)	B(11)–B(12)–B(7)	59.6(5)
C(2)–B(6)–B(11)	55.2(4)	B(7)–B(12)–B(8)	60.0(4)
B(11)–B(6)–B(10)	58.1(4)	B(8)–B(12)–B(9)	59.7(4)
B(10)–B(6)–B(5)	56.7(4)	B(9)–B(12)–B(10)	59.8(4)
B(5)–B(6)–Pd(1)	66.1(3)	B(10)–B(12)–B(7)	60.4$_5$(4)
(B) Other angles			
N(3)–C(2)–Pd(1)	110.2(3_5)	C(21)–Pd(1)–C(2)	115.5(2)
N(3)–C(2)–B(3)	120.8(5)	C(21)–Pd(1)–B(3)	152.6(2)
N(3)–C(2)–B(8)	119.2$_5$(4)	C(21)–Pd(1)–B(4)	151.5(3)
N(3)–C(2)–B(7)	118.4(5)	C(21)–Pd(1)–B(5)	108.9(2_5)
N(3)–C(2)–B(6)	119.7(4)	C(21)–Pd(1)–B(6)	93.0(2_5)
C(31A)–N(3)–C(2)	110.7(6_5)	C(11)–Pd(1)–C(21)	95.9(3)
C(32A)–N(3)–C(2)	110.4(6)	N(1)–C(11)–Pd(1)	173.6(6)
C(33A)–N(3)–C(2)	110.8(7)	C(12)–N(1)–C(11)	176.2(7)
C(31A)–N(3)–C(32A)	100.5(8)	N(2)–C(21)–Pd(1)	175.7(6)
C(31A)–N(3)–C(33A)	110.3(9)	C(22)–N(2)–C(21)	176.3(6)
C(32A)–N(3)–C(33A)	114.7(8)		
C(31B)–N(3)–C(2)	109.9(7)	C(121)–C(12)–N(1)	107(1)
C(32B)–N(3)–C(2)	116.2(9)	C(122)–C(12)–N(1)	108.4(8)
C(33B)–N(3)–C(2)	112.2(7)	C(123)–C(12)–N(1)	108.4(8)
C(31B)–N(3)–C(32B)	107(1)	C(121)–C(12)–C(122)	114(1)
C(31B)–N(3)–C(33B)	94.8(9)	C(121)–C(12)–C(123)	109(1)
C(22B)–N(3)–C(33B)	112(1)	C(122)–C(12)–C(123)	110(1)
C(11)–Pd(1)–C(2)	123.3(2)	C(221)–C(22)–N(2)	105.9(5)
C(11)–Pd(1)–B(3)	94.4(2)	C(222)–C(22)–N(2)	106.7(5)
C(11)–Pd(1)–B(4)	99.0(3)	C(223)–C(22)–N(2)	107.0(6)
C(11)–Pd(1)–B(5)	138.4(3)	C(221)–C(22)–C(222)	112.0$_5$(5)
C(11)–Pd(1)–B(6)	163.8(2)	C(221)–C(22)–C(222)	111.8(6)
		C(222)–C(22)–C(223)	112.8(6)

As in $[1,1\text{-}(PhMe_2P)_2\text{-}2,4\text{-}Me_2\text{-}1,2,4\text{-}PtC_2B_9H_9]$,[1] we may describe the metal co-ordination in terms of a distorted square-planar geometry with the isocyanide carbon atoms C(11) and C(21) lying *trans* to positions on the B(5)–B(6) and B(3)–B(4) bonds, respectively.

Unlike the co-ordination of Pt^{II} to the BCBCB face,[1]

TABLE 3

Summary of molecular parameters

Bond	Number, N	Range (Å)	Mean [a] (Å)
Pd–C$_{(cage)}$	1	2.600(6)	
Pd–B	4	2.223(7)—2.261(6)	2.24$_5$(2)
C–B	4	1.661(1)—1.711(8)	1.67$_5$(2)
B–B	21	1.71(1)—1.881(9)	1.79(4)
C–N$_{(amine)}$	1	1.550(7)	
N–C$_{(alkyl)}$	8	1.442(2)—1.58(2)	1.51(6)
Pd–C$_{(Bu^tCN)}$	2	2.022(7), 2.027(6)	
PdC–N$_{(Bu^tCN)}$	2	1.146(8), 1.150(9)	
C–C	6	1.44(2)—1.55(1)	1.50(5)
B–H	10	1.02(6)—1.20(7)	1.10(5)

Angle	Number, N	Range (°)	Mean (°)
C$_{(cage)}$–Pd–B	2	39.3(2), 40.6(2)	
B–Pd–B	3	46.0(3)—49.6(2)	48(2)
Pd–C–B	2	58.3(3), 59.3(3)	
B–C–B	3	63.2(4)—66.8(4)	66(2)
Pd–B–C	2	81.2(3), 81.4(3)	
B–B–C	6	55.2(4)—58.6(4)	57(1)
B–B–B	36	56.7(4)—64.3(4)	60(1_5)
Pd–B–B	6	64.2(3)—68.1(3_5)	66(1)
Pd–C$_{(cage)}$–N	1	110.2(3_5)	
B–C–N	4	118.4(5)—120.8(5)	119.$_5$(1)
C$_{(cage)}$–N–C$_{(alkyl)}$	6	109.9(7)—116.2(9)	112(2)
C$_{(alkyl)}$–N–C$_{(alkyl)}$	6	98.4(9)—113.7(7)	107(6)
C$_{(cage)}$–Pd–C$_{(cyano)}$	2	115.5(2), 123.3(2)	
B–Pd–C$_{(cyano)}$ [b]	4	93.0(2_5)—108.9(2_5)	99(7)
C$_{(cyano)}$–Pd–C$_{(cyano)}$	1	95.9(3)	
N–C$_{(cyano)}$–Pd	2	173.6(6), 175.7(6)	
C$_{(alkyl)}$–N–C$_{(cyano)}$	2	176.2(7), 176.3(6)	
C–C–N	6	105.9(5)—108.4(8)	107(1)
C–C–C	6	109(1)—114(1)	112(2)
H–B–Pd	4	107(3)—108(3)	107.7$_5$(5)
H–B–C	4	113.$_5$(4)—121(3)	119(3)
H–B–B	42	113(4)—130(3)	122(4)

[a] The e.s.d.s of the mean value are determined from the expression $\sigma^2 = \{\sum_{i=1}^{i=N}(\chi_i - \bar{\chi})^2\}/(N-1)$ where χ_i is the ith and $\bar{\chi}$ the mean of N similar types of parameter. [b] '*cis*' angles only.

TABLE 4

Least-squares planes data of the B(3)B(4)B(5)B(6) moiety

(A) The plane is represented in non-orthogonalised space by the equation $10.935x - 0.002y - 4.432z = 0.268$ Å. x, y, and z are the atomic fractional co-ordinates.

(B) Individual atomic deviations (Å) from the mean plane are: B(3) −0.01, B(4) +0.02, B(5) −0.02, B(6) +0.01, C(2) −0.30, and Pd(1) +1.70.

the metal-to-cage bonding in solution appears to be less distorted.

The Pd–C(2) bond, at 2.600(6) Å, represents little interaction and displaces the carbon atom to its preferred,[8,9] relatively low, cage-connectivity number of four. Since 2.6 Å represents a mean increase of *ca.* 0.15Å over the already weak Pt–C bonds in the 1,2,4-PtC_2B_9 metallacarbaborane [1] (and Pt^{II} and Pd^{II} share

[8] R. E. Williams, *Progr. Boron Chem.*, 1970, **2**, 37.
[9] W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1973, **95**, 4565.

the same planar covalent radius [10]) the strict description of the present polyhedron as either *closo* or *nido* is purely a formalism.
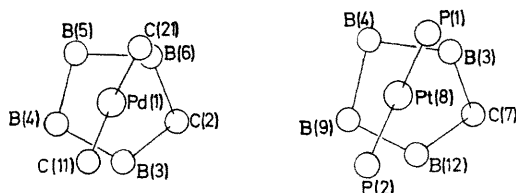

FIGURE 2 View of the co-ordination spheres of the d^8 metal atoms in [1,1-(Bu^{t}NC)$_2$-2-NMe$_3$-1,2-PdCB$_{10}$H$_{10}$] and [1-(η-C$_5$H$_5$)-8,8-(Et$_3$P)$_2$-1,2,7,8-CoC$_2$PtB$_8$H$_{10}$]

The co-ordination sphere of the d^8 metal atom bears direct comparison to that observed in [1-(η-C$_5$H$_5$)-8,8-(Et$_3$P)$_2$-1,2,7,8-CoC$_2$PtB$_8$H$_{10}$] † (Figure 3 of ref. 2), the product of the reaction between [Pt(*trans*-stilbene)-(PEt$_3$)$_2$] and [1-(η-C$_5$H$_5$)-1,2,4-CoC$_2$B$_8$H$_{10}$]. In both compounds a (non-planar) $\overline{\text{BBBBC}}$ face is co-ordinated by a d^8 metal atom whose neutral ligands show similar orientation with respect to that face. Whilst the formation of the Pd-carbaborane (V) is readily understood in terms of attack of the zerovalent palladium species on one of the B(1)C(2)B(3)BB ' open faces ' of the *closo*-2-NMe$_3$-2-CB$_{10}$H$_{10}$ octadecahedron, reaction of the platinum(0) complex with [1-(η-C$_5$H$_5$)-1,2,4-CoC$_2$B$_8$H$_{10}$] must either proceed quite differently to both predicted reaction paths or be followed by subsequent ' diamond-square–diamond ' intramolecular rearrangement [11] leading to the observed product. If such rearrangement does occur it may be that the inherent stability of square-planar d^8 metal complexes and preferred low cage connectivity of carbon atoms are partly responsible, since both are to some extent satisfied by the geometry adopted.

The Non-cage Atoms.—In the present study only those hydrogen atoms bound directly to the cage have been located. The B–H lengths determined range from 1.02(6) to 1.20(7) Å [mean 1.10(5) Å] and are, as expected,[12] shorter than the accepted [10] internuclear separation by an average 0.1 Å. Comparison of the mean H–B-(cage atom) angles (Table 3) again serves to demonstrate the deformation that the palladium atom produces in the icosahedron.

The amino-carbon atoms are disordered over two sets of three positions (types A and B) separated by an average of *ca.* 1.09 Å. Fractional populations are *ca.* 0.57 and 0.43, respectively. There is no evidence of nitrogen atom disorder, consistent with the solution

† *Crystal data:* C$_{19}$H$_{45}$B$_8$CoP$_2$Pt, $M = 692.3$, orthorhombic, space group $P2_12_12_1$, $a = 18.654(8)$, $b = 1441(1)$, $c = 12.800(3_5)$ Å, $U = 3441(2)$ Å^3, $Z = 4$, $D_C = 1.336$, $F(000) = 1368$ electrons, μ(Mo-$K\alpha$) = 49.8 cm^{-1}. M, D_C, F, and μ are not entirely correct since there is evidence of (probably disordered) toluene of solvation in the lattice. R = currently *ca.* 0.08 (metal and phosphorus atoms anisotropic). Intensity data were, unfortunately, recorded on the Syntex diffractometer during a period of variable-beam intensity. Although the analysis is sufficiently accurate to define the molecule as the [1,2,7,8-CoC$_2$-PtB$_8$] isomer we shall recollect the data and fully refine the structure at some future date.

n.m.r. studies, which suggest free rotation of the group about a fixed N–C bond.

The isocyanide ligands are related by an approximate C_2 axis bisecting the C–Pd–C bond. The Pd–C bond lengths are in excellent mutual agreement, and correspond precisely to the simple sum of covalent radii for square-planar Pd^{II} and sp-hybridised carbon. This, together with comparison with the corresponding distances in [PdCl$_2$(MeNH·C·HN)$_2$],[13] [PtCl$_2$(PhNC)$_2$],[14] [PtCl$_2$(EtNC)(PMeEtPh)],[15] and [Pt$_3$(Bu^{t}NC)$_6$] [16] (1.83—1.99 Å), suggests minimal, if any, M(d)→L(π^*) back donation in the present compound.

The isocyanide Pd–C–N and C–N–C angles deviate significantly from 180°, but these are probably simple consequences of efficient crystal packing. Considerable thermal motion is exhibited by the methyl groups of the C(11) ligand (Table 7) and is reflected in the relatively short C(12)–C bond lengths observed [mean value 1.45 Å *cf.* 1.54 Å for C(22)–C].

Non-bonded Contacts and Crystal Packing.—Figure 3 is a view of the crystal packing as seen along the *a* axis looking towards the origin. Inter- and intra-molecular non-bonded atomic distances which are less than the appropriate van-der-Waals sum have been listed in Table 5. Although only approximate, since the van-der-Waals radii of methyl groups have been estimated as 2.0

TABLE 5

Non-bonding contacts

Atom A [a]	Atom B	Position B	Contact (Å)
Intramolecular			
H(3)	C(31A) [b]	x, y, z	2.73(5)
H(3)	C(32B)	x, y, z	2.97(5$_5$)
H(6)	C(32A)	x, y, z	2.65(5)
H(7)	C(32B)	x, y, z	2.74(8)
H(11)	C(33B)	x, y, z	2.63(6)
Intermolecular			
H(3)	C(32B)	$\bar{x}, \bar{y}, \bar{z}$	2.94$_5$(5)
H(8)	C(32B)	$\bar{x}, \bar{y}, \bar{z}$	2.97(6)
C(33A)	H(4)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	2.78(5)
C(121)	C(223)	$x - \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$	3.83(3)

[a] Atom A has co-ordinates x, y, z. [b] Methyl groups taken to have van-der-Waals radius of 2.0 Å.

Å, these contacts may explain the greater population of type A aminomethyl sites, since there are a greater number of contacts to the type B groups

DISCUSSION

The ^{11}B n.m.r. spectra of the complexes (IV), (V), and (VI) are not sufficiently resolved to allow unambiguous

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[11] W. N. Lipscomb, ' Boron Hydrides,' Benjamin, New York, 1963.
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[14] B. Javonovic, Lj. Manojhovic-Muir, and K. W. Muir, *J.C.S. Dalton*, 1972, 1178.
[15] B. Javanovic and Lj. Manojhovic-Muir, *J.C.S. Dalton*, 1972, 1176.
[16] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 3.

structural assignments. Thus, it is not possible to determine if complexes (IV) and (VI) are isostructural with (V).

A difference in geometry could, in principle, arise if the products of the reaction were determined by thermodynamic control, *i.e.* the kinetically controlled product undergoes a polyhedral rearrangement of the type which has been observed [17] for $[1\text{-}\eta\text{-}C_5H_5\text{-}1,2\text{-}NiCB_{10}H_{11}]$. However, preliminary studies [18] on the palladium complex (V) have shown that isomerisation will only occur on heating to 130 °C in xylene. Although the driving force for such a rearrangement is thought to be the tendency of the polyhedral structure to achieve hetero-atom separation, which might be expected to vary on changing the metal from Ni to Pd or Pt, it seems unlikely that there could be such a difference in the activation parameters for the rearrangement of the various

(I)—(IV) involves nucleophilic attack on one of the $\overline{BCBBB}$ ' open faces '. It seems unlikely that the Ni^0 and Pt^0 species would react differently from the Pd^0 complex. Thus it is suggested that all the complexes are isostructural with the palladium species (V).

Attempts were made to examine the *exo*-polyhedral chemistry of the isocyanide species; however, the only reaction observed was the replacement of the Bu^tNC ligands of (V) by bis-1,2-diphenylphosphinoethane (diphos) to yield the insoluble yellow complex (VII).

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 MHz. ^{11}B and ^{31}P F.T. n.m.r. spectra were recorded on a JEOL PFT-100 spectrometer. The external references for the 32.08 MHz ^{11}B and 40.48
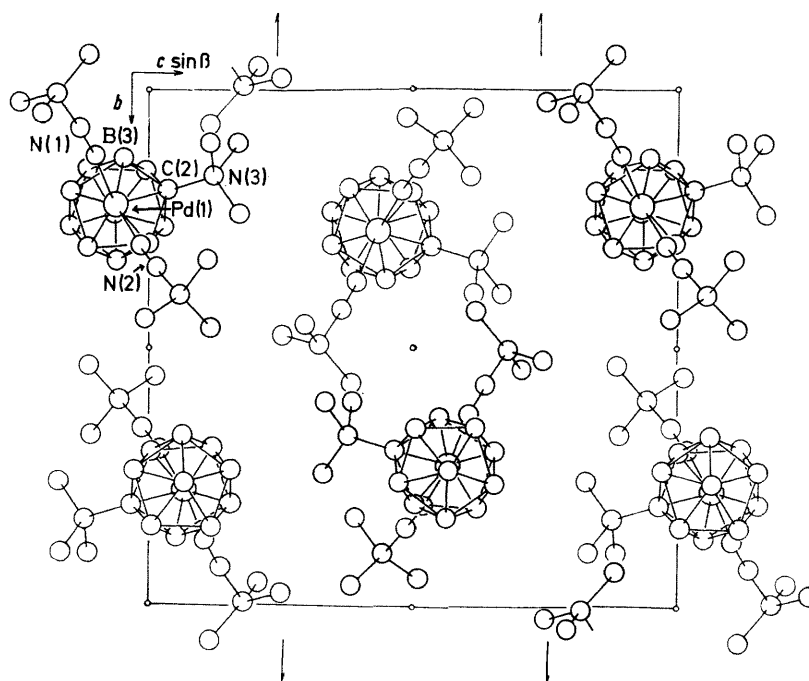

FIGURE 3 Molecular packing diagram, looking along the a axis, towards the origin. Hydrogen atoms are omitted for clarity. Only those symmetry operations necessary for generating the array are shown

metallacarbaboranes as to lead to rearrangement of the Ni and Pt complexes at room temperature, *i.e.* the conditions used in the synthesis of these species. It has been previously suggested [2] that the reaction of Ni^0, Pd^0, and Pt^0 with *closo*-C_2B_9 carbaborane involves nucleophilic attack by the metal species on one of the four equivalent boron atoms (Scheme 1 of ref. 2), the lowest unfilled molecular orbital being localised mainly on these atoms. Although nucleophilic attack on *closo*-$[CB_{10}H_{11}]^-$ or *closo*-$[2\text{-}NMe_3\text{-}2\text{-}CB_{10}H_{10}]$ has not been previously observed it is possible that the formation of the species

MHz ^{31}P spectra were $Et_2O\cdot BF_3$ and 85% H_3PO_4, respectively. I.r. spectra were measured on a Perkin-Elmer 457 spectrophotometer. All reactions were performed in a dry oxygen-free nitrogen atmosphere. Light petroleum refers to the fraction b.p. 40—60 °C.

The metal complexes $[Ni(cod)_2]$,[19] $[Pd(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$,[20] and $[Pt(trans\text{-}stilbene)(PEt_3)_2]$ [21] were prepared by the literature methods. Decaborane was used as the starting point for the synthesis of $[Me_4N]^+[CB_{10}H_{11}]^-$ and *closo*-$[2\text{-}Me_3N\text{-}2\text{-}CB_{10}H_{10}]$.[5]

Preparation of $[Me_4N]^+[1,1\text{-}(Bu^tNC)_2\text{-}1,2\text{-}NiCB_{10}H_{11}]^-$ (I). A solution of $[Me_4N]^+[CB_{10}H_{11}]^-$ (0.21 g, 1.0 mmol) in dry deoxygenated acetone (10 cm^3) was added dropwise with

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[18] W. E. Carroll, M. Green, and F. G. A. Stone, unpublished observations.

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[20] M. Sakakibara, Y. Takahashi, S. Sakai, and Y. Ishii, *Chem. Comm.*, 1969, 396.

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

stirring to a solution in acetone (15 cm³) if [Ni(cod)(Bu^{t}NC)$_2$] {prepared *in situ* from [Ni(cod)$_2$] (0.27 g, 1.0 mmol) and Bu^{t}NC (0.17 g, 2.0 mmol)}. After 16 h at room temperature diethyl ether (100 cm³) was added. The resultant precipitate was collected, washed with diethyl ether, and recrystallised from acetone to give orange *microcrystals* of (I) (0.22 g, 50%) (Found: C, 41.3; H, 9.9; N, 9.4. C$_{15}$H$_{41}$B$_{10}$N$_3$Ni requires C, 41.9; H, 9.6; N, 9.8%), ν$_{max.}$ (Nujol) 2 514sbr, 2 474vs, br (BH), 2 164vs (NC), and 2 135vs (NC) cm⁻¹. The ¹H n.m.r. spectrum [(CD$_3$)$_2$CO] showed resonances at τ 6.90 (s, 12 H, Me$_4$N) and 8.60 (s, 18 H, Bu^{t}N).

Preparation of [Me$_4$N]$^+$[1,1-(Bu^{t}NC)$_2$-1,2-PdCB$_{10}$H$_{11}$]⁻, (II).—An excess of Bu^{t}NC (0.11 cm³) was added (−15 °C) dropwise to a solution of [Pd(η-C$_5$H$_5$)(η-C$_3$H$_5$)] (0.21 g, 1.0 mmol) in light petroleum (20 cm³). The resultant orange precipitate of [Pd(Bu^{t}NC)$_2$] was washed with light petroleum and dissolved in dry deoxygenated acetone (10 cm³). Addition of [Me$_4$N]$^+$[CB$_{10}$H$_{11}$]⁻ (0.21 g, 1.0 mmol) to the acetone solution led to an immediate reaction, and the precipitation of a green-yellow solid. After 3 h the precipitate was collected and washed with acetone (5 cm³). Recrystallisation from ethanol–dimethylformamide afforded yellow *microcrystals* of (II) (0.15 g, 32%) (Found: C, 37.8; H, 8.7; N, 8.7. C$_{15}$H$_{41}$B$_{10}$N$_3$Pd requires C, 37.7; H, 8.7; N, 8.8%), ν$_{max.}$ (Nujol) 2 516sbr (BH), 2 494sbr (BH), 2 472vs, br (BH), 2 172vs (NC), and 2 151vs (NC) cm⁻¹. The ¹H n.m.r. spectrum [(CD$_3$)$_2$CO] showed resonances at τ 6.90 (s, 12 H, *Me$_4$N*) and 8.55 (s, 18 H, Bu^{t}N).

Preparation of [Me$_4$N]$^+$[1,1-(Et$_3$P)$_2$-1,2-PtCB$_{10}$H$_{11}$]⁻, (III).—A solution of [Me$_4$N]$^+$[CB$_{10}$H$_{11}$]⁻ (0.10 g, 0.5 mmol) in acetone (8 cm³) was added dropwise with stirring (room temperature) to a solution of [Pt(*trans*-stilbene)(PEt$_3$)$_2$] (0.30 g, 0.5 mmol) in acetone (10 cm³). After 12 h the solvent was removed *in vacuo*, and the residue was washed with light petroleum (4 × 20 cm³) to remove *trans*-stilbene. Slow evaporation of a solution of the residue in acetonitrile (20 cm³) gave bright yellow crystals of (III) (0.13 g, 41%) (Found: C, 32.0; H, 8.2; N, 2.8. C$_{17}$H$_{53}$B$_{10}$NP$_2$Pt requires C, 32.1; H, 8.4; N, 2.2%), ν$_{max.}$ (Nujol) 2 480sbr (BH) cm⁻¹. The ¹H n.m.r. spectrum (CD$_3$CN) showed resonances at τ 7.7 (s, 12 H, *Me$_4$N*), 8.08 (m, 12 H, PC*H$_2$*CH$_3$), and 8.95 (m, 18 H, PCH$_2$*CH$_3$*).

Preparation of [1,1-(Bu^{t}NC)$_2$-2-Me$_3$N-1,2-NiCB$_{10}$H$_{10}$], (IV).—Addition of a solution of *closo*-2-Me$_3$N-2-CB$_{10}$H$_{10}$ (0.12 g, 0.63 mmol) in acetone (10 cm³) to a solution of [Ni(cod)-(Bu^{t}NC)$_2$] {prepared from [Ni(cod)$_2$] (0.172 g, 0.63 mmol) and Bu^{t}NC (0.10 g, 1.25 mmol)} in toluene (10 cm³) gave after 3 h at room temperature a dark orange solution. The solvent was removed *in vacuo* and the residue chromatographed on an alumina-packed column. Elution with methylene chloride–toluene (1 : 1) gave an uncharacterised yellow solid. Further elution with methylene chloride gave an orange material, which on recrystallisation from methylene chloride–hexane afforded orange *microcrystals* of (IV) (0.13 g, 51%), m.p. >200 °C (decomp.) (Found: C, 40.8; H, 9.3; N, 9.5. C$_{14}$H$_{37}$B$_{10}$N$_3$Ni requires C, 40.6; H, 9.0; N, 10.2%), ν$_{max.}$ (Nujol) 2 502vs,br (BH), 1 175vs (NC), and 2 150vs (NC) cm⁻¹. The ¹H n.m.r. spectrum [(CD$_3$)$_2$CO] showed resonances at τ 6.57 (s, 9 H, NMe$_3$) and 8.50 (s, 18 H, Bu^{t}N). The ¹¹B n.m.r. spectrum [(CD$_3$)$_2$CO] showed resonances at 6.5(2), 15.5(1), and 20.0(2) p.p.m.

Preparation of [1,1-(Bu^{t}NC)$_2$-2-Me$_3$N-1,2-PdCB$_{10}$H$_{10}$], (V).—A solution of [Pd(Bu^{t}NC)$_2$] {prepared from [Pd(η-C$_5$H$_5$)(η-C$_3$H$_5$)] (0.53 g, 2.5 mmol)} in toluene (40 cm³) was

added dropwise to a solution of *closo*-2-Me$_3$N-2-CB$_{10}$H$_{10}$ (0.48 g, 2.5 mmol) in acetone (20 cm³). A yellow precipitate was rapidly formed and after 3 h the solvent was removed *in vacuo*. The residue was extracted with methylene chloride, and the solution filtered through charcoal. The resultant yellow solution was diluted with toluene and the methylene chloride slowly removed *in vacuo*. The remaining solution slowly deposited yellow microcrystals of (V) (1.0 g, 86%), m.p. 255—260 °C (decomp.) (Found: C, 36.5; H, 8.3; N, 8.9. C$_{14}$H$_{37}$B$_{10}$N$_3$Pd requires C, 36.4; H, 8.1; N, 9.1%), ν$_{max.}$ (Nujol) 2 512vs (BH), 2 438vs (BH), 2 180vs (NC), and 2 165vs (NC) cm⁻¹. The ¹H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 6.60 (s, 9 H, NMe$_3$) and 8.50 (s, 18 H, *Bu^t*N). The ¹¹B n.m.r. spectrum (CH$_3$CN) showed resonances at 6.09(4), 9.74(1), 19.94(3), and 25.72(2) p.p.m.

A solution of *nido*-2-Me$_3$N-2-CB$_{10}$H$_{12}$ (0.19 g, 1.0 mmol) in THF (20 cm³) was treated (−40 °C) with n-butyl-lithium (2 mmol). A white suspension formed and on warming to 10 °C *cis*-[PdCl$_2$(Bu^{t}NC)$_2$] (0.34 g, 1.0 mmol) was added. Reaction occurred instantly, with a deep red colour developing, eventually fading to a dark yellow colour. After stirring at room temperature overnight, the solvent was removed *in vacuo*, and the residue dissolved in methylene chloride and chromatographed on an alumina-packed column. Elution with methylene chloride–toluene (4 : 1) afforded a yellow material. Recrystallisation from methylene chloride–toluene afforded yellow *microcrystals* of (V) (0.15 g, 33%).

Preparation of [1,1-(Et$_3$P)$_2$-2-Me$_3$N-1,2-PtCB$_{10}$H$_{10}$], (VI). A solution of *closo*-2-Me$_3$N-2-CB$_{10}$H$_{10}$ (0.10 g, 0.5 mmol) in acetone (8 cm³) was added dropwise at room temperature to a solution of [Pt(*trans*-stilbene)(PEt$_3$)$_2$] (0.30 g, 0.5 mmol) in toluene (10 cm³). After 4 h the solvent was removed *in vacuo*. The residue was dissolved in methylene chloride, treated with charcoal, and filtered to give a light yellow solution. Addition of hexane, followed by evaporation of the methylene chloride gave *crystals* of (VI) (0.20 g, 64%), m.p. 264 °C (decomp.) (Found: C, 30.6; H, 8.0; N, 2.5. C$_{16}$H$_{49}$B$_{10}$NP$_2$Pt requires C, 30.9; H, 8.0; N, 2.3%), ν$_{max.}$ (Nujol) 2 530vs (BH) and 2 498vs (BH) cm⁻¹. The ¹H n.m.r. spectrum (CD$_2$Cl$_2$) showed resonances at τ 6.66 (s, 9 H, NMe$_3$), 8.04 (m, 12 H, PC*H$_2$*CH$_3$), and 8.90 (m, 18 H, PCH$_2$*CH$_3$*). The ³¹P n.m.r. spectrum (CH$_2$Cl$_2$, CDCl$_3$) showed a single sharp singlet at 2.29 p.p.m. with ¹⁹⁵Pt satellites (J_{PtP} = 3 103 Hz). The ¹¹B n.m.r. spectrum (CH$_2$Cl$_2$, CDCl$_3$) showed resonances at 5.48, 9.89, 12.10, 19.78, and 22.45 p.p.m.

Preparation of [1,1-(Ph$_2$PCH$_2$)$_2$-2-Me$_3$N-1,2-PdCB$_{10}$H$_{10}$], (VII).—A sample of (V) (0.10 g, 0.22 mmol) was suspended in benzene (20 cm³), diphos (0.17 g, 0.42 mmol) was added and the mixture heated (2 h) under reflux. A yellow precipitate formed on cooling; it was collected and washed with benzene to give *microcrystals* of (VII), m.p. 294—296 °C (0.11 g, 73%) (Found: C, 51.3; H, 6.0; N, 1.7. C$_{30}$H$_{43}$B$_{10}$-NP$_2$Pd requires C, 51.9; H, 6.2; N, 2.0%).

Crystal Structure Determination.—The complex (V) was recrystallised from acetone–toluene and formed bright yellow transparent prisms elongated along [010]. A single crystal, 0.030 × 0.048 × 0.025 cm, was mounted in a 0.05-cm diameter Lindemann capillary for easy handling, set on a Syntex *P*2$_1$ four-circle diffractometer, and the unit cell and intensity data recorded in a manner already described.²²

Experimental details were as follows. Fifteen reflections,

²² A. G. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

TABLE 6

Positional parameters [a] of the [(Bu^{t}NC)$_2$Pd(NCB$_{10}$)] fraction

Atom	x	y	z
Pd(1)	0.270 18(4)	−0.068 78(3)	0.222 86(3)
C(2)	0.0764(5)	0.0352(4)	0.1957(3)
B(3)	0.0776(6)	−0.0532(4)	0.1335$_5$(4)
B(4)	0.1057(7)	−0.1589(4)	0.1971(4)
B(5)	0.1468(8)	−0.1248(5)	0.3060(4)
B(6)	0.1459(6)	−0.0024(4)	0.2976(4)
B(7)	−0.0662(7)	−0.0050(5)	0.1537(5)
B(8)	−0.0466(7)	−0.1212(5)	0.1523(5)
B(9)	−0.0079(8)	−0.1585(5)	0.2614(5)
B(10)	0.0223(8)	−0.065(5)	0.3280(5)
B(11)	−0.0214(7)	0.0299(5)	0.2614(5)
B(12)	−0.1074(7)	−0.0675(6)	0.2360(5)
N(3)	0.1119(5)	0.1271(3)	0.1663(5)
C(11)	0.3520$_5$(6)	−0.1094(4)	0.1274(4)
N(1)	0.3948(5)	−0.1403(4)	0.0744(4)
C(12)	0.4450(8)	−0.1850(6)	0.0075(5)
C(121)	0.361(2)	−0.257(1)	0.025(1)
C(122)	0.572(1)	−0.212(1)	0.0458(9)
C(123)	0.443(1)	−0.1211(8)	−0.0663(7)
C(21)	0.4290(6)	−0.0203(4)	0.3016(4)
N(2)	0.5161(5)	0.0123(3)	0.3445(3)
C(22)	0.6262(5)	0.0586(5)	0.3953(4)
C(221)	0.6801(8)	0.1119(6)	0.3286(6)
C(222)	0.5793(8)	0.1189(6)	0.4598(5)
C(223)	0.7186(7)	−0.0118(6)	0.4410(5)

[a] Expressed as fractional co-ordinates of the unit-cell edges. The estimated standard deviations are shown in parentheses.

15° < 2θ < 27°, were centred and used to generate the cell dimensions, associated standard deviations, and orientation

exposure. Card images were generated locally;[23] of the 4 105 measured intensities, 3 319 were retained [$I \geqslant 2.5 \sigma$ (I)] and were used to solve and refine the structure. An absorption correction was applied but had little effect (maximum $A^* = 1.26$, minimum = 1.19).

Crystal Data.—C$_{14}$H$_{37}$B$_{10}$N$_3$Pd, $M = 461.97$, monoclinic, space group $P2_1/n$, $a = 10.947(3)$, $b = 15.194(4)$, $c = 15.804(4)$ Å, $\beta = 103.45(2)°$, $U = 2\,557(1)$ Å^3, $D_M = 1.15$ (flotation), $Z = 4$, $D_C = 1.200$, $F(000) = 952$, μ(Mo-$K_{\bar{a}}$) = 7.18 cm^{-1}.

The 3 319 significantly observed data were corrected for Lorentz and polarisation effects, and the position (in one asymmetric unit) of the palladium atom easily deduced from a three-dimensional Patterson synthesis. Positional and (isotropic) thermal parameters of this atom were refined by two cycles of full-matrix least-squares to ca. $R = 0.27$; from an accompanying difference electron density synthesis all non-hydrogen atoms were visible.

Since possible disordering of the amino-carbon atoms was apparent, parameters of the [(Bu^{t}NC)$_2$Pd(NCB$_{10}$)] fraction alone were subsequently refined, during which R fell to ca. 0.104 (Pd anisotropic). The better resolution afforded by the resulting difference synthesis showed the omitted carbon atoms in two sets of three partially occupied sites with fractional populations (determined by the relative mean peak heights) of 0.57 [C(31A, 32A, and 33A)] and 0.43 [C(31B, 32B, and 33B)].

With these populations invariant, parameters of all the located atoms were divided into five blocks containing

TABLE 7

Thermal parameters [a] of the [(Bu^{t}NC)$_2$Pd(NCB$_{10}$)] fraction (Å^2 × 10^3)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	45.3(0.5)	48.5(0.5)	40.6(0.5)	2.6(0.2)	4.1(0.2)	−11.7(0.2)
C(2)	46(3)	40(3)	41(3)	−1(3)	9(2)	−2(2)
B(3)	47(4)	47(4)	34(3)	−4(4)	2(3)	0$_{05}$(3)
B(4)	70(5)	37(4)	46(4)	−1(3)	8(3)	−6(3)
B(5)	81(5)	43(4)	40(4)	−7(4)	1(3)	3(3)
B(6)	52(4)	48(4)	34(3)	−5(3)	10(3)	−7(3)
B(7)	42(4)	53(4)	70(5)	−1(3)	7(3)	0$_{08}$(4)
B(8)	60(4)	50(4)	49(4)	−16(4)	8(3)	−5(3)
B(9)	90(6)	56(5)	49(4)	−28(4)	20(4)	−1(3)
B(10)	81(5)	66(5)	47(4)	−24(4)	29(4)	−9(4)
B(11)	53(4)	60(5)	67(5)	−3(4)	25(4)	−15(4)
B(12)	56(4)	79(5)	73(5)	−21(4)	28(4)	−17(5)
N(3)	68(3)	38(3)	58(3)	−5(3)	9(3)	3(2)
C(11)	49(4)	68(4)	58(4)	6(3)	8(3)	−17(3)
N(1)	58(3)	80(4)	66(4)	9(3)	17(3)	−22(3)
C(12)	82(5)	100(6)	80(5)	22(5)	39(4)	−30(5)
C(121)	329(22)	231(16)	357(22)	−164(16)	267(20)	−238(17)
C(122)	158(12)	430(27)	150(12)	184(16)	47(9)	−28(14)
C(123)	270(17)	144(10)	97(8)	59(11)	101(10)	11(7)
C(21)	51(4)	66(4)	53(4)	2(3)	7(3)	−15(3)
N(2)	48(3)	66(4)	45(3)	−1(3)	4(2)	−10(2)
C(22)	43(3)	70(4)	56(4)	−8(3)	−1(3)	−6(3)
C(221)	89(6)	97(6)	96(6)	−24(5)	33(5)	14(5)
C(222)	94(6)	97(6)	69(5)	−9(5)	18(4)	−40(4)
C(223)	63(5)	101(6)	92(6)	20(5)	−12(4)	17(5)

[a] The anisotropic thermal parameter 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.

matrix. Data were recorded within the range 2.9° ≤ 2θ ≤ 50.0° using graphite-monochromated Mo-K_α radiation and a θ : 2θ scan in 96 steps. Scan speeds varied from 0.0337° s^{-1} for sample counts ≤75 s^{-1} at the peak, to 0.4883° s^{-1} for counts ≥750 s^{-1}. The 400, 1̄16, and 2̄6̄2 reflections were measured once every batch of 28, but subsequent analysis of their intensities as a function of time indicated no significant crystal decomposition or machine variance over the 150 h

between 33 and 56 variables. Mixed refinement (amino-carbon atoms isotropic) converged R to 0.045 after four cycles, at which stage plausible positions for the ten-cage protons were taken from a difference map. The Hughes[24] weighting scheme was introduced with F^* set at 83.0

[23] A. G. Modinos, 'DRSYN,' a Fortran program for data analysis.
[24] E. W. Hughes, J. Amer. Chem. Soc., 1941, 63, 1737.

TABLE 8

Positional [a] and thermal [b] parameters of the amino-methyl carbon and cage hydrogen atoms

Atom	x	y	z	$U_j(\text{Å}^2 \times 10^3)$
C(31A)	0.197(1)	0.118(1)	0.103(1)	80(4)
C(32A)	−0.006(1)	0.172(1)	0.106(1)	71(3)
C(33A)	0.172(2)	0.180(1)	0.240(1)	89(4)
C(31B))	0.259(2)	0.135(1)	0.182(1)	75(5)
C(32B)	0.060(2)	0.150(1)	0.077(1)	94(6)
C(33B)	0.090(2)	0.202(1)	0.229(1)	61(4)
H(3)	0.092(5)	−0.044(3)	0.066(3)	50(16)
H(4)	0.131(5)	−0.216(4)	0.171(3)	56(16)
H(5)	0.204(5)	−0.157(4)	0.359(4)	66(18)
H(6)	0.205(4)	0.041(3)	0.345(3)	39(14)
H(7)	−0.130(7)	0.042(5)	0.102(5)	110(26)
H(8)	−0.107(5)	−0.158(4)	0.101(3)	58(17)
H(9)	−0.045(6)	−0.266(4)	0.282(4)	75(20)
H(10)	0.006(6)	−0.057(4)	0.391(4)	91(22)
H(11)	−0.054(5)	0.090(4)	0.288(3)	60(17)
H(12)	−0.206(5)	−0.071(4)	0.239(4)	68(18)

[a] See footnote a of Table 6. [b] The isotropic thermal parameter is defined as $q_j = \exp\{-8\pi^2 U_j(\sin^2\theta)/\lambda^2\}$. E.s.d.s in parentheses.

(absolute scale) and, incorporating the hydrogen atom positional and isotropic thermal parameters in a sixth

† For details of scheme see Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

block, all variables were refined to convergence. The mean shift : error ratio was 0.002. Final residuals are $R = 0.042$, $R_w = 0.052$. A final difference Fourier showed a maximum peak of *ca.* 0.70 e Å⁻³ near C(31A).

Scattering factors for neutral atoms were taken from references 25 (Pd, B) 26 (C, N), and 27 (H), those of Pd being corrected [28] for both parts of anomalous dispersion. Tables 6, 7, and 8 list the refined atomic parameters. A comparison of observed and calculated structure factor amplitudes appears as a Supplementary Publication No. SUP 21474 (14 pp., 1 microfiche). † Except for the preliminary data treatment all calculations were executed on the University of London CDC 7600 computer, using the ' X-Ray ' system of programs.[29]

[25] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.
[26] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
[27] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[28] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. III.
[29] Technical Report TR-192 of the Computer Science Centre, University of Maryland, June 1972.