Insertion of Platinum into an *ortho*-Carboranyl Boron–Hydrogen Bond. The Crystal and Molecular Structure of the Diphenyl(*ortho*-carboranyl)-phosphine Complex [PtCl($Ph_2PC_2B_{10}H_{10}$)($Ph_2PC_2B_{10}H_{11}$)] †

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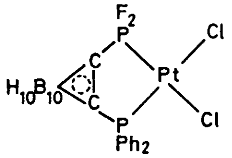
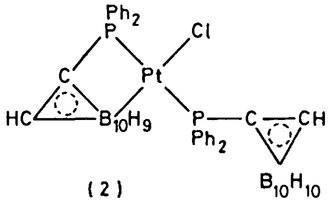
The molecular structure of the title complex has been determined by *X*-ray methods. The crystals are monoclinic, space group *I*2/*a*, with eight molecules in a unit cell of dimensions *a* = 26.122(3), *b* = 11.006(2), *c* = 29.775(3) Å, and β = 106.34(1)°. The structure has been refined by least-squares methods to *R* = 0.042 for 4 855 diffractometric intensities. The complex contains a $\overline{\text{Pt–P–C–B}}$ metallocycle, obtained by insertion of platinum into a B–H bond of a diphenyl(*ortho*-carboranyl)phosphine. A distorted square plane around platinum is completed by the phosphorus atom of a second $Ph_2PC_2B_{10}H_{11}$ ligand and by a chlorine atom. Both *ortho*-carboranyl cages have approximately icosahedral geometries. Selected bond lengths are: Pt–Cl 2.415(3), Pt–B 2.073(9), Pt–P(chelate) 2.279(3), and Pt–P(non-chelate) 2.305(2) Å.

Hill and Silva-Trivino[1] have recently prepared unsymmetrical *ortho*-carborane ditertiary phosphines (L) of the type ($R_2PC_2PR'R''$)$B_{10}H_{10}$ (R = C_6H_5 or NMe_2, R′ = NMe_2, R″ = F; and R = C_6H_5, R′ = R″ = NMe_2 or F), and treated them with platinum(II) nitriles to obtain well characterised complexes [$PtCl_2L$], in which L behaves as a chelating ligand. To extend our investigation of the electronic effects of phosphine substituents on metal–ligand bonding,[2-4] we decided to examine crystallographically the compound [$PtCl_2${($Ph_2PC_2PF_2$)$B_{10}H_{10}$}] (1), which contains highly electronegative fluorine atoms attached to phosphorus.



(1)



(2)

The low solubility of (1), which distinguishes it from other compounds of the series, prevented measurement of its n.m.r. parameters. During attempts at recrystallisation, (1) was treated with a variety of solvents, including benzene, chloroform, dichloromethane, and acetone.[5] The subsequent *X*-ray diffraction study quickly established that the recrystallisation procedure had caused (1) to undergo a chemical change. Nevertheless, the *X*-ray analysis was continued in order to establish the identity of the new compound. The results indicate that the recrystallisation product is a novel bis[diphenyl(*ortho*-carboranyl)phosphine] complex, (2). One of the phosphine ligands is unidentate, whereas the other is co-ordinated to the metal through both phosphorus and boron, with formation of a four-membered metallocycle.

EXPERIMENTAL

Crystal Data.—$C_{28}H_{41}B_{20}ClP_2Pt$, *M* = 886.3, Monoclinic, *a* = 26.122(3), *b* = 11.006(2), *c* = 29.775(3) Å, β = 106.34(1)°, *U* = 8 214.5 Å³, *Z* = 8, D_c = 1.433 g cm^{-3}, *F*(000) = 3 472, space group *I*2/*a* (C^6_{2h}, no. 15), equivalent positions $\pm(x, y, z)$, $\pm(\bar{x}, y, \frac{1}{2} - z) + (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, Mo-$K_\alpha$ radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 36.2 cm^{-1}.

Measurements.—A needle-shaped crystal of dimensions 0.053 × 0.016 × 0.013 cm, displaying the forms {10$\bar{1}$}, {001}, and {010}, was chosen for the analysis. The crystal system and the preliminary unit-cell dimensions were obtained from oscillation and Weissenberg photographs. Reflections were indexed on the basis of a body-centred unit cell, which gave a β angle much closer to 90° than an alternative C-centred cell. The systematically absent reflections were consistent with the space groups *Ia* (C^4_s, no. 9) and *I*2/*a* (C^6_{2h}, no. 15). The latter space group led to successful solution and refinement of the structure.

The orientation of the crystal on an Enraf–Nonius CAD-4F diffractometer, equipped with a graphite monochromator, and the final values of the unit-cell dimensions were determined from the setting angles of 25 reflections with $14 \leqslant \theta \leqslant 22°$. The intensities of all independent reflections with $2 \leqslant \theta(\text{Mo-}K_\alpha) \leqslant 25°$ were measured using continuous θ—2θ scans of 0.60° in θ, increased by 25% at each end of the scan range to allow for background effects. A reflection was counted either for 60 s or until $\sigma(I)/I \leqslant 0.03$, whichever took less time. The crystal orientation and the intensities of two reflections, periodically remeasured throughout the experiment, displayed no significant changes.

The integrated intensities and their standard deviations were derived in the way described elsewhere.[6] They were corrected for Lorentz, polarisation, and absorption effects. The transmission factors on F_o^2, obtained by Gaussian integration, were in the range 0.56—0.72. The structure analysis was carried out with 4 855 reflections for which $I \geqslant 5\sigma(I)$.

Structure Determination and Refinement.—The position of the platinum atom was determined from a Patterson synthesis and those of the other non-hydrogen atoms from the subsequent difference syntheses. A peak at a distance of 0.68 Å from a two-fold axis, and comparable in height with the peaks of phenyl carbon atoms, was thought to be associated with a disordered solvent molecule; it was included in all subsequent calculations and assigned a carbon scattering factor.

The final positional and thermal parameters of atoms (Table 1) were obtained by least-squares minimisation of the function $\Sigma(|F_o| - |F_c|)^2/\sigma^2(|F_o|)$. The parameters of

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† Semi-systematic name: chloro[1-diphenylphosphino-1,2-dicarba-*closo*-dodecaborane(12)-*P*][1-diphenylphosphino-1,2-dicarba-*closo*-dodecaboran-3-yl-B^3P]platinum.

different groups of atoms were refined in successive cycles. A detailed examination of the thermal parameters at a late stage of refinement allowed the carbon atoms of the *ortho*-carborane cages, C(25)—C(28) (Figure), to be distinguished from the boron atoms; such an identification of the carborane carbon atoms is compatible with structural and chemical evidence discussed later. The atomic scattering factors used, and the anomalous dispersion corrections for platinum, chlorine, and phosphorus atoms, were taken from ref. 7. No allowance was made for the scattering of hydrogen atoms.

TABLE 1

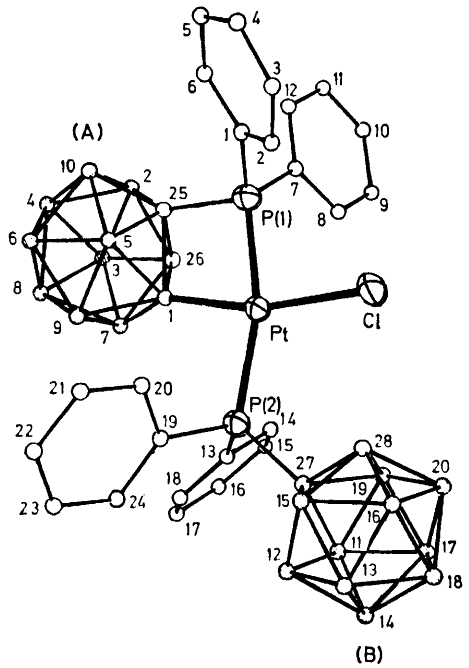
Fractional co-ordinates and vibrational parameters of atoms

Atom	x	y	z	$10^2U_{iso.}$/Å^2
Pt	0.119 94(1)	0.307 61(3)	0.090 27(1)	†
Cl	0.109 6(1)	0.159 5(2)	0.028 5(1)	†
P(1)	0.087 1(1)	0.172 9(2)	0.133 3(1)	†
P(2)	0.153 5(1)	0.479 8(2)	0.064 8(1)	†
C(1)	0.018 6(4)	0.130(1)	0.115 2(3)	4.5(2)
C(2)	−0.008 4(4)	0.134(1)	0.067 7(4)	5.8(3)
C(3)	−0.061 5(5)	0.094(1)	0.051 8(5)	7.8(4)
C(4)	−0.088 3(5)	0.057(1)	0.083 9(5)	8.6(4)
C(5)	−0.062 4(6)	0.060(1)	0.132 8(5)	9.4(4)
C(6)	−0.008 4(5)	0.099(1)	0.147 1(5)	7.9(4)
C(7)	0.127 7(3)	0.041(1)	0.156 8(3)	3.9(2)
C(8)	0.174 7(4)	0.027(1)	0.144 6(3)	5.2(2)
C(9)	0.208 8(5)	−0.069(1)	0.164 6(4)	6.7(3)
C(10)	0.191 9(5)	−0.152(1)	0.194 1(4)	6.7(3)
C(11)	0.144 7(5)	−0.138(1)	0.204 8(4)	7.1(3)
C(12)	0.112 2(4)	−0.040(1)	0.185 7(4)	5.7(3)
C(25)	0.095 4(4)	0.279(1)	0.182 3(3)	4.5(2)
C(26)	0.160 7(4)	0.306(1)	0.204 0(4)	4.0(2)
B(1)	0.123 5(4)	0.393(1)	0.153 0(4)	5.9(3)
B(2)	0.123 1(5)	0.263(1)	0.240 6(5)	5.6(3)
B(3)	0.170 2(6)	0.381(1)	0.256 0(5)	7.4(4)
B(4)	0.105 9(6)	0.397(2)	0.265 5(6)	7.9(4)
B(5)	0.061 4(5)	0.406(1)	0.165 6(4)	5.2(3)
B(6)	0.068 9(7)	0.491(2)	0.217 7(6)	8.4(5)
B(7)	0.171 4(6)	0.463(1)	0.203 3(5)	6.6(4)
B(8)	0.137 3(7)	0.523(2)	0.241 5(6)	8.8(5)
B(9)	0.107 8(6)	0.530(2)	0.179 1(6)	7.8(4)
B(10)	0.058 4(6)	0.327(1)	0.216 8(6)	7.3(4)
C(13)	0.219 9(3)	0.509(1)	0.104 3(3)	3.6(2)
C(14)	0.250 5(4)	0.402(1)	0.117 1(4)	5.4(3)
C(15)	0.301 3(5)	0.409(1)	0.149 9(4)	6.8(3)
C(16)	0.320 5(4)	0.521(1)	0.169 1(4)	6.0(3)
C(17)	0.291 0(5)	0.625(1)	0.155 3(4)	6.1(3)
C(18)	0.239 6(4)	0.617(1)	0.122 5(3)	5.0(2)
C(19)	0.108 4(3)	0.607(1)	0.062 6(3)	3.6(2)
C(20)	0.055 6(4)	0.577(1)	0.058 4(4)	5.5(3)
C(21)	0.018 2(5)	0.667(1)	0.056 2(5)	8.0(4)
C(22)	0.033 2(5)	0.789(1)	0.061 1(4)	7.2(3)
C(23)	0.085 8(5)	0.822(1)	0.064 6(4)	6.2(3)
C(24)	0.123 8(4)	0.732(1)	0.065 5(4)	5.2(3)
C(27)	0.165 4(3)	0.485(1)	0.005 1(3)	3.4(2)
C(28)	0.131 3(4)	0.386(1)	−0.033 6(3)	4.5(2)
B(11)	0.226 8(5)	0.511(1)	−0.004 7(5)	5.9(3)
B(12)	0.174 2(5)	0.618(1)	−0.024 6(4)	5.3(3)
B(13)	0.142 0(5)	0.586(1)	−0.084 5(5)	6.6(4)
B(14)	0.212 1(6)	0.575(1)	−0.061 6(5)	6.9(4)
B(15)	0.112 7(5)	0.535(1)	−0.041 0(4)	5.1(3)
B(16)	0.113 6(5)	0.439(1)	−0.088 8(4)	5.7(3)
B(17)	0.227 7(5)	0.410(1)	−0.051 7(5)	6.2(3)
B(18)	0.175 4(5)	0.462(1)	−0.102 2(4)	5.5(3)
B(19)	0.198 0(5)	0.366(1)	−0.009 6(4)	5.1(3)
B(20)	0.167 4(5)	0.332(1)	−0.068 7(5)	5.8(3)
C(29)	0.475 7(9)	0.659(2)	0.233 3(9)	18(1)

† Assigned anisotropic temperature factors of the form exp-$(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} h_i h_j a_i^* a_j^* U_{ij})$. The U_{ij} parameters ($\times 10^3$ Å^2) are:

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	45.5(2)	24.2(2)	29.3(2)	−4.0(2)	15.2(1)	−0.8(2)
Cl	93(2)	34(1)	45(1)	−15(1)	32(1)	−12(1)
P(1)	46(1)	31(1)	34(1)	−5(1)	15(1)	2(1)
P(2)	37(1)	26(1)	29(1)	0(1)	10(1)	1(1)

The refinement converged at R 0.042 and R' 0.062, with no parameter changing by more than 0.4 of its standard deviation. The final difference synthesis revealed two peaks of 1.2 e Å^{-3} close to the position of the platinum atom, and no other peaks higher than 0.8 e Å^{-3}. An analysis of $\langle(|F_o| - |F_c|)^2/\sigma^2(|F_o|)\rangle$ as a function of $|F_o|$ and sinθ established the adequacy of the weighting scheme employed. The observed and calculated structure amplitudes are presented in Supplementary Publication No. SUP 22668 (20 pp.).*



View of the molecular structure of $[PtCl(Ph_2PC_2B_{10}H_{10})(Ph_2PC_2B_{10}H_{11})]$. The vibrational ellipsoids of Pt, Cl, and P atoms display 50% probability. For clarity, the carbon and boron atoms are represented respectively by open and shaded circles of arbitrary size; they are labelled by numbers only, corresponding to those listed in Table 1

All calculations were carried out on the N.U.M.A.C. IBM 370 computer, using programs listed elsewhere.[8]

RESULTS AND DISCUSSION

The crystal structure is built of discrete $[PtCl(Ph_2PC_2B_{10}H_{10})(Ph_2PC_2B_{10}H_{11})]$ molecules, separated by van der Waals contacts, and also of disordered solvent molecules. The identity of the solvent was not established by this analysis, but the chemical history of the sample suggests that it may be acetone.

The molecular structure, shown in the Figure, displays a square-planar geometry around the platinum atom, with the two phosphorus atoms *trans* to one another. The *ortho*-carboranyl substituent of one phosphine ligand is also co-ordinated to platinum to form a four-membered metallocycle of the type Pt–P–C–B. As far as we are

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

aware, the molecular structure described here provides the first example of a crystallographically characterised complex of a B-metallated (*ortho*-carboranyl)phosphine.

In the phosphine ligands the geometry of the phenyl groups is normal: the C–C bond distances are 1.35(1)—1.43(1) Å and the C–C–C bond angles are 117(1)—122(1)°. The P–C(phenyl) bond lengths are 1.783(10)—1.829(7) Å, and the C–P–C angles deviate somewhat from the ideal tetrahedral value of 109° 28′ (Table 2).

TABLE 2

Selected interatomic distances and angles

(*a*) Bond lengths (Å)

Pt–Cl	2.415(3)	Pt–B(1)	2.073(9)
Pt–P(1)	2.279(3)	Pt–P(2)	2.305(2)
P(1)–C(1)	1.783(10)	P(2)–C(13)	1.829(7)
P(1)–C(7)	1.814(8)	P(2)–C(19)	1.816(9)
P(1)–C(25)	1.834(10)	P(2)–C(27)	1.888(10)
C(25)–C(26)	1.672(14)	C(27)–C(28)	1.658(12)
C(25)–B(1)	1.802(15)	C(27)–B(11)	1.732(16)
C(25)–B(2)	1.690(14)	C(27)–C(12)	1.751(16)
C(25)–B(5)	1.657(16)	C(27)–B(15)	1.733(13)
C(25)–B(10)	1.680(22)	C(27)–B(19)	1.692(16)
C(26)–B(1)	1.828(14)	C(28)–B(15)	1.706(16)
C(26)–B(2)	1.726(19)	C(28)–B(16)	1.685(16)
C(26)–B(3)	1.712(19)	C(28)–B(19)	1.702(15)
C(26)–B(7)	1.747(19)	C(28)–B(20)	1.702(19)
B(1)–B(5)	1.769(18)	B(11)–B(12)	1.776(18)
B(1)–B(7)	1.825(16)	B(11)–B(14)	1.771(19)
B(1)–B(9)	1.789(20)	B(11)–B(17)	1.789(20)
B(2)–B(3)	1.756(20)	B(11)–B(19)	1.756(19)
B(2)–B(4)	1.766(22)	B(12)–B(13)	1.779(17)
B(2)–B(10)	1.782(19)	B(12)–B(14)	1.740(22)
B(3)–B(4)	1.790(24)	B(12)–B(15)	1.792(18)
B(3)–B(7)	1.816(22)	B(13)–B(14)	1.771(19)
B(3)–B(8)	1.781(24)	B(13)–B(15)	1.774(21)
B(4)–B(6)	1.802(23)	B(13)–B(16)	1.770(20)
B(4)–B(8)	1.853(26)	B(13)–B(18)	1.777(21)
B(4)–B(10)	1.798(21)	B(14)–B(17)	1.857(21)
B(5)–B(6)	1.773(22)	B(14)–B(18)	1.805(18)
B(5)–B(9)	1.790(20)	B(15)–B(16)	1.772(18)
B(5)–B(10)	1.779(22)	B(16)–B(18)	1.787(20)
B(6)–B(8)	1.762(24)	B(16)–B(20)	1.807(18)
B(6)–B(9)	1.785(28)	B(17)–B(18)	1.817(16)
B(6)–B(10)	1.828(23)	B(17)–B(19)	1.721(21)
B(7)–B(8)	1.761(26)	B(17)–B(20)	1.744(18)
B(7)–B(9)	1.775(21)	B(18)–B(20)	1.798(19)
B(8)–B(9)	1.800(23)	B(19)–B(20)	1.758(17)

(*b*) Bond angles (°)

Cl–Pt–P(1)	90.6(1)	P(1)–Pt–P(2)	163.4(8)
Cl–Pt–P(2)	106.0(1)	P(1)–Pt–B(1)	73.6(3)
Cl–Pt–B(1)	164.0(3)	P(2)–Pt–B(1)	89.9(3)
Pt–P(1)–C(1)	120.5(3)	Pt–P(2)–C(13)	108.1(3)
Pt–P(1)–C(7)	117.7(3)	Pt–P(2)–C(19)	109.9(3)
Pt–P(1)–C(25)	93.2(3)	Pt–P(2)–C(27)	121.0(3)
C(1)–P(1)–C(7)	109.3(4)	C(13)–P(2)–C(19)	112.2(4)
C(1)–P(1)–C(25)	107.2(5)	C(13)–P(2)–C(27)	102.9(4)
C(7)–P(1)–C(25)	106.1(4)	C(19)–P(2)–C(27)	102.6(4)
P(1)–C(25)–C(26)	107.3(7)	P(2)–C(27)–C(28)	115.7(6)
P(1)–C(25)–B(1)	91.8(6)	P(2)–C(27)–B(11)	124.7(6)
P(1)–C(25)–B(2)	132.2(7)	P(2)–C(27)–B(12)	125.6(7)
P(1)–C(25)–B(5)	111.4(6)	P(2)–C(27)–B(15)	116.8(7)
P(1)–C(25)–B(10)	136.6(8)	P(2)–C(27)–B(19)	116.4(6)
Pt–B(1)–C(25)	101.4(6)	Pt–B(1)–B(7)	140.9(8)
Pt–B(1)–C(26)	112.7(7)	Pt–B(1)–B(9)	144.7(8)
Pt–B(1)–B(5)	114.6(6)		

The C_2B_{10} units of the *ortho*-carboranyl substituents, (A) and (B), are nearly regular icosahedra (Figure). Thus the bond angles display ranges of 55(1)—64(1) and 100(1)—117(1)° in (A) and 57(1)—65(1) and 103(1)—116(1)° in (B), compared with ideal icosahedral values of 60 and 108°.

The identification of the carboranyl carbon atoms on the basis of their temperature factors leads to formulation of both (A) and (B) as 1-*P*-1,2-dicarbadodecaboranes, as would be expected since (2) is derived from (1). A detailed inspection of bond lengths within the polyhedra was carried out in an attempt to obtain further confirmation of this formulation. Beal[9] has recently summarised bond lengths in *ortho*-carborane derivatives and pointed out that the carbon atoms display a covalent radius some 0.06 Å shorter than that of boron: the ranges of length shown by each type of bond (C–C 1.63—1.67, C–B 1.66—1.77, and B–B 1.69—1.85 Å) overlap with each other, but the average values (C–C 1.65, C–B 1.72, and B–B 1.77 Å) show little variation from structure to structure.[9–12] In (B) the mean lengths of the five bonds involving a given cage atom are greater than 1.76 Å, except for C(27) (1.713), C(28) (1.690), and B(19) (1.726 Å). The C(27)–C(28) bond [1.658(12) Å] is the shortest within the icosahedron, and the individual C–B and C–C distances [respectively 1.685(16)—1.751(16) and 1.721(21)—1.857(21) Å] appear unexceptional. In (A) the average bond length is shortest for C(25) (1.700 Å) and longest for B(1) (1.803 Å), thus confirming the conclusion that metallation has occurred at a boron rather than at a carbon atom. Other average bond lengths are greater than 1.77 Å, except for the atoms C(26) (1.737), B(2) (1.744), and B(5) (1.754 Å). The C(25)–C(26) bond [1.672(14) Å] is slightly longer than the C(25)–B(5) distance [1.657(16) Å]. The C(25)–B(1) and C(26)–B(1) bond lengths [1.802(15) and 1.828(14) Å] are exceptionally long, most probably because of their proximity to the four-membered chelate ring. Other C–B and B–B distances appear normal. The bond lengths in (A) thus tend to confirm the identification of C(25) and C(26) as carbon atoms, although they do not rule out the possibility of some disorder between the C(26), B(2), and B(5) positions.

The co-ordination sphere of the platinum atom displays significant deviations from ideal square-planar geometry. Thus the constraint imposed by formation of the four-membered chelate ring leads to an unusually acute P(1)–Pt–B(1) angle of 73.6(3)°, while the P(2)–Pt–Cl angle opens to 106.0(1)°. The atom B(1) deviates by 0.083(10) Å from the platinum co-ordination plane [defined by the atoms Pt, B(1), P(1), P(2), and Cl], while the displacements of the remaining atoms do not exceed ±0.016 Å. The atom C(25) is displaced from this plane by 0.027 Å only.

The rotational orientation of carborane (B) around the Pt–P(2) bond is such as to place the atoms C(27) and C(28) 0.07 and 0.66 Å away from the co-ordination plane of platinum. This leads to a C(28) · · · Cl intramolecular contact of 3.24 Å. Assuming the stereochemistry of C(28) is as expected for an *ortho*-carboranyl carbon atom, we estimate that the H · · · Cl contact involving the hydrogen atom bonded to C(28) is no longer than 2.4 Å. This value is 0.4 Å shorter than the sum of the appropriate van der Waals radii (2.8 Å) and it suggests, on the basis of the criterion of Hamilton and Ibers,[13] that carborane (B) and the chlorine ligand are linked by an intramolecular hydrogen bond of the type C–H · · · Cl.

The Pt–P(1) [2.279(3) Å] and Pt–P(2) [2.305(2) Å] bond lengths are in the range of Pt–P (*trans* to P) distances (2.28—2.32 Å) usually observed in monotertiary phosphine complexes of platinum(II).[14] They differ from each other by 0.026(4) Å, the shorter bond being that incorporated in the chelate ring. Formation of this ring also results in a contraction of the P(1)–C(25) bond [1.834(10) Å], which is 0.054(14) Å shorter than the P(2)–C(27) bond [1.888(10) Å], and in the unusually small Pt–P(1)–C(25) angle of 93.2(3)°.

Metallation of carborane (A) results in a Pt–B(1) σ-bonding distance of 2.073(9) Å. This distance is slightly shorter than the Pt–C(*ortho*-carborane) σ bond of 2.13(1) Å in $1\text{-}[\overline{\text{Pt}(\text{Pr}^n{}_2\text{P}\text{C}}\text{HCH}_2\text{CH}_3)(\text{PPr}^n{}_3)]\text{-}2\text{-}\text{C}_6\text{H}_5\text{-}1,2\text{-}\text{C}_2\text{-}\text{B}_{10}\text{H}_{10}$,[15] and it is practically the same as the mean value [2.079(5) Å] for Pt–C(alkyl) bonds in platinum(II) complexes in which the carbon-donor ligands are subject to low *trans* influence.[16] The Pt–Cl distance [2.415(3) Å] lies at the upper end of the range of values found in platinum(II) complexes,[17] thus indicating that the *trans* influence of the carboranyl boron atom is relatively high. Indeed, it is comparable with the *trans* influence of an sp^3-hybridised carbon atom, as is evident from the Pt–Cl(*trans* to C) distance of 2.415(5) Å in *trans*-$[\text{PtCl}(\text{CH}_2\text{SiMe}_3)(\text{PMe}_2\text{Ph})_2]$.[18] For alkyl, and now by extrapolation for σ-bonded carboranyl boron, high *trans* influence is thought to arise from the strongly covalent nature of the bond formed with platinum.

Metallocarboranes in which the metal atoms are π-bonded to the carborane cage [19] or involved in two-centre two-electron M–C(carborane) σ-bonding interactions [15] have been characterised crystallographically; the existence of three-centre M–H–B bridges has also been established.[20,21] We however present here the first crystallographic evidence for the existence of a metal–boron(carborane) σ bond.

Pertinent to this work is the study of Hoel and Hawthorne [22,23] of intramolecular oxidative addition in $[\text{IrCl}(1\text{-PMe}_2\text{-}1,2\text{-C}_2\text{-B}_{10}\text{H}_{11})_3]$, where spectroscopic evidence strongly indicates that insertion of iridium(I) into a B–H bond results in formation of an Ir–B σ bond incorporated into a four-membered Ir–P–C–B metallocycle. It has been further shown that the 1,2-, 1,7-, and $1,12\text{-C}_2\text{-B}_{10}\text{H}_{12}$ carboranes are susceptible to catalysed deuterium exchange at boron atoms, but not at carbon, and that they undergo intermolecular oxidative-addition reactions with iridium(I) species to form stable *B*-σ-carboranyliridium complexes.[23-25] It has therefore been suggested that in carboranes the BH groups are much more reactive with low-valent transition-metal complexes than are the CH groups, the relative reactivities being particularly high for the BH groups which are closest to the carbon atoms in the icosahedral cage.[26] The molecular structure of the platinum(II) complex described here supports these observations.

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