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**SYNTHESIS AND MOLECULAR STRUCTURE OF**  
*cis*-1-[(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>PPtP(CHC<sub>6</sub>H<sub>5</sub>)(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]-2-CH<sub>3</sub>-1,2-(σ-B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>)

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**Summary**

The title complex has been prepared from the reaction of *cis*-[(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub> with 1-Li-2-CH<sub>3</sub>-1,2-B<sub>10</sub>C<sub>2</sub>H<sub>10</sub> and the crystal structure determined by X-ray single-crystal analysis. Crystals are triclinic, space group *P* $\bar{1}$ , with *a* 13.826(5), *b* 15.269(5), *c* 13.234(4) Å and α 104.74(8), β 60.78(8), γ 107.46(8)°. The structure was solved by the heavy-atom method and refined to *R* 0.060 for 3855 independent reflections. The carboranyl group is σ-bonded to Pt through its C(1) atom. One phosphine is coordinated to the metal atom through its P atom, the other through its P atom and the C atom bonded to phosphorus of one benzyl side group, leading to a three-membered Pt–P–C chelate ring.

In a previous paper [1] we reported the synthesis and characterization of some cyclometallated bis(phosphino)platinum(II) complexes containing 1,2- or 1,7-dicarba-*closo*-dodecaborane(12) bonded through metal–carbon σ bonds. These complexes were prepared by treating *trans*-L<sub>2</sub>PtCl<sub>2</sub> (L = PEt<sub>3</sub>, P-*n*-Pr<sub>3</sub>) and 1-Li-2-R-1,2- or 1-Li-7-R-1,7-dicarba-*closo*-dodecaborane(12), (R = H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) in solution at room temperature or below. The special feature of such complexes is that the internal metallation involves the first carbon atom of an alkyl group of one of the coordinated phosphines with formation of an unusual three-membered Pt–P–C chelate ring, as has been shown by the recent crystal structure analysis of the PEt<sub>3</sub> [2] and P-*n*-Pr<sub>3</sub> [3] derivatives containing -2-CH<sub>3</sub>-1,2- and -2-C<sub>6</sub>H<sub>5</sub>-1,2-B<sub>10</sub>C<sub>2</sub>H<sub>10</sub> ligands, respectively. Furthermore, all these compounds appear to be square-planar distorted complexes having the two phosphine ligands in mutual *cis* positions.

Later, we prepared and characterized by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy the cyclometallated complex *cis*-1-[(MePh<sub>2</sub>P)Pt(PCH<sub>2</sub>Ph<sub>2</sub>)]-2-C<sub>6</sub>H<sub>5</sub>-1,2-( $\sigma$ -B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>) [4]. Here the three-membered chelate ring formation occurs through internal metallation at a C—H bond of one methyl substituent of the phosphine ligands. Recently, an intramolecular C—H addition in a trimethylphosphine complex of iron(0) with formation of a three-membered Fe—P—C ring has been also reported [5].

In order to obtain further insight into the intramolecular metallation reactions and to get information about the influence of the ligand system on the size of the chelate ring we have now prepared the carborane derivative of platinum(II) containing the tribenzylphosphine ligand. The compound was fully characterized by IR and  $^{31}\text{P}$  NMR spectroscopic techniques and formulated as *cis*-1-[(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>P]<sub>2</sub>PtP(CHC<sub>6</sub>H<sub>5</sub>)(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]-2-CH<sub>3</sub>-1,2-( $\sigma$ -B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>) (I). In order to prove unequivocally the ligand arrangement around the metal atom an X-ray structural investigation was performed.

## Experimental

### Synthesis and characterization of I

A solution of 2.5 mmol of 1-Li-2-CH<sub>3</sub>-1,2-B<sub>10</sub>C<sub>2</sub>H<sub>10</sub> in 10 ml of tetrahydrofuran [6] was added dropwise to a stirred solution of 1.5 mmol (0.55 g) of *cis*-[(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub> [7] in 20 ml of tetrahydrofuran under argon. After 20 h stirring at room temperature the resulting pale yellow solution was evaporated in vacuo to dryness. The solid residue was dissolved in dichloromethane and the solution washed with H<sub>2</sub>O. The organic layer was separated, dried with Na<sub>2</sub>SO<sub>4</sub>, and filtered. The filtrate was concentrated to small volume at reduced pressure on a rotary evaporator and then a white precipitate was obtained by addition of methanol. The crude product was separated by filtration and recrystallized from CHCl<sub>3</sub>/CH<sub>3</sub>OH to give white crystals of I (25% yield based on *cis*-[(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub>, m.p. 204–205°C uncorrected) in a capillary tube sealed under nitrogen. Anal.: Found: C, 55.67; H, 5.48%. C<sub>45</sub>H<sub>54</sub>B<sub>10</sub>P<sub>2</sub>Pt calcd.: C, 56.29; H, 5.67%.

The infrared spectrum (Nujol mull) of I shows, in addition to the bands due to the phosphine ligands, strong absorptions in the region 2580–2610 cm<sup>-1</sup>, which are assigned to  $\nu(\text{BH})$  of the dicarba-*closo*-dodecaborane(12). The  $^{31}\text{P}$  NMR spectrum of I in CDCl<sub>3</sub> was recorded at 24.28 MHz with a WP-60 FTR Bruker NMR spectrometer. It exhibits two doublets of relative total intensities 1 to 1 centered at  $\delta +8.5$  and  $\delta -22.7$  ppm, respectively (shifts relative to external 85% H<sub>3</sub>PO<sub>4</sub>, positive values are downfield), with  $J(\text{P—P})$  30 Hz (the  $^{31}\text{P}$  chemical shifts versus H<sub>3</sub>PO<sub>4</sub> are  $\pm 0.1$  ppm,  $J(\text{P—P})$  and  $J(\text{Pt—P}) \pm 1$  Hz). Each of the main peaks of the  $^{31}\text{P}$  resonances is flanked by satellites due to the coupling with the  $^{195}\text{Pt}$  isotope separated by  $J(^{195}\text{Pt—P})$  of 3190 Hz and 1493 Hz at low and high field, respectively. This NMR pattern is in agreement with a configuration in which the phosphine ligands are in mutual *cis* position. In addition, the phosphorus resonance values of I are comparable with those exhibited by the corresponding and structurally well-defined complexes *cis*-[Et<sub>3</sub>P]<sub>2</sub>P(CHCH<sub>3</sub>)Et<sub>2</sub>]-2-CH<sub>3</sub>-1,2-( $\sigma$ -B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>) (II) [2],

TABLE 1

FRACTIONAL COORDINATES ( $\times 10^4$ ) AND ISOTROPIC TEMPERATURE FACTORSESD's in parentheses; asterisks indicate anisotropic temperature factors.<sup>a</sup>

	X	Y	Z	B ( $\text{\AA}^2$ )
Pt	1772(0)	2341(0)	2559(0)	*
P(1)	1358(3)	3029(3)	4446(3)	*
P(2)	3628(3)	2375(3)	1503(3)	*
C(1)	151(10)	1942(9)	2639(11)	4.5(3)
C(2)	-396(10)	823(9)	2285(11)	4.7(3)
C(3)	317(13)	84(12)	1960(14)	6.9(4)
C(4)	99(11)	2486(10)	5695(12)	5.3(3)
C(5)	27(12)	2921(11)	6909(12)	5.8(3)
C(6)	527(14)	2540(12)	7378(14)	7.3(4)
C(7)	408(16)	2945(14)	8568(17)	8.9(5)
C(8)	-120(18)	3653(16)	9093(19)	10.0(6)
C(9)	-685(19)	4027(17)	8686(20)	10.9(7)
C(10)	-594(15)	3604(14)	7521(16)	8.3(5)
C(11)	1081(11)	4216(10)	4806(11)	5.2(3)
C(12)	1991(11)	4915(10)	3991(12)	5.4(3)
C(13)	2149(12)	4819(11)	2840(13)	6.1(4)
C(14)	2986(13)	5485(12)	2105(14)	7.1(4)
C(15)	3625(15)	6224(14)	2575(16)	8.4(5)
C(16)	3433(14)	6279(12)	3693(15)	7.3(4)
C(17)	2626(12)	5651(11)	4436(13)	6.2(4)
C(18)	2524(11)	3242(10)	4844(11)	5.2(3)
C(19)	3072(10)	2430(9)	4591(11)	4.7(3)
C(20)	2515(12)	1508(10)	4530(12)	5.7(3)
C(21)	3062(13)	802(11)	4360(13)	6.5(4)
C(22)	4148(13)	1000(12)	4277(14)	7.0(4)
C(23)	4713(13)	1910(12)	4314(14)	7.1(4)
C(24)	4191(12)	2644(11)	4479(13)	6.0(4)
C(25)	4309(11)	1497(10)	1502(12)	5.3(3)
C(26)	5361(11)	1338(10)	360(12)	5.6(3)
C(27)	5360(13)	1228(11)	-714(14)	6.5(4)
C(28)	6391(15)	1127(13)	-1778(16)	8.2(5)
C(29)	7331(14)	1098(13)	-1679(15)	7.8(5)
C(30)	7298(15)	1181(13)	-641(15)	7.8(5)
C(31)	6322(13)	1284(12)	430(14)	6.9(4)
C(32)	4767(11)	3390(10)	861(12)	5.2(3)
C(33)	5396(11)	3830(9)	1597(11)	5.0(3)
C(34)	6432(13)	3614(11)	1246(13)	6.5(4)
C(35)	7027(15)	4060(14)	1991(16)	8.4(5)
C(36)	6584(15)	4656(13)	2920(15)	7.9(5)
C(37)	5592(14)	4864(12)	3239(15)	7.3(4)
C(38)	4969(12)	4457(11)	2576(13)	6.0(3)
C(39)	2793(10)	1893(9)	751(11)	4.5(3)
C(40)	2924(10)	2289(9)	-231(10)	4.4(3)
C(41)	3181(12)	1725(11)	-1341(13)	6.1(4)
C(42)	3333(13)	2101(12)	-2285(14)	6.9(4)
C(43)	3257(14)	3018(13)	-2181(15)	7.4(4)
C(44)	3004(13)	3571(11)	-1112(13)	6.5(4)
C(45)	2852(11)	3196(10)	-156(12)	5.6(3)
B(1)	14(12)	1563(11)	1320(13)	4.7(3)
B(2)	-379(13)	2616(12)	2210(14)	5.2(4)
B(3)	-1019(13)	2427(12)	3689(14)	5.3(4)
B(4)	-957(13)	1300(12)	3699(14)	5.3(4)
B(5)	-1203(14)	680(12)	1575(15)	5.5(4)
B(6)	-1226(14)	1849(12)	1514(15)	5.8(4)
B(7)	-1878(17)	2358(16)	2985(19)	7.6(5)
B(8)	-2254(14)	1526(13)	3951(15)	5.8(4)
B(9)	-1816(14)	517(13)	3055(15)	5.8(4)
B(10)	-2386(14)	1153(13)	2607(15)	6.1(4)

(Continued)

TABLE 1 (continued)

	$B_{11}$	$B_{12}$	$B_{13}$	$B_{22}$	$B_{23}$	$B_{33}$
Pt	632(2)	236(4)	-590(4)	509(2)	29(4)	667(3)
P(1)	687(20)	277(31)	-560(33)	583(18)	16(36)	744(24)
P(2)	665(20)	225(32)	-526(33)	582(18)	89(36)	649(24)

$\alpha$  Anisotropic temperature factors ( $\times 10^5$ ) are in the form:  $\exp - [B_{11}h^2 + B_{12}hk + B_{13}kl + B_{23}kl + B_{22}k^2 + B_{33}l^2]$ .

*cis*-[n-Pr<sub>3</sub>PPt(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)n-Pr<sub>2</sub>]-2-C<sub>6</sub>H<sub>5</sub>-1,2-( $\sigma$ -B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>) (III) [3] and  
*cis*[(Ph<sub>2</sub>MeP)PtP(CH<sub>2</sub>)Ph<sub>2</sub>]-2-C<sub>6</sub>H<sub>5</sub>-1,2-( $\sigma$ -B<sub>10</sub>C<sub>2</sub>H<sub>10</sub>) (IV) [4].

#### Crystal data

PtP<sub>2</sub>B<sub>10</sub>C<sub>45</sub>H<sub>54</sub>,  $M = 960.1$ , triclinic,  $a$  13.826(5),  $b$  15.269(5),  $c$  13.234(4) Å,  $\alpha$  104.74(8),  $\beta$  60.78(8),  $\gamma$  107.46(8)°,  $U$  2306.3 Å<sup>3</sup>,  $D_c$  1.38,  $D_m$  1.42 (by flotation)  $Z = 2$ , Mo- $K_\alpha$  radiation,  $\lambda$  0.7107 Å,  $\mu$ (Mo- $K_\alpha$ ) 33.0 cm<sup>-1</sup>, space group  $P\bar{1}$  (from structure refinement). Cell parameters were determined from Weissenberg and precession photographs taken with Cu- $K_\alpha$  radiation and refined with an on-line automatic Siemens diffractometer. Single crystals were obtained by slow evaporation of a dichloromethane solution.

#### Intensity measurements

Three-dimensional intensity data were collected on a Siemens single-crystal diffractometer by the  $\theta - 2\theta$  scan technique with Mo- $K_\alpha$  radiation for a maximum  $2\theta$  angle of 54°. Reflections having  $I_0 < 3\sigma(I_0)$  were rejected, the remainder being corrected for Lorentz and polarization factors. 3855 independent reflections were used in the subsequent calculations. No correction for absorption was applied ( $\mu R$  0.38).

During data collection a decrease of the standard reflection intensity was observed suggesting a disordering of the crystal, due to X-ray exposure, which affects the accuracy of the structure analysis. This was partly avoided by correcting the intensities, which decreased by about 30% during the overall recording time with a nearly linear trend.

#### Structure determination and refinement

The structure was solved by conventional Patterson and Fourier methods. Least squares refinement with anisotropic temperature factors for the platinum and phosphorus atoms reduced  $R$  to 0.060. The hydrogen atoms were neglected and the final weighting scheme was  $w = 1/(A + |F_o| + B|F_o|^2)$  where  $A = 17.5$  and  $B = 0.0033$  were chosen so as to maintain  $w(|F_o| - |F_c|)^2$  nearly constant over all ranges of  $|F_o|$  and  $(\sin \theta/\lambda)$ . Scattering factors were calculated according to Moore [8]. Final atomic parameters are listed in Table 1 together with their estimated standard deviations. Observed and calculated structure factors are available from the authors (N.B.P.) on request.

### Calculations

All calculations were carried out on a CDC 6200 computer with programmes described in ref. 9.

### Results and discussion

The main results dealing with the structure of I is that a three-membered  $\text{Pt} \begin{smallmatrix} \text{P} \\ \text{C} \end{smallmatrix}$  chelate ring is formed instead of the usual less strained five-membered ring obtained through internal metallation of an *ortho* C—H bond of one phenyl group of the phosphine ligand. In fact the crystal structure consists of monomeric  $[(\text{C}_6\text{H}_5\text{CH}_2)_3\text{PPtP}(\text{CHC}_6\text{H}_5)(\text{CH}_2\text{C}_6\text{H}_5)_2]-2\text{-CH}_3-1,2-(\sigma\text{-B}_{10}\text{C}_2\text{H}_{10})$  units. The  $\text{Pt}^{\text{II}}$  atom is coordinated by the carboranyl group through its C(1) atom and by two phosphine ligands through its phosphorous atoms, the four-coordination being achieved by internal metallation involving the carbon atom bonded to P of a benzyl group of one phosphine ligand (see Fig. 1). A three-membered chelate ring is then formed, as already observed in the related  $\text{PEt}_3$  (II) [2] and  $\text{P-n-Pr}_3$  (III) [3] derivatives. Furthermore, as in II and III, the carboranyl group is bonded to the metal atom through a "pure"  $\sigma$  bond, as indicated by the Pt—C bond length of 2.09(1) Å and by the fact that the car-

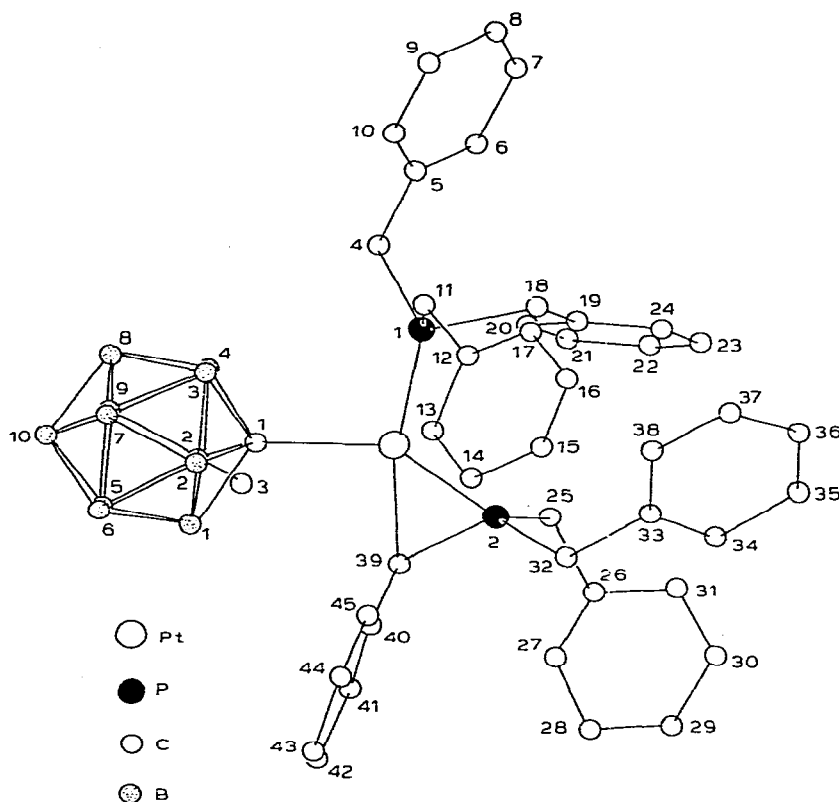


Fig. 1. A view of the molecule, with the numbering scheme for the atoms.

boranyl atoms adjacent to the coordinated C atom are nearly equidistant from the Pt at distances ranging from 3.31(1) to 3.42(2) Å. Such results further demonstrate that the bulky carboranyl ligands  $\sigma$ -bonded to a transition metal atom promote intramolecular cyclometallation reactions [10] and confirm that in Pt complexes the cyclometallation takes place with formation of a three-membered ring even when rings of sterically more favoured size could be formed.

The platinum and the four coordinated atoms are coplanar within  $\pm 0.04$  Å. The geometry of the three-membered Pt—P(2)—C(39) ring is very similar to that of the analogous rings in II and III and it is better described [3] in terms of a  $\pi$  olefin-like bond between Pt and a P(2)=C(39) double bond, rather than two Pt—C(39) and Pt—P(2)  $\sigma$  bonds, as can be seen from the trend of bond lengths and angles. In fact the P(2)—C(39) distance of 1.76(2) Å is shorter than the other P—C distances (from 1.85(2) to 1.87(1) Å) suggesting a certain amount of double bond character. The sum of the C—P—C angles around P(2), 331.6(7)°, greater than that around P(1) (303.5(7)°) further supports that the state of P(2) is closer to a  $sp^2$  than  $sp^3$  hybridization.

Bond lengths and angles of interest for the present compound and its analogues II and III are listed in Table 2. A comparison of such values shows that the geometry around the metal atom is very similar in the three complexes. It is noteworthy that the Pt—P(1) distance is significantly longer than Pt—P(2). The latter distance of 2.235(4) Å is near to values reported [11] for Et<sub>3</sub>P—Pt distances *trans* to chlorine which range from 2.226(7) to 2.247(6) Å. In contrast, the Pt—P(1) bond length of 2.302(4) Å is only slightly below the values reported for Et<sub>3</sub>P—Pt *trans* to the  $\sigma$ -carbon atom, which range from 2.310(7) to 2.362(5) Å [11]. This would suggest that C(39) exerts a *trans* influence greater than that of the carboranyl C(1) atom. However it must be borne in mind that

TABLE 2

BOND LENGTHS (Å) AND ANGLES (°) OF INTEREST WITH THEIR ESD's IN PARENTHESES

	Compound I	Compound II	Compound III
Pt—P(1)	2.302(4)	2.291(8)	2.286(5)
Pt—P(2)	2.235(4)	2.189(7)	2.202(5)
Pt—C(1)	2.09(1)	2.09(2)	2.13(1)
Pt—C(39)	2.15(1)	2.19(2)	2.17(2)
P(2)—C(39)	1.76(2)	1.73(3)	1.76(2)
P(2)—C(25)	1.85(2)	1.82(4)	1.81(2)
P(2)—C(32)	1.87(1)	1.87(4)	1.82(3)
P(1)—C(4)	1.86(1)	1.72(4)	1.83(2)
P(1)—C(11)	1.86(2)	1.82(3)	1.89(2)
P(1)—C(18)	1.85(2)	1.95(4)	1.86(2)
P(1)—Pt—P(2)	110.0(1)	109.2(2)	107.3(2)
P(1)—Pt—C(39)	158.2(4)	155.1(6)	154.7(5)
P(1)—Pt—C(1)	100.7(3)	103.4(7)	102.8(4)
P(2)—Pt—C(39)	47.3(4)	46.7(7)	47.5(5)
P(2)—Pt—C(1)	148.3(3)	147.4(7)	149.9(4)
C(1)—Pt—C(39)	101.0(5)	101.0(9)	102.4(6)
Pt—P(2)—C(39)	63.9(4)	66.7(8)	65.3(6)
Pt—C(39)—P(2)	68.8(5)	66.6(9)	67.3(6)

C(1)—Pt—P(2) and C(39)—Pt—P(1) fragments are far from linear, the angles at Pt being  $148.3(3)$  and  $158.2(4)^\circ$ , respectively. On the other hand, if the P(2) hybridization state is closer to  $sp^2$  a decrease of its covalent radius would be expected compared to that of P(1), which is closer to  $sp^3$  hybridization.

It has been shown that *cis*-compounds II, III and IV can be prepared starting from *trans*- [1] or *cis*- $L_2PtCl_2$  [4]. Model inspection suggests that the bulky carboranyl ligand destabilizes the *trans* isomer, mainly because of steric interactions with the phosphine organic substituents.

As far compound I is concerned, model inspection shows that the five-membered ring formation is sterically hindered both in *cis* and *trans* isomers. In fact the *trans* isomer appears to be destabilized in a way similar to that claimed above for II and III, whereas the *cis* configuration appears to be hindered by strong steric interaction between the metallated phenyl group and the carborane ligand.

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