

Synthesis of a Boron Analogue of Co-ordinated Cyclobutadiene; X-Ray Molecular Structures of *closo*- and *nido*- $L_2PtC_2B_6H_6R_2$

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Summary Reaction of *closo*-1,6- R_2 -1,6- $C_2B_6H_6$ ($R = H$ or Me) with $[Pt(\textit{trans}\text{-stilbene})L_2]$ ($L = PEt_3$ or PMe_3) affords *closo*- $[L_2PtC_2B_6H_6R_2]$ and *nido*- $[L_2PtC_2B_6H_6R_2]$ complexes which are structurally characterised by X-ray crystallography.

ZEROVALENT Ni, Pd, and Pt complexes readily undergo a stereoselective insertion reaction with 11- and 9-atom carboranes to give respectively *closo*- or *nido*-metallo-carboranes.^{1,2} In investigating related reactions of Pt^0 species† with the 8-atom *closo*- C_2B_6 carboranes we have found that both *closo*- and *nido*-metallo-carboranes are formed in the same reaction in contrast with the odd-atom systems.

The reaction (room temperature; light petroleum) of $[Pt(\textit{trans}\text{-stilbene})L_2]$ ($L = PMe_3$ or PEt_3) with *closo*-1,6- R_2 -1,6- $C_2B_6H_6$ ($R = H$ or Me) affords two isomeric products $[L_2PtC_2B_6H_6R_2]$, which can be separated by fractional crystallisation. When $L = PMe_3$ and $R = Me$ the major product is (I), which was found to occur in two yellow crystalline forms (α and β). Single-crystal X-ray diffraction studies were carried out on both forms establishing the molecular structure shown (Figure 1).

Crystal data: α -form, $M = 472.25$, monoclinic, space group $A2/a$, $a = 12.002(5)$, $b = 10.415(7)$, $c = 16.559(7)$ Å, $\beta = 102.47(3)^\circ$, $U = 2021(1)$ Å³, $Z = 4$, $D_c = 1.552$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 74.38$ cm⁻¹, $R = 0.07$ for 1162 reflections (Syntex $P2_1$, four-circle diffractometer). β -Form, $M = 472.25$, monoclinic, space group $P2_1/c$, $a = 11.892(4)$, $b = 9.280(4)$, $c = 18.724(8)$ Å, $\beta = 106.17(3)^\circ$, $U = 1984(1)$ Å³, $Z = 4$, $D_c = 1.580$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 76.19$ cm⁻¹, $R = 0.05$ for 2613 reflections. A crystal structure determination was also carried out on the related complex

$[(Me_3P)_2PtC_2B_6H_8]$, which established that it had a similar molecular geometry; $M = 444.19$, monoclinic, space group

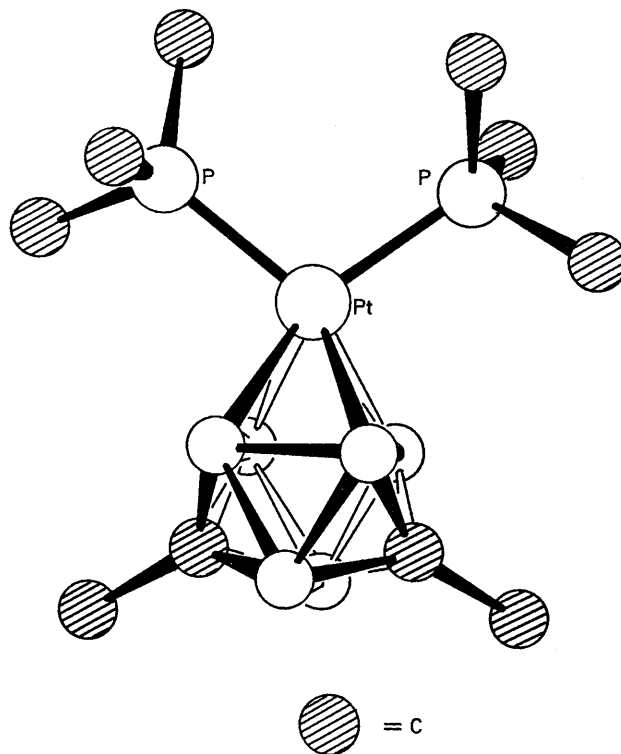


FIGURE 1. *closo*-1,1-(Me_3P)₂-6,8- Me_2 -1,6,8- $PtC_2B_6H_6$.

† Only the more stable *closo*-nickelacarborane could be isolated from the corresponding reaction of Ni^0 species.

$A2$, $a = 5.716(2)$, $b = 9.785(4)$, $c = 15.329(8)$ Å, $\beta = 94.24(3)^\circ$, $U = 885.2(6)$ Å³, $D_c = 1.725$ g cm⁻³, $Z = 2$, C_2 symmetry imposed, R ca. 0.12 for 767 data.

The complexes (I) have C_2 symmetry (a space group requirement for the α -form) and tricapped (Pt and two C atoms) trigonal prismatic polyhedral geometries.† Molecular parameters for the two forms are identical within experimental limits. The Pt–P bonds are 2.31 Å; the Pt–B bonds 2.20–2.25 Å; and the P–Pt–P angle 105°. The complex [(Me₃P)₂PtC₂B₆H₈] differs slightly with Pt–P at 2.42(2) Å, Pt–B bonds of 2.15(6) and 2.24(8) Å, a P–Pt–P angle of 100.3(5)°, and a greater angle between the planes containing the PtP₂ and PtC₂(cage) units [20° compared with 12° for (I)].

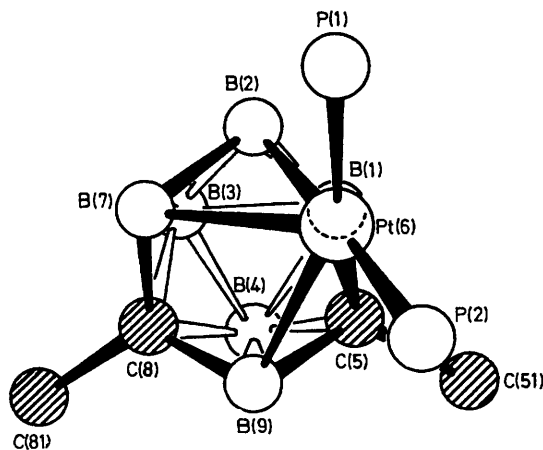


FIGURE 2. *nido*-6,6-(Et₃P)₂-5,8-Me₂-6,5,8-PtC₂B₆H₈.

Within the concept of a metallocarborane as a transition-metal complex containing a π -bonded carborane ligand, the platinacarboranes (I)§ represent a 1—4- η bonded boracyclobutadiene complex. Compared with other metallocarboranes the metal adopts an unusual low co-ordination number. Previously, Muettterties³ has commented on the possibility of preparing complexes of the type [(R₃P)₂PtB₅H₅] containing a π -bonded B₅H₅²⁻ ion (an analogue of cyclobutadiene), and one of the products [η^5 -C₅H₅FeC₂B₆H₈] of the polyhedral expansion reaction of 1,6-C₂B₆H₈ has been tentatively formulated⁴ as a complex in which only two

† The solution n.m.r. spectra of the complexes are consistent with the structure established for the solid state.

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¹ J. L. Spencer, M. Green, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1178; M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, in the press.

² M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 571.

³ E. L. Muettterties, *Pure Appl. Chem.*, 1972, **29**, 585.

⁴ M. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1973, **95**, 4565.

⁵ H. Hart and W. N. Lipscomb, *Inorg. Chem.*, 1968, **7**, 1070; T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *ibid.*, p. 1076.

boron and two carbon atoms bond to the iron atom. However, the complexes (I) provide the first structurally authenticated example of a boracyclobutadiene complex, serving to emphasise further the wide scope of metallocarborane chemistry, and suggesting that B₅H₅ could be a source of related complexes.

An X-ray diffraction study of the minor product (II) of the reaction of [Pt(*trans*-stilbene)(PEt₃)₂] with *closo*-1,6-Me₂-1,6-C₂B₆H₆ established the molecular structure shown (Figure 2).

Crystal data: M , 556.47, orthorhombic, space group $Pbca$, $a = 18.868(8)$, $b = 17.143(7)$, $c = 31.07(2)$ Å, $U = 10050(4)$ Å³, $Z = 16$, $D_c = 1.471$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 60.02$ cm⁻¹, $R = 0.07$ for 4569 reflections.

Thus the orange complex (II) is a *nido*-platinacarborane. Although the geometry still approximates to tricapped trigonal prismatic, in contrast with (I), the metal atom now lies in the prism with a boron atom providing the third cap.‡ The corresponding parameters of the two independent molecules in the asymmetric unit agree within experimental error and mean values are quoted.

There are two short [B(2), 2.19; C(5), 2.19 Å] and three long [B(1), 2.56; B(7), 2.52; B(9), 2.45 Å] bonds between the platinum and cage atoms, and there is a rough correlation that linkages *trans* to the phosphine groups are stronger. The metal-phosphorus distances of Pt–P(1), 2.287 and Pt–P(2), 2.340 Å are normal as are the P–Pt–P angle (99°) and all cage parameters with the exception of the non-bonding contact B(7)–B(9) of 2.48 Å responsible for the molecules formulation as a *nido*-species {cf. the corresponding distance of 2.52(7) Å in *nido*-[(Et₃P)₂PtC₂B₇H₇Me₂]}.²

In considering possible reaction paths for formation of the platinacarboranes [skeletal PtC₂B₆ and PtC₂B₇²] it is interesting to note that the apparent position of nucleophilic attack by Pt⁰ is not as predicted by M.O. calculations,⁵ and that in the species formed the polyhedral carbon atoms have only four cage connectivities.

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