Structural Consequences of Ligand and Metal Substitution in Metallacarbaboranes; the Crystal and Molecular Structures of 3-$[C_2H_4(NMe_2)_2]$3,1,2-$PdC_2B_9H_{11}$ and 3,3-$(PMe_3)_2$-3,1,2-$PdC_2B_9H_{11}$

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Summary The molecular structures of 3-$[C_2H_4(NMe_2)_2]$-3,1,2-$PdC_2B_9H_{11}$ and 3,3-$(PMe_3)_2$-3,1,2-$PdC_2B_9H_{11}$, determined by single-crystal *X*-ray diffraction, reveal a marked structural influence of the ligands *trans* to the $C_2B_9H_{11}$ cage, in that the amino-compound adopts a 'slipped' configuration, whereas when $(PMe_3)_2$ replaces

$C_2H_4(NMe_2)_2$ much more symmetrical metal-cage binding is observed; the phosphine compound also shows unexpected differences from the known and similar platinum derivative 3,3-$(PEt_3)_2$-3,1,2-$PtC_2B_9H_{11}$.

RECENT structural information from *X*-ray data on a series of metallacarbaboranes has illustrated both the general failure of electron-rich metal ions to complete the closed polyhedra predicted from the electron-counting rules (E.C.R.),[1] and the ability of such ions to distort carbaborane cage frameworks.[2,3] These structural anomalies have so far been associated with (i) the electronic configuration of the metal ion, since a progressive metal-cage opening occurs as the electron density on the metal increases,[2] and (ii) the hetero-atom nature of the cage itself, since different distortions occur in d^8 derivatives of 7-$CB_{10}H_{11}^-$, 7,9-$C_2B_9H_{11}^{2-}$, and 7,8-$C_2B_9H_{11}^{2-}$, and these have been rationalised in terms of variations in the metal-cage bonding.[3] It has also been pointed out recently that it is essential in such systems to ensure that 'extra' hydrogen atoms are not present in the cage framework to invalidate the E.C.R.[4]

We now report the preparation and *X*-ray crystal structures of two d^8 palladacarbaboranes, 3-$[C_2H_4(NMe_2)_2]$-3,1,2-$PdC_2B_9H_{11}$ (I), and 3,3-$(PMe_3)_2$-3,1,2-$PdC_2B_9H_{11}$ (II), which reveal for the first time marked structural changes in the MC_2B_9 fragment induced by a third factor, namely the ligands co-ordinated to the metal. These variations in polyhedral geometry are as significant as those produced by a change in metal electron configuration in certain cases.

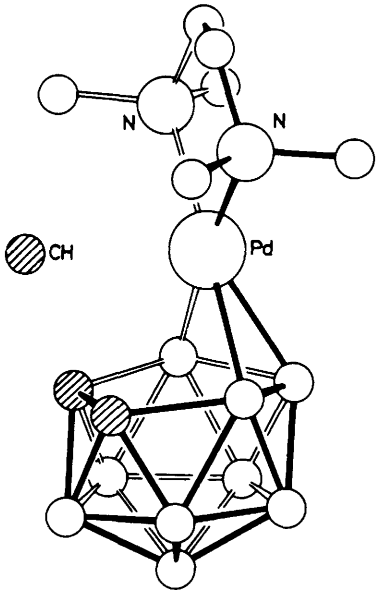

FIGURE 1. Molecular structure of 3-$[C_2H_4(NMe_2)_2]$-3,1,2-$PdC_2B_9H_{11}$ (I). (Hydrogen atoms omitted.)

The molecular structure of the dark green complex (I), prepared by reaction of $C_2H_4(NMe_2)_2PdCl_2$ with $Tl^+[3,1,2\text{-}TlC_2B_9H_{11}]^-$ [5] in CH_2Cl_2 solution, is shown in Figure 1, and that of the deep red compound (II),† prepared by direct displacement of $C_2H_4(NMe_2)_2$ from complex (I) by trimethylphosphine, is shown in Figure 2. Metal-cage distances and dihedral angles for each C_2B_3 face are given in the Table.

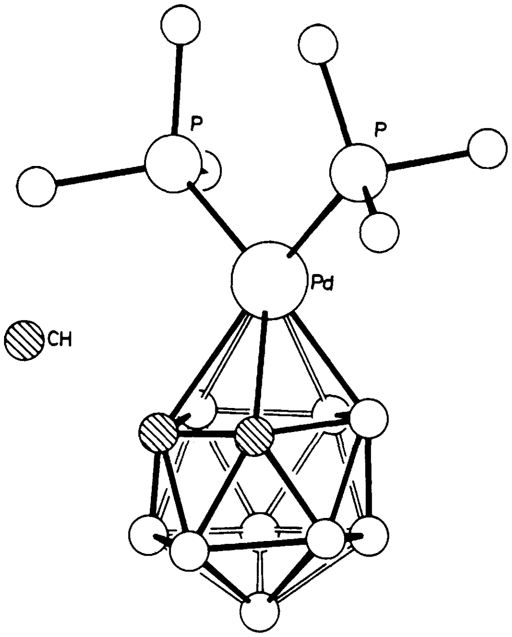

FIGURE 2. Molecular structure of 3,3-$(PMe_3)_2$-3,1,2-$PdC_2B_9H_{11}$ (II). (Hydrogen atoms omitted.)

Crystal data: $[C_2H_4(NMe_2)_2]_2PdC_2B_9H_{11}$ (I); $M = 355{\cdot}0$, monoclinic, space group $P2_1/c$, $a = 8{\cdot}4745(12)$, $b = 12{\cdot}3636(19)$, $c = 16{\cdot}7759(26)$ Å, $\beta = 109{\cdot}14(1)°$, $U = 1660{\cdot}5(4)$ Å^3, $D_c = 1{\cdot}420$ g cm^{-3}, $Z = 4$, μ(Mo-K_α) $= 10{\cdot}86$ cm^{-1}. *R* is currently 0·030 for 2070 independent observed reflections. $(PMe_3)_2PdC_2B_9H_{11}$ (II); $M = 391{\cdot}0$, monoclinic, space group $P2_1/c$; $a = 6{\cdot}7183(10)$, $b = 15{\cdot}5024(18)$, $c = 17{\cdot}9184(24)$ Å, $\beta = 101{\cdot}90(1)°$, $U = 1826{\cdot}1(4)$ Å^3, $D_c = 1{\cdot}422$ g cm^{-3}, $Z = 4$, μ(Mo-K_α) $= 11{\cdot}57$ cm^{-1}. *R* is currently 0·026 for 2214 independent observed reflections.‡

TABLE

	M-B/Å	M-B′/Å	M-C/Å	Dihedral angle C_2B_3/B_3/°
(I)	2·182(6), 2·182(6)	2·202(5)	2·623(4), 2·608(4)	165·5
(II)	2·260(5), 2·249(4)	2·315(5)	2·414(4), 2·492(4)	170·3
$(PEt_3)_2PtC_2B_9H_{11}$ ..	2·277(8), 2·283(8)	2·264(8)	2·530(7), 2·613(7)	171·0

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† Satisfactory analyses have been obtained for these compounds.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Clearly the $Pd(PMe_3)_2$ unit in (II) is bonded much more symmetrically, and with less distortion of the C_2B_9 cage, than is the $Pd[C_2H_4(NMe_2)_2]$ group in (I) so that the difference between Pd–B and Pd–C in (II) is only 0·18 Å compared with 0·43 Å in (I), and a value of 0·0 Å which would be expected in a symmetrically bonded Pd^{IV} (d^6) analogue.

Since $C_2H_4(NMe_2)_2$ is essentially a pure σ-donor, and PMe_3 is normally judged a moderate π-acceptor,[6] these results provide strong support for the idea that π-acceptor ligands reduce the antibonding character, and thus the effect, of the occupied $5e_1(p_y)$–d_{yz}^* orbital, which is both perpendicular to the PdL_2 plane, and responsible, in part, for the deviations from the regular *closo*-geometry observed in many d^8 metallacarbaboranes.[7] The replacement of trimethylphosphine by even stronger π-bonding ligands should therefore give rise to still more symmetrical structures, and indeed the tetraphenylcyclobutadiene complex $3\text{-}Ph_4C_4\text{-}3,1,2\text{-}PdC_2B_9H_9Me_2$ is reported to be a 'symmetrically bonded sandwich,'[8] although full details of the structure have not been published. In this molecule the delocalisation of the $5e_1(p_y)$–d_{yz}^* electrons on to the cyclobutadiene ligand may be so extensive that the complex could be formally regarded as one of (d^6)Pd^{IV} and $Ph_4C_4^{2-}$. Rotation of the PdP_2 plane in (II) by *ca.* 12° relative to the PdB_2 plane is almost certainly a packing effect since the ^1H n.m.r. spectrum ($CDCl_3$ solution) indicates complete equivalence of the phosphine ligands. This rotation, however, readily accounts for the difference in the Pd–C distances (2·41, 2·49 Å), since the carbon atom of the longer bond then lies closer to the plane of the $5e_1(p_y)$–d_{yz}^* orbital.

These results also illustrate surprising differences between structures containing metals with the same electron configuration [Pd^{II}, Pt^{II}, d^8], and similar ligands (*e.g.* PR_3). Although the $C_2B_9H_{11}$ cage in $3,3\text{-}(PEt_3)_2\text{-}3,1,2\text{-}PtC_2B_9H_{11}$[3] is virtually identical with that in (II), the metal-cage interaction in the platinacarbaborane is considerably less symmetrical [(Pt–C, mean) – (Pt–B, mean) = 0·30 Å, see Table] than that in (II) [(Pd–C, mean) – (Pd–B, mean) = 0·18 Å]. Further, if the structures are regarded as 'slipped,' then the 'slip parameter,' defined here as the distance the metal atom is displaced from a symmetrical position with respect to the planar B_4 unit (B5,9,11,12) of the lower pentagonal girdle (B5,6,9,11,12), gives a value of only 0·10 Å for (II) compared with 0·27 Å for the platinum compound. The extent of the slippage of the latter is emphasised by comparison with the value of 0·35 Å obtained for the amine derivative (I). Alternatively, if the 'slip parameter,' Δ, as defined earlier,[3] is used, the corresponding values are 0·26 Å for (II), 0·42 Å (PtC_2B_9 cage) and 0·52 Å (I). Whichever set of figures is considered, the structural consequences of changing the metal in otherwise similar compounds are clear, and appear to imply either that the π-acidity of alkylphosphine ligands decreases as $Pd(C_2B_9H_{11}) >> Pt(C_2B_9H_{11})$, or that *p*–*d* hybridisation (directing electron density away from the cage[3]) is more extensive for palladium than for platinum.

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