X-Ray Crystallographic and Theoretical Studies on 'Slipped' Metallacarboranes

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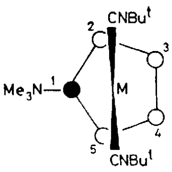
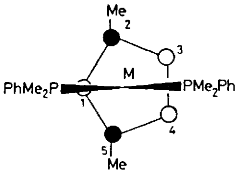
Summary Crystal structure analyses of the icosahedral metallacarborane complexes, skeletal $L_2MC_nB_{11-n}$ (L = R_3P, RNC; M = Pd, Pt; n = 1,2), have shown that the magnitude and direction of the slipped distortion depends on the substituents on the open pentagonal face of the ligand; extended Hückel calculations on model borane complexes have accounted for the observed geometries.

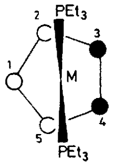
The 'slipped' distortion in the electron rich metallacarboranes $(C_2B_9H_{11})_2M^{n-}$ (M = Ni^{II}, Pd^{II}, Cu^{II} or Au^{II}, n = 2; M = Cu^{III} or Au^{III}, n = 1) was first noted ten years ago.[1] The electronic factors responsible for the 'slipping' are, however, still the subject of some controversy[2,3] and recently it has been suggested that the observed distortions may not result from a translation of the metal atom parallel to the face of the ligand, but rather from a folding of the ligand face co-ordinated to the metal.[3] A better understanding of the precise nature of the 'slipped' distortion and its electronic origins, has been realised from *X*-ray crystallographic studies on the following series of closely related icosahedral metallacarboranes: $(Bu^tNC)_2Pd$-$(1\text{-}NMe_3\cdot CB_{10}H_{10})$ (I), $(PhMe_2P)_2Pt(2,5\text{-}Me_2\cdot C_2B_9H_9)$ (II), and $(Et_3P)_2Pt(3,4\text{-}C_2B_9H_{11})$ (III). These complexes are all derived from a common *nido*-$B_{11}H_{11}{}^{2-}$ icosahedral parent ligand co-ordinated to d^{10} ML_2 fragments (M = Pd or Pt; L = PR_3 or CNR) and are therefore effectively iso-electronic. The complexes differ in the number and positions of the carbon atoms co-ordinated to the metal, as shown below, and therefore provide an opportunity for studying the influence of hetero-atoms on the 'slipped' distortion. *X*-Ray crystallographic details have been reported previously for (I) and (II)[4,5] and the relevant data for (III) are given below.



(I)



(II)

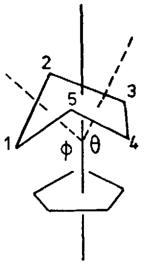


(III)

C● B○

Crystal Data: (III), $C_{14}H_{41}B_9PtP_2$, M = 563·8, monoclinic, space group $P2_1/n$, a = 9·375(4), b = 15·985(3), c = 16·033(7) Å, β = 93·56(5)°, U = 2398(2) Å^3, D_c = 1·561, Z = 4, μ(Mo-K_α) = 6·285 cm^{-1}. Data (6289 > 1·0σ) were recorded at *ca.* 215 K on a Syntex $P2_1$ four-circle diffractometer, and the structure was solved and refined by standard techniques to a current conventional R index of *ca.* 0·05. The molecular structure of (III) closely resembles that reported recently by Wallbridge *et al.*[3] for the isoelectronic gold complex $(Et_2NCS_2)Au(3,4\text{-}C_2B_9H_{11})$.†

The 'slipping' and 'folding' distortions in complexes (I)—(III) have been resolved into the following independent components. The slip of the central atom, Δ, has been defined with respect to the more planar non-bonded pentagonal face of boron atoms, planar within experimental error, with $+\Delta$ representing translation towards, and $-\Delta$ translation away from position 1. The lack of co-planarity of the top ligand face with the lower pentagon is defined by the dihedral angles ϕ and θ.



Table[a]

Complex	Δ	ϕ	θ	M–1[c]	M–2,5[b]	M–3,4[b]
(I)	−0·32	168	176	*2·600(6)*	2·250(7)	2·241(8)
(II)	−0·13	191	185	2·270(9)	*2·447(8)*[c]	2·258(9)
(III)	+0·43	175	175	2·267(10)	2·283(10)	*2·575(9)*[c]

[a] Distances in Å, angles in degrees. [b] Mean values. [c] Bond lengths in italics refer to metal–carbon bond lengths.

The Table summarises the distortion parameters Δ, ϕ, and θ together with some relevant bond lengths for (I) to (III). The 'slip' distortion is much larger in (I) and (III) than in (II), and more interestingly the direction of 'slip' is diametrically opposite in (I) and (III). The 'allylic' distortion shown by (III) is a common structural feature of electron-rich metallacarboranes,[1] but the complementary distortion shown by (I) (which may be described as 'dienylic') has not been noted previously for this type of compound. These crystallographic results therefore demonstrate unambiguously that the magnitude and direction of the 'slip' distortion is dependent on the substituents in the open face of the ligand.

The dihedral angle calculations (Table) indicate that non-planarity of the ligand face arises in each case from a

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

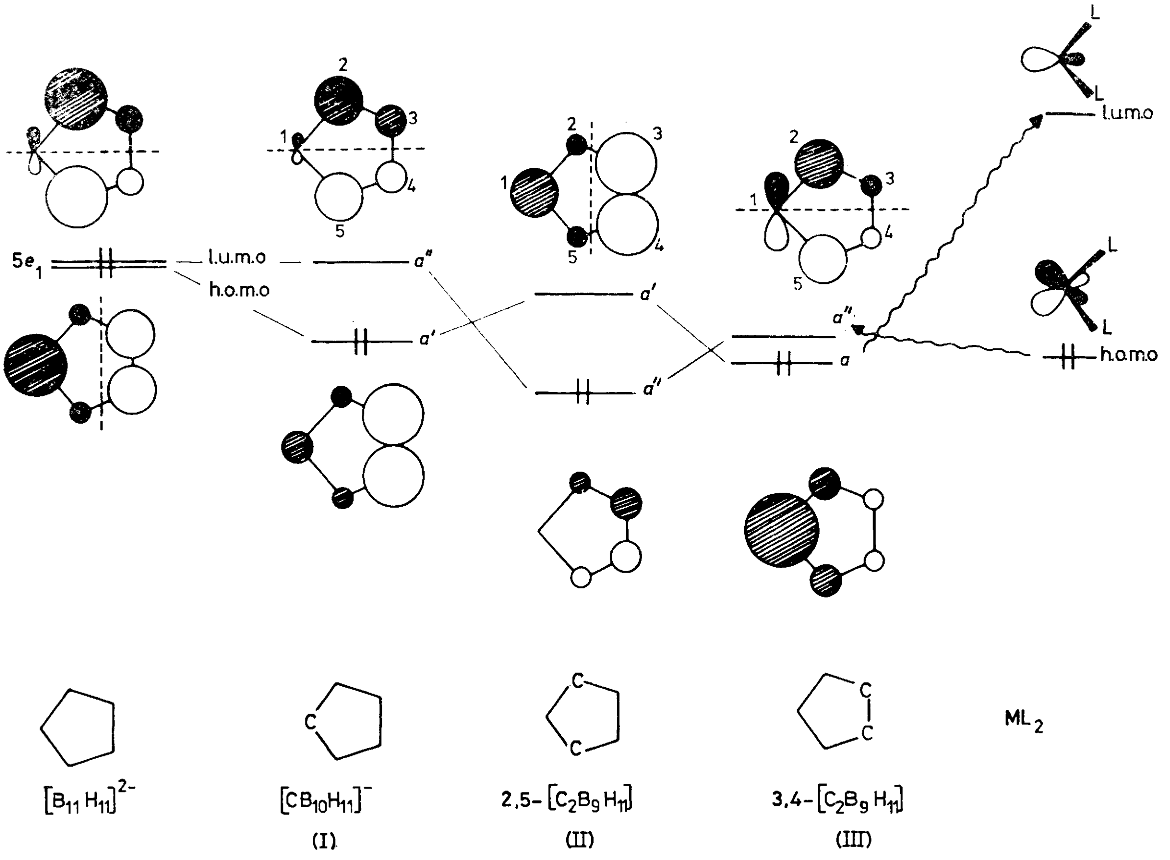

FIGURE. A schematic illustration of the L_2Pt–$C_nB_{11-n}H_{11}$ h.o.m.o.–l.u.m.o. interactions. The metal h.o.m.o. is a metal d_{xz}–p_x hybrid orbital which lies in the PtL_2 plane, and the l.u.m.o. is a s–p_z hybrid orbital. The latter has zero overlap with the $B_{11}H_{11}^{2-}$ $5e_1$ orbitals when $\Delta = 0$.

movement of the carbon atoms away from the metal atom and towards the non-bonded pentagonal face. The direction of 'slipping' in (I) and (II) is the same, although the dihedral angles are quite different. Thus the 'slipping' and 'folding' distortions do not bear a simple geometric relationship.

The electronic factors responsible for the 'slip' distortion in these complexes have been traced using Walsh diagrams based on extended Hückel calculations for $[(H_3P)_2Pt(B_{11}H_{11})]^{2-}$ and related carborane complexes.[6]

These calculations have shown that the equilibrium geometry in these complexes is particularly sensitive to the substituents on the open pentagonal face of ligand and the conformation taken up by the ML_2 fragment with respect to this face [see (I)—(III)]. These differences can be most simply related to the attainment of maximum overlap between the l.u.m.o's and h.o.m.o's of the d^{10} ML_2 fragment and the carborane ligand.[7] The relevant orbitals are illustrated schematically in the Figure.

The conformations of the molecules are decided primarily by the metal h.o.m.o.–ligand l.u.m.o. interactions, which are maximised when the nodal planes of the interacting pair of molecular orbitals are in coincidence, *i.e.* when the ML_2 fragment lies perpendicular to the mirror plane of symmetry in (I) and (III) and parallel to this plane in (II).

For the parent $B_{11}H_{11}^{2-}$ ligand the metal h.o.m.o.–ligand l.u.m.o. overlap is largest when the metal atom lies above the centre of the pentagonal face. This is not the case for the less symmetrical carborane ligands because carbon substitution into the $B_{11}H_{11}^{2-}$ skeleton has the effect of localising the ligand frontier orbitals on to the boron atoms of the open pentagonal face. These localisation effects are represented schematically in the Figure. The metal–ligand h.o.m.o.–l.u.m.o. interactions are increased by a negative 'slip' for the $CB_{10}H_{11}^-$ complex because of the pronounced localisation at the 3 and 4 positions. For 3,4-$C_2B_9H_{11}$ the increased localisation at the 1 position in the h.o.m.o. and the 1,2,5-positions in the l.u.m.o. encourage a positive 'slip'. These arguments therefore account simply for the alternant and significant 'slip' distortions observed for (I) and (III). For (II) a negative 'slip' distortion is indicated by the localisation of the l.u.m.o. at the 3,4 positions, but the magnitude of the distortion is limited by the loss of coincidence of the metal and ligand nodal planes as the distortion proceeds. The localisation of electron density on to the boron atoms in the frontier molecular orbitals also results in the strengthening of the metal–boron bonds at the expense of the metal–carbon bonds and therefore also accounts for the folding distortions described above.

We thank S.R.C. for a Research Studentship awarded to M.I.F. and Dr. J. L. Spencer for crystals of (III).

(*Received, 29th April* 1977; *Com.* 417.)

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