*Journal of Organometallic Chemistry*, 437 (1992) C1–C6
Elsevier Sequoia S.A., Lausanne
JOM 22781PC

Preliminary communication

# Steric and metal-centre control of two-, three- and four-orbital carborane–metal interaction in tin and platinum complexes of the $\{C_2B_8H_9X\}$ ligand, where X = H and Ph *,**

John D. Kennedy [a], Karl Nestor [a], Bohumil Štíbr [b], Mark Thornton-Pett [a] and George S.A. Zammit [a]

[a] *School of Chemistry, University of Leeds, Leeds LS2 9JT (UK)*
[b] *Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 25608 Řež near Prague (Czechoslovakia)*

(Received February 12, 1992)

**Abstract**

The cluster $^{11}B$ and $^{1}H$ NMR properties of the cluster species $[1,1\text{-}Me_2\text{-}1,2,3\text{-}SnC_2B_8H_{10}]$ (compound **1**), $[1,1\text{-}\{P(OMe)_3\}_2\text{-}1,2,3\text{-}PtC_2B_8H_{10}]$ (compound **2**) and $[1,1\text{-}\{P(OMe)_3\}_2\text{-}1,2,3\text{-}PtC_2B_8H_9\text{-}2\text{-}Ph]$ (compound **3**), together with single-crystal X-ray diffraction analyses of the platinum compounds, show that the metal-to-cluster bonding is substantially different for each of these three species, occurring predominantly *via* two, three and four orbitals respectively. The differences between compounds **2** and **3** constitute a rare example of a sterically induced change in metal oxidation state.

The Williams–Wade cluster-geometry electron-counting formalism [1–4] forms the basis of a beautiful structural and electronic rationalisation for much of the complex molecular chemistry based on polyhedral boron-containing clusters [3–6], and has been exceptionally useful in underpinning much of the development of the area over the last twenty years. However, boron-containing polyhedral structural types that are not in accord with this formalism, sometimes grossly so, sometimes more subtly, and which thereby in principle provide a basis for its rational and useful extension, have always been recognised [7]. These exceptions to the formalism have often engendered interesting discussion about their electronic structures, one problem being that analytical *experimental* criteria to discern among any supposed fundamental electronic features that may be associated with structural variations are notoriously hard to come by. As a specific example in this general

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Correspondence to: Dr. J.D. Kennedy.

* Dedicated to Professor Alwyn G. Davies in recognition of his contributions to organometallic chemistry.

** Contribution no. 20 from the Řež–Leeds Anglo–Czech Polyhedral Collaboration (A.C.P.C.).

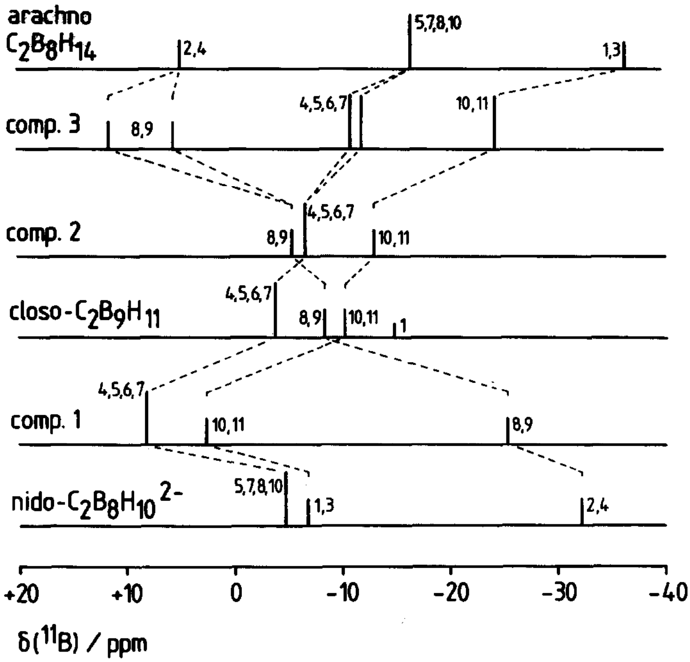

Fig. 1. Stick diagrams of the chemical shifts and relative intensities in the $^{11}$B NMR spectra of (from bottom to top) [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$, [1,1-$Me_2$-1,2,3-$SnC_2B_8H_{10}$] (compound **1**), [*closo*-2,3-$C_2B_9H_{11}$]$^{2-}$, [1,1-{$P(OMe)_3$}$_2$-1,2,3-$PtC_2B_8H_{10}$] (compound **2**), [2-Ph-1,1-{$P(OMe)_3$}$_2$-1,2,3-$PtC_2B_8H_9$] (compound **3**), and [*arachno*-6,9-$C_2B_8H_{14}$]. Dotted lines join equivalent positions.

context we now present preliminary results from structural and NMR experimental work that strongly suggest that no fewer than three distinct electronic structural types can be accommodated by the one basic eleven-vertex {*closo*-1,2,3-$MC_2B_8$} closed polyhedral cluster type.

We have found that reaction of the [*nido*-6-X-6,9-$C_2B_8H_9$]$^-$ anions with $Me_2SnCl_2$ or [$PtCl_2${$P(OMe)_3$}$_2$] gives the complexes [1,1-$Me_2$-1,2,3-$SnC_2B_8H_9X$] (X = H, compound **1**) or [1,1-{$P(OMe)_3$}$_2$-1,2,3-$PtC_2B_8H_9$-2-X] (X = H and Ph, compounds **2** and **3** respectively), all as white solids. The NMR properties [8*] of the tin compound [$Me_2SnC_2B_8H_{10}$] (compound **1**) are very similar to those [9] of the aluminium analogues [1-Et-1-($OEt_2$)-1,2,3-$AlC_2B_8H_{10}$] and [$H_{10}B_8C_2AlC_2B_8H_{10}$]$^-$ that have been structurally characterised [9] as $\mu$-6,9-metallated *nido*-6,9-dicarbaboranes with two-electron two-centre bonds from the metal to each of the 6,9 carbon atoms. This structural description is supported by the similarity of the NMR properties to those [10*] of the free [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ anion itself (Fig. 1, lowest two diagrams). This shows that the *nido* characteristics of the ligand are retained, and thus confirms that the metal interaction with the cluster is a two-orbital one (structure I). Conversely this indicates a quite specific location of an *endo* lone pair at each of the 6 and 9-positions in the free [$C_2B_8H_{10}$]$^{2-}$ ligand.

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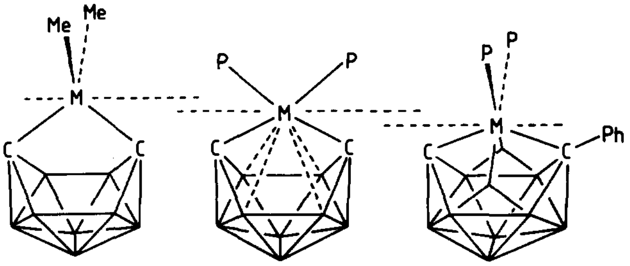
* Reference number with asterisk indicates a note in the list of references.



I II III

The cluster NMR properties of the unsubstituted platinum compound $[\{P(OMe)_3\}_2PtC_2B_8H_{10}]$ (compound **2**) are quite different [13*] to those of **1** and are very similar to those [14*] of the *closo* compound [*closo*-2,3-$C_2B_9H_{11}$] in which the {BH} vertex in the 1-position is held to have a classical three-orbital interaction with the rest of the cluster (Fig. 1, centre two diagrams). Both exhibit a close grouping in the central region of the $^{11}B$ spectrum. This similarity suggests that the metal atom in **2** has a similar three-orbital involvement with the $\{C_2B_8H_{10}\}$ fragment. This conclusion is supported by the results [16*] of a single-crystal X-ray diffraction analysis of this species (Fig. 2), which reveal a closer involvement of the metal atom with the cluster (structure II) than in the structurally characterised [9] aluminium species (with due allowances for difference in metal-atom size). In compound **2** each $P(OMe)_3$ ligand is *trans* to a carbon atom, and eclipses the other one.

By contrast, in the C-phenylated analogue, $[\{P(OMe)_3\}_2PtC_2B_8H_9$-2-Ph] (compound **3**) [16*], the steric effect of the C-phenyl group forces the $\{P(OMe)_3\}_2$ ligand sphere into a position orthogonal to that seen in the unsubstituted species **2** (Fig. 2). This 90° twist is associated with an even more compact association of the platinum atom with the cluster, and a further drastic change in cluster NMR properties [17*] which now closely resemble those [18*] of the unmetallated *arachno* cluster compound [6,9-$C_2B_8H_{14}$]. These factors indicate that the bonding to platinum in compound **3** can be regarded as a direct replacement, in $C_2B_8H_{14}$, of the two bonds to the bridging hydrogen atoms, and the two bonds to the *endo* hydrogen atoms, by four bonds to the platinum centre, so that the metal atom has a four-orbital involvement with the $\{C_2B_8H_9Ph\}$ unit, now with an overall 18-electron octahedral platinum(IV) configuration (structure III).

## Conclusion

In summary, we suggest that the successive changes to the $\{C_2B_8H_{10}\}$ fragment brought about first by replacement of $\{SnMe_2\}$ by $\{Pt[P(OMe)_3]_2\}$ (compound **1** → compound **2**) and secondly by the steric effect of the C-phenyl group in the 2-position (compound **2** → compound **3**) arise from successive changes from a two- to a three-orbital, and a three- to a four-orbital, metal-to-cluster interaction. These changes involve quite remarkable, and quite specific, electronic variation within the constraints of ostensibly very similar geometries for the $\{C_2B_8H_9X\}$ fragment.

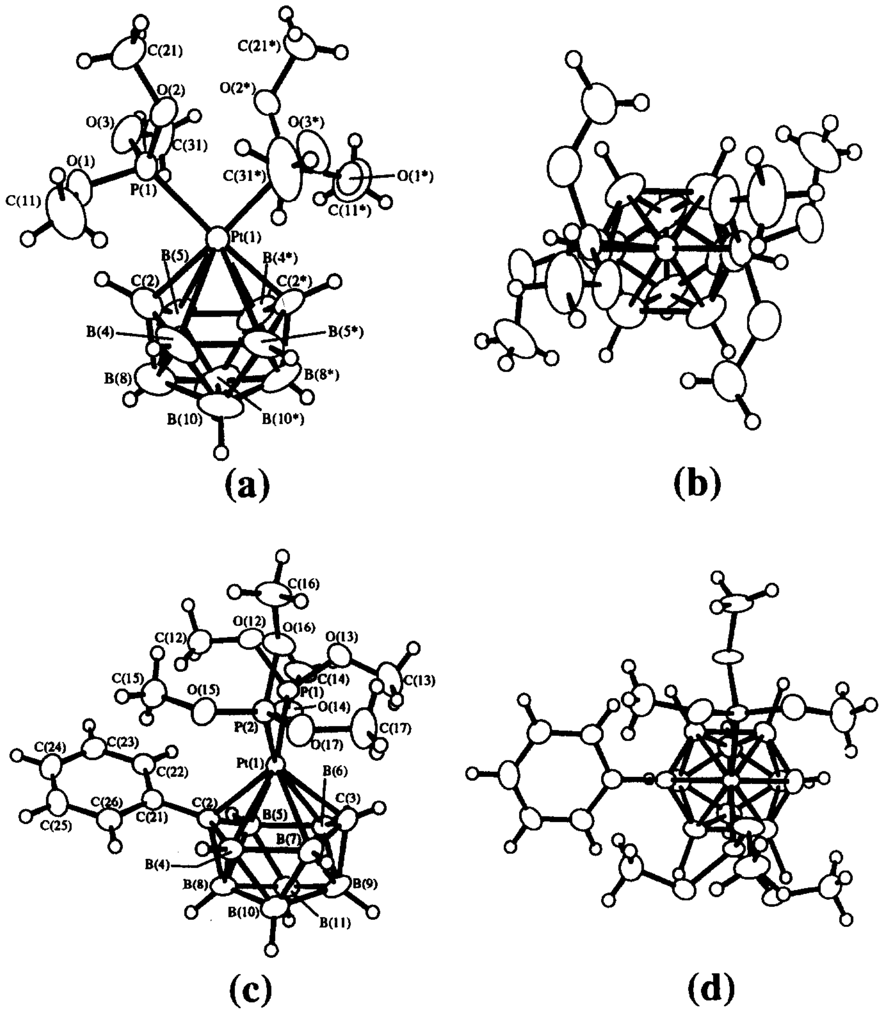


Fig. 2. Crystallographically determined molecular structure of (a) and (b) [1,1-$\{P(OMe)_3\}_2$-1,2,3-$PtC_2B_8H_{10}$] (compound 2) and (c) and (d) [2-Ph-1,1-$\{P(OMe)_3\}_2$-1,2,3-$PtC_2B_8H_9$] (compound 3). Selected interatomic distances for compound 2 are Pt(4)–C(2)C(3)(mean) 213.5(6), Pt–B(4)B(5)B(6)B(7)(mean) 255.2(7), C(2) · · · C(3) 320.7(8), and B(4)–B(7)/B(5)–B(6)(mean) 188.5(11) pm. For compound 3 the corresponding distances are 220.1(5), 239.6(6), 351.7(7) and 196.0(9) pm, and the corresponding distances in [$(OEt_2)(Et)AlC_2B_8H_{10}$] (from data in reference 9, no esd's available) are 203, 251, 309 and 265 pm respectively. The distances of the metal to the B(4)B(5)B(6)B(7) mean plane are 196.8(2), 175.9(2) and 190 pm respectively for compounds **2**, **3** and the aluminium species. C(2)–Pt(1)–C(3) is 97.4(3) and 106.1(3)° for compounds **2** and **3** respectively.

The differences between compounds **2** (X = H) and **3** (X = Ph) also show a quite remarkable sterically induced change in effective oxidation state.

**Acknowledgements.** We thank the SERC, the Czechoslovak Academy of Sciences (Grant no. 43204), the Royal Society, and Borax Research Ltd for support, and Drs. Scott Griffin and Dana Wagnerová for helpful cooperation.

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8 Cluster $^{11}B$ and $^{1}H$ NMR properties for compound **1** (this work, 294–297 K), and $^{11}B$ NMR properties for $[Et(OEt_2)AlC_2B_8H_{10}]$ and $[H_{10}B_8C_2AlC_2B_8H_{10}]^-$ (ambient temperature; values from reference 9, assignments by comparison with compound **1**) ordered as: (assignment) $\delta(^{11}B)$/ppm [$\delta(^{1}H)$/ppm in square brackets when measured]. Compound **1** ($CD_2Cl_2$ solution): (4,5,6,7) +8.1 [+3.30], (8,9) −25.5 [+1.59], (10,11) +2.5 [+2.89], (2,3)(CH) – [+4.61], (1) ($SnMe_2$) – [+0.92 {$^{2}J(^{119}Sn-^{1}H)$ 65.7 Hz}]. $[Et(OEt_2)AlC_2B_8H_{10}]$ ($C_6D_6$ solution): (4,5,6,7) +2.9, (8,9) −25.3, (10,11) +4.3, (2,3)(CH) – [+4.69]. $[H_{10}B_8C_2AlC_2B_8H_{10}]^-$ ($CD_2Cl_2$ solution): (4,5,6,7) +2.7, (8,9) −28.7, (10,11) +0.9 [numbering as for compounds **2** and **3** for convenience of comparison].

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10 Cluster $^{11}B$ and $^{1}H$ NMR properties for [*nido*-6,9-$C_2B_8H_{10}]^{2-}$ (taken from references 11 and 12, $CD_3CN$ solution, 294–297 K) ordered as for compound **1**. (5,7,8,10) −4.7 [+2.09], (1,3) −6.9 [+1.88], (2,4) −32.2 [−0.07], (6,9)(CH) – [+4.6] (Note there is change in numbering from 10-vertex *nido* to 11-vertex *closo* upon metal complexation – see Fig. 1).

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13 Cluster $^{11}B$ and $^{1}H$ NMR properties for compound **2** (this work, $CD_2Cl_2$ solution, 294–297 K) ordered as for compound **1**. (4,5,6,7) −6.8 [+1.88], (8,9) −5.4 [+3.45, $^{3}J(^{195}Pt-^{1}H)$ *ca.* 65 Hz], (10,11) −13.2 [+0.83], (2,3)(CH) – [+4.71], (1) ($P[OMe]_3$) – [+3.70 {$\delta$ $^{31}P$ +91.0, $^{1}J(^{195}Pt-^{31}P)$ 5508 Hz}].

14 Cluster $^{11}B$ and $^{1}H$ NMR properties for [*closo*-2,3-$C_2B_9H_{11}$] (taken from references 12 and 15, $CD_2Cl_2$ solution, 294–297 K ordered as for compound **1**. (1) −15.2 [+1.12], (4,5,6,7) −4.0 [+2.78], (8,9) −8.5 [+2.08], (10,11) −10.3 [+2.38], (2,3)(CH) – [+5.94].

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16 Crystal data for compound **2**. $C_8H_{28}B_8O_6P_2Pt$, $M = 563.82$, monoclinic, $a = 1330.9(2)$, $b = 1093.6(1)$, $c = 1516.5(1)$ pm, $\beta = 107.81(1)°$, $U = 2.0996(4)$ nm$^{-3}$, space group $C2/c$, $Z = 4$, $D_c = 1.78$ g cm$^{-3}$, $\mu = 69.21$ cm$^{-1}$, $F(000) = 991.94$, $R$ ($R_w$) = 0.0194 (0.0261) for the refinement of 1719 unique reflections with $F_o > 4.0\sigma(F_o)$ and $4.0 < 2\theta < 50.0°$. Crystal data for compound **3**. $C_{14}H_{32}B_8O_6P_2Pt$, $M = 639.92$, monoclinic, $a = 1054.5(2)$, $b = 1739.9(3)$, $c = 1315.9(2)$ pm, $\beta = 93.81(1)°$, $U = 2.4090(7)$ nm$^{-3}$, space group $P2_1/n$, $Z = 4$, $D_c = 1.76$ g cm$^{-3}$, $\mu = 57.34$ cm$^{-1}$, $F(000) = 1247.94$, $R$ ($R_w$) = 0.0295 (0.0394) for the refinement of 3671 unique reflections with $F_o > 4.0\sigma(F_o)$ and $4.0 < 2\theta < 50.0°$. All measurements were made on a Stoe STADI4 diffractometer using $\omega/\theta$ scans and graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda = 71.069$ pm). Both data-sets were corrected for absorption using azimuthal psi-scans. Both structures were solved using standard heavy-atom methods and were refined by full-matrix least-squares using SHELX76. Refinement was the same for both complexes. All non-hydrogen atoms were refined with anisotropic thermal parameters; the phenyl group of compound **3** was treated as a rigid body with idealised hexagonal symmetry (C–C = 139.5 pm). Methyl and phenyl (for compound **3**) hydrogen atoms were included in calculated positions (C–H = 96 pm) and were refined with an overall isotropic thermal parameter. Cluster-associated hydrogen atoms were located on difference maps and were freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$ was used in both cases. Tables of atomic coordinates and interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre.

17 Cluster $^{11}B$ and $^{1}H$ NMR properties for compound **3** (this work, $CDCl_3$ solution, 294–297 K) ordered as for compound **1**. (4,5) and (6,7) −12.2 [+1.99] and −13.3 [+1.55], (8) and (9) +5.4

[+3.95] and +11.4 [+4.09], (10,11) −24.4 [−0.52], (3)(CH) − [+5.20], (P[OMe]$_3$) − [+3.50 {$\delta$ $^{31}$P +95.8, $^1J$($^{195}$Pt–$^{31}$P) 5674 Hz}].

18 Cluster $^{11}$B and $^1$H NMR properties for [*arachno*-6,9-$C_2B_8H_{14}$] (taken from references 19 and 20, $CDCl_3$ solution, 294–297 K) ordered as for compound **1**. (5,7,8,10) −16.4 [+2.27], (2,4) +4.8 [+2.90], (1,3) −36.6 [+0.93], (6,9)(CH) − [+0.86 (*exo*), −0.67 (*endo*)], [$\delta$ ($^1$H) for $\mu$-H(4,7)/H(5,6) −2.85 (Note there is a change in numbering upon metal complexation as for [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ above).

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