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Effects of metal-centre orbital control on cluster character and electron distribution between borane and hydrocarbon ligands; significance of the structures of [μ-9,10-(SMe)-8,8-$(PPh_3)_2$-*nido*-8,7-$IrSB_9H_9$] and [μ-9,10-(SMe)-8-(η^4-C_5Me_5H)-*nido*-8,7-$RhSB_9H_9$]

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In [μ-9,10-(SMe)-8-(η^4-C_5Me_5H)-*nido*-8,7-$RhSB_9H_9$] the non-borane ligand has been found to prefer {η^4-C_5Me_5H} rather than {η^5-C_5Me_5} character, demonstrating factors behind (*a*) metallaborane core cluster control of exopolyhedral ligand-to-metal co-ordination modes, and (*b*) the stability of sixteen-electron transition-element centres that engender stable formally 'low' cluster-electron counts.

There is current interest in polyhedral boron-containing cluster compounds that deviate[1] from the dictates of the classical[2,3] Williams–Wade cluster geometry–electron-counting formalism or which exhibit other unusual cluster behaviour. In this general context there have recently been reports of (*a*) the unusual incidence of a tetrahapto η^4-C_5Me_5H ligand in [1-(η^5-C_5Me_5)-2-(η^4-C_5Me_5H)-*nido*-1,2-$Co_2B_3H_8$], which is suggested to be sterically driven to form this bidentate η^4 type of co-ordination rather than the η^5-C_5Me_5 ligand generally found in metallaborane chemistry,[4] and (*b*) unusual hydrogen-to-metal agostic interactions in [8-(η^2-$Ph_2PCH_2CH_2Ph_2$)-*nido*-8,7-$RhSB_9H_{10}$] which are proposed[5] in order to convert what can be regarded as a formal Wadian *closo* electron count into a *nido* one that would be perhaps interpretable as more consistent with the conventional eleven-vertex *nido* cluster structure. We now report preliminary results from two compounds that together generate additional significant perspective on these two interesting behavioural modes.

Reaction of essentially equimolar amounts (reaction scale 80 μmol) of μ-(MeS)SB_9H_{10}[6] **1** (schematic structure **I**) with [$IrCl(PPh_3)_3$] and *N*,*N*,*N′*,*N′*-tetramethylnaphthalene-1,8-diamine (tmnda) in CH_2Cl_2 at room temperature for 30 min, followed by chromatographic separation (TLC, silica gel G, CH_2Cl_2–C_6H_{14} 1 : 1), resulted in the isolation of red air-stable [μ-9,10-(SMe)-8,8-$(PPh_3)_2$-*nido*-8,7-$IrSB_9H_9$] **2** (R_f 0.34; 58%; schematic structure **II**), characterised by single-crystal X-ray diffraction analysis† (Fig. 1, upper) and NMR spectroscopy.‡ The compound has a *nido*-shaped eleven-vertex {$IrSB_9$} cluster, but has associated with it[5] a formally *closo* Wadian[3] eleven-vertex electron count if the metal centre is regarded as formally square-planar iridium(I).

An essentially equivalent procedure (reaction scale 250 μmol), but using [{Rh(η^5-C_5Me_5)Cl_2}$_2$] with **1** and tmnda, resulted in the isolation of yellow air-stable [μ-9,10-(SMe)-8-(η^4-C_5Me_5H)-*nido*-8,7-$RhSB_9H_9$] **3** (R_f 0.59; 21%; schematic structure **III**), also characterised by single-crystal X-ray diffraction analysis† (Fig. 1, lower) and NMR spectroscopy.‡ This has a tetrahapto bidentate pentamethylcyclopentadiene ligand, η^4-C_5Me_5H,

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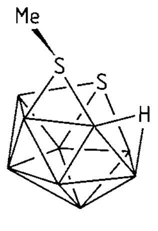
† Crystals of compounds **2** and **3** were both grown by diffusion of hexane into solutions of them in CH_2Cl_2. Data for **2** were collected at 200 K on a Stoe STADI4 diffractometer operating in the ω–θ scan mode, those for **3** at 160 K on a Siemens SMART CCD area-detector diffractometer with narrow ω-rotation frames. In both cases Mo-Kα radiation (λ = 0.710 73 Å) was used. The structures were solved by heavy-atom methods using SHELXS 86[7] and refined by full-matrix least squares (against all the unique F^2 data) using SHELXL 93.[8] Non-hydrogen atoms were refined with anisotropic displacement parameters. Restraints were applied to the phenyl rings of **2** such that they remained flat with overall C_{2v} symmetry. In both cases the hydrogen atoms associated with the ligands were constrained to idealised positions, whereas those associated with the cluster [including that with the mixed-atom site B/S(4) in **3** (see below)] were located on Fourier-difference maps and freely refined. Compound **2**, $C_{37}H_{42}B_9IrP_2S_2$, $M_r = 902.26$, crystal dimensions 0.38 × 0.28 × 0.14 mm, triclinic, space group $P1$, $a = 9.7888(11)$, $b = 11.1211(12)$, $c = 18.455(3)$ Å, $\alpha = 85.471(3)$, $\beta = 77.651(8)$, $\gamma = 79.813(8)°$, $Z = 2$, $U = 1929.9(4)$ Å^3, $D_c = 1.553$ g cm^{-3}; 8345 reflections were collected to $\theta = 25.0°$; 6793 unique reflections ($R_{int} = 0.0505$) were used in calculations after Lorentz-polarisation and absorption corrections ($\mu = 3.679$ mm^{-1}; azimuthal ψ scans, transmission factors 0.356–0.744). Final $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{\frac{1}{2}} = 0.0779$, conventional $R = 0.0318$ for F values of 5624 reflections with $F_o^2 > 2\sigma(F_o^2)$; $w = 1/[\sigma^2(F_o^2) + 0.0504P^2]$ where $P = (F_o^2 + 2F_o^2)/3$, goodness of fit = 1.020 for all F^2 values and 493 parameters. Maximum and minimum residual electron density 1.10 and −1.86 e Å^{-3} respectively. Compound **3**, $C_{11}H_{28}B_9RhS_2$, $M_r = 424.71$, crystal dimensions 0.42 × 0.40 × 0.08 mm, monoclinic, space group $P2_1/c$, $a = 14.4790(2)$, $b = 10.1752(2)$, $c = 14.9360(2)$ Å, $\beta = 114.936(1)°$, $Z = 4$, $U = 1868.24(5)$ Å^3, $D_c = 1.51$ g cm^{-3}; 11 398 reflections were collected to $\theta = 28.51°$ of which 4280 ($R_{int} = 0.0356$) were used in calculations after Lorentz-polarisation and absorption corrections ($\mu = 1.020$ mm^{-1}; based on repeated and equivalent data, transmission factors 0.741–0.794). The cluster was disordered across two positions related by a pseudo-mirror plane passing through atoms Rh(8), C(1) and C(6), and the midpoint of the C(3)–C(4) bond vector of the pentamethylcyclopentadiene ligand. It is disordered in a 9 : 1 ratio over two positions for which there are three types of atom: (*i*) Rh(8), B(3), B(10) and B(6) (labelling refers to highest-occupancy molecule) lie on the plane and are common to both molecules, (*ii*) B(1), B(4) and B(5) are related to B(2), S(7), B(11) respectively and interchange when going from the major- to minor-occupancy molecule and (*iii*) B(9) and S(91) which are unique to the major-occupancy molecule and are related to B(9′) and S(91′) of the minor-occupancy molecule. Atoms B(4) and S(7) were refined as mixed-occupancy atoms (9 : 1 B : S for the former and 9 : 1 S : B for the latter) and 'soft' rigid-bond and similarity restraints were applied to the displacement parameters of B(9), B(9′), S(91) and S(91′). Final $wR2 = 0.0694$, conventional $R = 0.0268$ for F values of 3765 reflections with $F_o^2 > 2\,\sigma(F_o^2)$; $w = 1/[\sigma^2(F_o^2) + 0.0321P^2 + 1.205P]$, with P as for **2**, goodness of fit = 1.098 for all F^2 values and 269 parameters. Maximum and minimum residual electron density 0.48 and −0.81 e Å^{-3} respectively. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/328.



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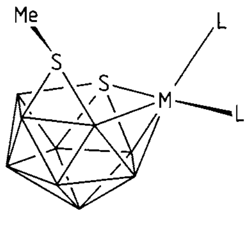

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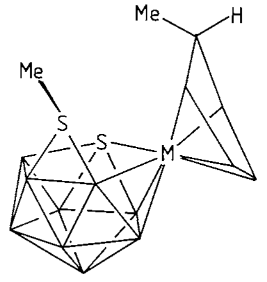

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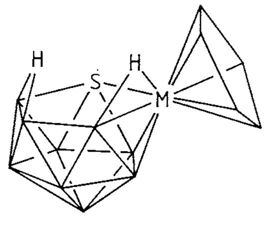

IV

which would complete a sixteen-electron square-planar rhodium(I) bonding sphere in the same manner as the two monodentate PPh_3 ligands would complete a formal iridium(I) bonding sphere in compound **2**. Hydrogen is incorporated into the $\{RhC_5Me_5\}$ unit with the generation of an approximation of rhodium(I) square-planar character, and a concomitant generation of *arachno*, rather than pyramidal *nido*, six-vertex cluster character for the $\{RhC_5\}$ unit. This contrasts to the several previously characterised *nido*-structured $\{MSB_9\}$ cluster compounds of general formulation [8-(arene)-*nido*-8,7-MSB_9H_{11}] [$\{$(arene)M$\}$ = $\{(\eta^6\text{-}C_6H_5Me)Fe\}$ **4a**, $\{(\eta^5\text{-}C_5Me_5)Co\}$ **4b**, $\{(\eta^5\text{-}C_5Me_5)Rh\}$ **4c** or $\{(\eta^5\text{-}C_5Me_5)Ir\}$ **4d**; schematic cluster configuration **IV**],[10–12] which retain pyramidal *nido* character in the $\{$(arene)M$\}$ unit and formally octahedral metal character. Significantly, the generation of the $\{\eta^4\text{-}C_5Me_5H\}$ unit in **3** effectively occurs in preference to an incorporation of hydrogen that would engender unambiguous rhodium(III) octahedral character and generate a formal *nido* electron count for the $\{RhSB_9\}$ unit that would then be consistent with its *nido* eleven-vertex cluster shape. That the $\{Rh(\eta^4\text{-}C_5Me_5H)\}$ unit also occurs in preference to the retention of the stable *nido* six-vertex $\{Rh(\eta^5\text{-}C_5Me_5)\}$ pyramidal unit is also noteworthy. The origins of this different behaviour of **3** compared to the set of compounds **4a**–**4d** presumably derive from the lack of mobility of the bridging SMe group in **3** compared to a relative lability of the bridging hydrogen system in **4a**–**4d**.

This interesting preference for $\{\eta^4\text{-}C_5Me_5H\}$ bidentate behaviour has two general connotations. (*a*) In [1-$(\eta^5\text{-}C_5Me_5)$-2-$(\eta^4\text{-}C_5Me_5H)$-*nido*-1,2-$Co_2B_3H_8$] an *arachno* six-vertex $\{Co(\eta^4\text{-}C_5Me_5H)\}$ subcluster is similarly adopted in preference to an *arachno* five-vertex $\{Co_2B_3H_9\}$ one. Here, it has been suggested that the η^4-$\{C_5Me_5H\}$ mode may be sterically enforced by the proximity of the two bulky $\{Co(C_5Me_5)\}$-based units, rather than by the electronic requirements of the cluster core.[4] By contrast, the η^4 mode observed here for compound **3**, in which there is no steric conflict, demonstrates that control by the electronic dictates of the metallaborane cluster core is also feasible. (*b*) For [8-$(\eta^2\text{-}Ph_2PCH_2CH_2PPh_2)$-*nido*-8,7-$RhSB_9H_{10}$], long-range interactions involving PPh hydrogen atoms and the otherwise sixteen-electron transition-element centre are invoked to propose an eighteen-electron centre and thence a 'correct' 26-electron *nido* eleven-vertex cluster-electron count.[5] In **3**, by contrast, the *nido*-shaped eleven-vertex $\{RhSB_9\}$ cluster effectively rejects the hydride moiety that would enable it to gain a 'correct' 26-electron *nido* count. There is no real evidence for any significant interaction between the rhodium centre and the hydrogen atoms of the $\{\eta^4\text{-}C_5Me_5H\}$ ligand, the two closest

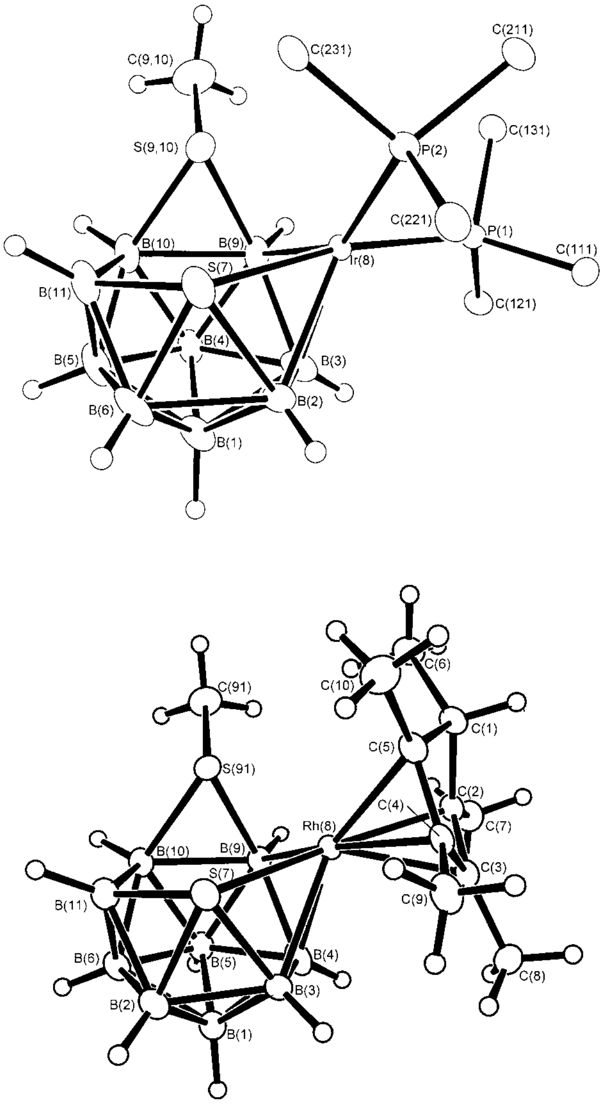

Fig. 1 The ORTEP-type diagrams[9] for the crystallographically determined molecular structures of compounds **2** (upper) and the major component (see footnote †) of **3** (lower). Ellipsoids are drawn at the 40% probability level with hydrogen atoms as circles of a small arbitrary radius. For **2** all phenyl atoms other than the *ipso*-carbons have been omitted for clairty. Selected interatomic distances (Å): for **2**, Ir(8)–P(1) 2.2916(13), Ir(8)–P(2) 2.3895(12), Ir(8)–S(7) 2.3902(14), Ir(8) · · · S(9,10) 2.6367(14), Ir(8)–B(2) 2.260(5), Ir(8)–B(3) 2.282(5), Ir(8)–B(9) 2.248(6), S(9,10)–B(9) 2.005(7), S(9,10)–B(10) 1.997(6), S(7)–B(2) 2.064(6), S(7)–B(6) 1.981(6), S(7)–B(11) 1.912(6), B(9)–B(10) 1.968(9) and B(10)–B(11) 1.912(9): for **3**, Rh(8) · · · C(1) 2.736(2), Rh(8)–C(2) 2.186(2), Rh(8)–C(3) 2.142(2), Rh(8)–C(4) 2.166(2), Rh(8)–C(5) 2.260(2), Rh(8)–B(3) 2.298(3), Rh(8)–B(4) 2.337(2), Rh(8)–S(7) 2.4107(6), Rh(8)–B(9) 2.254(3), Rh(8) · · · S(9,10) 2.4852(6), B(9)–S(9,10) 1.999(3), B(10)–S(9,10) 2.002(3), B(9)–B(10) 1.978(5) and B(10)–B(11) 1.940(4). For each of **2** and **3** there is little difference among the various metal-to-boron distances, emphasising the ambiguities of bonding interpretation and, in particular, the limitations of bonding models that involve or otherwise imply simplistic square-planar or octahedral models for transition-element centres

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‡ Cluster BH NMR data ($CDCl_3$, 294–297 K), ordered as $\delta(^{11}B)$ (relative to $BF_3{\cdot}OEt_2$) [$\delta(^1H)$ of directly attached hydrogen atom]: for **2**, +11.8 [+5.12], +6.2 [+3.39], +6.0 [+1.89], +3.6 [+2.93], −1.6 [+2.77], −5.8 [+2.97], −10.9 [+2.48], −20.2 [+2.03] and −31.2 [+1.32]; also $\delta(^1H)$ +2.41 (SMe) and $\delta(^{31}P)$ +20.8 and +11.2 [$^2J(^{31}P\text{–}^{31}P)$ 26.3 Hz]; for **3**, +16.5 [+2.53], +12.2 [+3.82], +10.4 [+2.88], +4.2 [+3.70], −2.3 [+2.06], −5.6 [+2.75], *ca.* −13.7 [+2.10], *ca.* −13.7 [+2.43] and −29.5 [+0.90]; also $\delta(^1H)$ +2.54 (3 H, SMe), +3.09 (1 H, br), +2.20 [3 H, d, $^3J(^1H\text{–}^1H)$ 1.6 Hz], +1.97 (3 H), +1.71 (3 H) and +1.31 (6 H) (accidental coincidence of two sets of C_5Me_5H methyl-proton resonances).

contacts being *ca*. 3.1 and *ca*. 3.4 Å, somewhat longer than distances to the closest borane-cluster hydrogen atoms on B(9), B(10) and B(11) which are in the range 2.90(3)–2.93(3) Å. There is, however, an increasingly closer approach of the methylated sulfur atom to the metal centre when **2** and **3** are compared [2.6367(14) and 2.4852(6) Å respectively] indicating an incipient twelve- rather than eleven-vertex *nido* cluster character.

Acknowledgements

Paper no. 59 from the Řež-Leeds Anglo-Czech Polyhedral Collaboration (ACPC). We thank the Government of the Basque Country, the EPSRC (UK), the Academy of Sciences of the Czech Republic, the Czech Grant Agency and the Royal Society (London) for support, and Professor Pascual Román of the University of the Basque Country, Bilbao, for his good offices.

References

1 See, for example, J. D. Kennedy and B. Štíbr, in *Current Topics in the Chemistry of Boron*, ed. G. W. Kabalka, Royal Society of Chemistry, Cambridge, 1994, pp. 285–292 and refs. therein.
2 R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 67.
3 K. Wade, *Chem. Commun.*, 1971, 792; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.
4 Y. Nishihara, K. J. Deck, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, 1993, **115**, 12224.
5 K. J. Adams, T. D. McGrath and A. J. Welch, *Acta Crystallogr., Sect. C*, 1995, **51**, 401.
6 J. Holub, A. E. Wille, B. Štíbr, P. J. Carroll and L. G. Sneddon, *Inorg. Chem.*, 1994, **33**, 4920.
7 G. M. Sheldrick, *Acta Crystallogr., Sect A.*, 1990, **46**, 467.
8 G. M. Sheldrick, SHELXL 93, Program for refinement of crystal structures, University of Göttingen, 1993.
9 P. McArdle, *J. Appl. Crystallogr.*, 1995, **28**, 65.
10 S.-O. Kang, P. J. Carroll and L. G. Sneddon, *Organometallics*, 1988, **7**, 772.
11 S.-O. Kang, P. J. Carroll and L. G. Sneddon, *Inorg. Chem.*, 1989, **28**, 96.
12 K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1991, 2657.

Received 28*th October* 1996; *Communication* 6/07342E