Eleven- and Twelve-vertex Polyhedral Metalladithiaborane Chemistry. Novel Compounds from the *arachno*-$[S_2B_9H_{10}]^-$ Anion: $[(PPh_3)_3H_2IrS_2B_9H_{10}]$, $[(PPh_3)_2HIrS_2B_9H_9]$ and $[(PPh_3)_2HRhS_2B_8H_8]$

Ramón Macías,[a] Josef Holub,[a,b] John D. Kennedy,[a] Bohumil Štíbr[a,b] and Mark Thornton-Pett[a]

[a] *School of Chemistry, University of Leeds, Leeds, UK LS2 9JT*
[b] *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 25068 Řež, near Prague, Czech Republic*

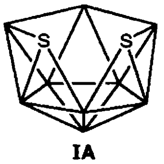
Reaction of the *arachno*-$[S_2B_9H_{10}]^-$ anion with $[IrCl(PPh_3)_3]$ yields (*a*) $[(PPh_3)_3H_2IrS_2B_9H_{10}]$, in which cluster–metal interaction occurs solely *via* heteroatom η^1 two-electron, two-centre, cluster-to-metal donation, and (*b*) $[(PPh_3)_2HIrS_2B_9H_9]$, which has a contiguous *nido*-type twelve-vertex cluster structure with η^5 cluster-to-metal donation, whereas reaction with $[RhCl(PPh_3)_3]$ results in one-atom cluster dismantlings to give *nido*-type eleven-vertex (*c*) $[(PPh_3)_2HRhS_2B_8H_8]$ and (*d*) $[(PPh_3)_2RhSB_9H_{10}]$, both with η^4 cluster-to-metal donation.

The chemistry of the dicarbaboranes[1] well exceeds that of the boranes themselves. Their metal complexes,[2] especially the twelve-vertex metalladicarbaboranes, are very well studied, and are often taken as the exemplars of polyhedral boron-containing chemistry. By comparison, the chemistry of other main-group polyhedral diheteroboranes is very limited, the best represented being that of the dithiaboranes. However, until very recently, only three dithiaborane building blocks were known: the eight-vertex *hypho* $\{S_2B_6\}$ system,[3] the nine-vertex *arachno* $\{S_2B_7\}$ system,[3,4] and the eleven-vertex *nido* $\{S_2B_9\}$ system.[5] Examples of $\{S_2B_8\}$ systems are not known. The known systems are now augmented by the eleven-vertex *arachno* system based on the $[S_2B_9H_{10}]^-$ anion **1** (schematic cluster structure **IA**).[6] This is readily accessible in high yield from the well-known[7–11] neutral precursor *nido*-SB_9H_{11} by treatment with base and elemental sulfur.[6] Its accessibility permits a ready assessment of its metal chemistry to compare with the well-examined metalladicarbaboranes. Here we report interesting preliminary results in this area.

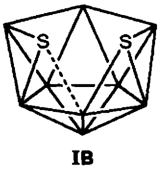
Reaction of $[IrCl(PPh_3)_3]$ with the *arachno*-$[S_2B_9H_{10}]^-$ anion **1** [tmndH$^+$ (proton sponge) salt] in CH_2Cl_2 at room temperatures for 7 h, followed by chromatographic separation (dichloromethane–hexane on silica G), yields two pale-yellow crystalline air-stable products, characterised by X-ray diffraction analysis[†] and NMR spectroscopy.[‡] The first, $[(PPh_3)_3H_2IrS_2B_9H_{10}]$ **2** (Fig. 1, Schematic **II**, 21% yield) exhibits simple heteroatom η^1 two-electron two-centre ligand-to-metal donation that is unsupported by additional metal bonding to the cluster: this has often previously been entertained for a cluster atom in a heteroborane, but never observed.[12] Interesting also in **2** is the partial opening of the $\{S_2B_9H_{10}\}$ cluster (hatched lines in **IB**): here there is an effective competition between the metal centre and the rest of the cluster for the sulfur atom that is coordinated to the metal atom. By contrast, the second product, $[(PPh_3)_2H\ IrS_2B_9H_9]$ **3**, Schematic **III**, 22% yield) has a twelve-vertex contiguous *nido* cluster, isostructural with that previously reported[5] for $[(C_5H_5)CoSe_2B_9H_9]$ **4**. In contrast to fluxional **4**, the iridium compound **3** is static in solution at room temperature.

In contrast to the $[IrCl(PPh_3)_3]$ reaction, the corresponding reaction of **1** with $[RhCl(PPh_3)_3]$ (CH_2Cl_2, *ca.* 294 K, *ca.* 7 h) yields, after chromatography (benzene on silica G), known[13] $[(PPh_3)_2RhSB_9H_{10}]$ **5** (Schematic **IV**, 10% yield) and orange crystalline air-stable $[(PPh_3)_2HRhS_2B_8H_8]$ **6** (Fig. 2 and schematic **V**, 15% yield), characterised by X-ray diffraction analysis[†] and NMR spectroscopy.[§] The known $\{MSB_9\}$ cluster of **5** and the new $\{MS_2B_8\}$ cluster of **6** have eleven-vertex *nido* shapes **IV** and **V**. No eleven-vertex $\{MS_2B_8\}$ clusters were previously known, but, more fundamentally, compound **6** demonstrates entry, in principle, into the $\{S_2B_8\}$ system, not previously accessed, *via* a one-boron dismantling process.Prompted by this, we experiment at present on dismantling from the non-metallated *arachno* $\{S_2B_9\}$ system with a view to obtaining unmetallated parent $\{S_2B_8\}$ cluster species. The one-sulfur dismantling to give the $\{MSB_9\}$ cluster of **5** is also of interest as it represents an ultimate of a one-sulfur loosening from the $\{S_2B_9\}$ residue exemplified successively, albeit in a somewhat different sense, by **3** then **2** above.

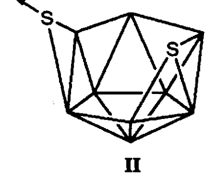
A rich and well-established metal–dicarbaborane chemistry derives from the mutually isomeric $[C_2B_9H_{12}]^-$ anions, both *via* addition to give twelve-vertex cluster compounds, and *via* cluster dismantling to give clusters with fewer than twelve vertices.[2] Our present results now presage a correspondingly



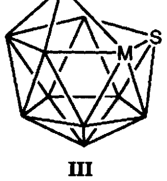
IA



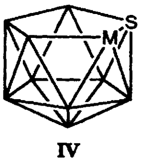
IB



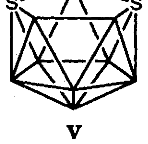
II



III



IV



V

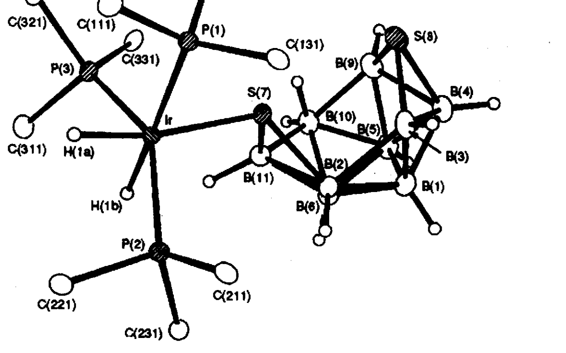


Fig. 1 ORTEP-type diagram[18] of the crystallographically determined molecular structure of $[(PPh_3)_3H_2IrS_2B_9H_{10}]$ **2**, with selected P-organyl atoms omitted for clarity. Selected interatomic dimensions are as follows: Ir–P(1) 2.3968(7), Ir–P(2) 2.3224(7), Ir–P(3) 2.3250(7), Ir–S(7) 2.4654(7), S(7)–B(2) 1.965(3), S(7)–B(11) 1.858(3), S(8)–B(3) 1.866(4), S(8)–B(4) 1.936(4), S(8)–B(9) 1.892(4), B(2)–B(3) 1.940(5), B(9)–B(10) 1.839(5), B(10)–B(11) 1.871(5) Å; P(2)–Ir–P(3) 145.32(2), P(1)–Ir–S(7) 88.45(2), P(2)–Ir–S(7) 109.20(3), P(3)–Ir–S(7) 92.63(2), B(2)–S(7)–B(11) 60.4(2), B(3)–S(8)–B(9) 98.4(2) B(9)–B(10)–B(11) 117.0(2)°

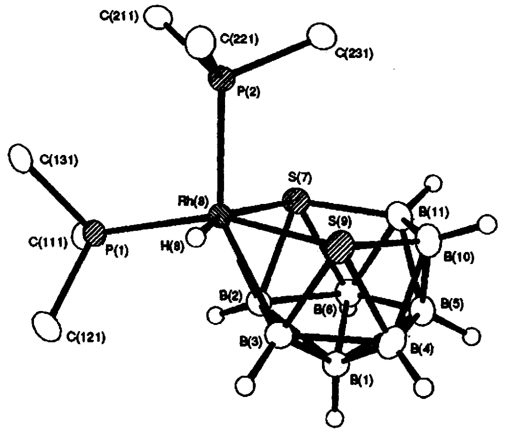


Fig 2 ORTEP-type diagram[18] of the crystallographically determined molecular structure of $[(PPh_3)_2HRhS_2B_8H_8]$ **6**, with selected P-organyl atoms omitted for clarity. Selected interatomic dimensions are as follows: Rh(8)–P(1) 2.3103(5), Rh(8)–P(2) 2.3604(5), Rh(8)–B(2) 2.242(2), Rh(8)–B(3) 2.240(2), Rh(8)–S(7) 2.4304(5), Rh(8)–S(9) 2.3567(5), S(7)–B(2) 2.024(2), S(7)–B(6) 1.989(2), S(7)–B(11) 1.926(2), S(9)–B(3) 2.023(2), S(9)–B(4) 2.001(2), S(9)–B(10) 1.913(2), B(10)–B(11) 1.738(2) Å; P(1)–Rh(8)–P(2) 103.43(2), S(7)–Rh(8)–S(9) 88.76(2), Rh(8)–S(7)–B(11) 109.24(7), Rh(8)–S(9)–B(10) 112.35(7), S(9)–B(10)–B(11) 113.93(14) and S(7)–B(11)–B(10) 115.68(14)°

rich metal–dithiaborane chemistry that may be derived from the $[S_2B_9H_{10}]^-$ anion **1** which is somewhat more accessible[6] than the $[C_2B_9H_{12}]^-$ species. The two chemistries will not, in general, be parallel: already, for example, we can note a tendency for metal–sulfur interaction and a corresponding loosening of the sulfur-cluster intimacy in the $\{S_2B_9\}$ system, whereas in the $\{C_2B_9\}$ system metal–boron interaction is favoured,[14,15] with a tendency to *avoid* carbon–metal interaction and with a corresponding consolidation of intracluster carbon bonding.

Contribution no. 49 from the Řež–Leeds Anglo-Czech Polyhedral Collaboration (ACPC). We thank the Basque Government, the Royal Society, The Academy of Sciences of the Czech Republic (Grant no. 432402), and Borax Research Ltd for support, and Dr R. A. Walker, Dr D. M. Wagnerová, Professor P. Román and Professor N. N. Greenwood for their good offices.

Received, 27th June 1994; Com. 4/03861D

Footnotes

† *Crystal data* for $C_{54}H_{53}B_9IrP_3S_2\cdot 2CH_2Cl_2$ **2**, $M = 1318.34$ (includes solvate), triclinic, space group $P\bar{1}$, $a = 13.6231(14)$, $b = 14.211(2)$, $c = 16.1294(15)$ Å, $\alpha = 75.332(6)$, $\beta = 93.223(13)$, $\gamma = 82.290(9)°$, $U = 2983.6(6)$ Å^3, $D_c = 1.467$ Mg m^{-3}, $Z = 2$, $F(000) = 1320$, μ(Mo-Kα) = 1.467 mm^{-1}, $T = 200$K. A total of 11309 reflections collected to 2θ 50.0° on a Stoe STADI4 diffractometer using ω-θ scans. The structure was solved by heavy-atom methods (SHELXS-86)[16] and refined anisotropically by full-matrix least squares analysis based on all unique F^2 (SHELXL-93).[17] Restraints were applied to the phenyl rings such that they remained flat with overall C_{2v} symmetry. Ligand hydrogen atoms were included with a riding model, cluster hydrogen atoms were freely refined. The asymmetric part of the unit cell contained two CH_2Cl_2 solvate molecules, one of which was disordered across two sites. The final $wR(F^2)$ for all 10515 unique reflections was 0.0574 with a conventional $R(F)$ of 0.0276 [for 9643 reflections with $I > 2.0\sigma(I)$] for 751 parameters.

For $C_{36}H_{40}B_9IrP_2S_2\cdot CH_2Cl_2$ **3**, $M = 973.16$ (includes solvate), monoclinic, space group $P2_1/c$, $a = 13.0029(10)$, $b = 18.7158(15)$, $c = 16.9832(13)$ Å, $\beta = 97.557(7)°$, $U = 4097.1(6)$ Å^3, $D_c = 1.578$ Mg m^{-3}, $Z = 4$, $F(000) = 1928$, μ(Mo-Kα) = 3.598 mm^{-1}, $T = 200$ K. Data collection, structure solution and structure refinement as for **2** except: 7468 data collected (7251 unique), final $wR(F^2)$ 0.0640, conventional $R(F)$ 0.0256 [for 5798 reflections with $I > 2.0\sigma(I)$] for 518 parameters. For brevity in this preliminary communication, a drawing of this compound, of known[5] structural type **III**, is not presented here.

For $C_{36}H_{39}B_8P_2S_2Rh$ **6**, $M = 787.12$, monoclinic, space group $P2_1/n$, $a = 12.1549(7)$, $b = 16.2146(10)$, $c = 19.1485(12)$ Å, $\beta = 92.082(7)°$, $U = 3771.4(4)$ Å^3, $D_c = 1.386$ Mg m^{-3}, $Z = 4$, $F(000) = 1608$, μ(Mo-Kα) = 0.675 mm^{-1}, $T = 200$ K. Data collection, structure solution and structure refinement as for **2** except: 6804 data collected (6635 unique), final $wR(F^2)$ 0.0554, conventional $R(F)$ 0.0220 [for 5762 reflections with $I > 2.0\sigma(I)$] for 465 parameters.

Atomic co-ordinates, bond lengths and angles, and thermal parameters for **2**, **3** and **6** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ *Selected NMR data* for **2**: ($CDCl_3$, 294–297 K) {ordered as: relative intensity $\delta(^{11}B)$ (rel. to BF_3OEt_2) [$\delta(^1H)$]}: 1BH +30.4 [+4.97], 1BH +20.6 [+4.71], 1BH +7.1 [+3.07], (1 + 1)BH *ca.* −1.5 [+3.28, +3.13], 1BH −12.5 [+2.04], (1 + 1)BH *ca.* −22.2 [+1.25, +0.73], and $1BH_2$ −35.8 [−0.07, −1.35 (*endo*)]. $\delta(^1H)$(IrH) −11.58 {$^2J(^{31}P$–$^1H)$ 124, 18 and 23 Hz} and −18.44 {$^2J(^{31}P$–$^1H)$ 9, 17 and 19 Hz}, $^2J(^1H$–$^1H)$ 5.9 Hz. $\delta(^{31}P)$ ($CDCl_3$, 233 K, rel. 85% H_3PO_4) +14.0 (*a*), +3.0 (*b*) and +1.85 (*c*), $^2J(^{31}P_a$–$^{31}P_b)$ 311 Hz, $^2J(^{31}P_a$–$^{31}P_c)$ 10 Hz, and $^2J(^{31}P_b$–$^{31}P_c)$ 16 Hz. For **3** ($CDCl_3$, 294–297 K) {ordered as above}: 1BH +15.3 {+4.08], 1BH +9.8 [+4.24], 1BH +4.0 [+2.28], 1BH +0.3 [+4.21], 1BH −6.7 [+3.29], (1 + 1)BH *ca.* −10.7 [+3.12, +1.29], 1BH −16.9 [+2.59], and 1BH −32.0 [+1.01]. δ (^1H) (IrH) −13.96 {^2J (^{31}P–^1H) 24 and 14 Hz}. δ (^{31}P) ($CDCl_3$, 231 K) +6.8 and +2.2, ^2J (^{31}P–^{31}P) 15 Hz.

§ *Selected NMR data* for **6**: ($CDCl_3$, 294–297 K) { ordered as above}: 1BH +12.0 [+4.07], (1 + 1) BH *ca.* +3.4 [+3.35, +3.53], (1 + 1) BH *ca.* −4.1 [+2.46, +2.05], 1BH −13.7 [+2.00], 1BH −16.8 [+2.03], and 1BH −28.1 [+1.72], $\delta(^1H)$(RhH) −11.98 {^2J $(^{31}P$–$^1H)_{mean}$ and ^1J (^{103}Rh–^1H) both *ca.* 15 Hz}. $\delta(^{31}P)$ ($CDCl_3$, 223 K) +41.5 {^1J (^{103}Rh–^{31}P) 132 Hz} and +30.5 {^1J (^{103}Rh–^{31}P) 125 Hz}, ^2J (^{31}P–^{31}P) 19.5 Hz.

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