METALLABORANE REACTION CHEMISTRY. PART 3. REACTION OF CARBON MONOXIDE WITH [6-H-6-(PPh₃)-6ᴾ,5ᶜ-μ-(2-Ph₂PC₆H₄)-*nido*-6-IrB₉H₁₂] AND THE ISOLATION AND CHARACTERISATION OF TWO *arachno*-6-MONOIRIDADECABORANES [6-(CO)-6-H-6,9-(PPh₃)₂-6ᴾ,5ᶜ-μ-(2-Ph₂PC₆H₄)-*arachno*-6-IrB₉H₁₁] AND *sym*-[6-(CO)-6-H-6,6-(PMe₂Ph)₂-9-(PPh₃)-*arachno*-6-IrB₉H₁₁]*

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It is a pleasure to dedicate this paper to Jaromir Plesek on the occasion of his 70th birthday, not only from the point of view of personal friendly acquaintance, but also from the points of view of past collaborative work, and of his stimulating contributions into polyhedral boron-containing cluster chemistry.

[6-(CO)-6-H-6,9-(PPh₃)₂-6ᴾ,5ᶜ-μ-(2-Ph₂PC₆H₄)-*arachno*-6-IrB₉H₁₁] (**1**) results from the reaction of [6-H-6-(PPh₃)-6ᴾ,5ᶜ-μ-(2-Ph₂PC₆H₄)-*nido*-6-IrB₉H₁₂] (**2**) with carbon monoxide in refluxing benzene. It is characterised by NMR spectroscopy and by single-crystal X-ray diffraction analysis. Crystals were triclinic, space group $P\bar{1}$, with $a = 10.688(2)$, $b = 13.114(3)$, $c = 22.356(5)$ Å, $\alpha = 78.33(2)$, $\beta = 89.482(10)$, $\gamma = 70.884(12)°$, and $Z = 2$. The compound is of the little-examined *arachno* ten-vertex metallaborane structural type. A second compound of this type, [6-(CO)-6-H-6,6-(PMe₂Ph)₂-9-(PPh₃)-*arachno*-6-IrB₉H₁₁] (**3**), isolated from a reaction system involving [Ir(CO)Cl(PPh₃)₂], PMe₂Ph and the [*nido*-B₉H₁₂]⁻ anion, has also been characterised crystallographically. Crystals were triclinic, space group $P\bar{1}$, with $a = 10.389(1)$, $b = 10.511(1)$, $c = 19.699(3)$ Å, $\alpha = 75.03(1)$, $\beta = 85.53(1)$, $\gamma = 74.88(1)°$, and $Z = 2$.
**Key words:** Metallaborane; X-Ray studies; NMR; Cluster; Reaction chemistry of metallaboranes.

The *nido* and *arachno* decaboranyl skeletons (both of schematic cluster shape **I**) are typified by the parent binary boranes *nido*-[B₁₀H₁₄] and *arachno*-[B₁₀H₁₄]²⁻ themselves[1,2]. They are both stable structural types, and many *nido* ten-vertex monometalla-

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* Parts 1 and 2: see refs[11,12].

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decaborane analogues of *nido*-[$B_{10}H_{14}$] are known. These are of general structural types as represented in structures **II–V** (ref.[3]).
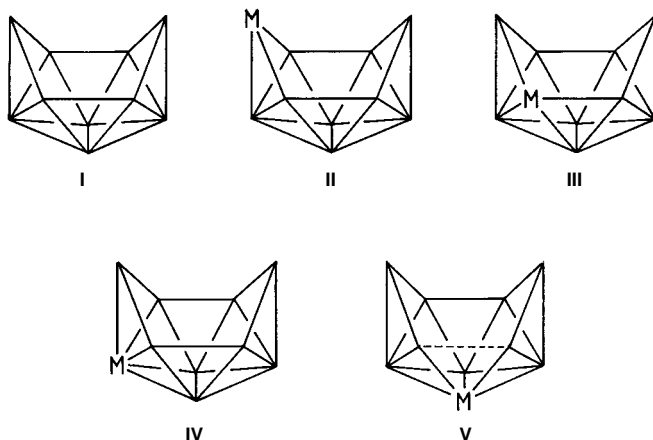
By contrast, examples of *arachno* ten-vertex monometallaboranes are surprisingly limited, even though many *arachno* ten-vertex heteroborane species in which the hetero-atom is not a metal are well known[4,5]. Reported *arachno* monometalladecaborane species consist of (i) a small family of *arachno*-6-platinadecaboranes [6,6-(PEt_3)$_2$-*arachno*-6-PtB$_9$H$_{11}$-9- L], where L can be an amine, a nitrile, a phosphime or a sulfide (structure **VI**)[6]; (ii) a family of three 6,9-bis(organyl isonitrile) rhodaboranes and irida-boranes [6,9-(RNC)$_2$-6-(η^5-C$_5$Me$_5$)-*arachno*-6-MB$_9$H$_{12}$] (structure **VII**)[7,8]; and (iii) one example of an *arachno*-5-metalladecaborane skeleton in the unusual compound [5-(η^6-C$_6$Me$_6$)-5-RuB$_9$H$_{12}$-6,9-μ-(NMe$_2$)-10-(PMe$_2$Ph)] (structure **VIII**)[9]. Of these, only struc-tural types **VII** and **VIII** have been characterised by diffraction studies[7–9].
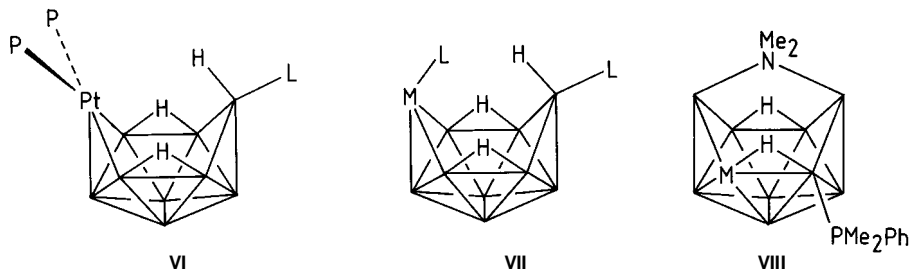
Here we report the isolation and characterisation of two new examples of this rela-tively uninvestigated *arachno* ten-vertex monometalladecaboranyl structural type. These are [6-(CO)-6-H-6,9-(PPh$_3$)$_2$-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*arachno*-6-IrB$_9$H$_{11}$] (**1**), iso-

lated in low yield from the reaction of [6-H-6-(PPh$_3$)-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$] (**2**) with carbon monoxide in refluxing benzene, and [6-(CO)-6-H-6,6-(PMe$_2$Ph)$_2$-9-(PPh$_3$)-*arachno*-6-IrB$_9$H$_{12}$] (**3**), isolated from a reaction system involving [Ir(CO)Cl(PPh$_3$)$_2$)], PMe$_2$Ph and the [*nido*-B$_9$H$_{12}$]$^-$ anion. Both compounds **1** and **3** are of structural type **VI**, previously uncharacterised crystallographically.

RESULTS AND DISCUSSION

Polyhedral metallaboranes that combine a redox-flexible transition-element centre with an electronically flexible open borane (B-frame) matrix should in principle undergo novel redox reactions with suitable substrates. In accord with this, we have reported that [6-H-6-(PPh$_3$)-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$] (**2**) and HC≡CH in refluxing benzene give [2,2-(PH$_3$)$_2$-2^P,1^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*closo*-IrB$_9$H$_7$-10-(PPh$_3$)] and [μ-1^P,2^C-(2-Ph$_2$PC$_6$H$_4$)-1-(η^2-α,ω-C$_4$H$_4$)-*isocloso*-IrB$_9$H$_7$-4-(PPh$_3$)] (refs[10,11]), whereas S=C=S under similar conditions gives [(μ-2,6),(μ-2,9)-(S.CS.S)$_2$-μ-2^P,1^C-(2-Ph$_2$PC$_6$H$_4$)-c*loso*-IrB$_9$H$_6$-10-(PPh$_3$)] (ref.[12]). These are all unusual products, and there is interest in examining reactions with other small-molecule substrates[13]. In accord with this, we have now examined the reaction of the *nido* compound **2** with carbon monoxide. In contrast to the above reactions, which yield closed species, the only metallaborane that we have been able to isolate in a characterisable form (in small yield) is the ten-vertex open *arachno* species [6-(CO)-6-H-6,9-(PPh$_3$)$_2$-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*arachno*-6-IrB$_9$H$_{11}$] (**1**).

Thus the passing of carbon monoxide through a refluxing solution of compound **2** in benzene, followed by repeated chromatography, gave a colourless, air-stable, crystalline solid in *ca* 2% yield. This was identified as [6-(CO)-6-H-6,9-(PPh$_3$)$_2$-μ-6^P,5^C-(2-Ph$_2$PC$_6$H$_4$)-*arachno*-6-IrB$_9$H$_{11}$] (**1**) by single-crystal X-ray diffraction analysis (Fig. 1 and Tables I and II). The compound is readily seen to be of the *nido/arachno* ten-vertex 6-metalladecaboranyl shape **II**, and is confirmed as *arachno* rather than *nido* by the disposition of the two bridging hydrogen atoms at B(5)B(10) and B(7)B(8) on the open face, and by the *endo* terminal hydrogen atom on the B(9) atom that is *exo*-substituted with the PPh$_3$ ligand. The general NMR similarities between compound **1** and other *arachno* ten-vertex species (see below and Fig. 3) also confirm this *arachno* ten-vertex categorization.

It is also convenient to report here a second new compound of the same structural type, *viz.* [6-(CO)-6-H-6,6-(PMe$_2$Ph)$_2$-9-(PPh$_3$)-*arachno*-6-IrB$_9$H$_{12}$] (**3**), which was isolated in modest yield from the reaction of the [*nido*-B$_9$H$_{12}$]$^-$ anion with an iridium species, possibly [Ir(CO)Cl(PMe$_2$Ph)(PPh$_3$)], resulting from the treatment of [Ir(CO)Cl(PPh$_3$)$_2$] with PMe$_2$Ph. Because of the uncertainty in the starting material, the synthetic route is not clear, but we report the structure and other details in view of the similarity to compound **1**.

Compound **3** was obtained by repeated chromatography as a colourless solid. NMR spectroscopy indicated an approximately 3 : 1 mixture of two components, of which

both were isomers of compound **3**. The minor one was the "symmetrical" isomer **3s** and the major component **3a** was probably the "asymmetric" isomer (see discussion in following paragraph). Recrystallisation from pentane–dichloromethane gave single crystals (<1% overall yield) which were identified by single-crystal X-ray diffraction analysis as the symmetric species **3s** (Fig. 2, Tables I and II). Dissolution of the single crystal used in the X-ray work showed the same 3 : 1 ratio of **3a** : **3s** by ^{1}H NMR spectroscopy. This suggests that there is an equilibrium in solution between the symmetric and asymmetric isomers, with the symmetric structure being adopted in the solid state. There are two precedents for both symmetric and asymmetric iridium configurations in other related *arachno*-type species. (i) First, the ten-vertex iridacarbaborane [6-(CO)-6-H-6,6-(PPh$_3$)$_2$-*arachno*-6,9-IrCB$_8$H$_{12}$] (**4**) is also isolated as a mixture of symmetrical and asymmetrical isomers[14]. The NMR spectra of this mixture and of the present system are closely related. For compound **4** it is the asymmetric species that crystallises out preferentially, but there appeared to be no equilibration between the symmetric and asymmetric isomers. (ii) Second, the nine-vertex iridaborane [4-(CO)-4-H-4,4-(PMe$_3$)$_2$-*arachno*-4-IrB$_8$H$_{12}$] (**5**) was isolated as the asymmetric isomer[15], and its chlorinated derivative [4-(CO)-4-H-4,4-(PMe$_3$)$_2$-*arachno*-4-IrB$_8$H$_{11}$-1-Cl] (**6**) is the symmetric isomer. Again there appeared to be no equilibration among isomers.

In each of compounds **1** and **3s** (Figs 1 and 2), the iridium atom at the 6-position bears a hydride, a carbonyl ligand and two triorganophosphine ligands. In compound **1**, one of the P-aryl groups is *ortho*-cycloboronated to B(5). This B(5) *ortho*-cycloboronation is as in the starting material **2**, suggesting no cage rearrangement during the course
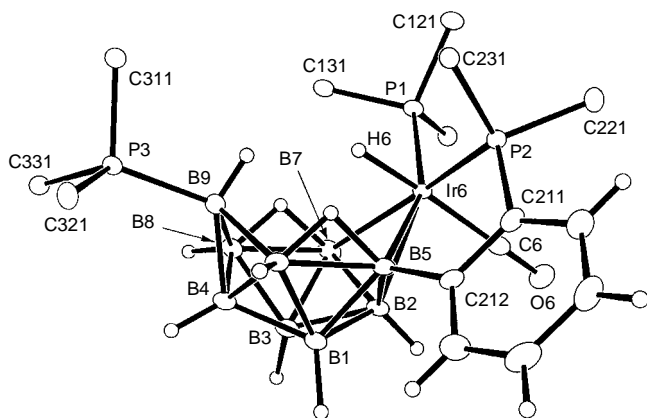

FIG. 1

ORTEP (ref.[43]) drawing of the crystallographically determined molecular structure of [6-(CO)-6-H-6,9-(PPh$_3$)$_2$-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*arachno*-6-IrB$_9$H$_{11}$] (**1**), with selected organyl group atoms omitted for clarity. Non-hydrogen atoms are shown with ellipses at the 30% probability level and hydrogen atoms are drawn as circles with a arbitrary small radius

of its formation. In each of the solid-state structures of **1** and **3s**, the disposition of these *exo*-polyhedral ligands is of the "symmetrical" (*sym*) configuration[14]. This configuration has the carbonyl group *trans* to hydride and the two phosphine ligands *transoid* to mutually similar boron linkages (schematic **X**). The alternative "asymmetric" (*asym*) configuration would have one phosphine and the carbonyl group *transoid* to the boron linkages, and the other phosphine *trans* to hydride (schematic **IX**). As mentioned in the previous paragraph, the principal component of the mixture from which the *sym* compound **3s** was crystallised was probably the *asym* isomer **3a**.

In each case the iridium centre can be regarded as octahedral iridium(III) based on (i) the four *exo*-polyhedral ligands together with (ii) two valencies directed towards two three-centre bonds Ir(6)B(2)B(5) and Ir(6)B(2)B(7). This *arachno* type of bonding

TABLE I
Selected interatomic distances (in Å) for $[6\text{-(CO)-6-H-6,9-(PPh}_3)_2\text{-}6^P,5^C\text{-}\mu\text{-(2-Ph}_2\text{PC}_6\text{H}_4)\text{-}arachno\text{-}6\text{-IrB}_9\text{H}_{11}]$ (**1**) and $sym\text{-}[6\text{-(CO)-6-H-6,6-(PMe}_2\text{Ph})_2\text{-9-(PPh}_3)\text{-}arachno\text{-}6\text{-IrB}_9\text{H}_{11}]$ (**3s**) with estimated standard deviations (e.s.d.'s) in parentheses

Distance	Compound		Distance	Compound	
	1	**3s**		**1**	**3s**
Ir6–P1	2.3375(9)	2.337(2)	Ir6–P2	2.338(1)	2.3290(15)
Ir6–C6	1.920(3)	1.922(5)	Ir6–H6	1.48(4)	1.49(3)
Ir6–B2	2.277(4)	2.273(6)			
Ir6–B5	2.316(4)	2.332(5)	Ir6–B7	2.310(4)	2.318(5)
B1–B2	1.759(5)	1.753(8)	B2–B3	1.754(5)	1.771(8)
B1–B4	1.768(5)	1.766(8)	B3–B4	1.775(5)	1.767(8)
B1–B3	1.781(5)	1.792(8)			
B1–B5	1.788(5)	1.782(8)	B3–B7	1.799(5)	1.758(8)
B1–B10	1.788(5)	1.767(8)	B3–B8	1.789(5)	1.771(7)
B2–B5	1.809(5)	1.788(8)	B2–B7	1.814(5)	1.782(8)
B4–B8	1.759(5)	1.740(7)	B4–B10	1.767(5)	1.750(7)
B4–B9	1.718(5)	1.721(7)			
B5–B10	1.895(5)	1.901(8)	B7–B8	1.883(5)	1.899(8)
B8–B9	1.883(5)	1.853(7)	B9–B10	1.865(5)	1.857(7)
C6–O6	1.140(4)	1.133(5)	C212–B5	1.590(5)	–
P3–B9	1.930(4)	1.929(5)			

mode is discussed elsewhere[15]. Three *arachno*-type species with bis(phosphine)carbonyl-hydridoiridium units have been previously investigated by single-crystal X-ray diffraction work. These are [*asym*-6-(CO)-6-H-6,6-(PPh$_3$)$_2$-*arachno*-6,9-IrCB$_8$H$_{12}$] (**4**)[14], [*sym*-4-(CO)-4-H-4,4-(PMe$_3$)$_2$-*arachno*-4-IrB$_8$H$_{11}$-1-Cl] (**6**)[15], and [*asym*-6-(CO)-6-H-6,6-(PMe$_3$)$_2$-9,9-(PMe$_2$Ph)$_2$-*arachno*-6,9-IrPtB$_8$H$_{10}$] (**7**)[16,17]. None of the three yielded sufficiently good diffraction data sets for good cluster hydrogen-atom location. Now, for compound **1** (in spite of solvate molecule disorder problems), and for compound **3**, the data are good enough for cluster hydrogen-atom location and refinement. In particular, the *endo*-located iridium-bound hydride, although previously reasonably presumed (from NMR evidence) in compounds **4**, **6** and **7** and related species[14–17], is confirmed for this
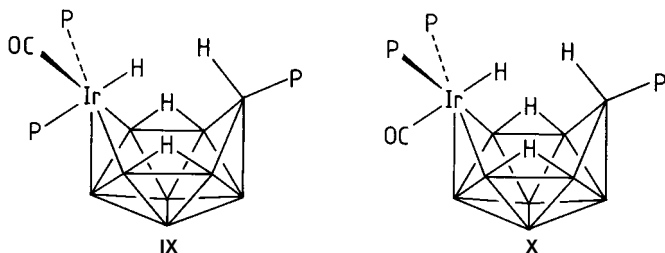
TABLE II
Selected angles (°) for [6-(CO)-6-H-6,9-(PPh$_3$)$_2$-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*arachno*-6-IrB$_9$H$_{11}$] (**1**) and *sym*-[6-(CO)-6-H-6,6-(PMe$_2$Ph)$_2$-9-(PPh$_3$)-*arachno*-6-IrB$_9$H$_{11}$] (**3s**) with e.s.d.'s in parentheses

Angle	Compound		Angle	Compound	
	1	**3s**		**1**	**3s**
C6–Ir6–B2	78.9(1)	81.6(2)	B2–Ir6–H6	100(2)	
C6–Ir6–B5	103.2(1)	101.2(2)	C6–Ir6–B7	97.6(1)	102.1(2)
C6–Ir6–P1	97.0(1)	92.4(2)	C6–Ir6–P2	95.3(1)	97.0(2)
C6–Ir6–H6	178(2)	168(2)			
B2–Ir6–B5	46.3(1)	45.7(2)	B2–Ir6–B7	46.6(1)	45.7(2)
B7–Ir6–B5	81.1(2)	80.5(2)	P1–Ir6–P2	109.37(3)	
B2–Ir6–P1	131.9(1)	133.5(2)	B2–Ir6–P2	118.9(1)	128.3(2)
B7–Ir6–P1	87.6(1)	164.0(1)	B5–Ir6–P1	158.0(9)	91.7(1)
B5–Ir6–P2	77.6(1)	158.9(1)	B7–Ir6–P2	157.2(1)	85.3(1)
B5–Ir6–H6	75(2)	74(2)	B7–Ir6–H6	83(2)	88(2)
P1–Ir6–H6	85(2)	77(2)	P2–Ir6–H6	84(2)	90(2)
O6–C6–Ir6	178.9(3)	168(2)			
C212–B5–Ir6	112.3(2)	–	C211–P2–Ir6	105.79(11)	–
C211–C212–B5	118.5(3)	–	C212–C211–P2	114.4(2)	–
B10–B5–Ir6	120.5(2)	119.6(3)	B8–B7–Ir6	121.7(2)	119.5(3)
B9–B10–B5	114.3(2)	114.3(3)	B9–B8–B7	113.5(2)	114.6(3)
B4–B9–P3	116.5(2)	118.2(3)			

Note P1 and P2 are oppositely labelled in compounds **1** and **3s**.

structural type. In compound **1**, C(6)–Ir(6)–H(6) is essentially linear at 178(2)°, but in compound **3** at 168(2)° it appears to deviate somewhat from linearity. Whether this difference is significant and plays a role in the solution equilibration properties (see above) cannot be assessed from the X-ray data.

The measured NMR data (Table III) for compound **1** are consistent with the molecular structure of Fig. 1, thus confirming that the crystal selected was representative of the bulk material. In the ^{11}B spectra, the general *arachno* ten-vertex characteristics are apparent, with $\delta(^{11}B)(1)$ and $\delta(^{11}B)(3)$ to extreme high-field shielding and $\delta(^{11}B)(2)$ and $\delta(^{11}B)(4)$ to extreme low-field. This shielding pattern is diagnostic of the ten-vertex *arachno* type, and is the inverse of typical ten-vertex *nido* behaviour[18,19]. Figure 3 (lower diagram) gives a stick representation of the chemical shifts and relative intensities in the ^{11}B NMR spectra of compound **1**, together with equivalent data for the related metallaborane $[6,9\text{-}(MeNC)_2\text{-}6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}arachno\text{-}6\text{-}IrB_9H_{12}]$ (**8**)[8] and the
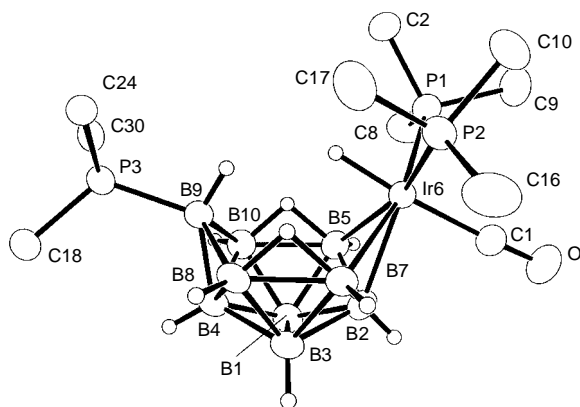

Fig. 2
ORTEP (ref.[43]) drawing of the crystallographically determined molecular structure of *sym*-[6-(CO)-6-H-6,6-(PMe$_2$Ph)$_2$-9-(PPh$_3$)-*arachno*-6-IrB$_9$H$_{11}$] (**3s**), with selected organyl group atoms omitted for clarity. Non-hydrogen atoms are shown with ellipses at the 25% probability level and hydrogen atoms are drawn as circles with an arbitrary small radius

carbametallaborane analogue [6-(CO)-6-H-6,6-(PPh$_3$)$_2$-*arachno*-6,9-IrCB$_8$H$_{12}$] (**4**)[14] for comparison. The data for these are also summarised in Table III for convenience of comparison. Provisional data for the *sym* compound **3s** are also included. The NMR data for this last species are not well defined: as discussed above, the compound appears to exist in solution as a 3 : 1 equilibrium mixture of the *asym* and *sym* isomers, **3a** and **3s**, respectively. Nevertheless, comparison of the spectra with those of compounds **1** and **4** permits a tentative assignment as indicated in Table III.

TABLE III
Measured NMR data for [6-(CO)-6-H-6,9-(PPh$_3$)$_2$-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*arachno*-6-IrB$_9$H$_{11}$] (**1**, CD$_2$Cl$_2$ at 294–297 K), together with cluster {BH} data for [(CO)(PPh$_3$)HIrB$_8$H$_{10}$CH$_2$] (**4**, data from ref.[14]) and [(C$_5$Me$_5$)(MeNC)IrB$_9$H$_{11}$(CNMe)] (**8**, data from ref.[8]) for comparison, and provisional data for *sym*-[6-(CO)-6-H-6,6-(PMe$_2$Ph)$_2$-9-(PPh$_3$)-*arachno*-6-IrB$_9$H$_{11}$] (**3s**, CDCl$_3$ at 300 K)

Assignment	**1**[a]		**4**		**8**		**3s**[b]
	δ(^{11}B)	δ(^{1}H)	δ(^{11}B)	δ(^{1}H)	δ(^{11}B)	δ(^{1}H)	δ(^{11}B)
2,4	*ca* +8	+4.56	+16	+5.05	+10.4	+3.83	*ca* +8
	ca +8	+3.68	+12	+4.20	+8.1	+3.99	*ca* +10
5,7,8,10	*ca* +5	–[c]	–13	+2.56	–11.7	+3.00	*ca* –11.5
	–9.1	+2.46	–13	+1.85			
	ca –18.5	+1.71	*ca* –18	+1.82	–20.7	+2.02	*ca* –17.5
	ca –18.5	+1.30[d]	*ca* –18	+2.58			
9	–22.3	+0.33[e]	[C]f	–[f]	–39.8	+0.32[f]	*ca* –23[g]
1,3	–32.2	+0.95	–33	+1.34	–34.7	+0.85	*ca* –33[h]
	–33.4	+1.14	–34	+0.95			
μ(5,10)	–	–1.94	–	–3.44	–	–3.55	–3.96[i]
μ(7,8)	–	–4.37	–	–4.67	–		
6	[Ir]	–13.41[j]	[Ir]	–16.66	[Ir]	–	–13.52[k]

[a] δ(^{31}P) at –50 °C: +12.8 (sharp), +7.9 (sharp) and *ca* +13.0 ppm (broad). [b] δ(^{31}P) of **3s** and **3a** mixture at –50 °C: +36.6 (sharp), +40.1 (sharp), *ca* +40 (sharp) and *ca* +15 ppm (broad). [c] *ortho*-Cyclophenylated position. [d] Tentative δ value. [e] *endo* BH resonance. [f] CH$_2$ position. [g] Partially resolved doublet structure at 333 K, arising from ^1J(^{31}P-^{11}B). [h] **3a** has δ(^{11}B) (1 and 3) *ca* –33 and *ca* –34.5. [i] Refers to δ(^{1}H) (μ-H) for **3s**, not δ(^{11}B); **3a** has δ(^{1}H)(μ-H) –3.47 and –3.62. [j] 1 : 2 : 1 triplet structure, repeated splitting 18 Hz. [k] 1 : 2 : 1 triplet, ^2J(^{31}P-^{1}H) 16 Hz; **3a** has δ(^{1}H) +14.20, doublet of doublets, ^2J(^{31}P-^{1}H) 10 and 55 Hz.

Compounds **1** and **3s** appear at first sight to deviate from the general *arachno* ten-vertex [11]B shielding pattern exhibited by compounds **4** and **8** in that their phosphine substituted ligand positions (hatched lines A in Fig. 3) are at considerably lower shielding than the corresponding MeN≡C substituted position in compound **8**. However, this is in the range of differential isocyanide *versus* phosphine ligand substituent effects, as recently noted in nine- and ten-vertex non-metal-containing *arachno* heteroboranes[5,20]. Compound **1** additionally appears to deviate in that the B-*ortho*-cyclophenylated boron atom in the 5-position (hatched lines B) is some 15 ppm less shielded than in the general trend for this position: however, this is within observed ranges of aromatic carbon *versus* terminal hydrogen substitution[12,20]. When these substituent effects are taken into account, the [11]B shielding patterns in all four species are very similar, consistent with the uniformity of the ten-vertex *arachno* structural categorization.
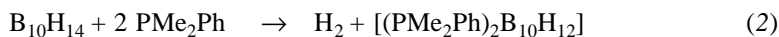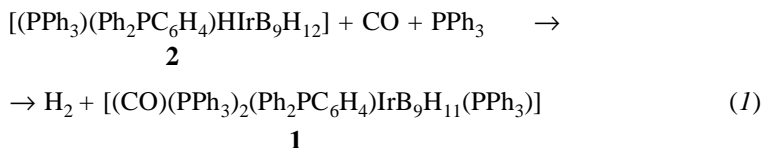
The ^{1}H shielding in compound **1** also parallels that in the two comparison compounds **4** and **8**, and there is a general parallel between $\delta(^{11}B)$ and $\delta(^{1}H)$ of gradient $\delta(^{11}B) : \delta(^{1}H)$ *ca* 12.5 : 1 (uppermost diagram in Fig. 3). The only apparent anomaly in this correlation concerns the $\delta(^{1}H)$ values for the *endo*-9-hydrogen atoms of compounds **1** and **8**. In the phosphine compound **1**, this is *ca* 1 ppm more shielded than the general

Fig. 3

NMR data for [6-(CO)-6-H-6,9-(PPh₃)₂-6^P,5^C-μ-(2-Ph₂PC₆H₄)-*arachno*-6-IrB₉H₁₁] (○, **1**), *sym*-[6-(CO)-6-H-6,6-(PMe₂Ph)₂-9-(PPh₃)-*arachno*-6-IrB₉H₁₁] (∇, **3s**), together with data for [(CO)(PPh₃)₂HIrB₈H₁₁CH₂] (**4**, ⬜, data from ref.[14]) and [(C₅Me₅)(MeNC)-IrB₉H₁₁(MeNC)] (**8**, △, data from ref.[8]) for comparison. The bottom three diagrams are representations of the chemical shifts and relative intensities in the [11]B spectra, with lines joining equivalent positions for the three species. For hatched lines A and B, see text. The top diagram is a plot of $\delta(^{1}H)$ *versus* $\delta(^{11}B)$ for the directly bound {BH} units of compounds **1**, **4** and **8**. The line drawn has slope $\delta(^{11}B) : \delta(^{1}H)$ *ca* 12.5 : 1, intercept +3.6 ppm in $\delta(^{1}H)$
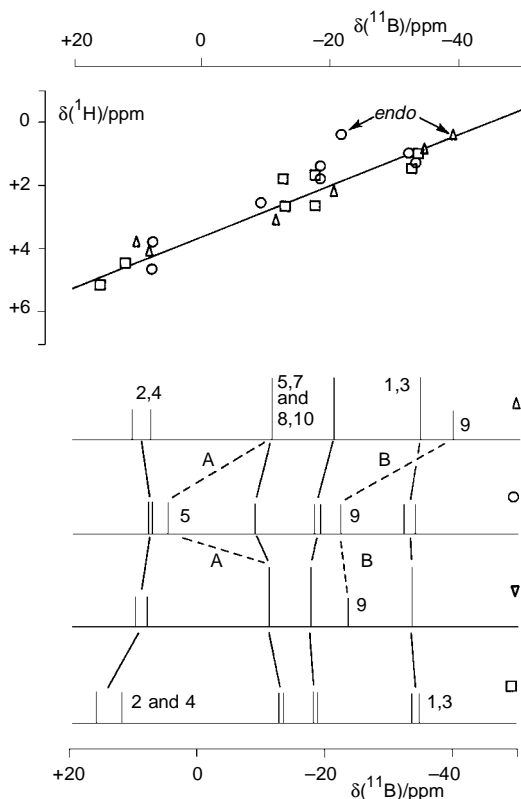
trend, in accord with general *endo* shielding behaviour[21]. In the MeN≡C species **8**, however, this is anomalously less shielded, and more in line with the BH(*exo*) shielding trend. This type of reduced ^{1}H shielding has been noted before, and has been attributed to the magnetic anisotropy of the MeN≡C grouping[7,8].

Mechanistically, the formation of the open *arachno* compound **1** with carbon monoxide is of interest in view of the cluster-closure reactions previously[11,12] encountered with HC≡CH and S=C=S. Compound **1** derives formally from the starting material **2** by (i) the addition of CO, (ii) a movement of hydrogen atoms about the open face, and (iii) the acquisition of an additional PPh$_3$ moiety that must arise from other molecules of the starting material. In spite of this complexity, the basic stoichiometry is very simple (Eq. (*1*)) and has similarities to the classic reaction[22] of *nido*-decaborane with two-electron donor ligands to give 6,9-bis(ligand)-*arachno*-decaboranes (*e.g.* Eq. (*2*))[19].

$$[(PPh_3)(Ph_2PC_6H_4)HIrB_9H_{12}] + CO + PPh_3 \quad \rightarrow$$
$$\mathbf{2}$$
$$\rightarrow H_2 + [(CO)(PPh_3)_2(Ph_2PC_6H_4)IrB_9H_{11}(PPh_3)] \qquad (1)$$
$$\mathbf{1}$$

$$B_{10}H_{14} + 2\ PMe_2Ph \quad \rightarrow \quad H_2 + [(PMe_2Ph)_2B_{10}H_{12}] \qquad (2)$$

Classically, *arachno* species may be generally formed from corresponding *nido* species by the effective net addition of a monodentate two-electron ligand. In both Eqs (*1*) and (*2*), the extra two electrons from the second of the two such ligands are countered by dihydrogen loss. The only previous instance of this parallel of reactions in ten-vertex metallaborane chemistry is in the reactions of organyl isocyanides[7,8] mentioned in the introduction. Much more typically, in metallaborane systems investigated so far, a variety of alternative behaviour supervenes[11,12,23–31]. This alternative behaviour can involve (i) partial or complete cluster closure, (ii) cluster rearrangement with retention of *nido* character, or (iii) cluster degradation. Previously examined reactions of this general type with *nido* iridadecaborane species such as [6-H-6-(PPh$_3$)-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$] (**2**) and its uncyclised parent [6-H-6,6-(PPh$_3$)$_2$-*nido*-6-IrB$_9$H$_{13}$] are those with PPh$_3$, HC≡CH and CS$_2$ (refs[10–21,31,32]). Of these, the reaction with PPh$_3$ in refluxing benzene induces rearrangement and ligand addition[32], or partial closure to *isonido*[31–33], the reaction with HC≡CH induces closure to *closo* and *isocloso*[10,11], and the reaction with CS$_2$ induces closure to *closo* only[12]. Now, with CO, another reaction type, *viz.* cluster *opening* to give *arachno*, is observed.

CONCLUSIONS

In view of this variety of metallaborane reaction behaviour, there is considerable interest in extending the study of the reactions of these *nido*-6-iridadecaboranes and other suitable metallaboranes to other simple electron-rich species[9,13,24–28,30,31,34]. In the general types of iridadecaborane reaction chemistry studied previously, more condensed *isonido* intermediates have often been invoked to account for the precise nature of the products[11,12,31,33,35–37]. The isolation of the *arachno* species **1** now introduces the possibility of significant, more expanded, *arachno*-type intermediates in the complex cluster redox processes that must be involved. The identification of other (coloured) products from this reaction system would be helpful in speculations about mechanisms when it becomes feasible to examine this reaction system on a larger scale, but we have not been able to characterise these so far.

EXPERIMENTAL

General

The compound [6-H-6-(PPh$_3$)-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$] (**2**) was prepared according to the literature method[35]. Solvents were dried prior to use. Benzene was distilled and stored over sodium wire under nitrogen. Preparative and analytical thin-layer chromatography (TLC) were performed in air using silica gel G (Fluka or Aldrich type GF 254) as the stationary phase as previously described[11]. Infrared spectra were recorded from KBr discs or as microcrystalline evaporates on PTFE film using a Polaris FTIR infrared spectrometer. For compound **1**, ^{11}B and ^{1}H NMR data were obtained in CDCl$_3$ solution at 294–297 K and at 9.40 T (corresponding to ν(^{1}H) at *ca* 400 MHz and ν(^{11}B) at *ca* 128 MHz) on a Bruker AM400 instrument, and ^{31}P NMR data in CD$_2$Cl$_2$ solution at 223 K and 2.35 T (corresponding to ν(^{31}P) at *ca* 40 MHz) using a JEOL FX100 instrument. For compound **3** all spectra were obtained for a CDCl$_3$ solution at 300 K at 11.75 T (ν(^{1}H) ν(^{11}B) and ν(^{31}P) at *ca* 500 MHz, 160 MHz and 200 MHz, respectively) on a Bruker ARX 500 instrument. Chemical shifts δ are given in ppm to high frequency (low field) of Ξ 100 MHz (SiMe$_4$) for ^{1}H (quoted ±0.05 ppm), Ξ 32.083971 MHz (nominally Et$_2$OBF$_3$ in CDCl$_3$) for ^{11}B (quoted ±0.5 ppm)[21], and Ξ 40.480730 MHz (nominally 85% H$_3$PO$_4$) for ^{31}P (quoted ±0.5 ppm), Ξ being defined as in ref.[38].

Preparation of [6-(CO)-6-H-9-(PPh$_3$)$_2$-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*arachno*-6-IrB$_9$H$_{11}$] (**1**)

Benzene (*ca* 10 ml) was distilled into a flask containing [6-H-6-(PPh$_3$)-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$] (**2**) (40 mg, 40 μmol). Carbon monoxide was then bubbled through the solution for *ca* 5 min at room temperature. The solution was then heated at reflux under a constant stream of CO for 16 h during which time little colour change from the initial yellow was noted. After cooling, the solution was reduced in volume *in vacuo*, applied to a preparative TLC plate, and developed using 70 : 30 v/v dichloromethane–light petroleum mixture (b.p. 80–100 °C) as eluting solvent. Several closely adjacent red, yellow and pink bands were evident under normal light, with an additional band being observed under UV light. The red and yellow bands (R_F *ca* 0.75; 19.5 mg total yield) contained a mixture of products which have so far defied definitive purification and characterisation, although spectroscopy shows that they do contain carbonyl, metal hydride and boron hydride moieties. The UV-active component was well separated from other components on the TLC plate and was identified after further chromatography and crystallisation as [6-(CO)-6-H-6,9-(PPh$_3$)$_2$-6^P,5^C-μ-(2-

$Ph_2PC_6H_4$)-*arachno*-6-IrB$_9$H$_{11}$] **1** (R_F 0.4; 1.5 mg; *ca* 1.3 μmol; 2%). IR (KBr disc and film on PTFE): $ν_{max}$, cm^{-1}: (CO) 1 980 (s); (Ir–H) 2 125 (m); (BH) 2 520 (s). Colourless, air-stable crystals suitable for single-crystal X-ray diffraction analysis were obtained *via* diffusion of pentane into a solution of the compound in CH_2Cl_2.

Isolation of [6-(CO)-6-H-6,6-(PMe$_2$Ph)$_2$-9-(PPh$_3$)-*arachno*-6-IrB$_9$H$_{12}$] (**3**)

A reaction to give [IrCl(CO)(PMe$_2$Ph)$_2$] (ref.[39]), using [IrCl(CO)(PPh$_3$)$_2$] and PMe$_2$Ph, gave a clean yellow microcrystalline solid, which, in view of the product **3**, was probably [IrCl(CO)(PMe$_2$Ph)(PPh$_3$)] rather than the desired [IrCl(CO)(PMe$_2$Ph)$_2$] (the reaction results are acknowledged to be erratic)[39]. To a sample of this (250 mg) was added a solution of [NEt$_4$][*nido*-B$_9$H$_{12}$] (112 mg, 450 μmol) in CH_2Cl_2 (15 ml), and the resulting mixture stirred for 45 min. The yellow solution was then filtered, reduced in volume, and applied to a preparative TLC plate, and developed using CH_2Cl_2–hexane 70 : 30 as liquid phase. This gave a colourless component (R_F 0.7), detected under UV illumination, and identified (see text) as a mixture of the *sym* and *asym* isomers of [6-(CO)-6-H-6,6-(PMe$_2$Ph)$_2$-9-(PPh$_3$)-*arachno*-6-IrB$_9$H$_{12}$] (**3s** and **3a**, respectively, see above) (50 mg, 57 μmol; 12% based on (NEt$_4$)[*nido*-B$_9$H$_{12}$]). Colourless crystals of the symmetric isomer (**3s**, 3 mg; 0.8%) suitable for single-crystal X-ray diffraction analysis were obtained by diffusion of pentane into a solution of the isomer mixture in CH_2Cl_2.

Single Crystal X-Ray Diffraction Analysis of [6-(CO)-6-H-6,9-(PPh$_3$)$_2$-6^P,5^C-μ-(2-Ph$_2$PC$_6$H$_4$)-*arachno*-6-IrB$_9$H$_{11}$] (**1**)

Crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite-monochromated MoKα X-radiation (λ = 0.71069 Å). The data set was corrected for absorption semi-empirically using azimuthal ψ-scans (maximum and minimum transmission factors 0.3799 and 0.4876, respectively).

The structure was determined by standard heavy-atom methods using SHELXS86 (ref.[40]), and was refined by full-matrix least-squares (based on F^2) using SHELXL93 (refs[41,42]). All data were used for refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters with the exception of a second CH_2Cl_2 molecule (this CH_2Cl_2 molecule proved to be so badly disordered that it could not be characterised at all and was therefore treated by refining the highest peaks in the region as partially occupied carbon atoms). Restraints were applied to the phenyl rings such that they were flat with overall C_{2v} symmetry, with the exception of the *ortho*-cycloboronated benzene ring to which no restraints were applied. The aromatic hydrogen atoms were included in calculated positions (C–H = 0.95 Å) and were assigned fixed isotropic thermal parameters of 1.2U_{eq} of the parent carbon atom. The hydrogen atoms associated with the cluster were all located on a Fourier difference synthesis and were freely refined with individual isotropic thermal parameters. The weighting scheme $w = [σ^2(F_o^2) + (0.0372P)^2 + 0.2691P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$, was used. The maximum peak of residual electron density was 1.123 e Å^{-3} and this was located in the region of the badly disordered CH_2Cl_2 solvate molecule. An ORTEP (ref.[43]) diagram of compound **1** is given in Fig. 1.

Crystal data for compound **1**: $C_{55}H_{55}B_9IrOP_3$. CH_2Cl_2, $M = 865.14$ (includes solvate molecules), 0.50 × 0.35 × 0.15 mm, triclinic, space group $P\bar{1}$, $a = 10.688(2)$ Å, $b = 13.114(3)$ Å, $c = 22.356(5)$ Å, α = 78.33(2)°, β = 89.48(1)°, γ = 70.88(2)°, $U = 1\,270.8(2)$ Å^3, $Z = 2$, $D_x = 1.474$ Mg m^{-3}, μ = 2.614 mm^{-1}, $F(000) = 1\,288$.

Data collection: 4.0 < 2θ < 50.0°, scan widths = 1.05 + α-doublet splitting, scan speeds 1.0–8.0° min^{-1}. Number of unique data collected = 10 200; number with $F_o > 4.0σ(F_o)$ = 8 902 (used only for calculation of R_1 below); $R_{sig} = Σ[σF_o^2]/Σ[F_o^2] = 0.0296$; $T = 200$ K.

Structure refinement: Number of parameters, $p = 713$; $R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o| = 0.0251$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.0651$; goodness of fit $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2} = 1.019$.

Single Crystal X-Ray Diffraction Analysis of [6-(CO)-6-H-6,6-(PMe$_2$Ph)$_2$-9-(PPh$_3$)-*arachno*-6-IrB$_9$H$_{12}$] (**3**)

Crystallographic measurements were carried out on a Siemens P4RA diffractometer operating in the ω-scan mode with variable scan speed, and using graphite-monochromated MoKα X-radiation (λ = 0.71073 Å). The data set was corrected using equivalent reflections and ψ-scan reflections (XEMP).

The structure was determined by standard heavy-atom methods using SHELXTL-PLUS(5.03) (ref.[42]) and was refined by full-matrix least-squares (based on F^2) using SHELXL93 (ref.[41]). The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms associated with the cluster were all located on a Fourier difference synthesis and were freely refined. The methyl- and phenyl-group hydrogen atoms were refined using the riding models AFIX 34 and AFIX 44, respectively. The weighting scheme $w = [\sigma^2(F_o^2) + (0.0372P)^2 + 0.2691P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$, was used. An ORTEP (ref.[43]) diagram of compound **3** is given in Fig. 2.

Crystal data for compound **3**: C$_{35}$H$_{49}$B$_9$IrOP$_3$, $M = 868.14$, $0.50 \times 0.40 \times 0.20$ mm, triclinic, space group $P\bar{1}$, $a = 10.389(1)$ Å, $b = 10.511(1)$ Å, $c = 19.699(3)$ Å, α = 75.03(1)°, β = 85.53(1)°, γ = 74.98(1)°, $U = 2\ 006.0(4)$ Å^3, $Z = 2$, $D_x = 1.437$ Mg m^{-3}, μ = 3.475 mm^{-1}, $F(000) = 868$.

Data collection: $4.0 < 2\theta < 55.0°$, scan widths = 1.05 + α-doublet splitting, scan speeds 1.0–8.0° min^{-1}. Number of unique data collected = 14 373; number with $F_o > 4.0\sigma(F_o) = 9\ 079$; $T = 298$ K.

Structure refinement: Number of parameters, $p = 519$; $R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o| = 0.0365$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.0795$; goodness of fit $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2} = 1.013$.

The tables of atomic coordinates and a full list of bond lengths and angles are available on request from the corresponding author.

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