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Metallaheteroborane chemistry: Part 16.† Contrasting metal to heteroborane bonding modes in isoelectronic $\{MC_2B_9\}$ and $\{MAs_2B_9\}$ clusters. Synthesis and characterisation of $[9\text{-}\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}nido\text{-}7,8\text{-}C_2B_9H_{12}]$, $[7\text{-}\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}nido\text{-}7,8\text{-}As_2B_9H_{10}]$ and $[7\text{-}\{M(CO)_2(\eta^7\text{-}C_7H_7)\}\text{-}nido\text{-}7,8\text{-}As_2B_9H_{10}]$, where M is Mo or W

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Received 13th June 2003, Accepted 11th September 2003
First published as an Advance Article on the web 30th September 2003

Structural details of previously reported $[9\text{-}\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}nido\text{-}7,8\text{-}C_2B_9H_{12}]$ **1** and $[7\text{-}\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}nido\text{-}7,8\text{-}As_2B_9H_{10}]$ **2**, and of the new compounds $[7\text{-}\{M(CO)_2(\eta^7\text{-}C_7H_7)\}\text{-}nido\text{-}7,8\text{-}As_2B_9H_{10}]$, where M is Mo **3** or W **4**, were established by ^1H and ^{11}B NMR spectroscopy and, for **1**, **2** and **3**, by single-crystal X-ray diffraction methods. The NMR data showed that the $\{C_2B_9\}$ and $\{As_2B_9\}$ cages were of the *nido* type, with each having a single bridging hydrogen atom on the open face of its cage. The X-ray diffraction study of **1** confirmed that the $\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}$ unit is attached *exo* to the cage by an unusual interaction of the iron atom with a B–H bond. X-Ray diffraction studies of **2** and **3** showed that the transition-element atoms bonded to arsenic donor sites. The dimensions in the {Fe–H–B} region are Fe(1)–B(9) 2.377(1), Fe(1)–H(9) 1.59(2), B(9)–H(9) 1.25(2) Å and Fe(1)–H(9)–B(9) 113(1)°. There was considerable disorder in the diarsenaborane cages and $(\eta^n\text{-}C_nH_n)$ sections of the molecules **2** and **3**. The principal interatomic distances of interest are Fe(1)–As(7) 2.334(1) Å and Mo(1)–As(7) 2.598(1) Å in **2** and **3**, respectively. The ^{57}Fe Mössbauer spectrum of **1**, obtained at 78 K, comprised a well-resolved doublet with measured parameters $\delta = 0.113$ mm s^{-1} and $\Delta E_Q = 1.94$ mm s^{-1}. The bonding in the {Fe–H–B} region of **1**, when compared with bonding in other ferraboranes, and with models that have been described for agostic hydrogen M–H–B and M–H–C interactions, is shown to be unique. Photolysis of **1** in tetrahydrofuran solution produces the known "mixed-sandwich" paramagnetic species $[3\text{-}(\eta^5\text{-}C_5H_5)\text{-}closo\text{-}3,1,2\text{-}FeC_2B_9H_{11}]$ **5** in 85% yield.

Introduction

The eleven-vertex *exo*-metallated dicarbaborane and diarsenaborane complexes $[9\text{-}\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}\text{-}nido\text{-}7,8\text{-}C_2B_9H_{12}]$ **1** and $[7\text{-}\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}\text{-}nido\text{-}7,8\text{-}As_2B_9H_{10}]$ **2** were prepared first by Todd and co-workers in 1975 and 1974 respectively.[2,3] Structures were proposed in which the $\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}$ unit was bound to the heteroborane cages by different donor sites. In **1** the site proposed was the B(9) atom adjacent to a carbon heteroatom, and in **2** it was an arsenic atom, *i.e.* the heteroatom rather than a boron site. There was no mention of any Fe–H–B bridge bond. Although both ^{11}B (70.6 MHz) and ^1H (220 MHz) NMR spectra were presented in the original papers, no X-ray diffraction analyses were reported and it was not possible fully to characterise the structures of **1** or **2** from the spectroscopy alone. In a continuation of our studies of the coordination chemistry of transition elements with heteroboranes,[1] we have now examined complexes **1** and **2** with X-ray diffraction techniques as well as higher-dispersion NMR spectroscopy (^{11}B at 160 MHz and ^1H at 500 MHz), and also by Mössbauer spectroscopy. Herein we report that the modes of bonding between the iron atoms and the heteroborane clusters in **1** and **2** are indeed significantly different. In **1** there is a novel {Fe–H–B} bridge, whereas in **2** an arsenic atom acts as a more conventional two-electron donor site. We also report the synthesis of the complexes $[7\text{-}\{M(CO)_2(\eta^7\text{-}C_7H_7)\}\text{-}nido\text{-}7,8\text{-}As_2B_9H_{10}]$, where M is Mo **3** or W **4**, the characterisation of both by NMR spectroscopy and of **3** by X-ray crystallography, and compare these compounds with the iron arsenaborane **2**. We also report that photolysis of **1** in tetrahydrofuran solution affords a route to the known paramagnetic species $[3\text{-}(\eta^5\text{-}C_5H_5)\text{-}closo\text{-}3,1,2\text{-}FeC_2B_9H_{11}]$, **5**, in a higher yield of 77% compared to the 25% yield from the previously reported route.[4,5]

The results that we present here relate not only to the large body of published work on the bonding between transition elements and cluster ligands in metallaboranes and metallaheteroboranes but also to discussions of agostic hydrogen interactions in organometallics[6] and in metallaheteroborane complexes.[7–11]

Results and discussion

Synthesis

Compound **1**, $[9\text{-}\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}nido\text{-}7,8\text{-}C_2B_9H_{12}]$, was prepared in 91% yield by the reaction between $[Fe(CO)_2(C_6H_{10})(\eta^5\text{-}C_5H_5)][PF_6]$ and the the caesium salt of $[nido\text{-}7,8\text{-}C_2B_9H_{12}]^-$ anion **6**, as previously described by Todd and co-workers.[2] In a manner similar to Todd and co-workers,[3] the ferradiarsenaborane $[7\text{-}\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}nido\text{-}7,8\text{-}As_2B_9H_{10}]$ **2** was prepared in 81% yield from the reaction between $[Fe(CO)_2(C_6H_{10})(\eta^5\text{-}C_5H_5)][PF_6]$ and the tetramethylammonium salt of the $[nido\text{-}7,8\text{-}As_2B_9H_{10}]^-$ anion **7** in a 1 : 1 molar ratio in CH_2Cl_2 solvent at room temperature for 7 h.

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† Part 15: ref. 1.

DOI: 10.1039/b306776a

Likewise, the molybdenum complex [7-{Mo(CO)$_2$(η^7-C$_7$H$_7$)}-*nido*-7,8-As$_2$B$_9$H$_{10}$] **3** was prepared by the reaction of the [NMe$_4$]$^+$ salt of [*nido*-7,8-As$_2$B$_9$H$_{10}$]$^-$ with [Mo(CO)$_3$(η^7-C$_7$H$_7$)]-[BF$_4$] in a 1 : 1 molar ratio in dichloromethane solvent at room temperature for 24 h (69%). Similarly, the tungsten derivative [7-{W(CO)$_2$(η^7-C$_7$H$_7$)}-*nido*-7,8-As$_2$B$_9$H$_{10}$] **4** was isolated from the reaction of [NMe$_4$][*nido*-7,8-As$_2$B$_9$H$_{10}$] with [W(CO)$_3$-(η^7-C$_7$H$_7$)][BF$_4$] in a 1 : 1 molar ratio in dichloromethane solvent at room temperature for 4 days (42%).

NMR spectroscopy

All compounds were examined using ^{11}B, ^{11}B-{^{1}H(broadband)}, ^{1}H, ^{1}H-{^{11}B(broadband)}, ^{1}H-{^{11}B(selective)}, [^{11}B–^{11}B]-COSY-{^{1}H} and [^{1}H–^{1}H]-COSY-{^{11}B} spectroscopy,[12,13] which distinguished any accidental coincidences of chemical shifts for different sites both in the ^{11}B and in the ^{1}H spectra, and also permitted the assignment of all the ^{11}B and ^{1}H resonances to their molecular positions as summarised in the Experimental section below. The metalladiheteroboranes discussed in this paper exhibit configuration **I** (compound **1**, see also Fig. 1 below), configuration **II** (compounds **2**, **3** and **4**, see Fig. 2 below) or the conventional twelve-vertex *closo* configuration **III** (compound **5**). All derive from the eleven-vertex *nido*-7,8-diheteroundecaborane skeleton **IV**.

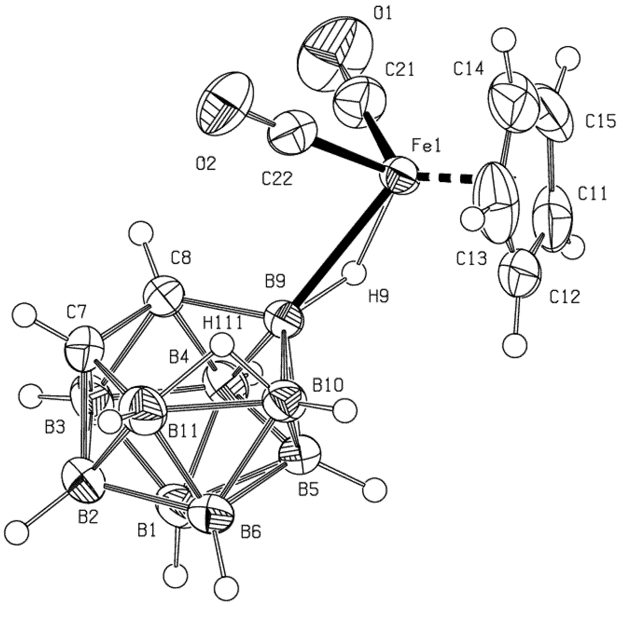


Fig. 1 A view of [9-{Fe(CO)$_2$(η^5-C$_5$H$_5$)}-7,8-*nido*-C$_2$B$_9$H$_{12}$] **1** showing the numbering scheme. Ellipsoids are drawn at the 30% probability level. Selected interatomic distances (Å) and angles (°); Fe(1)–C(21) 1.787(2), Fe(1)–C(22) 1.783(2), Fe(1)–B(9) 2.377(1), Fe(1)–H(9) 1.59(2), O(1)–C(21) 1.125(2), O(2)–C(22) 1.134(2), C(7)–C(8) 1.549(2), C(7)–B(11) 1.629(2), C(8)–B(9) 1.600(2), B(9)–B(10) 1.784(2), B(10)–B(11) 1.855(2), B(9)–H(9) 1.25(2), B(10)–H(111) 1.18(2), B(11)–H(111) 1.32(2); other B–B distances range 1.751(2)–1.808(3), B–C distances range 1.629(2)–1.729(2), C–C distances in cyclopentadienyl ring range 1.381(3)–1.404(3)) and Fe–C (cyclopentadienyl) range 2.075(2)–2.088(2); C(21)–Fe(1)–C(22) 93.29(9), C(21)–Fe(1)–B(9) 100.11(8), C(22)–Fe(1)–B(9) 77.95(7), Fe(1)–H(9)–B(9) 113(1), B(9)–Fe(1)–H(9) 26.3(7), C(21)–Fe(1)–H(9) 87.3(7), C(22)–Fe(1)–H(9) 101.5(7), O(2)–C(22)–Fe(1) 178.6(2), O(1)–C(21)–Fe(1) 178.4(2), C(8)–C(7)–B(11) 111.4(1), C(7)–C(8)–B(9) 114.7(1), C(8)–B(9)–B(10) 106.8(1), B(9)–B(10)–B(11) 101.3(1), C(7)–B(11)–B(10) 105.6(2), Fe(1)–B(9)–H(9) 36(1), B(11)–B(10)–H(111) 45.0(9).

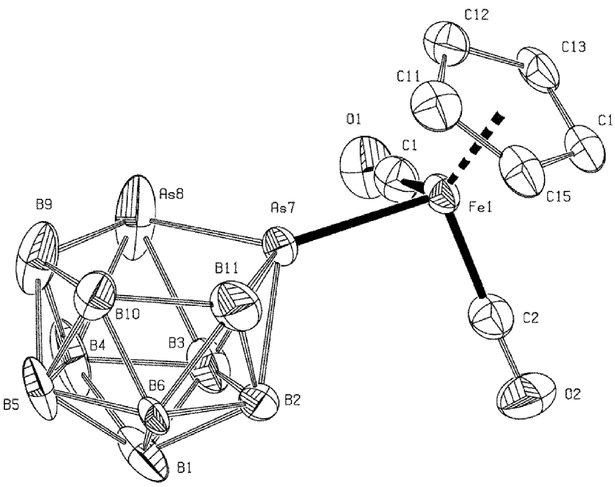
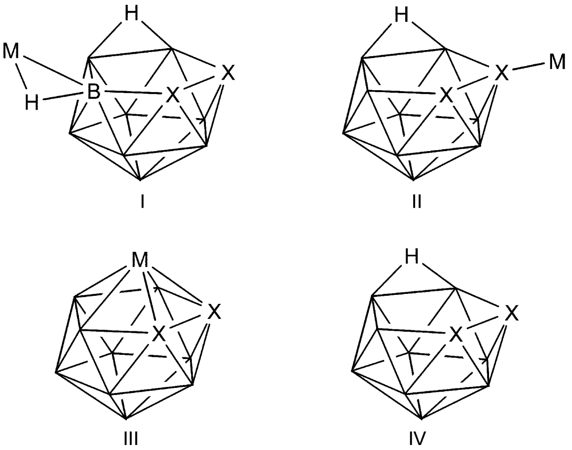


Fig. 2 A view of the *A*-enantiomer of [7-{Fe(CO)$_2$(η^5-C$_5$H$_5$)}-7,8-*nido*-As$_2$B$_9$H$_{10}$] **2** showing the numbering scheme. Ellipsoids are drawn at the 30% probability level and only the major conformer of the disordered system is shown. H atoms are omitted. Atom sites labelled as As8 and B11 are disordered and contain contributions from both B and As atoms. Selected interatomic distances (Å) and angles (°); Fe(1)–As(7) 2.334(1), Fe(1)–C(1) 1.778(6), Fe(1)–C(2) 1.759(7), C(1)–O(1) 1.131(8), C(2)–O(2) 1.150(9); C(1)–Fe(1)–C(2) 95.1(3), Fe(1)–C(1)–O(1) 178.0(6), Fe(1)–C(2)–O(2) 177.4(6), Fe(1)–As(7)–B(2) 118.3(2), Fe(1)–As(7)–B(3) 116.8(2)); distances between atoms B(1–6) range 1.755(8)–1.870(8), C–C distances in cyclopentadienyl rings range 1.40(2)–1.42(3) and Fe–C (cyclopentadienyl) range 2.06(2)–2.13(2).



The cluster ^{11}B and ^{1}H NMR behaviour of [9-{Fe(CO)$_2$-(η^5-C$_5$H$_5$)}-*nido*-7,8-C$_2$B$_9$H$_{12}$] **1**, formally a complex between the [*nido*-7,8-C$_2$B$_9$H$_{12}$]$^-$ anion **6** and the {Fe(CO)$_2$(η^5-C$_5$H$_5$)}$^+$ moiety *via* a unique {BH(*exo*)–Fe} linkage as discussed below, show strong similarities to those of its precursor anion **6**.[14] The mirror-plane symmetry exhibited by anion **6** in solution is however lost, so that separate ^{11}B resonances for the nine individual boron cluster positions could be distinguished, as opposed to the six-resonance 2 : 2 : 2 : 1 : 1 : 1 relative-intensity pattern seen for the free anion. Many of the chemical shifts δ(^{11}B) were similar to those in the [C$_2$B$_9$H$_{12}$]$^-$ anion **6**, except for the ^{11}B(9) position involved in the {B–H–Fe} linkage, shifted upfield by *ca.* 25 ppm, reflecting the electronic perturbation at the BH(9) site relative to the free anion **6**, and also the resonances for ^{11}B(5) and ^{11}B(10), flanking this coordinating site, concomitantly shifted downfield by *ca.* 15 and *ca.* 8 ppm, respectively. Interestingly, B(4), also flanking the {BH(9)Fe} site, was not so significantly affected. In the ^{1}H spectrum, the resonances from δ(^{1}H) +2.18 to +0.46 ppm associated with the {BH(*exo*)} units are in typical general ranges for {BH(*exo*)} units in polyhedral boron-containing cluster species. More interest in the present context derives from the two signals at δ(^{1}H) −3.33 and −12.9 ppm, typical of bridging {B–H–B} and {Fe–H–B} protons, respectively.[13–22] Of these, the resonance at −3.33 ppm is readily assigned to the B(9)B(10) bridging position by the ^{1}H-{^{11}B} and [^{1}H–^{1}H]-COSY experiments, and the resonance at −12.9 ppm for the hydrogen atom associated with B(9) was so assigned by the ^{1}H-{^{11}B} results; it showed no [^{1}H–^{1}H]-COSY ^3J(^{1}H–^{1}H) correlations to any adjacent

$\{H(\textit{exo})\}$ sites. This $\{Fe–H–B\}$ bridging proton resonance shows a doublet structure, with a measurable splitting arising from $^1J(^{11}B–^1H)$ of *ca.* 103 Hz, a value that is smaller than the values of *ca.* 140–170 Hz typically seen for $\{BH(\textit{exo})\}$ units.[13–22]

The ^{11}B NMR spectra of $[7\text{-}\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}\textit{nido}\text{-}7,8\text{-}As_2B_9H_{10}]$ **2**, $[7\text{-}\{Mo(CO)_2(\eta^7\text{-}C_7H_7)\}\text{-}\textit{nido}\text{-}7,8\text{-}As_2B_9H_{10}]$ **3** and $[7\text{-}\{W(CO)_2(\eta^7\text{-}C_7H_7)\}\text{-}\textit{nido}\text{-}7,8\text{-}As_2B_9H_{10}]$ **4** each similarly exhibit nine separate resonances, showing that the effective mirror-plane symmetry exhibited in solution by the uncomplexed starting $[\textit{nido}\text{-}7,8\text{-}As_2B_9H_{10}]^-$ anion[13] has been altered. Correspondingly, the ^1H NMR spectrum for the heteroborane cluster of each compound shows nine separate $\{BH(\textit{exo})\}$ resonances, now all in typical $\{BH(\textit{exo})\}$ ranges, and one bridging resonance in the typical $\{B–H–B\}$ bridging range. Since all three species exhibit arsenic-to-metal bonding rather than the $\{BH(\textit{exo})\}$-to-metal bonding of compound **1**, there are no dramatically matching shielding changes for any of the cluster ^{11}B or ^1H resonances upon complexation of anion **7**, although the B(2) and B(11) positions flanking the metal-coordinated As(7) atom do show increases in ^{11}B shielding compared to the precursor anion **7**, for example of 5 and 7 ppm, respectively, in the molybdenum compound **3**. The most striking difference between the precursor **7** and the molybdenum compound **3** is, however, the large downfield shift of *ca.* 10 ppm in the ^{11}B shielding associated with the BH(5) vertex that is antipodal to the As(7) site of metallation. These changes in the shielding of B(2), B(5) and B(11) also occur in compounds **2** and **4**. We have previously noted related antipodal NMR effects involving mutually antipodal cluster constituents and *exo*-sites in metallaheteroboranes.[13]

Compound $[3\text{-}(\eta^5\text{-}C_5H_5)\text{-}\textit{closo}\text{-}3,1,2\text{-}FeC_2B_9H_{11}]$, **5**, with the schematic cluster configuration **III**, afforded ^{11}B and ^1H NMR spectra characteristic of a paramagnetic species, exhibiting broadened resonances and a large chemical shift range, in this case with a $\delta(^{11}B)$ range of *ca.* 635 ppm at 300 K. The ^{11}B NMR spectrum consisted of six resonances in 1 : 2 : 2 : 1 : 2 : 1 relative intensity ratio, reflecting the effective C_s mirror-plane symmetry of this species in solution. Four of these resonances appeared with doublet structure, with observed splittings arising from couplings $^1J(^{11}B–^1H)$ of between *ca.* 105 and *ca.* 135 Hz, but the broadness of the other two resonances, in the region −450 to −520 ppm, was such as to preclude the resolution of any similar fine structure. Here it may be noted that, for broadened ^{11}B resonances, the apparent splitting observed will be smaller than the coupling constant $J(^{11}B–^1H)$ from which the splitting arises. It is also convenient to note that the very large chemical shift range associated with this paramagnetic species precluded completely efficient decoupling of all resonances at once in $^1H\text{-}\{^{11}B\}$ and $^{11}B\text{-}\{^1H\}$ broadband decoupling experiments on the equipment used. A comparison of the ^{11}B NMR data for compound **5** presented here with that previously reported[4] reveals the same basic features, for example in the large scale of the chemical shift range, but the splitting data were not previously detailed.

X-Ray diffraction studies

The original study of $[9\text{-}\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}\textit{nido}\text{-}7,8\text{-}C_2B_9H_{12}]$ **1** did not contain a report of the solid-state structure and the NMR spectroscopic study did not conclusively resolve what type of iron–carborane bonding was involved.[2] In the present study an X-ray diffraction analysis revealed that complex **1** has an eleven-vertex *nido*-C_2B_9-cage with the iron atom of the $\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}$ moiety bonded to the open $\{C_2B_3\}$-face with an $\{Fe–H–B\}$ linkage *via* the $\{BH(9)(\textit{exo})\}$ unit, Fig. 1. Each of the other $\{C_2B_9\}$ cage atoms is bonded to a terminal hydrogen atom and the bridging hydrogen atom in the $\{\textit{nido}\text{-}7,8\text{-}C_2B_9H_{12}\}$ cage is located between B(10) and B(11). Selected interatomic distances and angles are given in the caption to Fig. 1.

Within the $\{Fe–H–B\}$ linkage, the distance from Fe(1) to B(9) is 2.377(1) Å, while the Fe(1)–H(9) and B(9)–H(9) distances are 1.59(2) and 1.25(2) Å, respectively, with the Fe(1)–H(9)–B(9) angle 113(1)°. Thus the iron atom has bonding interactions with both the boron and hydrogen atoms B(9) and H(9) but it is not a cluster vertex. Comparison with published *nido*-ferraborane and ferracarborane structures (see Chart 1 for the basic structural types) shows that the situation in **1** is unique (Chart 1(a)). No other *nido*-cage compound has been reported with the type of M–H–B bonding observed in **1**. Previously reported *nido*-ferraborane[15,19,23,24] and ferraheteroborane structures[20,21] contain iron atoms incorporated as cluster cage atoms, most commonly with one or more Fe–H–B bridging interactions (Chart 1(b)). Another related type of bonding, found with essentially zwitterionic *closo*-carborane derivatives, has the iron atom bonded *exo* to the cluster as part of a weak B–H–Fe interaction with very little or no direct iron-to-boron bonding (Chart 1(c)).[25–27] An example here is the compound $[12\text{-}\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}\textit{closo}\text{-}1\text{-}CB_{11}H_{12}]$ **8**.[25,27] Lastly, several compounds are known with iron atoms that are *exo* bonded directly to a boron or carbon cage atom by a two-centre–two-electron bond as in $[2\text{-}\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}\textit{nido}\text{-}B_5H_8]$ **9** (Chart 1(d)).[24] Relevant iron–boron, iron–hydrogen and boron–hydrogen distances and Fe–H–B angles are listed in Table 1 for complexes for which standard uncertainty data have been reported on located hydrogen atoms.

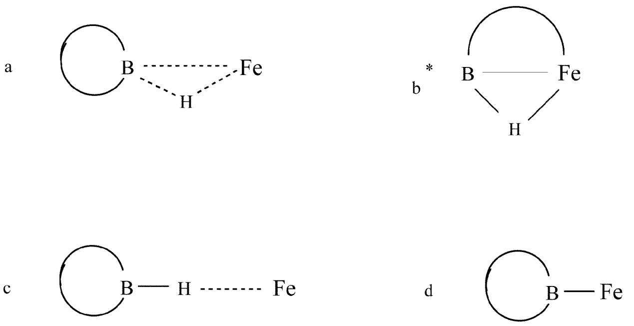


Chart 1 *nido*-Ferraborane and ferracarborane structures. * Ferraborane and ferracarborane clusters with H-atoms bridging Fe–B interactions. These clusters contain between 4 and 11 cluster vertices. They do not contain $\{Fe(C_5H_5)(CO)_2\}$ units. The ligand groups on the Fe atoms in these clusters are CO, PMe_3, 1,3,5-$Me_3C_6H_3$ or toluene.

As seen from Table 1, the iron–boron distance and the Fe–H–B angle in **1** clearly lie between those previously found in $\{Fe–H–B\}$ bridged units in ferraborane or ferracarborane clusters and those found in the the zwitterionic compounds that are formed between *closo* carborane anions or related metallacarborane species and the cations or $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]^+$ or $[M(CO)_2(\eta^5\text{-}C_5R_5)]^+$ {where M is Fe or Ru and R is H or Me}.[25–31] The molecular structures of a number of such zwitterionic compounds, such as $[12\text{-}\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}\textit{closo}\text{-}1\text{-}CB_{11}H_{12}]$ **8**,[27] $[12\text{-}\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}\text{-}\textit{closo}\text{-}CB_{11}H_{12}]$ **14**[28] and $[Re(CO)_3(\eta^5\text{-}(\mu\text{-}H)\text{-}\textit{exo}\text{-}\{Ru(CO)_2(\eta^5\text{-}C_5H_5)\}\text{-}7,8\text{-}C_2B_9H_{10}]$ **15**,[30] have been described in detail. These species contain 'unsupported' M–H–B bonds, *i.e.* there is no significant bonding between the transition-element atom and the nearest boron atom. In both **8** and **14**, the B–H distances are typical of terminal B–H bonds, at 1.18(2) and 1.18(3) Å, respectively, and the Fe–H–B angles are 141.1(8) and 152(2)°. These compounds have been described as zwitterionic in the sense of a carborane anion interacting weakly with a transition element moiety acting as a cation. Analogously, the structure of **15** shows a $\{\textit{closo}\text{-}ReC_2B_9\}$ cluster unit bonded to the $\{Ru(CO)_2(\eta^5\text{-}C_5H_5)\}$ unit *via* an unsupported Ru–H–B bond with Ru. . .B 2.694(13), B–H 1.67(10), Ru–H 1.75(10) Å and Ru–H–B 104(5)°.[30] Notwithstanding the standard uncertainty of the B–H distance in compound **15**, the B–H distance is exceptionally long for a terminal

Table 1 Interatomic distances and angles of ferraborane and ferracarborane complexes with Fe–H–B bridges

Complex	Fe–B/Å	Fe–H/Å	B–H/Å	Fe–H–B/°	Structure
1	2.377(1)	1.59(2)	1.25(2)	113(1)	1a
10[23]	2.223(11)	1.54	1.39	99	1b
	2.240(10)	1.58	1.45	95	
11[15]	2.183(2)	1.69(3)	1.29(3)	96.8	1b
	2.205(2)	1.53(3)	1.29(3)	99.8	
12[19]	2.077(5)	1.55(3)	1.31(3)	93(2)	1b
13[29]	2.20(1)	1.7(1)	1.3(1)	96(1)	1b
8[27]	2.593(2)	1.563(22)	1.18(2)	141.1(8)	1c
9[24]	2.035(3)	–	–	–	1d*

Key: [1,1,2,2-$(CO)_4$-1,2-$(PPh_3)_2$-1,2-*nido*-$FeIrB_2H_5$] **10**, *conjuncto*-[$B_4H_8Fe_4(CO)_{12}$] **11**, [5-{η^6–$C_6Me_3H_3$}-5-*nido*-FeB_9H_{13}] **12**, [NEt_4][WFe{μ-C(2,6-$Me_2C_6H_4$)}$(CO)_4$(η^6-$C_2B_{10}H_{10}Me_2$)] **13**, [12-{$Fe(CO)_2$(η^5-C_5H_5)}-1-*closo*-$CB_{11}H_{12}$] **8**, [2-{$Fe(CO)_2$(η^5-C_5H_5)}-*nido*-B_5H_8], **9**. *Note: other reported two-centre–two-electron Fe–B distances (Å) are: 1.959(6) in [{$Fe(CO)_2$(η^5-C_5H_5)}$B(OC_6H_4O)_2$] and 2.034(3) in [{$Fe(CO)_2$(η^5-C_5H_5)}BPh_2],[32] and 2.051(3) in [4-{$Fe(CO)_2$(η^5-C_5H_5)}-μ-2,3-PPh_2-*nido*-B_5H_7].[24]

B–H bond and it was suggested that **15** could be viewed as a compound showing "incipient hydride extraction".[30]

Comparison of the B–H distances in the {M–H–B} regions of the species **8**, **14** and **15** with our present compound **1** suggests that neither the zwitterionic "borane anion–transition element fragment cation" description nor the "incipient transition element hydride" description of the *exo* M–H–B interactions applies to the Fe–H–B bonding in **1**.

In the dicarbaborane section of **1** the range of boron–boron distances is 1.751(2)–1.855(2) Å and carbon–boron distances of 1.600(2)–1.729(2) Å in **1** are remarkably similar to the analogous distances in the carborane anion [7,8-*nido*-$C_2B_9H_{12}$]$^-$, **6**, of 1.754(3)–1.849(3) and 1.606(3)–1.726(3) Å, respectively.[7] A shortening of the B(9)–B(10) linkage in **1** by 0.033 Å is the largest change observed. It is noteworthy that the distances about boron vertex B(9) change very little. In the solid-state structure of **1** the hydrogen atom H(111) that bridges B(10) and B(11) is asymetrically placed with B(10)–H(111) and B(11)–H(111) distances of 1.18 (2) and 1.32(2) Å, respectively. This asymmetry and the distances involved are not unusual in borane and metallaborane clusters.

By contrast, the X-ray analysis of the molecular structure of the species [7-{$Fe(CO)_2$(η^5-C_5H_5)}-*nido*-7,8-$As_2B_9H_{10}$] **2** did not exhibit an {Fe–H–B} link. Rather, the metal-to-cluster linking is now *via* a direct iron–arsenic bond. The X-ray diffraction analysis of compound **2** revealed that it has an irregular eleven-vertex *nido*-diarsenaborane cluster geometry, with the iron atom of the {$Fe(CO)_2$(η^5-C_5H_5)} moiety bound *exo* to one of the two arsenic atoms in the open {As_2B_3}-face. The analysis revealed considerable disorder. Thus the crystal packing in **2** was such that the coordinates of the iron atom remain identical but that the arsenic atoms are disordered over five sites resulting in what initially appeared to be a quasi twelve-vertex "icosahedron". However, as the analysis proceeded, the array of cage atoms resolved into two distinct orientations of the {As_2B_9} cage in an occupancy ratio of 0.811 : 0.189. In the principal orientation, occupancy of the arsenic atom not bonded to iron is observed at the two adjacent sites in the {As_2B_3} open-face affording the *C*-[7-{$Fe(CO)_2$(η^5-C_5H_5)}-*nido*-7,8-$As_2B_9H_{10}$] **2a** and *A*-[7-{$Fe(CO)_2$(η^5-C_5H_5)}-*nido*-7,8-$As_2B_9H_{10}$] **2b** enantiomers, with the latter predominating (94%), Fig. 2. The cyclopentadienyl rings in **2** are equally disordered over two sites and each of the enantiomers of **2** has two conformations of the cyclopentadienyl rings in equivalent ratio. The considerable disorder in the crystal of **2** severely restricts the refinement of the structure, and a detailed discussion is thus curtailed. The iron–arsenic distance in **2**, 2.334(1) Å, is similar to that in the cluster compound [{$Fe(CO)_3$}$_2$-{$W(CO)_2$(η^5-C_5H_5)}{μ_3-As{$Fe(CO)_2$(η^5-C_5H_5)}}], 2.345(2) Å.[33] Other structural data are given in the legend to Fig. 2.

The molecular structure of [7-{$Mo(CO)_2$(η^7-C_7H_7)}-*nido*-7,8-$As_2B_9H_{10}$], **3**, the first η^1-ligated arsenaborane molybdenum complex to be structurally characterised, exhibited similar characteristics to **2**. Compound **3** also contained an irregular eleven-vertex *nido*-diarsenaborane cage with the molybdenum atom of the {$Mo(CO)_2$(η^7-C_7H_7)} moiety directly coordinated to an arsenic atom in the open {As_2B_3} face, Fig. 3. In the crystal that was analysed, there was similar disorder to that discussed in **2** above. Thus, the molecules were packed in such a way that in each molecule the coordinates of the {$Mo(CO)_2$-(η^7-C_7H_7)} unit remained identical while the arsenic atoms are disordered over four sites in a similar fashion as in **2**. There are thus two distinct orientations of the open {As_2B_3}-face with respect to the molybdenum unit, these two orientations having an occupancy ratio of 0.663 : 0.337. The major orientation (78%) shown in Fig. 3, is the *C*-[7-{$Mo(CO)_2$(η^7-C_7H_7)}-*nido*-7,8-$As_2B_9H_{10}$] enantiomer. Selected interatomic distances and angles for this orientation are given in the legend to Fig. 3. The molybdenum–arsenic bond length in **3** is 2.598(1) Å. It appears that no compound containing the {$Mo(CO)_2$(η^7-C_7H_7)}As} unit has been previously reported. However, comparison of the Mo–As bond length in **3** can be made with compounds containing {$Mo(CO)_5$As} and {$Mo(CO)_3$(η^5-C_5H_5)As} fragments, *viz.*, [$Mo(CO)_5$($AsPh_3$)] at 2.630(2) Å,[34] and [(μ_4-As)$_2$(η^5-C_5H_5)$_2$-$Fe_3Mo_2(CO)_{15}$] at 2.676(1) Å.[35] The {$Mo(CO)_2$(η^7-C_7H_7)As} fragment of **3** is found to have a "piano stool" type of arrangement similar to that observed in other metal tricarbonyl

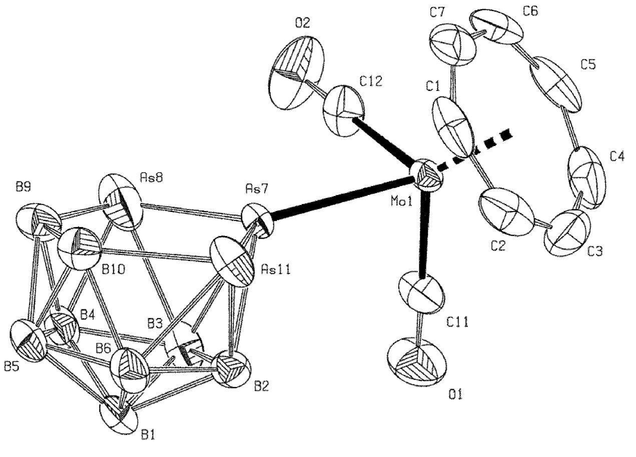


Fig. 3 A view of the *C* enantiomer of [7-{$Mo(CO)_2$(η^7-C_7H_7)}-7,8-*nido*-$As_2B_9H_{10}$] **3** showing the numbering scheme. Ellipsoids are drawn at the 30% probability level and only the major conformer of the disordered system is shown. H atoms are omitted. Atom sites labelled as B3, As8 and B11 are disordered and contain contributions from both B and As atoms. Selected interatomic distances (Å) and angles (°); Mo(1)–As(7) 2.598(1), Mo(1)–C(11) 2.016(8), Mo(1)–C(12) 2.003(8), O(1)–C(11) 1.141(9), O(2)–C(12) 1.141(9); distances between atoms B(1–6) range 1.72(1)–1.84(2), C–C distances in cycloheptatrienyl rings range 1.32(1)–1.41(1) and Mo–C (cycloheptatrienyl) range 2.250(9)–2.300(8); C(11)–Mo(1)–C(12) 86.6(4), C(11)–Mo(1)–As(7) 88.9(2), C(12)–Mo(1)–As(7) 80.2(2), Mo(1)–C(11)–O(1) 175.6(8), Mo(1)–C(12)–O(2) 178.7(9).

Table 2 Measured ^{57}Fe Mössbauer parameters (isomer shift (δ) and quadrupole nuclear splitting (ΔE_Q))[a] and ν(CO) absorptions[b] for [9-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}-7,8-*nido*-$C_2B_9H_{12}$] **1** and *B*-{$Fe(CO)_2(\eta^5$-$C_5H_5)$} substituted metallaborane complexes

Complex	δ/mm s^{-1}	ΔE_Q/mm s^{-1}	ν(CO)/cm^{-1}
[9-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}-7,8-*nido*-$C_2B_9H_{12}$] **1**	0.113	1.94	2059, 2008
[2-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}-*nido*-B_5H_8] **9**[18]	0.039	1.84	2005, 1947
[2,4-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}$_2$-*nido*-B_5H_7][18]	0.039	1.77	1996, 1936
[4-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}-μ-2,3-PPh_2-*nido*-B_5H_7][18]	0.024	1.82	1990, 1934

[a] Recorded at 78 K, δ values relative to natural α-iron foil. [b] Measured in a KBr pellet.

complexes.[36] The molybdenum atom is approximately equidistant from all seven carbon atoms of the {C_7H_7} unit, with an average Mo–C_{ring} distance of 2.280(8) Å.

Mössbauer spectroscopy

The ^{57}Fe Mössbauer spectrum of [9-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}-*nido*-7,8-$C_2B_9H_{12}$] **1** showed a well-resolved doublet with $\delta = 0.113$ mm s^{-1} (relative to natural α-iron foil) and with $\Delta E_Q = 1.94$ mm s^{-1}. Compared with previously reported data for *B*-{$Fe(CO)_2$-(η^5-C_5H_5)}-constructed ferraborane complexes,[18] the isomer shift value for **1** is significantly higher (Table 2), which suggests that the mode of bonding in **1** is different to that in other known ferraboranes, for example those based on the [2-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}-*nido*-B_5H_8], **9**, compound.[18] In view of the higher isomer shift for **1**, the dicarbaborane anion **3** must be a weaker σ-donor and/or a weaker π-acceptor than the pentaborane ligands in the ferraborane complexes. If the dicarbaborane cage is to be considered a weaker donor ligand, the carbonyl stretching frequencies in the infrared spectrum of **1** should be higher than in the corresponding ferraborane complexes. In this context, the observed stretching frequencies in compound **1** are clearly higher than those of [2-{$Fe(CO)_2$-(η^5-C_5H_5)}-*nido*-B_5H_8] **9**, [2,4-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}$_2$-*nido*-B_5H_7], and [4-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}(μ-2,3-PPh_2-*nido*-B_5H_7)], supporting the suggestion that the carborane ligand is a weaker donor, Table 2.

The {Fe–B–H} interaction in [9-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}-*nido*-7,8-$C_2B_9H_{12}$] 1

Compounds [$Re(CO)_3(\eta^5$-(μ-H)-*exo*-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}-7,8-$C_2B_9H_{10}$] **16**,[30] and [12-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}-*closo*-1-$CB_{11}H_{12}$] **8**,[25] have been described as zwitterionic species, with the positive charge localised on the iron-centred {$Fe(CO)_2(\eta^5$-$C_5H_5)$} moiety and with the negative charge dispersed throughout the carbaborane cage. Single-crystal X-ray analyses confirmed that the {Fe–H–B) interactions in **16** and **8** are very weak (Table 1) and in the case of **8**, the carbaborane anion has been described[20,21] as "non-coordinating". Further, for [$Re(CO)_3$-(η^5-(μ-H)-*exo*-{$Ru(CO)_2(\eta^5$-$C_5H_5)$}-7,8-$C_2B_9H_{10}$] **15**, it has been suggested[30] that the compound "almost has the appearance of a [$RuH(CO)_2(\eta^5$-$C_5H_5)$] molecule loosely bound to a neutral [$Re(CO)_3(\eta^5$-7,8-$C_2B_9H_{10})$] species". However, the solid-state structure of compound **1** is clearly not like those of **8**, **15** or **16**. The differences between **8**, **15** or **16** and **1** are also reflected in the observed splittings arising from the coupling constants $^1J(^{11}B$–$^1H)$ within the {M–H–B} links. These are *ca.* 80 and *ca.* 75 Hz in **15** and **16**, respectively,[30] compared to the observed splitting of 103 Hz arising from the $^1J(^{11}B$–$^1H)$ coupling constant in the {Fe–H–B} system in **1**. It has also been suggested that the coupling constant values in **15** and **16** may be typical of agostically involved hydrides.[30]

A question therefore arises concerning the description of the {Fe–B–H} interaction in **1** either as a three-centre–two-electron bond or as an *agostic* {B–H–Fe} three-centre–two-electron interaction. Although these descriptions have often been used interchangeably in metallacarborane chemistry, see for example ref. 30, the original designation of an "agostic hydrogen interaction" was applied to the donation of the σ-electrons of a non-metallic element-to-hydrogen (E–H) bond, where E was predominantly carbon, to an otherwise electron-deficient metal centre with *the hydrogen atom as part of a ligand which was attached to the metal by additional bonds.* An example would be an agostic β-C–H–M interaction involving the terminal methyl C–H unit of an ethyl group which is σ-bonded to the metal.[6] Chart 2(a) and (b) show the two most common situations with respect to the bonding involved in the {M–H–C} interactions.[6] The non-agostic contributions to the metal-to-ligand bonding could be either σ or π in nature and they are, in general, responsible for the location of the agostic H atom within reach of the coordination sphere of the metal atom. Thus, agostic {M–H–C} bonding interactions have been always supported by other metal–ligand interactions as seen in Chart 2. In the case of the ferradicarbaborane **1** there is no extra metal–ligand framework support of the {Fe–H–B} interaction. Lack of a supporting framework is also observed in other reported compounds such as [12-{$Fe(CO)_2(\eta^5$-$C_5H_5)$}-*closo*-1-$CB_{11}H_{12}$], **8**,[25] [12-{$Mo(CO)_3(\eta^5$-$C_5H_5)$}-*closo*-$CB_{11}H_{12}$], **14**,[28] and [$Re(CO)_3(\eta^5$-(μ-H)-*exo*-{$Ru(CO)_2(\eta^5$-$C_5H_5)$}-7,8-$C_2B_9H_{10}$], **15**.[30] Hence it might be more reasonable to describe the {Fe–H–B} bonding in **1** simply as a three-centre–two-electron bond rather than as agostic, and also similarly so to describe the {M–H–B} bonding in compounds **8**, **14** and, possibly, **15**. The differences in interatomic distances and angles among **1**, **8**, **14** and **15**, would be due to the different strengths of the interactions within the {M–H–B} linkages. It may be noted that in compounds **1**, **8** and **14**, the M–H–B angles are always more than 90° but less than 180°, being 113(1), 141.1(8) and 152(2)°, respectively, and the B–H distances are 1.25(2), 1.18(2) and 1.18(3) Å, respectively, reflecting the strength of the metal involvement with the H–B bonds.

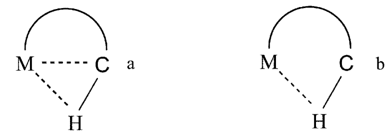


Chart 2

In the context of the above discussion there are some examples of metallaborane compounds for which the agostic description could in fact be regarded as more suitable. These are usually small metallaborane *arachno* or *hypho* cluster compounds such as [{$Fe(CO)(\eta^5$-$C_5H_5)$}$B_3H_7PPh_2$], **18**, which contains a {Fe–H–B} linking unit supported by a {B–P–Fe} strong ligand-to-metal grouping,[37] or non-cluster iron–borane complexes, *e.g.* [$Fe(CO)(PMe_3)_2${PhSC(H)=S(BH_3)}], **19**, which contains a {Fe–H–B} linking unit supported by a strong conventional {B–S–Fe} ligand-to-metal linkage.[38] Also it is of interest to note that there are examples of compounds which contain strong Fe–H bonds but very weak H ··· B attractive interactions. They are found in the {C_4B} borole complexes [(η^5-C_5H_5)Fe(H)(η^5-C_4Me_4BPh)] **20** and [(η^5-C_5H_4Me)Fe(H)-2,5-(η^5-$C_4Me_2H_2BPh$)] **21**.[39] In order to accommodate the Fe–H bonds in **20** and **21**, the mean planes containing the borole rings and the cyclopentadienyl rings are no longer parallel, the interplanar angles between the mean planes of the C_5- and C_4B-

rings being 164.3 and 165.2°. The Fe–H distances are typical of iron hydrides at 1.475(23) and 1.47(3) Å, respectively, but there are also weak iron hydride to boron interactions at 1.461(26) and 1.51(3) Å, respectively. In solution the related compound [(η^5-C_5H_5)Fe(H)(η^5-C_4H_4BPh)] establishes an equilibrium between the Fe–H ··· B bonded species and a Fe–H–C bonded agostic isomer. However, the borole complexes for which solid-state structures have been established, might be better described either as eighteen-electron iron organometallic complexes or as *nido* six-atom cluster analogues of B_6H_{10}, with no need to invoke any agostic behaviour, because the H ··· B distances are too long to support a convincing agostic bond description even though the borole ligand is π-bonded to the iron atom.

In conclusion, we would suggest that the term "agostic interaction" is used in metallaborane chemistry only when a weak {M–H–X} bridging linkage is supported by other, non-cluster bonding, metal-ligand interactions. Thus, in compound **1** and similar species, *e.g.* **8** and **14**, we would suggest that the {Fe–H–B} interactions in the solid state are best described as three-centre two-electron bonds and not as agostic interactions. On the other hand, compounds **18** and **19** could be considered as containing agostic {Fe–H–B} interactions. Importantly, whatever the chosen description, the structural details of the compound should be taken into account. Hence the Fe–H ··· B bonds in **20** and **21** would be best described as a terminal iron hydride with a very weak H ··· B interaction.

It is noteworthy that, if the coordinates of the midpoint (X) of the B(9)–H(9) bond in **1** are considered, then the environment of the iron atom in the {$Fe(CO)_2X$} part of **1** is that of a slightly irregular octahedron, with angles C(21)–Fe–C(22), C(21)–Fe–X and C(22)–Fe–X of 93, 94 and 88°, respectively. This observation suggests that the B(9)–H(9) bond functions as a two-electron ligand, interacting with the iron atom to form a three-centre–two-electron Fe–H–B bond and thereby rendering the iron atom an 18-electron centre.

In compound **2**, the donor properties of the arsenic atoms are clearly superior to those of the B–H bonds and therefore iron-arsenic coordination is preferred with the arsenic atom acting as a more straightforward two-electron donor.

Photolysis of [9-{$Fe(CO)_2$(η^5-C_5H_5)}-*nido*-7,8-$C_2B_9H_{12}$] 1

As part of this work, we also report here that photolysis of compound **1** in tetrahydrofuran afforded the paramagnetic ferracarbaborane [3-(η^5-C_5H_5)-*closo*-3,1,2-$FeC_2B_9H_{11}$] **5** in 85% yield. Overall, from [$Fe(CO)_2(C_6H_{10})$(η^5-C_5H_5)][PF_6] and the caesium salt of [*nido*-7,8-$C_2B_9H_{12}$]$^-$, the yield is 77%. Previously, the preparation of **5** had been reported from the reaction of an equimolar mixture of [C_5H_5]$^-$ and [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ **6** with [$FeCl_2$] in tetrahydrofuran at reflux temperature, followed by air oxidation,[4] but the yield was lower at 25%. Compound **5** has previously been structurally characterised by a single-crystal X-ray diffraction analysis.[5]

The photolytic conversion of **1** to **5** is complex, and in the process in THF solution, **1** appears to lose two CO groups and a hydrogen atom (or, possibly, one CO and one HCO radical). Photochemical decarbonylation reactions are well known in the chemistry of compounds containing the {$Fe(CO)_2$(η^5-C_5H_5)} group. These include ferraboranes,[37,40] for example the {B_5}-based cluster [2-{$Fe(CO)_2$(η^5-C_5H_5)}-*nido*-B_5H_8] **9** is reported to afford the six-vertex {FeB_5}-based cluster [2-(η^5-C_5H_5)-2-(CO)-2-*nido*-FeB_5H_8] **22** when photolysed in THF solution.[40] It is also noteworthy that photolysis of [2-{$Fe(CO)_2$(η^5-C_5H_5)}-*nido*-B_5H_8] **9** in pentane solution produces [$Fe(CO)_2$(η^5-C_5H_5)]$_2$ as the only soluble product. It is well known that the {$Fe(CO)_2$-(η^5-C_5H_5)} radical is a common initial photogenerated product from {$Fe(CO)_2$(η^5-C_5H_5)}-containing species and that THF is a radical-supporting solvent which sometimes becomes involved in the radical reactions. An example of this is observed in the photolysis of [6-{$Fe(CO)_2$(η^5-C_5H_5)}-*nido*-$B_{10}H_{13}$], in THF affording [1-(THF)-2-(η^5-C_5H_5)-*closo*-2,1-$FeCB_{10}H_{10}$].[41] In this general area, a reaction that is perhaps more similar to the conversion of **1** into **5** is the photolysis *in vacuo* of [μ-{$Fe(CO)_2$(η^5-C_5H_5)}-*nido*-2,3-$C_2B_4H_7$] **23**.[42,43] Two products are isolatable in approximately equal amounts: *viz.* diamagnetic orange [1-(η^5-C_5H_5)-1-(H)-*closo*-1,2,3-$FeC_2B_4H_6$], **24**, which from ^{1}H NMR spectroscopic evidence contains an Fe–H bond, and brown paramagnetic [1-(η^5-C_5H_5)-*closo*-1,2,3-$FeC_2B_4H_6$], **25**. Compounds **24** and **25** can be interconverted by acid–base and redox processes: thus, reaction of **24** with Na[H] followed by oxidation with air afforded **25**, whereas the conversion of **25** to **24** can be achieved by initial reaction with sodium amalgam then gaseous HCl. Hence, it appears that the conversion of **24** into **25** can occur either directly during photolysis or in steps. In our present work, we would propose that the photolytic conversion of [9-{$Fe(CO)_2$(η^5-C_5H_5)}-*nido*-7,8-$C_2B_9H_{12}$] **1** into [3-(η^5-C_5H_5)-*closo*-3,1,2-$FeC_2B_9H_{11}$] **5** may occur *via* the loss of two CO groups and subsequent transfer of a hydrogen atom onto the iron center as in **24**. It is not clear how the hydrogen atom is removed form this site but it seems unlikely that {$Fe(CO)_2$(η^5-C_5H_5)} radicals are involved significantly in hydrogen-atom removal since the yield of **5** is 85%.

Experimental

General procedures

All preparative experiments and crystallisation were carried out in an inert atmosphere. [$Fe(CO)_2(C_6H_{10})$(η^5-C_5H_5)][PF_6],[44] the caesium salt of [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion **6**,[45] and the [Me_4N]$^+$ salt of [*nido*-7,8-$As_2B_9H_{10}$]$^-$ anion **7**[46] were prepared by literature methods. Infrared spectra of compounds **1**–**5** were recorded from a KBr disk on a Perkin-Elmer Paragon FT-IR spectrometer. Carbon and hydrogen analyses were performed at University College Cork.

NMR spectra were recorded on Bruker ARX 250 and DRX 500 spectrometers, using ^{11}B, ^{11}B-{^{1}H(broadband)}, ^{1}H, ^{1}H-{^{11}B(broadband)}, ^{1}H-{^{11}B(selective)}, [^{11}B–^{11}B]-COSY]-{^{1}H} and [^{1}H–^{1}H]-COSY-{^{11}B} techniques in combined analytical procedures as described previously.[13] Chemical shifts δ are expressed in parts per million (ppm) to high frequency (low field) relative to Ξ 100 MHz for ^{1}H (nominally internal $SiMe_4$) and Ξ 32.083972 MHz for ^{11}B (nominally internal [$BF_3(OEt_2)$]), using deuterated solvent ^{2}D resonances as internal secondary standards. Splittings arising from couplings $J(^{11}B–^1H)$ are taken from resolution-enhanced (line-narrowed) ^{11}B spectra with digital resolution 4 Hz. For broadened ^{11}B resonances, the splitting observed will be smaller than the coupling constant $J(^{11}B–^1H)$ from which the splitting arises. Mössbauer spectroscopy was performed at 77 K on an apparatus which has been described previously.[47] The spectrum was fitted to a symmetric quadrupole doublet by using standard least-squares fitting procedures. Chemical isomer shift (δ) and quadrupole nuclear splitting (ΔE_Q) are expressed in millimetres per second (mm s^{-1}), relative to natural α-iron foil.

Synthesis of [9-{$Fe(CO)_2$(η^5-C_5H_5)}-*nido*-7,8-$C_2B_9H_{12}$] 1. To a solution of [$Fe(CO)_2(C_6H_{10})$(η^5-C_5H_5)][PF_6] (100 mg, 0.25 mmol) in acetone (10 mL) was added a solution of Cs[*nido*-7,8-$C_2B_9H_{12}$] (66 mg, 0.25 mmol) in acetone (10 mL). The reaction mixture was heated at reflux temperature for 1 h, cooled and filtered. The solvent was removed under reduced pressure. The mixture was dissolved in CH_2Cl_2 and subjected to preparative TLC(80 : 20 CH_2Cl_2–C_6H_{14}). The single major component was extracted into CH_2Cl_2 and crystallised from CH_2Cl_2–heptane, affording crystalline compound **1** as orange plates (71 mg, 91.0%) (Found: C, 34.9; H, 5.5. $C_9H_{17}B_9FeO_2$ requires C, 34.8; H 5.5%). IR (KBr): ν_{max} 2552(s, sh)(BH), 2521(s, br)(BH), 2059(vs)(CO), 2008(vs, sh)(CO) cm^{-1}. ^{11}B and ^{1}H NMR data for directly bound BH units (CD_2Cl_2, 300 K) {ordered as: assignment $\delta(^{11}B)$/ppm [(^1H)/ppm] ⟨splitting from $^1J(^{11}B–^1H)$/Hz⟩ where measurable}: BH(5) −1.7 [+1.95] ⟨129⟩, BH(3) −9.7 [+2.18] ⟨147⟩, BH(11) −16.9 [*ca.* +1.75], BH(2) −17.3 [*ca.* +1.75], BH(6) −21.4 [+1.18] ⟨135⟩, BH(4) −24.1 [+0.87], BH(10) −24.7 [+0.46], BH(1) −33.7 [+0.96] ⟨148⟩ and BH(9) −35.2 [−12.9] ⟨103⟩. Additional data are as follows: $\delta(^1H)$(carbaborane CH) +7.22 and +7.51, $\delta(^1H)(C_5H_5)$ +4.20, $\delta(^1H)$(μ-10,11-H) −3.33.

Photolysis of [9-{Fe(CO)$_2$(η^5-C$_5$H$_5$)}-*nido*-7,8-C$_2$B$_9$H$_{12}$] 1. An orange solution of compound **1** (60 mg, 0.19 mmol) in tetrahydrofuran (20 mL) was irradiated at room temperature for 12 h using a standard 60 W tungsten-filament light bulb placed 10 cm from the reaction flask. The resultant purple solution was filtered and the solvent removed under reduced pressure. The mixture was dissolved in CH_2Cl_2 and subjected to preparative TLC (60 : 40, CH_2Cl_2–C_6H_{14}). The major component was extracted into CH_2Cl_2 and crystallised from benzene–cyclohexane affording crystalline [3-(η^5-C$_5$H$_5$)-*closo*-3,1,2-FeC$_2$-B$_9$H$_{11}$] **5** as purple needles (41 mg, 85.4%) (Found: C, 32.5; H, 2.9. $C_7H_{16}B_9Fe$ requires C, 33.2; H, 6.4%). IR (KBr): ν_{max} 2593(w)(BH), 2538(s, br)(BH) cm^{-1}. ^{11}B-{^1H} NMR ($CDCl_3$, 300 K) {ordered as: $\delta(^{11}B)$/ppm (peak shape and relative intensity) [splitting from $J(^{11}B–^1H)$/Hz]}: *ca.* +122 (d, 1 B) [125], *ca.* +9 (s, 2 B) [105], *ca.* 0 (s, 2 B) [136], *ca.* −90 (s, 1 B) [127], *ca.* −455 (br, 2 B) and *ca.* −513 (br, 1 B).

Synthesis of [7-{Fe(CO)$_2$(η^5-C$_5$H$_5$)}-*nido*-7,8-As$_2$B$_9$H$_{10}$] 2. To a suspension of [Fe(CO)$_2$(C$_6$H$_{10}$)(η^5-C$_5$H$_5$)][PF$_6$] (0.07 g, 0.17 mmol) in CH_2Cl_2 (5 mL) was added a suspension of [Me$_4$N]-[*nido*-7,8-As$_2$B$_9$H$_{10}$] (0.063 g, 0.19 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 7 h. The solution was concentrated under reduced pressure and subjected to preparative TLC (100% CH_2Cl_2). The major component was extracted into CH_2Cl_2 and crystallised from CH_2Cl_2–heptane affording crystals of compound **2** as red blocks (60 mg, 81.3%) (Found: C, 19.7; H, 3.7. $C_7H_{15}As_2B_9FeO_2$ requires C, 19.4; H 3.5%). IR (KBr): ν_{max} 2539(m, sh)(BH), 2527(s, br)(BH), 2039(vs)(CO), 1993(vs, sh)(CO) cm^{-1}. ^{11}B and ^1H NMR data for directly bound BH units (CD_2Cl_2, 300 K) {ordered as: assignment $\delta(^{11}B)$/ppm [$\delta(^1H)$/ppm] ⟨splitting from $^1J(^{11}B–^1H)$/Hz⟩ where measurable}: BH(5) +10.7 [+3.86] ⟨144⟩, BH(9) +8.6 [+3.59] ⟨156⟩, BH(6) −4.0 [+2.69] ⟨152⟩, BH(11) −5.8 [+2.34] ⟨190⟩, BH(3) −7.8 [+2.73] ⟨163⟩, BH(10) −15.3 [+1.92] ⟨123⟩, BH(2) *ca.* −16.3 [+2.14], BH(4) *ca.* −16.3 [+1.74], BH(1) −28.3 [+2.40] ⟨150⟩. Additional data were as follows: $\delta(^1H)(C_5H_5)$ +4.80, $\delta(^1H)$(μ-H(10,11)) −4.40.

Synthesis of [7-{Mo(CO)$_2$(η^7-C$_7$H$_7$)}-*nido*-7,8-As$_2$B$_9$H$_{10}$] 3. To a suspension of [Mo(CO)$_3$(η^7-C$_7$H$_7$)][BF$_4$] (60 mg, 0.17 mmol) in CH_2Cl_2 (5 mL) was added a suspension of [Me$_4$N]-[*nido*-7,8-As$_2$B$_9$H$_{10}$] **3** (63 mg, 0.19 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 24 h. The solution was concentrated under reduced pressure and subjected to preparative TLC (100% CH_2Cl_2). The major component was extracted into CH_2Cl_2 and recrystallised from CH_2Cl_2–heptane affording crystals of [7-{Mo(CO)$_2$(η^7-C$_7$H$_7$)}-*nido*-7,8-As$_2$B$_9$H$_{10}$] **3** as red blocks (59 mg, 69%) (Found: C, 21.8; H, 3.5. $C_9H_{17}As_2B_9MoO_2$ requires C, 21.6; H, 3.4%). IR (KBr): ν_{max} 2526(m, sh)(BH), 2517(s)(BH), 2002(vs)(CO), 1956(vs, sh)(CO) cm^{-1}. ^{11}B and ^1H NMR data for directly bound BH units (CD_2Cl_2, 300 K) {ordered as: assignment $\delta(^{11}B)$/ppm [δ (^1H)/ppm] ⟨splitting from $^1J(^{11}B–^1H)$/Hz⟩ where measurable}: BH(5) +9.3 [+3.66] ⟨140⟩, BH(9) +6.5 [+3.45] ⟨146⟩, BH(6) −4.6 [+2.60] ⟨156⟩, BH(11) −6.3 [+2.22] ⟨153⟩, BH(3) −7.0 [+2.64] ⟨160⟩, BH(2) *ca.* −15.5 [+2.08], BH(10) *ca.* −15.5 [+1.75], BH(4) *ca.* −15.5 [+1.62], BH(1) −27.9 [+2.24] ⟨148⟩. Additionally: $\delta(^1H)(C_7H_7)$ +5.63, $\delta(^1H)$(μ-H(10,11)) −3.90.

Synthesis of [7-{W(CO)$_2$(η^7-C$_7$H$_7$)}-*nido*-7,8-As$_2$B$_9$H$_{10}$] 4. To a suspension of [W(CO)$_3$(η^7-C$_7$H$_7$)][BF$_4$] (75 mg, 0.17 mmol) in CH_2Cl_2 (15 mL) was added a suspension of [Me$_4$N][*nido*-7,8-As$_2$B$_9$H$_{10}$] **3** (56 mg, 0.17 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 4 days. The solution was concentrated under reduced pressure and subjected to preparative TLC (100% CH_2Cl_2). The major component was extracted into CH_2Cl_2 and recrystallised from CH_2Cl_2–heptane, affording crystals of [7-{W(CO)$_2$(η^7-C$_7$H$_7$)}-*nido*-7,8-As$_2$B$_9$H$_{10}$] **4** as dark red blocks (42 mg, 42.4%) (Found: C, 18.7; H, 3.1. $C_9H_{17}As_2B_9O_2W$ requires C, 18.4; H, 2.9%). IR (KBr): ν_{max} 2524(m)(BH), 2520(s, sh)(BH), 1992(vs)(CO), 1938(vs)(CO) cm^{-1}. ^{11}B and ^1H NMR data for directly bound BH units (CD_2Cl_2, 300 K) {ordered as: assignment $\delta(^{11}B)$/ppm [δ (^1H)/ppm] ⟨splitting from $^1J(^{11}B–^1H)$/Hz⟩ where measurable}: BH(5) +9.1 [+3.64] ⟨140⟩, BH(9) +5.7 [+3.51] ⟨145⟩, BH(6) −4.8 [+2.60] ⟨150⟩, BH(3) *ca.* −6.8 [+2.74], BH(11) *ca.* −6.8 [+2.26,], BH(10) −15.3 [+1.75] ⟨155⟩, BH(2) *ca.* −16.0 [+2.21], BH(4) *ca.* −16.0 [+1.77], BH(1) −28.0 [+2.26] ⟨149⟩. Additionally: δ ($^1H)(C_7H_7)$ +5.59, $\delta(^1H)$(μ-H(10,11)) −3.92.

Structure determinations of [9-{Fe(CO)$_2$(η^5-C$_5$H$_5$)}-*nido*-7,8-C$_2$B$_9$H$_{12}$] 1, [7-{Fe(CO)$_2$(η^5-C$_5$H$_5$)}-*nido*-7,8-As$_2$B$_9$H$_{10}$] 2 and [7-{Mo(CO)$_2$(η^7-C$_7$H$_7$)}-*nido*-7,8-As$_2$B$_9$H$_{10}$] 3

Data for all three structures were collected with a CAD4 diffractometer; structure solution used NRCVAX[48] and refinement was with SHELXL-97[49] PLATON[50] was used for the molecular graphics.

CCDC reference numbers 200271–200273.

See http://www.rsc.org/suppdata/dt/b3/b306776a/ for crystallographic data in CIF or other electronic format.

Crystal data

[9-{Fe(CO)$_2$(η^5-C$_5$H$_5$)}-*nido*-7,8-C$_2$B$_9$H$_{12}$], 1. $C_9H_{17}B_9FeO_2$, M = 310.38, triclinic, space group $P\bar{1}$, Z = 2, a = 6.8776(4), b = 9.9354(5), c = 11.7304(13) Å, α = 86.065(6), β = 78.903(8), γ = 74.073(5)°, U = 756.27(10) Å^3, D_c = 1.363 g cm^{-3}, $F(000)$ = 316, λ(Mo-Kα) = 0.71073 Å, μ = 0.986 mm^{-1}, T = 294 K, R = 0.0245 for 3133 data with $I > 2\sigma(I)$, $R_w(F^2)$ = 0.0653 for all 3455 unique reflections.

[7-{Fe(CO)$_2$(η^5-C$_5$H$_5$)}-*nido*-7,8-As$_2$B$_9$H$_{10}$], 2. $C_7H_{15}As_2B_9FeO_2$, M = 434.19, monoclinic, space group $P2_1/n$, Z = 4, a = 10.7338(9), b = 12.1033(11), c = 13.3083(17) Å, β = 111.132(10)°, U = 1612.7(2) Å^3, D_c = 1.728 g cm^{-3}, $F(000)$ = 805, λ(Mo-Kα) = 0.71073 Å, μ = 4.997 mm^{-1}, T = 293 K, R = 0.0488 for 2404 data with $I > 2\sigma(I)$, $R_w(F^2)$ = 0.1431 for all 3509 unique reflections.

[7-{Mo(CO)$_2$(η^7-C$_7$H$_7$)}-*nido*-7,8-As$_2$B$_9$H$_{10}$], 3. $C_9H_{17}As_2B_9MoO_2$, M = 500.30, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 11.6069(14), b = 10.8092(14), c = 14.188(2) Å, U = 1780.0(4) Å^3, D_c = 1.867 g cm^{-3}, $F(000)$ = 960, λ(Mo-Kα) = 0.71073 Å, μ = 4.422 mm^{-1}, T = 294 K, R = 0.0435 for 3191 data with $I > 2\sigma(I)$, $R_w(F^2)$ = 0.1106 for all 3871 measured data.

During the structure solution of **1** all hydrogen atoms were visible in the difference maps; a plot showing the hydrogen atom bridging the Fe1 and B(9} atoms is with the supplementary material. The two hydrogen atoms involved in bridging, *viz.* H(9) to B(9) and Fe(1), and H(10,11) to B(10) and B(11), were allowed freely to refine isotropically. Hydrogen atoms bonded to C(7), C(8), B(10) and B(11) were positioned at coordinates obtained from a difference map and were not refined. All other hydrogen atoms were treated as riding atoms using the SHELXL defaults (AFIX 43 for cyclopentadienyl hydrogen atoms (C–H 0.93 Å) and AFIX 153 for the hydrogen atoms bonded to B(1)–B(6) (B–H 1.10 Å)).

For **2** it soon became apparent that there was considerable disorder present in the structure; all atoms except those of the

$\{Fe(CO)_2\}$ moiety were disordered. A quasi-toroidal electron-density distribution found for the cyclopentadiene unit was consistent with the atoms of this ring system being equally disordered over two sets of sites; in the subsequent refinement process, the atoms were constrained to be planar pentagons with standard geometry. It was evident that the arsenic atom bonded to iron was disordered unequally over two adjacent locations and that the diarsenaborane cage was grossly disordered unequally over at least three orientations that occupied substantially the same volume element in the crystal lattice. After many trial refinements using combinations of DFIX restraints available in SHELXL-97, the best diarsenaborane cage models had overall occupancies of 0.811(3) and 0.189(3) for the two arsenic atoms bonded to iron. Because of the disorder no hydrogen atoms were visible in difference maps; those hydrogen atoms whose coordinates could be assigned on the basis of known geometry (using the HFIX options in SHELXL-97) were included in the refinement cycles as riding atoms. The boron atoms of the minor diarsenaborane cage were only allowed isotropic motion; all other non-hydrogen atoms were refined anisotropically.

In the crystal of **3** that was analysed, the molecules were packed in such a way that in each molecule the coordinates of the metal-based $\{Mo(CO)_2(\eta^7\text{-}C_7H_7)\}$ unit remain identical, whereas the arsenic atoms are disordered over four sites. There were two distinct orientations of the $\{As_2B_3\}$ open face with an occupancy ratio of 2 : 1. In the major orientation, which has the metal attached at As(7), arsenic occupancy was observed in the two positions adjacent to the metallated arsenic atom, affording an asymmetric unit containing both the enantiomers *C*-[7-$\{Mo(CO)_2(\eta^7\text{-}C_7H_7)\}$-*nido*-7,8-$As_2B_9H_{10}$] and *A*-[7-$\{Mo(CO)_2(\eta^7\text{-}C_7H_7)\}$-*nido*-7,8-$As_2B_9H_{10}$], with the former predominating (78%). Important interatomic distances and angles for the principal orientation of [7-$\{Mo(CO)_2(\eta^7\text{-}C_7H_7)\}$-*nido*-7,8-$As_2B_9H_{10}$] are given in the legend of Fig. 3

Acknowledgements

Thanks are due to EPSRC (UK) (J. D. K.) for funds for instrumentation and UCC for support to G. O'R.

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