Reactivity of *nido*-[2-{Fe(η-C_5H_5)}B_5H_{10}] with Some Transition-metal Hydride Complexes *

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The reaction of *nido*-[2-{Fe(η-C_5H_5)}B_5H_{10}] with [Mo(PMe_2Ph)$_4H_4$] gave capped-*closo*-[1-{Fe(η-C_5H_5)}-2-{Mo(PMe_2Ph)$_3$H}B_5H_7] which has been characterised by X-ray crystallography as well as by ^{11}B and ^1H NMR spectroscopy. The structure determination [monoclinic, space group $P2_1/c$, a = 15.586(5), b = 11.523(4), c = 19.186(4) Å, β = 106.23(2)°] reveals a capped-*closo* geometry with one Fe–Mo–B face being capped by a boron atom and the other having a triply bridging hydrogen atom. The isostructural tungsten compound capped-*closo*-[1-{Fe(η-C_5H_5)}-2-{W(PMe_3)$_3$H}B_5H_7] was similarly prepared from [W(PMe_3)$_3H_6$] and *nido*-[2-{Fe(η-C_5H_5)}B_5H_{10}]. Reaction between [Re(PMe_3)$_5$H] and *nido*-[2-{Fe(η-C_5H_5)}B_5H_{10}] gave a mixture of *nido*-[2-{Re(PMe_3)$_3$}B_5H_{10}] and the salt [Re(PMe_3)$_5H_2$]$^+$[*nido*-2-{Fe(η-C_5H_5)}B_5H_9]$^-$, a product of an acid–base reaction.

The reaction of boranes with a wide variety of transition-metal compounds has led to a diverse range of structurally characterised metallaboranes with polyhedral cage structures.[1] However, there are relatively few studies of the reactivity of metallaboranes. Some metallaboranes have been used as synthons in the stepwise synthesis of heterometallaboranes (or polymetallaboranes) by further reaction with metal complexes: these studies have been limited mainly to reactions between transition-metal chlorides and the larger, more stable metallaborane anions.[2–14] Here we describe studies on the reactions of the ferraborane *nido*-[2-{Fe(η-C_5H_5)}B_5H_{10}].

Results and Discussion

The ferraborane *nido*-[2-{Fe(η-C_5H_5)}B_5H_{10}] was first reported by Weiss and Grimes[15] from the reaction of Na(C_5H_5) and B_5H_9 with $FeCl_2$, however the isolated yield was low. A recent alternative synthesis from the reaction between [Fe(η-C_5H_5)(PMe_3)$_2$H] and B_5H_9 has been described by Kelland[16] which allows this compound to be prepared conveniently in gram quantities.

Treatment of *nido*-[2-{Fe(η-C_5H_5)}B_5H_{10}] with [Mo(PMe_2Ph)$_4H_4$] in toluene gave capped-*closo*-[1-{Fe(η-C_5H_5)}-2-{Mo(PMe_2Ph)$_3$H}B_5H_7] **1** as large cubic crystals. The crystal structure of **1** has been determined. The molecular structure is shown in Fig. 1, selected bond lengths and angles in Table 1, and fractional atomic coordinates in Table 2. All hydrogen atoms on the metallaborane cage were successfully located from Fourier-difference maps. The structure consists of a distorted capped-*closo* seven-vertex metallaborane. The Fe(η-C_5H_5) group occupies an apical position (1) with the Mo(PMe_2Ph)$_3$H group in an adjacent basal position (2). The Mo–Fe–B(3) face of the octahedral core is capped by B(123), and there is a hydrogen atom [H(1232)] bridging the B(123)–Mo(2) vector. A further interesting structural feature is the presence of a triply bridging hydrogen atom [H(1250)] over the Fe(1)–Mo(2)–B(5) face. Compound **1** was fully characterised by ^{11}B, ^1H and ^{31}P NMR spectroscopy and elemental analysis; the data are consistent with the molecular structure. The spectroscopic and analytical data characterising **1** and the other new compounds reported are presented in Table 3, and discussion in the text will be restricted to those points of interpretation which might not otherwise be clear. In each case, assignments have been established by consideration of relative chemical shifts, selective and broad-band ^1H-{^{11}B} decoupled spectra, ^1H-{$^{11}B_{broad\ band}$–$^1H_{selective}$} triple resonance

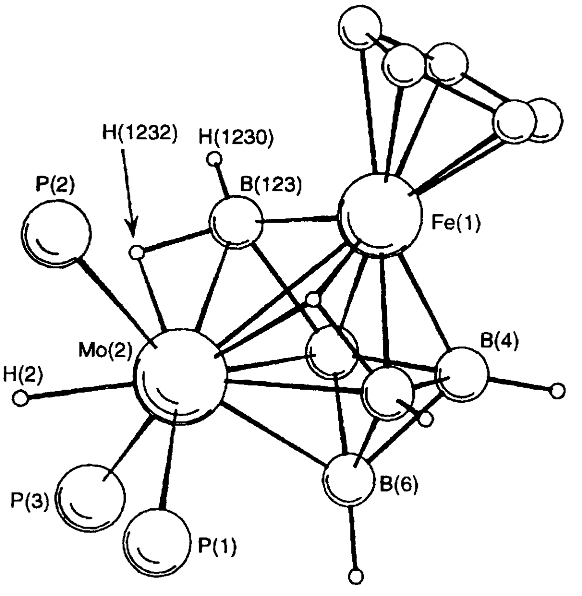

Fig. 1 Molecular structure of capped-*closo*-[1-{Fe(η-C_5H_5)}-2-{Mo(PMe_2Ph)$_3$H}B_5H_7] showing the adopted numbering scheme; the phosphine methyl and phenyl groups and organic hydrogen atoms are omitted for clarity

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Selected bond lengths (Å) and angles (°) for capped-*closo*-[1-{Fe(η-C_5H_5)}-2-{Mo($PMe_2Ph)_3$H}B_5H_7] **1**; estimated standard deviations are given in parentheses

Mo(2)–Fe(1)	2.822(1)	Mo(2)–B(123)	2.261(3)	B(3)–B(6)	1.748(4)	B(4)–B(5)	1.730(5)
Fe(1)–B(123)	1.996(3)	B(123)–B(3)	1.796(5)	B(4)–B(6)	1.698(4)	B(5)–B(6)	1.731(4)
Fe(1)–B(4)	2.024(3)	Fe(1)–B(3)	2.142(3)	Fe(1)–H(1250)	1.66(3)	Mo(2)–H(2)	1.739(9)
Mo(2)–B(3)	2.349(3)	Fe(1)–B(5)	2.176(3)	Mo(2)–H(1232)	1.81(3)	Mo(2)–H(1250)	1.95(3)
Mo(2)–B(6)	2.253(3)	Mo(2)–B(5)	2.443(3)	B(3)–B(4)	1.721(4)		
B(3)–Fe(1)–Mo(2)	54.43(8)	B(4)–Fe(1)–Mo(2)	80.51(9)	B(6)–B(3)–Mo(2)	64.8(1)	B(6)–B(3)–B(4)	58.6(2)
B(4)–Fe(1)–B(3)	48.7(1)	B(5)–Fe(1)–Mo(2)	56.79(8)	B(123)–B(3)–Fe(1)	60.1(1)	B(123)–B(3)–Mo(2)	64.5(1)
B(5)–Fe(1)–B(3)	72.4(1)	B(5)–Fe(1)–B(4)	48.5(1)	B(123)–B(3)–B(4)	122.2(2)	B(123)–B(3)–B(6)	127.7(2)
B(123)–Fe(1)–Mo(2)	52.67(9)	B(123)–Fe(1)–B(3)	51.3(1)	B(3)–B(4)–Fe(1)	69.2(2)	B(5)–B(4)–Fe(1)	70.4(2)
B(123)–Fe(1)–B(4)	100.0(1)	B(123)–Fe(1)–B(5)	106.1(1)	B(5)–B(4)–B(3)	95.3(2)	B(6)–B(4)–Fe(1)	103.3(2)
P(1)–Mo(2)–Fe(1)	124.2(1)	P(2)–Mo(2)–Fe(1)	94.01(2)	B(6)–B(4)–B(3)	61.5(2)	B(6)–B(4)–B(5)	60.7(2)
P(2)–Mo(2)–P(1)	88.15(2)	P(3)–Mo(2)–Fe(1)	126.5(1)	Mo(2)–B(5)–Fe(1)	75.04(9)	B(4)–B(5)–Fe(1)	61.1(2)
P(3)–Mo(2)–P(1)	95.64(2)	P(3)–Mo(2)–P(2)	124.2(1)	B(4)–B(5)–Mo(2)	98.2(2)	B(6)–B(5)–Fe(1)	96.3(2)
B(3)–Mo(2)–Fe(1)	47.87(8)	B(5)–Mo(2)–Fe(1)	48.17(7)	B(6)–B(5)–Mo(2)	62.6(1)	B(6)–B(5)–B(4)	58.8(2)
B(5)–Mo(2)–B(3)	64.3(1)	B(6)–Mo(2)–Fe(1)	69.35(8)	B(3)–B(6)–Mo(2)	70.6(1)	B(4)–B(6)–Mo(2)	106.8(2)
B(6)–Mo(2)–B(3)	44.6(1)	B(6)–Mo(2)–B(5)	43.0(1)	B(4)–B(6)–B(3)	59.9(2)	B(5)–B(6)–Mo(2)	74.3(1)
B(123)–Mo(2)–Fe(1)	44.56(8)	B(123)–Mo(2)–B(3)	45.8(1)	B(5)–B(6)–B(3)	94.3(2)	B(5)–B(6)–B(4)	60.6(2)
B(123)–Mo(2)–B(5)	90.2(1)	B(123)–Mo(2)–B(6)	89.6(1)	Mo(2)–B(123)–Fe(1)	82.8(1)	B(3)–B(123)–Fe(1)	68.6(2)
Mo(2)–B(3)–Fe(1)	77.7(1)	B(4)–B(3)–Fe(1)	62.1(2)	B(3)–B(123)–Mo(2)	69.7(1)	B(123)–H(1232)–Mo(2)	96.1(16)
B(4)–B(3)–Mo(2)	102.1(2)	B(6)–B(3)–Fe(1)	97.0(2)	Mo(2)–H(1250)–Fe(1)	102.7(14)	B(5)–H(1250)–Fe(1)	93.1(16)

Table 2 Fractional atomic coordinates for capped-*closo*-[1-{Fe(η-C_5H_5)}-2-{Mo($PMe_2Ph)_3$H}B_5H_7] **1**; organic hydrogen atoms are excluded

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Fe(1)	0.140 94(3)	0.453 94(4)	0.194 00(2)	C(15)	0.566 2(2)	0.226 9(3)	0.049 6(2)
Mo(2)	0.247 75(1)	0.332 21(2)	0.121 61(1)	C(16)	0.511 0(2)	0.306 7(3)	0.068 4(2)
P(1)	0.350 87(4)	0.164 34(6)	0.176 87(3)	C(17)	0.283 6(2)	0.482 8(3)	−0.028 4(2)
P(2)	0.126 74(4)	0.182 84(6)	0.066 44(4)	C(18)	0.423 7(2)	0.537 3(3)	0.094 0(2)
P(3)	0.347 97(5)	0.417 69(6)	0.057 07(4)	C(19)	0.161 1(2)	0.044 3(2)	0.035 9(1)
B(3)	0.250 6(2)	0.525 3(3)	0.161 4(2)	C(20)	0.158 2(2)	−0.058 6(3)	0.072 4(2)
B(4)	0.263 2(2)	0.508 3(3)	0.252 8(2)	C(21)	0.185 7(2)	−0.162 0(3)	0.048 2(2)
B(5)	0.260 5(2)	0.358 2(3)	0.250 5(2)	C(22)	0.215 8(2)	−0.162 6(3)	−0.012 1(2)
B(6)	0.333 7(2)	0.435 6(3)	0.214 9(2)	C(23)	0.219 5(2)	−0.061 8(3)	−0.048 9(2)
B(123)	0.150 6(2)	0.482 3(3)	0.093 9(2)	C(24)	0.193 1(2)	0.041 4(3)	−0.024 6(2)
C(1)	0.454 9(2)	0.199 8(3)	0.244 8(2)	C(25)	0.081 0(2)	0.559 2(3)	0.254 0(2)
C(2)	0.393 3(2)	0.077 2(2)	0.114 3(2)	C(26)	0.068 9(2)	0.444 5(4)	0.270 1(2)
C(3)	0.307 0(2)	0.046 1(2)	0.222 7(1)	C(27)	0.021 3(2)	0.388 3(4)	0.207 6(2)
C(4)	0.232 9(2)	0.062 4(3)	0.248 0(1)	C(28)	0.003 1(2)	0.470 7(5)	0.150 4(2)
C(5)	0.197 2(2)	−0.028 3(3)	0.278 5(2)	C(29)	0.041 6(2)	0.576 8(4)	0.181 1(2)
C(6)	0.235 0(2)	−0.137 0(3)	0.283 2(2)	H(2)	0.257(2)	0.263(2)	0.043 4(9)
C(7)	0.308 9(2)	−0.154 8(3)	0.259 8(2)	H(3)	0.261(2)	0.609(2)	0.137(1)
C(8)	0.345 3(2)	−0.063 8(3)	0.230 6(2)	H(4)	0.281(2)	0.573(2)	0.298(1)
C(9)	0.057 5(2)	0.240 8(3)	−0.020 0(2)	H(5)	0.272(2)	0.299(2)	0.295(1)
C(10)	0.039 4(2)	0.137 3(3)	0.106 9(2)	H(6)	0.406(1)	0.444(2)	0.230(1)
C(11)	0.423 5(2)	0.322 0(2)	0.026 4(1)	H(1230)	0.111(1)	0.542(2)	0.054(1)
C(12)	0.394 3(2)	0.256 5(3)	−0.036 5(1)	H(1232)	0.166(2)	0.414(2)	0.054(1)
C(13)	0.449 9(2)	0.177 2(3)	−0.056 1(2)	H(1250)	0.189(2)	0.325(2)	0.199(1)
C(14)	0.535 7(2)	0.162 1(3)	−0.012 6(2)				

spectra and [^{11}B-^{11}B]-{^{1}H} correlation spectroscopy (COSY) where indicated.

The reaction of *nido*-[2-{Fe(η-C_5H_5)}B_5H_{10}] with [W($PMe_3)_3H_6$] is remarkably clean and gave only one metallaborane product (^{11}B NMR spectrum) which was isolated as orange-red crystals. The NMR studies identified the product as capped-*closo*-[1-{Fe(η-C_5H_5)}-2-{W($PMe_3)_3$H}-B_5H_7] **2**, a structural analogue of **1**, in which a W($PMe_3)_3$H unit replaces the Mo($PMe_2Ph)_3$H unit (see Scheme 1).

The NMR spectra of **1** and **2** are very similar. The ^{11}B spectra of both compounds consist of five doublets of equal relative intensity, which collapse to singlets in the ^{11}B-{^{1}H} spectra. In each case the highest-frequency doublet (δ 94.3 for **1**, 91.3 for **2**) is significantly broader than the other resonances, and these chemical shifts are consistent with a face-capping boron atom in a metal-rich environment.[17] A ^{11}B–^{11}B COSY 45 spectrum was recorded for the tungsten analogue **2** and shows a number of correlations; the assignment will be discussed below.

The ^{1}H NMR spectra of compounds **1** and **2** show resonances which are assigned to a η-C_5H_5 group attached to the iron atom and PMe_2Ph groups for **1** or PMe_3 groups for **2**. Additionally, seven resonances sharpen in the ^{1}H-{^{11}B} broad-band decoupled spectra on comparison with the ^{1}H spectra and are thus assigned to hydrogens connected to boron nuclei; individual assignments were made using ^{1}H-{^{11}B} selective decoupling experiments. These experiments show that there are five resonances corresponding to the five terminal protons, one on each boron, and two inequivalent M–H–B bridging protons.

Only the assignment of the ^{11}B and ^{1}H-{^{11}B} NMR spectra of compound **2** will be described in any detail, the assignment of the data for **1** being essentially identical. From the relative position of its ^{11}B NMR resonance, the capping boron atom, B(123), can be assigned to the high-frequency doublet at δ 91.3. From ^{11}B–^{11}B COSY this capping boron atom is weakly coupling to one resonance (at δ − 14.9) which can be assigned to B(3), as the W–Fe–B(3) face is capped by B(123). The ^{1}H-{^{11}B} selective-decoupling experiments allow the protons attached to

Table 3 Analytical and spectroscopic data[a]

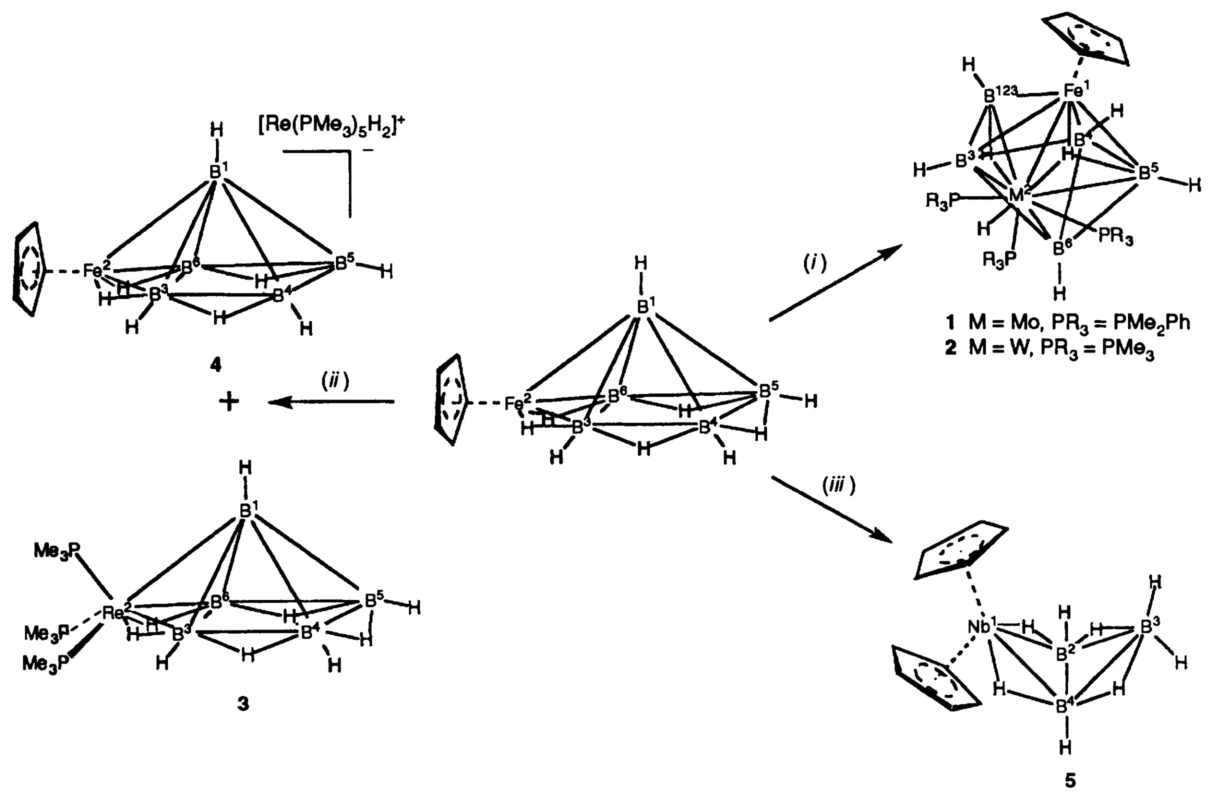
Compound	^{1}H-{^{11}B} NMR	^{11}B and ^{31}P-{^{1}H} NMR
1 *closo*-[1-{Fe(η-C$_5$H$_5$)}-2-{Mo(PMe$_2$Ph)$_3$H}B$_5$H$_7$][b] Dark red C, 50.6 (50.2); H, 6.6 (6.7)	9.22 [s, 1 H, H(4)] 9.12 [t, 1 H, *J*(H^{1230}–H^{1232}) = 12.5, H(1230)] 7.60 [t, 3 H, *J*(H–H) = 8, PPh] 7.44 [t, 3 H, *J*(H–H) = 8, PPh] 7.1, 7.0 (m, 9 H, PPh) 6.30 [t, 1 H, *J*(H–P) = 17, H(6)] 4.42 (s, 5 H, η-C$_5$H$_5$) 4.20 [t, 1 H, *J*(H^5–H^{1250}) = 8, H(5)] 1.52, 1.20, 1.16, 1.12, 1.01, 0.98 [6 × d, 3 H, *J*(H–P) = 8, PMe$_2$] 0.30 [br m, 1 H, H(2)] −0.91 [d, 1 H, *J*(H–P) = 15, H(3)] −8.34 [spt, 1 H, *J* = 12.5, H(1232)] −14.75 [br d, 1 H, *J*(H–P) = 19, H(1250)]	^{11}B: 94.3 [br d, 1 B, B(123)] 79.3 [d, 1 B, *J*(B–H) = 134, B(4)] 63.1 [d, 1 B, *J*(B–H) = 143, B(6)] 15.5 [br d, 1 B, B(5)] −9.0 [d, 1 B, *J*(B–H) = 126, B(3)] ^{31}P-{^{1}H}: 22.6 [dd, 1 P, *J*(P–P) = 25, 25] 6.5 [d, 2 P, *J*(P–P) = 25]
2 *closo*-[1-{Fe(η-C$_5$H$_5$)}-2-{W(PMe$_3$)$_3$H}B$_5$H$_7$] Orange-red *m/z* = 595 [*P*]$^+$ C, 28.2 (28.25); H, 6.6 (6.8)	10.10 [s, 1 H, H(4)] 9.86 [t, 1 H, *J*(H^{1230}–H^{1232}) = 12, H(1230)] 6.57 [t, 1 H, *J*(H–P) = 15, H(6)] 4.90 (s, 5 H, η-C$_5$H$_5$) 3.94 [t, 1 H, *J*(H^5–H^{1250}) = 9, H(5)] 1.45 [d, 9 H, *J*(H–P) = 8, PMe$_3$] 1.30 [d, 9 H, *J*(H–P) = 8, PMe$_3$] 1.16 [d, 9 H, *J*(H–P) = 8, PMe$_3$] −0.14 [ddd, 1 H, *J*(H–P) = 32, 53, 42, H(2)] −1.00 [d, 1 H, *J*(H–P) = 15, H(3)] −9.14 [spt, 1 H, *J* = 12, H(1232)] −14.97 [dd, 1 H, *J*(H^{1250}–H^5) = 10, *J*(H–P) = 15, H(1250)]	^{11}B: 91.3 [br d, 1 B, *J*(B–H) = 150, B(123)] 78.4 [d, 1 B, *J*(B–H) = 146, B(4)] 56.9 [d, 1 B, *J*(B–H) = 143, B(6)] 4.3 [d, 1 B, *J*(B–H) = 142, B(5)] −14.9 [d, 1 B, *J*(B–H) = 131, B(3)] ^{31}P-{^{1}H}:[c] −28.5 [dd, *J*(P–P) = 21, 26, *J*(P–W) = 191] −40.3 [dd, *J*(P–P) = 22, 26, *J*(P–W) = 174] −42.8 [dd, *J*(P–P) = 21, 22, *J*(P–W) = 140]
3 *nido*-[2-{Re(PMe$_3$)$_3$}B$_5$H$_{10}$] Yellow-orange *m/z* = 479 C, 23.0 (22.6); H, 8.2 (7.8)	7.47 [br s, 2 H, H(3) and H(6)] 4.17 [br s, 2 H, H(4) and H(5)] 1.28 [d, 27 H, *J*(H–P) = 8, 3PMe$_3$] 0.71 [br s, 2 H, H(3,4) and H(5,6)] −0.27 [br s, 1 H, H(1)] −1.45 [br s, 1 H, H(4,5)] −10.52 [br s, 2 H, H(2,6) and H(2,3)]	^{11}B: 48.2 [br d, 2 B, *J*(B–H) = 137, B(3), B(6)] −3.6 [d, 2 B, *J*(B–H) = 138, B(4), B(5)] −52.5 [d, 1 B, *J*(B–H) = 129, B(1)] ^{31}P-{^{1}H}: −33.7 (br s)
4 [Re(PMe$_3$)$_5$H$_2$]$^+$[*nido*-2-{Fe(η-C$_5$H$_5$)B$_5$H$_9$]$^-$ [d] Orange-brown oil	6.46 [s, 2 H, H(3) and H(6)] 3.93 (s, 5 H, η-C$_5$H$_5$) 3.77 [s, 2 H, H(4) and H(5)] 1.73 [d, 45 H, *J*(H–P) = 8, 5PMe$_3$] −1.10 [s, 1 H, H(1)] −4.53 [s, 2 H, H(3,4) and H(5,6)] −7.46 [sxt, 2 H, *J*(H–P) = 29, Re–H] −18.01 [s, 2 H, H(2,3) and H(2,6)]	^{11}B: 40.6 [d, 2 B, *J*(B–H) = 125, B(3) and B(6)] 15.5 [d, 2 B, *J*(B–H) = 106, B(4) and B(5)] −42.4 [d, 1 B, *J*(B–H) = 144, B(1)]

[a] Unless otherwise stated, all NMR spectroscopic data (*J* in Hz) are at room temperature in C$_6$D$_6$, mass spectral data are electron impact and only the parent-ion mass is given and elemental analyses (%) are the best results from two independent determinations. [b] The NMR data are in [^{2}H$_8$]toluene at room temperature, except for ^{31}P at 200 K. [c] In [^{2}H$_8$]toluene at 240 K. [d] All NMR data are in [^{2}H$_8$]tetrahydrofuran.

B(3) and B(123) to be assigned; H(3) is at δ −1.00 and H(1230) at δ 9.86. Triple-resonance experiments show that H(1230) is coupled to the M–H–B resonance at δ −9.14, this resonance is thus assigned to the bridging hydrogen H(1232). The ^{11}B–^{11}B COSY spectrum shows that B(3) is coupled to two resonances which are thus assigned to B(4) and B(6), but it is not possible unambiguously to assign each of these. By process of elimination, the remaining ^{11}B resonance at δ 4.3 is assigned to B(5). The selective-decoupling experiments show that the ^{1}H resonance at δ 3.94 can be assigned to H(5); in turn the triple-resonance experiments show that H(5) is coupled to H(1230). The ^{1}H resonance at δ −0.14 can be assigned to the W–H hydride, and the triple-resonance experiments in turn show that this resonance is coupled to the B–H resonance at δ 6.57. By elimination the resonance at δ 6.57 can be assigned to H(6), and it follows from the ^{1}H-{^{11}B} selective-decoupling experiments that the ^{11}B resonance at δ 56.9 is due to B(6). The remaining ^{11}B resonance at δ 78.4 must be due to B(4), and the ^{1}H resonance at δ 10.10 is due to H(4).

Finally, the selective-decoupling experiments enable the resonances at δ −14.75 (Mo) and −14.97 (W) to be assigned to the face-bridging hydrogen atom located in the structural determination. This M$_2$B-bridging proton appears as a doublet of doublets, due to coupling to the *trans* ^{31}P nucleus (*J* = 15 Hz) and coupling to H(5) (*J* = 10 Hz); this latter ^{1}H–^{1}H coupling was confirmed by selective decoupling and irradiation of the H(5) band caused the band due to the M$_2$B-bridging proton to collapse to a doublet. On cooling a [^{2}H$_8$]toluene solution of compound **2** to 200 K the broad W–H resonance at δ −0.14 sharpened to a doublet of doublet of doublets, whilst in the case of **1** the Mo–H resonance at δ 0.30 is partly obscured by the PMe$_2$ signal.

Compounds **1** and **2** have capped-octahedral *closo* structures with two metals occupying adjacent sites in the cluster. A



Scheme 1 (*i*) $[Mo(PMe_2Ph)_4H_4]$, toluene, 65 °C, 54 h, **1**; $[W(PMe_3)_3H_6]$, toluene, 75 °C, 19 h, **2**; (*ii*) $[Re(PMe_3)_5H]$, toluene; (*iii*) $[Nb(\eta\text{-}C_5H_5)_2H_3]$, 20 °C, 15 h, 50 °C, 30 min, column chromatography

skeletal electron count shows that both have seven pairs and are effectively isoelectronic with the hypothetical borane B_7H_7. If the metal centre (W or Mo) can be considered to donate four orbitals and three electrons to the cluster a satisfactory Lewis (valence bond) structure can be drawn.

The closest structural analogue of compounds **1** and **2** is the complex capped-*closo*-$[1,2\text{-}\{Co(\eta\text{-}C_5Me_5)\}_2B_5H_5]$ in which the Co atoms occupy the same positions in the borane cage as do the Fe and Mo(W) atoms in **1**(**2**).[17] Other structural analogues include capped-*closo*-$[1,2,3\text{-}\{Co(\eta\text{-}C_5R_5)\}_3B_4H_4]$ (R = H[18] or Me[17]).

Although a hydrogen atom bridging a M–M–B face is relatively rare, the ability of hydrogen to take part in four-centre three-electron bonds in borane structures is well established. For example, the *closo*-cobaltaboranes $[\{Co(\eta\text{-}C_5Me_5)\}_2B_5H_7]$ and $[\{Co(\eta\text{-}C_5Me_5)\}_2B_4H_6]$[17] exhibit ^1H NMR resonances at δ −14.76 and −13.00 assigned to triply bridging hydrogen atoms. The exact location of these hydrogens was not determined from the crystal structures. We note that the face-bridging hydrogen atoms in **1** and **2** are also found at high field [δ −14.75 (**1**) and −14.97 (**2**)].

The reaction of *nido*-$[2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_{10}]$ with a 2.5 molar excess of $[Re(PMe_3)_5H]$ in toluene gave an orange-brown solution from which an orange oil separated. This oil was soluble in tetrahydrofuran (thf) and has been characterised by ^1H, ^{11}B and ^{31}P NMR spectroscopy as the salt $[Re(PMe_3)_5H_2]^+$[*nido*-$2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_9]^-$ **4**. The orange-brown toluene solution was further purified by chromatography and crystallisation, giving a mixture of long yellow needles and small orange crystals; both types of crystals were identified as *nido*-$[2\text{-}\{Re(PMe_3)_3\}B_5H_{10}]$ **3** by NMR and mass spectroscopy.

The NMR spectroscopic data for compound **3** (Table 3) bears a close resemblance to those of the ferraborane starting material *nido*-$[2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_{10}]$.[15,16] Thus, the ^{11}B NMR spectrum consists of three doublets of relative intensity 2:2:1 which collapse to singlets on proton decoupling. The $^1H\text{-}\{^{11}B\}$ broad-band decoupled spectrum shows six resonances which are not observed in the ^1H spectrum and which are thus assigned to hydrogens on boron. From their relative positions, three of these resonances can be assigned to B–H terminal H atoms [at δ 7.47 (2 H), 4.17 (2 H) and −0.27 (1 H)], two resonances to B–H–B bridging H atoms [at δ 0.71 (2 H) and −1.45 (1 H)] and one resonance is assigned to M–H–B bridging H atoms [at δ −10.52 (2 H)]. The correlation of the Re–H–B ^1H NMR resonance with the ^{11}B NMR signal at δ 48.2 assigns this resonance to B(3) and B(6); H(3) and H(6) are similarly assigned. The high-field ^{11}B resonance at δ − 52.5 is characteristic of an apical boron atom, and the ^1H resonance at δ −0.27 is thus assigned to H(1); the remaining resonances are then assigned by elimination.

No noticeable change was observed in the B–H–B ^1H resonance at δ 0.71 when the ^{11}B frequency of either B(3) or B(6) was selectively irradiated and this result is unexpected. However, there are examples where related crystallographically characterised compounds have shown similar NMR behaviour.[19] It appears that in some cases it is necessary to decouple both ^{11}B nuclei for a B–H–B $^1H\text{-}\{^{11}B\}$ resonance to sharpen; however, experiments involving decoupling of both B(3) and B(6) simultaneously were not performed.

An electron count for $[\{Re(PMe_3)_3\}B_5H_{10}]$ gives eight pairs of electrons and is consistent with a six-vertex *nido* structure.

The ^{11}B NMR spectrum of the salt $[Re(PMe_3)_5H_2]^+$[*nido*-$2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_9]^-$ **4** consists of three doublets of relative intensity 2:2:1, all of which collapse to singlets in the $^{11}B\text{-}\{^1H\}$ broad-band decoupled spectrum. The ^1H NMR spectrum shows a singlet assigned to a cyclopentadienyl group, a doublet assigned to five equivalent trimethylphosphine groups and a sextet (δ −7.46) of relative intensity 2 assigned to two apparently equivalent rhenium hydrides coupling to five phosphorus atoms. In the $^1H\text{-}\{^{11}B\}$ broad-band decoupled NMR spectrum there are five resonances which sharpen relative to the ^1H spectrum; these have been assigned by selective $^1H\text{-}\{^{11}B\}$ decoupling experiments. For the boron cluster, an electron count of eight pairs is consistent with a *nido* six-vertex anion.

The reaction of *nido*-$[2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_{10}]$ with $[Re(PMe_3)_5H]$ gave products markedly different to those of the Group 6 phosphine hydrides. The increased number of trimethylphosphine ligands makes the rhenium complex more basic, and this presumably results in deprotonation of an acidic B–H–B bridging proton from the ferraborane, giving the $[\{Fe(\eta\text{-}C_5H_5)\}B_5H_9]^-$ anion as the $[Re(PMe_3)_5H_2]^+$ salt **4**. The reaction of the electron-rich iridium phosphine hydride $[Ir(PMe_3)_4H]$ with B_5H_9 also proceeds *via* an acid–base reaction, giving the salt $[Ir(PMe_3)_4H_2]^+[B_5H_8]^-$.[20] We have also observed that the reaction of $[Re(PMe_3)_5H]$ with $B_{10}H_{14}$ also results in abstraction of a bridging hydrogen atom giving the salt $[Re(PMe_3)_5H_2]^+[B_{10}H_{13}]^-$.[21]

The compound *nido*-$[2\text{-}\{Re(PMe_3)_3\}B_5H_{10}]$ **3** is the product of a rare example of metal-fragment exchange within a metallaborane cage, with the metal fragment $Fe(\eta\text{-}C_5H_5)$ being substituted by the isolobal fragment $Re(PMe_3)_3$. The relatively few examples of this type of process usually involve salt-metathesis type reactions.[22] The substitution reaction may proceed *via* an intermediate dimetallaborane which then eliminates $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2H]$. We note that **3** is isostructural with *nido*-$[2\text{-}\{Re(PMe_2Ph)_3\}B_5H_{10}]$[21] and *nido*-$[2\text{-}\{M(CO)_3\}B_5H_{10}]$ (M = Mn or Re).[23]

The reaction between *nido*-$[2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_{10}]$ and $[Nb(\eta\text{-}C_5H_5)_2H_3]$ in benzene at 50 °C gave a number of unidentified borane-containing products (NMR spectroscopy). Column chromatography gave a green compound and the ^1H and ^{11}B NMR spectra showed this to be the previously described *arachno*-$[\{Nb(\eta\text{-}C_5H_5)_2\}B_3H_8]$ **5**.[24] It appears that the first-formed products are decomposed or react on the column to give **5**.

The reactions and the structures proposed for the new compounds are shown in Scheme 1.

Experimental

All preparations, manipulations and reactions were carried out using standard techniques for handling air-sensitive materials (Schlenk line and glove-box). Solvents were predried over molecular sieves (4 or 5A) and then distilled from appropriate drying agents. Deuteriated solvents were stored over activated molecular sieves or sodium–potassium alloy. The following compounds were synthesised according to literature methods: $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2H]$,[25] $[Mo(PMe_2Ph)_4H_4]$,[26] $[W(PMe_3)_3H_6]$,[27] $[Re(PMe_3)_5H]$,[28] and $[Nb(\eta\text{-}C_5H_5)_2H_3]$.[29] The NMR spectra were obtained using Bruker AC-200 or AM-300 instruments: ^1H spectra were referenced internally with respect to the residual protiosolvent (C_6D_6, δ 7.10; $[^2H_8]$toluene, δ 2.05); ^{11}B and ^{31}P spectra were referenced internally relative to the deuterium lock signal using the SR command of standard Bruker software, with respect to the standards 85% H_3PO_4–D_2O (^{31}P) and $BF_3{\cdot}Et_2O$ (^{11}B). All chemical shifts are quoted in δ (ppm) and coupling constants in Hertz (Hz). On the Bruker AC-200, double-resonance $^1H\text{-}\{^{11}B\}$ broad-band and selectively decoupled spectra and triple-resonance $^1H\text{-}\{^{11}B_{broad\ band}\text{-}^1H_{selective}\}$ spectra were acquired using an external X-nucleus decoupler; the selectively decoupled spectra were acquired using an on-resonance minus off-resonance technique. On the Bruker AM-300, $^1H\text{-}\{^{11}B\}$ broad-band and selectively decoupled spectra were acquired in inverse mode using a BSV-7 broad-band decoupler or the TLO output respectively. Elemental analysis was performed by the Analysis Department of the Inorganic Chemistry Laboratory, Oxford University.

Preparations.—*nido*-$[2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_{10}]$. From the thesis of Kelland.[16] The compound $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2H]$[25] (4.0 g, 14.5 mmol) was treated with a solution of pentaborane(9) on toluene (64 cm^3, 0.25 mol dm^{-3}) and the mixture was stirred at 20 °C for 12 h. Silica gel (6 g) was added to the resulting mixture and volatiles were removed. The dry residue was transferred to an alumina chromatography column made up in light petroleum (b.p. 30–40 °C). Elution with light petroleum–diethyl ether (20:1) gave first a purple band and subsequently several other bands. The purple band was collected and solvent was removed under reduced pressure giving a dark purple solid which was recrystallised from pentane at −78 °C to give dark purple crystals of *nido*-$[2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_{10}]$. Yield 0.4 g (15%). Detailed studies of the other products of this reaction[16] will be reported separately.

Capped-*closo*-$[1\text{-}\{Fe(\eta\text{-}C_5H_5)\}\text{-}2\text{-}\{Mo(PMe_2Ph)_3H\}B_5H_7]$ **1**. A solution of $[Mo(PMe_2Ph)_4H_4]$ (2.177 g, 4.12 mmol) in toluene (20 cm^3) was added to a solution of *nido*-$[2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_{10}]$ (0.742 g, 4 mmol) in toluene (20 cm^3) in a Young's ampoule and the mixture heated to 65 °C for 54 h. The solution was concentrated under reduced pressure and chromatographed (silica gel, 35 × 200 mm). Elution with light petroleum (b.p. 40–60 °C) containing 2–5% diethyl ether gave three bands. The first band was yellow and shown to be $PMe_2Ph{\cdot}BH_3$. The second band was purple and ^1H and ^{11}B NMR spectroscopy indicated that it contained a mixture of compounds, even following a second chromatography. The third band was bright red and comprised the major fraction; the volatiles were removed under reduced pressure and any remaining $PMe_2Ph{\cdot}BH_3$ was removed by sublimation *in vacuo* onto a −196 °C probe. The residue was crystallised from diethyl ether and gave crystals of capped-*closo*-$[1\text{-}\{Fe(\eta\text{-}C_5H_5)\}\text{-}2\text{-}\{Mo(PMe_2Ph)_3H\}B_5H_7]$ suitable for X-ray diffraction. Yield 150 mg, 0.21 mmol, 5%.

Capped-*closo*-$[1\text{-}\{Fe(\eta\text{-}C_5H_5)\}\text{-}2\text{-}\{W(PMe_3)_3H\}B_5H_7]$ **2**. A solution of *nido*-$[2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_{10}]$ (0.41 g, 2.2 mmol) in toluene (25 cm^3) was added to a small Young's ampoule containing $[W(PMe_3)_3H_6]$ (1.42 g, 3.4 mmol) and the solution heated at 75 °C for 19 h. The resulting orange-brown solution was transferred to a small Schlenk tube, most of the volatiles were removed under reduced pressure and the residue chromatographed (silica gel, 35 × 110 mm). Gradual elution with light petroleum (b.p. 40–60 °C)–diethyl ether (30:70 increasing to 0:100) gave a bright orange band. This was collected and the volatiles removed under reduced pressure; the residue was crystallised from either boiling light petroleum (b.p. 40–60 °C) or diethyl ether and capped-*closo*-$[1\text{-}\{Fe(\eta\text{-}C_5H_5)\}\text{-}2\text{-}\{W(PMe_3)_3H\}B_5H_7]$ was isolated as orange-red microcrystals. Yield 150–200 mg, 12–15%.

Reaction of nido-$[2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_{10}]$ *with* $[Re(PMe_3)_5H]$: *synthesis of nido-*$[2\text{-}\{Re(PMe_3)_3\}B_5H_{10}]$ **3** *and* $[Re(PMe_3)_5H_2]^+$[*nido*-$2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_9]^-$ **4**. A solution of *nido*-$[2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_{10}]$ (220 mg, 1.2 mmol) in toluene (10 cm^3) was treated with a green solution of $[Re(PMe_3)_5H]$ (1.54 g, 2.71 mmol). The mixture immediately turned orange and after 5 min an orange-brown oil formed. The mixture was stirred at room temperature for 15 h and then heated to 60 °C for 15 min. The resulting orange solution was decanted from an orange oil. The oil was washed with diethyl ether (30 cm^3) and extracted into thf (10 cm^3); attempted crystallisation at −30 °C failed, and so the volatiles were removed under reduced pressure, and the oil dissolved in deuteriotetrahydrofuran and characterised by NMR spectroscopy as $[Re(PMe_3)_5H_2]^+$[*nido*-$2\text{-}\{Fe(\eta\text{-}C_5H_5)\}B_5H_9]^-$ **4**. The volatiles were removed from the toluene-soluble fraction of the reaction mixture under reduced pressure, and the residue was chromatographed (silica gel, 32 × 135 mm). Elution with light petroleum (b.p. 40–60 °C)–diethyl ether (95:5 to 35:65) gave a large yellow band. Elution with diethyl ether and thf gave small green and red bands which did not contain any borane products (as shown by ^{11}B NMR spectroscopy). The volatiles were removed under reduced pressure from the yellow band, and the residue dissolved in pentane (15 cm^3); cooling to −30 °C gave large orange crystals of *nido*-$[2\text{-}\{Re(PMe_3)_3\}B_5H_{10}]$ **3**. Yield *ca.* 80 mg, 0.16 mmol, 14%.

Table 4 Crystal structure data for capped-*closo*-[1-{Fe(η-C_5H_5)}-2-{Mo(PMe_2Ph)$_3$H}B_5H_7] **1**

Empirical formula	$C_{29}H_{46}B_5FeMoP_3$
M	693.4407
Crystal size/mm	0.2 × 0.3 × 0.5
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	15.586(5)
b/Å	11.523(4)
c/Å	19.186(4)
β/°	106.23(2)
U/Å^3	3308.5
Z	4
μ(Mo-Kα)/cm^{-1}	9.6993
D_c/g cm^{-3}	1.32
F(000)	1432
Radiation (λ/Å)	Mo-Kα (0.710 69)
2θ limits/°	3–50
ω Scan width	1 + 0.35 tan θ
hkl Ranges	−1 to 18, −1 to 13, −22 to 22
Scan mode	ω
Total reflections measured	7223
No. of observations [$I > 3\sigma(I)$]	4583
R (merge)	0.02
No. of variables	386
Observations/variables	11.87
Weighting scheme	Unit weights
Maximum, minimum peaks in final difference map/e Å^{-3}	0.3, −0.2
Shift/e.s.d. in final cycle	0.04
R	0.023
R'	0.024

Reaction of nido-[2-{Fe(η-C_5H_5)}B_5H_{10}] *with* [Nb(η-C_5H_5)$_2H_3$]. A solution of *nido*-[2-{Fe(η-C_5H_5)}B_5H_{10}] (10 mg, 54 μmol) and [Nb(η-C_5H_5)$_2H_3$] (38 mg, 168 μmol) in deuteriobenzene (0.4 cm^3) was sealed in a NMR tube (diameter 5 mm). This was kept at 20 °C for 15 h and then heated to 50 °C for 30 min. The tube was opened and the contents chromatographed (silica gel, 15 × 60 mm), giving only one green band on elution with light petroleum–diethyl ether (95 : 5). The band was collected and the volatiles removed under reduced pressure to give a low yield of a dark green to black solid. Proton and ^{11}B NMR spectra identified this as pure *arachno*-[{Nb(η-C_5H_5)$_2$}B_3H_8] **5**.

Crystal-structure Determination of capped-*closo*-[1-{Fe(η-C_5H_5)}-2-{Mo(PMe_2Ph)$_3$H}B_5H_7] **1**.—A crystal of compound **1** was sealed in a glass capillary under nitrogen and diffraction data collected on an Enraf-Nonius CAD4 diffractometer. Unit-cell parameters and the orientation matrix were determined from the positions of 25 accurately centred reflections and refined using least-squares procedures. During data collection three orientation controls were measured every 250 reflections, and three intensity standards were measured every 3600 s of exposure time. The crystal data are listed in Table 4. An absorption correction based on azimuthal scan data was applied,[30] and the data were corrected for Lorentz and polarisation effects. Equivalent reflections were merged and only those for which $I > 3\sigma(I)$ were included in the refinement.

The structure was solved by the Patterson method which located the Mo atom; all other non-hydrogen atoms were located from subsequent Fourier-difference syntheses and refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon were placed in calculated positions (C–H 0.96 Å) and refined riding on their supporting carbon atoms with a thermal parameter equal to 1.3 times the equivalent isotropic thermal parameter of the respective carbon atom. Hydrogens attached to boron were found in difference maps and their atomic positions refined. All calculations were performed on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford, using the Oxford CRYSTALS system[31] and the molecular structure was plotted using SNOOPI.[31] Atomic scattering factors and anomalous dispersion coefficients were taken from the usual sources.[32] The final difference map showed a residual peak of 0.3 e Å^{-3} at 1.4 Å from the Mo atom.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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