Synthesis of η-Cyclopentadienyl-polyborane Derivatives of Molybdenum and Tungsten†

H. Janet Bullick,[a] **Peter D. Grebenik,**[a] **Malcolm L. H. Green,**[b] **Andrew K. Hughes,**[*,b] **John B. Leach**[c] **and Patrick C. McGowan**[b]
[a] *School of Biological and Molecular Science, Oxford Brookes University, Gipsy Lane, Headington, Oxford OX3 0BP, UK*
[b] *Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK*
[c] *Department of Chemistry, Manchester Metropolitan University, John Dalton Building, Chester Street, Manchester M1 5GD, UK*

The reaction of $LiBH_4$ with $[Mo(\eta\text{-}C_5H_4Me)Cl_4]$ gives the dimetallaborane bicapped *closo*-$[\{Mo(\eta\text{-}C_5H_4R)\}_2B_5H_9]$, which has been characterised by X-ray crystallography. The reaction of $LiBH_4$ with $[W(\eta\text{-}C_5H_4R)Cl_4]$, for R = Me, gives *closo*-$[\{W(\eta\text{-}C_5H_4Me)H_2\}_2B_3H_7]$ or, for R = Pr^i, both *closo*-$[\{W(\eta\text{-}C_5H_4Pr^i)H_2\}_2B_3H_7]$ and *nido*-$[\{W(\eta\text{-}C_5H_4Pr^i)H_3\}B_4H_8]$. The reaction between $[Mo(\eta\text{-}C_5H_4Me)(PMe_3)_2Cl_2]$ and $LiBH_4$ yields bicapped *closo*-$[\{Mo(\eta\text{-}C_5H_4Me)\}_2B_5H_9]$ or *nido*-$[\{Mo(\eta\text{-}C_5H_4Me)(PMe_3)H\}B_4H_8]$, depending on the reaction conditions. Also $LiBH_4$ reacts with $[W(PMe_3)_3Cl_4]$ to give a mixture of *nido*-$[\{W(PMe_3)_2H_4\}B_4H_8]$ and *arachno*-$[\{W(PMe_3)_3H_3\}B_3H_8]$.

We have been interested in the synthesis of metallapolyboranes using monoborane precursor reagents and have shown previously that BH_3·thf (thf = tetrahydrofuran) reacts with a variety of transition-metal halides to give complexes which have polyborane ligands.[1–3] It is well established that the alkali-metal tetrahydroborates MBH_4 (M = Li, Na or K) react with transition-metal halide derivatives to give transition-metal tetrahydroborate complexes in which the BH_4^- ligand commonly bonds as a bidentate and, less often, as a mono- or tri-dentate ligand. In contrast, homologation reactions using MBH_4 which form metallapolyborane clusters with two or more boron atoms, and direct B–B or B–H–B bonds, are comparatively rare. Examples are the reactions of $LiBH_4$ with $[\{Ta(\eta\text{-}C_5Me_4R)Cl_2\}_2]$[4] and $[NbCl_5\{Li(C_5Me_4R)\}]$ (R = Me or Et).[5,6] Also the reaction of $[\{Co(\eta\text{-}C_5Me_5)Cl\}_2]$ with $LiBH_4$ gives the trimetallaborane *closo*-$[2,3,4\text{-}\{Co(\eta\text{-}C_5Me_5)\}_3\text{-}B_2H_4]$;[7] and the reaction of $[\{Co(\eta\text{-}C_5Me_5)Cl\}_2]$ with BH_3·thf gives a mixture of *nido*-$[1\text{-}\{Co(\eta\text{-}C_5Me_5)\}\text{-}2\text{-}\{(\eta^4\text{-}C_5Me_5H)\text{-}Co\}B_3H_8]$ and *arachno*-$[1\text{-}\{Co(\eta\text{-}C_5Me_5)\}B_4H_{10}]$.[8]

A number of dimetallaborane products have been isolated from various reactions of monoborane species (MBH_4 and BH_3·L) with cyclopentadienyl complexes of Groups 5 and 6. Ting and Messerle[4] have shown that the reaction of 2 equivalents of $LiBH_4$ with $[Ta_2(C_5Me_4R)_2(\mu\text{-}X)_4]$ (R = Me or Et, X = Cl or Br) produces $[Ta_2(C_5Me_4R)_2(\mu\text{-}X)_2B_2H_6]$. A crystal structure has been obtained of $[Ta_2(C_5Me_5)_2\text{-}(\mu\text{-}Br)_2B_2H_6]$, which reveals four equivalent M–H–B bridging hydrogen atoms and a Ta–Ta double bond bridged by a B_2H_6 ligand. Addition of 4 equivalents of $LiBH_4$ to $[Ta_2(C_5Me_4R)_2\text{-}(\mu\text{-}X)_4]$ (R = Me or Et, X = Cl or Br), or the addition of 2 equivalents of $LiBH_4$ to $[Ta_2(C_5Me_4R)_2(\mu\text{-}X)_2B_2H_6]$ gives $[\{Ta_2(C_5Me_4R)_2\}(B_2H_6)_2]$ in which the two remaining halide ligands have been replaced by a second B_2H_6 bridging ligand. Crossover studies have ruled out mechanisms containing mononuclear intermediates. The reaction of $NbCl_5$ with a mixture of $Li(C_5Me_5)$ and $NaBH_4$ is reported to produce $[\{Nb(C_5Me_5)\}_2(B_2H_6)_2]$ as a by-product to the main reaction, which gives $[Nb(C_5Me_5)_2(BH_4)]$;[5] the analogous complex $[\{Nb(\eta\text{-}C_5Me_4Et)\}_2(B_2H_6)_2]$ has recently been prepared, and structurally characterised.[6] Here we describe the reactions of $LiBH_4$ with some polyhalide derivatives of tungsten and molybdenum.

Results and Discussion

Reactions of $LiBH_4$ *with* $[M(\eta\text{-}C_5H_4R)Cl_4]$, (M = Mo *or* W, R = Me *or* Pr^i).—Treatment of $[Mo(\eta\text{-}C_5H_4Me)Cl_4]$ with an excess of $LiBH_4$ in diethyl ether gave, after chromatography, orange crystals of $[\{Mo(\eta\text{-}C_5H_4Me)\}_2B_5H_9]$ **1**. The molecular structure of **1** has been determined by a single crystal X-ray diffraction study, and views of the molecular structure are shown in Fig. 1; selected geometrical data are given in Table 1 and fractional atomic coordinates appear in Table 2. The molecule lies on a crystallographically imposed two-fold axis which passes through B(3) and H(3); thus, the atoms Mo(1) and Mo(1B) (and all other similarly labelled atoms) are related by this axis.

The high symmetry of $[\{Mo(\eta\text{-}C_5H_4Me)\}_2B_5H_9]$ **1** is shown by the presence of two molecular mirror planes (non-crystallographic), in addition to the crystallographic two-fold axis. The structure can be described as a distorted trigonal bipyramid [where B(3), Mo(1) and Mo(1B) define the trigonal

Table 1 Selected bond lengths (Å) and angles (°) for bicapped *closo*-$[\{Mo(\eta\text{-}C_5H_4Me)\}_2B_5H_9]$ **1**

Mo(1)–Mo(1B)	2.812(1)	Mo(1)–B(1)	2.21(1)
Mo(1B)–B(1)	2.24(1)	Mo(1)–B(2)	2.32(1)
Mo(1B)–B(2)	2.34(1)	Mo(1)–B(3)	2.17(1)
B(1)–B(2)	1.75(2)	B(1)–B(3)	1.71(1)
Mo(1)–H(211)	1.89(6)	Mo(1)–H(212)	1.79(6)
B(2)–H(211)	1.34(7)	B(2)–H(212)	1.36(7)
Mo(1)–B(1)–Mo(1B)	78.3(3)	Mo(1)–B(2)–Mo(1B)	74.2(3)
Mo(1)–B(3)–Mo(1B)	80.6(5)	B(1)–B(3)–B(1B)	123.4(11)
Mo(1)–H(211)–B(2)	89(3)	Mo(1)–H(212)–B(2)	95(4)

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* *Present address:* Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE, UK.

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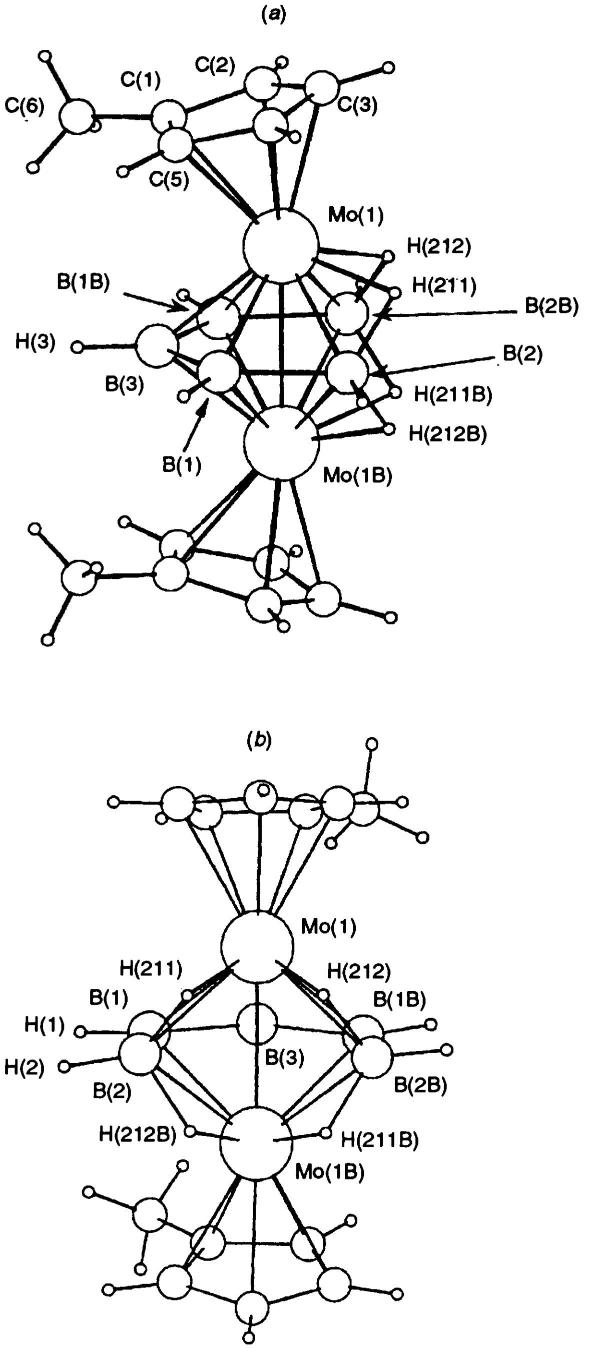


Fig. 1 (*a*), (*b*) Two views of the molecular structure of bicapped *closo*-$[\{Mo(\eta\text{-}C_5H_4Me)\}_2B_5H_9]$ **1** showing the adopted crystallographic numbering scheme, view (*b*) is 10° off the crystallographic two-fold axis. Atoms labelled B are related to their partners by the two fold axis

Table 2 Fractional atomic coordinates for bicapped *closo*-$[\{Mo(\eta\text{-}MeC_5H_4)\}_2B_5H_9]$ **1**; hydrogen atoms attached to carbon are excluded

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	0.063 35(4)	−0.213 97(5)	0.166 53(8)
C(1)	0.167 9(6)	−0.338 9(8)	0.144(1)
C(2)	0.202 8(5)	−0.234 2(9)	0.177(1)
C(3)	0.166 4(6)	−0.167 0(9)	0.037(1)
C(4)	0.107 2(7)	−0.225(1)	−0.084(1)
C(5)	0.107 3(6)	−0.331(1)	−0.020(1)
C(6)	0.194 4(8)	−0.440 5(9)	0.249(2)
B(1)	−0.062 7(6)	−0.284(1)	0.075(1)
B(2)	−0.068 3(7)	−0.140(1)	0.060(1)
B(3)	0.000 0	−0.351(1)	0.250 0
H(1)	−0.106(4)	−0.323(6)	−0.029(9)
H(2)	−0.118(4)	−0.123(7)	−0.049(9)
H(3)	0.000 0	−0.435(6)	0.250 0
H(211)	0.003(4)	−0.085(5)	0.079(9)
H(212)	0.084(4)	−0.092(5)	0.298(9)

plane, and B(1) and B(1B) are the apical atoms] with two identical capping B–H fragments [B(2) and B(2B)] over the Mo–Mo–B faces; thus, the structure is a trigonal bipyramid with two equatorial Mo atoms, and both Mo_2B faces capped by BH units. There are four equivalent Mo–H–B bridging hydrogen atoms between the Mo atoms and capping boron atoms. A skeletal electron count of the complex gives six electron pairs, which is effectively isoelectronic with *closo*-$[B_5H_5]^{2-}$, and the structure can be formally described as a bicapped analogue of *closo*-$[B_5H_5]^{2-}$. To our knowledge this is the first example of a bicapped metallaborane, although a number of bi-, tri-, and tetra-capped complexes are found in metal cluster chemistry. In contrast to metal clusters, it is also unique in being a bicapped cluster with both capping units sharing a common edge (the Mo–Mo bond), *cf.* $[Os_8(CO)_{22}]^{2-}$ and $[Re_8C(CO)_{24}]^{2-}$.[9,10]

The structure of **1** can also be viewed as a derivative of a triple-decker sandwich structure in which the two $[Mo(\eta\text{-}C_5H_4Me)]$ units comprise the outer units and the five boron atoms a central layer. The least-squares plane of the $\eta\text{-}C_5H_4Me$ rings is *ca.* 2.013 Å from the molybdenum atoms and the Mo–Mo distance is 2.812(1) Å.

The analytical and spectroscopic data for $[\{Mo(\eta\text{-}C_5H_4Me)\}_2B_5H_9]$ **1**, and for all the other new compounds described below, are given in Table 3. The assignments of the NMR data have been established by a combination of relative chemical shifts, selective and broadband $^1H\text{-}\{^{11}B\}$ decoupled spectra, $^1H\text{-}\{^{11}B_{broadband}\text{-}^1H_{selective}\}$ triple-resonance spectra and $[^{11}B\text{-}^{11}B]\text{-}\{^1H\}$ COSY spectroscopy. The molecular numbering scheme shown in Fig. 2 is used for compound **1** in the following discussion.

The ^{11}B NMR spectrum of **1** consists of two overlapping doublets (δ 61.6 and 59.7) and a doublet of triplets (δ 27.8) all of which collapse to singlets in the $^{11}B\text{-}\{^1H\}$ spectrum. The ^1H NMR spectrum shows resonances assigned to the equivalent $(\eta\text{-}C_5H_4Me)$ ligands. Additionally, in the $^1H\text{-}\{^{11}B\}$ broadband decoupled spectrum, four resonances sharpen giving a singlet at δ 6.34, a broad triplet at δ 5.53 and a singlet at δ 3.94; these peaks have relative intensities of 2:2:1 and there is a high-field doublet of intensity 4 at δ −7.01. A series of $^1H\text{-}\{^{11}B_{broadband}\text{-}^1H_{selective}\}$ triple-resonance experiments show that the triplet at δ 5.53 (assigned to B–H terminal hydrogen atoms) is coupled to the doublet at δ −7.01 (assigned to M–H–B bridging hydrogen atoms). A ^{11}B NMR spectrum was recorded with selective decoupling of the M–H–B ^1H resonance at δ −7.01, in which the high-field ^{11}B resonance collapses from a doublet of triplets to a doublet.

The ^{11}B NMR resonance at δ 61.6 is assigned to apical boron atoms B(1) and B(5), the resonance at δ 59.7 is assigned to the unique equatorial boron atom B(4), and the doublet of triplets at δ 27.8 is assigned to the face-capping boron atoms B(μ-1,2,3) and B(μ-2,3,5), this latter chemical shift is at extremely high field compared with other known examples of capped metallaboranes.[11–13] This anomaly may reflect the unusual electronic environment of these boron atoms. The splitting of the B(μ-2,3,5) ^{11}B NMR resonance is attributed to coupling with one terminal hydrogen B–H atom and two terminal M–H–B bridging hydrogen atoms.

Treatment of $[W(\eta\text{-}C_5H_4Pr^i)Cl_4]$ with an excess of $LiBH_4$ gives two or more products whose relative yields depend on the reaction conditions (Scheme 1). When using diethyl ether as the solvent, the isolated products were small yellow-green crystals of *closo*-$[\{W(\eta\text{-}C_5H_4Pr^i)H_2\}_2B_3H_7]$ **2** and *nido*-$[\{W(\eta\text{-}C_5H_4Pr^i)H_3\}B_4H_8]$ **3**. A third compound was incompletely characterised, but the available data are consistent with the formulation *arachno*-[{W(η-$C_5H_4Pr^i$)H_4}B_3H_8] **4**. The mixture of compounds **3** and **4** could not be separated by column chromatography. When the solvent for the reaction was tetrahydrofuran (thf), treatment of [W(η-$C_5H_4Pr^i$)Cl_4] with an excess of $LiBH_4$ for 5 d gave, after chromatography, two bands from which pure *closo*-[{W(η-$C_5H_4Pr^i$)H_2}$_2B_3H_7$] **2** and *nido*-[{W(η-$C_5H_4Pr^i$)H_3}B_4H_8] **3** were isolated. Shorter reaction times in thf also gave a low yield of *arachno*-[{W(η-$C_5H_4Pr^i$)H_4}B_3H_8] **4**.

The ^{11}B NMR spectrum of *closo*-[{W(η-$C_5H_4Pr^i$)H_2}$_2$-B_3H_7] **2** consists of two doublets of relative intensity 2:1, which collapse to singlets in the ^{11}B-{^1H} spectrum. In the ^1H NMR spectrum two sets of similar resonances are observed between δ 4 and 5 which are assigned to the ring protons of two inequivalent η-$C_5H_4Pr^i$ ligands, the associated $CHMe_2$ proton resonances are close to δ 2.4 and 1.0. Additionally, four signals appear at high field; resonances at δ −2.35 and −5.09 (each of intensity 2 relative to the isopropyl CH resonances) are assigned to two hydrides attached to each metal centre; these resonances show ^{183}W satellites which in total amount to approximately 14% of the integrated peak area, thus the hydrides are terminal W–H. The remaining signals at δ −12.11 and −12.59, each of relative intensity 2, sharpen in the ^1H-{^{11}B} broadband decoupled spectrum which also reveals two signals at δ 6.80 and 0.47, of relative intensities 2:1. Triple-resonance [^1H-{$^{11}B_{broadband}$–$^1H_{selective}$}] experiments show that the two B–H hydrogens at δ 6.80 are coupled strongly with the W–H–B hydrogen atoms at −12.59 and weakly with the W–H–B hydrogens at δ −12.11, also the unique B–H at δ 0.47 is coupled with the W–H–B hydrogens at δ −12.11, and the W–H signal at δ −5.09 is coupled with the W–H–B signal at δ −12.11. These NMR data indicate a complex with stoichiometry [{W(η-$C_5H_4Pr^i$)H_2}$_2B_3H_7$], and a structure containing two inequivalent [W(η-$C_5H_4Pr^i$)H_2] units, two equivalent BH units, a third unique BH unit and two pairs of bridging hydrogen atoms. The stoichiometry is supported by mass spectroscopy and microanalytical data. A skeletal electron count gives six electron pairs for a five-vertex cage, implying a *closo* structure as shown in Scheme 1. Since the singlet at δ −2.35 in the ^1H NMR spectrum has ^{183}W satellites and shows no coupling with any other proton resonance, it can be assigned to the hydrides on the apical W (position 1) in the trigonal bipyramid. The triple-resonance experiments can be accounted for by placing the W–H–B hydrogen atoms assigned to the resonance at δ −12.11 in a triply bridging position over the W(2)B(3)B(5) and W(2)B(4)B(5) faces. The ^1H resonance at δ −5.09 is a triplet with ^{183}W satellites, and is thus assigned as a W–H hydride on the equatorial W, and is coupled to the W–H–B face bridging atoms at δ −12.11. The other W–H–B resonance (δ −12.59) is a doublet due to coupling with the B–H resonance of the equatorial boron atoms (δ 6.80). The possibility that the W–H–B hydrogens at δ −12.59 are also triply bridging across the W–B–W face can be discounted by the fact they show no coupling to the hydrides on the equatorial tungsten. As the cluster is electron-deficient with only six electron pairs it is not possible to draw a satisfactory valence-bond structure (Scheme 1) unless the W–H–B hydrogens are placed in a face-bridging position. This structural feature is consistent with the interpretation of the NMR data presented above.

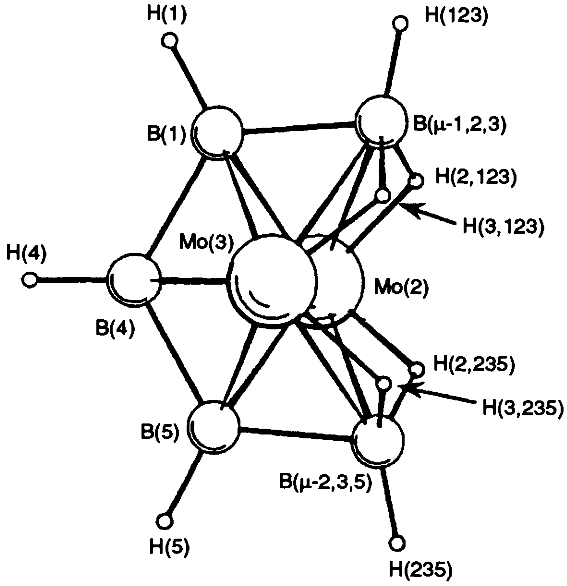
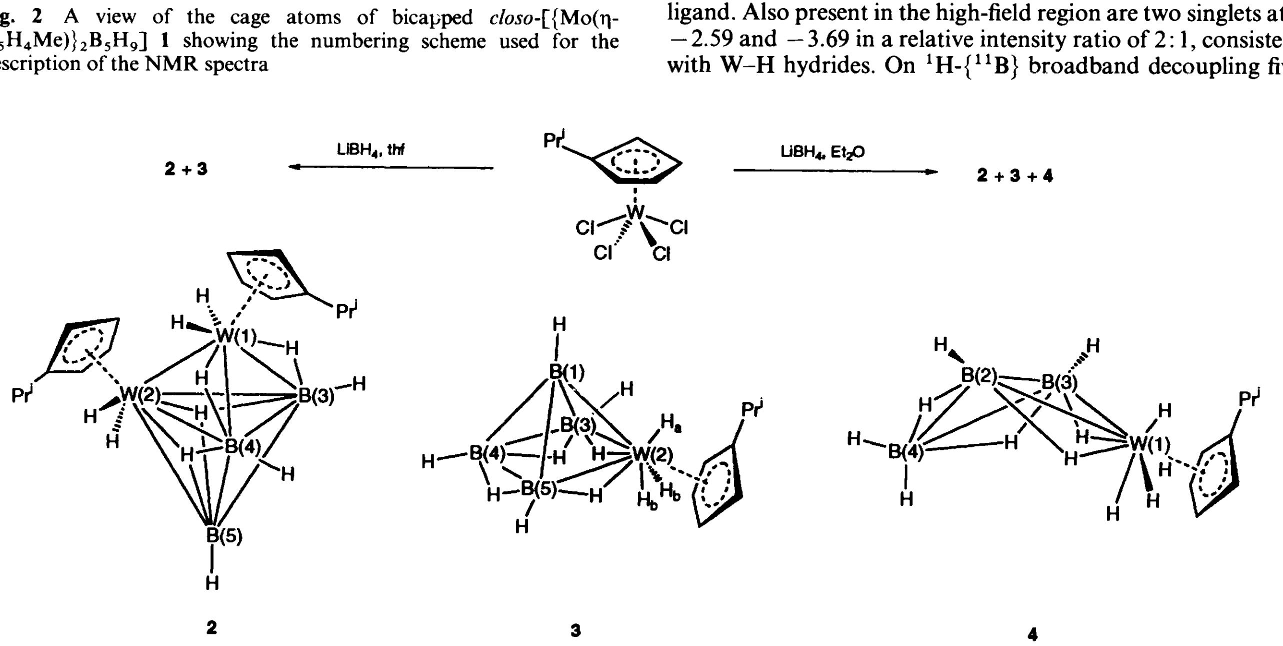


Fig. 2 A view of the cage atoms of bicapped *closo*-[{Mo(η-C_5H_4Me)}$_2B_5H_9$] **1** showing the numbering scheme used for the description of the NMR spectra

The ^{11}B NMR spectrum of *nido*-[{W(η-$C_5H_4Pr^i$)H_3}B_4H_8] **3** consists of three doublets of intensity 1:2:1, all of which collapse to singlets on broadband proton decoupling. The ^1H-{$^{11}B_{broadband}$} NMR spectrum suggests that the molecule is non-rigid, and the room-temperature spectrum shows several broad signals between δ 0 and −10. The ^1H NMR spectrum at 255 K is much sharper and shows resonances assigned to a η-$C_5H_4Pr^i$ ligand. Also present in the high-field region are two singlets at δ −2.59 and −3.69 in a relative intensity ratio of 2:1, consistent with W–H hydrides. On ^1H-{^{11}B} broadband decoupling five



Scheme 1 The products of the reaction of [W(η-$C_5H_4Pr^i$)Cl_4] with $LiBH_4$ in ethereal solvents

Table 3 Spectroscopic and analytical data[a]

Compound	^{1}H-{^{11}B} NMR data	^{11}B and ^{31}P NMR data
1 bicapped *closo*-$[\{Mo(\eta\text{-}C_5H_4Me)\}_2B_5H_9]$[b] Orange Mass spectrum: m/z = 413 [P^+] C 34.6 (34.9); H 5.6 (5.6)	6.34 [s, 2 H, H(1) and H(5)] 5.53 [t, 2 H, J(H–H) = 11, H(235) and H(123)] 5.18 [m, 4 H, $\eta\text{-}C_5\mathit{H}_4Me$] 5.12 [m, 4 H, $\eta\text{-}C_5\mathit{H}_4Me$] 3.94 [s, 1 H, H(4)] 1.89 (s, 6 H, 2 × Me) −7.01 [d, 4 H, J(H–H) = 11, H(2,123), H(3,123), H(2,235) and H(3,235)]	^{11}B: 61.6 [d, 2 B, J(B–H) = 188, B(μ_3-1,2,3) and B(μ_3-2,3,5)] 59.7 [d, 1 B, J(B–H) = 190, B(4)] 27.8 [d, 2 B, J(B–H) = 134, B(1) and B(5)]
2 *closo*-$[\{W(\eta\text{-}C_5H_4Pr^i)H_2\}_2B_3H_7]$[c] Yellow-green Mass spectrum: m/z = 620 C 30.9 (30.7): H 5.5 (5.3)	6.80 [br s, 2 H, H(3) and H(4)] 4.89 [t, 2 H, J(H–H) ≈ 2.4, $\eta\text{-}C_5\mathit{H}_4Pr^i$, ring 1] 4.84 [t, 2 H, J(H–H) ≈ 2.4, $\eta\text{-}C_5\mathit{H}_4Pr^i$, ring 1] 4.79 [t, 2 H, J(H–H) ≈ 2.5, $\eta\text{-}C_5\mathit{H}_4Pr^i$, ring 2] 4.58 [t, 2 H, J(H–H) ≈ 2.5, $\eta\text{-}C_5\mathit{H}_4Pr^i$, ring 2] 2.51 [sept, 1 H, J(H–H) = 7, $C\mathit{H}Me_2$] 2.39 [sept, 1 H, J(H–H) = 7, $C\mathit{H}Me_2$] 0.98 [d, 6 H, J(H–H) = 7, $CH\mathit{Me}_2$] 0.96 [d, 6 H, J(H–H) = 7, $CH\mathit{Me}_2$] 0.47 [br s, 1 H, H(5)] −2.35 [s, 2 W–H, J(W–H) = 62] −5.09 [t, 2 W–H, J(H–H) = 5, J(W–H) = 60] −12.11 [br s, 2 H, H(2,3) and H(2,4)] −12.59 [d, 2 H, J(H–H) = 15, H(1,3) and H(1,4)]	^{11}B: 17.6 [d, 2 B, J(B–H) = 154, B(3) and B(4)] −20.4 [d, 1 B, J(B–H) = 154, B(5)]
3 $[\{W(\eta\text{-}C_5H_4Pr^i)H_3\}B_4H_8]$[d] Orange-yellow oil	6.02 [s, 1 H, H(4)] 4.30 (m, 4 H, $\eta\text{-}C_5\mathit{H}_4Pr^i$) 3.09 [s, 2 H, H(3) and H(5)] 2.20 [sept, 1 H, J(H–H) = 6.7, $C\mathit{H}Me_2$] 1.14 [s, 1 H, H(1)] 0.83 [d, 6 H, J(H–H) = 6.7, $CH\mathit{Me}_2$] −2.31 [s, 2 H, H(3,4) and H(4,5)] −2.59 (s, 2 H, 2 × WH_b) −3.69 (s, 1 H, WH_a) −8.28 [s, 2 H, H(2,3) and H(2,5)]	^{11}B: 7.6 [d, 1 B, J(B–H) = 162, B(4)] −13.1 [d, 2 B, J(B–H) = 150, B(3) and B(5)] −34.0 [d, 1 B, J(B–H) = 156, B(1)]
4 $[\{W(\eta\text{-}C_5H_4Pr^i)H_4\}B_3H_8]$[e] Mixture with $[\{W(\eta\text{-}C_5H_4Pr^i)H_3\}B_4H_8]$	5.07 (s, 1 H, H_{exo} or H_{endo}) 4.38 (br s, 4 H, $\eta\text{-}C_5\mathit{H}_4Pr^i$) 3.20 (s, 1 H, H_{endo} or H_{exo}) 2.10 (sept, 1 H, $C\mathit{H}Me_2$) 1.27 [s, 2 H, H(1) and H(3)] 0.80 (d, 6 H, $CH\mathit{Me}_2$) −0.40 [s, 2 H, H(3,4) and H(1,4)] −2.05 (s, 4 × W–H) −8.10 [s, 2 H, H(2,3) and H(1,2)]	^{11}B: 1.9 [t, 1 B, J(B–H) = 130, B(4)] −44.3 [d, 2 B, J(B–H) = 140, B(1) and B(3)]

Table 3 (*contd.*)

Compound	$^1H\text{-}\{^{11}B\}$ NMR data	^{11}B and ^{31}P NMR data
5 *closo*-$[\{W(\eta\text{-}C_5H_4Me)H_2\}_2B_3H_7]$[f] Yellow-green C 25.3 (25.6); H 4.4 (4.4)	6.58 [br s, 2 H, H(3) and H(4)] 4.91 (m, 2 H, $\eta\text{-}C_5H_4Me$) 4.62 (2 × m, 4 H, $\eta\text{-}C_5H_4Me$) 4.46 (m, 2 H, $\eta\text{-}C_5H_4Me$) 1.67 (s, 3 H, Me) 1.63 (s, 3 H, Me) 0.75 [br s, 1 H, H(5)] −2.12 [s, 2 W–H, *J*(W–H) = 60, W–H] −5.01 [t, 2 W–H, *J*(W–H) = 54, *J*(H–H) = 5.3, W–H] −12.09 [br s, 2 H, H(1,3) and H(1,4) or H(2,3) and H(2,4)] −12.59 [d, 2 H, *J*(H–H) = 15, H(1,3) and H(1,4) or H(2,3) and H(2,4)]	^{11}B: 17.3 [d, 2 B, B(3) and B(4)] −19.7 [d, 1 B, B(5)]
6 $[\{Mo(\eta\text{-}C_5H_4Me)(PMe_3)H\}B_4H_8]$[g] Orange-brown	4.45 [s, 1 H, H(4)] 4.27 (br s, 1 H, $\eta\text{-}C_5H_4Me$) 4.01 (br s, 1 H, $\eta\text{-}C_5H_4Me$) 3.87 (br s, 1 H, $\eta\text{-}C_5H_4Me$) 3.74 (br s, 1 H, $\eta\text{-}C_5H_4Me$) 3.51 [s, 1 H, H(3) or H(5)] 2.61 [s, 1 H, H(5) or H(3)] 1.67 (s, 3 H, $\eta\text{-}C_5H_4Me$) 1.65 [s, 1 H, H(1)] 1.03 [d, 9 H, *J*(H–P) = 9, PMe_3] −2.12 [s, 1 H, H(4,5) or H(3,4)] −2.50 [s, 1 H, H(3,4) or H(4,5)] −5.03 [d, 1 H, *J*(H–P) = 42, Mo–H] −8.34 [s, 1 H, H(2,3) or H(2,5)] −10.82 [s, 1 H, H(2,5) or H(2,3)]	^{11}B: 16.5 [d, 1 B, *J*(B–H) = 156, B(1)] 14.0 [d, 1 B, *J*(B–H) = 167, B(3) or B(5)] 7.1 [d, 1 B, *J*(B–H) = 150, B(5) or B(3)] 9.3 [d, 1 B, *J*(B–H) = 156, B(4)] $^{31}P\text{-}\{^1H\}$: 2.4 (s)
7 *nido*-$[\{W(PMe_3)_2H_4\}B_4H_8]$ Orange-brown oil	5.49 [s, 1 H, H(4)] 3.09 [s, 2 H, H(3) and H(5)] 1.32 [d, 18 H, *J*(H–P) = 9, 2 × PMe_3] 1.14 [s, 1 H, H(1)] −1.87 [t, 4 H, *J*(H–P) = 40, 4 × W–H] −2.31 [s, 2 H, H(3,4) and H(4,5)] −6.94 [s, 2 H, H(2,3) and H(2,5)]	^{11}B: 2.0 [d, 1 B, *J*(B–H) = 154, B(4)] −12.1 [d, 2 B, *J*(B–H) = 146, B(3) and B(5)] −30.1 [d, 1 B, *J*(B–H) = 154, B(1)] ^{31}P: −16.3 [app d, 2P, J_{app} = 7.6, *J*(P–W) = 110]

[a] Unless otherwise stated, all NMR data are at room temperature in $[^2H_6]$benzene, at 200 (^1H), 64.2 (^{11}B) or 81.0 MHz (^{31}P). Microanalytical data are given as the best results from at least two independent determinations, calculated values are given in parentheses. [b] NMR data in $[^2H_8]$toluene. [c] ^1H NMR data in $[^2H_6]$benzene at 300 MHz, ^{11}B NMR data in $[^2H_8]$toluene at 64.2 MHz. [d] ^1H and ^{11}B NMR data in $[^2H_8]$toluene at 255 K. [e] ^1H NMR in $[^2H_6]$benzene at 300 MHz, ^{11}B NMR in $[^2H_6]$benzene at 96.3 MHz. [f] ^1H NMR in $[^2H_6]$benzene at 300 MHz, ^{11}B NMR in $[^2H_8]$toluene at 96.3 MHz. [g] ^1H, ^{11}B and ^{31}P NMR in $[^2H_8]$toluene.

signals sharpen and these were completely assigned (Table 3) by selective decoupling experiments.

The NMR data for **3** indicate the presence of a [W(η-$C_5H_4Pr^i$)H_3] unit, two equivalent BH units and two inequivalent BH units and, on the basis of NMR integrals, an overall stoichiometry corresponding to [{W(η-$C_5H_4Pr^i$)H_3}-B_4H_8]. An electron count for this formula gives seven electron pairs, indicating a metal subrogated analogue of *nido*-B_5H_9. On the basis of the multiplicity of the ^{11}B resonances the structure is base-subrogated, with a [W(η-$C_5H_4Pr^i$)H_3] unit replacing a BH unit and contributing two electrons and three orbitals to the skeletal frame.

The observation of two different hydride resonances in the ^1H NMR spectrum of **3** at 255 K indicates a structure with one unique hydride (H_a) and two equivalent hydride ligands (H_b). Spin-saturation transfer experiments show that H(2,3) and H(2,5) exchange with all three of the tungsten hydrides. Variable-temperature experiments above 255 K confirm this result, with the relevant peaks beginning to coalesce. Below 255 K, the spectra show a number of further decoalescences which have not been fully investigated since the low-temperature limits of these decoalescences cannot be attained. The data suggest an exchange process which at high temperature apparently equivalences all the W–H and W–H–B protons; a second (lower temperature) process has not been fully investigated, but it is clear from the spectra that the W–H protons are involved in at least two different exchange processes.

These variable-temperature NMR studies provide some valuable data on the structure of complex **3**. Thus, in the intermediate temperature regime (255 K), the complex has some symmetry element which makes two of the hydride ligands equivalent. The molecular structure in Scheme 1 satisfies the requirements of a symmetry element which makes two hydrides equivalent, and two boron sites equivalent; this structure corresponds with the intermediate regime. In this structure the η-$C_5H_4Pr^i$ ring centroid, the W atom, the unique hydride and B(1) and B(4) are coplanar with a molecular mirror plane. The high-temperature NMR data suggest exchange of W–H and W–H–B within this molecule; we have previously observed similar fluxional behaviour in *nido*-MB_4 complexes closely related to **3** where M–H–B and M–H are in exchange.[14]

As described above, the reaction of [W(η-$C_5H_4Pr^i$)Cl_4] with $LiBH_4$ in diethyl ether gave a second compound **4** as an inseparable mixture with **3**. Following the full characterisation of the latter we have obtained a partial characterisation of **4** by examining the remaining resonances in the spectra of a mixture of **3** and **4**. The ^{11}B NMR spectrum assigned to **4** consists of two resonances, a triplet (δ 1.9) and a doublet (δ −44.3), in an intensity ratio 1 : 2, both peaks collapsing to singlets in the ^{11}B-{$^1H_{broadband}$} spectrum. The ^1H NMR spectrum shows a multiplet at δ 4.38 assigned to a C_5H_4 ring, together with a septet (δ 2.10) and a doublet (δ 0.80) assigned to the isopropyl group. In the ^1H-{$^{11}B_{broadband}$} spectrum five resonances sharpen. These resonances were assigned by examination of the ^1H-{^{11}B} selectively decoupled spectra. It is not possible to distinguish any signals that might be unequivocally assigned to a metal hydride resonance for [{W(η-$C_5H_4Pr^i$)H_4}B_3H_8], however a broad singlet at δ − 1.65 may be attributed to this, as it shows no ^{11}B coupling. It is also possible that fluxional processes may also occur in complex **4** as already observed for *nido*-[{W(η-$C_5H_4Pr^i$)H_3}B_4H_8] **3**[14] and *arachno*-[{W-(PMe_3)$_3H_3$}B_3H_8],[2] and such fluxionality might possibly obscure the hydride resonance.

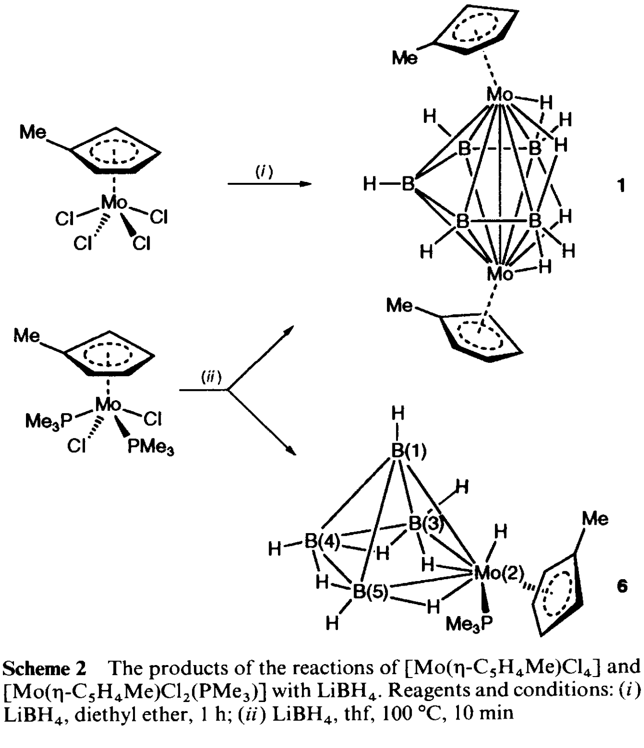
From the NMR data available, we consider the most likely structure for **4** to be an *arachno* four-vertex butterfly disposition with the metal subrogating a wing tip. For example, a comparison of ^1H and ^{11}B NMR shifts with known *arachno* four-vertex metallaboranes shows some close similarities.[15,16] A satisfactory skeletal electron count for such a structure would require the metal centre to contribute three electrons to the cluster which would require a [W(η-$C_5H_4Pr^i$)H_4] unit.

Treatment of [W(η-C_5H_4Me)Cl_4] with an excess of $LiBH_4$ in diethyl ether gave a large number of borane products (^{11}B NMR), in contrast to the analogous reaction of [W(η-$C_5H_4Pr^i$)Cl_4]. Work-up by column chromatography gave only one product in significant yield, which was isolated as yellow-green microcrystals and characterised as *closo*-[{W(η-C_5H_4Me)H_2}$_2B_3H_7$] **5**, a direct structural analogue of **2**.

Reaction of [Mo(η-C_5H_4Me)(PMe_3)$_2Cl_2$] *with* $LiBH_4$.—The product distribution from the reaction of $LiBH_4$ with [Mo(η-C_5H_4Me)(PMe_3)$_2Cl_2$] is also highly dependent on temperature and reaction time (Scheme 2). Heating a thf solution of the reactants at 55–65 °C for several hours gave PMe_3·BH_3 as the only boron-containing product. In contrast, heating rapidly to 100 °C for several minutes produced a number of products in varying yields. Work-up by either column chromatography or solvent extraction gave [{Mo(η-C_5H_4Me)}$_2B_5H_9$] **1** (described above) and *nido*-[{Mo(η-C_5H_4Me)(PMe_3)H}B_4H_8] **6**.

The yield of *nido*-[{Mo(η-C_5H_4Me)(PMe_3)H}B_4H_8] **6** was low and the compound was characterised by NMR spectroscopy only. The ^{11}B NMR spectrum consists of four doublets of equal intensity, all of which collapse to singlets on ^1H decoupling. The ^1H NMR spectrum consists of resonances assigned to η-C_5H_4Me and PMe_3 groups and a broad doublet assigned to a Mo–H hydride resonance. In the ^1H-{^{11}B} broadband decoupled NMR spectrum of **6** eight resonances of equal intensity sharpen and were assigned by ^1H-{^{11}B} selective decoupling experiments (Table 3). Irradiating at the ^{11}B frequency corresponding to a chemical shift of either δ 14.0 or 16.5 caused the ^1H M–H–B signal at δ −8.34 to sharpen; this resonance appeared to sharpen more clearly when the ^{11}B resonance at δ 14.0 was irradiated, and the latter correlation with the δ 16.5 resonance has been interpreted as a spurious result, due to the two ^{11}B resonances being too close for satisfactory selective irradiation. However, this observation could also be interpreted as the M–H–B hydrogen atom bridging the Mo–B–B face.

The NMR data for **6** are consistent with a [Mo(η-C_5H_4Me)(PMe_3)H] fragment attached to a borane cage



Scheme 2 The products of the reactions of [Mo(η-C_5H_4Me)Cl_4] and [Mo(η-C_5H_4Me)Cl_2(PMe_3)] with $LiBH_4$. Reagents and conditions: (*i*) $LiBH_4$, diethyl ether, 1 h; (*ii*) $LiBH_4$, thf, 100 °C, 10 min

which has four inequivalent BH groups, giving an overall stoichiometry of $[\{Mo(\eta\text{-}C_5H_4Me)(PMe_3)H\}B_4H_8]$. A skeletal electron count for this formula gives seven electron pairs for a five-vertex structure, indicating a *nido* structure. It is possible to assign several structures to this molecule. One possible structure which is consistent with the data is derived from a base-subrogated analogue of pentaborane(9), with asymmetry introduced by the chiral Mo centre; thus, if the borane cage and $\eta\text{-}C_5H_4Me$ ligand are each considered as one substituent on the metal atom, then the metal is pseudo-tetrahedral with four different substituents (Scheme 2).

A number of preliminary spin-saturation transfer experiments were also performed on $[\{Mo(\eta\text{-}C_5H_4Me)(PMe_3)H\}B_4H_8]$, and revealed that fluxional processes are occurring in this molecule. Thus, the M–H resonance at δ −5.03 is exchanging with the M–H–B resonances at δ −8.34 and −10.82. These fluxional processes will not be further discussed in the present work.

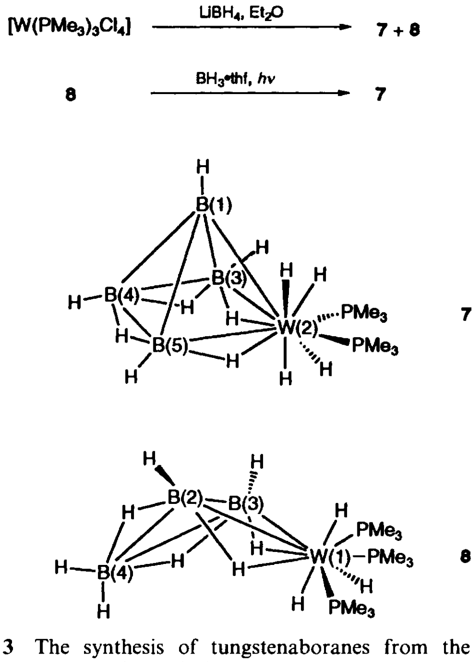
Reaction of $[W(PMe_3)_3Cl_4]$ *with* $LiBH_4$.—Treatment of $[W(PMe_3)_3Cl_4]$ with an excess of $LiBH_4$ for 2 h gave a brown oil which ^{11}B NMR spectroscopy showed to contain a new metallaborane **7** in addition to the known compound *arachno*-$[\{W(PMe_3)_3H_3\}B_3H_8]$ **8**[2] (Scheme 3). When the reaction was performed for 5 h, only pure **8** was isolated. It was not possible to isolate **7** in a pure form, as it does not crystallise free of **8**.

The photolysis of *arachno*-$[\{W(PMe_3)_3H_3\}B_3H_8]$ **8** in the presence of an excess of $BH_3{\cdot}thf$ gives only two products after chromatography, namely $PMe_3{\cdot}BH_3$ and *nido*-$[\{W(PMe_3)_2H_4\}B_4H_8]$; the NMR data of this second product are identical to the second product from the reaction of $[W(PMe_3)_3Cl_4]$ and an excess of $LiBH_4$ (Scheme 3).

The ^{11}B NMR spectrum of *nido*-$[\{W(PMe_3)_2H_4\}B_4H_8]$ **7** consists of three doublets of relative intensity 1:2:1 which collapse to singlets in the $^{11}B\text{-}\{^1H\}$ spectrum. The ^1H NMR spectrum shows resonances assigned to two PMe_3 ligands and four tungsten-bound hydrides. The $^1H\text{-}\{^{11}B\}$ broadband decoupled NMR spectrum shows five singlet resonances which sharpen relative to the ^1H NMR spectrum; three resonances at δ 5.49, 3.09 and 1.14 are in the intensity ratio 1:2:1, whilst the signals at δ −2.31 and −6.94 are in the intensity ratio 2:2. The $^1H\text{-}\{^{11}B\}$ selective decoupling experiments were used to assign further the connectivities of the boron and hydrogen atoms.

The NMR data are consistent with a $[W(PMe_3)_2H_4]$ unit, with two inequivalent phosphine ligands (^{31}P NMR), connected to a $[B_4H_4(\mu\text{-}H)_4]$ unit, consisting of two equivalent B–H groups and two inequivalent B–H groups. An electron count indicates a *nido* structure for $[\{W(PMe_3)_2H_4\}B_4H_8]$. The compound *nido*-$[\{W(PMe_3)_2H_4\}B_4H_8]$ is thus a base subrogated analogue of pentaborane(9) with a $[W(PMe_3)_2H_4]$ unit replacing a BH unit in the base of the square pyramid (Scheme 2), and contributing two electrons to the cluster count.

In conclusion, the reactions and structures proposed for the new compounds are shown in Schemes 1–3.



Scheme 3 The synthesis of tungstenaboranes from the reaction between $[W(PMe_3)_3Cl_4]$ and $LiBH_4$

Experimental

All preparations, manipulations and reactions were carried out using standard techniques for handling air-sensitive materials (Schlenk line and glove-box). Solvents were pre-dried over molecular sieves (4 Å or 5 Å) and then distilled from appropriate drying agents. Deuteriated solvents were stored over activated molecular sieves or sodium–potassium alloy; $LiBH_4$ was obtained from Aldrich and used as received. The following compounds were synthesised according to literature methods: $[W(PMe_3)_3Cl_4]$,[17] $[W(\eta\text{-}C_5H_4Pr^i)Cl_4]$,[18] $[W(\eta\text{-}C_5H_4Me)Cl_4]$,[18] $[Mo(\eta\text{-}C_5H_4Me)Cl_4]$,[18] $[Mo(\eta\text{-}C_5H_4Me)(PMe_3)_2Cl_2]$.[19] The NMR spectra were obtained using Bruker AC-200 or AM-300 instruments. Proton NMR spectra were referenced internally with respect to the residual protio solvent ($[^2H_6]$benzene δ 7.10, $[^2H_8]$toluene δ 2.05). In the case of ^{11}B, ^{13}C and ^{31}P NMR, spectra were referenced internally relative to the deuterium lock signal using the SR command of standard Bruker software, with respect to 85% H_3PO_4–D_2O (^{31}P) and $BF_3{\cdot}OEt_2$ (^{11}B). All chemical shifts are quoted in δ (ppm) and coupling constants in Hz. On the Bruker AC-200 instrument, double-resonance $^1H\text{-}\{^{11}B\}$ broadband and selective decoupled spectra and triple-resonance $^1H\text{-}\{^{11}B_{broadband}\text{-}{}^1H_{selective}\}$ 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 instrument, $^1H\text{-}\{^{11}B\}$ broadband and selective decoupled spectra were acquired in inverse mode using a BSV-7 broadband decoupler or the TLO output respectively. Elemental analysis was performed by the Analysis Department of the Inorganic Chemistry Laboratory, Oxford University.

Chromatographic separations of product mixtures were typically performed as follows. The reaction mixture was concentrated under reduced pressure to *ca.* 5 cm³; approximately 5–10 g of silica gel (Fluka, type GF254, 60–120 mesh) were added, and the remaining solvent was removed under reduced pressure until a free flowing 'sand' was obtained. A glass chromatography column (typically 2–5 cm diameter, 100–600 mm long) was filled with silica gel and light petroleum (b.p. 40–60 °C) and deoxygenated by passing nitrogen-saturated solvent through it. The 'sand' was then tipped onto the column, under a flow of nitrogen, through a PVC transfer tube. The column was then eluted initially using light petroleum, but adding increasing proportions of more polar solvents until product bands were eluted. Given the low yields and the oxygen sensitive nature of the isolated products, no attempts were made to measure R_f values using TLC.

Synthesis of $[\{Mo(\eta\text{-}C_5H_4Me)\}_2B_5H_9]$ **1**.—A slurry of $[Mo(\eta\text{-}C_5H_4Me)Cl_4]$ (1.0 g, 3.16 mmol) and $LiBH_4$ (0.24 g, 11.02 mmol) in diethyl ether (30 cm³) at −80 °C was stirred and then allowed to warm to room temperature. After 1 h the solvent was removed from the resulting black solution under reduced pessure. The residue was chromatographed (silica gel, 2.3 × 8.7 cm) and elution with light petroleum gave a dark green band which rapidly decomposed on the column. Further elution with light petroleum (b.p. 40–60 °C) containing 16–40% diethyl ether gave a bright orange band. Removal of solvent under reduced pressure and recrystallisation from diethyl ether gave orange crystals of [{Mo(η-C_5H_4Me)}$_2B_5H_9$] **1**. Yield *ca.* 10–20 mg (0.75–1.5%).

Synthesis of closo-[{W(η-$C_5H_4Pr^i$)H_2}$_2B_3H_7$] **2**, [{W(η-$C_5H_4Pr^i$)H_3}B_4H_8] **3** *and* [{W(η-$C_5H_4Pr^i$)H_4}B_3H_8] **4**.—A Young's ampoule was charged with a mixture of [W(η-$C_5H_4Pr^i$)Cl_4] (1.0 g, 2.3 mmol) and $LiBH_4$ (0.194 g, 8.9 mmol). The vessel was cooled to −80 °C and cold diethyl ether (30 cm^3) added. The mixture was stirred and allowed to warm to room temperature. After 1 h the dark homogeneous solution was transferred to a Schlenk vessel and the volatiles removed under reduced pressure. The black oily residue was extracted with toluene (15 cm^3) and the solution was chromatographed (silica gel, 26 × 60 mm). Elution with light petroleum (b.p. 40–60 °C) containing 2.5% diethyl ether gave a small yellow band. Elution with light petroleum containing 5–10% diethyl ether gave a larger green-yellow band. On some occasions a purple band was observed on the top of the green-yellow band. Each fraction was collected and the volatiles removed under reduced pressure and the residue was crystallised from light petroleum. The first yellow band failed to crystallise; the solvent was removed to give an oil which was identified as a mixture of [{W(η-$C_5H_4Pr^i$)H_3}B_4H_8] **3** and [{W(η-$C_5H_4Pr^i$)H_4}B_3H_8] **4**. The second yellow band gave microcrystals of *closo*-[{W(η-$C_5H_4Pr^i$)H_2}$_2B_3H_7$] **2**, yield 50 mg (3.5%). The purple band, after two recrystallisations, gave purple-black crystals of an unidentified organometallic compound, yield typically 10 mg.

Alternative Synthesis of [{W(η-$C_5H_4Pr^i$)H_3}B_4H_8] **3**.—A slurry of [W(η-$C_5H_4Pr^i$)Cl_4] (1.0 g, 2.3 mmol) and $LiBH_4$ (0.25 g, 11.4 mmol) in thf (30 cm^3) was stirred at −80 °C. On warming to room temperature the mixture turned dark brown and was stirred for a further 5 d. The solvent was removed under reduced pressure, giving a black material which was chromatographed (silica gel, 2.3 × 6.5 cm). Elution with light petroleum containing 2.5% diethyl ether gave a brown-yellow band and a second orange band. The brown-yellow band failed to crystallise from light petroleum and removal of solvent gave a brown oil of [{W(η-$C_5H_4Pr^i$)H_3}B_4H_8] **3**, yield *ca.* 10 mg (1.3%). The orange band gave no tractable products.

Synthesis of closo-[{W(η-C_5H_4Me)H_2}$_2B_3H_7$] **5**.—A mixture of [W(η-C_5H_4Me)Cl_4] (0.995 g, 2.46 mmol) and $LiBH_4$ (0.277 g, 12.7 mmol) in a Young's ampoule was cooled to −80 °C. Diethyl ether (50 cm^3) at −80 °C was added and the contents of the ampoule warmed to room temperature with stirring. After 1 h the solution was decanted, the volatiles removed under reduced pressure and the residue chromatographed (silica gel, 2.6 × 17 cm). Elution with light petroleum (b.p. 40–60 °C) gave a yellow band which contained a mixture of borane compounds (NMR). Elution with 7% diethyl ether gave a green band, with apparent partial degradation of the column, and elution with pure diethyl ether gave a brown band, which did not contain any boron compounds (^{11}B NMR). The green band was recrystallised from pentane giving small green needle crystals of *closo*-[{W(η-C_5H_4Me)H_2}$_2B_3H_7$] **5**. Yield *ca.* 20 mg (1.4%).

Synthesis of [{Mo(η-C_5H_4Me)(PMe_3)H}B_4H_8] **6**.—A mixture of [Mo(η-C_5H_4Me)(PMe_3)$_2Cl_2$] (0.225 g, 0.70 mmol) and $LiBH_4$ (0.45 g, 20.66 mmol) in thf (20 cm^3) was heated under partial vacuum at 100 °C for 5–10 min. The solution was cooled and the solvent removed under reduced pressure giving a brown solid. Extraction with pentane and recrystallisation gave a dark brown solid and a few orange-brown crystals which were carefully removed and dissolved in deuteriotoluene and identified as [{Mo(η-C_5H_4Me)(PMe_3)H}B_4H_8] **6**.

The reaction was repeated under identical conditions but with a different work-up as follows. The solvent was removed under reduced pressure and the solid obtained was extracted with a 1 : 1 mixture of toluene–light petroleum (b.p. 100–120 °C) and chromatographed (silica gel, 2.6 × 4.8 cm). Elution with light petroleum containing 2.5% diethyl ether gave a bright orange band and a dark orange band. The first orange band gave [{Mo(η-C_5H_4Me)}$_2B_5H_9$] **1** and the second darker orange band contained a mixture of materials. No [{Mo(η-C_5H_4Me)(PMe_3)H}B_4H_8] **6** was obtained despite it being present in the reaction mixture prior to chromatography.

Synthesis of [{W(PMe_3)$_3H_3$}B_3H_8] **8**.—A slurry of [W(PMe_3)$_3Cl_4$] (3.06 g, 5.5 mmol) in diethyl ether (40 cm^3) was cooled to −80 °C and a slurry of $LiBH_4$ (0.518 g, 24 mmol) in diethyl ether (20 cm^3) was added. The mixture was warmed to room temperature and stirred for 5 h, producing a brown solution over a grey-brown solid. The solution was filtered and the solvent removed under reduced pressure giving an oily brown residue. This residue was extracted with pentane (150 cm^3) giving an orange-brown solution. Repeated recrystallisations at −80 °C produced brown crystals of [{W(PMe_3)$_3H_3$}B_3H_8] **8**. Yield 0.4 g (0.88 mmol, 16%).

Synthesis of [{W(PMe_3)$_2H_4$}B_4H_8] **7**.—A yellow solution of [{W(PMe_3)$_3H_3$}B_3H_8] (0.581 g, 1.3 mmol) in thf (10 cm^3) was cooled to −80 °C and treated with BH_3·thf (3 cm^3 of 1 mol dm^{-3} solution, 3 mmol). The mixture was photolysed for 7 h, giving a dark brown solution. The volatiles were removed under reduced pressure and the residue was chromatographed. Elution with diethyl ether–light petroleum (2 : 98) gave a small pale yellow-orange band, gradual elution with diethyl ether–light petroleum (25 : 75 becoming 100 : 0) gave an orange-brown band. The solvent was removed under reduced pressure from this second band, giving an orange brown oil of [{W(PMe_3)$_2H_4$}B_4H_8] **7**. Yield 45 mg (9%). The small yellow-orange band contained some PMe_3·BH_3.

Crystal Structure Determination for [{Mo(η-C_5H_4Me)}$_2B_5H_9$] **1**.—The crystal data are listed in Table 4. A crystal of **1** was sealed in a glass capillary under nitrogen and diffraction

Table 4 Crystal structure data for bicapped *closo*-[{Mo(η-C_5H_4Me)}$_2B_5H_9$] **1**

Empirical formula	$C_{12}H_{23}B_5Mo_2$
M	413.244
Crystal size/mm	0.3 × 0.4 × 0.5
Space group	*C*2/*c*
a/Å	16.824(13)
b/Å	12.117(9)
c/Å	8.010(6)
α, γ/°	90
β/°	106.07(10)
U/Å^3	1569
Z	4
μ (Mo-Kα)/cm^{-1}	1.7494
D_c/g cm^{-3}	1.75
F(000)	816
Radiation (λ/Å)	Mo-Kα (0.710 69)
2θ limits/°	3–50
ω Scan width	1 + 0.35 tan θ
Zone	*h*, *k*, ±*l*
Scan mode	ω–2θ
Total unique data	1607
No. of observations	1322
R (merge)	0.036
Structure solution method	Direct
No. of variables	100
Observations/variables	13.2
Weighting scheme	unit weights
Max., min. peaks in final difference map/e Å^{-3}	1.1, 0.5
Root mean squared shift/e.s.d. in final least-squares cycle	0.03
R^a	0.045
R'^b	0.049

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$.

data collected on an Enraf-Nonius CAD4F 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.

An absorption correction based on azimuthal scan data was applied,[20] 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 direct methods 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 H(1), H(2) and H(211) were found in difference maps, hydrogen H(3) was placed (in a special position) and hydrogen H(211) was placed in a position equivalent to H(212) *via* the molecular (non-crystallographic) symmetry; all B–H hydrogens were refined with a fixed isotropic thermal parameter. All calculations were performed on a MicroVAX 3800 in the Chemical Crystallography Laboratory, Oxford, using the Oxford CRYSTALS system[21] and plotted using SNOOPI. Atomic scattering factors and anomalous dispersion coefficients were taken from the usual sources.[22]

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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