Alkyne–Carbaborane Coupling at a Molybdenum Centre: Crystal Structure of [*closo*-3,3,3-$(CO)_3$-8,3-{σ:η^2-C(H)=C(H)-$SiMe_3$}-3,1,2-$MoC_2B_9H_{10}$]†

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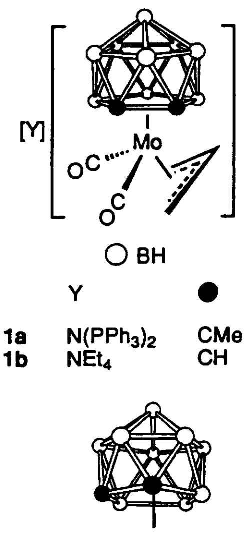
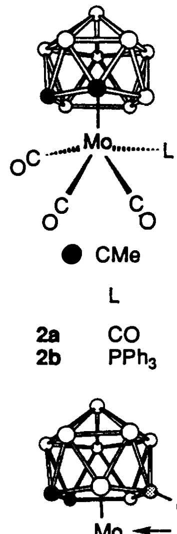
In CH_2Cl_2 the complex [*closo*-1,2-Me_2-3-(η-PhC_2Ph)-3-(CO)-3-(PPh_3)-3,1,2-$MoC_2B_9H_9$] decomposed to yield a mixture of [*closo*-1,2-Me_2-3,3,3-$(CO)_3$-3-(PPh_3)-3,1,2-$MoC_2B_9H_9$] and [*closo*-1,2-Me_2-3,3-$(CO)_2$-3-(PPh_3)-8,3-{σ:η^2-C(Ph)=C(H)Ph}-3,1,2-$MoC_2B_9H_8$]. Protonation ($HBF_4·Et_2O$) of [NEt_4][*closo*-3-(η-C_3H_5)-3,3-$(CO)_2$-3,1,2-$MoC_2B_9H_{11}$], in CH_2Cl_2 at −78 °C, in the presence of an excess of $Me_3SiC≡CSiMe_3$, afforded a chromatographically separable mixture of [*closo*-3,3-(η-$Me_3SiC_2SiMe_3$)$_2$-3-(CO)-3,1,2-$MoC_2B_9H_{11}$] and [*closo*-3,3,3-$(CO)_3$-8,3-{σ:η^2-C(H)=C(H)$SiMe_3$}-3,1,2-$MoC_2B_9H_{10}$]. The latter complex forms *via* the intermediacy of $Me_3SiC≡CH$, generated by HF cleavage of $Me_3SiC≡CSiMe_3$, and its structure was established by X-ray diffraction. The molybdenum atom is ligated on one side by three CO groups, and on the other by the open pentagonal face of the *nido*-1,2-C_2B_9 cage framework. The boron atom located in the β site with respect to the two carbons carries a vinyl substituent C(H)=C(H)$SiMe_3$, and this exopolyhedral group is η^2 co-ordinated to the molybdenum atom [Mo–C 2.43(1) and 2.55(1) Å]. Treatment of [N$(PPh_3)_2$][*closo*-1,2-Me_2-3-(η-C_3H_5)-3,3-$(CO)_2$-3,1,2-$MoC_2B_9H_9$] and $Me_3SiC≡CH$ with $HBF_4·Et_2O$ gives initially the complex [*closo*-1,2-Me_2-3,3-(η-Me_3SiC_2H)$_2$-3-(CO)-3,1,2-$MoC_2B_9H_9$], which subsequently rearranges to [*closo*-1,2-Me_2-3-(η-Me_3SiC_2H)-3-(CO)-8,3-{σ:η^2-C(H)=C(H)$SiMe_3$}-3,1,2-$MoC_2B_9H_8$]. Use of $Me_3SiC≡CD$ in this synthesis, combined with NMR studies, suggests that insertion of the alkyne into the cage B–H bond proceeds *via* the intermediacy of a molybdenum vinylidene species. The NMR data (^1H, $^{13}C-\{^1H\}$, $^{11}B-\{^1H\}$, and $^{31}P-\{^1H\}$) for the new compounds are reported and discussed in relation to the structures proposed.

We have recently reported the synthesis of the molybdenum complex salts [Y][*closo*-1,2-R'_2-3-(η-C_3H_5)-3,3-$(CO)_2$-3,1,2-$MoC_2B_9H_9$] [Y = N$(PPh_3)_2$, R′ = Me **1a**; Y = NEt_4, R′ = H **1b**] and have studied some protonation reactions of these species in the presence of donor molecules [CO, PPh_3, CH_2=CHCH=CH_2, or RC≡CR (R = Me or Ph)].[1] Thus treatment of **1a** with $HBF_4·Et_2O$ in the presence of CO or PPh_3 affords the compounds [*closo*-1,2-Me_2-3,3,3-$(CO)_3$-3-L-3,1,2-$MoC_2B_9H_9$] (L = CO **2a** or PPh_3 **2b**). Protonation of the reagents **1** with $HBF_4·Et_2O$ in the presence of MeC≡CMe yields the bis(alkyne) complexes [*closo*-1,2-R'_2-3,3-(η-MeC_2Me)$_2$-3-(CO)-3,1,2-$MoC_2B_9H_9$] (R′ = Me **3a** or H **3b**). If a mixture of **1a** and PhC≡CPh is treated with $HBF_4·Et_2O$ and PPh_3 is added, the compound [*closo*-1,2-Me_2-3-(η-PhC_2Ph)-3-(CO)-3-(PPh_3)-3,1,2-$MoC_2B_9H_9$] **3c** is formed. In this paper further studies involving alkyne complexes are described.



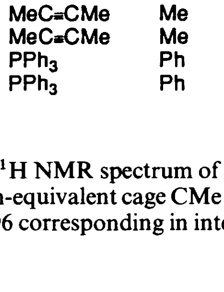
O BH ●

	Y	●
1a	N$(PPh_3)_2$	CMe
1b	NEt_4	CH

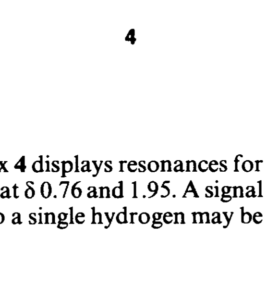


● CMe

	L
2a	CO
2b	PPh_3



	L	R	●
3a	MeC≡CMe	Me	CMe
3b	MeC≡CMe	Me	CH
3c	PPh_3	Ph	CMe
3d	PPh_3	Ph	CH



● CMe ○ BH ◎ B

4

Results and Discussion

If CH_2Cl_2 solutions of compound **3c** are left at ambient temperatures for about 24 h decomposition occurs to give a chromatographically inseparable mixture of the previously characterised species [*closo*-1,2-Me_2-3,3,3-$(CO)_3$-3-(PPh_3)-3,1,2-$MoC_2B_9H_9$] **2b**[1a] and the new compound [*closo*-1,2-Me_2-3,3-$(CO)_2$-3-(PPh_3)-8,3-{σ:η^2-C(Ph)=C(H)Ph}-3,1,2-$MoC_2B_9H_8$] **4**. When complex **3c** was left under a CO atmosphere only **2b** was formed. Although **4** was not isolated pure, entirely free of **2b**, it was fully identified by the NMR data given in Tables 1 and 2, and discussed below. Moreover, the unusual η^2-co-ordination to the molybdenum of the vinyl substituent on the cage is a structural feature also found in a related molecule studied by X-ray diffraction, as described later.

The ^1H NMR spectrum of complex **4** displays resonances for the non-equivalent cage CMe groups at δ 0.76 and 1.95. A signal at δ 4.96 corresponding in intensity to a single hydrogen may be

† *Supplementary Data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Hydrogen-1 and carbon-13 NMR data[a] for the new compounds

Compound	δ (^{1}H)[b]	δ (^{13}C)[c]
3d	2.18 (s, br, 1 H, CH), 3.50 (s, br, 1 H, CH), 7.25–7.47 (m, 25 H, Ph)	236.3 [d, CO, *J*(PC) 13], 216.1, 210.3 (br, C≡C), 133.4–129.3 (Ph), 50.7, 46.4 (br, CH)
4	0.76 (s, 3 H, CMe), 1.95 (s, 3 H, CMe), 4.96 (s, 1 H, =CH), 7.10–8.15 (m, 25 H, Ph)	235.4 [d, CO, *J*(PC) 22], 232.7 [d, CO, *J*(PC) 34], 141.1–127.3 (Ph), 82.7 (vbr, =CPh), 78.0 (*C*HPh), 74.8, 65.8 (br, *C*Me), 26.0, 25.4 (C*Me*)
5	0.34 (s, 9 H, MeSi), 2.96 (s, br, 1 H, CH), 3.41 (s, br, 1 H, CH), 4.13 [d, 1 H, =CH, *J*(HH) 17], 5.54 [d, 1 H, =CH, *J*(HH) 17]	[d] 228.2, 224.6, 223.0 (CO), 96.2 [*C*(H)SiMe$_3$], 49.9, 45.5 (br, CH), 0.5 (MeSi)
6a	0.37 (s, 18 H, MeSi), 0.47 (s, 18 H, MeSi), 3.25 (s, br, 2 H, CH)	233.0 (CO), 179.0, 160.5 (C≡C), 48.6 (br, CH), 1.2, 0.5 (MeSi)
6b	3.29 (s, br, 2 H, CH of C$_2$B$_9$H$_{11}$), 9.21 (s, 2 H, ≡CH), 9.81 (s, 2 H, ≡CH)	222.7 (CO), 157.4, 136.2 (C≡C), 52.1 (br, CH of C$_2$B$_9$H$_{11}$)
6c	0.40 (s, 18 H, MeSi), 1.90 (s, 6 H, CMe), 10.20 (s, 2 H, ≡CH)	228.8 (CO), 177.2 (≡CH), 149.0 (≡CSi), 70.6 (br, *C*Me), 28.2 (C*Me*), −0.5 (MeSi)
7a[e]	−0.25 (s, 9 H, MeSi), 0.41 (s, 9 H, MeSi), 1.09 (s, 3 H, CMe), 1.89 (s, 3 H, CMe), 2.20 [s, 1 H, =C(H)Si], 2.65 [s, 1 H, =C(H)B], 10.87 (s, 1 H, ≡CH)	230.0 (CO), 194.3 (≡CH), 174.5 (≡CSi), 96.5 [vbr, =C(H)B], 79.0, 72.0 (*C*Me), 55.7 [=C(H)Si], 30.0, 27.0 (C*Me*), −0.2, −1.0 (MeSi)

[a] Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz. [b] Measured at ambient temperatures in CD$_2$Cl$_2$ unless otherwise stated. Proton resonances for terminal BH groups occur as broad unresolved peaks in the range δ *ca.* −2 to +3. [c] Hydrogen-1 decoupled, measured at ambient temperatures in CD$_2$Cl$_2$. Chemical shifts are positive to high frequency of SiMe$_4$. [d] Signal due to B*C*H=CHSi carbon nucleus is presumably very broad and therefore not observed. [e] Measured at 230 K.

Table 2 Boron-11 NMR * data for the new compounds

Compound	δ(^{11}B)
3d	0.4 (1 B), −4.0 (1 B), −5.3 (1 B), −5.9 (2 B), −9.5 (1 B), −16.4 (3 B)
4	13.5 (1 B, BCPh), 7.4 (1 B), −0.7 to −10.9 (7 B)
5	21.0 (1 B, BCH), 2.1 (1 B), −6.7 (2 B), −9.0 (2 B), −13.7 (2 B), −16.7 (1 B)
6a	−0.5 (1 B), −5.6 (3 B), −7.3 (1 B), −10.9 (2 B), −15.0 (2 B)
6b	−0.1 (1 B), −3.6 (2 B), −5.5 (1 B), −9.9 (2 B), −14.3 (3 B)
6c	0.5 (1 B), −2.1 (1 B), −3.7 (1 B), −5.1 (3 B), −7.2 (3 B)
7a	18.6 (1 B, BCH), −0.6 (1 B), −1.6 (1 B), −4.5 (1 B), −6.9 (5 B)

* Hydrogen-1 decoupled, measured at ambient temperatures in CD$_2$Cl$_2$. Chemical shifts (δ) in ppm are positive to high frequency of BF$_3$·Et$_2$O (external). Signals ascribed to more than one boron nucleus may result from overlapping peaks, and do not necessarily indicate symmetry equivalence.

ascribed to the vinylic proton of the C(H)Ph group. In the ^{13}C-{^{1}H} NMR spectrum diagnostic doublet resonances for the CO ligands are seen at δ 235.4 [*J*(PC) 22] and 232.7 [*J*(PC) 34 Hz], while peaks for the cage CMe groups are observed at δ 74.8 and 65.8 (*C*Me) and at 26.0 and 25.4 (C*Me*).[2] The resonance occurring at δ 78.0 is attributable to the *C*(H)Ph nucleus, an assignment confirmed by a DEPT (distortionless enhancement by polarisation transfer) spectrum showing that this carbon atom is bonded to one proton. A signal at δ 82.7 is assigned to the carbon atom of the *C*(Ph) group attached to the boron atom. This peak is very broad, a common feature due to the quadrupolar effect of the adjacent ^{11}B nucleus. The resonance for the boron atom carrying the C(Ph) substituent is seen in the ^{11}B-{^{1}H} NMR spectrum (Table 2) at δ 13.5, in the expected range.[2] The ^{31}P-{^{1}H} NMR spectrum shows a singlet peak for the PPh$_3$ ligand at δ 54.2.

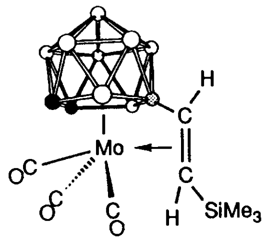
The formation of compound **4** in the decomposition of **3c** implies that the ligated PhC≡CPh molecule in the precursor has inserted into a cage B–H vertex. Efforts were therefore directed towards discovering other reactions leading to complexes with structures having exopolyhedral vinyl groups similar to that of **4**.

The complex [*closo*-3-(η-PhC$_2$Ph)-3-(CO)-3-(PPh$_3$)-3,1,2-MoC$_2$B$_9$H$_{11}$] **3d** was prepared by treating a CH$_2$Cl$_2$ solution containing **1b** and PhC≡CPh with HBF$_4$·Et$_2$O followed by addition of PPh$_3$. However, it proved to be very stable in solution and did not undergo the decomposition described above for **3c**. Similarly, complex **3a** [1a] was also stable in solution, and there was no evidence for insertion of one of its but-2-yne ligands into a cage B-H bond. Reactions with the alkynes Me$_3$SiC≡CSiMe$_3$ and Me$_3$SiC≡CH were then investigated since these alkynes are known to co-ordinate readily to metal centres.

Treatment of the salt **1b** and an excess of Me$_3$SiC≡CSiMe$_3$ in CH$_2$Cl$_2$ at −78 °C with HBF$_4$·Et$_2$O (1.1 molar equivalent) afforded a mixture of the two compounds [*closo*-3,3,3-(CO)$_3$-8,3-{σ:η^2-C(H)=C(H)SiMe$_3$}-3,1,2-MoC$_2$B$_9$H$_{10}$] **5** and [*closo*-3,3-(η-Me$_3$SiC$_2$SiMe$_3$)$_2$-3-(CO)-3,1,2-MoC$_2$B$_9$H$_{11}$] **6a** separated by column chromatography. Formation of **6a** in this reaction is not unexpected, in view of the earlier syntheses of the structurally similar compounds **3a** and **3b** by a similar procedure. The ^{1}H and ^{13}C-{^{1}H} NMR spectra of **6a** are in agreement with its formulation. In the ^{1}H NMR spectrum resonances for the SiMe$_3$ groups are seen at δ 0.37 and 0.47, and there is a broad peak at δ 3.25 for the cage CH vertices. The ^{13}C-{^{1}H} NMR spectrum displays a resonance for the CO group at δ 233.0. Peaks at δ 179.0 and 160.5 are ascribed to the ligated carbon atoms of the alkyne ligands, and the chemical shifts are in accord with these groups functioning formally as three-electron donors.[3] The observation of two signals indicates that the alkyne molecules are not rotating on the NMR time-scale about an axis through the metal atom and the midpoint of the C≡C bonds. The cage CH groups give rise to a broad peak at δ 48.6.

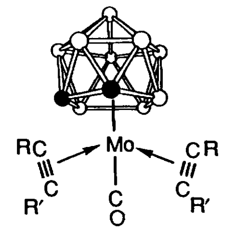
The formation of complex **5** was unexpected, but its structure was firmly established by a single-crystal X-ray diffraction study. There are two crystallographically independent molecules in the asymmetric unit. Only molecule 1 is discussed herein and selected bond distances and angles are listed in Table 3 and the structure is shown in Fig. 1. As expected the metal atom is ligated on one side by three CO groups deviating slightly from linearity (average Mo–C–O 174°). On the other side the open pentagonal face of the *nido*-C$_2$B$_9$ cage is co-ordinated to the molybdenum atom in the usual pentahapto manner, although the Mo(1)–B(4) connectivity [2.29(2) Å] is appreciably shorter than those between Mo(1) and B(3) [2.44(2) Å] and between Mo(1) and B(5) [2.40(2) Å]. Interest focuses on the vinyl group attached to B(4) which is η^2 co-ordinated to the molybdenum [Mo(1)–C(6) 2.43(1), Mo(1)–C(7) 2.55(1), C(6)–C(7) 1.42(2) Å]. The various groups attached to the molybdenum thus provide the metal with the necessary number of electrons for a filled valence shell.

The NMR data for compound **5** are in accord with the



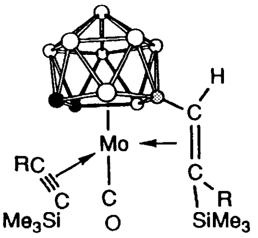
● CH ○ BH ◎ B

5



○ BH

	R	R′	●
6a	SiMe$_3$	SiMe$_3$	CH
6b	H	H	CH
6c	H	SiMe$_3$	CMe
6d	H	H	CMe



● CMe ○ BH ◎ B

	R
7a	H
7b	D

structure established by X-ray diffraction. The ^{1}H NMR spectrum reveals the presence of the alkene protons of the $C(H)$=$C(H)SiMe_3$ group with doublet signals at δ 4.13 and 5.54 [J(HH) 17 Hz]. The magnitude of the ^{1}H–^{1}H coupling establishes that the two protons of the vinyl group are transoid,[4] as found in the solid-state structure (Fig. 1). The ^{13}C-{^{1}H} NMR spectrum shows resonances at δ 228.2, 224.6 and 223.0 for the three non-equivalent CO ligands. A peak at δ 96.2 is assigned to the olefinic carbon C(H)SiMe$_3$. The signal due to the exopolyhedral vinyl-carbon atom bonded to the boron atom in the open pentagonal face of the cage ligating the molybdenum is not seen in the spectrum. This is not unusual,[2] and is very probably due to the quadrupolar effect of the neighbouring B(4) atom (Fig. 1) broadening the resonance so that it is lost in the noise. However, in the ^{11}B-{^{1}H} NMR spectrum there is a characteristic peak for a single boron nucleus attached to an exopolyhedral carbon group at δ 21.0, which remains as a singlet in the fully coupled spectrum.

The origin of the BC(H)=C(H)SiMe$_3$ group in complex **5** is of interest. It seemed that it must have originated by insertion of a Me$_3$SiC≡CH ligand into a B–H bond, and that the alkyne required for this reaction had been generated *in situ* by HF cleavage of one of the SiMe$_3$ groups from Me$_3$SiC≡CSiMe$_3$. This was confirmed when **5** was prepared by treating a mixture of **1b** and an excess of Me$_3$SiC≡CH with HBF$_4$·Et$_2$O. The latter reagent often contains traces of HF. In this reaction also cleavage of Me$_3$Si groups evidently occurred, as an additional product was the very air-unstable species [*closo*-3,3-(η-HC$_2$-H)$_2$-3-(CO)-3,1,2-MoC$_2$B$_9$H$_{11}$] **6b**. However, no reaction occurred between **7a**, described later, and HBF$_4$·Et$_2$O, implying that desilylation of the alkyne takes place prior to its co-ordination to the metal centre.

The complex **6b** was characterised spectroscopically. In the IR spectrum the CO ligand gives rise to a strong band at 2059 cm^{-1}, and in the ^{13}C-{^{1}H} NMR spectrum the resonance for this group is at δ 222.7. The ligated carbon atoms of the two HC≡CH molecules resonate at δ 157.4 and 136.2, and the peak for the cage CH vertices occurs at δ 52.1.[2] In the ^{1}H NMR spectrum the signal for the latter is observed as a broad peak at δ 3.29, while resonances for the alkyne protons occur at δ 9.21 and 9.81. The observation in both the ^{13}C-{^{1}H} and ^{1}H NMR spectra of two peaks for the HC≡CH ligands indicates that they are not rotating on the NMR time-scale.

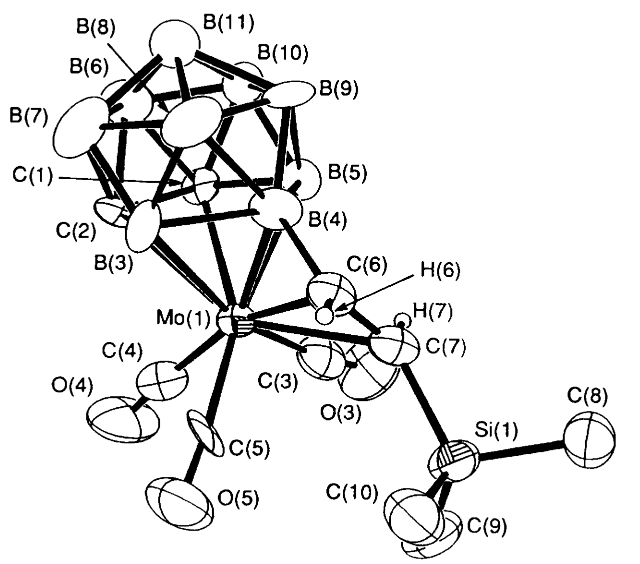


Fig. 1 The molecular structure of [*closo*-3,3,3-(CO)$_3$-8,3-{σ:η^2-C(H)=C(H)SiMe$_3$}-3,1,2-MoC$_2$B$_9$H$_{10}$] **5** (molecule 1), showing the crystallographic labelling scheme

Further insight into the formation of complexes of type **4** and **5**, having vinyl groups exopolyhedrally linked to a carbaborane cage, was gained by treating mixtures of **1a** and an excess of Me$_3$SiC≡CH with a slight deficiency of HBF$_4$·Et$_2$O at room temperature. At this temperature, the alkyne HC≡CH generated by desilylation is lost faster from the solution than at −78 °C. When this same reaction was allowed to proceed for a short time (*ca.* 5 min) the complex [*closo*-1,2-Me$_2$-3,3-(η-Me$_3$Si-C$_2$H)$_2$-3-(CO)-3,1,2-MoC$_2$B$_9$H$_9$] **6c** was formed. If, however, the reaction is allowed to proceed for several hours, complex **6c** is converted into [*closo*-1,2-Me$_2$-3-(η-Me$_3$SiC$_2$H)-3-(CO)-8,3-{σ:η^2-C(H)=C(H)SiMe$_3$}-3,1,2-MoC$_2$B$_9$H$_8$] **7a**, and none of **6c** remains.

The ^{1}H and ^{13}C-{^{1}H} NMR data for complex **7a** were measured at 230 K since the resonances at this temperature were somewhat sharper than those obtained at room temperature, indicating that the complex was exhibiting a degree of fluxional behaviour. However, the difference between the chemical shift patterns seen at ambient and low temperatures was minimal. In the ^{1}H NMR spectrum a resonance at δ 10.87 is readily assigned to the alkyne proton of the η^2-co-ordinated Me$_3$SiC≡CH ligand. Peaks at δ −0.25 and 0.41 are attributable to the SiMe$_3$ substituents on the basis of their shifts and relative intensities. The two non-equivalent cage CMe vertices give rise to singlets at δ 1.09 and 1.89. The olefinic protons of the BC(H)=C(H)-SiMe$_3$ group appear at δ 2.20 and 2.65, and their occurrence as singlets rather than doublets indicates that they are cisoid with respect to one another across the ligated C=C bond. This is in contrast to the situation with compound **5**, as discussed above. In the ^{13}C-{^{1}H} NMR spectrum of **7a** the ligated carbon atoms of the η-Me$_3$SiC≡CH molecule are observed at δ 194.3 and 174.5 with the former peak being appreciably more intense than the latter. The signal at δ 194.3 is therefore assigned to the ≡CH nucleus. The chemical shifts are in the range diagnostic for an alkyne donating four electrons to a metal centre,[3] and it is noteworthy that complex **7a** contrasts with **4** and **5** in having one less group co-ordinated to the molybdenum atom. Peaks in the ^{13}C-{^{1}H} NMR spectrum of **7a** for the vinylic carbons of the BC(H)=C(H)SiMe$_3$ moiety occur at δ 96.5 and 55.7. The former is very broad and the latter sharp, so the peak at 96.5 may be assigned to the BC(H) nucleus for the reasons discussed

Table 3 Selected internuclear distances (Å) and angles (°) for [*closo*-3,3,3-$(CO)_3$-8,3-{σ:η^2-C(H)=C(H)$SiMe_3$}-3,1,2-$MoC_2B_9H_{10}$] **5**, with estimated standard deviations in parentheses

Molecule 1

Mo(1)–C(1)	2.37(1)	Mo(1)–C(2)	2.38(1)	Mo(1)–B(3)	2.44(2)	Mo(1)–B(4)	2.29(2)
Mo(1)–B(5)	2.40(2)	Mo(1)–C(3)	1.98(2)	Mo(1)–C(4)	2.04(1)	Mo(1)–C(5)	1.95(2)
Mo(1)–C(6)	2.43(1)	Mo(1)–C(7)	2.55(1)	C(1)–C(2)	1.64(2)	C(1)–B(5)	1.69(2)
C(1)–B(6)	1.72(2)	C(1)–B(10)	1.75(2)	C(2)–B(3)	1.61(2)	C(2)–B(6)	1.81(2)
C(2)–B(7)	1.69(2)	B(3)–B(4)	1.84(2)	B(3)–B(7)	1.72(2)	B(3)–B(8)	1.72(2)
B(4)–B(5)	1.83(2)	B(4)–B(8)	1.76(2)	B(4)–B(9)	1.74(2)	B(4)–C(6)	1.53(2)
B(5)–B(9)	1.76(2)	B(5)–B(10)	1.74(2)	B(6)–B(7)	1.85(2)	B(6)–B(10)	1.75(2)
B(6)–B(11)	1.76(3)	B(7)–B(8)	1.84(3)	B(7)–B(11)	1.80(3)	B(8)–B(9)	1.77(2)
B(8)–B(11)	1.77(2)	B(9)–B(10)	1.77(2)	B(9)–B(11)	1.77(3)	B(10)–B(11)	1.77(3)
C(3)–O(3)	1.17(2)	C(4)–O(4)	1.15(2)	C(5)–O(5)	1.20(2)	C(6)–C(7)	1.42(2)
C(7)–Si(1)	1.86(1)	Si(1)–C(8)	1.89(2)	Si(1)–C(9)	1.80(2)	Si(1)–C(10)	1.83(2)
C(3)–Mo(1)–C(4)	76.4(6)	C(3)–Mo(1)–C(5)	104.2(6)	C(4)–Mo(1)–C(5)	78.6(6)	C(3)–Mo(1)–C(6)	105.6(5)
C(5)–Mo(1)–C(6)	81.2(5)	C(3)–Mo(1)–C(7)	73.7(5)	C(5)–Mo(1)–C(7)	81.5(5)	Mo(1)–B(4)–C(6)	76.2(8)
Mo(1)–C(3)–O(3)	173(1)	Mo(1)–C(4)–O(4)	174(1)	Mo(1)–C(5)–O(5)	175(1)	Mo(1)–C(6)–B(4)	66.1(7)
Mo(1)–C(6)–C(7)	78.4(8)	B(4)–C(6)–C(7)	123(1)	Mo(1)–C(7)–C(6)	68.7(7)	Mo(1)–C(7)–Si(1)	126.9(6)
C(6)–C(7)–Si(1)	127(1)	C(7)–Si(1)–C(8)	107.7(6)	C(7)–Si(1)–C(9)	111.6(7)	C(8)–Si(1)–C(9)	109.3(7)
C(7)–Si(1)–C(10)	108.9(7)	C(8)–Si(1)–C(10)	107.5(7)	C(9)–Si(1)–C(10)	111.7(8)		

Molecule 2

Mo(2)–C(51)	2.36(1)	Mo(2)–B(52)	2.32(2)	Mo(2)–B(53)	2.41(2)	Mo(2)–C(52)	1.96(1)
Mo(2)–C(53)	2.02(2)	Mo(2)–C(54)	2.33(2)	Mo(2)–C(55)	2.51(3)	C(51)–B(53)	1.69(2)
C(51)–B(54)	1.71(3)	C(51)–B(56)	1.72(2)	C(51)–C(51a)	1.51(2)	B(52)–B(53)	1.83(2)
B(52)–B(55)	1.78(2)	B(52)–C(54)	1.41(3)	B(53)–B(55)	1.72(2)	B(53)–B(56)	1.84(2)
B(54)–B(56)	1.74(2)	B(54)–B(57)	1.80(3)	B(55)–B(56)	1.82(2)	B(55)–B(57)	1.79(2)
B(55)–B(55a)	1.86(3)	B(56)–B(57)	1.79(2)	C(52)–O(52)	1.17(2)	C(53)–O(53)	1.16(3)
C(54)–C(55)	1.41(3)	C(55)–Si(2)	1.61(3)	Si(2)–C(56)	1.78(2)	Si(2)–C(57)	1.79(4)
C(52)–Mo(2)–C(53)	77.1(5)	C(52)–Mo(2)–C(54)	93.8(5)	C(53)–Mo(2)–C(54)	164.6(8)	C(52)–Mo(2)–C(55)	73.8(5)
C(52)–Mo(2)–C(52a)	105.4(9)	C(53)–Mo(2)–C(52a)	77.1(5)	C(54)–Mo(2)–C(52a)	93.8(5)	C(55)–Mo(2)–C(52a)	73.8(5)
Mo(2)–B(52)–C(54)	73(1)	Mo(2)–C(52)–O(52)	175(1)	Mo(2)–C(53)–O(53)	169(2)	Mo(2)–C(54)–B(52)	72(1)
Mo(2)–C(54)–C(55)	80(2)	B(52)–C(54)–C(55)	152(2)	Mo(2)–C(55)–C(54)	66(1)	Mo(2)–C(55)–Si(2)	147(2)
C(54)–C(55)–Si(2)	147(2)	C(55)–Si(2)–C(56)	111.4(9)	C(55)–Si(2)–C(57)	108(2)	C(56)–Si(2)–C(57)	110(1)
C(56)–Si(2)–C(56a)	107(2)						

earlier. The remaining peaks in the spectrum are as expected, with the resonance for the CO ligand at δ 230.0, four peaks for the cage CMe groups at δ 79.0 and 72.0 (*C*Me), and 30.0 and 27.0 (C*Me*), and two signals for the $SiMe_3$ substituents at δ −0.2 and −1.0. In the ^{11}B-{^{1}H} NMR spectrum the diagnostic resonance for the boron atom attached to the exopolyhedral vinyl group is seen at δ 18.6.[2]

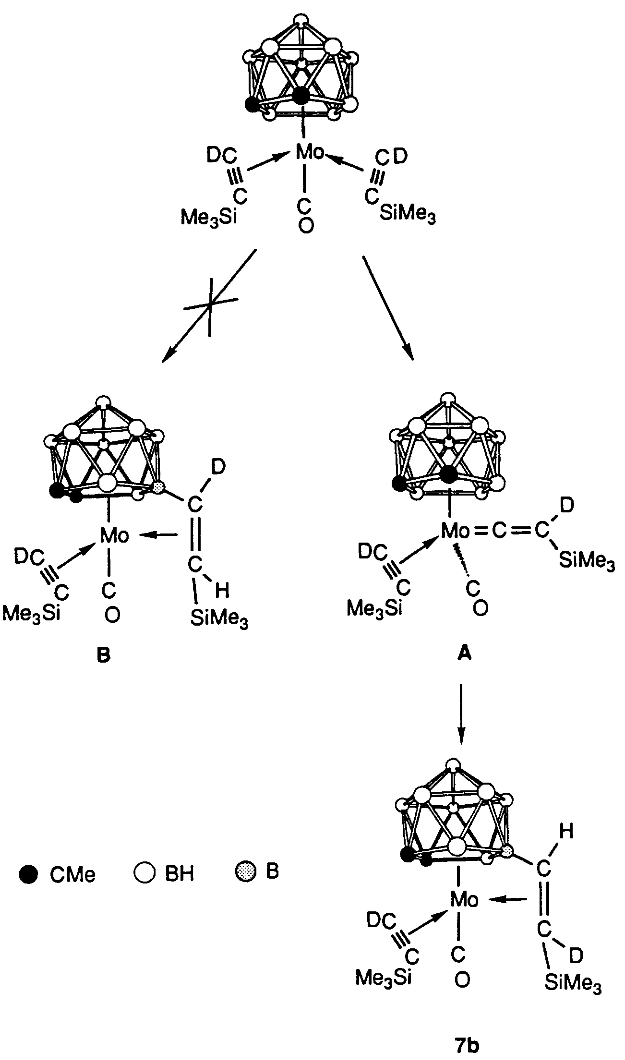
Although, as described above, compound **6c** is labile and readily transforms into the thermodynamically more stable complex **7a**, it was possible to obtain NMR data for the former species (Tables 1 and 2) from the spectra of a mixture in which it predominated. A relatively deshielded signal in the ^{1}H NMR spectrum at δ 10.20 is due to the HC≡ nuclei of the two co-ordinated $Me_3SiC{\equiv}CH$ molecules. Resonances for the cage CMe groups appear in the ^{1}H NMR spectrum at δ 1.90, and in the ^{13}C-{^{1}H} NMR spectrum at δ 70.6 (*C*Me) and 28.2 (C*Me*). The apparent equivalence of these groups implies that the carbaborane cage is rotating about an axis through the molybdenum atom and the centroid of the CCBBB face of the ligating cage. Peaks in the ^{13}C-{^{1}H} NMR spectrum at δ 149.0 and 177.2 are ascribed to the Me_3Si*C*≡CH and $Me_3SiC{\equiv}$*C*H nuclei, respectively; these shifts being consistent with the alkyne groups formally acting as three electron donors.[3]

It is noteworthy that the complex [*closo*-1,2-Me_2-3,3-(η-$HC_2H)_2$-3-(CO)-3,1,2-$MoC_2B_9H_9$] **6d** was formed as a minor product (*ca.* 10%) with **6c** and was detected from the ^{1}H NMR spectrum of mixtures of the two species. Thus there are two singlets at δ 9.40 and 10.14 ascribable to the alkyne protons of **6d**, each peak corresponding to two protons. The two cage methyl groups give rise to a resonance at δ 2.37. Like **6b**, complex **6d** is unstable.

In order to gain further understanding of the pathway for the formation of complex **7a** through the intermediacy of **6c**, the synthesis was repeated using $Me_3SiC{\equiv}CD$ instead of $Me_3SiC{\equiv}CH$. This reaction (see Experimental section) afforded the deuteriated complex [*closo*-1,2-Me_2-3-(η-Me_3SiC_2D)-3-(CO)-8,3-{σ:η^2-C(H)=C(D)$SiMe_3$}-3,1,2-$MoC_2B_9H_8$] **7b**. As expected, for the latter ν_{max}(CO) in the IR spectrum (1984 cm^{-1}) was identical with that for **7a**, and the ^{11}B-{^{1}H} NMR spectra of the two species were also the same.

In the ^{1}H NMR spectrum of complex **7b** there were no resonances at δ 2.20 or 10.87 as found in the spectrum of **7a**, but in the ^{2}H NMR spectrum there were corresponding signals at δ 2.33 (=CD) and 10.92 (≡CD). The ^{13}C-{^{1}H} NMR spectrum of **7b** was crucial in establishing the site of the ^{2}H nucleus in the vinyl group. Most peaks in the spectra of **7a** and **7b** are the same, as expected. However, in the ^{13}C-{^{1}H} NMR spectrum of **7b** there is a peak at δ 195.5, very broad due to unresolved ^{2}H–^{13}C coupling, and a triplet signal at δ 56.8 [*J*(^{2}H–^{13}C) 24 Hz]. The former resonance is clearly due to the $Me_3SiC{\equiv}$*C*D nucleus and corresponds to the peak seen in the spectrum of **7a** at δ 194.3. The triplet signal in the spectrum of **7b** relates to that at δ 55.7 for **7a** which was assigned to the BC(H)=*C*(H)$SiMe_3$ nucleus, as discussed above. It follows, therefore, that a C(D)$SiMe_3$ moiety rather than a C(H)$SiMe_3$ group must be present in **7b**, leading to the conclusion that formation of the complexes **7** proceeds through hydrogen migration as depicted in Scheme 1, intermediate **A**. Insertion of the resultant vinylidene group into the B–H bond in the cage which is in the β site with respect to the two carbon vertices in the CCB*B*B ring would then afford the final product.

The alternative pathway shown involving hydroboration of the alkyne at the molybdenum centre would afford a species with structure **B** having a pendant BC(D)=C(H)$SiMe_3$ group. The intermediacy of a vinylidene fragment, as in **A**, in the formation of **7** or the related species **5** is supported by studies



Scheme 1

which show that terminal alkylidene groups ligating Mo or W readily insert into cage B-H bonds.[2] Also the rearrangement M(η-RC≡CH) ⟶ M=C=C(H)R shown in Scheme 1 is well documented in the literature, and has been discussed from a theoretical standpoint.[5] Although the pathways to compounds **5** and **7** involve hydrogen migration from one carbon centre in $Me_3SiC{\equiv}CH$ to the other, the formation of **4** must occur *via* hydroboration of the co-ordinated PhC_2Ph ligand.

In conclusion, as far as we are aware, the insertion of alkyne groups into a B-H bond of a carbametallaborane cage is without precedent. Other insertion reactions based on use of the reagents **1** are under investigation.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen, using Schlenk-tube techniques. Solvents were distilled from appropriate drying agents under nitrogen before use. Light petroleum refers to that fraction of b.p. 40–60 °C. Chromatography columns (*ca.* 15 cm in length and 2 cm in diameter) were packed with silica gel (Aldrich, 70–230 mesh). The NMR spectra (Tables 1 and 2) were recorded with a Bruker AMX360 instrument operating at 90.6 for ^{13}C, 115.5 for ^{11}B, and 145.8 MHz for ^{31}P. Chemical shifts (δ) for phosphorus are positive to high frequency of 85% H_3PO_4 (external). The IR spectra were recorded in CH_2Cl_2, unless otherwise stated, using a Bruker IFS 25 FT-IR spectrometer. The reagents **1** and **3c** were prepared as described previously.[1a] Tetrafluoroboric acid was an 85% solution of $HBF_4{\cdot}Et_2O$ in Et_2O, as supplied by Aldrich. Green *microcrystals* of [*closo*-3-(η-PhC_2Ph)-3-(CO)-3-(PPh_3)-3,1,2-$MoC_2B_9H_{11}$] **3d** were prepared (78% yield) by the method used to obtain **3c**[1a] (Found: C, 60.6; H, 5.2. $C_{35}H_{36}B_9MoOP$ requires C, 60.3; H, 5.2%); ν_{max}(CO) at 1969 cm^{-1}. ^{31}P-{^1H} NMR (CD_2Cl_2): δ 53.9.

Formation of [*closo*-1,2-Me_2-3,3-$(CO)_2$-3-(PPh_3)-8,3-{σ:η^2-C(Ph)=C(H)Ph}-3,1,2-$MoC_2B_9H_8$] **4**.—A CD_2Cl_2 solution (0.5 cm^3) of complex **3c** (0.03 g, 0.04 mmol) was placed in an NMR tube and allowed to stand at room temperature for *ca.* 24 h, during which time the colour changed from green to yellow, and NMR measurements showed no signals due to **3c**. Chromatography of the solution at −20 °C and elution of the column with CH_2Cl_2–light petroleum (1:1) gave a yellow eluate. Solvent was removed *in vacuo* and the residue afforded a microcrystalline mixture (0.01 g, *ca.* 1:3) of **2b**[1a] and [*closo*-1,2-Me_2-3,3-$(CO)_2$-3-(PPh_3)-8,3-{σ:η^2-C(Ph)=C(H)Ph}-3,1,2-$MoC_2B_9H_8$] **4**; ν_{max}(CO) at 1968s and 1896vs cm^{-1} (in light petroleum). ^{31}P-{^1H} NMR (CD_2Cl_2): δ 54.2; see also Tables 1 and 2.

Reactions with $Me_3SiC{\equiv}CSiMe_3$ *and* $Me_3SiC{\equiv}CH$.—(*i*) Addition of $HBF_4{\cdot}Et_2O$ (0.13 cm^3, 0.73 mmol) to a CH_2Cl_2 (10 cm^3) solution of complex **1b** (0.30 g, 0.66 mmol) and $Me_3SiC{\equiv}CSiMe_3$ (0.56 g, 3.29 mmol) at −78 °C gave a deep red colouration. The mixture was warmed slowly to room temperature and stirred for 3 h. Solvent was removed *in vacuo*, and the residue was pre-adsorbed on silica and chromatographed on the same support. Elution with light petroleum removed a red fraction. After removal of solvent *in vacuo* the residue was crystallised from CH_2Cl_2–light petroleum (20 cm^3, 1:19) to give red *microcrystals* of [*closo*-3,3,3-$(CO)_3$-8,3-{σ:η^2-C(H)=C(H)$SiMe_3$}-3,1,2-$MoC_2B_9H_{10}$] **5** (0.09 g, 32%) (Found: C, 29.0; H, 5.7. $C_{10}H_{21}B_9MoO_3Si$ requires C, 29.3; H, 5.2%); ν_{max}(CO) at 2045vs, 1990m, and 1951vs cm^{-1}. Further elution of the column with CH_2Cl_2–light petroleum (1:1) yielded an orange fraction which, after removal of solvent *in vacuo* and crystallisation from CH_2Cl_2–light petroleum as for **5**, gave orange *microcrystals* of [*closo*-3,3-(η-$Me_3SiC_2SiMe_3$)$_2$-3-(CO)-3,1,2-$MoC_2B_9H_{11}$] **6a** (0.11 g, 27%) (Found: C, 38.2; H, 8.3. $C_{19}H_{47}B_9MoOSi_4$ requires C, 38.2; H, 7.9%); ν_{max}(CO) at 2009 cm^{-1}.

(*ii*) In a similar experiment, treatment of a mixture of complex **1b** (0.30 g, 0.66 mmol) and $Me_3SiC{\equiv}CH$ (0.46 cm^3, 3.25 mmol) with an excess of $HBF_4{\cdot}Et_2O$ (0.13 cm^3, 0.73 mmol) at −78 °C gave compound **5** (0.08 g, 28%) and yellow *microcrystals* of [*closo*-3,3-(η-HC_2H)$_2$-3-(CO)-3,1,2-$MoC_2B_9H_{11}$] **6b** (0.04 g, 20%); ν_{max}(CO) at 2059 cm^{-1}

(*iii*) A CH_2Cl_2 (20 cm^3) solution containing complex **1a** (0.10 g, 0.11 mmol) and $Me_3SiC{\equiv}CH$ (0.05 cm^3, 0.35 mmol) at room temperature was treated with a deficiency of $HBF_4{\cdot}Et_2O$ (0.01 cm^3, 0.06 mmol) and the mixture was stirred for 5 min. Solvent was removed *in vacuo*, the residue extracted with CH_2Cl_2–light petroleum (10 cm^3, 1:1) and chromatographed. Elution with the same solvent mixture gave a yellow fraction from which solvent was removed *in vacuo* to give a 9:1 mixture (0.02 g, 69% based on $HBF_4{\cdot}Et_2O$ used) of brown *microcrystals* of [*closo*-1,2-Me_2-3,3-(η-Me_3SiC_2H)$_2$-3-(CO)-3,1,2-$MoC_2B_9H_9$] **6c** [ν_{max}(CO) at 2033 cm^{-1}] and [*closo*-1,2-Me_2-3,3-(η-HC_2H)$_2$-3-(CO)-3,1,2-$MoC_2B_9H_9$] **6d**.

(*iv*) A CH_2Cl_2 (20 cm^3) solution of complex **1a** (0.10 g, 0.11 mmol) and $Me_3SiC{\equiv}CH$ (0.05 cm^3, 0.35 mmol) was treated with a deficiency of $HBF_4{\cdot}Et_2O$ (0.01 cm^3, 0.06 mmol), and the mixture was stirred overnight. Solvent was removed *in vacuo*, the residue extracted with CH_2Cl_2-light petroleum (10 cm^3, 1:1) and the extracts chromatographed at −20 °C. Elution with the same solvent mixture gave a red eluate. Solvent was removed *in vacuo* to yield red oily *microcrystals* of [*closo*-1,2-Me_2-3-(η-Me_3SiC_2H)-3-(CO)-8,3-{σ:η^2-C(H)=C(H)$SiMe_3$}-3,1,2-$MoC_2B_9H_8$] **7a** (0.02 g, 69% based on $HBF_4{\cdot}Et_2O$ used).

Mass spectrum m/z: 481 (M^+), 453 (M^+ − CO) and 355 (M^+–CO–$Me_3SiC{\equiv}CH$). ν_{max}(CO) at 1984 cm^{-1}.

(*v*) A Et_2O (10 cm^3) solution of $Me_3SiC{\equiv}CH$ (0.50 cm^3, 3.5 mmol) was treated with $LiBu^n$ (7 mmol, 3.5 cm^3 of a 2.0 mol dm^{-3} solution in cyclohexane) at −78 °C. After warming the mixture slowly to *ca.* 0 °C, D_2O (5 cm^3) was slowly added. The ether layer was separated to give a *ca.* 0.35 mol dm^{-3} solution of $Me_3SiC{\equiv}CD$ in Et_2O. This solution was then used to prepare [*closo*-1,2-Me_2-3-(η-Me_3SiC_2D)-3-(CO)-8,3-{σ:η^2-C(H)=C(D)$SiMe_3$}-3,1,2-$MoC_2B_9H_8$] **7b**, using a similar procedure to that described for **7a**.

Crystal Structure Determination and Refinement.—Crystals of compound **5** were grown by slow diffusion of light petroleum into a CH_2Cl_2 solution of the complex. The X-ray measurements were obtained from a rectangular crystal (0.08 × 0.26 × 0.36 mm) the optical homogeneity and anisotropic (biaxial) nature of which were verified on a Zeiss Photomicroscope II. Data were collected on an Enraf-Nonius CAD4-F automated diffractometer in the ω–2θ mode at a varied scan rate (0.43–3.44° min^{-1}) and in the range 2θ 3.0–40.0° (*h* 0–11, *k* 0–12, *l* 0–33). The monitored check reflections measured as a function of time (every 2 h) showed no significant variations (< 1.0%). Therefore, crystal stability and electronic hardware reliability were confirmed. Lorentz and polarisation corrections as well as an empirical absorption correction (transmission factors: minimum, 0.697; maximum, 1.458) were applied to all intensity data. Of the 3122 collected reflections, 2786 were independent of which 2015 reflections had $F \geqslant 4.0\sigma(F)$. Examination of the resultant data revealed the conditions: $0kl$, $k = 2n$; $h0l$, $l = 2n$; $0k0$, $k = 2n$; and $00l$, $l = 2n$ which are consistent with space group *Pbcm*. Final unit-cell dimensions and standard deviations were obtained by least-squares refinement of twenty-five well centred high-angle reflections (27 < 2θ < 40°). Crystal data and relevant parameters are summarised in Table 4.

A crystallographic analysis (direct methods) of the reduced data using the SHELXTL-PC[6] package of programs located all non-hydrogen atoms which were anisotopically refined using the conventional full-matrix least-squares method. The SHELXTL-PC package and the density calculation dictated Z = 12. Molecule 1 relates to eight of the twelve molecules at a multiplicity of 1.0, whereas molecule 2 has a multiplicity of 0.5 which is equivalent to four molecules. This is because the atoms Mo(2), B(52), B(54), B(57), C(53), O(53), C(54), C(55), Si(2) and C(57) of molecule 2 are located at crystallographic special positions with coordinates (x, y, 0.25) and therefore define a crystallographic mirror plane. The atoms C(51a), B(53a), B(55a), B(56a), C(52a), O(52a) and C(56a) were generated from the symmetry-related atoms. Although the two molecules clearly have the same gross structure, the refined parameters for molecule 2 are not as reliable as those for molecule 1, and so only the latter were discussed earlier. After the application of a secondary extinction correction [$g = 7(4) \times 10^{-5}$ e^{-2}], the residual factors, $R = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, stabilised with an average shift/error value of 5.4×10^{-2}. Hydrogen atoms H(6) and H(7) which are bonded to C(6) and C(7) were located by Fourier difference mapping. All other hydrogen atomic positions were calculated (C–H 0.96 and B–H 1.10 Å) and allowed to ride on their respective bonding atoms with fixed isotropic thermal parameters (80 and 60 × 10^{-3} Å^2, respectively).[6,7] The minimised quantity was $\Sigma w||F_o| - |F_c||^2$ and the weighting scheme was $w^{-1} = \sigma^2(F) + 0.0041|F|^2$. The final electron-density map displayed some residual density (Table 4) in the vicinity of the Mo atom, as is normal. However, elsewhere only a random fluctuating background was observed. Atomic scattering factors and associated anomalous dispersion correction factors were taken from the usual source.[8] Final fractional atomic coordinates for non-hydrogen atoms are presented in Table 5.

Table 4 Data for crystal structure analysis of compound **5**

Molecular formula	$C_{10}H_{21}B_9MoO_3Si$
M	410.6
Crystal system	Orthorhombic
Space group	*Pbcm* (no. 57)
a/Å	12.3261(9)
b/Å	13.512(4)
c/Å	35.250(3)
U/Å^3	5860(2)
Z	12
D_c/g cm^{-3}	1.396
$F(000)$	2472
μ(Mo-Kα)/cm^{-1}	7.18
T/K	292
Scan range (ω/°)	1.15 + 0.34 tan θ
Radiation	Mo-Kα ($\bar{\lambda}$ = 0.71073 Å)
Data-to-parameter ratio	6.0:1
R,R' (R_{all})	0.079, 0.094 (0.117)
S (Goodness of fit)	1.74
Residual density (maximum, minimum/e Å^{-3})	1.29, −1.16

Table 5 Atomic coordinates (× 10^4) for complex **5**, with estimated standard deviations in parentheses

Atom	x	y	z
Molecule 1			
Mo(1)	1 822(1)	1 358(1)	5 818(1)
C(1)	288(9)	1 811(10)	6 186(3)
C(2)	103(11)	2 133(10)	5 741(3)
B(3)	171(13)	1 233(9)	5 442(5)
B(4)	523(12)	166(12)	5 744(4)
B(5)	544(12)	587(11)	6 237(4)
B(6)	−1 032(13)	2 071(14)	6 066(4)
B(7)	−1 080(14)	1 711(14)	5 559(5)
B(8)	−791(12)	373(12)	5 564(5)
B(9)	−594(11)	−10(13)	6 040(5)
B(10)	−751(13)	1 024(11)	6 342(5)
B(11)	−1 568(15)	912(14)	5 932(5)
C(3)	2 888(12)	1 277(10)	6 237(4)
O(3)	3 422(10)	1 197(10)	6 508(4)
C(4)	2 441(12)	2 753(10)	5 847(5)
O(4)	2 856(11)	3 518(9)	5 841(4)
C(5)	2 710(13)	1 405(9)	5 361(5)
O(5)	3 182(10)	1 431(9)	5 064(4)
C(6)	1 560(9)	−333(9)	5 602(4)
C(7)	2 511(10)	−424(10)	5 825(4)
Si(1)	3 864(3)	−871(3)	5 665(1)
C(8)	4 115(12)	−2 110(10)	5 895(4)
C(9)	4 925(13)	−28(12)	5 799(4)
C(10)	3 826(15)	−1 066(12)	5 153(5)
Molecule 2			
Mo(2)	8 220(1)	1 129(1)	2 500
C(51)	9 936(11)	590(10)	2 714(3)
B(52)	9 417(15)	2 449(13)	2 500
B(53)	9 633(13)	1 682(14)	2 920(6)
B(54)	11 179(20)	494(16)	2 500
B(55)	10 650(11)	2 446(12)	2 763(4)
B(56)	11 026(13)	1 202(13)	2 910(6)
B(57)	11 639(18)	1 757(17)	2 500
C(52)	7 256(13)	1 099(10)	2 943(4)
O(52)	6 746(10)	1 085(11)	3 224(4)
C(53)	7 669(17)	−275(14)	2 500
O(53)	7 193(13)	−1 012(12)	2 500
C(54)	8 360(18)	2 849(14)	2 500
C(55)	7 223(19)	2 748(23)	2 500
Si(2)	6 062(7)	3 293(7)	2 500
C(56)	5 907(17)	4 069(17)	2 905(7)
C(57)	5 027(31)	2 366(23)	2 500

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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