DALTON
FULL PAPER

Amine–nitrile coupling in amino-monocarbollide complexes of molybdenum

Shaowu Du, Jason A. Kautz, Thomas D. McGrath and F. Gordon A. Stone *

Department of Chemistry and Biochemistry, Baylor University, Waco, TX 76798-7348, USA

Received 19th December 2001, Accepted 13th February 2002
First published as an Advance Article on the web 20th March 2002

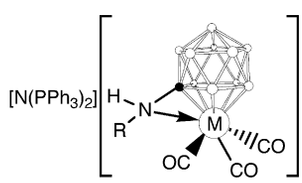
The Mo^0 molybdenacarbaborane trianion $[1\text{-}NH_2\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]^{3-}$ is formed *in situ* from the reaction between $[7\text{-}NH_2\text{-}nido\text{-}7\text{-}CB_{10}H_{10}]^{3-}$ and $[Mo(CO)_4\{NH(CH_2)_5\}_2]$ in THF solution (THF = tetrahydrofuran). In the absence of nitriles, oxidation of this trianion by $CH_2{=}CHCH_2Br$ gives the Mo^{II} complex $[1,2\text{-}\mu\text{-}NH_2\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]^-$, isolated as its $[N(PPh_3)_2]^+$ salt. However, in the presence of nitriles NCR, the same oxidation ultimately affords the species $[N(PPh_3)_2][1,2\text{-}\mu\text{-}\{NHC(R){=}NH\}\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ in which amidine groups form a bridge between the carbon atom of the cage and the molybdenum, as a consequence of coupling of the nitrile with the cage-bound NH_2 group. The acetamidine product $[N(PPh_3)_2][1,2\text{-}\mu\text{-}\{NHC(Me){=}NH\}\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ is also formed by reaction of $[7\text{-}NH_2\text{-}nido\text{-}7\text{-}CB_{10}H_{12}]^-$ with $[Mo(CO)_6]$ in refluxing NCMe, and its structure was confirmed by an X-ray diffraction study. Further oxidation of this species by I_2 in the presence of $CNBu^t$ gives the Mo^{IV} derivatives $[1,2\text{-}\mu\text{-}\{NHC(Me){=}NH\}\text{-}2,2\text{-}(CNBu^t)_2\text{-}2\text{-}L\text{-}2\text{-}I\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ (L = CO, $CNBu^t$), of which the tris(isocyanide) complex has been studied by X-ray diffraction.

Introduction

Although the *C*-amine substituted carbaboranes $7\text{-}NR_3\text{-}nido\text{-}7\text{-}CB_{10}H_{12}$ (R = H, alkyl) have been known for several decades,[1,2] their chemistry has scarcely been explored.[3–8] One aspect of these carbaboranes' chemistry that is of particular interest lies in complexes formed by these ligands where one or more of the groups R is a hydrogen atom. In this situation, the presence of the N–H group makes additional functionalization possible.[1,6] Moreover, in the parent carbaboranes $7\text{-}NHR_2\text{-}nido\text{-}7\text{-}CB_{10}H_{12}$ (R = H, alkyl), treatment with one equivalent of base affords the anions $[7\text{-}NR_2\text{-}nido\text{-}7\text{-}CB_{10}H_{12}]^-$ in which the nitrogen centre has been deprotonated first; removal of either of the two *endo*-polyhedral bridging H atoms requires addition of further base.[7]

These amino-carbaboranes are also precursors to transition-metal complexes containing the *C*-amine and -amino ligands $[7\text{-}NR_3\text{-}nido\text{-}7\text{-}CB_{10}H_{10}]^{2-}$ and $[7\text{-}NR_2\text{-}nido\text{-}7\text{-}CB_{10}H_{10}]^{3-}$, respectively. Recently in our laboratories, it was shown that the carbaborane $7\text{-}NH_2Bu^t\text{-}nido\text{-}7\text{-}CB_{10}H_{12}$ reacts with $[RhCl(PPh_3)_3]$ in refluxing toluene to give 16-electron $[1\text{-}NH_2Bu^t\text{-}2\text{-}Cl\text{-}2\text{-}PPh_3\text{-}closo\text{-}2,1\text{-}RhCB_{10}H_{10}]$.[9] This contrasts with the earlier work of Hawthorne *et al.*, in which the non-*N*-substituted carbaborane $7\text{-}NH_3\text{-}nido\text{-}7\text{-}CB_{10}H_{12}$ was found to react with the same rhodium reagent in methanolic KOH solution to give the anion $[1\text{-}NH_2\text{-}2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}closo\text{-}2,1\text{-}RhCB_{10}H_{10}]^-$.[10] Significantly, the latter rhodium–carbaborane complex, upon mild thermolysis, forms dimeric $[2,2'\text{-}\mu\text{-}H\text{-}\{1,2'\text{-}\mu\text{-}NH_2\text{-}2\text{-}PPh_3\text{-}closo\text{-}2,1\text{-}RhCB_{10}H_{10}\}_2]^-$, in which each of the $\mu\text{-}NH_2$ units forms a bridge between the cage-carbon atom of one $\{RhCB_{10}\}$ cluster and the rhodium centre of the other.[10]

In earlier work,[11] we found that interaction of the carbaborane anion $[7\text{-}NHBu^t\text{-}nido\text{-}7\text{-}CB_{10}H_{12}]^-$ with $[Mo(CO)_6]$ in refluxing NCMe results in dihydrogen elimination and formation of the novel molybdenacarbaborane $[1,2\text{-}\mu\text{-}NHBu^t\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]^-$, isolated as the $[N(PPh_3)_2]^+$ salt **1a**, which contains an intramolecular $NHBu^t$ bridging moiety. Analogous tungsten (**1b**) and chromium (**1c**) species were prepared similarly. The same molybdenum complex is also obtained by treating the carbaborane trianion $[7\text{-}NHBu^t\text{-}nido\text{-}7\text{-}CB_{10}H_{10}]^{3-}$ with $[Mo(CO)_3(NCMe)_3]$ initially to give *in situ* $[1\text{-}NHBu^t\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]^{3-}$ which, upon oxidation with $CH_2{=}CHCH_2Br$, is converted to $[1,2\text{-}\mu\text{-}NHBu^t\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]^-$, again isolated as the $[N(PPh_3)_2]^+$ salt **1a**.[11]



	M	R
1a	Mo	Bu^t
1b	W	Bu^t
1c	Cr	Bu^t
2a	Mo	H
2b	W	H
2c	Cr	H

● C ○ BH

Seeking to prepare salts of the analogous anion $[1,2\text{-}\mu\text{-}NH_2\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]^-$ we have found that in the presence of nitriles the synthesis did not proceed as expected. The nature of the observed products and their chemistry are described herein.

Results and discussion

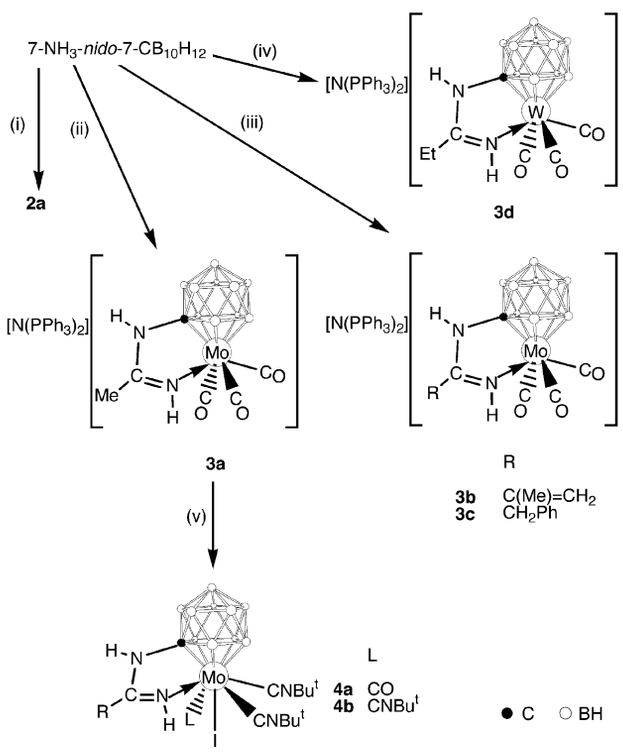
Synthetic methodologies similar to those which afforded **1a**, but here employing the carbaborane anions $[7\text{-}NH_2\text{-}nido\text{-}7\text{-}CB_{10}H_{12}]^-$ or $[7\text{-}NH_2\text{-}nido\text{-}7\text{-}CB_{10}H_{10}]^{3-}$, respectively, failed to afford $[N(PPh_3)_2][1,2\text{-}\mu\text{-}NH_2\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ **2a**. Instead, the product obtained from both routes was $[N(PPh_3)_2][1,2\text{-}\mu\text{-}\{NHC(Me){=}NH\}\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ **3a** (Scheme 1). This and related species **3** arise from a coupling of the cage-carbon bound NH_2 unit with a nitrile molecule, as discussed in more detail below.

DOI: 10.1039/b111562f

Table 1 Analytical and physical data

Compound	Yield (%)	ν_{max}(CO), ν_{max}(NC)*[a]/cm^{-1}	Analysis (%)[b] C	H	N
2a [N(PPh$_3$)$_2$][1,2-μ-NH$_2$-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]	18	2008 s, 1940 m, 1887 s	55.6 (55.6)	5.3 (4.9)	3.2 (3.2)
3a [N(PPh$_3$)$_2$][1,2-μ-{NHC(Me)=NH}-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]	25	2010 s, 1910 s	53.7 (53.8)[c]	4.9 (4.9)	4.4 (4.4)
3b [N(PPh$_3$)$_2$][1,2-μ-{NHC{C(Me)=CH$_2$}=NH}-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]	14	2010 s, 1908 s	51.8 (51.6)[d]	5.5 (4.7)	4.4 (4.0)
3c [N(PPh$_3$)$_2$][1,2-μ-{NHC(CH$_2$Ph)=NH}-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]	16	2009 s, 1908 s	58.8 (58.7)	5.1 (5.0)	4.8 (4.3)
3d [N(PPh$_3$)$_2$][1,2-μ-{NHC(Et)=NH}-2,2,2-(CO)$_3$-*closo*-2,1-WCB$_{10}$H$_{10}$]	24	2003 s, 1809 s	53.6 (53.2)[e]	5.2 (5.5)	4.4 (3.7)
4a [1,2-μ-{NHC(Me)=NH}-2,2-(CNBu^t)$_2$-2-CO-2-I-*closo*-2,1-MoCB$_{10}$H$_{10}$]	37	2184 s,* 2010 m	27.9 (27.8)	5.6 (5.6)	9.2 (9.3)
4b [1,2-μ-{NHC(Me)=NH}-2,2,2-(CNBu^t)$_3$-2-I-*closo*-2,1-MoCB$_{10}$H$_{10}$]	36	2187 m,* 2165 s*	32.3 (32.3)[f]	6.4 (6.5)	10.2 (10.5)

[a] Measured in CH_2Cl_2; broad medium-intensity bands observed at *ca.* 2550 cm^{-1} in the spectra of all compounds are due to B–H absorptions. [b] Calculated values are given in parentheses. [c] Crystallizes with 0.5 mol equivalent of CH_2Cl_2. [d] Crystallizes with 1.5 mol equivalent of CH_2Cl_2. [e] Crystallizes with 2 mol equivalent of THF. [f] Crystallizes with 0.5 mol equivalent of H_2O.



Scheme 1 Synthesis of compounds **2a**, **3** and **4**. *Reagents and conditions*: (i) Bu^{n}Li (3 equiv.), [Mo(CO)$_4${NH(CH$_2$)$_5$}$_2$], CH$_2$=CHCH$_2$Br and [N(PPh$_3$)$_2$]Cl successively in THF; (ii) Bu^{n}Li (1 equiv.) in THF, then [Mo(CO)$_6$] in refluxing NCMe, then [N(PPh$_3$)$_2$]Cl in CH_2Cl_2; (iii) Bu^{n}Li (3 equiv.), [Mo(CO)$_4${NH(CH$_2$)$_5$}$_2$], NCR, CH$_2$=CHCH$_2$Br and [N(PPh$_3$)$_2$]Cl successively in THF; (iv) Bu^{n}Li (1 equiv.) in THF, then [W(CO)$_6$] in refluxing NCEt, then [N(PPh$_3$)$_2$]Cl in CH_2Cl_2; (v) CNBu^t (4 equiv.) and I_2 in CH_2Cl_2.

An alternative route, which avoids nitriles, was found to the salt **2a**. When the carbaborane trianion [7-NH$_2$-*nido*-7-CB$_{10}$H$_{10}$]$^{3-}$ is treated with [Mo(CO)$_4${NH(CH$_2$)$_5$}$_2$], in THF solution, the trianionic molybdenacarbaborane species [1-NH$_2$-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]$^{3-}$ is formed *in situ*. Addition to this of CH$_2$=CHCH$_2$Br followed by [N(PPh$_3$)$_2$]Cl, and chromatographic work-up, gave modest yields of [N(PPh$_3$)$_2$][1,2-μ-NH$_2$-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$] **2a**. As observed in one of the routes to **1a**, discussed above, the allyl bromide serves only as an oxidizing agent.[11] The intense violet colour of the product appears to be typical of species having this intramolecular bridge between the molybdenum atom and one of the atoms in the ligating CBBBB face of the carbaborane. This phenomenon has been noted previously both in the complexes **1**, which contain an M–NHBu^t–C(cage) bridge,[11] and in the species [2,2,2-(CO)$_3$-2,3-μ-I-*n*-L-*closo*-2,1-MoCB$_{10}$H$_9$] (L = thioether; *n* = 7, 11), which have an Mo–I–B(cage) bridge.[12]

Data characterizing compound **2a** are given in Tables 1 and 2. As expected, the NMR data for **2a** are very similar to those for **1a**. In particular, the NH$_2$ protons give rise to a broad resonance at δ 2.50 in **2a**, to be compared with δ 2.41 for the NH proton in **1a**. The cage-carbon atom in **2a** is seen as a broad resonance at δ 96.1 in the $^{13}C\{^1H\}$ NMR spectrum, whereas this signal occurs at δ 100.1 in **1a**. The most significant difference between these two compounds' NMR data is seen in their $^{11}B\{^1H\}$ NMR spectra. For all of the compounds **1**, the two different substituents (H, Bu^t) on nitrogen cause the anions overall to be asymmetric, resulting in 10 separate resonances (with some coincident) for the cluster boron atoms. In **2a**, this is not the case, and the mirror symmetry of the anion is reflected by the 1 : 2 : 4 : 1 : 2 pattern observed in its $^{11}B\{^1H\}$ NMR spectrum (two resonances of intensity 2 coincide).

To date we have been unable to isolate **2b**, the tungsten analogue of **2a**. The characteristic violet colour of such a product was observed by qualitative thin-layer chromatographic analysis of a reaction mixture obtained from interaction of Li[7-NH$_2$-*nido*-7-CB$_{10}$H$_{12}$] and [W(CO)$_4$(COD)] (COD = 1,5-cyclo-C$_8$H$_{12}$) in refluxing THF. However, the species so identified appears to be very unstable and could not be isolated.

Although it was noted above that when [7-NH$_2$-*nido*-7-CB$_{10}$H$_{12}$]$^-$ is treated with [Mo(CO)$_6$] in refluxing NCMe a coupling reaction takes place between the nitrile and the cage-bound amino group, when the same anion and [Cr(CO)$_6$] are heated to reflux in NCEt solution, the only product that could be isolated upon addition of [N(PPh$_3$)$_2$]Cl and work-up appears to be [N(PPh$_3$)$_2$][1,2-μ-NH$_2$-2,2,2-(CO)$_3$-*closo*-2,1-CrCB$_{10}$H$_{10}$] **2c**. The poor isolated yield of only 2% was primarily a consequence of instability during chromatography. This characteristically violet compound shows three bands as expected in its infrared spectrum, at 1996 s, 1936 m and 1892 s cm^{-1}. Microanalysis results were equally consistent with the proposed formulation. In its ^1H NMR spectrum, a broad singlet, corresponding in intensity to two protons and assigned to a μ-NH$_2$ group, is seen at δ 1.88 (*cf.* δ 1.79 for the μ-N*H*Bu^t proton in **1c**). In the $^{13}C\{^1H\}$ NMR spectrum the cage-carbon atom signal appears as a broad resonance at δ 109.4 (*cf.* δ 106.5 for **1c**). However, the carbonyl region of the same spectrum is less straightforward: although two resonances are observed in the expected regions

Table 2 ^{1}H, ^{13}C, and ^{11}B NMR data [a]

Compound	^{1}H δ [b]	^{13}C δ [c]	^{11}B δ [d]
2a	7.68–7.46 (m, 30 H, Ph), 2.50 (br s, 2 H, NH_2)	240.5 (CO × 2), 232.9 (CO), 134.1–126.8 (Ph), 96.1 (br, cage C)	5.1 (1 B), 0.7 (2 B), −11.5 (4 B), −12.1 (1 B), −18.7 (2 B)
3a	7.69–7.47 (m, 30 H, Ph), 5.42, 4.68 (br m × 2, 1 H × 2, NH × 2), 1.76 (s, 3 H, Me)	250.6 (CO), 239.1 (CO × 2), 170.9 (NCN), 134.1–126.8 (Ph), 102.1 (br, cage C), 20.5 (Me)	−4.0 (1 B), −4.8 (2 B), −7.8 (2 B), −12.1 (1 B), −12.6 (2 B), −15.0 (2 B)
3b	7.69–7.46 (m, 30 H, Ph), 5.58 (br m, 1 H, NH), 5.13, 5.11 (br m × 2, 1 H × 2, $=CH_2$), *ca.* 5.0 (br, sh, 1 H, NH), 1.74 (br m, 3 H, Me)	250.0 (CO), 238.9 (CO × 2), 172.1 (NCN), 135.4 [=*C*(Me)], 134.1–126.8 (Ph), 119.2 ($=CH_2$), 101.9 (br, cage C), 19.5 (Me)	−4.0 (1 B), −4.7 (2 B), −7.9 (2 B), −12.1 (1 B), −12.7 (2 B), −14.9 (2 B)
3c	7.68–7.46 (m, 30 H, PPh), 7.39–7.04 (m, 5 H, CH_2*Ph*), 5.55, 4.72 (br s × 2, 1 H × 2, NH × 2), 3.34 (s, 2 H, CH_2)	250.4 (CO), 239.0 (CO × 2), 172.8 (NCN), 134.1–126.8 (Ph), 101.9 (br, cage C), 39.8 (CH_2)	−4.2 (1 B), −4.7 (2 B), −7.9 (2 B), −12.2 (3 B), −15.1 (2 B)
3d	7.66–7.46 (m, 30 H, Ph), 5.52, 5.27 (br m × 2, 1 H × 2, NH × 2), 2.07 [q, 2 H, *J*(HH) = 8, CH_2], 0.9 (t, 3 H, Me)	242.8 [CO, *J*(WC) = 112], 232.6 [CO × 2, *J*(WC) = 132], 177.2 (NCN), 134.1–126.8 (Ph), 96.4 (br, cage C), 26.4 (CH_2), 10.6 (Me)	−5.0 (1 B), −8.7 (4 B), −12.9 (1 B), −14.5 (2 B), −15.8 (2 B)
4a	5.23, 5.21 (br m × 2, 1 H × 2, NH × 2), 1.84 (s, 3 H, Me), 1.55 (s, 18 H, Bu^t)	216.0 (CO), 169.8 (NCN), 147.0 (br, C≡N), 108.9 (br, cage C), 59.0 (CMe_3), 29.3 (CMe_3), 20.1 (Me)	8.2 (1 B), 1.9 (2 B), −4.2 (4 B), −11.1 (1 B), −12.8 (2 B)
4b	5.21, 5.08 (br m × 2, 1 H × 2, NH × 2), 1.77 (s, 3 H, Me), 1.54 (s, 18 H, Bu^t), 1.38 (s, 9 H, Bu^t)	167.2 (NCN), 157.1 (br, C≡N), 153.4 (br, C≡N × 2), 105.0 (br, cage C), 57.8 (CMe_3 × 2), 57.5 (CMe_3), 29.9 (CMe_3 × 2), 29.7 (CMe_3), 20.1 (Me)	5.2 (1 B), 3.7 (2 B), −4.6 (2 B), −6.3 (2 B), −11.3 (1 B), −14.1 (2 B)

[a] Chemical shifts (δ) in ppm, coupling constants (J) in Hz, measurements at ambient temperatures in CD_2Cl_2. [b] Resonances for terminal BH protons occur as broad unresolved signals in the range δ *ca.* −1 to +3. [c] ^{1}H-decoupled chemical shifts are positive to high frequency of $SiMe_4$. [d] ^{1}H-decoupled chemical shifts are positive to high frequency of $BF_3{\cdot}Et_2O$ (external).

(δ *ca.* 248 and *ca.* 243, in the ratio 2 : 1), some additional peaks are also seen. Moreover, in the ^{11}B{^{1}H} NMR spectrum the resonance at δ *ca.* −18, of relative intensity 2, appears to be split into two peaks of unit intensity; the spectrum is otherwise very similar to that of both **1c** (albeit here having mirror symmetry) and **2a**. We believe that this may result from the presence in solution of a second species, very similar to **2c**. The nature of this second species, however, is not clear but it may be speculated to be, for example, a dimeric relative in which two {1-NH_2-2,2,2-$(CO)_3$-*closo*-2,1-$CrCB_{10}H_{10}$} cores are linked by inter-anion rather than intra-anion NH_2 bridges, as in [2,2′-μ-H-{1,2′-μ-NH_2-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$}$_2$]$^-$.[10]

The compound $[N(PPh_3)_2]$[1,2-μ-{NHC(Me)=NH}-2,2,2-$(CO)_3$-*closo*-2,1-$MoCB_{10}H_{10}$] **3a** introduced above was prepared by two different routes. It can be isolated either from the reaction between the carbaborane trianion [7-NH_2-*nido*-7-$CB_{10}H_{10}$]$^{3-}$ and $[Mo(CO)_3(NCMe)_3]$ in THF/NCMe at room temperature, followed by oxidation with CH_2=$CHCH_2Br$, or from the reaction of the monoanionic carbaborane [7-NH_2-*nido*-7-$CB_{10}H_{12}$]$^-$ with $[Mo(CO)_6]$ in refluxing NCMe. In both cases, work-up simply required addition of $[N(PPh_3)_2]Cl$ and chromatographic purification, but the latter route gives the product in rather superior yields.

Although the gross structure of the anion of **3a** could be reasonably inferred from its NMR data, an X-ray diffraction study was necessary to confirm the detailed architecture. The resulting structure is shown in Fig. 1. Therein it is seen that an acetamidine moiety is linked both to the cage-carbon atom and to the molybdenum vertex to form a five-membered ring which appears to be unstrained. The C(1)–N(1) [1.445(4) Å] and Mo–N(2) [2.190(3) Å] distances are quite normal. Within the amidine unit, C(5)–N(1) is 1.335(5) Å and C5–N(2) is 1.287(5) Å, suggesting that there may be some greater localization of double bond character between C(5) and N(2) than between C(5) and N(1). However, the angles C(5)–N(2)–Mo [121.6(3)°], C(5)–N(1)–C(1) [121.0(3)°] and N(2)–C(5)–N(1) [117.9(3)°] are all close to 120°, as are the two C(6)–C(5)–N angles, indicative of sp^2 hybridization at all three atoms of the amidine backbone. Interestingly, whereas in the anion of **1b** the tungsten vertex is laterally slipped towards the cage-carbon atom to accommodate the geometric demands of the μ-$NHBu^t$ unit,[11] in **3a** the metal vertex is much more symmetrically disposed with respect to the five atoms in the *pentahapto* coordinating carbaborane $\overline{CBBBB}$ face.

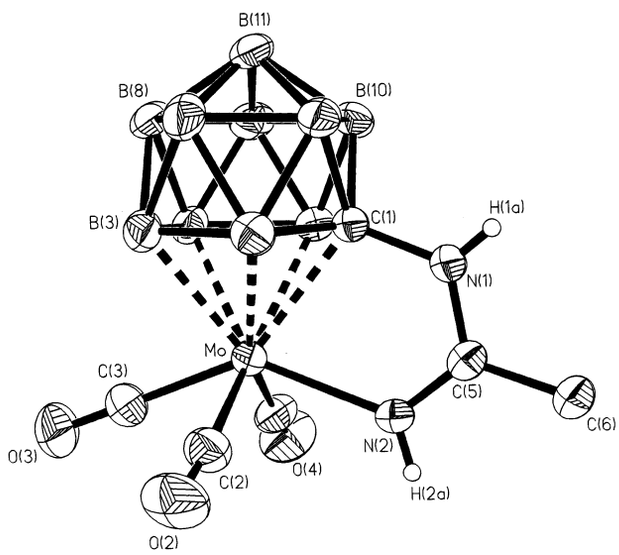


Fig. 1 Structure of the anion of **3a** showing the crystallographic labeling scheme. Hydrogen atoms, except H(1a) and H(2a), are omitted and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Mo–C(3) 1.967(4), Mo–C(2) 2.005(5), Mo–C(4) 2.018(5), Mo–N(2) 2.190(3), Mo–B(4) 2.335(5), Mo–B(3) 2.359(5), Mo–B(5) 2.368(4), Mo–C(1) 2.383(3), Mo–B(2) 2.386(4), C(1)–N(1) 1.445(4), N(1)–C(5) 1.335(5), C(5)–N(2) 1.287(5); C(3)–Mo–N(2) 138.8(2), C(2)–Mo–N(2) 82.8(2), C(4)–Mo–N(2) 81.7(2), N(2)–Mo–C(1) 71.78(12), N(1)–C(1)–Mo 107.5(2), C(5)–N(2)–Mo 121.6(3), C(5)–N(1)–C(1) 121.0(3), N(2)–C(5)–N(1) 117.9(3).

Mechanistically, formation of the acetamidine moiety appears straightforward. The intermediate [1-NH_2-2,2,2-$(CO)_3$-*closo*-2,1-$MoCB_{10}H_{10}$]$^{3-}$ upon oxidation gains a vacant metal coordination site, which becomes occupied by NCMe to give transient [1-NH_2-2,2,2-$(CO)_3$-2-NCMe-*closo*-2,1-$MoCB_{10}H_{10}$]$^-$. Intramolecular attack by the amino group upon the

metal-activated nitrile, followed by redistribution of H atoms, then gives the observed anion. In the synthesis of compound **1a** by analogous routes, an *N*-Bu^t relative of **3a** is not observed. Arguably, an intermediate of the form [1-NHBu^t-2,2,2-(CO)$_3$-2-NCMe-*closo*-2,1-MoCB$_{10}$H$_{10}$]$^-$ in the formation of **1a** would be relatively disfavored for both steric and electronic reasons: the larger and more basic NHBu^t moiety could compete with NCMe more successfully than NH_2 to fill the vacant site produced on the metal upon oxidation. The addition of primary amines to nitriles is a well-known route to amidines.[13]

The compounds [N(PPh$_3$)$_2$][1,2-μ-{NHC{C(Me)=CH$_2$}=NH}-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$] **3b** and [N(PPh$_3$)$_2$][1,2-μ-{NHC(CH$_2$Ph)=NH}-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$] **3c** are related to **3a**, but were obtained by slightly different routes. As in the preparation of **2a**, the molybdenacarbaborane trianion [1-NH$_2$-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]$^{3-}$ was formed *in situ* from [7-NH$_2$-*nido*-7-CB$_{10}$H$_{10}$]$^{3-}$ and [Mo(CO)$_4${NH(CH$_2$)$_5$}$_2$] in THF solution. Addition of the nitriles NCC(Me)=CH$_2$ or NCCH$_2$Ph, prior to oxidation with CH$_2$=CHCH$_2$Br and work-up as for **3a**, gave the salts **3b** and **3c**, respectively. The compound [N(PPh$_3$)$_2$][1,2-μ-{NHC(Et)=NH}-2,2,2-(CO)$_3$-*closo*-2,1-WCB$_{10}$H$_{10}$] **3d** was formed by a method similar to one of those by which its molybdenum analogue **3a** was prepared. Interaction of the carbaborane monoanion [7-NH$_2$-*nido*-7-CB$_{10}$H$_{12}$]$^-$ and [W(CO)$_6$] in refluxing NCEt, and similar work-up, gave **3d** in a yield close to that of **3a** obtained by the parallel route.

Compounds **3a**–**3d** are characterized by the data given in Tables 1 and 2. The ^{11}B{^{1}H} NMR spectra of all four compounds are very similar, and the appearance of 6 resonances in the ratio 1 : 2 : 2 : 1 : 2 : 2 (with some coincidences) reflects the mirror symmetry of all of these anions. In their ^{1}H and ^{13}C{^{1}H} NMR spectra, resonances are seen in typical positions for all of the organic groups bound to the central carbon of the amidine moiety. This central carbon atom itself resonates at δ 170.9 (**3a**), 172.1 (**3b**), 172.8 (**3c**) and 177.2 (**3d**), and proved to be a useful diagnostic for confirming that the NCMe/NH$_2$ coupling had taken place. Similarly, the two different NH protons gave rise to two broad peaks, each of unit intensity, in the ^{1}H NMR spectra of compounds **3**. Of these, the signal to higher frequency [range δ 5.42 (**3a**) to 5.58 (**3b**)] is always significantly sharper than that to lower frequency [range δ 4.68 (**3a**) to 5.27 (**3d**)]. It is likely that the NH group giving rise to the sharper of these two peaks is the one that is directly bonded to the metal. The broadening of the other peak is due to the proximity of this proton to the carbaborane cluster and consequent coupling to quadrupolar boron nuclei. This assignment is consistent with the solid-state structure of **3a** which suggested greater double-bond character for the amidine C–N bond involving the molybdenum-bound nitrogen atom. A broad resonance in the ^{13}C{^{1}H} NMR spectra assigned to the cage-carbon atom is seen at around δ 102 for the molybdenum species **3a**–**3c** and at δ 96.4 for the tungsten compound **3d**.

In earlier work we have shown that the Mo–N bond in the anion of compound **1a** is "lifted-off" upon protonation in the presence of ligands L to give species of general formulation [1-NH$_2$Bu^t-2,2,2-(CO)$_3$-2-L-*closo*-2,1-MoCB$_{10}$H$_{10}$] (L = CO, phosphines).[11] Similar treatment of **3a**, however, did not yield any isolatable products; it appears that the amidine moiety is only stable when coordinated to the metal centre.

Compound **1a** was also shown to react with CNBu^t and I$_2$ to give the Mo^{IV} species [1,2-μ-NHBu^t-2,2,2-(CNBu^t)$_3$-2-I-*closo*-2,1-MoCB$_{10}$H$_{10}$].[11] Clearly it was of interest to examine the behaviour of compound **3a** with the same reagents, and in particular to determine whether the amidine moiety survives the reaction conditions or, indeed, if it undergoes some additional coupling with a metal-bound isocyanide. Thus a CH$_2$Cl$_2$ solution of compound **3a** was treated with I$_2$ and CNBu^t (4 equivalents), thereby affording two neutral products in good combined yield. These two Mo^{IV} species are of formulation [1,2-μ-{NHC(Me)=NH}-2,2-(CNBu^t)$_2$-2-L-2-I-*closo*-2,1-MoCB$_{10}$H$_{10}$] [L = CO (**4a**), CNBu^t (**4b**)]. In both compounds the amidine linkage appeared to have remained intact. This was further confirmed by an X-ray diffraction study of **4b**, which yielded the structure shown in Fig. 2. The formally eight-coordinate molybdenum atom is seen to be *pentahapto* ligated by the CBBBB face of the carbaborane with, in addition, bonds to an amidine nitrogen, three isocyanides and an iodide. The Mo(1)–I(1) distances [2.9135(6) and 2.9093(6) Å for the two crystallographically independent molecules] are normal, and the I(1)–Mo(1)–(CB$_4$ centroid) angles (178.1 and 178.7°) are close to linearity. However, as Fig. 2 clearly shows, the Mo–I vector is somewhat tilted away from being orthogonal to the plane of the carbaborane face. Indeed, in contrast to the situation with **3a**, the Mo vertex in **4b** is significantly laterally slipped away from the cage-carbon atom. This may be to minimize steric repulsions between the amidine and the bulky CNBu^t ligands.

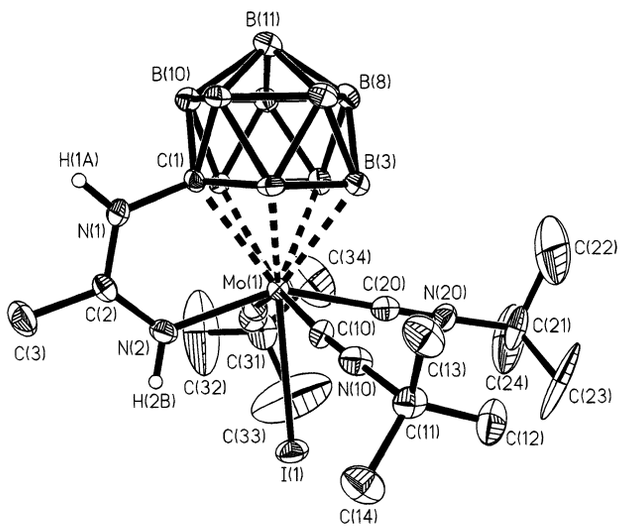


Fig. 2 Structure of molecule **4b** showing the crystallographic labeling scheme. Only one of the two crystallographically independent molecules is shown; the other is geometrically very similar. Hydrogen atoms, except H(1A) and H(2B), are omitted and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°) for the molecule shown are: Mo(1)–B(4) 2.356(6), Mo(1)–B(3) 2.371(6), Mo(1)–B(5) 2.402(6), Mo(1)–B(2) 2.436(6), Mo(1)–C(1) 2.472(5), Mo(1)–C(20) 2.073(6), Mo(1)–C(30) 2.101(6), Mo(1)–C(10) 2.121(5), Mo(1)–N(2) 2.191(5), Mo(1)–I(1) 2.9135(6), C(1)–N(1) 1.462(7), N(1)–C(2) 1.311(7), C(2)–N(2) 1.307(8); N(2)–Mo(1)–C(1) 69.5(2), C(20)–Mo(1)–I(1) 73.6(2), C(30)–Mo(1)–I(1) 74.5(2), C(10)–Mo(1)–I(1) 74.39(14), N(2)–Mo(1)–I(1) 77.15(13), C(2)–N(1)–C(1) 121.3(5), N(2)–C(2)–N(1) 117.2(5), N(1)–C(1)–Mo(1) 107.1(3), C(2)–N(2)–Mo(1) 124.9(4).

Spectroscopic data characterizing **4a** and **4b** are given in Tables 1 and 2. In their ^{11}B{^{1}H} NMR spectra, molecular mirror symmetry is again evidenced by the 1 : 2 : 2 : 2 : 1 : 2 pattern of intensities, and there has been a significant general downfield shift of the resonances compared with those of the precursor **3a**, consistent with the higher metal oxidation state in compounds **4**. Signals are seen in typical positions in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **4a** and **4b** for the isocyanide ligands and, in particular, only one type of isocyanide is seen in **4a**. This indicates that the carbonyl ligand in **4a** is located *transoid* to the amidine moiety, preserving the molecular mirror symmetry. Peaks attributed to the acetamidine moiety are also observed, with the NH protons again seen as broad signals, at δ 5.21 and 5.23 for **4a** and at δ 5.08 and 5.21 for **4b**, somewhat deshielded compared to **3a**. In their ^{13}C{^{1}H} NMR spectra, the central carbon of the NCN backbone resonates at δ 169.8 in **4a** and δ 167.2 in **4b**, close to the corresponding parameter in **3a**.

Conclusion

The complexes **2**, like compounds **1** described recently,[11] demonstrate that the [7-NHR-*nido*-7-$CB_{10}H_{10}$]$^{3-}$ (R = H or Bu^t) group can function formally as an eight-electron ($6\pi + 2\sigma$) donor to a d^6 metal ion. This ability may be useful in the synthesis of monocarbollide complexes of early transition elements. Moreover, the coupling of NCR molecules with the {1,2-μ-NH_2-*closo*-2,1-$MCB_{10}H_{10}$}$^-$ cage system to generate C–N bonds in the reactions leading to the complexes **3** is, as far as we are aware, without precedent. The methodology may possibly be exploited by oxidizing the species [1-NH_2-2,2,2-$(CO)_3$-*closo*-2,1-$MoCB_{10}H_{10}$]$^{3-}$ in the presence of other reactive substrates.

Experimental

General

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk line techniques. Solvents were stored over and distilled from appropriate drying agents under nitrogen prior to use. Petroleum ether here refers to that fraction of boiling point 40–60 °C. Chromatography columns (typically *ca.* 15 cm in length and *ca.* 2 cm in diameter) were packed with silica gel (Acros, 60–200 mesh). NMR spectra were recorded at the following frequencies: ^1H 360.1, ^{13}C 90.6 and ^{11}B 115.5 MHz. The carbaborane 7-NH_3-*nido*-7-$CB_{10}H_{12}$ was prepared according to the literature method;[14] all other materials were used as received.

Syntheses

[$N(PPh_3)_2$][1,2-μ-NH_2-2,2,2-$(CO)_3$-*closo*-2,1-$MoCB_{10}H_{10}$]. The carbaborane 7-NH_3-*nido*-7-$CB_{10}H_{12}$ (0.28 g, 1.88 mmol) was dissolved in THF (30 cm^3) and cooled to *ca.* 0 °C. To this solution was added Bu^nLi (2.3 cm^3, 2.5 M solution in hexanes, 5.75 mmol). After warming to room temperature and stirring for 1 h, solid [$Mo(CO)_4\{NH(CH_2)_5\}_2$] (0.72 g, 1.90 mmol) was added. The mixture was stirred for a further 3 h and then CH_2=$CHCH_2Br$ (0.23 g, 1.90 mmol) added. After 1 h, [$N(PPh_3)_2$]Cl (1.10 g, 1.92 mmol) was added and stirring continued overnight. Solvent was removed *in vacuo*, and the residue was taken up in CH_2Cl_2 (*ca.* 3 cm^3) and chromatographed. Elution with neat CH_2Cl_2 removed a purple fraction which, upon evaporation of the solvent *in vacuo*, gave violet microcrystals of [$N(PPh_3)_2$][1,2-μ-NH_2-2,2,2-$(CO)_3$-*closo*-2,1-$MoCB_{10}H_{10}$] **2a** (0.30 g).

Compounds [$N(PPh_3)_2$][1,2-μ-{NHC(R)=NH}-2,2,2-$(CO)_3$-*closo*-2,1-$MCB_{10}H_{10}$] [M = Mo, R = Me, C(Me)=CH_2, CH_2Ph; M = W, R = Et]. (i) The carbaborane 7-NH_3-*nido*-7-$CB_{10}H_{12}$ (0.28 g, 1.88 mmol) was dissolved in THF (10 cm^3) and the mixture cooled to *ca.* 0 °C. To this was added Bu^nLi (0.76 cm^3, 1.90 mmol). After stirring for 1 h, solvent was removed *in vacuo*. The residue was redissolved in NCMe (30 cm^3), [$Mo(CO)_6$] (0.50 g, 1.89 mmol) was added, and the mixture heated to reflux for 3 h. After evaporation of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 (30 cm^3) and treated with [$N(PPh_3)_2$]Cl (1.00 g, 1.83 mmol) for 1 h. Solvent was removed *in vacuo* and the residue taken up in CH_2Cl_2 (*ca.* 5 cm^3) and applied to a chromatography column. Elution with neat CH_2Cl_2 removed an orange fraction which, after removal of solvent *in vacuo*, gave orange microcrystals of [$N(PPh_3)_2$][1,2-μ-{NHC(Me)=NH}-2,2,2-$(CO)_3$-*closo*-2,1-$MoCB_{10}H_{10}$] **3a** (0.42 g).

Compound **3a** was also prepared as follows: To a solution of 7-NH_3-*nido*-7-$CB_{10}H_{12}$ (0.50 g, 3.35 mmol) in THF (20 cm^3) at *ca.* −40 °C was added Bu^nLi (3 cm^3, 7.5 mmol). After warming to room temperature, a solution of [$Mo(CO)_3(NCMe)_3$)] {prepared *in situ* from [$Mo(CO)_6$] (1.00 g, 3.79 mmol) in NCMe (20 cm^3)} was added *via* a cannula. After 1 h, CH_2=$CHCH_2Br$ (0.46 g, 3.81 mmol) was added, followed by [$N(PPh_3)_2$]Cl (1.80 g, 3.29 mmol) and the mixture stirred overnight. Evaporation and then chromatography as above afforded orange microcrystals of **3a** (0.50 g, 16%).

(ii) The carbaborane 7-NH_3-*nido*-7-$CB_{10}H_{12}$ (0.28 g, 1.88 mmol) was dissolved in THF (30 cm^3) and cooled to *ca.* 0 °C. To this solution was added Bu^nLi (2.3 cm^3, 2.5 M solution in hexanes, 5.75 mmol). After warming to room temperature and stirring for 1 h neat NCC(Me)=CH_2 (2.0 cm^3, 1.6 g, 24 mmol) was added, followed by solid [$Mo(CO)_4\{NH(CH_2)_5\}_2$] (0.72 g, 1.90 mmol). The mixture was stirred a further 3 h and treated with CH_2=$CHCH_2Br$ (0.23 g, 1.90 mmol). After 1 h, [$N(PPh_3)_2$]Cl (1.10 g, 1.92 mmol) was added and stirring continued overnight. Solvent was removed *in vacuo*, and the residue was taken up in CH_2Cl_2 (*ca.* 3 cm^3) and chromatographed. Elution with neat CH_2Cl_2 removed an orange fraction which, upon removal of solvent *in vacuo*, gave [$N(PPh_3)_2$][1,2-μ-{NHC{C(Me)=CH_2}=NH}-2,2,2-$(CO)_3$-*closo*-2,1-$MoCB_{10}H_{10}$] **3b** (0.24 g) as an orange solid.

(iii) A similar procedure, using $NCCH_2Ph$ (0.30 cm^3, 0.33 g, 2.83 mmol) instead of NCC(Me)=CH_2, afforded orange microcrystals of [$N(PPh_3)_2$][1,2-μ-{NHC(CH_2Ph)=NH}-2,2,2-$(CO)_3$-*closo*-2,1-$MoCB_{10}H_{10}$] **3c** (0.30 g).

(iv) Following a route similar to the former of those that gave compound **3a**, Li[7-NH_2-*nido*-7-$CB_{10}H_{12}$] and [$W(CO)_6$] (0.66 g, 1.88 mmol) in refluxing NCEt (30 cm^3) after 8 h gave [$N(PPh_3)_2$][1,2-μ-{NHC(Et)=NH}-2,2,2-$(CO)_3$-*closo*-2,1-$WCB_{10}H_{10}$] **3d** (0.45 g) as orange microcrystals following chromatographic work-up.

Reaction of 3a with $CNBu^t$ and I_2. Compound **3a** (0.20 g, 0.221 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and $CNBu^t$ (0.10 cm^3, 0.9 mmol) was added, followed by I_2 (0.056 g, 0.221 mmol). The mixture was stirred overnight. After removal of solvent *in vacuo*, the residue was taken up in CH_2Cl_2 (*ca.* 2 cm^3) and chromatographed. Elution with CH_2Cl_2–petroleum ether (2 : 1) removed first an orange–red band which, upon removal of solvent *in vacuo* and crystallization from CH_2Cl_2–petroleum ether, gave red crystals of [1,2-μ-{NHC(Me)=NH}-2,2-(CNBu^t)$_2$-2-CO-2-I-*closo*-2,1-$MoCB_{10}H_{10}$] **4a** (0.050 g). Further elution with the same solvent mixture afforded a second yellow–brown fraction which, after removal of solvent *in vacuo* and crystallization from CH_2Cl_2–petroleum ether, gave dark-green crystals of [1,2-μ-{NHC(Me)=NH}-2,2,2-$(CNBu^t)_3$-2-I-*closo*-2,1-$MoCB_{10}H_{10}$] **4b** (0.053 g).

Crystallography

Experimental data for compounds **3a** and **4b** are recorded in Table 3. Diffracted intensities for **3a** were collected on an Enraf-Nonius CAD4 diffractometer using Mo-Kα X-radiation (λ = 0.71073 Å). Final unit cell dimensions were determined from the setting angles of 25 accurately centered reflections. Intensity data were corrected for Lorentz and polarization effects after which a numerical absorption correction based on the measurements of the various crystal faces was applied. X-Ray intensity data for **4b** were collected on a Siemens SMART CCD area-detector three-circle diffractometer using Mo-Kα X-radiation. For three settings of φ, narrow data 'frames' were collected in 0.3° increments of ω. The substantial redundancy in data allowed empirical absorption corrections (SADABS)[15] to be applied using multiple measurements of equivalent reflections. The data frames were integrated using SAINT.[15]

Both structures were solved with conventional direct methods and refined by full-matrix least-squares on all F^2 data using SHELXTL version 5.03 and SHELXL-97.[16,17] All non-hydrogen atoms were assigned anisotropic displacement parameters. The locations of the cage-carbon atoms were verified by examination of the appropriate internuclear distances

Table 3 Data for crystal structure analyses of compounds **3a**·0.25CH_2Cl_2 and **4b**·0.5H_2O·0.5CH_2Cl_2

	3a·0.25CH_2Cl_2	**4b**·0.5H_2O·0.5CH_2Cl_2
Chemical formula	$C_{42.25}H_{45.5}B_{10}Cl_{0.5}MoN_3O_3P_2$	$C_{18.5}H_{44}B_{10}ClIMoN_5O_{0.5}$
M	927.02	710.98
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$P2_12_12_1$
a/Å	31.235(4)	9.9624(10)
b/Å	12.4030(11)	19.591(2)
c/Å	24.733(2)	34.329(3)
β/°	101.160(11)	
Z	8	8
U/Å^3	9401(2)	6699.9(11)
μ(Mo-Kα)/cm^{-1}	4.17	14.12
T/K	293	173
Reflections measured	8493	41803
Independent reflections	8329	15318
R_{int}	0.0362	0.0408
$wR2$ (all data), $R1$ [a]	0.0983, 0.0440	0.1074, 0.0458 [b]

[a] $F_o > 4\sigma(F_o)$. [b] Flack parameter = 0.06(2).

and the magnitudes of their isotropic thermal displacement parameters. Hydrogens on the amidine groups were located in difference Fourier syntheses and their positional parameters freely refined; the remaining hydrogen atoms were included in calculated positions and allowed to ride on their parent atoms. All hydrogen atoms were assigned fixed isotropic thermal parameters, $U_{iso}(H) = 1.2 \times U_{iso}$(parent) or $U_{iso}(H) = 1.5 \times U_{iso}(C)$ for methyl groups.

Compound **3a** co-crystallized with one-quarter molecule of CH_2Cl_2 per formula unit in close proximity to an inversion centre but with all atoms lying in general sites (8*f*). The site occupancy factors for the carbon and chlorine atoms of the asymmetric portion of the solvent molecule were assigned based upon a reasonable refinement of the thermal parameters corresponding to Cl(1). Thus, Cl(1) was refined with a fixed occupancy of 0.5, corresponding to one-quarter molecule per formula unit, and C(90) was included with a site occupancy factor of 0.25, as is required by site multiplicity. The C–Cl bond distances were restrained to reasonable values; hydrogen atoms were included in calculated positions.

In the crystal structure of **4b** the asymmetric unit comprises two independent molybdenacarbaborane molecules plus one molecule each of H_2O and CH_2Cl_2. The water molecule was disordered over two distinct sites, for which the oxygen atoms were refined with equivalent anisotropic displacement parameters and with half occupancy in each site; no hydrogen atoms were included. The fully ordered CH_2Cl_2 molecule was refined with hydrogen atoms in calculated positions and with the two chlorine atoms having equivalent anisotropic displacement parameters. One CNBu^t ligand in **4b** had methyl substituents disordered over two positions by an approximate 60° rotation about the C(21)–N(20) bond. The major and minor components were refined in parts with fixed occupancies of 0.70 and 0.30, respectively, and with equivalent anisotropic thermal parameters for the atoms in each set of disordered methyl groups. While **4b** is not chiral, it crystallizes in a chiral space group; the value of the Flack parameter 0.06(2) indicates that the correct axial system was chosen to describe the structure.[18]

CCDC reference numbers 176997 and 176998.

See http://www.rsc.org/suppdata/dt/b1/b111562f/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Robert A. Welch Foundation for support (Grant AA-1201), and Dr. J. C. Jeffery, Bristol University, United Kingdom, for assistance with the structure determination of **4b**.

References

1 D. E. Hyatt, D. A. Owen and L. J. Todd, *Inorg. Chem.*, 1966, **5**, 1749.
2 W. H. Knoth, *J. Am. Chem. Soc.*, 1967, **89**, 1274.
3 D. E. Hyatt, F. R. Scholer, L. J. Todd and J. L. Warner, *Inorg. Chem.*, 1967, **6**, 2229.
4 W. H. Knoth, *Inorg. Chem.*, 1971, **10**, 598.
5 J. Plesek, T. Jelínek, E. Drdáková, S. Hermánek and B. Stíbr, *Collect. Czech. Chem. Commun.*, 1984, **49**, 1559.
6 T. Jelínek, J. Plesek, S. Hermánek and B. Stíbr, *Collect. Czech. Chem. Commun.*, 1985, **50**, 1376.
7 J. C. Jeffery, P. A. Jelliss, J. Karban, V. N. Lebedev and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1997, 1219.
8 J. H. Morris, K. W. Henderson and V. A. Ol'shevskaya, *J. Chem. Soc., Dalton Trans.*, 1998, 1951.
9 J. C. Jeffery, V. N. Lebedev and F. G. A. Stone, *Inorg. Chem.*, 1996, **35**, 2967.
10 J. A. Walker, C. A. O'Con, L. Zheng, C. B. Knobler and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 1983, 803.
11 S. Du, T. D. McGrath, J. A. Kautz and F. G. A. Stone, *Inorg. Chem.*, 2001, **40**, 6563.
12 S. Du, T. D. McGrath, J. A. Kautz and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 2001, 2791.
13 W. Kantlehner, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 6 (ed. E. Winterfeldt), p. 546.
14 W. H. Knoth, J. L. Little, J. R. Lawrence, F. R. Scholer and L. J. Todd, *Inorg. Synth.*, 1968, **11**, 33.
15 G. M. Sheldrick, SADABS, A Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996; SAINT, Bruker AXS, Madison, WI, 1997.
16 SHELXTL version 5.03, Bruker AXS, Madison, WI, 1995.
17 G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.
18 H. D. Flack and G. Bernardinelli, *J. Appl. Crystallogr.*, 2000, **33**, 1143.