Synthesis, Molecular Structure, and Nuclear Magnetic Resonance Spectra of the Anionic Monocarbametallaborane $[NEt_4][(CO)_3(PPh_3)(OH)$-*closo*-$MoCB_{10}H_{10}]\cdot CH_2Cl_2$ *

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Reaction between *arachno*-$[B_{10}H_{14}]^{2-}$ and a mixture of $[Mo(CO)_3(MeCN)_3]$ and PPh_3 results in the formation of the twelve-vertex *closo*-carbamolybdaborane anion $[1,1,1,1\text{-}(CO)_3(PPh_3)\text{-}2\text{-}(OH)$-*closo*-$1,2\text{-}MoCB_{10}H_{10}]^-$, isolated in 50% yield as its tetraethylammonium salt. Crystals of $[NEt_4][(CO)_3(PPh_3)MoC(OH)B_{10}H_{10}]\cdot CH_2Cl_2$ are triclinic, space group $P\bar{1}$ (no. 2), with a = 962.0(3), b = 1 006.9(3), c = 2 156.3(3) pm, α = 95.10(3), β = 100.55(3), and γ = 101.63(2)°, and Z = 2. The structure was refined to R = 0.0505, R' = 0.0507 using 4 427 observed data $[I > 2\sigma(I)]$. Magnetic multiple-resonance spectroscopy was used for the tentative assignment of the ^{11}B and ^1H n.m.r. spectra.

Some seventeen years ago Wegner *et al.*[1] reported the photolytic reaction between tetrahydrofuran(thf) solutions of Na[*nido*-$B_{10}H_{13}$] and $[Mo(CO)_6]$ to give the anion $[1,1,1,1\text{-}(CO)_4\text{-}2\text{-}(OH)$-*closo*-$1,2\text{-}MoCB_{10}H_{10}]^-$ (**1**), equation (1). Treatment

$$[Mo(CO)_6] + [B_{10}H_{13}]^- \xrightarrow{h\nu} \underset{(\mathbf{1})}{[(CO)_4MoC(OH)B_{10}H_{10}]^-} + CO + H_2 \quad (1)$$

of this monoanion with sodium hydride gave a quantitative yield of the dianion $[1,1,1\text{-}(CO)_3\text{-}\mu\text{-}2,1\text{-}(\overline{COO)\text{-}closo\text{-}1,2\text{-}MoC}B_{10}H_{10}]^{2-}$ (**2**) [equation (2)] which was characterized by single-crystal *X*-ray diffraction analysis and shown to have an exopolyhedral Mo(1)–C(2) ester-type linkage as shown in Figure 1. Treatment of either compound (**1**) or (**2**) with aqueous base was reported to give the eleven-vertex *nido* dianion $[(CO)_4MoB_{10}H_{12}]^{2-}$ (**3**), which was believed to have the doubly H-bridged *nido* configuration (I).[1]

$$\underset{(\mathbf{1})}{[(CO)_4MoC(OH)B_{10}H_{10}]^-} + H^- \longrightarrow \underset{(\mathbf{2})}{[(CO)_3(CO\overline{O)MoC}B_{10}H_{10}]^{2-}} + H_2 \quad (2)$$

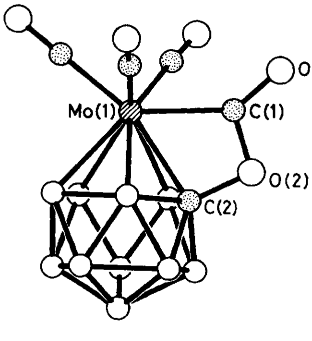
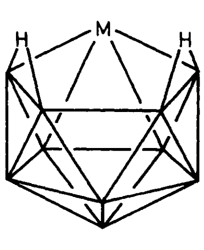
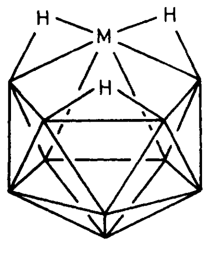


Figure 1. Representation of the crystallographically determined molecular structure of the $[(CO)_3(\overline{COO)MoC}B_{10}H_{10}]^{2-}$ dianion (**2**) (from ref. 1). Reported interatomic distances are Mo–C(1) 213, C(1)–O(1) 129, C(1)–O(2) 137, and C(2)–O(2) 145 pm. Distances from the molybdenum atom to the carbon atoms of carbonyl groups average at 197(2) pm, C–O distances within carbonyl ligands 116(2) pm, and intracluster B–C and B–B distances at 170(1) and 181(1) pm respectively. The molybdenum–cluster atom distances are 230(1) to C(2), 238(1) to B(3),B(6), and 244(1) pm to B(4),B(5)

Incidental to more extensive work in our laboratories concerned with the preparation and behaviour of eleven-vertex *nido* molybda- and wolframa-boranes of doubly H-bridged configuration (I) and triply H-bridged configuration (II),[2] we have isolated a phosphine-substituted analogue of compound (**1**), *viz.* the tetraethylammonium salt of the anion $[1,1,1,1\text{-}(CO)_3(PPh_3)\text{-}2\text{-}(OH)$-*closo*-$1,2\text{-}MoCB_{10}H_{10}]^-$, compound (**4**), for which we here report the molecular structure and n.m.r. properties. Some related work on ten-vertex *nido* molybda- and wolframa-boranes is described in ref. 3.



(I)



(II)

Results and Discussion

The reaction between $[NEt_4]_2[$*arachno*-$B_{10}H_{14}]$ and $[Mo(CO)_3(MeCN)_2(PPh_3)]$ (prepared *in situ* as described below) proceeds rapidly and smoothly under mild conditions (30 min at ambient temperature in CH_2Cl_2 solution). Chromatography thence yielded an air-stable crystalline solid, compound (**4**), as the only chromatographically mobile metallaborane product. N.m.r. and i.r. spectroscopy indicated a molybdaborane species with ten boron atoms and *exo*-polyhedral carbonyl and phosphine ligands on the metal, with the absence of bridging hydrogen proton resonances suggesting a closed species. However, the nuclear shielding patterns were not similar to those of the eleven-vertex *closo*-type $\{MB_{10}\}$ metallaboranes that have been reported (M = Fe, Ru, Os, or Rh),[4–7] nor to those[2] of the more open *nido* $\{MoB_{10}\}$ clusters of

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* Tetraethylammonium 2,2,2-tricarbonyl-1-hydroxy-2-triphenylphosphine-*closo*-1-carba-2-molybdadodecaborate(1 –)–dichloromethane (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Interatomic distances (pm) for the carbamolybdaborane anion of compound (**4**), with estimated standard deviations (e.s.d.s) in parentheses *

(*a*) Around molybdenum			
Mo(1)–C(1)	200.9(9)	Mo(1)–C(2)	240.9(7)
Mo(1)–C(3)	197.6(8)	Mo(1)–C(4)	196.6(8)
Mo(1)–P	256.6(4)	Mo(1)–B(3)	240.3(8)
Mo(1)–B(4)	240.1(8)	Mo(1)–B(5)	235.4(9)
Mo(1)–B(6)	235.3(8)		
(*b*) Around the polyhedral carbon atom C(2)			
C(2)–O(2)	142.6(8)	C(2)–B(3)	172.8(10)
C(2)–B(6)	170.4(10)	C(2)–B(7)	169.6(11)
C(2)–B(11)	171.5(11)		
(*c*) Boron–boron			
B(3)–B(4)	181.1(11)	B(3)–B(7)	176.9(11)
B(3)–B(8)	178.0(11)	B(4)–B(5)	180.4(11)
B(4)–B(8)	177.0(11)	B(4)–B(9)	178.1(11)
B(5)–B(6)	182.8(12)	B(5)–B(9)	178.6(12)
B(5)–B(10)	178.9(11)	B(6)–B(10)	177.6(12)
B(6)–B(11)	177.3(11)	B(7)–B(8)	176.8(12)
B(7)–B(11)	175.1(12)	B(7)–B(12)	175.6(13)
B(8)–B(9)	176.7(12)	B(8)–B(12)	177.5(12)
B(9)–B(10)	177.7(13)	B(9)–B(12)	177.3(13)
B(10)–B(11)	172.9(13)	B(10)–B(12)	176.8(13)
B(11)–B(12)	174.5(13)		
(*d*) Others			
C(1)–O(1)	114.6(8)	C(3)–O(3)	115.0(7)
C(4)–O(4)	114.8(8)	P–C(11)	182.6(5)
P–C(21)	182.1(5)	P–C(31)	184.2(5)
(*e*) Intramolecular contact			
C(1)···O(2)	292.0		

* Phenyl groups were refined as rigid hexagons with C–C and C–H distances of 139.5 and 108.0 pm respectively.

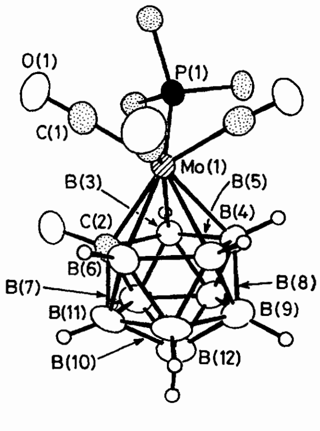

Figure 2. Crystallographically determined molecular structure of the $[(CO)_3(PPh_3)MoC(OH)B_{10}H_{10}]^-$ monoanion of (**4**), with the PPh_3 atoms, except *ipso*-C_3P omitted for clarity. All H atoms were located except for that on the hydroxyl group on C(2). Although C(1)–O(1) nearly eclipses this COH group (Figure 3) the O(2)–C(1) distance is non-bonding at 292.0 pm (*cf.* Figure 1)

Table 2. Selected interatomic angles (°) for the carbamolybdaborane anion of compound (**4**), with e.s.d.s in parentheses

(*a*) At the molybdenum atom			
C(1)–Mo(1)–P	75.2(3)	C(2)–Mo(1)–P	110.9(2)
C(3)–Mo(1)–P	75.9(3)	C(4)–Mo(1)–P	124.3(2)
C(1)–Mo(1)–C(4)	76.1(3)	C(2)–Mo(1)–B(3)	42.0(3)
C(2)–Mo(1)–B(6)	41.9(2)	B(3)–Mo(1)–B(4)	44.3(2)
B(4)–Mo(1)–B(5)	79.9(3)	B(5)–Mo(1)–B(6)	45.7(2)
(*b*) At the polyhedral carbon atom C(2)			
Mo(1)–C(2)–B(3)	68.8(4)	Mo(1)–C(2)–B(6)	67.3(4)
O(2)–C(2)–B(3)	120.4(5)	O(2)–C(2)–B(6)	120.6(5)
B(3)–C(2)–B(6)	112.7(5)	B(3)–C(2)–B(7)	62.3(5)
B(6)–C(2)–B(11)	62.5(5)	B(7)–C(2)–B(11)	61.8(5)
(*c*) At various boron atoms			
C(2)–B(3)–B(4)	107.0(5)	B(3)–B(4)–B(5)	106.6(6)
Mo(1)–B(3)–C(2)	69.2(4)	Mo(1)–B(4)–B(3)	67.9(4)
Mo(1)–B(3)–B(4)	67.8(4)	B(4)–B(5)–B(6)	106.9(5)
Mo(1)–B(5)–B(6)	67.1(4)	Mo(1)–B(6)–C(2)	70.8(4)
Mo(1)–B(6)–B(5)	67.2(4)	C(2)–B(6)–B(5)	106.6(5)
(*d*) Others			
Mo(1)–P–C(11)	119.2(2)	Mo(1)–C(1)–O(1)	176.8(5)
Mo(1)–P–C(21)	115.0(2)	Mo(1)–C(3)–O(3)	174.8(5)
Mo(1)–P–C(31)	111.8(2)	Mo(1)–C(4)–O(4)	178.8(5)

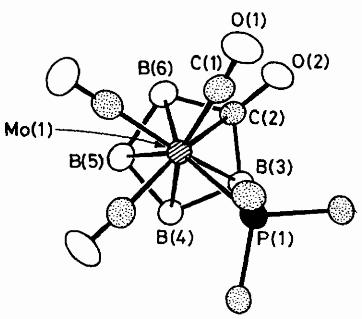

Figure 3. View of the metal and its circumjacent atoms in compound (**4**), viewed approximately perpendicular to the C(2)B(3)B(4)B(5)B(6) plane

configurations (**I**) and (**II**), and we therefore carried out a single-crystal *X*-ray study to establish the structural type. This revealed that compound (**4**) was the CH_2Cl_2 solvate of the ionic species $[NEt_4][1,1,1\text{-}(CO)_3(PPh_3)\text{-}2\text{-}(OH)\text{-}closo\text{-}1,2\text{-}MoCB_{10}H_{10}]$. The structure of the anion is shown in Figure 2, and interatomic distances and angles are given in Tables 1 and 2 respectively. All hydrogen atoms were located except for the hydroxy H on O(2) which is however reasonably inferred from the non-paramagnetic nature of the complex and n.m.r. spectroscopy (Table 3). The twelve-vertex *closo* $\{MoCB_{10}\}$ cluster is clearly analogous to that of the tetracarbonyl species (**1**) reported (but not structurally characterized) by Wegner *et al.*,[1] equation (1) above; in compound (**4**) a triphenylphosphine ligand replaces one of the carbonyl groups on the metal atom in compound (**1**).

The anion of compound (**4**) (Figure 2) differs from the dianion of compound (**2**) (Figure 1 above) in having no *exo* polyhedral cyclic ester-type linkage. Although the C(1)–O(1) carbonyl group almost eclipses the cluster C(2)-bound hydroxy grouping in compound (**4**) (Figure 3), the distance O(2)–C(1) is clearly non-bonding at 292.0 pm, and Mo(1)–C(1)–O(1) at 176.8(5)° deviates little from linearity.

Within the monocarbamonometallaborane cluster of compound (**4**) the Mo(1)–C(2) distance at 240.9(7) pm is longer than that constrained by the cyclic ester [230(1) pm] in compound (**2**), whereas the other intracluster distances are similar for both (**2**) and (**4**). Thus, although the molybdenum–boron distances appear to be marginally shorter in (**4**), this is not statistically significant and in any event is probably an artefact arising from hydrogen atom inclusion in the crystallographic data analysis of (**4**) but not of (**2**). The interboron distances between adjacent

Table 3. Measured n.m.r. parameters for compound (4); CD_3CN solution at 304 K unless otherwise specified[a]

Peak designator	Assignment[b]	$\delta(^{11}B)$/p.p.m.[c,d]	Observed $[^{11}B-^{11}B]$ COSY correlations[e]	$\delta(^1H)$/p.p.m.[d,f,g]
A	12 (9)	−1.8 (1 B)	Ds Em Fs	+2.58 (1 H)
B	4,5 (7,11)	−5.1 (2 B)	Cs Fs	+1.22 (2 H)
C	3,6	−9.2 (2 B)	Bs D? E?	+2.46 (2 H)
D	8,10	−10.6 (2 B)	As D? Fm	+1.67 (2 H)
E	7,11 (4,5)	−12.0 (2 B)	Am C?	+1.90 (2 H)
F	9 (12)	−14.2 (1 B)	As Bs Dm	+1.12 (1 H)

[a] Additional data: $\delta(^{31}P)$ +51.9 p.p.m. (CD_3CN solution at 243 K). $\delta(^{13}C)$ (aromatic) +133.8 [d, $J(^{31}P-^{13}C)$ *ca.* 10 Hz], +129.8 (s), and +127.7 p.p.m. [d, $J(^{31}P-^{13}C)$ *ca.* 10 Hz]; $\delta(^{13}C)(NEt_4)$ +7.1 (CH_3) and +52.5 p.p.m. (CH_2); *ipso*-CP and CO carbons not detected [CD_2Cl_2 solution at 294 K with {^1H (broad-band noise)} decoupling]. [b] Possible alternative assignments in parentheses [COSY interpretation ambiguous; non-parenthetic assignments at present favoured on basis of weaker correlations between the B(3,6) and B(7,11) pairs flanking the C(2) position (see, for example, Figure 5 in ref. 15)]. [c] ±0.5 p.p.m. to high field (low frequency) of $BF_3(OEt_2)$ in $CDCl_3$. [d] Relative intensities in parentheses. [e] s = Strong, m = intermediate, ? = uncertain. [f] ±0.05 p.p.m.; $\delta(^1H)$ related to directly bound B atoms by $^1H-\{^{11}B$ (selective)} spectroscopy. [g] Also $\delta(^1H)(OH)$ +3.54 at 294 K and +4.28 p.p.m. at 203 K in CD_2Cl_2 solution.

pairs of the Mo(1)-bound atoms B(3), B(4), B(5), and B(6), which average 181.4(13) pm, appear to be longer than the other interboron distances which average 177.1(11) pm (e.s.d. of average distance in parentheses). Not included in this latter average is the apparently short B(10)–B(11) distance of 172.9(13) pm, although this again may not be a statistically significant shortening. A final structural point is that there is no apparent phosphine *versus* carbonyl differential *trans* influence on the intracluster distances.

In terms of the Williams–Wade cluster-geometry and electron-counting rules[8,9] the anion in compound (4) is a *closo*-$[B_{12}H_{12}]^{2-}$ analogue in which the molybdenum centre contributes three orbitals and two electrons to the formal cluster electron count. In metal-complex terms the $\{B_{10}H_{10}C(OH)\}^{3-}$ moiety can be regarded as a pentahapto three-orbital ligand and the molybdenum as an 18-electron d^4 molybdenum(II) centre with seven principal valence orbitals in a '4:3 piano-stool' configuration.

The monocarbamolybdaborane (4) is consistently obtainable in *ca.* 50% yield from $[Mo(CO)_3(MeCN)_2(PPh_3)]$ (5) and this, together with its constitution, suggests carbonyl transfer from a second molecule of $[Mo(CO)_3(MeCN)_2(PPh_3)]$ during its formation. Confirmation that intermolecular carbonyl transfer does not occur prior to the addition of $[B_{10}H_{14}]^{2-}$ to the reaction mixture was achieved by isolating the product formed by the reaction of PPh_3 and $[Mo(CO)_3(MeCN)_3]$, equation (3).

$$[Mo(CO)_3(MeCN)_3] + PPh_3 \longrightarrow \underset{(5)}{[Mo(CO)_3(MeCN)_2(PPh_3)]} + MeCN \quad (3)$$

A yellow precipitate formed when equimolar solutions of PPh_3 and $[Mo(CO)_3(MeCN)_3]$ in CH_2Cl_2–MeCN were cooled to *ca.* 0 °C. The air-sensitive product was soluble in CH_2Cl_2, thf, and MeCN. Proton n.m.r. of a solution in CD_2Cl_2 revealed the presence of three different methyl-proton environments of equivalent intensity. Peaks at δ 1.776 and 1.788 p.p.m. correspond to methyl groups in acetonitrile ligands co-ordinated to the molybdenum atom. The peak at δ 1.94 p.p.m. is consistent with free acetonitrile. Inequivalence of the two co-ordinated MeCN ligands indicates that one of them is *trans* to the phosphine ligand.

We have also observed the anion of compound (4) as a product in small quantities (⩽ *ca.* 2%) from the reaction between NH_2Et and $[7,7,7,7-(CO)_3(PPh_3)$-*nido*-$7-MoB_{10}H_{13}]^-$ [of triply H-bridged configuration (II)],[3] the other polyhedral boron-containing product identified from this reaction being *closo*-$[B_6H_6]^{2-}$ which is also formed in the decomposition of compound (4) in CD_3CN solution in air. The carbonyl cluster insertion in the synthesis of compound (4) is of interest because precedents for this are photolytic processes such as that in equation (1) above,[1] or the photolytic formation of *closo*-$[(\eta^5-C_5H_5)FeC(OEt_2)B_{10}H_{10}]$ from $[(\eta^5-C_5H_5)(CO)_2FeB_{10}H_{13}]$,[10] although non-photolytic insertions do occur, for example in the formation of *isonido*-$[(PPh_3)(Ph_2PC_6H_4-o)IrC(OH)B_8H_6(OMe)]$[11] and *closo*-$[(PPh_3)(OCOMe)HIrCB_8H_7(PPh_3)]$.[12]

The 1:2:2:2:2:1 relative intensity patterns in the ^1H and ^{11}B n.m.r. spectra (Table 3) indicate a time-average mirror-plane symmetry for the anion of (4), which contrasts with the asymmetric solid-state structure and suggests a ready rotational fluxionality in the η^5-carborane–metal bonding which will of course be associated with a 'turnstile' contrarotation of the $\{(CO)_3(PPh_3)\}$ *exo*-polyhedral metal-bound ligand system. $^1H-\{^{11}B\}$ N.m.r. spectroscopy at 203 K gives a spectrum similar to that at room temperature, *i.e.* also indicating a 1:2:2:2:2:1 pattern; $\Delta G^{\ddagger}_{203}$ for the fluxional process is therefore low (⩽ *ca.* 40 kJ mol^{-1}). However, the resonance at +3.54 p.p.m. at room temperature is shifted downfield to +4.28 p.p.m. at 203 K (CD_2Cl_2 solution): this we assign to the OH proton on the polyhedral cluster carbon atom C(2). The fluxionality implies that any bonding-directing influence of *exo*-phosphine *vis-a-vis* cage carbon is not strong, as is also indicated by the interatomic distances, as discussed above.

Two-dimensional $[^{11}B-^{11}B]$-COSY[13] spectroscopy permits a tentative assignment of the ^{11}B resonances to structural positions. There is an ambiguity in this present case as there is no *a priori* provision for distinguishing between the C(2)-bound and Mo(1)-bound boron positions, thus unfortunately preventing a definitive estimation of molybdenum *versus* carbon antipodal effects. The precedent of weaker couplings $^1J(^{11}B-^{11}B)$ for B–B connectivities in $\{CB_2\}$ deltahedral faces[14,15] [which are associated with correspondingly stronger couplings $^1J(^{13}C-^{11}B)$[16]] would favour one alternative over the other as summarized in Table 3. The ^{11}B resonances are however closely grouped within a $\delta(^{11}B)$ range of 13 p.p.m. which is small compared to polyhedral ^{11}B shielding ranges,[15] and so lack of definitive assignment is perhaps not so critical in view of present very limited knowledge of the factors which may influence polyhedral nuclear shielding. The ^1H resonances similarly are closely grouped, as expected from general parallels between $\delta(^{11}B)$ and $\delta(^1H)$ of directly bound *exo*-hydrogens,[15,17] although in this context the shielding of $^1H(4,5)$ does seem to be anomalously high (by ⩾ *ca.* 1 p.p.m.).

Table 4. Fractional atomic co-ordinates (× 10^4) for compound (**4**), with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	2 518.2(5)	2 231.4(5)	2 092.8(2)	B(7)	4 511(8)	3 971(7)	3 672(3)
P	3 686(1)	3 537(1)	1 281(1)	B(8)	3 143(8)	4 882(7)	3 459(3)
C(1)	3 707(6)	1 015(6)	1 759(3)	B(9)	1 465(8)	3 801(8)	3 480(4)
C(2)	4 169(6)	2 596(5)	3 108(3)	B(10)	1 828(9)	2 221(8)	3 692(3)
C(3)	854(6)	2 519(6)	1 474(3)	B(11)	3 681(9)	2 352(8)	3 823(3)
C(4)	1 182(6)	425(6)	1 883(3)	B(12)	3 032(9)	3 777(8)	4 054(4)
O(1)	4 354(5)	273(5)	1 582(2)	Cl(1)	1 597(3)	6 883(3)	5 551(1)
O(2)	5 432(4)	2 122(4)	3 027(2)	Cl(2)	2 874(3)	8 635(3)	4 718(1)
O(3)	−178(5)	2 662(5)	1 148(2)	C(1S)	2 593(10)	7 005(9)	4 940(4)
O(4)	381(6)	−620(5)	1 761(2)	N	7 627(6)	8 301(6)	3 394(3)
C(11)	5 617(3)	4 346(3)	1 484(2)	C(1Na)	8 195(10)	7 141(9)	3 167(5)
C(12)	6 558(3)	3 740(3)	1 878(2)	C(1Nb)	9 247(18)	8 602(41)	3 437(20)
C(13)	8 052(3)	4 258(3)	1 986(2)	C(2N)	9 907(10)	7 527(11)	3 212(5)
C(14)	8 605(3)	5 382(3)	1 699(2)	C(3Na)	7 922(10)	9 569(10)	3 042(5)
C(15)	7 664(3)	5 988(3)	1 305(2)	C(3Nb)	6 954(39)	7 836(24)	2 640(16)
C(16)	6 170(3)	5 470(3)	1 198(2)	C(4N)	7 275(11)	9 198(10)	2 321(5)
C(21)	2 885(4)	4 943(3)	1 030(2)	C(5Na)	5 951(11)	7 747(11)	3 247(5)
C(22)	2 311(4)	5 019(3)	395(2)	C(5Nb)	6 882(25)	9 205(54)	3 808(24)
C(23)	1 714(4)	6 125(3)	232(2)	C(6N)	5 219(14)	8 846(13)	3 499(6)
C(24)	1 690(4)	7 155(3)	705(2)	C(7Na)	8 215(14)	8 910(13)	4 075(6)
C(25)	2 264(4)	7 078(3)	1 341(2)	C(7Nb)	7 630(46)	7 076(20)	3 753(9)
C(26)	2 861(4)	5 972(3)	1 503(2)	C(8N)	7 947(19)	7 612(18)	4 487(8)
C(31)	3 527(4)	2 420(4)	536(2)	H(3)	4 672(48)	4 745(44)	2 671(20)
C(32)	4 717(4)	2 423(4)	250(2)	H(4)	1 375(51)	4 701(49)	2 418(23)
C(33)	4 581(4)	1 533(4)	−302(2)	H(5)	−128(51)	1 801(47)	2 638(22)
C(34)	3 254(4)	639(4)	−569(2)	H(6)	2 479(49)	315(51)	3 054(22)
C(35)	2 064(4)	636(4)	−283(2)	H(7)	5 641(63)	4 372(56)	3 854(26)
C(36)	2 201(4)	1 526(4)	269(2)	H(8)	3 330(51)	6 015(52)	3 555(23)
B(3)	3 903(7)	4 126(6)	2 862(3)	H(9)	503(62)	4 206(57)	3 625(27)
B(4)	1 975(7)	4 051(7)	2 738(3)	H(10)	1 050(56)	1 572(53)	3 960(25)
B(5)	1 130(7)	2 367(7)	2 879(3)	H(11)	4 275(63)	1 733(60)	4 086(28)
B(6)	2 582(8)	1 465(7)	3 095(3)	H(12)	3 360(66)	4 188(63)	4 581(31)

Experimental

The compound $[NEt_4]_2[$*arachno*-$B_{10}H_{14}]$ was made from *nido*-$[B_{10}H_{13}]^-$ by reduction with $[BH_4]^-$. This was essentially according to the literature,[18] as was the preparation of $[Mo(CO)_3(MeCN)_3]$ from $[Mo(CO)_6]$.[19]

N.M.R. Spectroscopy.—This was performed at 2.35 and 9.40 T on JEOL FX100 and Bruker AM 400 instruments, respectively; $[^{11}B-^{11}B]$-COSY[5,7] and $^1H-\{^{11}B(\text{selective})\}$[20–22] experiments were essentially as described elsewhere. Other n.m.r. spectroscopy was straightforward, although ^{31}P spectra were recorded at low temperatures to maximize thermal decoupling of ^{10}B and ^{11}B nuclei from the phosphine ligand resonances.[23] Chemical shifts $\delta(^1H)$, $\delta(^{31}P)$, $\delta(^{11}B)$, and $\delta(^{13}C)$ are given to high frequency (low field) of $\Xi = 100$ ($SiMe_4$), $\Xi = 40.480\,730$ (nominally 85% H_3PO_4), $\Xi = 32.083\,971$ $[BF_3(OEt_2)$ in $CDCl_3]$,[15] and $\Xi = 25.145\,004$ MHz ($SiMe_4$) respectively.

Preparation of Compound (**4**).—Triphenylphosphine (260 mg, 1.0 mmol) in CH_2Cl_2 (10 cm^3) was added to a stirred solution of $[Mo(CO)_3(MeCN)_3]$ (300 mg, 1 mmol) in MeCN (*ca*. 50 cm^3) at room temperature under N_2. After stirring for 5 min, a solution of $[NEt_4]_2[B_{10}H_{14}]$ (460 mg, 1.2 mmol) in CH_2Cl_2–MeCN (1:1, 30 cm^3) was added and stirring continued for 30 min. After reducing the reaction mixture to a small volume under reduced pressure (rotary evaporator), repeated t.l.c. (silica G, Fluka GF254, on plates 200 × 200 × 1 mm) in air resulted in the isolation of $[NEt_4][(CO)_3(PPh_3)MoC(OH)B_{10}H_{10}]$ (**4**) (R_f 0.1 using 9:1 CH_2Cl_2–MeCN as eluting medium) as a yellow solid (400 mg, 0.5 mmol, *ca*. 50%), soluble in CH_2Cl_2, thf, and MeCN. Compound (**4**) is air stable in the solid state but decomposes over several hours in acetonitrile solution in air to give $[B_6H_6]^{2-}$ as the only identifiable boron hydride [$\delta(^{11}B)$ −15.8 p.p.m.] in viable yield (*ca*. 40%). Compound (**4**) had $\nu_{max.}(CO)$ at 1 910, 1 925, 2 000; $\nu(BH)$ at 2 420, 2 490, 2 540; and $\nu(OH)$ at 3 600 cm^{-1} (Nujol mull). N.m.r. properties are given in Table 3. A crystal suitable for single-crystal *X*-ray diffraction analysis was grown by the slow diffusion of n-hexane into a concentrated dichloromethane solution of (**4**).

Preparation of Compound (**5**).—Triphenylphosphine (130 mg, 0.5 mmol) in dichloromethane (10 cm^3) was added to $[Mo(CO)_3(MeCN)_3]$ (150 mg, 0.5 mmol) in acetonitrile (30 cm^3) at room temperature under N_2. After stirring for 5 min the solution was cooled to *ca*. 0 °C to effect precipitation. Supernatant liquid was removed and the solid washed with dichloromethane (3 × 5 cm^3) and hexane (2 × 10 cm^3) under nitrogen. The pale yellow air-sensitive solid was isolated in *ca*. 90% yield (250 mg, 0.44 mmol) {Found: C, 57.2; H, 4.25; N, 6.85. $[Mo(CO)_3(MeCN)_2(PPh_3)]\cdot MeCN$ requires C, 57.3; H, 4.25; N, 7.45%}; $\nu_{max.}(CO)$ at 1 805, 1 823, 1 921; $\nu(CN)$ at 2 250, 2 280 cm^{-1}.

X-Ray Crystallographic Analysis.—All measurements were carried out with a Nicolet P3/F diffractometer operating in the ω—2θ scan mode with graphite-monochromated Mo-K_α radiation ($\lambda = 71.069$ pm) following a standard procedure described elsewhere.[24] The structure was solved by standard heavy-atom methods using the SHELX program system.[25] An empirical absorption correction[26] was applied after the structure was determined.

All non-hydrogen atoms of the carbamolybdaborane anion

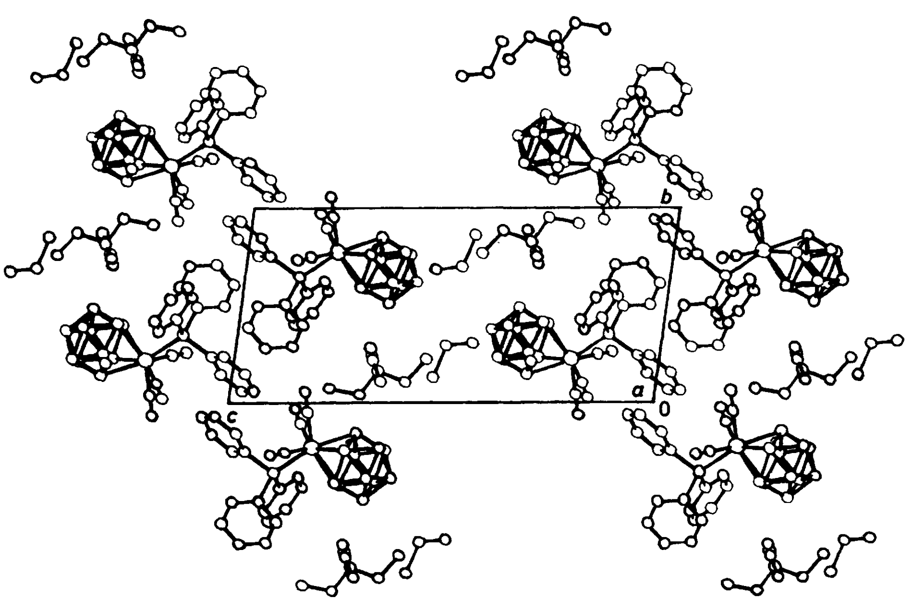

Figure 4. Crystal-packing diagram for $[NEt_4][(CO)_3(PPh_3)MoC(OH)B_{10}H_{10}]\cdot CH_2Cl_2$ (4); view direction (1,0,0)

were assigned anisotropic thermal parameters. Phenyl groups were refined as rigid hexagons (C–C 139.5 pm), with hydrogen atoms included in calculated positions (C–H 108.0 pm) and an overall isotropic thermal parameter for each group. All boron hydrogens were located experimentally and were freely refined with individual isotropic thermal parameters.

The methylene carbon atoms of the tetraethylammonium cation were disordered and each was refined over two positions with the overall site occupancy factors constrained to sum to one. Non-hydrogen atoms were assigned isotropic thermal parameters and hydrogen atoms were introduced in calculated positions with one overall thermal parameter.

The final refinement was weighted according to $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ in which the parameter g was included to give a flat analysis of variance with increasing sinθ and $[F_o/F_o(\text{max.})]$.

Fractional atomic co-ordinates are given in Table 4 and a packing diagram is shown in Figure 4.

Crystal data for (**4**). $[NEt_4][(CO)_3(PPh_3)MoC(OH)B_{10}H_{10}]\cdot CH_2Cl_2$, $C_{31}H_{48}B_{10}Cl_2MoNO_4P$, $M = 804.65$, triclinic, $a = 962.0(3)$, $b = 1\,006.9(3)$, $c = 2\,156.3(3)$ pm, $\alpha = 95.10(3)$, $\beta = 100.55(3)$, $\gamma = 101.63(2)^\circ$, $U = 1.994(1)$ nm^3, space group $P\bar{1}$ (no. 2), $Z = 2$, $D_c = 1.34$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 4.75$ cm^{-1}, $F(000) = 826$, $T = 290$ K.

Data collection. Scans from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0^\circ$, 4 981 unique data, 4 427 with $[I > 2\sigma(I)]$.

Structure refinement. Number of parameters, 427; weighting factor $g = 0.0003$, $R = 0.0505$, $R' = 0.0507$.

Acknowledgements

We thank the S.E.R.C. for support, and for a maintenance grant (to I. M.), and Dr. M. Thornton-Pett for crystallographic consultations.

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Received 26*th November* 1986; *Paper* 6/2286