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Macropolyhedral boron-containing cluster chemistry. Cluster assembly about a molybdenum centre. Formation of the 19-vertex $[(\text{CO})_2\text{MoB}_{16}\text{H}_{15}\text{C}_2\text{Ph}]^-$ anion.

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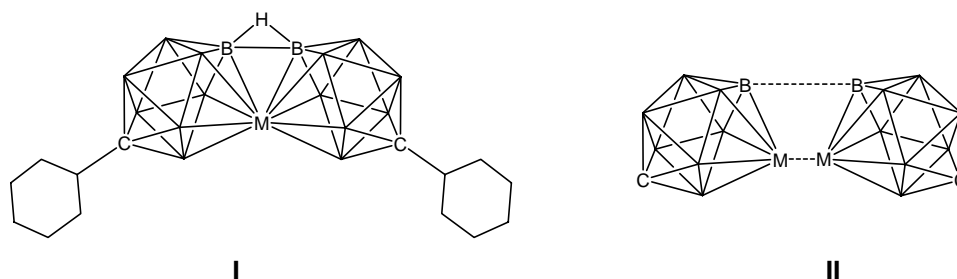
Fusion of nine-vertex [1-Ph-*nido*-1-CB₈H₁₁] with [Mo(CH₃CN)₃(CO)₃] in the presence of tetramethylnaphthalenediamine gives the nineteen-vertex macropolyhedral metallaborane anion $[(\text{CO})_2\text{MoB}_{16}\text{H}_{15}\text{C}_2\text{Ph}]^-$ with a molybdenum(VI) twelve-atom coordination sphere.

One conception of future achievable large borane cluster molecules predicts species that consist of condensed borons-only cores surrounded by boron-hydride outer skins.^{1,2} The architectures of many of these might be expected to mimic the assemblies of boron atoms that are seen within allotropes of elemental boron, but with peripheral valencies bound to hydrogen atoms.³⁻⁵ Computational work suggests that globular species such as B₁₇H₂₁ and B₈₄H₅₄, based on elemental boron assemblies, may represent future architectural principles.^{4,5} In terms of known species, such structures are approached by assemblies such as the {PdB₂₀} unit of [(PPh₃)₂(PPh₂)₂Pd₃B₂₀H₁₆Pd(PPh₃)]⁴ and the {IrB₁₈} unit of [(PMe₃)₂COIrB₂₆H₂₄Ir(PMe₃)₂].³ In the formation of these latter two compounds, smaller boron hydride units assemble and fuse about a transition-element centre.⁶ The experimental yields of these larger globular metallaborane species are, however, exceedingly small. Consequently, there is merit in prospecting for higher-yield assembly-fusion systems to facilitate development. Higher-yield fusions of five-vertex {C₂B₃} and six-vertex {C₂B₄} units about iron and cobalt centres have been observed,⁷ but the application of such routes to the fusion of larger clusters is not established, although potential feasibility is thereby suggested. We surmised that use of earlier transition-element centres, with fewer electrons, high formal oxidation states, and higher orbital and coordination-number availabilities, could have use as nuclei for such assembly-fusions. We have now been able to establish an instance of such an assembly fusion, in the reaction of [Mo(CO)₃(MeCN)₃]⁸ with [1-Ph-*nido*-1-CB₈H₁₁],⁹ and non-nucleophilic base, to give the air-stable nineteen-vertex $[(\text{CO})_2\text{MoB}_{16}\text{C}_2\text{Ph}_2\text{H}_{15}]^-$ anion **1** in a yield of 31 %. We have also obtained **1** from the otherwise closely related reaction using [Mo(CO)₃(C₇H₈)], but yields are very variable (zero to 70 %) and we have not been able to achieve consistency of good yield over many attempts and over several variations of conditions.

Thus, the reaction of [1-Ph-*nido*-1-CB₈H₁₁] {formed *in situ* from [4-Ph-*arachno*-4-CB₈H₁₃] (500 mg; 2.65 mmol) in toluene (25 ml) by heating to reflux temperature overnight}⁹ with N,N,N',N'-tetramethylnaphthalene-1,8-diamine (tmnd; 615 mg; 2.87 mmol) and [Mo(CO)₃(CH₃CN)₃] (700 mg, 2.65 mmol) in toluene (25 ml) at reflux temperature for 5 hours, followed by preliminary purification by 'flash chromatography' using silica-gel and subsequent TLC separation on silica-gel-G (Fluka, type GF₂₅₄), revealed a single major golden component (*R_F* ca. 0.3; 80 / 20 CH₂Cl₂ / hexane as liquid phase). This was identified as the [tmndH]⁺ salt **1a** of the $[(\text{CO})_2\text{MoB}_{16}\text{H}_{15}\text{C}_2\text{Ph}_2]^-$ anion **1** (308

mg, 420 μ mol, 31 %) by single crystal X-ray diffraction analysis (Figure 1),¹⁰ together with NMR spectroscopy, mass spectrometry and elemental analysis.¹¹

The basic double-cluster configuration of **1** approximates closely to the C_{2v} symmetry that is consistent with its solution NMR properties. This configuration is based on a nineteen-vertex $\{MoC_2B_{16}\}$ assembly (schematic I) that factorises into two *closo* ten-vertex $\{MoCB_8\}$ subcluster units that join with the molybdenum atom in common (schematic II). Monometallamonocarbaborane $\{MCB_8\}$ *closo* ten-vertex single-cluster species are known, but rare.¹² The two subclusters additionally link by a BHB unit, in which the hydrogen atom takes up a position equivalent to what would otherwise be a $\{BH(exo)\}$ site in each subcluster. This bridging hydrogen atom has an interestingly low nuclear shielding, with NMR $\delta(^1H)$ at + 7.17 ppm ($CDCl_3$). The overall architecture in this intercluster fusion region has some parallels with the apparently unbridged solid-state structure of $[(C_5Me_5)Co(C_2Me_2B_4H_3)CoH(C_2Me_2B_4H_3)Co(C_5Me_5)]$,¹³ and with the hydrogen-bridged structure in $[Cl_2TaC_4B_{18}H_{21}]$.¹⁴ The last compound, like **1**, is an earlier transition-element compound. These latter two species, as far as we are aware, constitute the only other known reasonably close cluster-fusion parallels. In the cobalt compound, the non-bridged interboron distance is 1.758(5) Å, and in the hydrogen-bridged tantalum species 1.870(4) Å. The equivalent linkage B(1)-B(1') in **1** at 1.707(4) Å shows a stronger fusion than in the other two species. The bonding around the B(1)-B(1') intercluster fusion in **1** is in fact generally strong, with Mo(2)-B(1) and Mo(2)-B(1'), both at 2.150(3) Å, markedly shorter than the other Mo-B distances, which all exceed 2.44 Å; interestingly, also, B(1)-B(4) and B(1)-B(4') are short for deltahedral interboron distances, at 1.662(5) and 1.657(5) Å respectively, and are in the range associated with localised interboron two-electron two-centre σ -bonds. In anion **1** the molybdenum atom is sited in a ten-boron cleft in the basic double-cluster assembly (compare references 3 and 4), with its formally molybdenum(VI) coordination periphery completed by the two CO ligands to give a sixteen-electron d^0 transition-element centre, with an overall nearest-neighbour atomic coordination number of 12.



In view of the elusiveness of high-yield routes to fused multi-cluster boron-containing species other than the *syn* and *anti* isomers of $B_{18}H_{22}$, this synthesis of the $[(CO)_2MoB_{16}H_{15}C_2Ph_2]^-$ anion **1** in reasonable yield in a straightforward synthesis from relatively easily made, or otherwise readily available, starting substrates,^{8,9} should now permit the development of a macropolyhedral chemistry that compliments that derived from the $B_{18}H_{22}$ isomers. The principle for the method also offers possibilities for development into a more generically applicable cluster-fusion method.

Acknowledgements

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Captions for Figure

Figure 1. Molecular structure of the $[(\text{CO})_2\text{MoB}_{16}\text{H}_{15}\text{C}_2\text{Ph}_2]^-$ anion **1**, as determined crystallographically in its $[\text{tmndH}]^+$ salt **1a**.¹⁰ Selected interatomic distances (Å) are as follows: from Mo(2) to B(1) 2.150(3), to B(1') 2.150(3), to B(3) 2.446(3), to B(3') 2.535(3), to B(5) 2.531(3), to B(5') 2.447(3), to B(6) 2.448(3), to B(6') 2.534(3), to B(9) 2.551(3), to B(9') 2.441(3), to C(21) 2.037(3) and to C(22) 2.018(3); C(21)-O(23) and C(22)-O(24) are 1.143(3) and 1.146(3); B(1) to B(1') is 1.707(4), with B(1)-B(4) and B(1)-B(4') also short at 1.662(5) and 1.657(4) (see text); conversely B(6)-B(9) and B(6')-B(9') (shown unconnected in the Figure) are 'long' at 1.978(2) and 1.971(4), showing a tendency towards more open 'isonido' ten-vertex geometry, as often observed in metal-containing *closo*-type ten-vertex borane cluster species.¹⁵ Other cluster interboron distances are in the range 1.733(4) to 1.872(4) Å, with carbon-boron distances in the range 159.7(4) to 162.1(4) Å. The C(21)-Mo(2)-C(22) angle is 89.27(11)°

Data for deposition

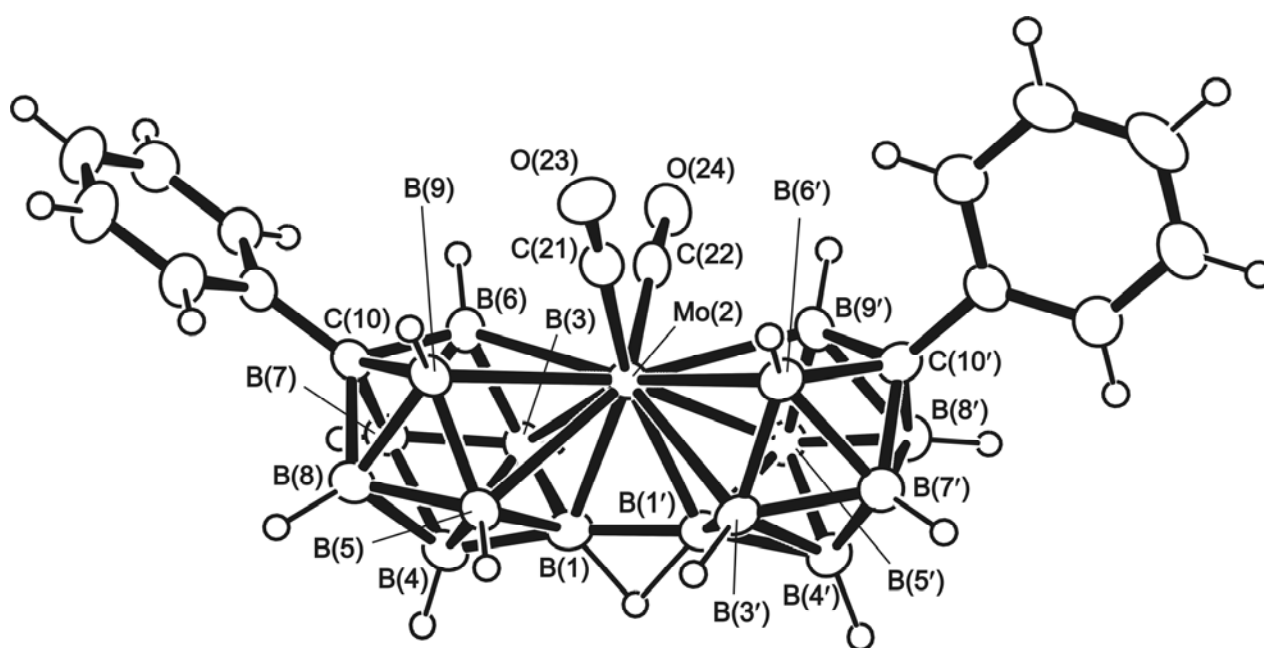
Crystallographic data for the previously unreported $[\text{C}_{10}\text{H}_6(\text{NMe}_2)\text{H}]^+$ salt **1a** of the $[(\text{CO})_2\text{MoB}_{16}\text{H}_{15}\text{C}_2\text{Ph}_2]^-$ anion **1** are deposited at the Cambridge Crystallographic Data Centre, CCDC, deposition number CCDC 239168; These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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10. Crystallographic data for the previously unreported $[\text{C}_{10}\text{H}_6(\text{NMe}_2)\text{H}]^+$ salt **1a** of the $[(\text{CO})_2\text{MoB}_{16}\text{H}_{15}\text{C}_2\text{Ph}_2]^-$ anion **1** are as follows: $\text{C}_{30}\text{H}_{44}\text{B}_{16}\text{MoN}_2\text{O}_2$: $M = 733.57$, triclinic (yellow prism from $\text{CH}_2\text{Cl}_2/\text{hexane}$), Space Group $P1$, $a = 9.2973(1) \text{ \AA}$, $b = 10.9837(2) \text{ \AA}$, $c = 11.3302(2) \text{ \AA}$, $\alpha = 117.822(1)^\circ$, $\beta = 96.567(1)^\circ$, $\gamma = 106.629(1)^\circ$, $U = 937.58(3) \text{ \AA}^3$, $D_{\text{calc}} = 1.299 \text{ Mg m}^{-3}$, $Z = 1$, Mo- K_α , $\lambda = 0.7107 \text{ \AA}$, $\mu = 0.382 \text{ mm}^{-1}$, $T = 150(2) \text{ K}$, $R_1 = 0.0277$ for 7009 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.0651$ for all 7061 unique reflections; CCDC 239168.
11. NMR data for anion **1**, salt **1a** in CDCl_3 , 298 K, δ in ppm, ordered as assignment, $\delta(^{11}\text{B})$ rel. $\text{BF}_3(\text{OEt}_2)$ [$\delta(^1\text{H})$ rel. SiMe_4]: B- μ -H(1,1') +60.9 [+7.17], BH(3,3';5,5') +2.4 [+2.13], BH(4,4') +8.4 [+3.41], BH(7,7';8,8') -15.7 [+3.08] and BH (6,6',9,9') -19.1 [-0.02]; IR spectrum $\nu(\text{CO})$ 1971.5 and 2020 cm^{-1} ; elemental analysis: found C 48.9, H 6.2, N 3.6 %; $\text{C}_{30}\text{H}_{44}\text{B}_{16}\text{MoN}_2\text{O}_2$ requires C 49.1, H 6.1, N 3.8 %; negative-ion mass spectrometry (electrospray) gave an $(m/z)(\text{max.})$ isotopomer envelope corresponding to $\text{C}_{16}\text{H}_{25}\text{B}_{16}\text{MoO}_2$ (molecular ion M for the anion **1**), with no significant H or H_2 loss, with a base-peak isotopomer envelope corresponding to $\{M - 2\text{CO}\}$, and a second principal fragmentation corresponding to $\{M - \text{CO}\}$.
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Figure 1



Suggestion for graphical abstract

Fusion of [1-Ph-*nido*-1-CB₈H₁₁] with [Mo(CH₃CN)₃(CN)₃] gives the nineteen-vertex macropolyhedral metallaborane anion [(CO)₂MoB₁₆H₁₅C₂Ph]⁻ with a molybdenum(VI) twelve-atom coordination sphere.

