The bis-molybdenum(0) trianion [1,3,6-{Mo(CO)$_3$}-3,6-(μ-H)$_2$-1,1,1-(CO)$_3$-2-Ph-*closo*-1,2-MoCB$_9$H$_7$]$^{3-}$ and its use as a scaffold in the assembly of heteropolymetallic complexes

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The title trianion reacts successively with cationic transition-metal fragments to afford a heterotrimetallic Mn–Mo–Pt species.

The cyclopentadienide anion [C$_5$H$_5$]$^−$ ranks among the most important ligands in organometallic chemistry.[1] For over 35 years, the di- and tri-anionic carborane ligands [*nido*-C$_2$B$_9$H$_{11}$]$^{2−}$ and [*nido*-CB$_{10}$H$_{11}$]$^{3−}$, respectively, which are isolobal with [C$_5$H$_5$]$^−$, have been known to behave similarly in that all three anions can act as *pentahapto*, 6π-electron donors to transition-metal centres.[2,3] Among the 12-vertex metallacarboranes so formed, the monocarbon cluster species are relatively scarce, and until recently sub-icosahedral complexes were especially rare.[4] However, contemporary advances in the chemistry of intermediate-sized monocarboranes, initiated by Brellochs,[5] permit an expansion of the number of monocarbon metallacarboranes with eleven vertices or fewer. To this end we have synthesized the 11-vertex metallacarboranes [1,1,1-(CO)$_3$-2-Ph-*closo*-MCB$_9$H$_9$]$^{2−}$ (M = Re, Mn)[6,7] and are exploring their chemistry. In expanding this work to other elements, we have discovered the related (but significantly different) title trianion, upon which we now report.

Treatment of [NEt$_4$][6-Ph-*nido*-6-CB$_9$H$_{11}$][5,8] in thf with Bu^{n}Li (2 equiv.), followed by [Mo(NCMe)$_3$(CO)$_3$][9] and then [NEt$_4$]I, afforded [NEt$_4$]$_3$[1,3,6-{Mo(CO)$_3$}-3,6-(μ-H)$_2$-1,1,1-(CO)$_3$-2-Ph-*closo*-1,2-MoCB$_9$H$_7$] **1a** (Scheme 1),† isolated by precipitation and recrystallization. The analogous tungsten species **1b** was formed similarly using [W(NCMe)$_3$(CO)$_3$][9] as the transition-metal reagent. The trianions of compounds **1** both show nine separate resonances (with one coincidence) in their ^{11}B{^{1}H} NMR spectra, indicative of an asymmetric structure, whilst their ^{1}H NMR spectra each reveal two broad quartets of unit integral around δ −1.1 and −5.4 (**1a**) and δ −1.7 and −6.1 (**1b**), typical of three-centre, two-electron B–HM agostic-type bonds.[10] These features, allied with the observation of several CO stretching bands in their IR spectra, suggested the presence of two metal centres with one being a vertex and one located in an exopolyhedral site, a situation confirmed by an X-ray diffraction study upon **1a** (Fig. 1).‡ This established that the trianion consists of a {*closo*-1,2-MoCB$_9$H$_9$} core that bears an exopolyhedral {Mo(CO)$_3$} fragment that is anchored to the cluster *via* an Mo–Mo dative bond [Mo(1)–Mo(2) = 3.1212(4) and 3.1801(5) Å (2 independent anions)] and two agostic-type B–HMo interactions [B(3)···Mo(2) = 2.399(4)

and 2.438(4) Å; B(6)···Mo(2) = 2.490(4) and 2.451(4) Å]. The latter involve boron vertices that are γ and β, respectively, to the carbon atom in the CBBBBB face of the carborane ligand.

Both of the molybdenum centres in **1a** (and similarly the two tungstens in **1b**) are formally zerovalent. Formation of these complexes provides a surprising contrast with the related 12-vertex species [1,2-R$_2$-3,3,3-(CO)$_3$-*closo*-3,1,2-MC$_2$B$_9$H$_9$]$^{2−}$ (M = Cr, Mo, W; R = H, Me),[11] prepared similarly from [7,8-R$_2$-*nido*-7,8-C$_2$B$_9$H$_9$]$^{2−}$ dianions with either [M(CO)$_6$] (under photolysis[11a] or [M(NCMe)$_3$(CO)$_3$] (at room temperature),[11b] but which lack the auxiliary exopolyhedral unit. The latter moiety in **1a** is not displaced by MeCN, nor by CO, and other attempts to abstract this fragment were also unsuccessful. Evidently in the present system the {1,1,1-(CO)$_3$-2-Ph-*closo*-1,2-MCB$_9$H$_9$} trianion core and the second {M(CO)$_3$} unit are mutually stabilizing, despite the absence of a formal anion–cation interaction as is normally
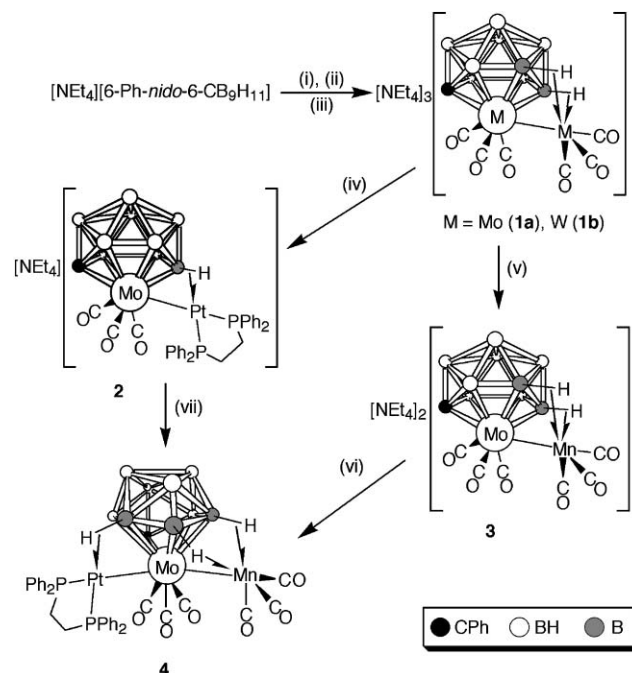
Scheme 1 *Reagents and conditions*: i, Bu^{n}Li (2 equiv.), THF; ii, [M(NCMe)$_3$(CO)$_3$] in THF; iii, [NEt$_4$]I (2 equiv.); iv, **1a** with [PtCl$_2$(dppe)] and Tl[PF$_6$] (2 equiv.) in MeCN; v, **1a** with [Mn(NCMe)$_3$(CO)$_3$][PF$_6$] in MeCN; vi, [PtCl$_2$(dppe)] and Tl[PF$_6$] (2 equiv.) in CH$_2$Cl$_2$; vii, [Mn(NCMe)$_3$(CO)$_3$][PF$_6$] in CH$_2$Cl$_2$.

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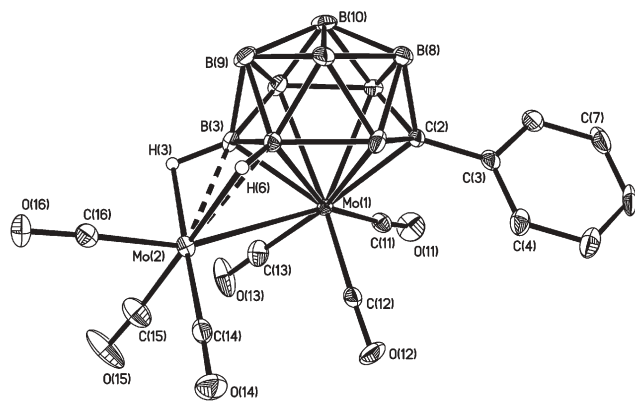
Fig. 1 Structure of one of two crystallographically independent trianions of **1a** (thermal ellipsoids at 40% probability). Selected distances (Å) are: Mo(1)–Mo(2) 3.1212(4), Mo(1)–C(2) 2.263(3), Mo(1)–B(3) 2.247(4), Mo(1)–B(4,5,6,7) range 2.497(4)–2.598(4), Mo(2)···B(3) 2.399(4), Mo(2)···B(6) 2.490(4). The other trianion is structurally very similar.

invoked in such systems. It is notable that the 2 : 1 metal : carborane stoichiometry in the products **1** is obtained regardless of the reactant ratio. Similar, but not well defined, dimetal products have been proposed as products from reaction of [7,8-R_2-$nido$-7,8-$C_2B_9H_9$]$^{2-}$ with excess [M(CO)$_6$] (M = Mo, W) in refluxing thf.[11a]

Like the above mentioned Re and Mn dianions,[6,12] the trianion of **1a** proved a useful synthon in reacting with cationic transition-element fragments to give heteropolymetallic complexes. With {Pt(dppe)}$^{2+}$, the monoanionic salt [NEt$_4$][1,3-{Pt(dppe)}-3-(μ-H)-1,1,1-(CO)$_3$-2-Ph-$closo$-1,2-MoCB$_9$H$_8$] **2**† is obtained, its structure also confirmed by X-ray diffraction (Fig. 2).‡ The exopolyhedral {Mo(CO)$_3$} moiety of the precursor has been lost and is replaced by a {Pt(dppe)} unit [Mo(1)–Pt(1) = 2.7114(2) Å], with the latter supported by an additional B–HPt agostic-type bond [Pt(1)–B(3) = 2.3114(19) Å] that utilizes the γ-BH in the molybdenum-coordinating C$BB$$B$$B$$B$ belt and a longer interaction with a β-BH [Pt(1)–B(6) = 2.4063(19) Å]. Compound **2** resembles the related neutral {L$_2$Pt–MC$_2$B$_n$} species (M = W, n = 9; M = Mo, n = 10)[11b,13] in which exopolyhedral {PtL$_2$} moieties are
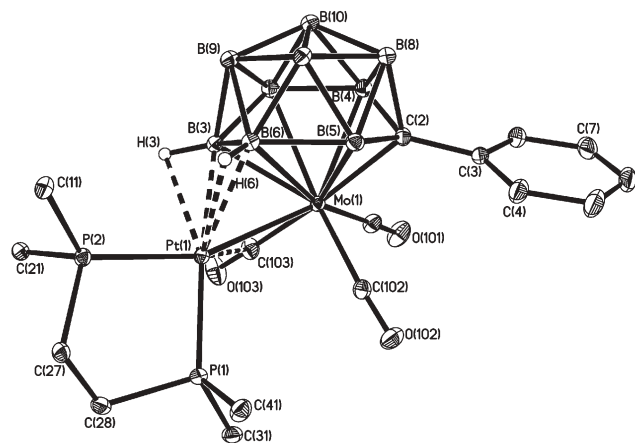
Fig. 2 Structure of the anion of **2**. Selected distances (Å) are: Mo(1)–Pt(1) 2.7114(2), Mo(1)–C(2) 2.2111(17), Mo(1)–B(3) 2.3172(19), Mo(1)–B(4,5,6,7) range 2.453(2)–2.6169(19), Pt(1)–B(3) 2.3114(19), Pt(1)···B(6) 2.4063(19), Pt(1)···C(103) 2.6201(18).

similarly attached to the cluster *via* a Pt–M bond and a single B$_\beta$–HPt agostic-type bridge.

Compound **2** shows spectroscopic properties consistent with the solid-state structure, with much higher CO stretching frequencies as expected upon reduction of the overall anionic charge by two units. Again the ^{11}B{^{1}H} NMR spectrum displays nine signals (with one coincidence), showing the molecule to be asymmetric, whilst the observation of only one CO resonance (^{13}C NMR) indicates free rotation of the {Mo(CO)$_3$} unit with respect to the ligating carborane surface. It cannot be said whether the Mo–Pt bond is retained in solution, as the CO signal does not reveal any corroborating ^{195}Pt satellites. Nevertheless, the two phosphorus centres are inequivalent (^{31}P NMR), strongly suggesting that the platinum fragment remains static in solution. Given the absence of any signal for a B–HPt unit in the ^{1}H NMR data, however, the exact nature of this species in solution is not clear.

In contrast with the above, treatment of **1a** with sources of {Mn(CO)$_3$}$^+$ afforded a bimetallic dianion, isolated as the salt [NEt$_4$]$_2$[1,3,6-{Mn(CO)$_3$}-3,6-(μ-H)$_2$-1,1,1-(CO)$_3$-2-Ph-$closo$-1,2-MoCB$_9$H$_7$] **3**.† The overall bimetal–carborane core of **3** was shown by a preliminary X-ray diffraction study‡ to be very similar to that of **1a**, with the {Mn(CO)$_3$}$^+$ cation replacing the neutral {Mo(CO)$_3$} unit so that the overall charge is reduced by one. Again the exopolyhedral group is anchored *via* a metal–metal bond [Mo–Mn = 2.951(3) and 2.949(4) Å (2 independents; approximate distances)] and two B–HMn agostic-type bridges. Similarly, NMR data for **3** reveal the asymmetry of the dianion in solution with nine ^{11}B{^{1}H} NMR resonances (three coincide), whilst in the ^{1}H NMR spectrum are seen two broad signals (δ −5.3 and −9.0) for the two B–HMn units.

Similar to that of **1a**, the anion of **3** also reacts with the {Pt(dppe)}$^{2+}$ dication, in this case giving the neutral, hetero-trimetallic species [1,3,6-{Mn(CO)$_3$}-1,7-{Pt(dppe)}-3,6,7-(μ-H)$_3$-1,1,1-(CO)$_3$-2-Ph-$closo$-MoCB$_9$H$_6$] **4**. Conversely, compound **4** can also be obtained from **2** with {Mn(CO)$_3$}$^+$ (see Scheme 1), as has been confirmed qualitatively (^{11}B NMR). The structure of **4** (Fig. 3)‡ consists of a V-shaped trimetal unit (Mn–Mo–Pt) supported by the carborane ligand. Both of the exopolyhedral metal centres are bonded to the central molybdenum [Mo–Pt = 2.7318(5) and 2.7323(5) Å; Mo–Mn = 3.0275(9) and 3.0588(9) Å; Mn–Mo–Pt = 82.06(2) and 82.55(2)° (2 independent molecules)]. Similar to the prototype species **2**, the Pt centre is close to two {BH} vertices with the ostensible primary B–HPt interaction now using a β-{BH}, and an additional close approach to the γ-{BH}. Likewise, the Mn centre parallels compound **3** and uses both β- and γ-{BH} units in forming two B–HMn interactions. The γ-{BH} vertex therefore appears to be involved in bonding to all three metal centres.

Spectroscopic data for **4** are in agreement with the solid-state structure. Similar to **2** and **3**, the exopolyhedral fragments in **4** appear not to be fluxional on the NMR time scale. Thus, six separate CO resonances are seen in the ^{13}C{^{1}H} NMR spectrum and there are three very broad, high field signals in the ^{1}H NMR spectrum (δ *ca.* −8.8, *ca.* −9.9, *ca.* −11.4) corresponding to the three agostic-type interactions that support the *exo*-metal centres. Arguably, the most shielded of these may be assigned to the γ-{BH} as this is the one associated with all three metals—although, surprisingly, there is no similarly affected resonance in the ^{11}B NMR data.
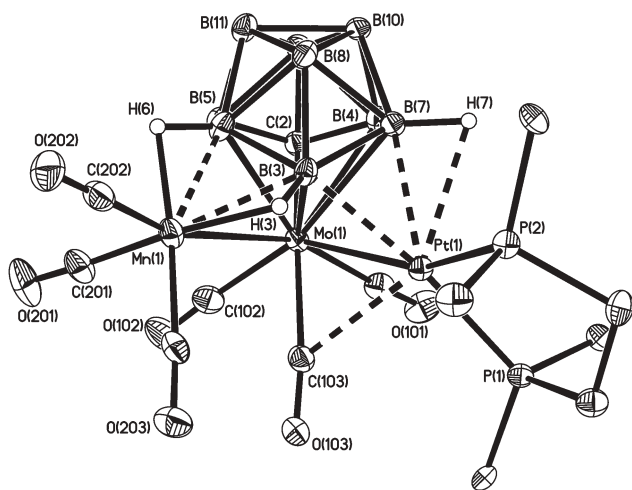
Fig. 3 Structure of one of two crystallographically independent molecules of **4**. Selected distances (Å) and angles (°) are: Mo(1)–Pt(1) 2.7318(5), Mo(1)–Mn(1) 3.0275(9), Mo(1)–C(2) 2.223(5), Mo(1)–B(3) 2.300(6), Mo(1)–B(4,5,6,7) range 2.404(6)–2.617(6), Mn(1)···B(3) 2.219(6), Mn(1)···B(6) 2.167(6), Pt(1)···B(3) 2.260(6), Pt(1)···B(7) 2.371(6), Pt(1)···C(103) 2.516(5); Mn(1)–Mo(1)–Pt(1) 82.06(2). The other molecule is structurally very similar.

The new complexes **1** extend our studies of eleven-vertex {*closo*-1,2-MCB$_9$} metallacarboranes beyond the Mn triad and provide both comparisons and contrasts with the behaviour found in previous studies upon the related MnCB$_9$, ReCB$_9$ and MoC$_2$B$_9$ clusters.[6,11,12] In addition, the neutral and formally zerovalent exopolyhedral {M(CO)$_3$} moieties in **1** are notable in that they are not anchored to the metallacarborane surface by formal anion–cation attraction, a feature that is without any well-defined precedent in metallacarborane chemistry. This moiety in **1a** is easily displaced by transition-metal cations, which we have exploited to assemble the heterotrimetallic species **4** in a stepwise manner. In all of this, the central molybdenacarborane core does not undergo any redox chemistry. However, the latter possibility does complicate the reactions of **1a** with other, more susceptible transition-metal fragments. Conversely, this reactivity of **1a** upon oxidation is an equally rich and fascinating area, and we continue to explore both of these themes in eleven-vertex molybdenacarborane chemistry.

Notes and references

† Satisfactory microanalyses were obtained for all compounds. For **1a**: Orange crystals; yield 61%. IR (MeCN): ν_{max}(CO) 1916 s, 1878 vs, 1791 vs, 1746 s cm^{-1}. ^{1}H NMR (360.1 MHz, 298 K, CD$_3$CN) δ *ca.* −1.1 (vbr q, *J*(BH) = *ca.* 120 Hz, B–HMo), *ca.* −5.4 (br q, *J*(BH) = *ca.* 115 Hz, B–HMo); ^{13}C{^{1}H} NMR (90.6 MHz, 298 K, CD$_3$CN) δ 236.0, 229.3 (CO), 67.6 (br, cage C); ^{11}B{^{1}H} NMR (115.5 MHz, 298 K, CD$_3$CN, unit integral except where indicated) δ 28.1, 10.3, −0.6, −6.6, −8.7, −15.2, −22.2 (2B), −24.7. For **1b**: Red-orange crystals; yield 60% IR (MeCN): ν_{max}(CO) 1918 s, 1870 vs, 1791 s, 1732 s cm^{-1}. ^{1}H NMR (CD$_3$CN) δ *ca.* −1.7 (vbr q, *J*(BH) = *ca.* 110 Hz, 1H, B–HW), *ca.* −6.1 (vbr q, *J*(BH) = *ca.* 100 Hz, 1H, B–HW); ^{13}C{^{1}H} NMR (CD$_3$CN) δ 229.8, 220.0 (br, CO),

65.2 (br, cage C); ^{11}B{^{1}H} NMR (CD$_3$CN) δ 23.7, 9.2, −0.8, −12.2, −14.0, −18.1, −25.6 (2B), −29.0. For **2**: Dark red crystals; yield 54%. IR (CH$_2$Cl$_2$): ν_{max}(CO) 1968 s, 1907 m, 1882 s cm^{-1}. B–HPt not observed in ^{1}H NMR. ^{13}C{^{1}H} NMR (CD$_3$CN) δ 224.0 (CO), 110.5 (br, cage C); ^{11}B{^{1}H} NMR (CD$_3$CN) δ 17.9, 12.9, 9.8, 3.7, *ca.* −9.8 (sh), −11.2, −13.4 (2B), −18.3; ^{31}P{^{1}H} NMR (145.8 MHz; 298 K, CD$_3$CN) δ 59.0 [*J*(PtP) = 3190 Hz, *J*(PP) = 32 Hz], 55.2 [*J*(PtP) = 4405 Hz]. For **3**: Black-green microcrystals; yield 67%. IR (CH$_2$Cl$_2$): ν_{max}(CO) 1993 s, 1938 s, 1899 s, 1830 w cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$) δ *ca.* −5.3, *ca.* −9.0 (br m × 2, B–HMn × 2); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 224.0 (vbr, CO), 214.7 (vbr, CO), 68.2 (br, cage C); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$) δ 26.0, 11.0, 2.4, −11.6 (3B), −24.0, −25.0, −27.5. For **4**: Dark red microcrystals; yield 68%. IR (CH$_2$Cl$_2$): ν_{max}(CO) 2526 br w, 2044 vs, 2017 vs, 1996 br m, 1948 br s cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$) δ *ca.* −8.8, *ca.* −9.9, *ca.* −11.4 (vbr m × 3, B–HMn × 2 and B–HPt). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 227.0, 222.9, 222.4, 219.7, 214.3, 208.0 (br, CO), 117.8 (br, cage C); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$) δ 19.1, 18.0 (2B), 9.0, −3.4, −8.8 (2B), −16.0 (2B); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 59.6 [br, *J*(PtP) = 4120 Hz], 58.2 [br, *J*(PtP) = 4660 Hz].

‡ *Crystal data*. For all determinations: Bruker-Nonius X8 Apex CCD diffractometer, Mo-Kα radiation, *T* = 110(2) K. Crystals of **3** were badly twinned and hence only a preliminary determination was possible. Data for **1**: C$_{37}$H$_{74}$B$_9$Mo$_2$N$_3$O$_6$, M_r = 946.16, orthorhombic, *Pca*2$_1$, *a* = 26.518(2), *b* = 17.1036(11), *c* = 20.3798(17) Å, *V* = 9243.4(12) Å^3, *Z* = 8 (2 independents), μ = 0.587 mm^{-1}, *F*(000) = 3952. 206587 reflections collected (θ_{max} = 33.76°), 32248 unique (R_{int} = 0.0838), R_1 = 0.0899, wR_2 = 0.1043 for refinement on all F^2 data. Flack parameter 0.049(19). For **2**·$\frac{1}{2}$CH$_2$Cl$_2$: C$_{44.5}$H$_{59}$B$_9$ClMoNO$_3$P$_2$Pt, M_r = 1141.64, monoclinic, *P*2$_1$/*n*, *a* = 14.4426(9), *b* = 22.8219(14), *c* = 15.1963(10) Å, β = 101.002(3)°, *V* = 4916.8(5) Å^3, *Z* = 4, μ = 3.256 mm^{-1}, *F*(000) = 2276. 88217 reflections collected (θ_{max} = 35.74°), 21411 unique (R_{int} = 0.0382), R_1 = 0.0394, wR_2 = 0.0607 for refinement on all F^2 data. For **4**·1$\frac{1}{8}$CH$_2$Cl$_2$: C$_{40.125}$H$_{40.25}$B$_9$Cl$_{2.25}$MnMoO$_6$P$_2$Pt, M_r = 1203.44, monoclinic, *C*2/*c*, *a* = 56.424(3), *b* = 11.4786(5), *c* = 38.7221(17) Å, β = 129.6520(10)°, *V* = 19309.1(15) Å^3, *Z* = 16 (2 independents), μ = 3.638 mm^{-1}, *F*(000) = 9396. 102923 reflections collected (θ_{max} = 29.35°), 23919 unique (R_{int} = 0.0630), R_1 = 0.0765, wR_2 = 0.1082 for refinement on all F^2 data. CCDC 270993–270995 for **1a**, **2** and **4**, respectively. See http://www.rsc.org/suppdata/cc/b5/b505841d/ for crystallographic data in CIF or other electronic format.

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