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Oxidation of 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$_7$]$^{3-}$: Metal and Boron Vertex Substitution and Cluster Expansion[§]

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Protonation of the 11-vertex bis-molybdenum−monocarbollide salt [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$_7$] (**1**) with H[BF$_4$]·OEt$_2$ in the presence of CO and [NEt$_4$]I results in molybdenum oxidation and cage expansion to yield 12-vertex [NEt$_4$][2,2,2-(CO)$_3$-8-OH-2-I-1-Ph-*closo*-2,1,8-MoC$_2$B$_9$H$_9$] (**5**). In contrast, oxidation of **1** with Ag[BF$_4$] in the presence of CNBu^t similarly results in metal oxidation but also in cage substitution to give 11-vertex [1,1,1,1,3-(CNBu^t)$_5$-2-Ph-*closo*-1,2-MoCB$_9$H$_8$] (**6**). The latter is oxidized in air to afford an icosahedral, cage expansion species [8-NHBu^t-2,2-(CNBu^t)$_2$-2-(=O)-1-Ph-*closo*-2,1,8-MoC$_2$B$_9$H$_9$] (**7**). Oxidation of **1** with PhSSPh results in retention of both molybdenum atoms to give the bis-thiolato-bridged complex [1-{Mo(μ-SPh)$_2$(CO)$_4$}-2-Ph-*closo*-1,2-MoCB$_9$H$_9$]$^-$, isolated as its [N(PPh$_3$)$_2$]$^+$ salt (**8**).

Introduction

We have recently reported the synthesis of the novel title trianion, isolated as the salt [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$_7$] (**1**) (see Chart 1), and shown that its high negative charge allows it to react readily with cationic transition metal−ligand fragments.[1] In these reactions the central molybdenum−monocarbollide core acts as a scaffold upon which heteropolymetallic species are formed, with the cluster molybdenum vertex remaining formally zerovalent and the exo-polyhedral {Mo(CO)$_3$} unit being lost.[1] The {1,1,1-(CO)$_3$-2-Ph-*closo*-1,2-MoCB$_9$H$_9$}$^{3-}$ core in **1** is related to the long-known[2,3] molybdenum−dicarbollide species [1,2-R$_2$-3,3,3-(CO)$_3$-*closo*-3,1,2-MoC$_2$B$_9$H$_9$]$^{2-}$ (**2**; R = H, Me, etc.), which—along with their 13-vertex analogues[3,4]—similarly have a rich heterometallic chemistry.[3−6] It has already been noted[1] that some transition element fragments cause oxidation of **1** rather than giving bi- or trimetallic Mo(0)-containing species, and compounds **2** also readily undergo oxidation reactions to Mo^{II} species and beyond.[5,7−12] We herein report upon the behavior of **1** upon oxidation with a variety of reagents, with these results detailing examples of cluster substitution at both metal and boron vertexes and also cluster expansion to yield molybdenum−*di*carbollide complexes.

Results and Discussion

It has long been known that the formally zerovalent molybdenum center in the cyclopentadienyl-molybdenum tricarbonyl anion [Mo(CO)$_3$(η-C$_5$H$_5$)]$^-$, which has similarities to the {1,1,1-(CO)$_3$-2-Ph-*closo*-1,2-MoCB$_9$H$_9$}$^{3-}$ core of **1**, undergoes protonation to yield an Mo^{II}−hydride species.[13] Similarly, it has been proposed[14] that protonation of the monocarbollide trianion [2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{11}$]$^{3-}$ (**3**), itself also comparable to the core of **1**, successively gives Mo^{II}−hydride and Mo^{IV}−dihydride species, [2,2,2-(CO)$_3$-2-H-*closo*-2,1-MoCB$_{10}$H$_{11}$]$^{2-}$ and [2,2,2-(CO)$_3$-2,2-(H)$_2$-*closo*-2,1-MoCB$_{10}$H$_{11}$]$^-$, respectively. The latter reaction was performed in the presence of CO, so that subsequent H$_2$ elimination from the dihydride complex gave the molybdenum(II) tetracarbonyl species [2,2,2,2-(CO)$_4$-*closo*-2,1-MoCB$_{10}$H$_{11}$]$^-$ (**4**),[14] which, like **2**, forms the basis for an extensive area of chemistry.[14−19] Recognizing the potential of **1** to form an 11-vertex analogue of **4** under similar conditions, thus allowing a more expansive study of 11-vertex molybdenum−monocarbollide chemistry, a CO-saturated MeCN solution of

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[§] This paper is dedicated to my friend and one-time collaborator Dr. José Antonio Abad, Universidad de Murcia, on the occasion of his retirement.

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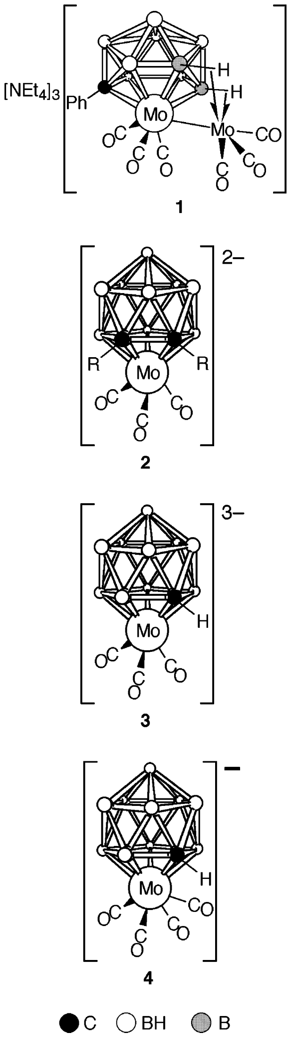
10.1021/om0600543 CCC: \$33.50

Chart 1



compound **1** was treated with $H[BF_4]\cdot OEt_2$. However, the compound so obtained in rather low yield was initially identified by an X-ray diffraction study as $[NEt_4][2,2,2\text{-}(CO)_3\text{-}8\text{-}OH\text{-}2\text{-}I\text{-}1\text{-}Ph\text{-}\mathit{closo}\text{-}2,1,8\text{-}MoC_2B_9H_9]$ (**5**). The source of the molybdenum-bound iodide was recognized as being derived from residual $[NEt_4]I$ that contaminated the precursor **1**. Upon addition of $[NEt_4]I$ (1 equiv) to the reaction mixture, yields of **5** were considerably improved. Interestingly, in the absence of CO no product could be isolated.

The structure determined for the anion of **5** is shown in Figure 1. This is seen to consist of a 12-vertex molybdenum(II)−dicarbollide cluster in which the molybdenum bears three CO ligands and one iodide (Mo(1)−I(1) is 2.9126(2) Å), the second metal in the starting trianion having been lost. One of the cage-carbon atoms bears the original Ph group, while the second unusually carries a terminal hydroxyl function (C(8)−O(8) = 1.386(3) Å). This {COH} unit almost certainly results from protonation of a metal-bound CO molecule, followed by cage insertion of a COH fragment, a process that has parallels with the formation of molybdenum−monocarbollide species from the reaction of molybdenum carbonyls with polyhedral boranes discovered many years ago by Muetterties and co-workers.[20]

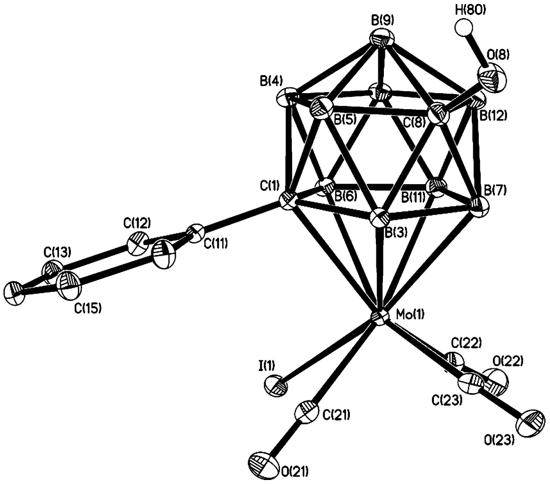


Figure 1. Structure of one of the crystallographically independent anions of **5** showing the crystallographic labeling scheme. In this and subsequent figures, thermal ellipsoids are drawn with 40% probability, and for clarity only chemically significant hydrogen atoms are shown. Selected distances (Å) and angles (deg): Mo(1)−I(1) 2.9126(2), Mo(1)−C(21) 2.040(2), Mo(1)−C(22) 1.998(2), Mo(1)−C(23) 1.964(2), Mo(1)−C(1) 2.3880(19), Mo(1)−B(3) 2.311(2), Mo(1)−B(6) 2.402(2), Mo(1)−B(7) 2.359(2), Mo(1)−B(11) 2.433(2), C(8)−O(8) 1.386(3); C(21)−Mo(1)−I(1) 74.21(6), C(22)−Mo(1)−I(1) 73.32(7), C(23)−Mo(1)−I(1) 125.10(6).

Spectroscopic data for compound **5** are listed in Tables 1 and 2. Resonances are seen in typical positions and appropriate ratios for the Et and Ph moieties in both ^1H and $^{13}C\{^1H\}$ NMR spectra, while the carbonyl ligands give rise to peaks at δ 228.2 (2 × CO) and 225.3 in the latter spectrum. Two separate signals are also seen in this spectrum for the two types of cage-carbon atoms: the {*C*−Ph} vertex resonates at δ 41.3, whereas the {*C*−OH} vertex is significantly deshielded by the oxygen atom and by its distance from the metal center and resonates at δ 95.2. In the $^{11}B\{^1H\}$ NMR spectrum, the absence of cluster symmetry is revealed in the presence of nine separate resonances (three are coincident) in the range −1.1 to −12.9, typical for a 12-vertex *closo*-dicarbametallaborane.[21]

Although complex **1** underwent an oxidation reaction upon treatment with protons, a number of other oxidizing species (including cationic transition metal fragments[1]) failed to yield isolatable metallacarborane products. However, with Ag^+ in the presence of excess $CNBu^t$, a species was obtained that exhibits features resulting from two types of oxidation process. Thus, reaction in MeCN of **1** with $Ag[BF_4]$ and $CNBu^t$ (1:4:10 molar ratio) afforded 11-vertex $[1,1,1,1,3\text{-}(CNBu^t)_5\text{-}2\text{-}Ph\text{-}\mathit{closo}\text{-}1,2\text{-}MoCB_9H_8]$ (**6**). The spectroscopic data for **6** showed several C≡N stretching bands in the IR spectrum, along with corresponding bands in the NMR spectra. Thus, in the ^1H NMR spectrum, two signals attributable to Bu^t groups are seen at δ 1.41 and 1.18 in the ratio 4:1, of which integration relative to peaks for the cage-bound phenyl protons indicated the presence of a total of five $CNBu^t$ ligands in **6**. Similarly, two sets of resonances for the isocyanide moieties were seen in the $^{13}C\{^1H\}$ NMR spectrum, with the C≡N nuclei resonating at δ 147.2 and 142.7; the lower intensity and greater broadness of the former peak were consistent with it belonging to a boron-bound CN group. Correspondingly with this, the $^{11}B\{^1H\}$ NMR spectrum suggested a symmetric structure with four resonances

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Table 1. Analytical and Physical Data

compd	color	yield/%	ν_{max}[a]/cm^{-1}	anal. %[b]		
				C	H	N
[NEt_4][2,2,2-$(CO)_3$-2-I-1-Ph-8-OH-*closo*-2,1,8-$MoC_2B_9H_9$] (**5**)	red	54	2097 w, 2035 vs, 1951 vs	34.7 (34.5)	5.4 (5.3)	2.3 (2.1)
[1,1,1,1,3-$(CNBu^t)_5$-2-Ph-*closo*-1,2-$MoCB_9H_8$] (**6**)	yellow	48	2180* m sh, 2140* s, 2091* s, 2053* s	48.1 (48.3)[c]	7.6 (7.4)	8.2 (8.4)
[8-$NHBu^t$-2,2-$(CNBu^t)_2$-2-(═O)-1-Ph-*closo*-2,1,8-$MoC_2B_9H_9$] (**7**)	violet	95	2173* m, 2146 m*	47.2 (47.4)	7.7 (7.4)	7.6 (7.5)
[$N(PPh_2)_2$][1-{Mo(μ-SPh)$_2$(CO)$_4$}-2-Ph-*closo*-1,2-$MoCB_9H_9$] (**8**)	dark red	48	2050 vs, 1972 s, 1951 vs	53.8 (53.7)[d]	4.2 (4.2)	1.2 (1.0)

[a] Measured in CH_2Cl_2, CO or *CN stretching frequencies; medium-intensity bands observed at ca. 2500−2550 cm^{-1} in the spectra of all compounds are due to B−H adsorptions. [b] Calculated values are given in parentheses. [c] Cocrystallizes with 1.5 molar equiv of CH_2Cl_2. [d] Cocrystallizes with 1 molar equiv of CH_2Cl_2.

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

compd	^{1}H (δ)[b]	^{13}C (δ)[c]	^{11}B (δ)[d]
5	7.22 (m, 2H, cage-*Ph*), 7.12 (m, 2H, cage-*Ph*), 7.03 (m, 1H, cage-*Ph*), 3.26 (q, ^3J(HH) = 6, 8H, NCH_2), 1.39 (t, 12H, NCH_2CH_3), 1.22 (br, CO*H*)	228.2 (2 × CO), 225.3 (CO), 145.0, 127.4, 125.2, 124.7 (Ph), 95.2 (br, cage *C*OH), 41.3 (br, cage *C*Ph), 25.6 (NCH_2), 7.5 (NCH_2CH_3)	−1.1, −3.4, −6.4, −8.1, −9.3, −10.0, −12.9 (3B)
6	7.12 (m, 2H, cage-*Ph*), 7.02 (m, 2H, cage-*Ph*), 6.93 (m, 1H, cage-*Ph*), 1.41 (s, 36H, Bu^t), 1.18 (s, 9H, cage-CN*Bu*^{t})	147.2 (br, cage−*C*≡N), 143.2 (Ph), 142.7 (br, Mo−*C*≡N), 127.4, 125.6, 125.0 (Ph), 56.8 (vbr, cage C), 54.3 (cage−CN*C*Me_3), 53.9 (Mo−CN*C*Me_3), 30.3 (Mo−CNC*Me*$_3$), 29.9 (cage−CNC*Me*$_3$)	1.0 (B(3)), −5.6 (2B), −8.2 (2B), −14.9 (4B)
7	7.05−6.85 (m, 5H, Ph), 2.35 (br, 1H, N*H*Bu^t), 1.60, 1.47, 1.28 (s × 3, 9H × 3, Bu^t × 3)	160.5 (br, Mo−*C*≡N), 159.4 (br, Mo−*C*≡N), 143.2, 127.4, 125.6, 125.0 (Ph), 74.7 (br, cage C), 66.3 (vbr, cage C), 54.3 (N(H)*C*Me_3), 53.9 (Mo−CN*C*Me_3 × 2), 30.0 (N(H)C*Me*$_3$), 29.9 (Mo−CNC*Me*$_3$ × 2)	1.2, 3.5 (2B), −5.6 (2B), −8.9, −12.9 (2B), −14.7
8	7.71 (m, 2H, cage-*Ph*), 7.58−7.12 (m, 40H, PPh and SPh), 7.01 (m, 2H, cage-*Ph*), 6.84 (m, 1H, cage-*Ph*)	219.7, 203.2, 201.1, 196.0 (CO), 167.6 (br, S−Ph), 150.0 (cage-Ph), 137.8−126.0 (Ph), 64.5 (br, cage C)	99.1, 11.8, 9.3 (3B), 0.5, −10.3 (3B)

[a] Chemical shifts (δ) in ppm, coupling constants (*J*) in hertz; measurements at ambient temperature 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); resonances are of unit integral except where indicated. Where a peak is ascribed to more than one boron atom, this may arise from coincidence and does not necessarily indicate symmetry equivalence.

in the ratio 1:2:2:4, of which one at δ 1.0 remained a singlet upon retention of proton coupling and is assigned as the *B*−$CNBu^t$ vertex. An X-ray diffraction study confirmed the above observations, with the structure determined for **6** being that shown in Figure 2. The molecule possesses both molecular and crystallographic mirror symmetry, with a Mo(II) center that bears four isocyanide ligands and a substituted carborane ligand. One BH vertex in the open face of the carborane, namely that which is γ with respect to the carbon atom in the molybdenum-bound $\overline{\mathrm{CBB}\mathit{B}\mathrm{BB}}$ belt, has undergone substitution and bears a fifth isocyanide unit (B(3)−C(31) = 1.525(5) Å). The latter renders the carborane zwitterionic, with replacement of H$^-$ by neutral $CNBu^t$ reducing by one the charge upon the {CB_9} ligand. Formally, this substitution may be viewed as an Ag$^+$-promoted oxidation of a boron-bound hydride (eq 1),[19]

$$\{B{-}H\}^- + Ag^+ + L \rightarrow \{B{-}L\} + {}^1/_2H_2 + Ag \qquad (1)$$

and hence the observation that the silver cations cause oxidation both at the molybdenum and at a cage vertex. It is also worthy of note that the boron hydride that is replaced is the one that is most distant from the cage carbon in the metal-bound CB_5 belt; it would be expected that this is the most hydridic and therefore the most susceptible to such substitution.

Compound **6** is unstable, and its yellow solutions are readily oxidized in air, to give almost quantitatively a deep violet compound, [8-$NHBu^t$-2,2-$(CNBu^t)_2$-2-(═O)-1-Ph-*closo*-2,1,8-$MoC_2B_9H_9$] (**7**). Initial identification of **7** was made by an X-ray diffraction study, which showed the structure to be that in Figure 3. The molecule is seen to be another cage expansion product, akin to compound **5**, but in the present case its composition is considerably more novel. The basic cluster structure in **7** is similar to that in **5**, with the molybdenum occupying a vertex in a closed {2,1,8-MoC_2B_9} framework. A second carbon vertex, bearing an $NHBu^t$ substituent, has been introduced in the cage in this case via an apparent insertion of one $CNBu^t$ molecule. The insertion of cyano moieties into boranes,[22−24] carboranes,[22,23,25] and even metallaboranes[26] is a well-established means of introducing a carbon vertex into a polyboron framework. It is perhaps significant that the site of insertion of the new {CX} vertex in **5** and in **7** (X = OH and $NHBu^t$, respectively) with respect to the Mo and {CPh} vertexes is identical. We note that in relative terms this site is also the one favored for insertion of a {Pt(dppe)} unit into an {$MnCB_9$} cluster that is isolobal with the {$MoCB_9$} core of **1**.[27]

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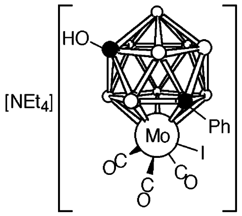
Chart 2



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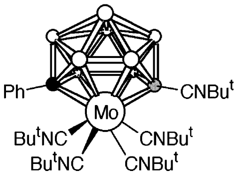

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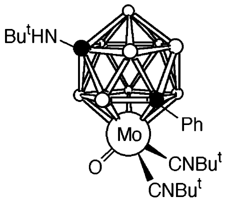

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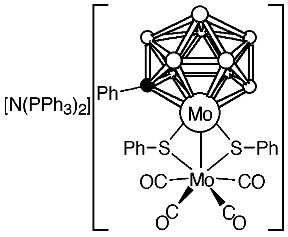

8

● C ○ BH ◍ B

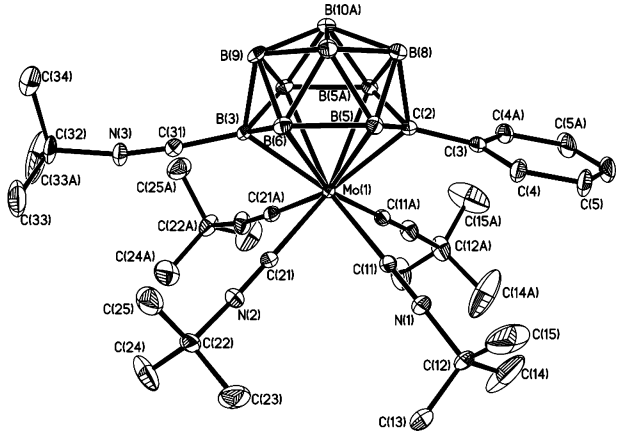

Figure 2. Structure of one whole molecule of **6** showing the crystallographic labeling scheme. Selected distances (Å) and angles (deg): Mo(1)−C(11) 2.111(2), Mo(1)−C(21) 2.081(3), Mo(1)−C(2) 2.203(3), Mo(1)−B(3) 2.220(4), Mo(1)−B(5) 2.492(3), Mo(1)−B(6) 2.533(2), B(3)−C(31) 1.525(5); C(21)−Mo(1)−C(21A) 77.74(14), C(21)−Mo(1)−C(11A) 118.62(10), C(21)−Mo(1)−C(11) 72.59(11), C(11)−Mo(1)−C(11A) 76.64(12), C(31)−B(3)−Mo(1) 131.1(3) (symmetry operation to generate equivalent atoms: A, $-x+1$, y, z).

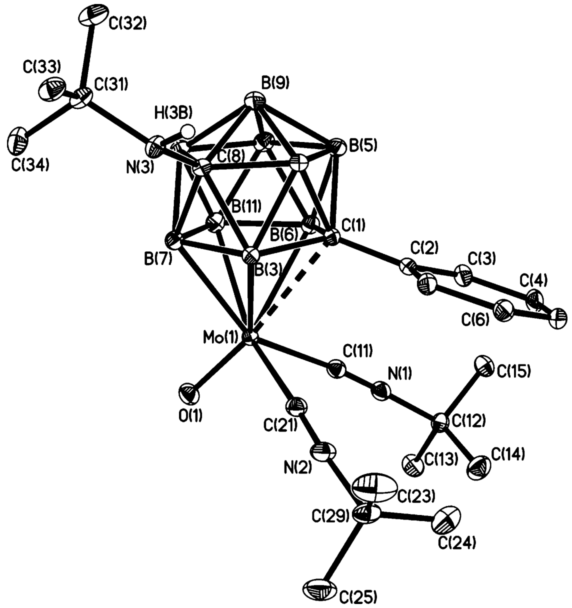

Figure 3. Structure of compound **7** showing the crystallographic labeling scheme. Selected distances (Å) and angles (deg): Mo(1)−O(1) 1.6999(12), Mo(1)−C(11) 2.0934(16), Mo(1)−C(21) 2.0918(16), Mo(1)···C(1) 2.5752(15), Mo(1)−B(3) 2.3949(18), Mo(1)−B(6) 2.4559(17), Mo(1)−B(7) 2.3685(18), Mo(1)−B(11) 2.3849(17), C(8)−N(3) 1.440(2); O(1)−Mo(1)−C(21) 99.30(6), O(1)−Mo(1)−C(11) 97.97(6), C(21)−Mo(1)−C(11) 84.58(6).

In addition to the dicarbollide ligand, the molybdenum center in **7** also bears two unadulterated CNBu^t ligands (Mo(1)−C(11) = 2.0934(16), Mo(1)−C(21) = 2.0918(16) Å) and one oxide group (Mo(1)−O(1) is 1.6999(12) Å). The molybdenum··· oxygen distance is typical of a Mo═O double bond,[28] and this assisted in identifying this atom crystallographically. This assignment is also reasonable on the basis of the reaction conditions that favor formation of **7**. Thus, although traces of **7** are observed when solutions of **6** are stored under N$_2$ at −30 °C for several weeks, the same solutions quite readily turn violet upon exposure to the atmosphere. Some conversion of **6** to **7** is also seen during column chromatographic purification on silica, even under N$_2$. Although the source of the oxide group is very likely to be atmospheric oxygen and/or moisture, the precise details of the formation of **7** are not clear, nor—as with **5**—is the process that leads to carbon vertex insertion well defined. An additional unusual feature of the structure of **7** is the Mo(1)···C(1) distance, which, at 2.5752(15) Å, is very long—especially long when compared with the corresponding distance of 2.3880(19) Å in compound **5**, itself perhaps slightly long. The reason for this elongation is not clear: there are no other anomalously long (or short) distances within the {MoC$_2$B$_9$} polyhedron of **7**. One explanation may be that in the solid-state structure the bulky phenyl and *tert*-butyl groups are on the same side of the molecule, and conceivably the Mo(1)···C(1) lengthening is a consequence of this. Clearly there is some strong electronic preference for the {Mo(═O)(CNBu^t)$_2$} fragment to adopt this conformation with respect to the ligating face of the carborane ligand, but a detailed theoretical treatment would be necessary to probe this further.

Cluster electron counting in compound **7** is also problematic. If the oxide moiety is formally considered to be dianionic, with

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the dicarbollide ligand also a dianion, then the molybdenum must be considered in the +4 oxidation state. However, this leaves the metal as having an only 16-electron configuration ($d^2 + 6\pi$ electrons from the dicarbollide ligand + 4 from the two isocyanides + 4 from the oxide), so that the $\{MoC_2B_9\}$ core is two electrons short of a normal *closo* cluster electron count.[29] Typically, such species would be termed *hypercloso*[30] and would not have the pseudo-icosahedral cluster geometry observed here.[31] We note, however, that the 12-vertex {Pt-MnCB$_9$} species mentioned above that are obtained from {Pt(dppe)} insertion into an $\{MnCB_9\}$ cluster are similarly electron deficient but also retain a conventional *closo*-type architecture.[27]

Spectroscopic data for compound **7** (Tables 1 and 2) are rather more straightforward. The two isocyanide units give rise to two C≡N stretching bands in its IR spectrum, at ν_{max} 2173 and 2146 cm^{-1}, some 30 cm^{-1} higher than those in well-defined Mo^{II}–dicarbollide species such as [1,2-R_2-3,3,3,3-(CNBu^t)$_4$-*closo*-3,1,2-$MoC_2B_9H_9$] (R = H, Me).[32] In the ^{1}H NMR spectrum, all three of the Bu^t groups are chemically inequivalent and give rise to three peaks, at δ 1.60, 1.47, and 1.28. In the $^{13}C\{^1H\}$ NMR spectrum, however, the Bu^t units of the molybdenum-bound isocyanides appear equivalent (although these are merely coincidences), while the carbons of their C≡N units appear as broad resonances at δ 160.5 and 159.4. Surprisingly, the ^{11}B-$\{^1H\}$ NMR spectrum revealed six peaks in the range δ 1.2 to −14.7, a range that is more typical of a *closo* structure than a *hypercloso* one and indeed is similar to the chemical shift range (−1.1 to −12.9) observed for compound **5**. Moreover, the peaks for **7** are in the ratio 1:2:2:1:2:1, a pattern that is suggestive of molecular mirror symmetry, but this is clearly due to coincidence.

Some years ago it was shown that the Mo^0 dianion **2** (R = H) upon reaction with PhSSPh underwent successive oxidation processes that led to a family of unusual dinuclear species containing Mo^{II}, Mo^{III}, and Mo^{IV} centers.[8,9,11] It was clearly of interest to examine for similar behavior in the case of compound **1**, and accordingly the metallacarborane was treated in MeCN with a 5-fold excess of PhSSPh. Upon addition of [N(PPh$_3$)$_2$]-Cl and chromatographic workup, a dark red dimolybdenum species was isolated in good yields. Although initial spectroscopic analysis indicated the presence of Mo, CO, SPh, and carborane moieties, an X-ray diffraction experiment was necessary in order to definitively identify the product. The compound is [N(PPh$_3$)$_2$][1-{Mo(μ-SPh)$_2$(CO)$_4$}-2-Ph-*closo*-1,2-$MoCB_9H_9$] (**8**), of which the structure of the anion is shown in Figure 4.

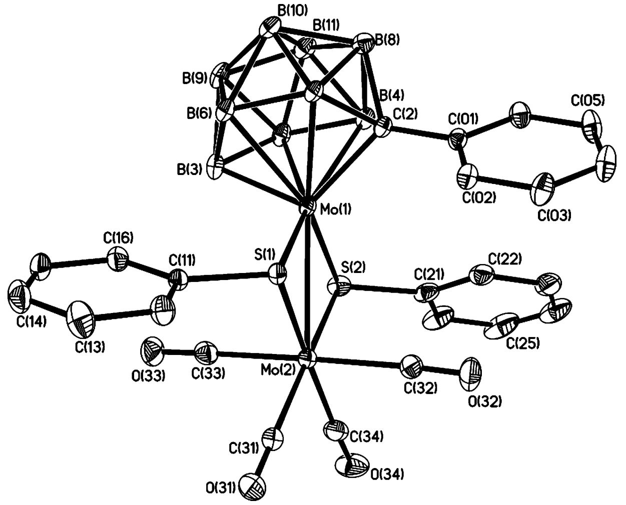

Figure 4. Structure of the anion of compound **8** showing the crystallographic labeling scheme. Selected distances (Å) and angles (deg): Mo(1)−Mo(2) 2.8424(6), Mo(1)−C(2) 2.0537(18), Mo(1)−B(3) 2.084(2), Mo(1)−B(4) 2.392(2), Mo(1)−B(5) 2.410(2), Mo(1)−B(6) 2.396(2), Mo(1)−B(7) 2.398(2), Mo(1)−S(1) 2.4349(6), Mo(1)−S(2) 2.4338(7), Mo(2)−S(1) 2.4839(7), Mo(2)−S(2) 2.4772(7), Mo(2)−C(31) 2.047(2), Mo(2)−C(32) 2.038(2), Mo(2)−C(33) 2.063(2), Mo(2)−C(34) 2.059(2); S(1)−Mo(1)−Mo(2) 55.511(17), S(2)−Mo(1)−Mo(2) 55.352(15), S(2)−Mo(1)−S(1) 110.81(2), S(1)−Mo(2)−Mo(1) 53.896(14), S(2)−Mo(2)−Mo(1) 53.924(18), S(2)−Mo(2)−S(1) 107.770(19), Mo(1)−S(1)−Mo(2) 70.594(16), Mo(1)−S(2)−Mo(2) 70.724(17).

Anions of **8** retain the closed 11-vertex {2-Ph-1,2-$MoCB_9H_9$} core of the precursor **1**, but, unlike the products of the other reactions of **1**, the cluster molybdenum vertex (Mo(1)) no longer bears carbonyl ligands and in addition a second molybdenum center (Mo(2)) remains within the complex. This latter metal atom bears four terminal CO ligands and is bonded to the cluster Mo vertex via two bridging {μ-SPh} units and an Mo−Mo connectivity (Mo(1)−Mo(2) = 2.8424(6) Å), which is rather longer than that (2.8153(12) Å) in the related Mo^{II}−Mo^{II} species [(3,3′-μ-SPh)$_4$-(*closo*-3,1,2-$MoC_2B_9H_{11}$)$_2$].[11] The thiolate bridges are somewhat asymmetric, each of the sulfur atoms being closer to the cluster molybdenum atom (Mo(1)−S(1) = 2.4349(6), Mo(1)−S(2) = 2.4338(7) Å) than to the exo-polyhedral one (Mo(2)−S(1) = 2.4839(7), Mo(2)−S(2) = 2.4772(7) Å).

Spectroscopic data for compound **8** are listed in Tables 1 and 2. In its NMR spectra, as noted, ^{1}H and ^{13}C resonances are evident for the anion, cluster, and thiolate Ph groups, along with a broad peak at δ 64.5 in the $^{13}C\{^1H\}$ NMR spectrum for the cage carbon atom and four separate signals (δ 219.7, 203.2, 201.1, and 196.0) for the four carbonyl ligands. The inequivalence of the CO groups indicates some rigidity in the Mo···Mo interconnection, so that the entire {Mo(μ-SPh)$_2$Mo(CO)$_4$} unit is envisaged as being static with respect to the carborane face. Significantly, the $^{11}B\{^1H\}$ NMR data for **8** show five resonances in the range δ +99.1 to −10.3 in the ratio 1:1:3:1:3, also consistent with an asymmetric structure.

Conclusion

Earlier studies with the *closo*-icosahedral molybdacarboranes **2** and **4**, and related species, have demonstrated their diverse reactivity with both metal−ligand fragments and with oxidizing agents. In our preliminary communication on the trianion **1** we have reported on its reactions with transition metal cations,[1] and we have now shown here that it also undergoes a broad range of reactions upon treatment with different oxidizing systems. Among the products are relatively simple, substituted species such as **6** and the more complex substitution product **8**, along with the rather more unexpected derivatives **5** and **7**, which are the results of cluster carbon atom insertion. Some of these species are without close precedent in metallacarbollide chemistry. Given the rich chemistry already demonstrated for **2** and **4**, and a similar wealth of results for rhena- and manganacarborane dianions [1,1,1-(CO)$_3$-2-Ph-*closo*-1,2-MCB_9H_9]$^{2-}$,[15] species that are analogous to the core of **1**, it will be of interest

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to expand still further upon the chemistry of **1**. Likewise, contemporary advances in the chemistry of the smaller monocarboranes[33] are opening the door for studies of smaller molybdenum−monocarborane species, for which there has already been one report[34] and which is an avenue with great potential that we are currently exploring. Our studies of these and related systems, as well as our attempts to identify other trace products in these reactions, such as the product of the decomposition of **7**, are continuing.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk-line techniques. Solvents were stored over and freshly distilled from appropriate drying agents 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). Filtration through Celite typically employed a plug ca. 5 cm in length and 2 cm in diameter. NMR spectra were recorded at the following frequencies (MHz): ^{1}H, 360.1; ^{13}C, 90.6; and ^{11}B, 115.5. The reagents [NEt$_4$][6-Ph-*nido*-6-CB$_9$H$_{11}$][33c,35] and [Mo(NCMe)$_3$(CO)$_3$][36] were prepared according to the literature; all other materials were used as received.

Synthesis of [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$_7$]. A THF (20 mL) solution of [NEt$_4$][6-Ph-*nido*-6-CB$_9$H$_{11}$] (0.41 g, 1.25 mmol) was cooled to −78 °C, and Bu^{n}Li (1.0 mL, 2.50 M solution in hexanes, 2.50 mmol) was added. After the mixture was allowed to warm to ca. −20 °C, a THF (120 mL) solution of [Mo(NCMe)$_3$(CO)$_3$] (0.79 g, 2.61 mmol) was introduced via a cannula. The solution was stirred for 6 h, [NEt$_4$]I (0.65 g, 2.53 mmol) was added, and stirring continued overnight. An orange solid that formed was collected by filtration and washed with copious amounts of THF, and then dissolved in 20 mL of MeCN. Slow diffusion of Et$_2$O (60 mL) in this solution at 20 °C afforded, after 3 days, orange crystals of [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$_7$] (**1**; 0.72 g).

Synthesis of [NEt$_4$][2,2,2-(CO)$_3$-8-OH-2-I-1-Ph-*closo*-2,1,8-MoC$_2$B$_9$H$_9$]. An MeCN (20 mL) mixture of the salt **1** (0.24 g, 0.25 mmol) and [NEt$_4$]I (0.064 g, 0.25 mmol) was cooled to −20 °C and saturated with CO, and then H[BF$_4$]·OEt$_2$ (70 μL, 54 wt % solution in Et$_2$O, 0.50 mmol) was added. The mixture was allowed to slowly warm to ambient temperature while CO bubbling was maintained and stirring continued for a further 1 h. All volatiles were removed in vacuo, and the residue was washed with Et$_2$O (2 × 20 mL) and then was extracted with THF−Et$_2$O (1:3, 30 mL). The extract was filtered (Celite), and the filtrate, after evaporation of solvent in vacuo, gave [NEt$_4$][2,2,2-(CO)$_3$-8-OH-2-I-1-Ph-*closo*-2,1,8-MoC$_2$B$_9$H$_9$] (**5**; 0.095 g) as a red microcrystalline solid.

Reaction of 1 with Ag[BF$_4$] and CNBu^t. An MeCN solution (20 mL) of compound **1** (0.24 g, 0.25 mmol) was cooled to −20 °C, and Ag[BF$_4$] (0.20 g, 1.03 mmol) was added. After stirring for 5 min, CNBu^t (0.12 mL, 0.095 g, 2.5 mmol) was introduced via syringe. The mixture was stirred overnight and was then filtered (Celite), concentrated, and transferred to the top of a chromatography column. A yellow fraction was eluted with CH$_2$Cl$_2$, which, after removal of solvent in vacuo, afforded [1,1,1,1,3-(CNBu^t)$_5$-2-Ph-*closo*-1,2-MoCB$_9$H$_8$] (**6**; 0.085 g) as a yellow crystalline solid.

Traces of compound **7** are also observed during chromatographic purification of **6**, probably a consequence of the presence of adventitious moisture and/or oxygen in the silica. However, **7** is more conveniently prepared as described below.

Preparation of [8-NHBu^t-2,2-(CNBu^t)$_2$-2-(=O)-1-Ph-*closo*-2,1,8-MoC$_2$B$_9$H$_9$]. A drop of water was added to a CH$_2$Cl$_2$ solution of compound **6** (0.106 g, 0.15 mmol). The mixture immediately became violet upon exposure to air, whereafter stirring was continued for 30 min. Volatiles were removed in vacuo, and the remaining solid was washed with petroleum ether (2 × 20 mL) to give violet microcrystals of [8-NHBu^t-2,2-(CNBu^t)$_2$-2-(=O)-1-Ph-*closo*-2,1,8-MoC$_2$B$_9$H$_9$] (**7**; 0.079 g).

Compound **7** itself slowly decomposes in solution, giving another, red species that appears also to be a molybdacarborane, but which unfortunately has defied identification.

Synthesis of [N(PPh$_3$)$_2$][1-{Mo(μ-SPh)$_2$(CO)$_4$}-2-Ph-*closo*-1,2-MoCB$_9$H$_9$]. A cooled (−20 °C) MeCN (25 mL) solution of compound **1** (0.24 g, 0.25 mmol) was treated with PhSSPh (0.28 g, 1.28 mmol), and the vigorously stirred mixture was allowed to slowly warm to ambient temperature; stirring was continued overnight. Solid [N(PPh$_3$)$_2$]Cl (0.15 g, 0.26 mmol) was added and the mixture stirred a further 2 h before evaporation in vacuo. The residue was extracted into CH$_2$Cl$_2$ (ca. 10 mL), and the extract was filtered and transferred to the top of a chromatography column. A dark red band was eluted with CH$_2$Cl$_2$−petroleum ether (4:1), which, after removal of solvent in vacuo, yielded [N(PPh$_2$)$_2$][1-{Mo(μ-SPh)$_2$(CO)$_4$}-2-Ph-*closo*-1,2-MoCB$_9$H$_9$] (**8**; 0.13 g) as a dark red crystalline solid.

Structure Determinations. Experimental data for compounds **5**−**8** are reported in Table 3. Diffraction data were acquired at 110(2) K using a Bruker-Nonius X8 Apex area-detector diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). Several sets of data frames were collected at different θ values for various initial values of ϕ and ω, each frame covering a 0.5° increment of ϕ or ω. The data frames were integrated using SAINT;[37] the substantial redundancy in data allowed empirical absorption corrections (SADABS)[37] to be applied on the basis of multiple measurements of equivalent reflections.

The structures were solved (SHELXS-97) via conventional direct methods and were refined (SHELXL-97) by full-matrix least-squares on all F^2 data using SHELXTL.[37,38] 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 and the magnitudes of their isotropic thermal displacement parameters. The molybdenum-bound oxygen atom in **7** was similarly identified. All hydrogen atoms were set riding on their parent atoms in calculated positions with the exception of the O−H hydrogens in **5**, which were refined with a "rotating group" model that maximized the electron density at the calculated position,[38] and the N−H hydrogen in **7**, which was allowed positional refinement. All hydrogen atoms were assigned fixed isotropic thermal parameters calculated as $U_{\mathrm{iso}}(\mathrm{H}) = 1.2 \times U_{\mathrm{iso}}(\mathrm{parent})$, or $U_{\mathrm{iso}}(\mathrm{H}) = 1.5 \times U_{\mathrm{iso}}(\mathrm{parent})$ for methyl hydrogens.

For **5**, there were two formula units in the independent unit, differing primarily in the disposition of the cations. The structure was otherwise straightforward and treated as described above. Crystals of **6** contained one half-molecule of **6**, plus one half-molecule of a solvate that was tentatively identified as pentane, in the asymmetric fraction of the unit cell. Both of these moieties lay across a crystallographic mirror plane, with that through **6** coinciding with the molecular mirror plane through Mo(1), C(2), B(3), B(8), and B(9). Although the solvate was poorly defined and likely

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[37] *APEX 2*, version 1.0; Bruker AXS: Madison, WI, 2003−2004.

[38] *SHELXTL*, version 6.12; Bruker AXS: Madison, WI, 2001.

Table 3. Crystallographic Data for Compounds 5−8

	5	**6**·C_5H_{12}	**7**	**8**·CH_2Cl_2
formula	$C_{19}H_{35}B_9IMoNO_4$	$C_{37}H_{70}B_9MoN_5$	$C_{22}H_{42}B_9MoN_3O$	$C_{60}H_{56}B_9Cl_2Mo_2NO_4P_2S_2$
fw	661.61	778.21	557.82	1341.19
space group	$P2_1/c$	$Cmc2_1$	$Pbca$	$P\bar{1}$
a, Å	17.4418(5)	14.867(3)	12.1448(7)	10.724(2)
b, Å	17.9056(5)	17.634(3)	16.2297(11)	15.387(3)
c, Å	17.6865(5)	17.202(3)	29.596(2)	19.162(4)
α, deg	90	90	90	98.622(9)
β, deg	96.299(1)	90	90	96.983(9)
γ, deg	90	90	90	99.202(9)
V, Å^3	5490.3(3)	4509.4(14)	5833.5(7)	3051.3(10)
Z	8	4	8	2
ρ_{calc}, g cm^{-3}	1.601	1.146	1.270	1.460
μ(Mo Kα), mm^{-1}	1.629	0.322	0.470	0.667
wR_2, R_1 (all data)[a]	0.0677, 0.0422	0.0946, 0.0472	0.0863, 0.0651	0.0887, 0.0406
wR_2, R_1 [$F_o > 4\sigma(F_o)$]	0.0633, 0.0276	0.0907, 0.0373	0.0774, 0.0352	0.0836, 0.0329

[a] $wR_2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum w(F_o^2)^2]^{1/2}$; $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

suffered from considerable further (untreated) disorder, a model with only the central CH_2 unit disordered over two positions gave a satisfactory refinement. Some restraints were necessary in order to achieve a reasonable convergence. One molecule of CH_2Cl_2 as solvate cocrystallized with one formula unit of **8** in the asymmetric portion of the unit cell. This solvate was well behaved and fully refined without difficulty as above.

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Supporting Information Available: Full details of the crystal structure analyses in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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