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Unprecedented Cage-Carbon to Cage-Boron NMe_3 Transfer in a Monocarbon Molybdenacarborane†

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The reagent $Li_2[7\text{-}NMe_3\text{-}nido\text{-}7\text{-}CB_{10}H_{10}]$ reacts with $[Mo(CO)_3(NCMe)_3]$ in THF–NCMe (THF = tetrahydrofuran) to give a molybdenacarborane intermediate which, upon oxidation by $CH_2{=}CHCH_2Br$ or I_2 and then addition of $[N(PPh_3)_2]Cl$, gives the salts $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}X\text{-}3\text{-}NMe_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ (X = Br (**1**) or I (**2**)). During the reaction, the cage-bound NMe_3 substituent is transferred from the cage-carbon atom to an adjacent cage-boron atom, a feature established spectroscopically in **1** and **2**, and by X-ray diffraction studies on several of their derivatives. When $[Rh(NCMe)_3(\eta^5\text{-}C_5Me_5)][BF_4]_2$ is used as the oxidizing agent, the trimetallic compound $[2,2,2\text{-}(CO)_3\text{-}7\text{-}\mu\text{-}H\text{-}2,7,11\text{-}\{Rh_2(\mu\text{-}CO)(\eta^5\text{-}C_5Me_5)_2\}\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_9]$ (**10**) is formed, the NMe_3 group being lost. Reaction of **1** in CH_2Cl_2 with $Tl[PF_6]$ in the presence of donor ligands L affords neutral zwitterionic compounds $[2,2,2\text{-}(CO)_3\text{-}2\text{-}L\text{-}3\text{-}NMe_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ for L = PPh_3 (**4**) or $CNBu^t$ (**5**), and $[2\text{-}Bu^tC{\equiv}CH\text{-}2,2\text{-}(CO)_2\text{-}3\text{-}NMe_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ (**6**) when L = $Bu^tC{\equiv}CH$. When **1** is treated with $CNBu^t$ and X_2, the metal center is oxidized, and in the products obtained, $[2,2,2,2\text{-}(CNBu^t)_4\text{-}2\text{-}Br\text{-}3\text{-}X\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ (X = Br (**7**), I (**8**)), the B–NMe_3 bond is replaced by B–X. In contrast, treatment of **2** with I_2 and *cyclo*-1,4-$S_2(CH_2)_4$ in CH_2Cl_2 results in oxidative substitution of the cluster and retention of the NMe_3 group, giving $[2,2,2\text{-}(CO)_3\text{-}2\text{-}I\text{-}3\text{-}NMe_3\text{-}6\text{-}\{cyclo\text{-}1,4\text{-}S_2(CH_2)_4\}\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_9]$ (**9**). The unique structural features of the new compounds were confirmed by single-crystal X-ray diffraction studies upon **6**, **7**, **9** and **10**.

Introduction

Transition-metal complexes of the trianionic monocarbollide ligand $[nido\text{-}7\text{-}CB_{10}H_{11}]^{3-}$ had until recently received relatively little attention compared with the wealth of information available on the corresponding complexes of the dicarbollide ligand $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ and its derivatives.[1] The carboranes $7\text{-}NR_3\text{-}nido\text{-}7\text{-}CB_{10}H_{12}$ (R = H, alkyl)[2] are also precursors to monocarbollide metal complexes, affording species 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.[2d,3] The potential of these amino-*nido*-carboranes for synthesis has, however, been but little exploited. Moreover, recent work has revealed some subtle differences in the nature of the products obtained in their reactions with low-valent transition-metal compounds. Thus, whereas, for example, the carboranes $7\text{-}NR_3\text{-}nido\text{-}7\text{-}CB_{10}H_{12}$ (NR_3 = NMe_3, NH_2Bu^t, NMe_2Bu^t) all react with $[Ru_3(CO)_{12}]$ in toluene at reflux temperatures to yield the cluster compounds $[1\text{-}NR_3\text{-}2,2\text{-}(CO)_2\text{-}7,11\text{-}(\mu\text{-}H)_2\text{-}2,7,11\text{-}\{Ru_2(CO)_6\}\text{-}closo\text{-}2,1\text{-}RuCB_{10}H_8]$,[4] the *nido*-carboranes show some variation in their reactivity with $[RhCl(PPh_3)_3]$ for different groups R.[5] In methanolic KOH solution, $7\text{-}NH_3\text{-}nido\text{-}7\text{-}CB_{10}H_{12}$ reacts with $[RhCl(PPh_3)_3]$ to give salts of $[1\text{-}NH_2\text{-}2,2\text{-}(PPh_3)_2\text{-}2$-

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† The new compounds described in this paper are based on icosahedral *closo*-1-carba-2-molybdenadodecaborane frameworks, and although all are chiral, they here occur as racemates. The substituted boron vertices that herein are numbered 3, 6, 7, and 11 could equally be labeled 6, 3, 11 and 7, respectively. In each case, the former is used, in accordance with IUPAC convention.

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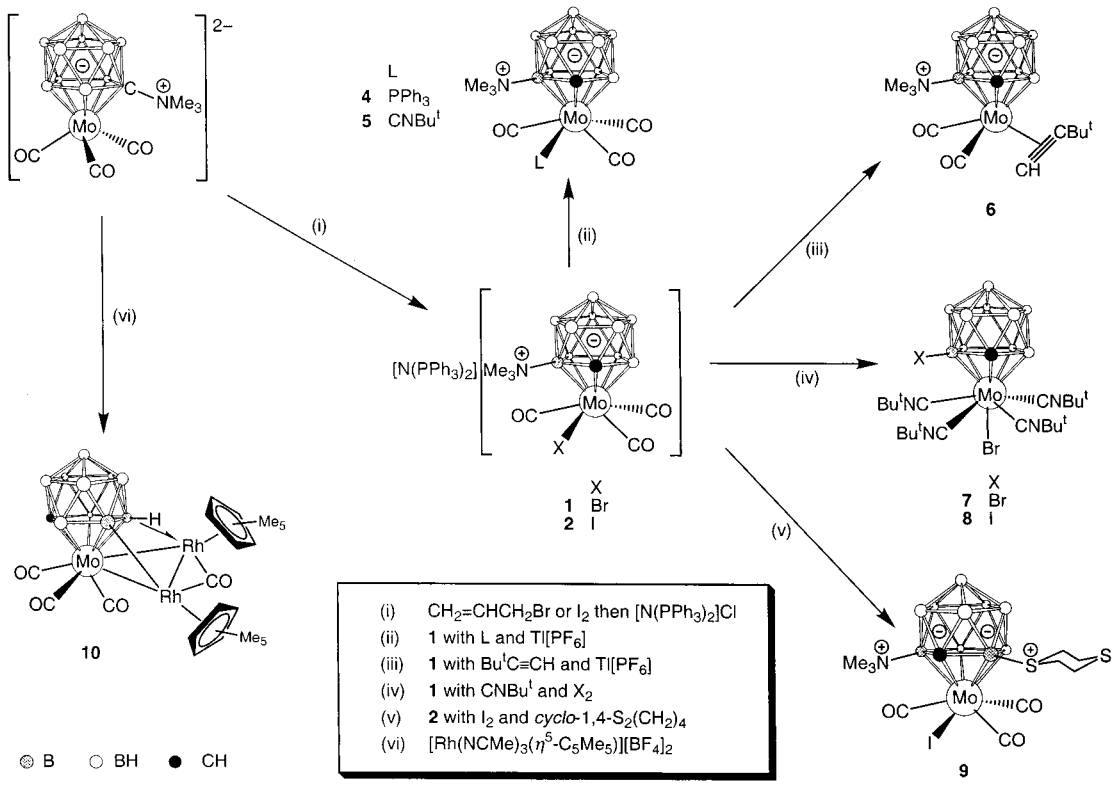
Scheme 1



H-*closo*-2,1-$RhCB_{10}H_{10}]^-$, of which the $[Bu^n_4N]^+$ salt is converted in refluxing methanol to the dimeric species $[Bu^n_4N]$-[2,2′-μ-H-{1,2′-μ-NH_2-2-PPh_3-*closo*-2,1-$RhCB_{10}H_{10}$}$_2$]$^-$.[5a] In contrast, the carborane 7-NMe_3-*nido*-7-$CB_{10}H_{12}$ with the same rhodium reagent in refluxing methanol yields primarily 18-electron [1-NMe_3-2,7-$(PPh_3)_2$-2-H-2-Cl-*closo*-2,1-$RhCB_{10}H_9$], along with 16-electron [1-NMe_3-2-PPh_3-2-Cl-*closo*-2,1-$RhCB_{10}H_{10}$].[5b] Moreover, 7-NH_2Bu^t-*nido*-7-$CB_{10}H_{12}$ reacts with $[RhX(PPh_3)_3]$ (X = Cl or Br) in refluxing toluene to give 16-electron [1-NH_2Bu^t-2-PPh_3-2-X-*closo*-2,1-$RhCB_{10}H_{10}$] as the only products.[5c]

These differences in reactivity of the carboranes 7-NR_3-*nido*-7-$CB_{10}H_{12}$ toward $[RhX(PPh_3)_3]$ have led us to explore their behavior in reactions with other transition-metal systems. We have recently reported[6] the synthesis of the monoanionic molybdenacarborane salt $[N(PPh_3)_2][1,2$-μ-$NHBu^t$-2,2,2-$(CO)_3$-*closo*-2,1-$MoCB_{10}H_{10}]$, which contains a novel intramolecular $NHBu^t$ bridge between molybdenum and the cage-carbon atom. This species is obtained upon oxidation of trianionic [1-$NHBu^t$-2,2,2-$(CO)_3$-*closo*-2,1-$MoCB_{10}H_{10}]^{3-}$. The latter was targeted for synthesis because of its isolobal relationship with the ubiquitous dicarbollide dianion [3,3,3-$(CO)_3$-*closo*-3,1,2-$MoC_2B_9H_{11}]^{2-}$.[7] In concert with that work, we attempted to prepare another analogue of the latter anion, namely the dianionic molybdenacarborane [2,2,2-$(CO)_3$-1-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}]^{2-}$, with a view to examining comparable reactivity. However, as we report herein, this last species is very readily oxidized undergoing an unprecedented cage-carbon to cage-boron transfer of the NMe_3 group. The nature and reactivity of the product is discussed, as are some related reactions.

Results and Discussion

The molybdenum dicarbollide dianion [3,3,3-$(CO)_3$-*closo*-3,1,2-$MoC_2B_9H_{11}]^{2-}$ has previously been used to prepare [3-(η^3-C_3H_5)-3,3-$(CO)_2$-*closo*-3,1,2-$MoC_2B_9H_{11}]^-$ by reaction with CH_2=$CHCH_2Br$.[8] Employing an ostensibly parallel monocarbollide system, we planned to treat a THF solution of [7-NMe_3-*nido*-7-$CB_{10}H_{10}]^{2-}$ with $[Mo(CO)_3(NCMe)_3]$ in NCMe, in the expectation of generating in situ the monocarbollide species [2,2,2-$(CO)_3$-1-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}]^{2-}$. However, the latter in reaction with CH_2=$CHCH_2Br$ did not afford the anticipated anion [1-NMe_3-2-(η^3-C_3H_5)-2,2-$(CO)_2$-*closo*-2,1-$MoCB_{10}H_{10}]^-$. Instead, the product isolated following addition of $[N(PPh_3)_2]Cl$ was $[N(PPh_3)_2]$[2-Br-2,2,2-$(CO)_3$-3-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}$] (**1**; Scheme 1). In addition to oxidizing the molybdenum center, the allyl bromide also serves as a bromide source. Most significant, however, is that during the course of reaction the NMe_3 group that had been bonded to the cage-carbon atom has transferred to an adjacent boron atom (B_α) in the C*B*B*B* belt that ligates the molybdenum vertex.

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Table 1. Analytical and Physical Data

cmpd	color	yield/%	ν_{max}(CO)[a]/cm^{-1}	anal./%[b] C	H	N
[N(PPh$_3$)$_2$][2-Br-2,2,2-(CO)$_3$-3-NMe$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$] (**1**)	red	27	2013 s, 1933 s, 1896 s	52.4 (52.3)	5.1 (5.0)	3.0 (2.8)
[N(PPh$_3$)$_2$][2,2,2-(CO)$_3$-2-I-3-NMe$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$] (**2**)	red	13	2006 s, 1932 s, 1894 s	51.3 (51.0)	5.0 (5.2)	3.0 (2.5)[c]
[2,2,2-(CO)$_3$-2-PPh$_3$-3-NMe$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$] (**4**)	yellow	63	2017 s, 1956 s, 1906 s	45.5 (45.4)	5.5 (5.2)	2.3 (2.1)[d]
[2-CNBu^t-2,2,2-(CO)$_3$-3-NMe$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$] (**5**)	yellow	71	2170 m,[e] 2038 s, 1985 s, 1930 s	31.9 (31.9)	6.3 (6.2)	6.2 (6.2)
[2-Bu^{t}C≡CH-2,2-(CO)$_2$-3-NMe$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$] (**6**)	purple	89	2039 s, 1979 s	33.3 (34.0)	6.9 (6.9)	3.3 (3.3)
[2,2,2,2-(CNBu^t)$_4$-2,3-Br$_2$-*closo*-2,1-MoCB$_{10}$H$_{10}$] (**7**)	orange	43	2213 w,[e] 2184 s[e]	35.5 (35.1)	6.5 (6.4)	7.4 (7.8)
[2,2,2,2-(CNBu^t)$_4$-2-Br-3-I-*closo*-2,1-MoCB$_{10}$H$_{10}$] (**8**)	orange	43	2208 w,[e] 2181 s[e]	32.2 (32.0)	5.9 (5.9)	6.7 (6.9)[d]
[2,2,2-(CO)$_3$-2-I-3-NMe$_3$-6-{*cyclo*-1,4-S$_2$(CH$_2$)$_4$}-*closo*-2,1-MoCB$_{10}$H$_9$] (**9**)	red	47	2019 s, 1958 m, 1922 s	21.1 (21.5)	4.4 (4.3)	2.4 (2.3)
[2,2,2-(CO)$_3$-7-μ-H-2,7,11-{Rh$_2$(μ-CO)(η^5-C$_5$Me$_5$)$_2$}-*closo*-2,1-MoCB$_{10}$H$_9$] (**10**)	brown	20	1998 s, 1939 m, 1826 m	36.8 (36.9)	5.0 (5.0)	

[a] Measured in CH_2Cl_2; the broad medium-intensity band observed at ~2500−2550 cm^{-1} in the spectra of all compounds is due to B−H absorptions. [b] Calculated values are given in parentheses. [c] Cocrystallizes with 1 mol equiv of thf. [d] Cocrystallizes with 0.5 mol equiv of CH_2Cl_2. [e] ν_{max}(N≡C).

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

cmpd	^{1}H/δ[b]	^{13}C/δ[c]	^{11}B/δ[d]
1	7.69−7.25 (m, 30H, Ph), 3.06 (s, 9H, Me), ca. 3.03 (sh, br s, 1H, cage CH)	246.5, 236.7, 229.9 (CO × 3), 134.1−126.8 (Ph), 67.4 (br, cage C), 57.7 (NMe$_3$)	8.3 (1B),* −2.0 (1B), −3.8 (2B), −7.5 (1B), −8.4 (1B), −10.8 (1B), −13.4 (1B), −16.8 (2B)
2	7.68−7.25 (m, 30H, Ph), 3.24 (br s, 1H, cage CH), 3.06 (s, 9H, Me)	244.3, 234.6, 229.2 (CO × 3), 134.1−126.8 (Ph), 60.7 (br, cage C), 57.9 (NMe$_3$)	8.1 (1B),* −1.7 (1B), −3.4 (2B), −7.1 (1B), −9.3 (1B), −11.6 (1B), −13.4 (1B), −16.6 (1B), −17.3 (1B)
4	7.52−7.31 (m, 15H, Ph), 2.95 (s, 9H, Me), 1.63 (br s, 1H, cage CH)	235.7 (d, CO, J(PC) = 8), 232.7 (d, CO, J(PC) = 31), 230.3 (d, CO, J(PC) = 33), 134.0−129.0 (Ph), 57.4 (NMe$_3$), 56.2 (br, cage C)	11.4 (1B),* 2.8 (1B), −3.1 (1B), −4.9 (2B), −10.4 (1B), −11.7 (1B), −14.1 (2B), −16.5 (1B)
5	3.00 (s, 9H, NMe$_3$), 2.70 (br s, 1H, cage CH), 1.53 (s, 9H, Bu^t)	233.6, 229.8, 226.3 (CO × 3), 153.9 (t, CN, J(NC) = 18), 60.8 (*C*Me$_3$), 57.1 (NMe$_3$), 54.7 (br, cage C), 30.3 (C*Me$_3$*)	9.2 (1B)*, 1.3 (1B), −3.8 (2B), −5.5 (1B), −10.4 (1B), −12.4 (2B), −15.3 (1B), −16.0 (1B)
6	10.06 (br s, 1H, C≡CH), 4.38 (br s, 1H, cage CH), 2.45 (s, 9H, NMe$_3$), 1.69 (s, 9H, Bu^t)	230.3, 225.0 (CO × 2), 223.3 (C≡*C*H), 175.0 (C≡*C*Bu^t), 57.6 (br, cage C), 56.9 (NMe$_3$), 41.6 (*C*Me$_3$), 31.3 (C*Me$_3$*)	12.6 (1B),* 2.5 (1B), 1.9 (1B), −2.2 (1B), −3.5 (1B), −5.0 (1B), −10.4 (1B), −12.4 (1B), −14.1 (2B)
7	2.42 (br s, 1H, cage CH), 1.52 (s, 36H, Bu^t)	152.0 (br, CN), 62.2 (br, cage C), 58.2 (*C*Me$_3$), 29.8 (C*Me$_3$*)	10.1 (1B + 1B*), 4.4 (1B), −3.3 (1B), −3.7 (1B), −6.5 (3B), −15.7 (1B), −17.8 (1B)
8	2.28 (br s, 1H, cage CH), 1.52 (s, 36H, Bu^t)	149.1 (br, CN), 62.7 (br, cage C), 58.5 (*C*Me$_3$), 29.5 (C*Me$_3$*)	11.1 (1B), 4.7 (1B), −2.6 (2B), −5.7 (1B + 1B*), ca. −6.1 (sh, 2B), −15.8 (2B)
9	3.89 (br m, 1H, CH$_2$), 3.55−3.42 (m, 2H, CH$_2$), 3.28−3.21 (m, 3H, CH$_2$), 3.09 (s, 9H, NMe$_3$), ca. 3.08 (sh, br s, 1H, cage CH), 2.99−2.82 (m, 2H, CH$_2$)	235.2, 224.3, 223.3 (CO × 3), 58.1 (NMe$_3$), 57.8 (br, cage C), 42.3, 40.2, 27.3, 26.6 (CH$_2$ × 4)	7.7 (1B),* −2.4 (1B), −4.3 (2B), −5.8 (2B), −6.6 (1B),* −7.9 (1B), −17.3 (1B), −18.2 (1B)
10	1.79, 1.76 (s × 2, 15H × 2, C$_5$Me$_5$ × 2), 1.71 (br s, 1H, cage CH), ca. −14.0 (vbr m, 1H, B−H⇀Rh)	251.1,[e] 225.1, 221.5 (CO × 3), 108.4 (d, *C*$_5$Me$_5$, J(RhC) = 4), 106.0 (d, *C*$_5$Me$_5$, J(RhC) = 6), 44.0 (br, cage C), 9.8, 9.3 (s × 2, Me × 2)	56.7 (1B, B−Rh), 29.3 (1B, B−H⇀Rh, J(HB) = 70), −3.7 (1B), −5.6 (1B), −6.8 (1B), −8.4 (1B), −10.9 (1B), −11.8 (1B), −14.3 (1B), −18.3 (1B)

[a] Chemical shifts (δ) in ppm, coupling constants (J) in hertz, 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·Et_2O (external). Signals ascribed to more than one boron nucleus result from overlapping peaks and do not indicate symmetry equivalence. Peaks marked with an asterisk are assigned to cage-boron nuclei bearing non-H substituents. [e] Resonance due to Rh−Rh-bridging CO not observed.

Spectroscopic data for compound **1** are given in Tables 1 and 2. Initially, however, the exact constitution of this species was not clear. In addition to peaks due to an [N(PPh$_3$)$_2$]$^+$ cation (confirmed by ^{31}P{^{1}H} NMR), the only significant features of the ^{1}H and ^{13}C{^{1}H} NMR spectra were resonances attributable to the NMe$_3$ substituent and three inequivalent

Mo-bound carbonyl ligands. Integration of the ^{1}H NMR spectrum indicated one cation per NMe_3 group, implying the molybdenacarborane to be monoanionic. Reasonably deducing the presence of a metal-bound bromide for overall neutrality, compound **1** was initially incorrectly formulated as $[N(PPh_3)_2][2\text{-Br-}2,2,2\text{-}(CO)_3\text{-}1\text{-}NMe_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$, with the NMe_3 moiety assumed still to be attached to the cage-carbon atom. A preliminary X-ray diffraction experiment (see later) appeared to support this, as the anion crystallizes with the NMe_3 group lying across a crystallographic mirror plane and with the carborane ligand therefore having apparent crystallographic mirror symmetry. However, in the $^{11}B\{^1H\}$ NMR spectrum of **1**, 10 separate resonances are seen (some are coincident), of which one signal remained a singlet in a fully coupled ^{11}B spectrum. Both of these features are consistent with a reduction in cluster symmetry due to substitution at a boron vertex, and it was realized that the available NMR data could better be explained if the NMe_3 substituent was bound to a cage-boron atom. Indeed, the chemical shift of this boron atom (δ 8.3) is typical for B-amine features in related systems.[9] A shoulder observed at $\delta \sim 3.03$ in the ^{1}H NMR spectrum of **1**, which is almost obscured by the signal for the methyl groups, may be tentatively assigned as the cage CH resonance. This proposal would also be consistent with the X-ray result with disorder precluding the distinguishing of cage-boron versus cage-carbon vertices. For the same reason, a distinction also could not yet be made between the amine being attached to α or β boron atoms in the CBBBB belt bonded to molybdenum. Thus, it was not at this stage unambiguously established if **1** was the 3-NMe_3 or the 7-NMe_3 isomer.

The structure ultimately assigned for the anion of **1** is shown in Figure 1. The site for the cage-carbon is based on the results for closely related structures discussed later. A molybdenum atom is ligated on one side by three carbonyls and a bromide [Mo−Br 2.771(3) Å], and on the other side by an 8-NMe_3-*nido*-7-$CB_{10}H_{10}$ carborane in a conventional pentahapto fashion. The B(2)−N(1) distance, at 1.613(8) Å, is normal.

In seeking analogues of **1** which might afford a more satisfactory crystallographic result, we found that the corresponding iodo compound $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}I\text{-}3\text{-}NMe_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ (**2**) could be obtained by using I_2 instead of $CH_2{=}CHCH_2Br$ as oxidant in the reaction by which compound **1** was formed. Data characterizing **2** are given in Tables 1 and 2, showing this species to have very similar spectroscopic properties to those of compound **1**, as would be expected. In particular, the broad proton resonance diagnostic for the cage CH group is seen at δ 3.24 and is now clearly distinguishable from the NMe_3 proton resonance at δ 3.06. The $^{11}B\{^1H\}$ NMR spectrum again reveals a resonance at δ 8.1, assigned to the B−NMe_3 group as it remains a singlet in a fully coupled ^{11}B NMR spectrum. Unfortunately, **2** also failed to yield crystals suitable for an accurate X-ray analysis. Isolated yields of **1** and **2** were low.

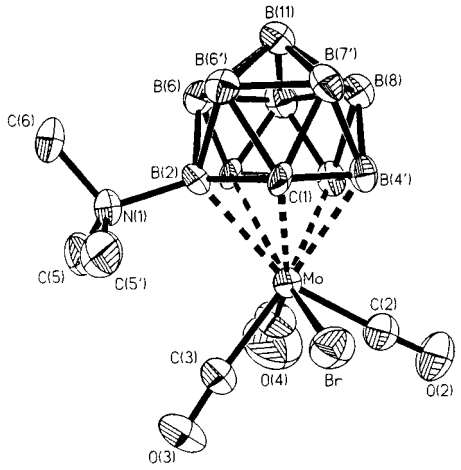


Figure 1. Structure of the anion of $[N(PPh_3)_2][2\text{-Br-}2,2,2\text{-}(CO)_3\text{-}3\text{-}NMe_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ (**1**) showing the crystallographic labeling scheme. In this and in Figures 2−5, thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity except where chemically important. Selected internuclear distances (Å) and angles (deg): Mo−C(4) 1.799(12), Mo−C(2) 1.961(9), Mo−C(3) 2.010(8), Mo−C(1) 2.31(4), Mo−B(4) 2.347(5), Mo−B(2) 2.452(8), Mo−B(3) 2.47(5), Mo−Br 2.771(3), B(2)−N(1) 1.613(8), C(2)−O(2) 1.132(9), C(3)−O(3) 1.142(8), C(4)−O(4) 1.19(2); C(1)−Mo−Br 72.1(5), B(4)−Mo−Br 130.12(14), B(4)^a−Mo−Br 85.20(14), B(2)−Mo−Br 104.94(6), B(3)−Mo−Br 140.6(4), B(3)−B(2)−N(1) 125.6(9), N(1)−B(2)−B(6) 113.3(5), N(1)−B(2)−C(1) 125.3(8), N(1)−B(2)−Mo 114.7(4). Symmetry code (*a*): $-x+1, y, z$.

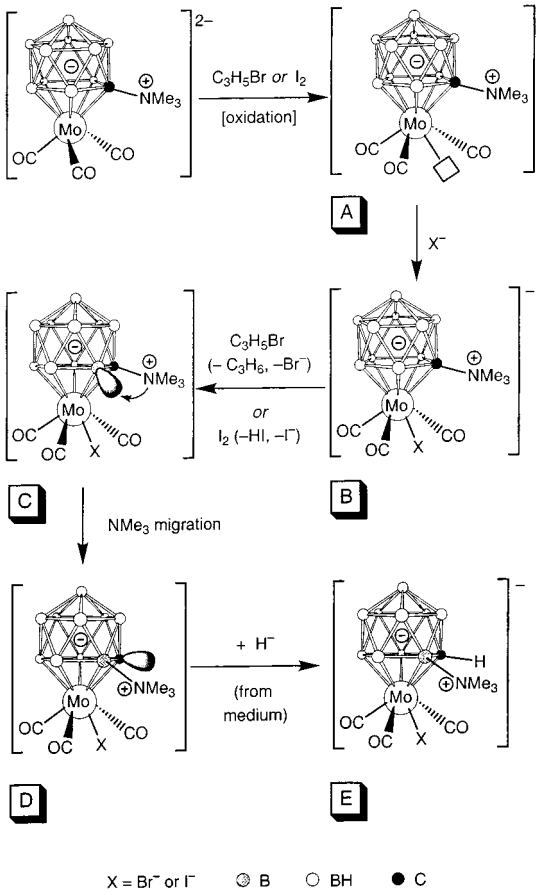
Evidently, side reactions occur, but formation of other identifiable molybdenacarborane products was not observed.

Unresolved at present is the manner by which the NMe_3 group is transferred from carbon to boron in the formation of **1** and **2**. However, a plausible pathway is indicated in Scheme 2, of which several steps have precedent.[10] Oxidation of the Mo^0 dianion with allyl bromide or iodine would afford the electronically unsaturated neutral Mo^{II} species $[1\text{-}NMe_3\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ (**A**) together with halide. The latter would ligate the metal center to form the saturated anionic complex $[1\text{-}NMe_3\text{-}2,2,2\text{-}(CO)_3\text{-}2\text{-}X\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]^-$ (**B**). In the next step affording **C**, iodine or allyl bromide abstracts H^- from a cage $BH^{\delta-}$ vertex, thereby creating a vacant site on a boron atom adjacent to the $CNMe_3$ unit, causing the NMe_3 group to migrate (**D**). The electron deficient carbon center must then scavenge H^- from other species present in solution to yield the anions **E**, cage BH groups being a likely source of hydride. This would perhaps account for the formation of **1** and **2** in poor yield. The removal of H^- from **B** by iodine also occurs in the reaction of the monoanion $[2,2,2,2\text{-}(CO)_4\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]^-$ with iodine in THF which gives $[2,2,2\text{-}(CO)_3\text{-}2\text{-}I\text{-}7\text{-}\{O(CH_2)_4\}\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]^-$. In this process, the I^- formed by reduction of iodine again ligates the metal center, but a THF molecule coordinates to a vacant site created on the boron atom.[10] It is noteworthy that in the synthesis of **1** and **2** the solvent is THF. Hence, it would in principle be possible for a THF molecule to attach itself to the naked boron in **C** obviating any need for NMe_3 migration. That this does not occur might suggest an intramolecular three-

(9) Franken, A.; Du, S.; Jelliss, P. A.; Kautz, J. A.; Stone, F. G. A. *Organometallics* **2001**, *20*, 1597.

(10) Du, S.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **2001**, 2791.

Scheme 2



center C−N−B mechanism for transfer of the NMe_3 moiety rather than the amine's ability to displace a THF molecule, otherwise a species having both $CNMe_3$ and $BO(CH_2)_4$ groups in the molybdenum-ligating CBBBB ring would form.

To explore their chemistry more fully, derivatives of **1** and **2** were sought. When the reaction that gave **1** was repeated using $[Mo(CO)_3(NCMe)_2(PPh_3)]$ instead of $[Mo(CO)_3(NCMe)_3]$, it was anticipated that $[N(PPh_3)_2][2\text{-Br-}2,2\text{-}(CO)_2\text{-}2\text{-}PPh_3\text{-}3\text{-}NMe_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$, a product analogous to **1**, might be obtained. However, the only product isolated after chromatographic workup was the known molybdenum complex $[N(PPh_3)_2][2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]$ (**3**),[11] identified spectroscopically. It is not possible to say whether a B−NMe_3 species analogous to **1** is formed and subsequently decomposes, or if this reaction follows a different route whereby the NMe_3 unit is simply lost.

Treatment of compound **1** with $Tl[PF_6]$ and ligands L results in TlBr elimination and formation of the neutral, zwitterionic complexes $[2,2,2\text{-}(CO)_3\text{-}2\text{-L-}3\text{-}NMe_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ for L = PPh_3 (**4**) or $CNBu^t$ (**5**) and the species $[2\text{-}Bu^tC{\equiv}CH\text{-}2,2\text{-}(CO)_2\text{-}3\text{-}NMe_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ (**6**) when L = $Bu^tC{\equiv}CH$. Data characterizing compounds **4**−**6** are given in Tables 1 and 2. For all three products, the $^{11}B\{^1H\}$ NMR spectra show 10 resonances (some coincide),

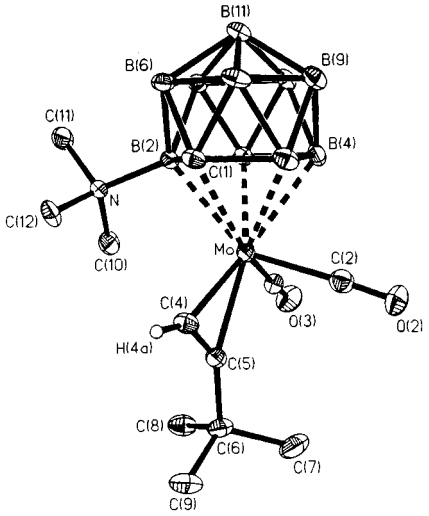


Figure 2. Structure of $[2\text{-}Bu^tC{\equiv}CH\text{-}2,2\text{-}(CO)_2\text{-}3\text{-}NMe_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ (**6**) showing the crystallographic labeling scheme. Selected internuclear distances (Å) and angles (deg): Mo−C(3) 1.995(3), Mo−C(2) 2.002(3), Mo−C(4) 2.044(3), Mo−C(5) 2.104(2), Mo−B(5) 2.357(3), Mo−C(1) 2.385(2), Mo−B(4) 2.396(3), Mo−B(2) 2.416(3), Mo−B(3) 2.431(3), B(2)−N 1.613(3), C(2)−O(2) 1.138(3), C(3)−O(3) 1.139(3), C(4)−C(5) 1.291(4); C(3)−Mo−C(4) 116.35(10), C(2)−Mo−C(4) 98.78(10), C(3)−Mo−C(5) 81.19(10), C(2)−Mo−C(5) 87.17(10), C(4)−Mo−C(5) 36.22(10), C(4)−Mo−C(1) 87.96(9), C(5)−Mo−C(1) 123.81(9), C(4)−Mo−B(2) 104.10(10), C(5)−Mo−B(2) 126.06(9), N−B(2)−C(1) 122.4(2), N−B(2)−B(7) 117.8(2), N−B(2)−B(6) 114.1(2), N−B(2)−B(3) 125.3(2), N−B(2)−Mo 109.64(14), C(5)−C(4)−Mo 74.4(2), C(4)−C(5)−C(6) 140.9(2), C(4)−C(5)−Mo 69.3(2), C(6)−C(5)−Mo 149.8(2).

in keeping with the anticipated asymmetry of the cluster. Here again, one signal in each spectrum remains a singlet upon retention of proton coupling and is relatively deshielded, resonating in the range δ 9.4−12.6. These are attributed to the boron vertices carrying an NMe_3 group. In the ^1H and $^{13}C\{^1H\}$ NMR spectra for **4**−**6**, peaks due the NMe_3 unit are also observed, confirming that this group is retained in the products. Moreover, broad resonances diagnostic for the cage CH groups are seen at $\delta(^1H)$ 1.63 (**4**), 2.70 (**5**), and 4.38 (**6**), and at δ (^{13}C) 56.2 (**4**), 54.7 (**5**), and 57.6 (**6**).[12] The significant deshielding of the cage CH proton resonance in the alkyne complex **6**, compared with **4** and **5**, is consistent with the corresponding parameters for analogous anionic species based on the $[nido\text{-}7\text{-}CB_{10}H_{11}]^{3-}$ carborane ligand.[11]

Single crystals of compound **6** were analyzed by X-ray diffraction methods, revealing the structure shown in Figure 2. The data were of sufficient quality unambiguously to establish that the NMe_3 group is attached to a cage-boron atom in an α position in the *C*BBB*B* face of the carborane ligand. Thus, the site of NMe_3 substitution in all of the foregoing species **1**, **2**, and **4**−**6** is reasonably assigned as being the 3-position. The carborane moiety in **6** is structurally very similar to that in **1**, the B(2)−N distance (1.613(3) Å) being essentially identical with the corresponding parameter in **1**. Two carbonyl ligands are also terminally bonded to molybdenum in a normal fashion. The final element of the molybdenum coordination sphere is the alkyne group $Bu^tC{\equiv}CH$, whose contact-carbon atoms are bonded to the metal center at distances Mo−C(4) 2.044(3) and Mo−C(5)

(11) Ellis, D. D.; Franken, A.; Jelliss, P. A.; Stone, F. G. A.; Yu, P.-Y. *Organometallics* **2000**, *19*, 1993.

(12) Brew, S. A.; Stone, F. G. A. *Adv. Organomet. Chem.* **1993**, *35*, 135.

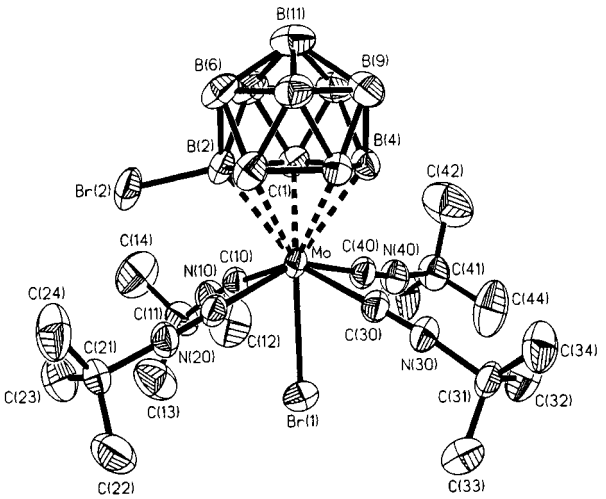


Figure 3. Structure of [2,2,2,2-$(CNBu^t)_4$-2,3-Br_2-*closo*-2,1-$MoCB_{10}H_{10}$] (**7**) showing the crystallographic labeling scheme. Selected internuclear distances (Å) and angles (deg): Mo−B(3) 2.368(5), Mo−B(4) 2.392(5), Mo−B(2) 2.408(5), Mo−B(5) 2.462(5), Mo−C(1) 2.469(5), Mo−Br(1) 2.6873(7), B(2)−Br(2) 2.003(5); B(2)−Mo−Br(1) 142.34(13), C(1)−Mo−Br(1) 143.81(12), C(1)−B(2)−Br(2) 121.3(3), B(7)−B(2)−Br(2) 113.7(3), B(6)−B(2)−Br(2) 107.4(3), B(3)−B(2)−Br(2) 130.4(3).

2.104(2) Å and which has an internal C(4)−C(5) distance of 1.291(4) Å. In accord with the alkyne ligand acting formally as a four-electron donor, in the $^{13}C\{^1H\}$ NMR spectrum, the ligated carbon atoms resonate at δ 175.0 and 223.3.[13] In the related molybdenum complex $[N(PPh_3)_2][2\text{-}Bu^tC{\equiv}CH\text{-}2,2\text{-}(CO)_2\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]$, the contact carbons of the alkyne resonate at δ 164.4 and 196.4,[11] also in the range for a four-electron donor alkyne. To our knowledge, compound **6** is the first structurally characterized metal−alkyne complex in metal−monocarbollide chemistry.

We have previously shown that the Mo^{II} complexes $[2,2,2,2\text{-}(CO)_4\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]^-$ and $[1,2\text{-}\mu\text{-}NHBu^t\text{-}2,2,2\text{-}(CO)_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]^-$, upon treatment with I_2 and $CNBu^t$, are oxidized to Mo^{IV} species $[2,2,2,2\text{-}(CNBu^t)_4\text{-}2\text{-}I\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]$[10] and $[1,2\text{-}\mu\text{-}NHBu^t\text{-}2,2,2\text{-}(CNBu^t)_3\text{-}2\text{-}I\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$,[6] respectively. Given the relationship of **1** to the two described Mo^{II} anions, it was of interest to examine the reactivity of **1** under similar conditions. Accordingly, CH_2Cl_2 solutions of compound **1** were treated with both Br_2 and I_2 in the presence of $CNBu^t$. Simplistically, it was expected that the product obtained might be of general formulation $[2,2,2\text{-}(CNBu^t)_3\text{-}2\text{-}X\text{-}2\text{-}Y\text{-}3\text{-}NMe_3\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ (X, Y = Br or I). In practice, however, the boron-bound NMe_3 unit is lost in the reaction, and the products isolated are $[2,2,2,2\text{-}(CNBu^t)_4\text{-}2\text{-}Br\text{-}3\text{-}X\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{10}]$ (X = Br (**7**), I (**8**)).

The two products **7** and **8** were fully characterized by the data presented in Tables 1 and 2. Compound **7** was additionally studied by X-ray diffraction methods, which established the structure shown (Figure 3). This determination reveals that a bromine atom is attached to an α boron atom in the five-membered C*B*BB*B* ring that is bonded to molybdenum, with B(2)−Br(2) 2.003(5) Å. It may reasonably be assumed that it is this boron atom which formerly carried the NMe_3 substituent. Thus, the molybdenum atom is η^5-coordinated on one side by an 8-Br-*nido*-7-$CB_{10}H_{10}$ carborane group and on the other by a bromide and four $CNBu^t$ ligands. The Mo−Br(1) distance, 2.6873(7) Å, is rather shorter than in **1** and is consistent with the higher molybdenum oxidation state in **7**. This bromide is sited trans to the centroid of the CBBBB carborane face, with Br(1)−Mo-centroid 178.8°. The Mo-centroid distance, 1.902 Å, is somewhat longer than that (1.877 Å) in $[2,2,2,2\text{-}(CNBu^t)_4\text{-}2\text{-}I\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]$;[10] likewise, the average Mo−($CNBu^t$) separation in **7** is ∼2.126 Å, perceptibly longer than in this analogue, where the corresponding parameter is ∼2.111 Å. These two species otherwise have very similar architectures.

The NMR parameters for compounds **7** and **8** are mutually very similar and, moreover, closely resemble the corresponding data for the related Mo^{IV} species $[2,2,2,2\text{-}(CNBu^t)_4\text{-}2\text{-}X\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]$ (X = Br, I).[10] In both the ^1H and $^{13}C\{^1H\}$ NMR spectra of **7** and **8**, signals for an NMe_3 group are clearly absent. The ^1H NMR spectra show a broad resonance for the cage CH unit at δ 2.42 (**7**) and 2.28 (**8**) of relative intensity 1, and a sharp signal at δ 1.52 of relative intensity 36 that corresponds to the four Bu^t groups. In the $^{13}C\{^1H\}$ NMR spectra, the cage-carbons resonate at δ 62.2 (**7**) and 62.7 (**8**), respectively. The expected patterns of resonances for the isocyanide ligands' three types of C atom environments are also seen in typical positions, with the contact carbon atoms of these groups seen as broad, unresolved triplets at δ 152.0 (**7**) and 149.1 (**8**). Compounds **7** and **8**, likewise, both have similar $^{11}B\{^1H\}$ NMR spectra, with the only significant difference between the two sets of data being the chemical shift of that boron atom bearing the halogen. For **7**, the substituted boron atom resonates at δ 10.1 and for **8** at δ −5.7. This difference in shielding of ∼15 ppm for bromide versus iodide substituents is very typical.[14] Indeed, this fact in conjunction with the microanalytical data serves to confirm the identity of the halogens present in compound **8**.

Whereas the anion $[2,2,2,2\text{-}(CO)_4\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_{11}]^-$ with I_2 and $CNBu^t$ undergoes metal oxidation, as mentioned previously, the same anion reacts with I_2 and thioethers L to give cage-substituted products $[2,2,2\text{-}(CO)_3\text{-}2,3\text{-}\mu\text{-}I\text{-}n\text{-}L\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_9]$ (n = 7, 11) and $[2,2,2\text{-}(CO)_3\text{-}2\text{-}I\text{-}3,11\text{-}L_2\text{-}closo\text{-}2,1\text{-}MoCB_{10}H_9]$.[10] As the former of these two product types contains a novel iodide bridge between molybdenum and a cage-boron atom, and given that the anion of **2** already contains a molybdenum-bound iodide, it was clearly of interest to investigate whether similar reactivity occurs with compound **2**. Because compound **1** is converted to **2** by treatment with I_2, to avoid unnecessary complications, compound **2** alone was chosen as substrate here. Thus, treatment of a CH_2Cl_2 solution of **2** with I_2 and 1,4-dithiane gave a product which initial NMR analysis showed to contain both the NMe_3 feature and a dithiane group. A single-crystal

(13) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

(14) Sprecher, R. F.; Aufderheide, B. E.; Luther, G. W. III; Carter, J. C. *J. Am. Chem. Soc.* **1974**, *96*, 4404.

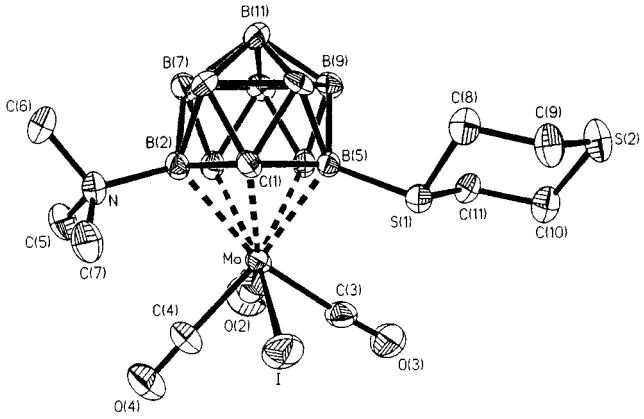


Figure 4. Structure of [2,2,2-(CO)$_3$-2-I-3-NMe$_3$-6-{*cyclo*-1,4-S$_2$(CH$_2$)$_4$}-*closo*-2,1-MoCB$_{10}$H$_9$] (**9**) showing the crystallographic labeling scheme. Selected internuclear distances (Å) and angles (deg): Mo−B(5) 2.353(11), Mo−B(4) 2.354(10), Mo−B(3) 2.387(10), Mo−C(1) 2.404(9), Mo−B(2) 2.452(11), Mo−I 2.8703(11), B(2)−N 1.629(13), B(5)−S(1) 1.924(10); B(5)−Mo−I 94.0(3), C(1)−Mo−I 81.6(2), B(2)−Mo−I 107.3(3), N−B(2)−C(1) 123.2(8), N−B(2)−B(3) 127.3(8), N−B(2)−Mo 116.8(6), C(1)−B(5)−S(1) 123.8(7), B(4)−B(5)−S(1) 124.8(7), S(1)−B(5)−Mo 108.6(5).

X-ray diffraction study established that the product was [2,2,2-(CO)$_3$-2-I-3-NMe$_3$-6-{*cyclo*-1,4-S$_2$(CH$_2$)$_4$}-*closo*-2,1-MoCB$_{10}$H$_9$] (**9**). Retention of the cage NMe$_3$ group in this reaction presents an interesting contrast with the formation of **7** and **8**.

A perspective view of a molecule of **9** is shown in Figure 4. The complex is seen to consist of an {Mo(CO)$_3$I} fragment that is η^5-coordinated to an 8-NMe$_3$-11-{*cyclo*-1,4-S$_2$(CH$_2$)$_4$}-*nido*-7-CB$_{10}$H$_9$ carborane ligand. Both the amine and the thioether substituents are bonded to boron atoms that are in α positions with respect to the cage-carbon atom in the C*B*BB*B* face that ligates molybdenum. The B(2)−N and B(5)−S(1) distances, 1.629(13) and 1.924(10) Å, respectively, are unremarkable. Likewise, the Mo−I separation, 2.8703(11) Å, is quite typical.

Compound **9** may be considered formally to be doubly zwitterionic and as such may be compared with the closely related compounds [2,2,2-(CO)$_3$-2-I-3,11-L$_2$-*closo*-2,1-MoCB$_{10}$H$_9$] (L = thioether or ether)[10] alluded to earlier. In these latter species, however, the substituents are at α and β sites of the carborane C*B*BB*B* belt. Their sequential formation,[10] via a β-monosubstituted cluster complex, contrasts with the formation of **9** from α-monosubstituted **1**. We have observed that when metals are pentahapto coordinated by *nido*-7-CB$_{10}$H$_{11}$ cages, those B−H vertices which are at β sites in the metal ligated CB*B*B*B* ring are activated toward substitution via hydride abstraction (by Me$^+$, H$^+$, etc.)[9,11,15] or via oxidation (by I$_2$).[10] It may be that in metal-coordinated *n*-L-*nido*-7-CB$_{10}$H$_{10}$ carboranes (L = two-electron donor, *n* = 8 or 9), the α B−H vertices in the C*B*BB*B* ring are activated to a second substitution regardless of whether L is attached at an α (*n* = 8, as here) or a β (*n* = 9)[10] boron site.

Spectroscopic data characterizing compound **9** are given in Tables 1 and 2. The ^{1}H and ^{13}C{^{1}H} NMR spectra confirm the presence of both NMe$_3$ and *cyclo*-1,4-S$_2$(CH$_2$)$_4$ groups. A singlet at δ 3.09 (of relative intensity 9) in the ^{1}H NMR spectrum and a peak at δ 58.1 in the ^{13}C{^{1}H} NMR spectrum are assigned to the amine methyl groups. Several multiplets in the range δ ~3.9−2.8 in the ^{1}H NMR spectrum are attributed to the dithiane methylene protons, with four corresponding resonances between δ 42.3 and 26.6 in the ^{13}C{^{1}H} NMR spectrum. In the ^{11}B{^{1}H} NMR spectrum, 10 resonances are seen (some are coincident), in keeping with the cluster asymmetry. Of these, two remain singlets in a fully coupled ^{11}B NMR spectrum, at δ 7.7 and −6.6, and are assigned to the boron atoms bearing the NMe$_3$ and thioether substituents, respectively.

Although compounds **1** and **2** were themselves characterized, and had their identity well supported by the preparation and characterization of several derivatives, the precise nature of their presumed precursor [1-NMe$_3$-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]$^{2-}$ remains unclear. Nevertheless, the existence of the dianionic molybdenum complex is reasonable on the basis of other known metallacarboranes synthesized from [7-NMe$_3$-*nido*-7-CB$_{10}$H$_{10}$]$^{2-}$, for example, [1-NMe$_3$-2,2-(CNBu^t)$_2$-*closo*-2,1-PdCB$_{10}$H$_{10}$], characterized by X-ray diffraction.[16] Indeed, although the carborane dianion [7-NMe$_3$-*nido*-7-CB$_{10}$H$_{10}$]$^{2-}$ has not itself been isolated, that it retains the C−NMe$_3$ linkage during its formation is adequately demonstrated by the observation that oxidative closure of this carborane gives 2-NMe$_3$-*closo*-2-CB$_{10}$H$_{10}$, in which the amine moiety remains bonded to the cage-carbon atom.[2c,17]

Several unsuccessful attempts were made to identify [1-NMe$_3$-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]$^{2-}$ indirectly by making derivatives. An endeavor was made to prepare the neutral complex [2,2,2,2-(CO)$_4$-1-NMe$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$] by oxidizing CO-saturated solutions of the dianion [2,2,2-(CO)$_3$-1-NMe$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]$^{2-}$ with [Fe(η^5-C$_5$H$_5$)$_2$][BF$_4$], but this was unsuccessful. Earlier we have shown[11] that addition of HBF$_4$ to CO-saturated solutions containing the species [2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{11}$]$^{3-}$ affords the monoanion [2,2,2,2-(CO)$_4$-*closo*-2,1-MoCB$_{10}$H$_{11}$]$^-$. However, similar treatment of [1-NMe$_3$-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]$^{2-}$ led only to decomposition.

It was also hoped that addition of suitable cationic metal−ligand fragments to solutions of [1-NMe$_3$-2,2,2-(CO)$_3$-*closo*-2,1-MoCB$_{10}$H$_{10}$]$^{2-}$ would yield bimetallic complexes in which the cationic metal group would be bound to the cage by exopolyhedral B−H→M bonds.[18] If successful, this would produce a species with a uninegative charge and perhaps increase stability. However, no isolable products were obtained from several experiments of this type. Nevertheless, when the salt [Rh(NCMe)$_3$(η^5-C$_5$Me$_5$)][BF$_4$]$_2$ was added to the described molybdenacarborane dianion in 1:1 molar ratio, a product was isolated which ^{1}H NMR spectroscopy revealed

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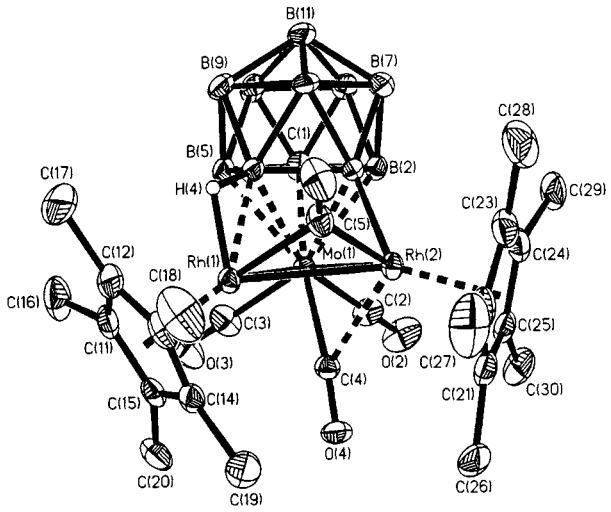

Figure 5. Structure of one of the crystallographically independent molecules of [2,2,2-$(CO)_3$-7-μ-H-2,7,11-{$Rh_2(\mu$-CO)(η^5-$C_5Me_5)_2$}-*closo*-2,1-$MoCB_{10}H_9$] (**10**) showing the crystallographic labeling scheme. Selected internuclear distances (Å) and angles (deg): Mo(1)−C(2) 2.016(4), Mo(1)−C(3) 2.027(5), Mo(1)−C(4) 2.029(4), Mo(1)−B(3) 2.253(4), Mo(1)−B(4) 2.286(4), Mo(1)−B(2) 2.329(4), Mo(1)−C(1) 2.378(4), Mo(1)−B(5) 2.379(4), Mo(1)−Rh(2) 2.7809(5), Mo(1)−Rh(1) 2.8294(6), Rh(1)−C(5) 2.113(4), Rh(1)−B(4) 2.317(4), B(4)−H(4) 1.25(4), H(4)−Rh(1) 1.60(4), Rh(1)−Rh(2) 2.7975(6), Rh(2)−C(5) 1.965(4), Rh(2)−B(3) 2.124(4), Rh(2)−C(4) 2.477(4); B(4)−H(4)−Rh(1) 108(3), Rh(2)−Mo(1)−Rh(1) 59.81(2), Rh(2)−Rh(1)−Mo(1) 59.232(11), C(4)−Rh(2)−Mo(1) 44.95(9), Mo(1)−Rh(2)−Rh(1) 60.957(14), Rh(2)−B(3)−Mo(1) 78.82(14), Mo(1)−B(4)−Rh(1) 75.84(13), O(4)−C(4)−Mo(1) 162.4(3), O(4)−C(4)−Rh(2) 120.6(3), O(5)−C(5)−Rh(2) 142.1(4), O(5)−C(5)−Rh(1) 131.2(3), Rh(2)−C(5)−Rh(1) 86.6(2).

contained two different pentamethylcyclopentadienyl moieties. Accordingly, adjustment of the reactant stoichiometry to 2:1 (Rh/Mo) afforded in reasonable yield a brown trimetal species identified as [2,2,2-$(CO)_3$-7-μ-H-2,7,11-{$Rh_2(\mu$-CO)-(η^5-$C_5Me_5)_2$}-*closo*-2,1-$MoCB_{10}H_9$] (**10**).

The detailed architecture of compound **10** was established by an X-ray diffraction study. The molecule has the structure shown in Figure 5. Two crystallographically independent molecules of **10** are found in each asymmetric fraction of the unit cell. The two are almost identical, and therefore, only one is discussed here. Compound **10** has considerable similarity to the dicarbollide derivatives [1,2-R_2-3,3,3-$(CO)_3$-8-μ-H-3,4,8-{$Rh_2(\mu$-H)(η^5-$C_5Me_5)_2$}-*closo*-3,1,2-$MC_2B_9H_7$] (M = Mo, W; R = H, Me), which are formed from [1,2-R_2-3,3,3-$(CO)_3$-*closo*-3,1,2-$MC_2B_9H_9]^{2-}$ via a parallel synthetic approach, and for which the compound with M = W and R = Me was the subject of X-ray diffraction analysis.[19] In the present compound, the dirhodium fragment {$Rh_2(\mu$-CO)(η^5-$C_5Me_5)_2$} is bonded to two cluster boron atoms and to the molybdenum center. One rhodium-to-boron interaction is a direct sigma bond, with Rh(2)−B(3) 2.124(4) Å, while the other is a B−H⇀Rh agostic-type linkage, with Rh(1)−B(4) 2.317(4), Rh(1)−H(4) 1.60(4), and B(4)−H(4) 1.25(4) Å. These two Rh−B distances are similar to the corresponding values (2.11(2) and 2.39(2) Å, respectively) in the previous tungsten dicarbollide species. Within the triangle of metal atoms, distances are Rh(1)−Rh(2) 2.7975(6), Rh(1)−Mo(1) 2.8294(6), and Rh(2)−Mo(1) 2.7809(5) Å; the corresponding Rh−Rh distance in the tungsten species is rather longer, at 2.859(1) Å. However, in the latter case, the connectivity is hydride bridged, whereas in **10**, a carbonyl ligand bridges the two rhodium atoms. This carbonyl bridge is somewhat asymmetric, with Rh(2)−C(5) (1.965(4) Å) being shorter than Rh(1)−C(5) (2.113(4) Å). Three further carbonyl ligands are bonded to the molybdenum vertex, of which two are approximately linear (Mo(1)−C(2)−O(2) is 179.2(4)°; Mo(1)−C(3)−O(3) is 177.8(4)°), while the third is slightly bent (Mo(1)−C(4)−O(4) is 162.4(3)°). This last carbonyl has partial bridging character, with a long interaction to Rh(2) (Rh(2)···C(4) 2.477(4) Å). A similar situation was observed in the related tungsten species mentioned previously.

Compound **10** may be viewed as being formed via a redox process. The molybdenum(0) center in the precursor is oxidized to molybdenum(+II), with two corresponding one-electron reductions of each of the rhodium centers from +III to +II. This is comparable with the process whereby compounds **1** and **2** are synthesized. However, in the case of **10**, the NMe_3 group is lost during the reaction. Notably, one boron vertex loses a hydride in forming the direct B−Rh σ linkage, while the cage-carbon atom formally gains a hydride after the NMe_3 group is lost. Whether it is the same hydride that is involved in both steps can only be speculated.

Physical and spectroscopic data for compound **10** are given in Tables 1 and 2. In its $^{11}B\{^1H\}$ NMR spectrum, 10 separate resonances are seen, in keeping with the molecular asymmetry. The boron atom that is σ-bonded to rhodium resonates at δ 56.7, while the adjacent boron vertex involved in the B−H⇀Rh linkage gives rise to a signal at δ 29.3. Upon retention of proton coupling, the latter peak is split into a doublet with J(HB) = 70 Hz. All of these parameters are quite typical for these features in such systems.[12] In the related rhodium−molybdenum and −tungsten dicarbollide species alluded to previously, the σ-bonded boron resonates at $\delta(^{11}B)$ ∼35−45, and that of the agostic-type linkage, at $\delta(^{11}B)$ ∼20−25, with corresponding coupling constant J(HB) also ∼70 Hz.[19] In the ^1H NMR spectrum of **10**, the agostic proton is observed as a very broad resonance at rather high field, δ ca. −14, for which no additional coupling information could be resolved. The cage CH proton gives rise to a broad singlet at δ 1.71, while the two C_5Me_5 units are seen as singlets at δ 1.76 and 1.79. These two units also show characteristic resonances in the $^{13}C\{^1H\}$ NMR spectrum, with their contact carbon atoms giving rise to a pair of doublets at δ 106.0 (J(RhC) 4 Hz) and 108.4 (J(RhC) 6 Hz). The cage-carbon atom resonates at δ 44.0, while the three molybdenum-bound carbonyl ligands are seen at typical positions of δ 221.5, 225.1, and 251.1. Of these, the one at highest frequency is assigned as the carbonyl with partial bridging character to rhodium.

Conclusion

The formation of the molybdenacarborane anions in **1** and **2** from their precursor [2,2,2-$(CO)_3$-1-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}]^{2-}$ appears to occur via a process that involves

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both a metal oxidation and an oxidative substitution of a cluster B−H bond, the latter resulting in a transfer of the trimethylamine moiety from the cage-carbon atom to an adjacent boron vertex. Compounds **1** and **2** undergo typical reactions of molybdenacarboranes. The metal-bound halide may be replaced by donor ligands to give neutral, zwitterionic species. With $CNBu^t$ and bromine or iodine, the Mo^{II} center is oxidized to Mo^{IV}, with concomitant replacement of $B-NMe_3$ by B−halide; whereas, by contrast, with iodine and a thioether, a cluster B−H bond is oxidized and replaced by B−thioether.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using Schlenk line techniques. Some subsequent manipulations were performed in the air, where indicated. Solvents were distilled from appropriate drying agents under nitrogen prior to use. Petroleum ether refers to that fraction of boiling point 40−60 °C. Chromatography columns (typically ∼15 cm in length and ∼2 cm in diameter) were packed with silica gel (Acros, 60−200 mesh). NMR spectra were recorded at the following frequencies: ^{1}H 360.1, ^{13}C 90.6, ^{31}P 145.8, and ^{11}B 115.5 MHz. The compounds 7-NMe_3-*nido*-7-$CB_{10}H_{12}$[20] and [{Rh(μ-Cl)Cl(η^5-C_5Me_5)}$_2$][21] were obtained by literature methods; [Mo(CO)$_3$(NCMe)$_2$(PPh_3)][22] was prepared in situ and used without isolation. All other reagents were used as received.

Synthesis of [N(PPh_3)$_2$][2,2,2-(CO)$_3$-2-X-3-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}$] (X = Br, I). (i) The compound 7-NMe_3-*nido*-7-$CB_{10}H_{12}$ (0.73 g, 3.82 mmol) was suspended in THF (20 mL), the mixture was cooled to about −40 °C, and Bu^nLi (3.1 mL, 7.75 mmol, 2.5 M solution in hexanes) was added. The resulting suspension was warmed to −10 °C, and a solution of [Mo(CO)$_3$(NCMe)$_3$] (prepared in situ from [Mo(CO)$_6$] (1.00 g, 3.79 mmol) refluxed in NCMe (20 mL)) was added by cannula. After warming to room temperature and stirring for 1 h, a dark red solution was obtained which was treated with CH_2═$CHCH_2Br$ (0.46 g, 3.80 mmol). The resultant mixture was stirred overnight, and [N(PPh_3)$_2$]Cl (2.18 g, 3.80 mmol) was added. After stirring for a further 3 h, the mixture was filtered and the filtrate slowly evaporated in air to give ∼1.1 g of dark red crystals. The crystals were washed with ice-cold acetone (3 × 20 mL) and dried in vacuo, to give pure [N(PPh_3)$_2$][2-Br-2,2,2-(CO)$_3$-3-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}$] (**1**) (1.02 g).

(ii) Compound **2** was prepared similarly, using I_2 (0.97 g, 3.82 mmol) as oxidizing agent in place of CH_2═$CHCH_2Br$. Following purification by column chromatography, with CH_2Cl_2 as eluant, [N(PPh_3)$_2$][2,2,2-(CO)$_3$-2-I-3-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}$] (**2**) (0.51 g) was isolated as a dark red powder.

Attempted Preparation of [N(PPh_3)$_2$][2-Br-2,2-(CO)$_2$-2-PPh_3-3-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}$]. Following a procedure similar to that by which compound **1** was formed, a suspension of 7-NMe_3-*nido*-7-$CB_{10}H_{12}$ (0.73 g, 3.82 mmol) in THF (20 mL) was treated with Bu^nLi (3.1 mL, 7.75 mmol), followed by an NCMe (20 mL) solution of [Mo(CO)$_3$(NCMe)$_2$(PPh_3)] (3.80 mmol). After 1 h, CH_2═$CHCH_2Br$ (0.46 g, 3.80 mmol) was added and the mixture stirred overnight. Thereafter, [N(PPh_3)$_2$]Cl (2.18 g, 3.80 mmol) was added. The mixture was stirred 3 h and then evaporated in vacuo. The residue was taken up in the minimum volume of CH_2Cl_2 (∼5 mL), filtered through a Celite pad, and applied to the top of a chromatography column. Elution with CH_2Cl_2 gave a yellow fraction that was identified by infrared and multinuclear NMR spectroscopy as the previously reported species [N(PPh_3)$_2$][2,2,2-(CO)$_3$-2-PPh_3-*closo*-2,1-$MoCB_{10}H_{11}$][11] (**3**) (0.35 g, 8%).

Synthesis of [2,2,2-(CO)$_3$-2-L-3-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}$] (L = PPh_3, $CNBu^t$) and [2,2-(CO)$_2$-2-Bu^tC≡CH-3-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}$]. (i) A mixture of compound **1** (0.20 g, 0.20 mmol), PPh_3 (0.08 g, 0.31 mmol), and Tl[PF_6] (0.076 g, 0.22 mmol) was stirred in CH_2Cl_2 (15 mL) for 12 h. After filtration through a Celite pad, solvent was removed in vacuo and the residue taken up in CH_2Cl_2 (∼2 mL) and transferred to a chromatography column. Elution with CH_2Cl_2−petroleum ether (3:1) gave a yellow fraction which, upon evaporation of solvent in vacuo, yielded yellow microcrystals of [2,2,2-(CO)$_3$-2-PPh_3-3-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}$] (**4**) (0.081 g). ^{31}P{^{1}H} NMR: δ 53.2.

(ii) By a similar procedure, using $CNBu^t$ (23 μL, 0.017 g, 0.20 mmol) in place of PPh_3, yellow microcrystals of [2-$CNBu^t$-2,2,2-(CO)$_3$-3-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}$] (**5**) (0.064 g) were obtained.

(iii) Similarly, reaction of **1** with Tl[PF_6] in the presence of Bu^tC≡CH (70 μL, 0.047 g, 0.57 mmol) afforded purple microcrystalline [2-Bu^tC≡CH-2,2-(CO)$_2$-3-NMe_3-*closo*-2,1-$MoCB_{10}H_{10}$] (**6**) (0.075 g).

Synthesis of [2,2,2,2-($CNBu^t$)$_4$-2-Br-3-X-*closo*-2,1-$MoCB_{10}H_{10}$] (X = Br, I). (i) To a CH_2Cl_2 (40 mL) solution of **1** (0.40 g, 0.40 mmol) was added $CNBu^t$ (0.19 mL, 0.14 g, 1.68 mmol) followed by Br_2 (0.065 g, 0.41 mmol). The solution was stirred for 2 h, and the solvent was allowed to evaporate in air. The residue was taken up in CH_2Cl_2 (∼2 mL) and chromatographed. Elution with CH_2Cl_2−petroleum ether (2:1), followed by evaporation of the solvent in air, gave orange microcrystals of [2,2,2,2-($CNBu^t$)$_4$-2,3-Br_2-*closo*-2,1-$MoCB_{10}H_{10}$] (**7**) (0.123 g).

(ii) Similarly, reaction of **1** (0.10 g, 0.10 mmol) with $CNBu^t$ (45 μL, 0.033 g, 0.40 mmol) and I_2 (0.026 g, 0.10 mmol) yielded orange microcrystalline [2,2,2,2-($CNBu^t$)$_4$-2-Br-3-I-*closo*-2,1-$MoCB_{10}H_{10}$] (**8**) (0.033 g).

Synthesis of [2,2,2-(CO)$_3$-2-I-3-NMe_3-6-{*cyclo*-1,4-$S_2(CH_2)_4$}-*closo*-2,1-$MoCB_{10}H_9$]. Iodine (0.074 g, 0.29 mmol) was added to a mixture of compound **2** (0.30 g, 0.29 mmol) and 1,4-dithiane (0.035 g, 0.29 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 12 h, and then solvent was removed in vacuo. The residue was redissolved in the minimum amount of CH_2Cl_2 (∼2 mL) and chromatographed. Elution with CH_2Cl_2−petroleum ether (3:1) removed a red fraction which, upon evaporation of solvent in vacuo and crystallization from CH_2Cl_2−petroleum ether, yielded red crystals of [2,2,2-(CO)$_3$-2-I-3-NMe_3-6-{*cyclo*-1,4-$S_2(CH_2)_4$}-*closo*-2,1-$MoCB_{10}H_9$] (**9**) (0.084 g).

Synthesis of [2,2,2-(CO)$_3$-7-μ-H-2,7,11-{Rh_2(μ-CO)(η^5-C_5Me_5)$_2$}-*closo*-2,1-$MoCB_{10}H_9$]. The carborane 7-NMe_3-*nido*-7-$CB_{10}H_{12}$ (0.24 g, 1.25 mmol) was suspended in THF (30 mL) at ca. −40 °C, and Bu^nLi (1.0 mL, 2.5 mmol) was added. The suspension was stirred and warmed to ca. −10 °C before solid [Mo(CO)$_4$(piperidine)$_2$] (0.47 g, 1.24 mmol) was added. After stirring for 2 h at room temperature, a filtered solution of [Rh(NCMe)$_3$(η^5-C_5Me_5)][BF_4]$_2$ (prepared in situ from [{Rh(μ-Cl)Cl(η^5-C_5Me_5)}$_2$] (0.80 g, 1.3 mmol) and Ag[BF_4] (1.0 g, 5.14 mmol) in NCMe (10 mL)) was added to the reaction mixture by syringe. The resultant mixture was stirred for a further 2 h. Solvent was removed in vacuo and the residue chromatographed. Elution with CH_2Cl_2−petroleum ether (3:2) gave a brown fraction from which solvent was removed in vacuo. Crystallization from CH_2Cl_2−petroleum ether yielded dark

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Table 3. Crystallographic Data for **1**, **6**, **7**, **9**·CH_2Cl_2 and **10**

	1	**6**	**7**	**9**·CH_2Cl_2	**10**
formula	$C_{43}H_{49}B_{10}BrMoN_2O_3P_2$	$C_{12}H_{29}B_{10}MoNO_2$	$C_{21}H_{46}B_{10}Br_2MoN_4$	$C_{12}H_{28}B_{10}Cl_2IMoNO_3S_2$	$C_{25}H_{40}B_{10}MoO_4Rh_2$
fw	987.73	423.40	718.48	700.31	814.43
space group	*Cmca*	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a, Å	26.998(2)	8.9100(9)	11.0575(9)	12.5499(7)	20.368(3)
b, Å	17.926(2)	25.796(2)	12.304(1)	24.115(3)	15.829(3)
c, Å	18.963(2)	9.0850(5)	14.726(2)	9.4584(6)	21.202(4)
α, deg			93.883(9)		
β, deg		98.749(6)	103.008(9)	111.609(5)	113.713(3)
γ, deg			114.451(7)		
V, Å^3	9177(1)	2063.8(3)	1747.5(3)	2661.3(4)	6259(2)
Z	8	4	2	4	8
ρ_{calc}, g cm^{-3}	1.444	1.363	1.365	1.748	1.729
T, K	293	173	293	293	173
μ(Mo Kα), cm^{-1}	12.80	6.41	26.80	20.27	14.69
wR2 (all data), R1[a]	0.1098, 0.0533	0.0566, 0.0235	0.0893, 0.0419	0.1197, 0.0508	0.0864, 0.0350

[a] Refinement was block full-matrix least-squares on all F^2 data: $wR2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum w(F_o^2)^2]^{1/2}$; $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 4\sigma(F_o)$.

brown crystals of [2,2,2-$(CO)_3$-7-μ-H-2,7,11-{$Rh_2(\mu$-CO)(η^5-$C_5Me_5)_2$}-*closo*-2,1-$MoCB_{10}H_9$] (**10**) (0.20 g).

Structure Determinations. Experimental data for compounds **1**, **6**, **7**, **9** and **10** are recorded in Table 3. Diffracted intensities for **1**, **6**, **7** and **9** were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα X-radiation ($\lambda = 0.71073$ 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 numerical (**1**, **7**, and **9**) or semi-empirical (**6**) absorption corrections based on the measurements of the various crystal faces or azimuth scans of ψ data, respectively, were applied.

Low-temperature X-ray intensity data for **10** were collected on a Siemens SMART CCD area-detector three-circle diffractometer using Mo Kα X-radiation. For four settings of φ, narrow data "frames" were collected for 0.3° increments of ω. Almost a full sphere of data was obtained. The substantial redundancy in data allowed empirical absorption corrections (SADABS)[23] to be applied using multiple measurements of equivalent reflections. The data frames were integrated using SAINT.[23]

The 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.[24,25] 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 acetylene hydrogen [H(4a)] in **6** and the agostic B−H→Rh hydrogens [H(4) and H(34)] in **10** were located in difference Fourier syntheses; their positional parameters were refined with fixed isotropic thermal parameters [U_{iso}(H) = 1.2 × U_{iso}(parent)]. The remaining hydrogen atoms were included in calculated positions and allowed to ride on their parent atoms with fixed isotropic thermal parameters [U_{iso}(H) = 1.2 × U_{iso}(parent), or U_{iso}(H) = 1.5 × U_{iso}(C) for methyl hydrogens].

The anionic unit of **1** is bisected by a crystallographic mirror plane (Wyckoff positions 8*f*) which contains the Mo atom, two carbonyl ligands [C(2), O(2), C(3), and O(3)], the nitrogen and one methyl group of the trimethylamine substituent [N(1) and C(6)], and several cage boron atoms [B(2), B(8), and B(11)]. The remaining carbonyl ligand [C(4) and O(4)] along with the Br atom are disordered across this mirror in general positions (16*e*), each refined with one-half occupancy. This disorder is the likely cause of the unusually short Mo−C(4) and unusually long Mo−Br and C(4)−O(4) distances determined in this experiment. Unfortunately, the crystallographically imposed mirror does not correspond to a true molecular mirror, making the assignment of the cage-carbon atom from X-ray data ambiguous. In this regard, the location of this atom was assigned on the basis of NMR spectroscopic information and by analogy with compound **6**. Thus, the cage-carbon atom and its symmetry related boron atom [B(3)] were included in disordered general positions (16*e*), and each refined with one-half occupancy. The nitrogen atom of the $[N(PPh_3)_2]^+$ cation was located at Wyckoff position 8*e* ($^3/_4$, $-y + {}^1/_2$, $^3/_4$) with full occupancy.

The coordinating $\overline{CBBBB}$ face (including the α-substituted Br) of the carborane cage in **7** was disordered around a pseudo 2-fold rotation axis which bisects the ring through B(3) and the C(1)−B(5) bond. The atoms of the major and minor component ring systems were restrained to equivalent positions, and respective occupancies were refined in parts to 96.4% and 3.6%. The Br(2A)−B(2A) distance was fixed at 2.00(2) Å. Also, the methyl groups on one of the $CNBu^t$ ligands were disordered by a 63° rotation about the C(11)−N(10) bond axis. The major and minor components were refined in parts, including hydrogen atoms, with occupancies of 56.9% and 43.1%, respectively.

Compound **9** cocrystallized with a molecule of dichloromethane in the asymmetric unit. The solvent molecule was fully ordered and refined without restraint; hydrogen atoms were included in calculated positions. Small residual density peaks (<2.0 e Å^{-3}) near the positions of the heavy metal atoms in the final difference map of compound **10** indicate an inability to completely correct for X-ray absorption effects on poorly formed, irregularly shaped crystals.

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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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