

Unprecedented Cage-Carbon to Cage-Boron NMe₃ Transfer in a Monocarbon Molybdenacarborane[†]

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The reagent Li₂[7-NMe₃-*nido*-7-CB₁₀H₁₀] reacts with [Mo(CO)₃(NCMe)₃] in THF–NCMe (THF = tetrahydrofuran) to give a molybdenacarborane intermediate which, upon oxidation by CH₂=CHCH₂Br or I₂ and then addition of [N(PPh₃)₂]-Cl, gives the salts [N(PPh₃)₂][2,2,2-(CO)₃-2-X-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (X = Br (**1**) or I (**2**)). During the reaction, the cage-bound NMe₃ 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(η⁵-C₅Me₅)](BF₄)₂ is used as the oxidizing agent, the trimetallic compound [2,2,2-(CO)₃-7-μ-H-2,7,11-{Rh₂(μ-CO)(η⁵-C₅Me₅)₂}-*closo*-2,1-MoCB₁₀H₉] (**10**) is formed, the NMe₃ group being lost. Reaction of **1** in CH₂Cl₂ with Ti[PF₆] in the presence of donor ligands L affords neutral zwitterionic compounds [2,2,2-(CO)₃-2-L-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] for L = PPh₃ (**4**) or CNBu^t (**5**), and [2-Bu^tC≡CH-2,2-(CO)₂-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (**6**) when L = Bu^tC≡CH. When **1** is treated with CNBu^t and X₂, the metal center is oxidized, and in the products obtained, [2,2,2,2-(CNBu^t)₄-2-Br-3-X-*closo*-2,1-MoCB₁₀H₁₀] (X = Br (**7**), I (**8**)), the B–NMe₃ bond is replaced by B–X. In contrast, treatment of **2** with I₂ and *cyclo*-1,4-S₂(CH₂)₄ in CH₂Cl₂ results in oxidative substitution of the cluster and retention of the NMe₃ group, giving [2,2,2-(CO)₃-2-I-3-NMe₃-6-{*cyclo*-1,4-S₂(CH₂)₄}-*closo*-2,1-MoCB₁₀H₉] (**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*-7-CB₁₀H₁₁]³⁻ had until recently received relatively little attention compared with the wealth of information available on the corresponding complexes of the dicarbollide ligand [*nido*-7,8-C₂B₉H₁₁]²⁻ and its derivatives.¹ The carboranes 7-NR₃-*nido*-7-CB₁₀H₁₂ (R = H, alkyl)² are also precursors to monocarbollide metal complexes, affording species containing the C-amine and -amino ligands [7-NR₃-*nido*-7-CB₁₀H₁₀]²⁻ and [7-NR₂-*nido*-7-CB₁₀H₁₀]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-NR₃-*nido*-7-CB₁₀H₁₂ (NR₃ = NMe₃, NH₂Bu^t, NMe₂Bu^t) all react with [Ru₃(CO)₁₂] in toluene at reflux temperatures to yield the cluster compounds [1-NR₃-2,2-(CO)₂-7,11-(μ-H)₂-2,7,11-{Ru₂(CO)₆}-*closo*-2,1-RuCB₁₀H₈],⁴ the *nido*-carboranes show some variation in their reactivity with [RhCl(PPh₃)₃] for different groups R.⁵ In methanolic KOH solution, 7-NH₃-*nido*-7-CB₁₀H₁₂ reacts with [RhCl(PPh₃)₃] to give salts of [1-NH₂-2,2-(PPh₃)₂-2-

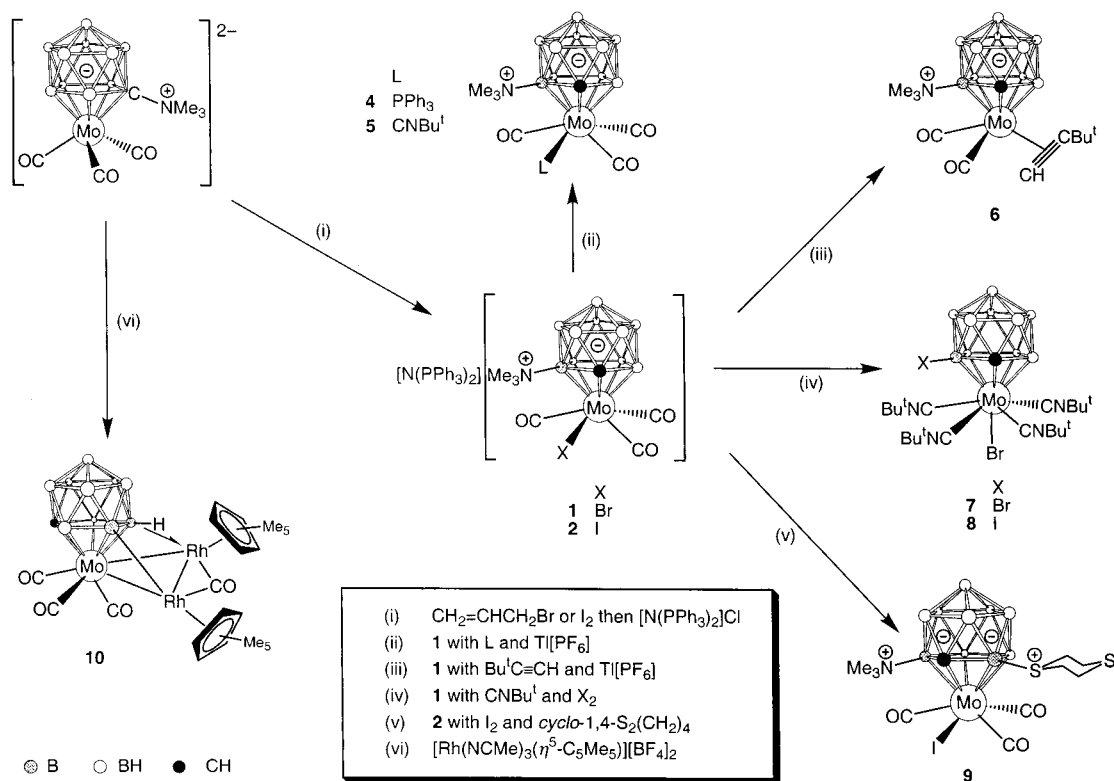
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[†] The new compounds described in this paper are based on icosahedral *closo*-1-carba-2-molybdenadodecaborane frameworks, and although all are chiral, they here occur as racemates. The substituted boron vertices that herein are numbered 3, 6, 7, and 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-RhCB₁₀H₁₀]⁻, of which the [Buⁿ₄N]⁺ salt is converted in refluxing methanol to the dimeric species [Buⁿ₄N]-[2,2'-μ-H-{1,2'-μ-NH₂-2-PPh₃-*closo*-2,1-RhCB₁₀H₁₀}₂]⁻.^{5a} In contrast, the carbaborane 7-NMe₃-*nido*-7-CB₁₀H₁₂ with the same rhodium reagent in refluxing methanol yields primarily 18-electron [1-NMe₃-2,7-(PPh₃)₂-2-H-2-Cl-*closo*-2,1-RhCB₁₀H₉], along with 16-electron [1-NMe₃-2-PPh₃-2-Cl-*closo*-2,1-RhCB₁₀H₁₀].^{5b} Moreover, 7-NH₂Bu^t-*nido*-7-CB₁₀H₁₂ reacts with [RhX(PPh₃)₃] (X = Cl or Br) in refluxing toluene to give 16-electron [1-NH₂Bu^t-2-PPh₃-2-X-*closo*-2,1-RhCB₁₀H₁₀] as the only products.^{5c}

These differences in reactivity of the carbaboranes 7-NR₃-*nido*-7-CB₁₀H₁₂ toward [RhX(PPh₃)₃] have led us to explore their behavior in reactions with other transition-metal systems. We have recently reported⁶ the synthesis of the monoanionic molybdenum carbaborane salt [N(PPh₃)₂][1,2-μ-NHBu^t-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀], 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-MoCB₁₀H₁₀]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-MoC₂B₉H₁₁]²⁻.⁷ In concert

with that work, we attempted to prepare another analogue of the latter anion, namely the dianionic molybdenum carbaborane [2,2,2-(CO)₃-1-NMe₃-*closo*-2,1-MoCB₁₀H₁₀]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 NMe₃ 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-MoC₂B₉H₁₁]²⁻ has previously been used to prepare [3-(η³-C₃H₅)-3,3-(CO)₂-*closo*-3,1,2-MoC₂B₉H₁₁]⁻ by reaction with CH₂=CHCH₂Br.⁸ Employing an ostensibly parallel monocarbollide system, we planned to treat a THF solution of [7-NMe₃-*nido*-7-CB₁₀H₁₀]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-NMe₃-*closo*-2,1-MoCB₁₀H₁₀]²⁻. However, the latter in reaction with CH₂=CHCH₂Br did not afford the anticipated anion [1-NMe₃-2-(η³-C₃H₅)-2,2-(CO)₂-*closo*-2,1-MoCB₁₀H₁₀]⁻. Instead, the product isolated following addition of [N(PPh₃)₂]Cl was [N(PPh₃)₂][2-Br-2,2,2-(CO)₃-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (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 NMe₃ group that had been bonded to the cage-carbon atom has transferred to an adjacent boron atom (B_α) in the CBBBB belt that ligates the molybdenum vertex.

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Table 1. Analytical and Physical Data

cmpd	color	yield/%	$\nu_{\max}(\text{CO})^a/\text{cm}^{-1}$	anal./% ^b		
				C	H	N
[N(PPh ₃) ₂][2-Br-2,2,2-(CO) ₃ -3-NMe ₃ - <i>closo</i> -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 - <i>closo</i> -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 - <i>closo</i> -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 - <i>closo</i> -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-2,2,2-(CO) ₃ -3-NMe ₃ - <i>closo</i> -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 - <i>closo</i> -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- <i>closo</i> -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-{ <i>cyclo</i> -1,4-S ₂ (CH ₂) ₄ }- <i>closo</i> -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 }- <i>closo</i> -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 CH₂Cl₂; 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 CH₂Cl₂. ^e $\nu_{\max}(\text{N}\equiv\text{C})$.

Table 2. ¹H, ¹³C, and ¹¹B 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 \times 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 \times 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, $J(\text{PC}) = 8$), 232.7 (d, CO, $J(\text{PC}) = 31$), 230.3 (d, CO, $J(\text{PC}) = 33$), 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 \times 3), 153.9 (t, CN, $J(\text{NC}) = 18$), 60.8 (CMe ₃), 57.1 (NMe ₃), 54.7 (br, cage C), 30.3 (CMe 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 \times 2), 223.3 (C≡CH), 175.0 (C≡CBu ^t), 57.6 (br, cage C), 56.9 (NMe ₃), 41.6 (CMe ₃), 31.3 (CMe 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 (CMe ₃), 29.8 (CMe 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 (CMe ₃), 29.5 (CMe 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 \times 3), 58.1 (NMe ₃), 57.8 (br, cage C), 42.3, 40.2, 27.3, 26.6 (CH ₂ \times 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 \times 2, 15H \times 2, C ₅ Me ₅ \times 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 \times 3), 108.4 (d, C ₅ Me ₅ , $J(\text{RhC}) = 4$), 106.0 (d, C ₅ Me ₅ , $J(\text{RhC}) = 6$), 44.0 (br, cage C), 9.8, 9.3 (s \times 2, Me \times 2)	56.7 (1B, B–Rh), 29.3 (1B, B–H→Rh, $J(\text{HB}) = 70$), -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 CD₂Cl₂. ^b Resonances for terminal BH protons occur as broad unresolved signals in the range δ ca. -1 to +3. ^c ¹H-decoupled chemical shifts are positive to high frequency of SiMe₄. ^d ¹H-decoupled chemical shifts are positive to high frequency of BF₃·Et₂O (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(PPh₃)₂]⁺

cation (confirmed by ³¹P{¹H} NMR), the only significant features of the ¹H and ¹³C{¹H} NMR spectra were resonances attributable to the NMe₃ substituent and three inequivalent

Mo-bound carbonyl ligands. Integration of the ¹H NMR spectrum indicated one cation per NMe₃ 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(PPh₃)₂][2-Br-2,2,2-(CO)₃-1-NMe₃-*closo*-2,1-MoCB₁₀H₁₀], with the NMe₃ 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 NMe₃ group lying across a crystallographic mirror plane and with the carborane ligand therefore having apparent crystallographic mirror symmetry. However, in the ¹¹B{¹H} NMR spectrum of **1**, 10 separate resonances are seen (some are coincident), of which one signal remained a singlet in a fully coupled ¹¹B 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 NMe₃ 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 δ ~3.03 in the ¹H 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-NMe₃ or the 7-NMe₃ 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-NMe₃-*nido*-7-CB₁₀H₁₀ 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(PPh₃)₂][2,2,2-(CO)₃-2-I-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (**2**) could be obtained by using I₂ instead of CH₂=CHCH₂Br 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 NMe₃ proton resonance at δ 3.06. The ¹¹B{¹H} NMR spectrum again reveals a resonance at δ 8.1, assigned to the B–NMe₃ group as it remains a singlet in a fully coupled ¹¹B NMR spectrum. Unfortunately, **2** also failed to yield crystals suitable for an accurate X-ray analysis. Isolated yields of **1** and **2** were low.

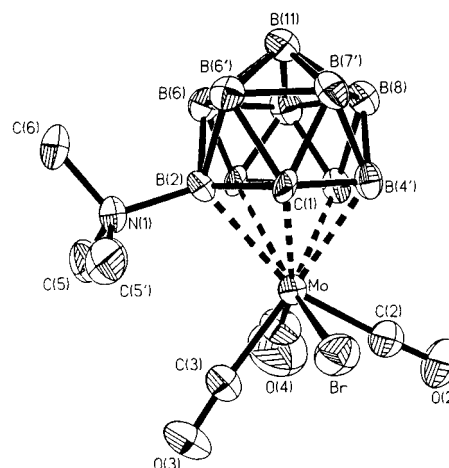


Figure 1. Structure of the anion of [N(PPh₃)₂][2-Br-2,2,2-(CO)₃-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (**1**) showing the crystallographic labeling scheme. In this and in Figures 2–5, thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity except where chemically 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)^{iv}–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): $-x + 1, y, z$.

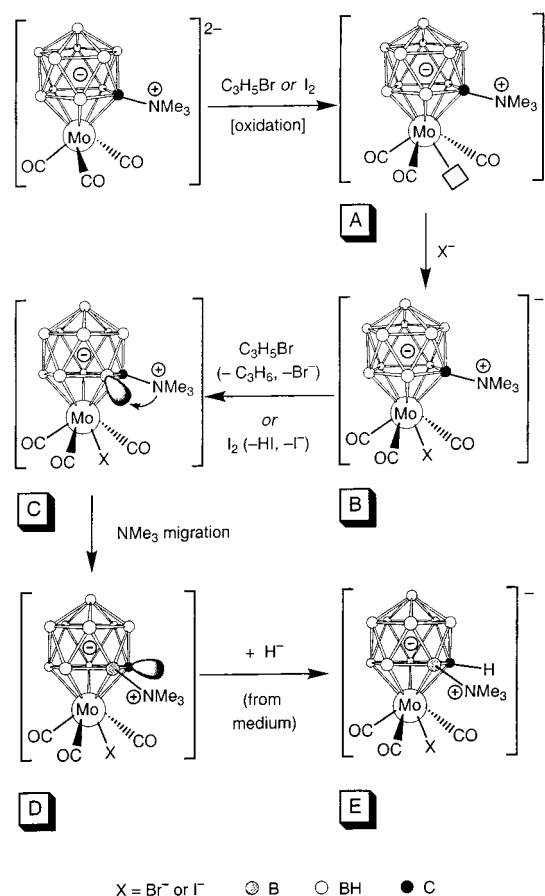
Evidently, side reactions occur, but formation of other identifiable molybdenacarborane products was not observed.

Unresolved at present is the manner by which the NMe₃ 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 Mo⁰ dianion with allyl bromide or iodine would afford the electronically unsaturated neutral Mo^{II} species [1-NMe₃-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀] (**A**) together with halide. The latter would ligate the metal center to form the saturated anionic complex [1-NMe₃-2,2,2-(CO)₃-2-X-*closo*-2,1-MoCB₁₀H₁₀][–] (**B**). In the next step affording **C**, iodine or allyl bromide abstracts H[–] from a cage BH^{δ–} vertex, thereby creating a vacant site on a boron atom adjacent to the CNMe₃ unit, causing the NMe₃ 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-(CO)₄-*closo*-2,1-MoCB₁₀H₁₁][–] with iodine in THF which gives [2,2,2-(CO)₃-2-I-7-{O(CH₂)₄}-*closo*-2,1-MoCB₁₀H₁₀][–]. 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 NMe₃ migration. That this does not occur might suggest an intramolecular three-

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Scheme 2



center C–N–B mechanism for transfer of the NMe₃ moiety rather than the amine's ability to displace a THF molecule, otherwise a species having both CNMe₃ and BO(CH₂)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(PPh₃)] instead of [Mo(CO)₃(NCMe)₃], it was anticipated that [N(PPh₃)₂][2-Br-2,2-(CO)₂-2-PPh₃-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀], a product analogous to **1**, might be obtained. However, the only product isolated after chromatographic workup was the known molybdenum complex [N(PPh₃)₂][2,2,2-(CO)₃-2-PPh₃-*closo*-2,1-MoCB₁₀H₁₁] (**3**),¹¹ identified spectroscopically. It is not possible to say whether a B–NMe₃ species analogous to **1** is formed and subsequently decomposes, or if this reaction follows a different route whereby the NMe₃ unit is simply lost.

Treatment of compound **1** with Tl[PF₆] and ligands L results in TlBr elimination and formation of the neutral, zwitterionic complexes [2,2,2-(CO)₃-2-L-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] for L = PPh₃ (**4**) or CNBu^t (**5**) and the species [2-Bu^tC≡CH-2,2-(CO)₂-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (**6**) when L = Bu^tC≡CH. Data characterizing compounds **4–6** are given in Tables 1 and 2. For all three products, the ¹¹B{¹H} NMR spectra show 10 resonances (some coincide),

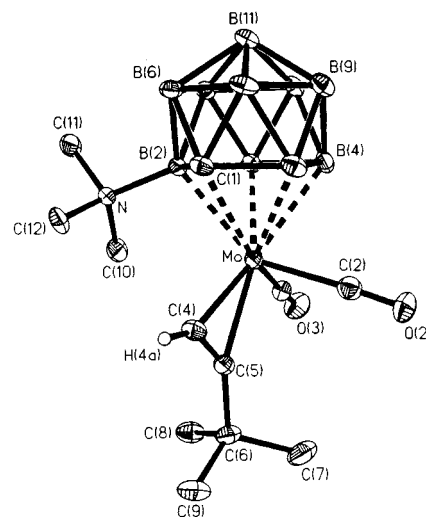


Figure 2. Structure of [2-Bu^tC≡CH-2,2-(CO)₂-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (**6**) showing the crystallographic labeling scheme. Selected internuclear distances (Å) and angles (deg): Mo–C(3) 1.995(3), Mo–C(2) 2.002(3), Mo–C(4) 2.044(3), Mo–C(5) 2.104(2), Mo–B(5) 2.357(3), Mo–C(1) 2.385(2), Mo–B(4) 2.396(3), 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 NMe₃ group. In the ¹H and ¹³C{¹H} NMR spectra for **4–6**, peaks due the NMe₃ 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 δ (¹H) 1.63 (**4**), 2.70 (**5**), and 4.38 (**6**), and at δ (¹³C) 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*-7-CB₁₀H₁₁]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 NMe₃ group is attached to a cage-boron

atom in an α position in the CBBBB face of the carborane ligand. Thus, the site of NMe₃ 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≡CH, whose contact-carbon atoms are bonded to the metal center at distances Mo–C(4) 2.044(3) and Mo–C(5)

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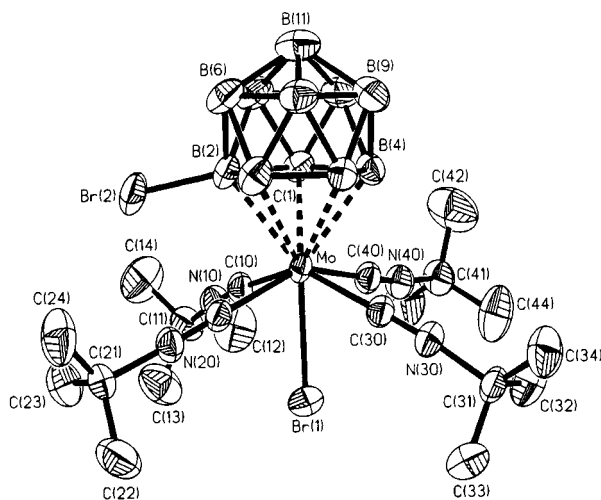


Figure 3. Structure of [2,2,2,2-(CNBu^t)₄-2,3-Br₂-closo-2,1-MoCB₁₀H₁₀] (**7**) showing the crystallographic labeling scheme. Selected internuclear distances (Å) and angles (deg): Mo–B(3) 2.368(5), Mo–B(4) 2.392(5), Mo–B(2) 2.408(5), Mo–B(5) 2.462(5), Mo–C(1) 2.469(5), Mo–Br(1) 2.6873(7), B(2)–Br(2) 2.003(5); 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 ¹³C{¹H} NMR spectrum, the ligated carbon atoms resonate at δ 175.0 and 223.3.¹³ In the related molybdenum complex [N(PPh₃)₂][2-Bu^tC≡CH-2,2-(CO)₂-closo-2,1-MoCB₁₀H₁₁], 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-(CO)₄-closo-2,1-MoCB₁₀H₁₁][−] and [1,2-μ-NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀][−], upon treatment with I₂ and CNBu^t, are oxidized to Mo^{IV} species [2,2,2,2-(CNBu^t)₄-2-I-closo-2,1-MoCB₁₀H₁₁]¹⁰ and [1,2-μ-NHBu^t-2,2,2-(CNBu^t)₃-2-I-closo-2,1-MoCB₁₀H₁₀]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, CH₂Cl₂ solutions of compound **1** were treated with both Br₂ and I₂ in the presence of CNBu^t. Simplistically, it was expected that the product obtained might be of general formulation [2,2,2-(CNBu^t)₃-2-X-2-Y-3-NMe₃-closo-2,1-MoCB₁₀H₁₀] (X, Y = Br or I). In practice, however, the boron-bound NMe₃ unit is lost in the reaction, and the products isolated are [2,2,2,2-(CNBu^t)₄-2-Br-3-X-closo-2,1-MoCB₁₀H₁₀] (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 CBBBB ring that is bonded to molybdenum, with B(2)–Br(2) 2.003(5) Å. It may reason-

ably be assumed that it is this boron atom which formerly carried the NMe₃ substituent. Thus, the molybdenum atom is η⁵-coordinated on one side by an 8-Br-*nido*-7-CB₁₀H₁₀ 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-(CNBu^t)₄-2-I-closo-2,1-MoCB₁₀H₁₁]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-(CNBu^t)₄-2-X-closo-2,1-MoCB₁₀H₁₁] (X = Br, I).¹⁰ In both the ¹H and ¹³C{¹H} NMR spectra of **7** and **8**, signals for an NMe₃ 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 ¹³C{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 ¹¹B{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 micro-analytical data serves to confirm the identity of the halogens present in compound **8**.

Whereas the anion [2,2,2,2-(CO)₄-closo-2,1-MoCB₁₀H₁₁][−] with I₂ and CNBu^t undergoes metal oxidation, as mentioned previously, the same anion reacts with I₂ and thioethers L to give cage-substituted products [2,2,2-(CO)₃-2,3-μ-I-*n*-L-closo-2,1-MoCB₁₀H₉] (*n* = 7, 11) and [2,2,2-(CO)₃-2-I-3,11-L₂-closo-2,1-MoCB₁₀H₉].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 I₂, to avoid unnecessary complications, compound **2** alone was chosen as substrate here. Thus, treatment of a CH₂Cl₂ solution of **2** with I₂ and 1,4-dithiane gave a product which initial NMR analysis showed to contain both the NMe₃ feature and a dithiane group. A single-crystal

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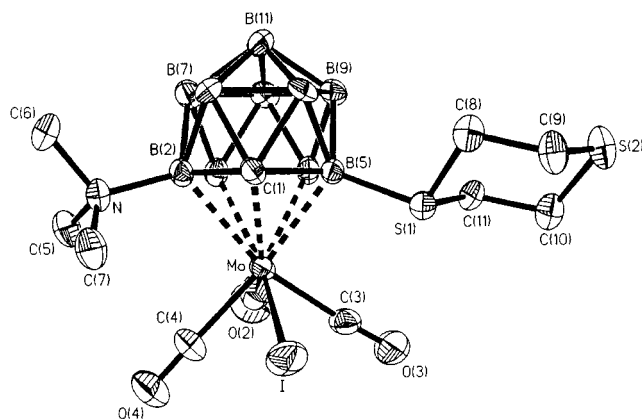


Figure 4. Structure of [2,2,2-(CO)₃-2-I-3-NMe₃-6-{*cyclo*-1,4-S₂(CH₂)₄}-*closo*-2,1-MoCB₁₀H₉] (**9**) showing the crystallographic labeling scheme. Selected internuclear distances (Å) and angles (deg): Mo–B(5) 2.353(11), Mo–B(4) 2.354(10), Mo–B(3) 2.387(10), Mo–C(1) 2.404(9), Mo–B(2) 2.452(11), Mo–I 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-NMe₃-6-{*cyclo*-1,4-S₂(CH₂)₄}-*closo*-2,1-MoCB₁₀H₉] (**9**). Retention of the cage NMe₃ 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)₃I} fragment that is η⁵-coordinated to an 8-NMe₃-11-{*cyclo*-1,4-S₂(CH₂)₄}-*nido*-7-CB₁₀H₉ 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 CBBBB 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-L₂-*closo*-2,1-MoCB₁₀H₉] (L = thioether or ether)¹⁰ alluded to earlier. In these latter species, however, the substituents are at α and β sites of the carborane CBBBB 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-CB₁₀H₁₁ cages, those B–H vertices which are at β sites in the metal ligated CBBBB ring are activated toward substitution via hydride abstraction (by Me⁺, H⁺, etc.)^{9,11,15} or via oxidation (by I₂).¹⁰ It may be that in metal-coordinated *n*-L-*nido*-7-CB₁₀H₁₀ carboranes (L = two-electron donor, *n* = 8 or 9), the α B–H vertices in the CBBBB 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 ¹H and ¹³C{¹H} NMR spectra confirm the presence of both NMe₃ and *cyclo*-1,4-S₂(CH₂)₄ groups. A singlet at δ 3.09 (of relative intensity 9) in the ¹H NMR spectrum and a peak at δ 58.1 in the ¹³C{¹H} NMR spectrum are assigned to the amine methyl groups. Several multiplets in the range δ ~3.9–2.8 in the ¹H NMR spectrum are attributed to the dithiane methylene protons, with four corresponding resonances between δ 42.3 and 26.6 in the ¹³C{¹H} NMR spectrum. In the ¹¹B{¹H} NMR spectrum, 10 resonances are seen (some are coincident), in keeping with the cluster asymmetry. Of these, two remain singlets in a fully coupled ¹¹B NMR spectrum, at δ 7.7 and –6.6, and are assigned to the boron atoms bearing the NMe₃ 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-NMe₃-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀]²⁻ remains unclear. Nevertheless, the existence of the dianionic molybdenum complex is reasonable on the basis of other known metallacarboranes synthesized from [7-NMe₃-*nido*-7-CB₁₀H₁₀]²⁻, for example, [1-NMe₃-2,2-(CNBu)₂-*closo*-2,1-PdCB₁₀H₁₀], characterized by X-ray diffraction.¹⁶ Indeed, although the carborane dianion [7-NMe₃-*nido*-7-CB₁₀H₁₀]²⁻ has not itself been isolated, that it retains the C–NMe₃ linkage during its formation is adequately demonstrated by the observation that oxidative closure of this carborane gives 2-NMe₃-*closo*-2-CB₁₀H₁₀, in which the amine moiety remains bonded to the cage-carbon atom.^{2c,17}

Several unsuccessful attempts were made to identify [1-NMe₃-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀]²⁻ indirectly by making derivatives. An endeavor was made to prepare the neutral complex [2,2,2-(CO)₄-1-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] by oxidizing CO-saturated solutions of the dianion [2,2,2-(CO)₃-1-NMe₃-*closo*-2,1-MoCB₁₀H₁₀]²⁻ with [Fe(η⁵-C₅H₅)₂][BF₄], but this was unsuccessful. Earlier we have shown¹¹ that addition of HBF₄ to CO-saturated solutions containing the species [2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₁]³⁻ affords the monoanion [2,2,2-(CO)₄-*closo*-2,1-MoCB₁₀H₁₁]⁻. However, similar treatment of [1-NMe₃-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀]²⁻ led only to decomposition.

It was also hoped that addition of suitable cationic metal–ligand fragments to solutions of [1-NMe₃-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀]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(η⁵-C₅Me₅)] [BF₄]₂ was added to the described molybdenacarborane dianion in 1:1 molar ratio, a product was isolated which ¹H NMR spectroscopy revealed

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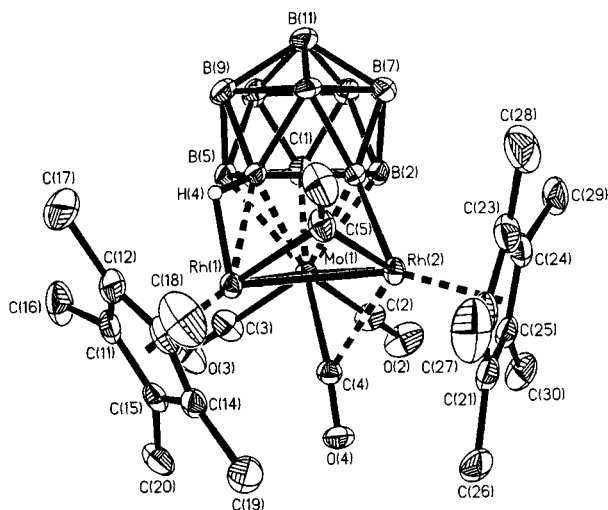


Figure 5. Structure of one of the crystallographically independent molecules of [2,2,2-(CO)₃-7- μ -H-2,7,11-{Rh₂(μ -CO)(η^5 -C₅Me₅)₂}-*closo*-2,1-MoCB₁₀H₉] (**10**) showing the crystallographic labeling scheme. Selected internuclear distances (Å) and angles (deg): Mo(1)–C(2) 2.016(4), Mo(1)–C(3) 2.027(5), 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 binuclear species identified as [2,2,2-(CO)₃-7- μ -H-2,7,11-{Rh₂(μ -CO)(η^5 -C₅Me₅)₂}-*closo*-2,1-MoCB₁₀H₉] (**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-R₂-3,3,3-(CO)₃-8- μ -H-3,4,8-{Rh₂(μ -H)(η^5 -C₅Me₅)₂}-*closo*-3,1,2-MC₂B₉H₇] (M = Mo, W; R = H, Me), which are formed from [1,2-R₂-3,3,3-(CO)₃-*closo*-3,1,2-MC₂B₉H₉]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 {Rh₂(μ -CO)(η^5 -C₅Me₅)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 NMe₃ 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 NMe₃ 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 ¹¹B{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 $J(\text{HB}) = 70$ 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 $\delta(^{11}\text{B}) \sim 35$ –45, and that of the agostic-type linkage, at $\delta(^{11}\text{B}) \sim 20$ –25, with corresponding coupling constant $J(\text{HB})$ 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 C₅Me₅ units are seen as singlets at δ 1.76 and 1.79. These two units also show characteristic resonances in the ¹³C{¹H} NMR spectrum, with their contact carbon atoms giving rise to a pair of doublets at δ 106.0 ($J(\text{RhC})$ 4 Hz) and 108.4 ($J(\text{RhC})$ 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-NMe₃-*closo*-2,1-MoCB₁₀H₁₀]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–NMe₃ 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: ¹H 360.1, ¹³C 90.6, ³¹P 145.8, and ¹¹B 115.5 MHz. The compounds 7-NMe₃-*nido*-7-CB₁₀H₁₂²⁰ and [Rh(μ-Cl)Cl(η⁵-C₅Me₅)₂]²¹ were obtained by literature methods; [Mo(CO)₃(NCMe)₂(PPh₃)]²² was prepared in situ and used without isolation. All other reagents were used as received.

Synthesis of [N(PPh₃)₂][2,2,2-(CO)₃-2-X-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (X = Br, I). (i) The compound 7-NMe₃-*nido*-7-CB₁₀H₁₂ (0.73 g, 3.82 mmol) was suspended in THF (20 mL), the mixture was cooled to about –40 °C, and BuⁿLi (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 CH₂=CHCH₂Br (0.46 g, 3.80 mmol). The resultant mixture was stirred overnight, and [N(PPh₃)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(PPh₃)₂][2-Br-2,2,2-(CO)₃-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (**1**) (1.02 g).

(ii) Compound **2** was prepared similarly, using I₂ (0.97 g, 3.82 mmol) as oxidizing agent in place of CH₂=CHCH₂Br. Following purification by column chromatography, with CH₂Cl₂ as eluant, [N(PPh₃)₂][2,2,2-(CO)₃-2-I-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (**2**) (0.51 g) was isolated as a dark red powder.

Attempted Preparation of [N(PPh₃)₂][2-Br-2,2-(CO)₂-2-PPh₃-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀]. Following a procedure similar to that by which compound **1** was formed, a suspension of 7-NMe₃-*nido*-7-CB₁₀H₁₂ (0.73 g, 3.82 mmol) in THF (20 mL) was treated with BuⁿLi (3.1 mL, 7.75 mmol), followed by an NCMe (20 mL) solution of [Mo(CO)₃(NCMe)₂(PPh₃)] (3.80 mmol). After 1 h, CH₂=CHCH₂Br (0.46 g, 3.80 mmol) was added and the mixture stirred overnight. Thereafter, [N(PPh₃)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 CH₂Cl₂ (~5 mL), filtered through a Celite pad, and applied to the top of a chromatography column. Elution with CH₂Cl₂ gave a yellow fraction that was identified by infrared and multinuclear NMR spectroscopy as the previously reported species [N(PPh₃)₂][2,2,2-(CO)₃-2-PPh₃-*closo*-2,1-MoCB₁₀H₁₁]¹¹ (**3**) (0.35 g, 8%).

Synthesis of [2,2,2-(CO)₃-2-L-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (L = PPh₃, CNBu^t) and [2,2-(CO)₂-2-Bu^tC≡CH-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀]. (i) A mixture of compound **1** (0.20 g, 0.20 mmol), PPh₃ (0.08 g, 0.31 mmol), and Ti[PF₆]₃ (0.076 g, 0.22 mmol) was stirred in CH₂Cl₂ (15 mL) for 12 h. After filtration through a Celite pad, solvent was removed in vacuo and the residue taken up in CH₂Cl₂ (~2 mL) and transferred to a chromatography column. Elution with CH₂Cl₂–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-PPh₃-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (**4**) (0.081 g). ³¹P{¹H} NMR: δ 53.2.

(ii) By a similar procedure, using CNBu^t (23 μL, 0.017 g, 0.20 mmol) in place of PPh₃, yellow microcrystals of [2-CNBU^t-2,2,2-(CO)₃-3-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (**5**) (0.064 g) were obtained.

(iii) Similarly, reaction of **1** with Ti[PF₆]₃ 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-NMe₃-*closo*-2,1-MoCB₁₀H₁₀] (**6**) (0.075 g).

Synthesis of [2,2,2,2-(CNBU^t)₄-2-Br-3-X-*closo*-2,1-MoCB₁₀H₁₀] (X = Br, I). (i) To a CH₂Cl₂ (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 Br₂ (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 CH₂Cl₂ (~2 mL) and chromatographed. Elution with CH₂Cl₂–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-Br₂-*closo*-2,1-MoCB₁₀H₁₀] (**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 I₂ (0.026 g, 0.10 mmol) yielded orange microcrystalline [2,2,2,2-(CNBU^t)₄-2-Br-3-I-*closo*-2,1-MoCB₁₀H₁₀] (**8**) (0.033 g).

Synthesis of [2,2,2-(CO)₃-2-I-3-NMe₃-6-{cyclo-1,4-S₂(CH₂)₄}-*closo*-2,1-MoCB₁₀H₉]. 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 CH₂Cl₂ (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 CH₂Cl₂ (~2 mL) and chromatographed. Elution with CH₂Cl₂–petroleum ether (3:1) removed a red fraction which, upon evaporation of solvent in vacuo and crystallization from CH₂Cl₂–petroleum ether, yielded red crystals of [2,2,2-(CO)₃-2-I-3-NMe₃-6-{cyclo-1,4-S₂(CH₂)₄}-*closo*-2,1-MoCB₁₀H₉] (**9**) (0.084 g).

Synthesis of [2,2,2-(CO)₃-7-μ-H-2,7,11-{Rh₂(μ-CO)(η⁵-C₅Me₅)₂}-*closo*-2,1-MoCB₁₀H₉]. The carborane 7-NMe₃-*nido*-7-CB₁₀H₁₂ (0.24 g, 1.25 mmol) was suspended in THF (30 mL) at ca. –40 °C, and BuⁿLi (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(η⁵-C₅Me₅)] [BF₄]₂ (prepared in situ from [Rh(μ-Cl)Cl(η⁵-C₅Me₅)₂] (0.80 g, 1.3 mmol) and Ag[BF₄] (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 CH₂Cl₂–petroleum ether (3:2) gave a brown fraction from which solvent was removed in vacuo. Crystallization from CH₂Cl₂–petroleum ether yielded dark

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Table 3. Crystallographic Data for **1**, **6**, **7**, **9**·CH₂Cl₂ and **10**

	1	6	7	9 ·CH ₂ Cl ₂	10
formula	C ₄₃ H ₄₉ B ₁₀ BrMoN ₂ O ₃ P ₂	C ₁₂ H ₂₉ B ₁₀ MoNO ₂	C ₂₁ H ₄₆ B ₁₀ Br ₂ MoN ₄	C ₁₂ H ₂₈ B ₁₀ Cl ₂ IMoNO ₃ S ₂	C ₂₅ H ₄₀ B ₁₀ MoO ₄ Rh ₂
fw	987.73	423.40	718.48	700.31	814.43
space group	<i>Cmca</i>	<i>P2₁/n</i>	<i>P1</i>	<i>P2₁/c</i>	<i>P2₁/n</i>
<i>a</i> , Å	26.998(2)	8.9100(9)	11.0575(9)	12.5499(7)	20.368(3)
<i>b</i> , Å	17.926(2)	25.796(2)	12.304(1)	24.115(3)	15.829(3)
<i>c</i> , 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)		
<i>V</i> , Å ³	9177(1)	2063.8(3)	1747.5(3)	2661.3(4)	6259(2)
<i>Z</i>	8	4	2	4	8
ρ _{calc.} , g cm ⁻³	1.444	1.363	1.365	1.748	1.729
<i>T</i> , 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-{Rh₂(μ-CO)(η⁵-C₅Me₅)₂}-*closo*-2,1-MoCB₁₀H₉] (**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 [$U_{iso}(H) = 1.2 \times U_{iso}(\text{parent})$]. The remaining hydrogen atoms were included in calculated positions and allowed to ride on their parent atoms with fixed isotropic thermal parameters [$U_{iso}(H) = 1.2 \times U_{iso}(\text{parent})$], or $U_{iso}(H) = 1.5 \times U_{iso}(C)$ for methyl hydrogens].

The anionic unit of **1** is bisected by a crystallographic mirror plane (Wyckoff positions 8f) 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 (16e), 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 (16e), and each refined with one-half occupancy. The nitrogen atom of the [N(PPh₃)₂]⁺ cation was located at Wyckoff position 8e ($3/4, -y + 1/2, 3/4$) with full occupancy.

The coordinating 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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