

Synthesis and Reactivity of the Monocarbon Molybdenacarborane Anion [1,2- μ -NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀][−]

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The reagent Li[7-NHBu^t-nido-7-CB₁₀H₁₂] reacts with [Mo(CO)₆] in NCMe at reflux temperatures, followed by addition of [N(PPh₃)₂]Cl, to give [N(PPh₃)₂][1,2- μ -NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀] (1). The tungsten (2) and chromium (3) analogues were similarly obtained, but the latter is unstable and was isolated in low yield. An X-ray diffraction study of 2 confirmed that the exo-polyhedral NHBu^t group forms a bridge between the cage-carbon atom and the tungsten. For 1, this intramolecular donor bond is lifted on protonation in the presence of donor molecules L (CO, PPh₃, PMe₃, PEt₃, PMe₂Ph) when zwitterionic complexes [1-NH₂Bu^t-2,2,2-(CO)₃-2-L-closo-2,1-MoCB₁₀H₁₀] (4) are formed. In contrast, protonation with HCl gives a salt [N(PPh₃)₂][1-NH₂Bu^t-2,2,2-(CO)₃-2-Cl-closo-2,1-MoCB₁₀H₁₀] (5). Complex 1 in CH₂Cl₂ with CNBu^t is oxidized by iodine, affording [1,2- μ -NHBu^t-2,2,2-(CNBu^t)₃-2-I-closo-2,1-MoCB₁₀H₁₀] (6a). Treatment of 1 with [CuCl(PPh₃)₄] in the presence of Ti[PF₆] yields the bimetallic compound [exo-{Cu(PPh₃)₃}-1,2- μ -NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀] (8), whereas reaction with [AuCl(PPh₃)₃] and Ti[PF₆] affords a mixture of [1,2- μ -NHBu^t-2-{Au(PPh₃)₃}-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀] (9) and [Au(PPh₃)₂][2,2'- μ -Au-{1,2- μ -NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀}₂] (10a). In solution, 9 disproportionates, giving 10a. The [N(PPh₃)₂]⁺ salt (10b) is readily prepared by treating 1 with [AuCl(THT)] (THT = tetrahydrothiophene) and Ti[PF₆], and its structure was determined by X-ray diffraction.

Introduction

Although the charge-compensated carborane 7-NH₂Bu^t-nido-7-CB₁₀H₁₂ was first reported many years ago by Todd et al.,¹ the potential of this molecule as a precursor for synthesizing a variety of metallocarboranes has only recently become apparent.² Studies have shown that it reacts with [Ru₃(CO)₁₂] in toluene at reflux temperatures to yield the cluster compound [1-NH₂-Bu^t-2,2-(CO)₂-7,11-(μ -H)-2,2,7,11-{Ru₂(CO)₆}-closo-2,1-Ru-CB₁₀H₈].^{2a} With [RhX(PPh₃)₃] (X = Cl or Br) in toluene, 7-NH₂Bu^t-nido-7-CB₁₀H₁₂ affords the 16-electron zwitterionic species [1-NH₂Bu^t-2-X-2-PPh₃-closo-2,1-RhCB₁₀H₁₀].^{2b} These compounds with 1 mol equiv of CNBu^t give the 18-electron complexes [1-NH₂Bu^t-2-X-2-PPh₃-2-CNBu^t-closo-2,1-RhCB₁₀H₁₀]. However, employment of an excess of the isocyanide in the reaction leads to the elimination of HX to produce the complexes [1-NHBu^t-2,2-(CNBu^t)₂-2-PPh₃-closo-2,1-RhCB₁₀H₁₀]. In the latter, the nido-carborane cage formally functions as the trianion [7-NHBu^t-nido-7-CB₁₀H₁₀]^{3−}, whereas in the charge-compensated complexes, the ligand is the dianion [7-NH₂Bu^t-nido-7-CB₁₀H₁₀]^{2−}. These amino-substituted carboranes are isolobal with the anions [nido-7-CB₁₀H₁₁]^{3−} and [nido-7,8-C₂B₉H₁₁]^{2−}, respectively, which form transition-metal complexes readily.³ The facility with which a ligated [7-NH₂Bu^t-nido-7-CB₁₀H₁₀]^{2−} group transforms into a [7-NHBu^t-nido-7-CB₁₀H₁₀]^{3−}

fragment is demonstrated by the synthesis of arene-rhodium complexes (e.g., [1-NHBu^t-2-(η^6 -C₆H₃Me₃-1,3,5)-closo-2,1-Rh-CB₁₀H₁₀]) by treating [1-NH₂Bu^t-2-Cl-2-PPh₃-closo-2,1-RhCB₁₀H₁₀] with an arene in the presence of Ag[BF₄].^{2c} Interestingly, when 7-NH₂Bu^t-nido-7-CB₁₀H₁₂ is treated with 1 equiv of LiBuⁿ, the monoanion [7-NHBu^t-nido-7-CB₁₀H₁₂][−] is produced, with the deprotonation of either of the two endo-polyhedral μ -H groups requiring addition of further lithium reagent.⁴

These results have led us to prepare other examples of metal complexes containing pentahapto coordinated [7-NH₂Bu^t-nido-7-CB₁₀H₁₀]^{2−} and [7-NHBu^t-nido-7-CB₁₀H₁₀]^{3−} moieties derived from the parent species 7-NH₂Bu^t-nido-7-CB₁₀H₁₂, and in this paper we describe several group 6 metal complexes which demonstrate the versatility of the aminocarborane ligand.

Results and Discussion

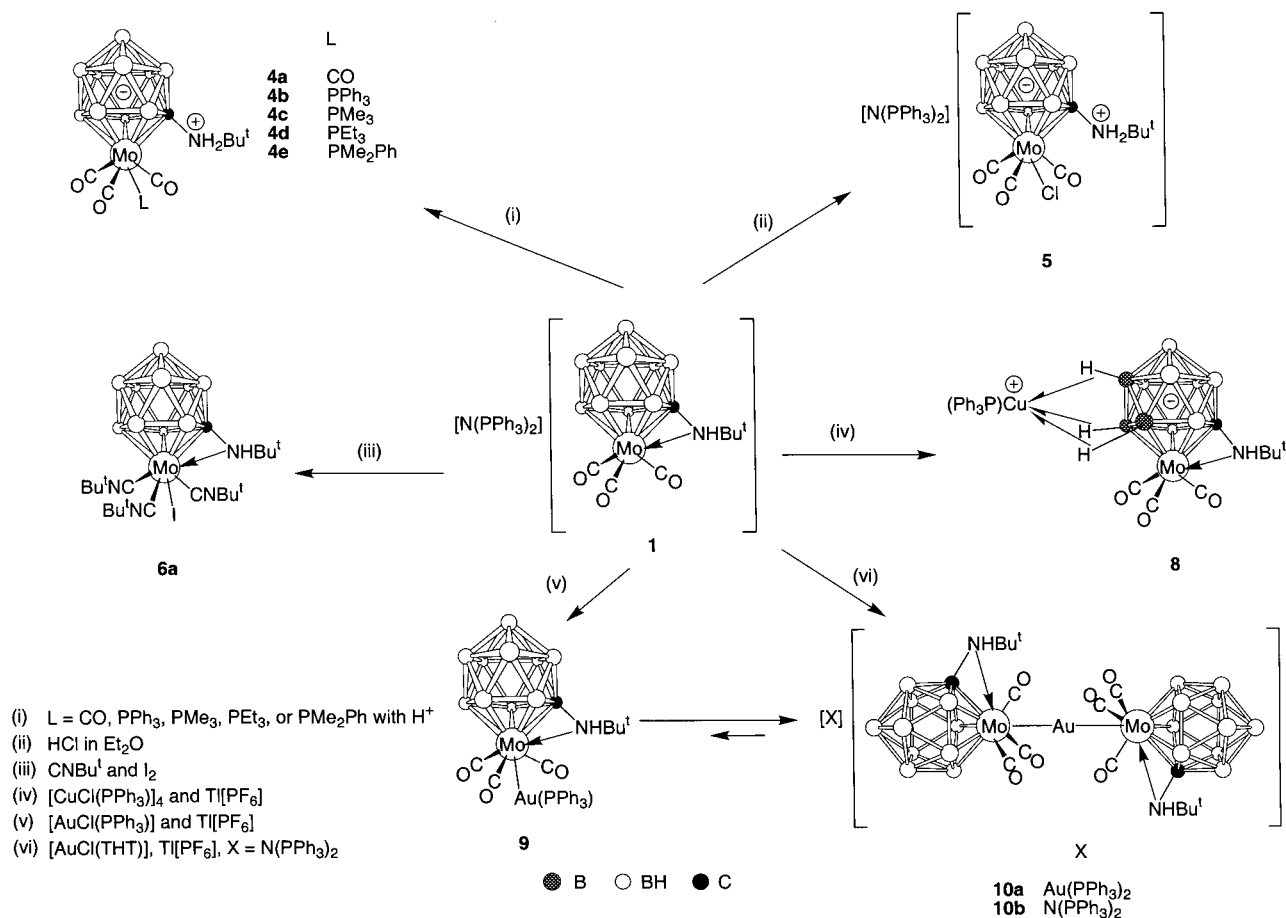
In an earlier work, we prepared the [NEt₄]⁺ salt of the allylmolybdenadecarbollide complex [3-(η^3 -C₃H₅)-3,3-(CO)₂-closo-3,1,2-MoC₂B₉H₁₁][−] by treating Ti₂[3,3,3-(CO)₃-closo-3,1,2-MoC₂B₉H₁₁] with CH₂=CHCH₂Br, followed by the addition of [NEt₄]Cl.⁵ Using a similar methodology, we anticipated obtaining a related monocarbollide molybdenum species [1-NHBu^t-2-(η^3 -C₃H₅)-2,2-(CO)₂-closo-2,1-MoCB₁₀H₁₀]^{2−} by deprotonating 7-NH₂Bu^t-nido-7-CB₁₀H₁₂ with 3 equiv of LiBuⁿ to generate [7-NHBu^t-nido-7-CB₁₀H₁₀]^{3−}, following which the addition of [Mo(CO)₃(NCMe)₃] would afford the trianion [1-NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀]^{3−} in situ. Treatment of the latter with CH₂=CHCH₂Br and [N(PPh₃)₂]Cl was expected to give [N(PPh₃)₂][1-NHBu^t-2-(η^3 -C₃H₅)-2,2-(CO)₂-

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- (1) Hyatt, D. E.; Owen, D. A.; Todd, L. J. *Inorg. Chem.* **1966**, *5*, 1749.
- (2) (a) Lebedev, V. N.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1996**, *15*, 1669. (b) Jeffery, J. C.; Lebedev, V. N.; Stone, F. G. A. *Inorg. Chem.* **1996**, *35*, 2967. (c) Jeffery, J. C.; Jelliss, P. A.; Lebedev, V. N.; Stone, F. G. A. *Organometallics* **1996**, *15*, 4737.
- (3) Grimes, R. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 1, Chapter 9. Grimes, R. N. *Coord. Chem. Rev.* **2000**, *200–202*, 773.

- (4) Jeffery, J. C.; Jelliss, P. A.; Karban, J.; Lebedev, V. N.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1997**, 1219.
- (5) Dossett, S. J.; Li, S.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1993**, 1585.

Scheme 1



closo-2,1-MoCB₁₀H₁₀]. Instead, the trianion was merely oxidized by the allyl bromide, and the final product isolated after the addition of [N(PPh₃)₂]Cl was [N(PPh₃)₂][1,2- μ -NHBu^t-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀] (**1**; Scheme 1).

It was subsequently found that **1** could be more straightforwardly prepared by the interaction of the lithium salt of the monoanionic carborane [7-NHBu^t-*nido*-7-CB₁₀H₁₂]⁻ with [Mo(CO)₆] in refluxing NCMc. The two face-bridging protons of the carborane are reduced and eliminated as dihydrogen with a concomitant two-electron oxidation of molybdenum. Addition of the salt [N(PPh₃)₂]Cl and subsequent chromatography then gave **1** in yields superior to that of the above route. Although microanalytical and spectroscopic data were obtained for **1** (Tables 1–3), an X-ray diffraction study was required to establish definitively the molecular structure of the anion. Unfortunately, repeated efforts to obtain good quality crystals were unsuccessful. Hence, using a similar synthetic procedure, tungsten and chromium analogues of **1** were prepared in the expectation that one of these complexes would provide suitable crystals. The tungsten complex [N(PPh₃)₂][1,2- μ -NHBu^t-2,2,2-(CO)₃-*closo*-2,1-WCB₁₀H₁₀] (**2**) yielded crystals that were satisfactory for X-ray diffraction analysis, but the chromium analogue (**3**) was isolated in only poor yield, primarily as a consequence of its relative instability during chromatography.

The structure of the anion of **2** is shown in Figure 1, and selected internuclear distances and angles are listed in Table 4. The tungsten atom is coordinated on one side by three CO molecules with little deviation from linearity in the W–C–O bonds. On the other, a 7-NHBu^t-*nido*-7-CB₁₀H₁₀ fragment is attached to the metal in a pentahapto manner by its open

CBBB face. However, the exo-polyhedral NHBu^t group is also bonded to the metal [N(1)–W = 2.291(3) Å, C(1)–N(1)–W = 67.1(2)°]. The differences in the W–B(2) (2.338(4) Å) and W–B(5) (2.344(4) Å) versus W–B(3) (2.410(4) Å) and W–B(4) (2.405(4) Å) distances indicate some slippage of the metal atom toward C(1) to accommodate attachment of the amino fragment. Overall, the tungsten atom, formally W^{II} (d⁴), acquires an 18-electron configuration because the 7-NHBu^t-*nido*-7-CB₁₀H₁₀ moiety can be regarded as contributing eight electrons (6 π + 2 σ) to the valence shell while the CO ligands add a further six. Rhodium complexes have been described in which {1-NH₂-2-PPh₃-*closo*-2,1-RhCB₁₀H₁₀} units form dimers via μ -NH₂ groups bridging between metal centers.⁶ As far as we are aware, the intramolecular mode of bridge bonding for an exo-polyhedral amino substituent to a metal seen in **2** has not been previously reported. However, the dianion [2,2,2-(CO)₃-1,2- μ -CO₂-*closo*-2,1-MoCB₁₀H₁₀]²⁻, described by Wegner et al. some 30 years ago,⁷ does contain a similar intramolecular bridge. In this latter species, an ester-type CO₂ linkage connects the molybdenum and cage-carbon vertices, and the carborane unit may likewise be viewed as an eight-electron (6 π + 2 σ) donor to the metal center.

The spectroscopic data for **2** are in agreement with the structure determined by X-ray diffraction. Moreover, the data

- (6) (a) Walker, J. A.; O'Con, C. A.; Zheng, L.; Knobler, C. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1983**, 803. (b) Chizhevsky, I. T.; Pisareva, I. V.; Petrovskii, P. V.; Bregadze, V. I.; Yanovsky, A. I.; Struchkov, Y. T.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1993**, 32, 3393.
 (7) Wegner, P. A.; Guggenberger, L. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1970**, 92, 3473.

Table 1. Analytical and Physical Data

compound	color	% yield	$\nu_{\max}(\text{CO})^a/\text{cm}^{-1}$	anal./% ^b		
				C	H	N
[N(PPh ₃) ₂][1,2- μ -NHBu ^t -2,2,2-(CO) ₃ - <i>closo</i> -2,1-MoCB ₁₀ H ₁₀] (1)	violet	61	2005 s, 1938 m, 1884 s	57.0 (57.4)	5.5 (5.5)	3.0 (3.0)
[N(PPh ₃) ₂][1,2- μ -NHBu ^t -2,2,2-(CO) ₃ - <i>closo</i> -2,1-WCB ₁₀ H ₁₀] (2)	violet	24	2001 s, 1925 m, 1872 s	47.3 (46.9)	4.7 (4.6)	2.5 (2.4) ^e
[N(PPh ₃) ₂][1,2- μ -NHBu ^t -2,2,2-(CO) ₃ - <i>closo</i> -2,1-CrCB ₁₀ H ₁₀] (3)	violet	8	1994 vs, 1938 s, 1891 s	54.3 (54.4)	5.3 (5.3)	2.8 (2.8) ^d
[1-NH ₂ Bu ^t -2,2,2-(CO) ₃ -2-PPh ₃ - <i>closo</i> -2,1-MoCB ₁₀ H ₁₀] (4b)	yellow	39	2030 s, 1974 m, 1893 s	48.0 (48.3)	5.5 (5.6)	1.7 (2.2)
[1-NH ₂ Bu ^t -2,2,2-(CO) ₃ -2-PMe ₃ - <i>closo</i> -2,1-MoCB ₁₀ H ₁₀] (4c)	yellow	60	2028 s, 1968 m, 1882 s	28.9 (28.8)	6.5 (6.6)	3.1 (3.0)
[1-NH ₂ Bu ^t -2,2,2-(CO) ₃ -2-PEt ₃ - <i>closo</i> -2,1-MoCB ₁₀ H ₁₀] (4d)	yellow	49	2025 s, 1965 m, 1879 s	33.3 (33.5)	7.1 (7.2)	2.7 (2.8)
[1-NH ₂ Bu ^t -2,2,2-(CO) ₃ -2-PMe ₂ Ph- <i>closo</i> -2,1-MoCB ₁₀ H ₁₀] (4e)	yellow	31	2029 s, 1969 m, 1887 s	36.2 (36.8)	6.1 (6.2)	2.4 (2.7)
[N(PPh ₃) ₂][1-NH ₂ Bu ^t -2,2,2-(CO) ₃ -2-Cl- <i>closo</i> -2,1-MoCB ₁₀ H ₁₀] (5)	orange-red	95	2026 s, 1950 vs, 1891 s	51.8 (51.9)	5.2 (5.1)	2.7 (2.7) ^e
[1,2- μ -NHBu ^t -2,2,2-(CNBu ^t) ₃ -2-I- <i>closo</i> -2,1-MoCB ₁₀ H ₁₀] (6a)	pink	51	2187 m, ^f 2163 s ^f	35.6 (35.6)	7.0 (7.0)	8.3 (8.3)
[1,2- μ -NHBu ^t -2,2,2-(CNBu ^t) ₃ -2-I- <i>closo</i> -2,1-WCB ₁₀ H ₁₀] (6b)	pink	9	2184 m, ^f 2149 s ^f	31.8 (31.5)	6.2 (6.2)	7.1 (7.3)
[1-NHBu ^t -2,2,2-(CNBu ^t) ₂ -2,2-(CO) ₂ -2-I- <i>closo</i> -2,1-WCB ₁₀ H ₁₀] (7)	orange	11	2202 s, ^f 2024 s	28.3 (27.8)	5.5 (5.2)	5.8 (5.7)
[<i>exo</i> -{Cu(PPh ₃) ₃ }-1,2- μ -NHBu ^t -2,2,2-(CO) ₃ - <i>closo</i> -2,1-MoCB ₁₀ H ₁₀] (8)	violet	41	2029 s, 1979 m, 1910 m	44.6 (44.1)	4.9 (5.1)	2.1 (2.0)
[1,2- μ -NHBu ^t -2-{Au(PPh ₃) ₃ }-2,2,2-(CO) ₃ - <i>closo</i> -2,1-MoCB ₁₀ H ₁₀] (9)	orange-red	36	2037 s, 1979 w, 1931 s	37.0 (37.1)	4.2 (4.3)	1.7 (1.7)
[Au(PPh ₃) ₂][2,2'- μ -Au-{1,2- μ -NHBu ^t -2,2,2-(CO) ₃ - <i>closo</i> -2,1-MoCB ₁₀ H ₁₀ } ₂] (10a)	dark red	23	2027 s, 1939 s	37.5 (37.1)	4.4 (4.3)	1.7 (1.7)

^a Measured in CH₂Cl₂; the broad medium-intensity band observed ca. 2500–2550 cm⁻¹ in the spectra of all of the compounds is due to B–H absorptions. ^b Calculated values are given in parentheses. ^c Cocrystallizes with 2 mol equiv of CH₂Cl₂. ^d Cocrystallizes with 1.5 mol equiv of CH₂Cl₂. ^e Cocrystallizes with 1 mol equiv of CH₂Cl₂. ^f $\nu_{\max}(\text{N}\equiv\text{C})$.

are very similar to those for compounds **1** and **3**; thus, it may confidently be assumed that the anions of all three of the salts have similar structures. Each species displays three CO stretching bands in its infrared spectrum (Table 1). In the ¹H NMR spectra, a diagnostic peak for the NH group is observed at δ 2.41 (**1**), 2.78 (**2**), and 1.79 (**3**), these signals being broad because of unresolved ¹⁴N–¹H coupling. In the ¹³C{¹H} NMR spectra, the resonances for the cage-carbon nuclei are also broad through attachment to both boron and nitrogen and are seen respectively at δ 100.1 (**1**), 91.9 (**2**), and 106.5 (**3**).

In the investigation of the chemistry of complexes **1–3**, attention was focused on the molybdenum species **1** because of its synthesis in good yield. In CO-saturated CH₂Cl₂ solutions, protonation with HBF₄·Et₂O afforded an oily solid. Repeated attempts to obtain analytically pure samples failed as the product readily reverted to precursor **1**. However, on the basis of spectroscopic data, the product can be provisionally formulated as the charge-compensated complex [1-NH₂Bu^t-2,2,2,2-(CO)₄-*closo*-2,1-MoCB₁₀H₁₀] (**4a**). The IR spectrum displays four carbonyl stretching bands (2085 s, 2026 vs, 1980 w, and 1950 s cm⁻¹), in contrast with the three bands seen in the spectrum of **1**. The NMR data (Tables 2 and 3) are in complete accord with the proposed formulation. Thus, in the ¹H spectrum, there is a broad resonance for the NH₂ group at δ 5.88 (rel int 2). The chemical shift for the NH group in **1** is at an appreciably higher field. A single CO resonance (δ 222.3) is seen in the ¹³C{¹H} NMR spectrum of **4a**, whereas in **1**, the metal ligated NHBu^t group introduces an asymmetry, resulting in the observation of three resonances for the nonequivalent CO ligands. Moreover, the cage ¹³C{¹H} and ¹¹B{¹H} NMR parameters for **4a** closely parallel those of the phosphine-substituted compounds **4b–e** discussed in the following paragraphs.

In contrast with an inability to isolate an analytically pure sample of **4a**, treatment of a CH₂Cl₂ solution of **1** with HBF₄·Et₂O followed by PPh₃ gave [1-NH₂Bu^t-2,2,2-(CO)₃-2-PPh₃-*closo*-2,1-MoCB₁₀H₁₀] (**4b**). It was also found that if CH₂Cl₂ solutions of **1** were treated directly with PMe₃, PEt₃ and PMe₂Ph, respectively, and the crude reaction mixtures were chromatographed without the addition of HBF₄·Et₂O, the complexes [1-NH₂Bu^t-2,2,2-(CO)₃-2-L-*closo*-2,1-MoCB₁₀H₁₀] (L = PMe₃ (**4c**), PEt₃ (**4d**), or PMe₂Ph (**4e**)) were formed. Evidently, initially produced anionic species [N(PPh₃)₂][1-NHBu^t-2,2,2-(CO)₃-2-L-*closo*-2,1-MoCB₁₀H₁₀] are very readily protonated during the chromatography procedure. Indeed, examination of the spectroscopic properties of the initial reaction mixture in the synthesis of **4d** gave strong evidence for the presence of a species [1-NHBu^t-2,2,2-(CO)₃-2-PEt₃-*closo*-2,1-MoCB₁₀H₁₀]⁻. The IR spectrum revealed CO stretching bands which can be assigned to such an anion at 2000 vs, 1927 m, and 1886 s cm⁻¹. Moreover, the ¹H, ¹³C{¹H}, and ¹¹B{¹H} NMR spectra displayed peaks for the expected groups present, with chemical shifts different from those of **4d**. For example, there were resonances for the CO ligands at δ 239.3 ($J(\text{PC}) = 7$ Hz) and 235.4 ($J(\text{PC}) = 28$ Hz) in the ¹³C{¹H} NMR spectrum to be compared with those in the spectrum of **4d** at δ 233.1 ($J(\text{PC}) = 7$ Hz) and 232.3 ($J(\text{PC}) = 29$ Hz). Similarly, whereas in **4d** the cage-carbon peak appeared at δ 83.0, in the transient anionic complex, the signal was seen at δ 100.2. In addition, the ¹¹B{¹H} NMR spectrum implied the presence of mirror symmetry, consistent with a “lifting off” of the N–Mo bond.

Protonation of **1** in CH₂Cl₂ with HCl does not yield a neutral zwitterionic complex; instead, a salt [N(PPh₃)₂][1-NH₂Bu^t-2,2,2-

Table 2. ^1H and ^{13}C NMR Data^a

compd	$^1\text{H}/\delta^b$	$^{13}\text{C}/\delta^c$
1	7.66–7.44 (m, 30H, Ph), 2.41 (br s, 1H, NH), 0.98 (s, 9H, Bu ^t)	240.6 (2 × CO), 234.2 (CO), 134.1–126.6 (Ph), 100.1 (br, cage C), 58.2 (CMe ₃), 29.4 (CMe ₃)
2	7.66–7.44 (m, 30H, Ph), 2.78 (br s, 1H, NH), 0.99 (s, 9H, Bu ^t)	237.5 (CO), 237.3 (CO), 227.7 (CO), 134.1–126.7 (Ph), 91.9 (br, cage C), 59.0 (CMe ₃), 29.1 (CMe ₃)
3	7.66–7.46 (m, 30H, Ph), 1.79 (br s, 1H, NH), 1.00 (s, 9H, Bu ^t)	248.6 (2 × CO), 244.6 (CO), 134.1–126.8 (Ph), 106.5 (br, cage C), 59.0 (CMe ₃), 29.5 (CMe ₃)
4a	5.88 (br s, 2H, NH ₂), 1.41 (s, 9H, Bu ^t)	222.3 (CO), 82.8 (br, cage C), 68.7 (CMe ₃), 28.2 (CMe ₃)
4b	7.60–7.30 (m, 15H, Ph), 5.29 (br s, 2H, NH ₂), 1.18 (s, 9H, Bu ^t)	232.7 (d, 2 × CO, <i>J</i> (PC) = 29), 231.6 (d, CO, <i>J</i> (PC) = 8), 135.2–128.9 (Ph), 83.3 (br, cage C), 69.2 (CMe ₃), 28.1 (CMe ₃)
4c	5.61 (br s, 2H, NH ₂), 1.80 (d, 9H, PMe ₃ , <i>J</i> (PH) = 10), 1.42 (s, 9H, Bu ^t)	231.3 (d, 2 × CO, <i>J</i> (PC) = 31), 229.7 (d, CO, <i>J</i> (PC) = 8), 82.8 (br, cage C), 69.0 (CMe ₃), 28.2 (CMe ₃), 18.3 (d, PMe ₃ , <i>J</i> (PC) = 33)
4d	5.70 (br s, 2H, NH ₂), 2.19 (dq, 6H, PCH ₂ Me, <i>J</i> (PH) = 8, <i>J</i> (HH) = 8), 1.42 (s, 9H, Bu ^t), 1.22 (dt, 9H, PCH ₂ Me, <i>J</i> (PH) = 16)	233.1 (d, CO, <i>J</i> (PC) = 7), 232.3 (d, 2 × CO, <i>J</i> (PC) = 29), 83.0 (br, cage C), 69.1 (CMe ₃), 28.2 (CMe ₃), 20.5 (d, PCH ₂ Me, <i>J</i> (PC) = 27), 8.8 (br, PCH ₂ Me)
4e	7.72–7.42 (m, 5H, Ph), 5.03 (br s, 2H, NH ₂), 2.09 (d, 6H, PMe ₂ , <i>J</i> (PH) = 10), 1.02 (s, 9H, Bu ^t)	231.7 (d, 2 × CO, <i>J</i> (PC) = 28), 229.3 (d, CO, <i>J</i> (PC) = 7), 131.7–128.2 (Ph), 83.2 (br, cage C), 68.3 (CMe ₃), 27.8 (CMe ₃), 17.6 (d, PMe ₂ , <i>J</i> (PC) = 33)
5	7.68–7.46 (m, 30H, Ph), 6.78 (br s, 2H, NH ₂), 1.35 (s, 9H, Bu ^t)	252.8 (CO), 238.0 (2 × CO), 135.0–126.7 (Ph), 80.0 (br, cage C), 65.9 (CMe ₃), 27.0 (CMe ₃)
6a	2.15 (br s, 1H, NH), 1.51 (s, 9H, CNBu ^t), 1.51 (s, 9H, CNBu ^t), 1.47 (s, 9H, CNBu ^t), 1.17 (s, 9H, NHBu ^t)	154.2 (br, 2 × Mo–CN), 153.0 (br, Mo–CN), 100.0 (br, cage C), 58.1 (2 × CMe ₃), 57.9 (CMe ₃), 57.8 (CMe ₃), 30.2 (CMe ₃), 30.1 (CMe ₃), 29.9 (CMe ₃), 29.7 (CMe ₃)
6b	2.87 (br s, 1H, NH), 1.52 (s, 9H, CNBu ^t), 1.51 (s, 9H, CNBu ^t), 1.48 (s, 9H, CNBu ^t), 1.21 (s, 9H, NHBu ^t)	146.5 (br, W–CN), 145.8 (br, 2 × W–CN), 90.2 (br, cage C), 58.1 (2 × CMe ₃), 57.8 (2 × CMe ₃), 30.5 (CMe ₃), 30.4 (CMe ₃), 29.9 (CMe ₃), 29.8 (CMe ₃)
7	^d 9.60 (s, 1H, NH), 1.57 (s, 9H, Bu ^t), 1.48 (s, 9H, Bu ^t), 1.38 (s, 9H, Bu ^t)	^d 204.1 (CO, <i>J</i> (WC) = 114), 202.3 (CO, <i>J</i> (WC) = 73), 137.2 (t, CN, <i>J</i> (NC) = 21, <i>J</i> (WC) = 105), 135.5 (t, CN, <i>J</i> (NC) = 21, <i>J</i> (WC) = 98), 77.6 (br, cage C), 69.2 (NHCMe ₃), 59.0 (br, 2 × CNMe ₃), 30.1 (CNCMe ₃), 30.0 (CNCMe ₃), 29.7 (NHCMe ₃)
8	7.54–7.15 (m, 15H, Ph), 2.67 (br s, 1H, NH), 1.02 (s, 9H, Bu ^t)	226.8 (CO), 223.3 (2 × CO), 134.0–128.5 (Ph), 103.0 (br, cage C), 60.5 (CMe ₃), 29.0 (CMe ₃)
9	7.61–7.48 (m, 15H, Ph), 2.29 (br s, 1H, NH), 0.98 (s, 9H, Bu ^t)	231.4 (d, CO, <i>J</i> (PC) = 4), 230.8 (d, CO, <i>J</i> (PC) = 4), 215.0 (d, CO, <i>J</i> (PC) = 4), 134.5–127.1 (Ph), 103.3 (br, cage C), 59.3 (CMe ₃), 29.9 (CMe ₃)
10a	7.66–7.45 (m, 30H, Ph), 2.48 (br s, 2H, NH), 1.21, 1.20 (2 × s, 2 × 9H, 2 × Bu ^t)	231.6 (CO), 231.5 (CO), 231.1 (CO), 231.0 (CO), 215.9 (br, 2 × CO), 134.6–129.7 (Ph), 103.3 (br, cage C), 59.7, 59.7 (2 × CMe ₃), 29.8 (br, 2 × CMe ₃)

^a Chemical shifts (δ) in ppm, coupling constants (*J*) in hertz, and measurements at ambient temperatures in CD₂Cl₂. ^b Resonances for terminal BH protons occur as broad unresolved signals in the range of δ ca. –1 to 3. ^c ^1H decoupled; chemical shifts are quoted as positive to high frequency of SiMe₄. ^d Compound is a mixture of two isomers.

Table 3. ^{11}B and ^{31}P NMR Data^a

compd	$^{11}\text{B}\{^1\text{H}\}/\delta^b$	$^{31}\text{P}\{^1\text{H}\}/\delta^c$
1	5.0 (1B), 1.5 (1B), –0.7 (1B), –9.1 (3B), –10.6 (1B), –12.4 (1B), –16.8 (1B), –20.0 (1B)	
2	4.1 (1B), –3.3 (1B), –5.7 (1B), –9.4 (1B), –11.6 (2B), –12.7 (2B), –18.6 (1B), –21.3 (1B)	
3	6.2 (1B), 4.9 (1B), 3.9 (1B), –7.3 (2B), –9.4 (1B), –10.5 (1B), –12.9 (1B), –16.2 (1B), –19.5 (1B)	
4a	4.0 (1B), –3.1 (2B), –5.8 (1B), –6.7 (2B), –9.8 (2B), –13.3 (2B)	
4b	–0.1 (1B), –3.0 (2B), –6.3 (1B), –7.9 (2B), –9.9 (2B), –14.2 (2B)	45.6
4c	–0.9 (1B), –3.8 (2B), ca. –7.4 (sh, 1B), ca. –7.9 (2B), –10.9 (2B), –15.1 (2B)	8.8
4d	–0.8 (1B), –3.9 (2B), –8.0 (3B), –11.1 (2B), –14.9 (2B)	30.3
4e	–0.6 (1B), –3.8 (2B), –6.9 (1B), –8.4 (2B), –10.0 (2B), –14.8 (2B)	12.3
5	2.6 (3B), –4.8 (1B), –8.8 (2B), –11.8 (2B), –15.6 (2B)	
6a	10.9 (1B), 6.1 (1B), 4.9 (1B), –2.2 (1B), –3.3 (1B), –9.0 (1B), –10.3 (1B), –12.3 (1B), –15.4 (1B), –17.0 (1B)	
6b	7.4 (1B), 0.1 (1B), –0.9 (1B), –6.4 (1B), –7.9 (1B), –10.6 (2B), –12.6 (1B), –14.4 (1B), –18.2 (1B)	
7	^d 7.5 (1B + 1B), –1.7 (4B + 4B), –5.5 (1B), –8.2 (2B), –8.5 (2B) –9.4 (1B), –15.9 (2B), –16.6 (2B)	
8	9.8 (1B), 1.3 (1B), –7.0 (1B), ca. –8.7 (2B), ca. –9.3 (1B), –11.4 (1B), –14.4 (2B), –18.5 (1B)	10.5 (br)
9	12.5 (1B), 4.9 (1B), 3.4 (1B), –5.1 (1B), ca. –6.0 (sh, 1B), ca. –6.9 (sh, 1B), –7.3 (1B), –10.2 (1B), –14.5 (1B), –17.3 (1B)	52.8
10a	11.5 (1B), 4.5 (1B), 3.0 (1B), –5.1 (1B), ca. –5.9 (sh, 1B), –7.5 (2B), –10.4 (1B), –14.6 (1B), –17.4 (1B)	45.6

^a Chemical shifts (δ) in ppm, coupling constants (*J*) in hertz, and measurements at ambient temperatures in CD₂Cl₂. ^b $^{11}\text{B}\{^1\text{H}\}$ chemical shifts (δ) are positive to high frequency of BF₃·Et₂O (external). Signals ascribed to more than one boron nucleus may result from overlapping peaks and do not necessarily indicate symmetry equivalence. ^c $^{31}\text{P}\{^1\text{H}\}$ chemical shifts (δ) are positive to high frequency of H₃PO₄ (external). ^d Compound is a mixture of two isomers.

(CO)₃-2-Cl-*closo*-2,1-MoCB₁₀H₁₀] (**5**) is formed. The acid has a coordinating anion Cl[–] which ligates the vacant site on the metal atom.

Compounds **4** and **5** were characterized by the data given in Tables 1–3. For **4d**, an X-ray diffraction study was carried out. The molecule is shown in Figure 2, and some selected bond distances and angles are listed in Table 5. This study confirms that protonation of **1** occurs at the nitrogen atom, with the vacant site thus created on the molybdenum being occupied by a neutral donor molecule L or by Cl[–] in the case of **5**. In the latter and in the neutral charge-compensated molecules **4**, the [7-NH₂-Bu^t-*nido*-7-CB₁₀H₁₀]^{2–} fragment formally donates six electrons

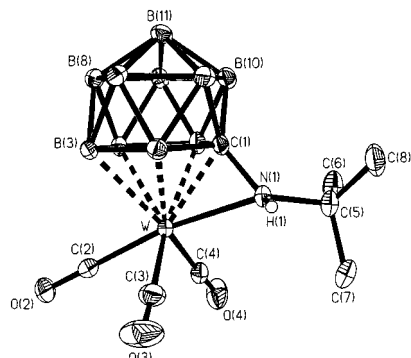
to the metal center rather than the eight donated from the [7-NHBu^t-*nido*-7-CB₁₀H₁₀]^{3–} group in precursor **1**.

In contrast to the relatively straightforward reaction of **1** with alkylphosphines, similar treatment of **1** with CNBu^t resulted in an intractable mixture of products and considerable associated decomposition. However, it is known that the anion [2,2,2,2-(CO)₄-*closo*-2,1-MoCB₁₀H₁₁]^{8–} reacts with CNBu^t in the presence of I₂ to give an Mo^{IV}-isocyanide complex, [2,2,2,2-(CNBu^t)₄-2-I-*closo*-2,1-MoCB₁₀H₁₁]⁹, and a similar strategy was

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

Table 4. Selected Internuclear Distances (Å) and Angles (deg) for the Anion of [N(PPh₃)₂][1,2- μ -NHBu^t-2,2,2-(CO)₃-*closo*-2,1-WCB₁₀H₁₀] (2)

		Distance (Å)					
W–C(4)	1.986(4)	W–C(3)	1.998(4)	W–C(2)	2.004(4)	W–C(1)	2.181(3)
W–N(1)	2.291(3)	W–B(2)	2.338(4)	W–B(5)	2.344(4)	W–B(4)	2.405(4)
W–B(3)	2.410(4)	C(1)–N(1)	1.443(4)	C(2)–O(2)	1.149(5)	C(3)–O(3)	1.148(5)
C(4)–O(4)	1.152(5)	N(1)–C(5)	1.499(4)				
		Angle (deg)					
C(4)–W–C(3)	105.3(2)	C(4)–W–C(2)	82.8(2)	C(3)–W–C(2)		80.9(2)	
C(4)–W–C(1)	114.00(14)	C(3)–W–C(1)	114.3(2)	C(2)–W–C(1)		151.15(14)	
C(4)–W–N(1)	94.53(13)	C(3)–W–N(1)	91.4(2)	C(2)–W–N(1)		170.80(13)	
C(1)–W–N(1)	37.55(11)	N(1)–W–B(2)	66.63(12)	N(1)–W–B(5)		71.44(12)	
N(1)–W–B(4)	109.99(12)	N(1)–W–B(3)	107.21(12)	N(1)–C(1)–B(10)		136.4(3)	
N(1)–C(1)–B(6)	129.1(3)	N(1)–C(1)–B(2)	105.1(3)	N(1)–C(1)–B(5)		114.6(3)	
N(1)–C(1)–W	75.4(2)	O(2)–C(2)–W	178.8(4)	O(3)–C(3)–W		175.3(4)	
O(4)–C(4)–W	176.5(4)	C(1)–N(1)–C(5)	127.8(3)	C(1)–N(1)–W		67.1(2)	
C(5)–N(1)–W	137.3(2)						

**Figure 1.** Structure of the anion of [N(PPh₃)₂][1,2- μ -NHBu^t-2,2,2-(CO)₃-*closo*-2,1-WCB₁₀H₁₀] (2) showing the crystallographic labeling scheme. Thermal ellipsoids are shown at the 40% probability level. For clarity, only the H(1) hydrogen atom is shown.

therefore applied to the present system. Thus, treatment of the Mo^{II} compound **1** with CNBu^t and iodine gave the Mo^{IV} complex [1,2- μ -NHBu^t-2,2,2-(CNBu^t)₃-2-I-*closo*-2,1-MoCB₁₀H₁₀] (**6a**). In contrast, a similar reaction of **2** gave a mixture of [1,2- μ -NHBu^t-2,2,2-(CNBu^t)₃-2-I-*closo*-2,1-WCB₁₀H₁₀] (**6b**) and [1-NHBu^t-2,2,2-(CNBu^t)₂-2,2-(CO)₂-2-I-*closo*-2,1-WCB₁₀H₁₀] (**7**). Data characterizing compounds **6** and **7** are given in Tables 1–3 and are entirely consistent with the assigned formulations.

For compounds **6a** and **6b**, the ¹H NMR spectra show a characteristic broad resonance for a single NH proton at δ 2.15 (**6a**) and δ 2.87 (**6b**). These spectra also each show three inequivalent CNBu^t proton resonance positions, consistent with the NHBu^t group being bonded to the metal center and thereby imparting molecular asymmetry. Broad peaks at δ 100.0 (**6a**) and δ 90.2 (**6b**) in the ¹³C{¹H} NMR spectra are assigned to the cage-carbon atoms and are comparable to those in the parent compounds **1** and **2**, respectively. The absence of mirror symmetry is also confirmed by the ¹¹B{¹H} NMR spectra, which reveal 10 inequivalent cage B atoms for both **6a** and **6b** (the spectrum of **6b** has one coincidence), similar to the corresponding spectra for compounds **1–3** where the NHBu^t unit also bridges to the metal center. The presence of the metal-bound iodide in **6** is inferred both from the need for overall neutrality and by analogy with the above known iodotetrakis(isocyanide) species that were prepared similarly.⁹

In compounds **6a** and **6b**, as in their precursors, the carborane ligand [7-NHBu^t-*nido*-7-CB₁₀H₁₀]³⁻ again functions as an eight-electron (6 π + 2 σ) donor. For compound **7**, this is not the case. Here, the same carborane unit formally donates 6 π electrons to

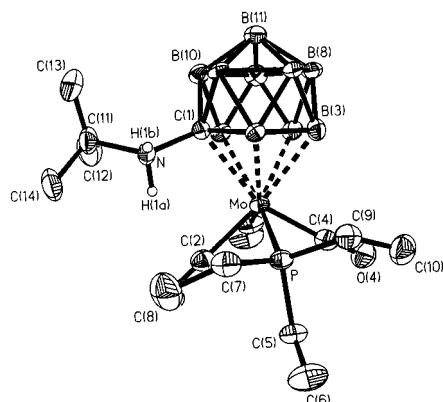
the metal center. This distinction arises from the most noteworthy feature of compound **7**, namely, that it does not have a μ -NHBu^t group. Instead, four ligands, two carbonyls and two isocyanides, are bound to the tungsten center in addition to the iodide and carborane groups. Interestingly, the carbonyl ligands are sufficiently strongly bound to the W^{IV} center that they are not displaced by the now pendant NHBu^t group. The NMR spectra of **7** also show some notable features. A resonance corresponding to a single NH proton is seen in the ¹H NMR spectrum at δ 9.60, significantly lower field than in any of the preceding compounds. In the ¹³C{¹H} NMR spectrum, the broad, cage-carbon atom resonance at δ 77.6 is to rather higher field than that in precursor **2**. Indeed, these two parameters clearly distinguish complex **7** from all of the compounds (**1–3**, **6**, and **8–10**) in which the NHBu^t unit has a bridging role. The ¹H and ¹³C{¹H} NMR spectra of **7** show two sets of resonances associated with the W-bound carbonyl and isocyanide ligands. However, if free inversion is reasonably assumed for the central N atom in the NHBu^t group, then the carborane ligand, and hence the whole molecule, should appear symmetric on the NMR time scale. The two carbonyl and two isocyanide ligands should then appear mutually equivalent and give rise to only one set of NMR resonances. In this connection, it is relevant to note that, in [1-NHBu^t-2,2,2-(CO)₃-2-PET₃-*closo*-2,1-MoCB₁₀H₁₀]⁻ (the precursor to **4d** discussed previously), the noncoordinated NHBu^t also appears to invert freely, as evidenced by the symmetry of its ¹¹B{¹H} NMR spectrum. These features in the NMR spectra of **7** are attributed not to asymmetry but to the compound existing as a mixture of two isomers differentiated by the two CO ligands being mutually disposed either *cisoid* or *transoid* about the W center. In the ¹¹B{¹H} NMR spectrum, there is also evidence for the presence of two closely related isomeric species with some of the resonances duplicated (see Table 3). A related tungsten species, [2,2-(CNBu^t)₂-2,2-(CO)₂-2-I-*closo*-2,1-WCB₁₀H₁₁]⁹ has been similarly prepared from [2,2,2,2-(CO)₄-*closo*-2,1-WCB₁₀H₁₁]⁻ but shows no such isomerism in the metal-bonded ligands. This may indicate some involvement of the μ -NHBu^t group during the formation of **7**, and its presence or lifting off may play some role in sterically or electronically directing the site of isocyanide attack.

The ready reaction of **1** with H⁺, as in the formation of compounds **4b** and **5**, prompted the treatment of **1** with the [M(PPh₃)₃]⁺ (M = Cu, Au) cations, isolobal with the proton, in the likelihood that bimetallic products would result. Thus, interaction of **1** with [CuCl(PPh₃)₄] in the presence of Ti[PF₆]₆ gave the heterobimetallic species [*exo*-{Cu(PPh₃)₃}-1,2- μ -NHBu^t-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀] (**8**). The site of attachment of the *exo*-polyhedral copper fragment in **8** cannot

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

Table 5. Selected Internuclear Distances (Å) and Angles (deg) for [1-NH₂Bu^t-2,2,2-(CO)₃-2-PEt₃-*closo*-MoCB₁₀H₁₀] (**4d**)

		Distance (Å)					
Mo–C(4)	1.986(2)	Mo–C(2)	2.001(2)	Mo–C(3)	2.003(2)	Mo–B(4)	2.372(2)
Mo–B(5)	2.386(2)	Mo–B(2)	2.400(2)	Mo–B(3)	2.403(2)	Mo–C(1)	2.461(2)
Mo–P	2.5625(6)	C(1)–N	1.527(2)	C(2)–O(2)	1.149(2)	C(3)–O(3)	1.135(2)
C(4)–O(4)	1.135(2)	N–C(11)	1.547(2)				
		Angle (deg)					
C(4)–Mo–C(2)	106.35(8)	C(4)–Mo–C(3)	76.10(8)	C(2)–Mo–C(3)	74.29(9)		
C(4)–Mo–C(1)	156.79(7)	C(2)–Mo–C(1)	96.85(7)	C(3)–Mo–C(1)	111.77(7)		
C(4)–Mo–P	77.52(6)	C(2)–Mo–P	77.37(6)	C(3)–Mo–P	133.49(6)		
B(4)–Mo–P	136.13(5)	B(5)–Mo–P	148.39(5)	B(2)–Mo–P	78.56(5)		
B(3)–Mo–P	92.93(5)	C(1)–Mo–P	107.56(4)	N–C(1)–B(5)	126.53(14)		
N–C(1)–B(6)	109.96(13)	N–C(1)–B(10)	118.42(13)	N–C(1)–B(2)	113.20(13)		
N–C(1)–Mo	107.00(10)	O(2)–C(2)–Mo	175.9(2)	O(3)–C(3)–Mo	178.1(2)		
O(4)–C(4)–Mo	173.5(2)	C(1)–N–C(11)	128.6(2)				

**Figure 2.** Structure of [1-NH₂Bu^t-2,2,2-(CO)₃-2-PEt₃-*closo*-2,1-MoCB₁₀H₁₀] (**4d**) showing the crystallographic labeling scheme. Thermal ellipsoids are shown at the 40% probability level. For clarity, all of the hydrogen atoms except H(1a) and H(1b) are omitted.

definitively be established without an X-ray diffraction study, but unfortunately, suitable single crystals could not be grown. However, it is reasonably assumed that the copper atom is bonded to a triangular B₃ face via three agostic B–H → Cu linkages, as depicted in Scheme 1. This is by analogy with the closely related species [2,2,2-(CO)₃-2-PPh₃-7,8,12-(μ-H)₃-7,8-12-{Cu(PPh₃)}-*closo*-2,1-MoCB₁₀H₈] characterized by X-ray diffraction, which is obtained similarly from the [2,2,2-(CO)₃-2-PPh₃-*closo*-2,1-MoCB₁₀H₁₁][−] anion.¹⁰ No signals were observed in the ¹H NMR spectrum of **8** that may be attributed to the protons involved in the three B–H → Cu linkages, presumably a consequence of dynamic behavior in solution that is fast on the NMR time scale.¹⁰ In the ³¹P{¹H} NMR spectrum, the exo-polyhedral {Cu(PPh₃)} moiety gives rise to a signal at δ 10.5, which is broadened by the adjacent quadrupolar copper and boron nuclei. The position of the NH proton resonance (at δ 2.67 in the ¹H NMR spectrum) and that of the cage carbon atom (at δ 103.0 in the ¹³C{¹H} NMR spectrum) combined with the cluster asymmetry revealed by the ¹¹B{¹H} NMR spectrum indicate that the molecule has a core structure very similar to that in **1**.

When a mixture of **1** and [AuCl(PPh₃)] was treated with Ti[PF₆], a mixture of products was obtained which was separated chromatographically. The two species formed were ultimately identified as the expected gold–molybdenum compound [1,2-μ-NHBu^t-2-{Au(PPh₃)}-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀] (**9**) and an unexpected salt [Au(PPh₃)₂][2,2'-μ-Au-{1,2-μ-NHBu^t-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀}]₂ (**10a**). However, initial analysis of each of these distinct fractions showed them

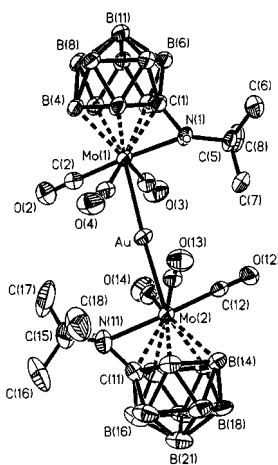
apparently to contain very similar mixtures. In particular, the ³¹P{¹H} NMR spectra of both showed two peaks (at δ 45.6 and 52.8) of approximately similar intensities. It became clear that, following separation, the two products readily disproportionate to reestablish an equilibrium mixture of the two. Indeed, ³¹P{¹H} NMR analysis of the two fractions immediately after chromatographic separation showed them each to predominantly contain only one species, with a mixture of two species becoming increasingly evident within a few hours in solution. When the composition of the anticipated product **9** was considered, it was apparent that two molecules of **9** may disproportionate into an [Au(PPh₃)₂]⁺ cation plus an anion of the form [Au{MoCB₁₀}₂][−]. The bis(triphenylphosphine)gold cation corresponds to the peak seen in the ³¹P{¹H} NMR at δ 45.6 (lit.¹¹ δ 45.0). Such disproportionations where cations [Au(PR₃)₂]⁺ are formed by dissociation in solution of complexes containing {Au(PR₃)} units have precedent, for example, in tungsten–carbyne chemistry¹² and in auraborane chemistry.¹³ To test this hypothesis, compound **1** (2 mol equiv) was treated with [AuCl(THT)] (THT = tetrahydrothiophene) and Ti[PF₆], with the aim of forming the proposed trimetallic Mo–Au–Mo species with a linear Au^I center bridging two molybdenum vertices. The resulting product was identified and characterized, including the use of an X-ray diffraction study, as [N(PPh₃)₂]-[2,2'-μ-Au-{1,2-μ-NHBu^t-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀}]₂ (**10b**), discussed below. Comparison of the infrared and ¹H and ¹¹B{¹H} NMR spectra of **10a** with those of **10b** confirmed that the two contain the same anion.

Compound **9** shows a broad resonance in its ¹H NMR spectrum, corresponding to a single NH proton at δ 2.29, and a further broad resonance at δ 103.3 in its ¹³C{¹H} NMR spectrum, which is assigned to the cage-carbon atom. These two chemical shifts are close to those seen in the spectra of the parent **1** and indicate the NHBu^t group to be bridging between the C(1) and Mo(2) atoms of the icosahedral cluster. This is further supported by the molecular asymmetry indicated in the ¹¹B{¹H} NMR spectrum, which shows 10 distinct resonances. The {Au(PPh₃)} fragment is confirmed to be bonded to the molybdenum vertex, because the three metal-bonded carbonyls all appear as doublets in the ¹³C{¹H} NMR spectrum, with three-bond coupling constants *J*(PC) of 4 Hz each. Similar to **9**, the anion of compounds **10a** and **10b** shows a broad NH proton resonance (at δ 2.48) in the ¹H NMR spectrum, a broad resonance at δ 103.3 in its ¹³C{¹H} NMR spectrum, and 10 resonances (two coincide) in its ¹¹B{¹H} NMR spectrum.

(11) (a) Westland, A. D. *Can. J. Chem.* **1969**, *47*, 4135. (b) Yau, J.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1997**, 1103.(12) Carriedo, G. A.; Howard, J. A. K.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2545.(13) Wynd, A. J.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1174.(10) Ellis, D. E.; Franken, A.; Jelliss, P. A.; Kautz, J. A.; Stone, F. G. A.; Yu, P.-Y. *J. Chem. Soc., Dalton Trans.* **2000**, 2509.

Table 6. Selected Internuclear Distances (Å) and Angles (deg) for the Anion of [N(PPh₃)₂][2,2'-μ-Au-{1,2-μ-NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀}₂] (**10b**)

		Distance (Å)					
Mo(1)–C(2)	2.033(7)	Mo(1)–C(3)	2.046(6)	Mo(1)–C(4)	2.059(6)	Mo(1)–C(1)	2.198(5)
Mo(1)–N(1)	2.319(4)	Mo(1)–B(2)	2.339(6)	Mo(1)–B(5)	2.340(6)	Mo(1)–B(4)	2.411(5)
Mo(1)–B(3)	2.424(6)	Mo(1)–Au	2.7377(9)	C(1)–N(1)	1.433(6)		
Au–Mo(2)	2.7422(8)	Mo(2)–C(12)	2.026(5)	Mo(2)–C(13)	2.038(6)	Mo(2)–C(14)	2.053(6)
Mo(2)–C(11)	2.195(5)	Mo(2)–N(11)	2.298(5)	Mo(2)–B(15)	2.335(6)	Mo(2)–B(12)	2.338(6)
Mo(2)–B(14)	2.405(5)	Mo(2)–B(13)	2.422(5)	C(11)–N(11)	1.427(7)		
		Angle (deg)					
C(2)–Mo(1)–C(3)	82.4(2)	C(2)–Mo(1)–C(4)	82.2(2)	C(3)–Mo(1)–C(4)	125.2(2)		
C(2)–Mo(1)–C(1)	146.8(2)	C(3)–Mo(1)–C(1)	110.4(2)	C(4)–Mo(1)–C(1)	110.9(2)		
C(2)–Mo(1)–N(1)	175.8(2)	C(3)–Mo(1)–N(1)	97.7(2)	C(4)–Mo(1)–N(1)	94.4(2)		
C(1)–Mo(1)–N(1)	36.9(2)	C(2)–Mo(1)–Au	82.2(2)	C(3)–Mo(1)–Au	63.0(2)		
C(4)–Mo(1)–Au	62.9(2)	C(1)–Mo(1)–Au	130.97(12)	N(1)–Mo(1)–Au	94.15(10)		
N(1)–C(1)–Mo(1)	76.2(3)	O(2)–C(2)–Mo(1)	178.5(6)	O(3)–C(3)–Mo(1)	171.2(5)		
O(4)–C(4)–Mo(1)	169.7(5)	C(1)–N(1)–Mo(1)	66.9(2)	Mo(1)–Au–Mo(2)	170.80(2)		
C(12)–Mo(2)–C(13)	82.0(2)	C(12)–Mo(2)–C(14)	85.0(2)	C(13)–Mo(2)–C(14)	124.6(2)		
C(12)–Mo(2)–C(11)	145.3(2)	C(13)–Mo(2)–C(11)	110.5(2)	C(14)–Mo(2)–C(11)	110.4(2)		
C(12)–Mo(2)–N(11)	177.1(2)	C(13)–Mo(2)–N(11)	98.8(2)	C(14)–Mo(2)–N(11)	92.2(2)		
C(11)–Mo(2)–N(11)	36.9(2)	C(12)–Mo(2)–Au	80.88(13)	C(13)–Mo(2)–Au	63.15(14)		
C(14)–Mo(2)–Au	61.7(2)	C(11)–Mo(2)–Au	133.83(14)	N(11)–Mo(2)–Au	96.98(13)		
N(11)–C(11)–Mo(2)	75.5(3)	O(12)–C(12)–Mo(2)	178.0(5)	O(13)–C(13)–Mo(2)	171.5(5)		
O(14)–C(14)–Mo(2)	170.1(5)	C(11)–N(11)–Mo(2)	67.6(3)				

**Figure 3.** Structure of the anion of [N(PPh₃)₂][2,2'-μ-Au-{1,2-μ-NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀}₂] (**10b**) showing the crystallographic labeling scheme. Thermal ellipsoids are shown at the 40% probability level. For clarity, only the H(1) and H(11a) hydrogen atoms are shown.

However, in the ¹H NMR spectrum, a pair of signals is seen for the Bu^t group. In the ¹³C{¹H} NMR spectrum, there is also doubling of the resonances for the Bu^t group and the CO ligands, although here some of the pairs are not fully resolved. The N atom of the μ-NHBu^t group is chiral, and the anion of **10** therefore contains two chiral centers. Thus, one set of NMR signals is attributed to the *R/S* diastereomeric pair and the other set to the *R/R* plus *S/S* racemic mixture.

The X-ray diffraction study of the salt **10b** confirmed its structure. Selected geometric parameters are listed in Table 6, and the anion is shown in Figure 3. Two {1,2-μ-NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀} units are coordinated to the central Au atom in an approximately linear fashion [Mo(1)–Au–Mo(2) = 170.80(2)°], with molybdenum–gold distances Mo(1)–Au = 2.7377(9) Å and Mo(2)–Au = 2.7422(8) Å. The gross architecture of the two metallacarborane residues is the same as that seen in the anion of **2**. On one side, each molybdenum

atom is ligated in a pentahapto fashion by the CBBB face of the carborane, with an additional bond to the C _{cage}-bound NHBu^t group [Mo(1)–N(1) = 2.319(4) Å with Mo(1)–N(1)–C(1) = 66.9(2)°; Mo(2)–N(11) = 2.298(5) Å with Mo(2)–N(11)–

C(11) = 67.6(3)°]. In addition to the bond to gold, each molybdenum atom is coordinated on the other side by three carbonyl ligands (Mo–CO distances 2.026(5)–2.059(6) Å). These distances are slightly longer than the Mo–CO distances in **4d** or even the W–CO distances in **2**. This feature is presumably a consequence of accommodating the additional steric demands of coordination to gold. Each molybdenum atom bears one CO ligand (namely, that which is trans to N), with Mo–C–O close to linearity. For these two carbonyls, Au⋯C is greater than 3.1 Å. The four remaining CO groups have Mo–C–O angles around 170°, with the C–O vector directed slightly away from the central Au atom. Moreover, the carbon atoms of these four CO groups all lie rather close to Au, with Au⋯C distances in the range 2.528(6)–2.574(5) Å and with the associated Au–Mo–C angles lying between 61.7(2) and 63.15(14)°. These parameters are typical for linear semibridging carbonyl groups of type III, according to the classification of Crabtree and Lavin.¹⁴ As would be expected, the apparent geometrically bridging character has little perceptible effect on spectroscopic properties, because there is little or no actual interaction between Au and CO. Hence, these are essentially Mo-terminal carbonyls. The present system mirrors that noted in the simpler, but nonetheless related, complex [(η⁵-C₅H₅)W(CO)₃{Au(PPh₃)₃}],¹⁵ which was similarly classified.¹⁴

More closely related to the anion of **10** are the species [μ-Au-{M(η⁵-C₅H₅)(CO)₃}₂][−] (M = Cr, Mo, W),^{16,17} for which the chromium complex has been characterized by single-crystal X-ray diffraction methods.¹⁷ The Cr–Au–Cr angle (162.2(3)°) is rather more distorted from linearity than the Mo–Au–Mo angle in **10**, and there are again close Au⋯C approaches (2.40(6)–2.61(6) Å) involving two of the three carbonyl ligands bound to each chromium. The axes of these CO groups, in addition, are directed away from the central Au atom and have associated Au–Cr–C angles in the range 62(2)–68(2)°. Although this complex was not analyzed in the work of Crabtree and Lavin,¹⁴ these four CO ligands in this chromium species must again be placed in the type III linear semibridging class.

(14) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1986**, *25*, 805.(15) Wilford, J. B.; Powell, H. M. *J. Chem. Soc. A* **1969**, 8.(16) Usón, R.; Laguna, A.; Laguna, M.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, 366.(17) Braunstein, P.; Schubert, U.; Burgard, M. *Inorg. Chem.* **1984**, *23*, 4057.

Conclusion

The complexes described herein are, as far as we are aware, the first to be reported in which metals of group 6 are coordinated by the groups $[7\text{-NH}_2\text{Bu}^t\text{-nido-7-CB}_{10}\text{H}_{10}]^{2-}$ and $[7\text{-NHBu}^t\text{-nido-7-CB}_{10}\text{H}_{10}]^{3-}$. The products obtained are zwitterionic, neutral, or anionic in nature, with the metal in a II^+ or, for **6** and **7**, a IV^+ oxidation state. Of particular interest is the role played by the $[7\text{-NHBu}^t\text{-nido-7-CB}_{10}\text{H}_{10}]^{3-}$ moiety, which functions formally as an eight-electron ($6\pi + 2\sigma$) donor to the metal center in **1** or **2** and several derivatives and a 6π -electron donor in **7**. The ($6\pi + 2\sigma$) bonding mode suggests that the group has considerable potential as a ligand for metals with d^6 or fewer d electrons. Moreover, protonation in the presence of a donor of species having the $\mu\text{-NHBu}^t$ attachment allows the addition of a further ligand to the metal center. The structural similarity between the anion present in the salts **10** and the anion $[\mu\text{-Au}\{-\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}_2]^-$ creates an interesting valence-electron correlation between the ubiquitous cyclopentadienide anion functioning formally in its customary manner in the 6π -electron donor mode and the $[7\text{-NHBu}^t\text{-nido-7-CB}_{10}\text{H}_{10}]^{3-}$ anion in **10** acting as an eight-electron ($6\pi + 2\sigma$) donor.

Experimental Section

General Considerations. All of the reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using Schlenk-line techniques. Solvents were distilled from appropriate drying agents under nitrogen prior to use. Petroleum ether refers to that fraction of boiling point between 40 and 60 °C. Chromatography columns (typically ca. 15 cm in length and ca. 2 cm in diameter) were packed with silica gel (Acros, 60–200 mesh). NMR spectra were recorded at the following frequencies (MHz): ^1H , 360.1; ^{13}C , 90.6; ^{31}P , 145.8; ^{11}B , 115.5. The carborane $7\text{-Bu}^t\text{NH}_2\text{-nido-7-CB}_{10}\text{H}_{12}$ and the reagents $[\text{CuCl}(\text{PPh}_3)]_4$,¹⁸ $[\text{AuCl}(\text{PPh}_3)]$,¹⁹ and $[\text{AuCl}(\text{SC}_4\text{H}_8)]$ ²⁰ were prepared according to the literature.

Synthesis of the Salts $[\text{N}(\text{PPh}_3)_2][1,2\text{-}\mu\text{-NHBu}^t\text{-2,2,2-(CO)}_3\text{-closo-2,1-MoCB}_{10}\text{H}_{10}]$ ($\text{M} = \text{Cr, Mo, W}$). (i) The reagent $\text{Li}[7\text{-NHBu}^t\text{-nido-7-CB}_{10}\text{H}_{12}]^4$ was prepared by adding LiBu^n (2.0 mL, 5.0 mmol, 2.5 M solution in hexane) to $7\text{-NH}_2\text{Bu}^t\text{-nido-7-CB}_{10}\text{H}_{12}$ (1.00 g, 4.87 mmol) in THF (25 mL). After the addition of $[\text{Mo}(\text{CO})_6]$ (1.31 g, 4.96 mmol) and NCMe (40 mL), the mixture was heated to reflux temperatures for 2 h. The salt $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (2.87 g, 5.00 mmol) was added, and the volume of the solvent was reduced in vacuo. The mixture was then chromatographed, eluting with CH_2Cl_2 –petroleum ether (3:1). Removal of solvent in vacuo gave violet crystals of $[\text{N}(\text{PPh}_3)_2][1,2\text{-}\mu\text{-NHBu}^t\text{-2,2,2-(CO)}_3\text{-closo-2,1-MoCB}_{10}\text{H}_{10}]$ (**1**; 2.73 g) after crystallization from CH_2Cl_2 layered with petroleum ether.

Compound **1** was also prepared as follows: a suspension of $[\text{Mo}(\text{CO})_6]$ (0.64 g, 2.42 mmol) in NCMe (20 mL) was heated to reflux for 5 h to form $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ in situ. Meanwhile, $7\text{-NH}_2\text{Bu}^t\text{-nido-7-CB}_{10}\text{H}_{12}$ (0.50 g, 2.43 mmol) was dissolved in THF (25 mL), LiBu^n (3.0 mL, 7.5 mmol) was added, and the mixture was stirred for 2 h at room temperature. When formation of the molybdenum reagent was complete (IR), the NCMe solution containing it was added via a cannula to the THF solution of the carborane salt. The resulting brown-yellow mixture was stirred for 1 h, following which $\text{CH}_2=\text{CHCH}_2\text{Br}$ (0.30 g, 2.48 mmol) was added. The color changed gradually to purple. After 1 h, $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (1.40 g, 2.44 mmol) was added, and after a further 1 h, the solvent was partially evaporated in vacuo and the remaining material chromatographed. Elution with neat CH_2Cl_2 gave a purple fraction which, after the removal of solvent in vacuo, afforded **1** as a microcrystalline purple solid (1.00 g, 45%).

(ii) Proceeding as for compound **1**, $7\text{-NH}_2\text{Bu}^t\text{-nido-7-CB}_{10}\text{H}_{12}$ (0.50 g, 2.43 mmol) was treated with LiBu^n (1.0 mL, 2.50 mmol) in THF (20 mL), and $[\text{W}(\text{CO})_6]$ (0.86 g, 2.44 mmol) in NCEt (30 mL) was added. The resultant mixture was heated to reflux temperature for 8 h, followed by the addition of $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (1.41 g, 2.46 mmol). After the partial removal of solvent in vacuo, the remainder was chromatographed (twice, using CH_2Cl_2 as the eluant). Removal of solvent in vacuo and crystallization (CH_2Cl_2 –petroleum ether) of the residue afforded violet crystals of $[\text{N}(\text{PPh}_3)_2][1,2\text{-}\mu\text{-NHBu}^t\text{-2,2,2-(CO)}_3\text{-closo-2,1-WCB}_{10}\text{H}_{10}]$ (**2**; 0.58 g).

(iii) A THF (25 mL) solution of the reagent $7\text{-NH}_2\text{Bu}^t\text{-nido-7-CB}_{10}\text{H}_{12}$ (0.20 g, 0.97 mmol) was treated with LiBu^n (0.4 mL, 1.0 mmol). After being stirred for 2 h at room temperature, solvent was removed in vacuo, and NCEt (25 mL) and $[\text{Cr}(\text{CO})_6]$ (0.21 g, 0.95 mmol) were added. The mixture was heated at reflux for 6 h. After the removal of solvent in vacuo, the residue was taken up in CH_2Cl_2 (5 mL) and $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (0.56 g, 0.98 mmol) added. After filtration of the suspension through a Celite plug, the solution was chromatographed rapidly. Elution with neat CH_2Cl_2 gave a purple fraction, from which violet prisms of $[\text{N}(\text{PPh}_3)_2][1,2\text{-}\mu\text{-NHBu}^t\text{-2,2,2-(CO)}_3\text{-closo-2,1-CrCB}_{10}\text{H}_{10}]$ (**3**; 0.067 g) were obtained following crystallization twice from CH_2Cl_2 layered with petroleum ether.

Synthesis of $[1\text{-NH}_2\text{Bu}^t\text{-2,2,2-(CO)}_3\text{-2-L-closo-2,1-MoCB}_{10}\text{H}_{10}]$ ($\text{L} = \text{CO, PPh}_3, \text{PMe}_3, \text{PEt}_3, \text{PMe}_2\text{Ph}$). (i) Compound **1** (0.20 g, 0.22 mmol) in CH_2Cl_2 (20 mL) was cooled to 0 °C, and the solution was saturated with CO. The reagent $\text{HBF}_4\cdot\text{OEt}_2$ (36 μL , 0.22 mmol, 54% solution in Et_2O) was added, and the mixture was warmed to room temperature over 1 h with continued passage of CO. Concentration of the resulting yellow solution and the addition of excess Et_2O afforded an oily yellow solid. Attempts to further purify the product $[1\text{-NH}_2\text{Bu}^t\text{-2,2,2-(CO)}_3\text{-2,1-MoCB}_{10}\text{H}_{10}]$ (**4a**) by crystallization or chromatography were unsuccessful.

(ii) Compound **1** (0.20 g, 0.22 mmol) in CH_2Cl_2 (20 mL) at -30 °C was treated with $\text{HBF}_4\cdot\text{OEt}_2$ (36 μL , 0.22 mmol). The resulting dark red-brown solution was stirred at this temperature for 30 min, and PPh_3 (0.28 g, 1.07 mmol) was added. After the mixture was warmed and stirred at room temperature for a further 1 h, solvent was removed in vacuo. The residue was taken up in CH_2Cl_2 , and the mixture was chromatographed. A yellow fraction was eluted with CH_2Cl_2 –petroleum ether– MeCO_2H (150:50:1), from which yellow microcrystals of $[1\text{-NH}_2\text{Bu}^t\text{-2,2,2-(CO)}_3\text{-2-PPh}_3\text{-closo-2,1-MoCB}_{10}\text{H}_{10}]$ (**4b**; 0.055 g) were obtained after the removal of solvent in vacuo and crystallization from a CH_2Cl_2 solution layered with petroleum ether.

(iii) To a solution of compound **1** (0.20 g, 0.22 mmol) in CH_2Cl_2 (25 mL) was added PMe_3 (0.22 mL, 0.22 mmol, 1.0 M solution in THF), and the mixture was stirred at room temperature for 1 h. The solvent was reduced in volume, and the mixture was chromatographed. A yellow fraction was eluted with CH_2Cl_2 , from which $[1\text{-NH}_2\text{Bu}^t\text{-2,2,2-(CO)}_3\text{-2-PMe}_3\text{-closo-2,1-MoCB}_{10}\text{H}_{10}]$ (**4c**; 0.061 g) was isolated as a yellow microcrystalline powder after crystallization from a CH_2Cl_2 solution layered with petroleum ether.

(iv) Proceeding as for compound **4c**, compound **1** (0.20 g, 0.22 mmol) and PEt_3 (0.11 mL, 0.09 g, 0.74 mmol) gave $[1\text{-NH}_2\text{Bu}^t\text{-2,2,2-(CO)}_3\text{-2-PEt}_3\text{-closo-2,1-MoCB}_{10}\text{H}_{10}]$ (**4d**; 0.054 g) as yellow crystals.

(v) Similarly, compound **1** (0.20 g, 0.22 mmol) and PMe_2Ph (0.15 mL, 0.15 g, 1.05 mmol) yielded $[1\text{-NH}_2\text{Bu}^t\text{-2,2,2-(CO)}_3\text{-2-PMe}_2\text{Ph-closo-2,1-MoCB}_{10}\text{H}_{10}]$ (**4e**; 0.036 g) as yellow microcrystals.

Synthesis of $[\text{N}(\text{PPh}_3)_2][1\text{-NH}_2\text{Bu}^t\text{-2,2,2-(CO)}_3\text{-2-Cl-closo-2,1-MoCB}_{10}\text{H}_{10}]$. A CH_2Cl_2 (25 mL) solution of **1** (0.20 g, 0.22 mmol) at -50 °C was treated with HCl (0.25 mL, 0.25 mmol, 1.0 M solution in Et_2O). The mixture was warmed to room temperature and stirred for 2 h, affording a deep-red solution. Removal of solvent in vacuo afforded a red microcrystalline solid, which was washed several times with Et_2O to give an almost quantitative yield of $[\text{N}(\text{PPh}_3)_2][1\text{-NH}_2\text{Bu}^t\text{-2,2,2-(CO)}_3\text{-2-Cl-closo-2,1-MoCB}_{10}\text{H}_{10}]$ (**5**; 0.20 g).

Synthesis of $[1,2\text{-}\mu\text{-NHBu}^t\text{-2,2,2-(CNBu}^t\text{)}_3\text{-2-I-closo-2,1-MoCB}_{10}\text{H}_{10}]$. Compound **1** (0.20 g, 0.22 mmol) dissolved in CH_2Cl_2 (20 mL) with CNBu^t (0.10 mL, 0.074 g, 0.89 mmol) added was treated with I_2 (0.055 g, 0.22 mmol). The resultant mixture was stirred for 12 h. Solvent was reduced in volume and the remainder transferred to the top of a chromatography column. Elution with CH_2Cl_2 –petroleum ether (3:1)

(18) Jardine, F. H.; Rule, J.; Vohra, A. G. *J. Chem. Soc. A* **1970**, 238.

(19) Bruce, M. I.; Nicholson, B. K.; Bin Shawkataly, O. *Inorg. Synth.* **1989**, 26, 325.

(20) Uson, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, 26, 85.

gave a pink eluant. After the removal of solvent in vacuo, the residue was crystallized from CH₂Cl₂–petroleum ether to afford [1,2- μ -NHBu^t-2,2,2-(CNBu^t)₃-2-I-closo-2,1-MoCB₁₀H₁₀] (**6a**; 0.076 g) as pink crystals.

Synthesis of [1-NHBu^t-2,2-(CNBu^t)₂-2,2-(CO)₂-2-I-closo-2,1-WCB₁₀H₁₀] and [1,2- μ -NHBu^t-2,2,2-(CNBu^t)₃-2-I-closo-2,1-WCB₁₀H₁₀]. To a solution of compound **2** (0.38 g, 0.38 mmol) in CH₂Cl₂ were added CNBu^t (0.17 mL, 0.13 g, 1.56 mmol) and then I₂ (0.096 g, 0.38 mmol). The reactants were stirred for 12 h. Partial evaporation of solvent in vacuo followed by chromatography of the remainder, eluting first with CH₂Cl₂–petroleum ether (1:1), gave a yellow fraction which, after the solvent was removed in vacuo, yielded [1-NHBu^t-2,2-(CNBu^t)₂-2,2-(CO)₂-2-I-closo-2,1-WCB₁₀H₁₀] (**7**; 0.030 g) as an orange solid. Further elution with CH₂Cl₂–petroleum ether (3:1) afforded a pink band, from which [1,2- μ -NHBu^t-2,2,2-(CNBu^t)₃-2-I-closo-2,1-WCB₁₀H₁₀] (**6b**; 0.025 g) was obtained as a pink powder after the removal of solvent in vacuo.

Synthesis of Bimetallic Complexes. (i) Compound **1** (0.20 g, 0.22 mmol) and [CuCl(PPh₃)₃]₄ (0.08 g, 0.055 mmol) were dissolved in CH₂Cl₂ (25 mL), and Ti[PF₆] (0.076 g, 0.22 mmol) was added. After being stirred for 2 h, the mixture was filtered through a Celite plug, the solvent was partially removed in vacuo, and the remainder was applied to the top of a chromatography column. A purple fraction was eluted with CH₂Cl₂ which, after the removal of solvent in vacuo and recrystallization (CH₂Cl₂–petroleum ether) of the residue, afforded [exo-{Cu(PPh₃)₃}-1,2- μ -NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀] (**8**; 0.064 g) as violet crystals.

(ii) The salt Ti[PF₆] (0.076 g, 0.22 mmol) was added to a CH₂Cl₂ (25 mL) solution containing **1** (0.20 g, 0.22 mmol) and [AuCl(PPh₃)₂] (0.11 g, 0.22 mmol). The reactants were stirred for 2 h, following which the mixture was filtered through a Celite plug. After the partial removal of solvent in vacuo, the remainder was chromatographed, eluting with CH₂Cl₂–petroleum ether (2:1). A dark-red fraction was obtained which, after the removal of solvent, afforded [1,2- μ -NHBu^t-2-{Au(PPh₃)₂}-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀] (**9**; 0.066 g) as red microcrystals. Further elution with neat CH₂Cl₂ gave a second red fraction which, upon the removal of solvent in vacuo, gave as a dark-red microcrystalline powder [Au(PPh₃)₂][2,2'- μ -Au-{1,2- μ -NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀}₂] (**10a**; 0.043 g). The isolated solid **9** likely contains some **10a** and vice versa, as a consequence of the disproportionation discussed earlier; this, however, has no effect on the microanalytical results.

(iii) A CH₂Cl₂ (25 mL) solution of **1** (0.20 g, 0.22 mmol) was treated with [AuCl(THT)] (0.035 g, 0.11 mmol) and Ti[PF₆] (0.038 g, 0.11 mmol). The mixture was stirred for 2 h, following which the products were filtered through a Celite plug. Solvent was reduced in volume in vacuo to ca. 5 mL, and the mixture was chromatographed. A red fraction was eluted with CH₂Cl₂ from which, after the removal of solvent in vacuo and crystallization from CH₂Cl₂ layered with petroleum ether, [N(PPh₃)₂][2,2'- μ -Au-{1,2- μ -NHBu^t-2,2,2-(CO)₃-closo-2,1-MoCB₁₀H₁₀}₂] (**10b**; 0.051 g, 31%) was obtained as red crystals. IR (CH₂Cl₂): $\nu_{\max}(\text{CO})$ 2028 s, 1940 s cm⁻¹. Anal. Found (calcd) for C₅₃H₇₂AuB₂₀Cl₂Mo₂N₃O₆P₂ (**10b**·CH₂Cl₂): C, 40.5 (40.2); H, 5.0 (4.6); N, 2.7 (2.6).

Structure Determinations of 2, 4d, and 10b. Experimental data are recorded in Table 7. Diffracted intensities were collected on an Enraf-Nonius CAD4 diffractometer using Mo K α X-radiation ($\lambda = 0.71073$ Å). Final unit cell dimensions were determined from the setting angles of 25 accurately centered reflections. Intensity data were

Table 7. Crystallographic Data for **2**·2CH₂Cl₂, **4d**, and **10b**·CH₂Cl₂

	2 ·2CH ₂ Cl ₂	4d	10b ·CH ₂ Cl ₂
formula	C ₄₆ H ₅₄ B ₁₀ Cl ₄ - N ₂ O ₃ P ₂ W	C ₁₄ H ₃₆ B ₁₀ Mo- NO ₃ P	C ₅₃ H ₇₂ AuB ₂₀ Cl ₂ - Mo ₂ N ₃ O ₆ P ₂
fw	1178.60	501.45	1585.02
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1
<i>a</i> , Å	9.8637(7)	12.4537(10)	12.427(2)
<i>b</i> , Å	15.146(2)	10.0216(12)	17.498(5)
<i>c</i> , Å	18.481(2)	19.863(2)	18.785(3)
α , deg	91.484(10)		117.51(2)
β , deg	104.077(7)	94.749(8)	100.115(14)
γ , deg	97.696(9)		97.51(2)
<i>V</i> , Å ³	2649.0(5)	2470.5(5)	3459.8(13)
<i>Z</i>	2	4	2
ρ_{calc} , g cm ⁻³	1.478	1.348	1.521
<i>T</i> , K	173	293	293
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	24.84	6.11	26.43
wR2 (all data), R1 ^a	0.0709, 0.0304	0.0593, 0.0236	0.0956, 0.0407

^a Refinement was block full-matrix least-squares on all of the *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 σ (*F*_o).

corrected for Lorentz and polarization effects, after which appropriate absorption corrections were applied.

The structures were solved with conventional direct methods and refined by full-matrix least-squares on all *F*² data using SHELXTL version 5.03²¹ and SHELXL-97.²² All of the non-hydrogen atoms were assigned anisotropic displacement parameters. The locations of the cage-carbon atoms were verified by examination of the appropriate internuclear distances, as well as the magnitudes of their isotropic thermal displacement parameters. The amine protons in all three of the structures were located in difference Fourier syntheses and refined with fixed isotropic thermal parameters [*U*_{iso}(H) = 1.2*U*_{iso}(N)]. 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 protons].

Compound **2** cocrystallized with two molecules of CH₂Cl₂ in the asymmetric unit. The molecule corresponding to C(100) was fully ordered and refined without restraint; hydrogen atoms were included in the calculated positions. The second solvent molecule, corresponding to C(200), was disordered over several positions; no hydrogen atoms were included. Compound **10b** cocrystallized with one fully ordered CH₂Cl₂ molecule per formula unit, which was refined without restraint; hydrogen atoms were included in calculated positions.

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Supporting Information Available: Crystallographic data available (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) SHELXTL, version 5.03; Bruker AXS: Madison WI, 1995.

(22) Sheldrick, G. M. SHELXL-97; University of Göttingen: Göttingen, Germany, 1997.