

Review

# Metal complexes of monocarbon carboranes bearing C-amine or -amino substituents

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## Abstract

Icosahedral metal–monocarbollide complexes in which the carbon atom of the {*nido*-CB<sub>10</sub>} fragment carries an *exo*-polyhedral –NR<sub>3</sub> or –NR<sub>2</sub> group have an extensive chemistry. This is illustrated with complexes of ruthenium, osmium, rhodium, molybdenum, tungsten and rhenium. Many complexes with molecular structures new to the metallocarborane field have been discovered, and it has been shown that it is possible to introduce functional groups into the {*nido*-CB<sub>10</sub>} cage system in many different ways.

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## 1. Introduction

Molecules with structures in which a metal ion is a vertex in a cage framework of boron and carbon atoms occupy a major domain of chemistry, forming a bridge between that of the main group elements and the transition elements [1]. The first such metallocarboranes were identified in Hawthorne's laboratory [2,3], and contained a metal ion, two carbon and nine boron atoms combining to form a {*closo*-MC<sub>2</sub>B<sub>9</sub>} icosahedral cage framework. From the earliest work it was recognized that these compounds might be viewed as metal complexes in which a metal is ligated in a pentahapto manner by the open face of a [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup> dianion. The formalism is useful because it emphasizes the isolobal relationship between the carborane dianion and the ubiquitous [C<sub>5</sub>H<sub>5</sub>]<sup>-</sup> monoanion of cyclopentadienide

metal complex chemistry, which also coordinates in a pentahapto manner.

Metallocarborane chemistry has grown enormously since its beginnings in 1965. However, until recent times compounds based on {*closo*-3,1,2-MC<sub>2</sub>B<sub>9</sub>} structures have largely dominated the field. Now there is a growing interest in metallocarboranes with polyhedral structures other than those that are icosahedral, and also interest in species with more than two carbon atoms in the cage [4–6]. Surprisingly the study of species with only one carbon atom in the polyhedral framework has been largely neglected. However, following the isolation of metal dicarbollides such as [3-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)-*closo*-3,1,2-FeC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], from reactions between metal salts and salts of [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup>, it was logical that the monocarbon trianion [*nido*-7-CB<sub>10</sub>H<sub>11</sub>]<sup>3-</sup> would react in a similar manner to afford monocarbon metallocarboranes with icosahedral frameworks. Indeed this was demonstrated soon thereafter, when a few monocarbollide complexes, e.g., [*commo*-2,2'-Ni-(*closo*-2,1-NiCB<sub>10</sub>H<sub>11</sub>)<sub>2</sub>]<sup>2-</sup>, were isolated [7]. Since this initial report, however, monocarbon species have received very little attention [4].

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In an attempt to remedy this situation studies on the chemistry of monocarbollide metallacarboranes have been initiated in our laboratory, with the work focused on compounds where the metal is a vertex in a  $\{closo-2,1-MCB_{10}\}$  cage system. Moreover, the compounds we are investigating are of the ‘piano-stool’ type, with a  $\{nido-7-CB_{10}H_{11}\}$  group coordinated on one side of the metal atom and with the conventional ligands of coordination chemistry (CO,  $PR_3$ , CNR, alkynes, etc.) on the other. This structural arrangement, where different coordinating groups are located within the coordination sphere of the metal, allows for reactions to occur between the ligands themselves, or between the latter and the BH or CH vertices of the cage. Reactions of other molecules with the coordinated ligands are also possible. If the BH or CH vertices are involved, the cage adopts a non-spectator role and formation of unusual cage-substitution products is possible [8]. Piano-stool type complexes therefore offer the opportunity to develop new chemistry that is larger in scope than that arising from molecules with sandwich structures.

Our work has concentrated on two types of piano-stool monocarbollide metallacarboranes. In the first, the carborane moiety is the  $[nido-7-CB_{10}H_{11}]^{3-}$  group. In the second, the carbon of the *nido*- $CB_{10}$  fragment carries either an  $-NR_3$  or an  $-NR_2$  group. The amine- and the amino-substituted compounds are the subject of this review. The reader is referred elsewhere for a review of studies on compounds where the metal is ligated by the  $[nido-7-CB_{10}H_{11}]^{3-}$  group [9].

Dianions of formulation  $[7-NR_3-nido-7-CB_{10}H_{10}]^{2-}$  are charge-compensated species with the charge reduced by one compared with  $[nido-7-CB_{10}H_{11}]^{3-}$ . As such they are therefore isoelectronic with the dianion  $[nido-7,8-C_2B_9H_{11}]^{2-}$ . If the carbon atom carries an *exo*-polyhedral  $NR_2$  fragment, however, then the anion  $[7-NR_2-nido-7-CB_{10}H_{10}]^{3-}$  is isoelectronic with  $[nido-7-CB_{10}H_{11}]^{3-}$ . These relationships allow the synthesis of hitherto unknown monocarbollide metallacarboranes, many displaying novel structures and undergoing new reactions. It should be noted that some full-sandwich complexes of general formulation  $[M\{\eta^5-(amine)CB_{10}H_{10}\}_2]$  were among the first monocarbollide metal complexes to be isolated [7]. However, since they were of the full- rather than the half-sandwich type, they do not have the potential for the development of new chemistry as do those compounds described herein.

## 2. Ruthenium and osmium compounds

The observation that *nido-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>13</sub>* reacts readily with  $[Ru_3(CO)_{12}]$  to yield the mononuclear ruthenium complex  $[3,3,3-(CO)_3-closo-3,1,2-RuC_2B_9H_{11}]$  [10] stimulated a study to determine whether the isolobal mono-

carboranes  $7-NR_3-nido-7-CB_{10}H_{12}$  would undergo a similar reaction to yield complexes of formulation  $[1-NR_3-2,2,2-(CO)_3-closo-2,1-RuCB_{10}H_{10}]$ . In practice the reactions followed a different course, affording triruthenium cluster compounds [11]. Thus  $7-NMe_3-nido-7-CB_{10}H_{12}$  with  $[Ru_3(CO)_{12}]$  in toluene at reflux temperatures gave  $[1-NMe_3-2,2-(CO)_2-7,11-(\mu-H)_2-2,7,11-\{Ru_2(CO)_6\}-closo-2,1-RuCB_{10}H_8]$  (**1a**). Similar reactions with other carboranes  $7-NR_3-nido-7-CB_{10}H_{12}$  yielded the species  $[1-NR_3-2,2-(CO)_2-7,11-(\mu-H)_2-2,7,11-\{Ru_2(CO)_6\}-closo-2,1-RuCB_{10}H_8]$  (**1b**,  $NR_3 = NH_2Bu^+$ ; **1c**,  $NR_3 = NMe_2Bu^+$ ). Compound **1d**, the osmium analogue of **1a**, has been synthesized from  $[Os_3(CO)_{12}]$  and  $7-NMe_3-nido-7-CB_{10}H_{12}$  [12]. The molecular structures of **1a** and **1d** were established by X-ray diffraction studies, and on the basis of their similar NMR data it may be inferred that **1b,c** have similar structures. The compounds, which are zwitterionic in character, have a triangular array of ruthenium or osmium atoms bridged by the  $\{7-NMe_3-nido-7-CB_{10}H_{10}\}$  group. One metal atom is pentahapto coordinated to the cage and the other two form three-center two-electron  $B-H \rightarrow M$  ( $M = Ru$  or  $Os$ ) interactions. The three-center bonds involve the two borons in the  $\beta$ -sites with respect to the carbon in the  $\overline{CBBBB}$  ring. The clusters are electronically saturated since the carbonyl ligands contribute 16 electrons and the monocarbon *nido*-carborane cage formally donates 8 electrons, 4 to the pentahapto coordinated metal center and two each to the other two metal atoms. Thus with 24 valence electrons from the metal atoms the overall cluster electron count is 48, in accord with adherence to the 18-electron rule.

Treatment of **1a** with  $PPh_3$  in toluene gives the complex  $[1-NMe_3-2,2-(CO)_2-7-\mu-H-2,7,11-\{Ru_2(\mu-H)(PPh_3)(CO)_5\}-closo-2,1-RuCB_{10}H_8]$  (**2**), also having a triangular array of ruthenium atoms. In **2** one metal atom  $[Ru(1)]$  carries two CO groups and forms a  $\{closo-2,1-RuCB_{10}\}$  framework as in the complexes **1**. Two CO molecules and the  $PPh_3$  group ligate a second Ru atom  $[Ru(2)]$ , with the phosphine transoid to  $Ru(1)$ , while the third Ru atom  $[Ru(3)]$  is terminally attached to three CO molecules. The  $Ru(2)-Ru(3)$  connectivity is bridged by a hydrido ligand, and in addition both of these metal atoms are linked to the  $CB_{10}$  framework through boron atoms in the  $\beta$  sites of the  $\overline{CBBBB}$  ring coordinated to  $Ru(1)$ . Atom  $Ru(2)$  is involved in a three-center, two electron  $B-H \rightarrow Ru$  bond, while atom  $Ru(3)$  forms a direct  $Ru-B$   $\sigma$ -bond, with the result that the  $\{7-NMe_3-nido-7-CB_{10}H_9\}$  group bridges the  $Ru_3$  triangle via a combination of  $\eta^5-\overline{CBBBB}$ ,  $B-H \rightarrow Ru$ , and  $B-Ru$  interactions. In addition to X-ray diffraction studies, NMR is an important structural tool in this area. Thus the  $^1H$  spectrum of **2** reveals signals for the  $\mu-H$  ligand at  $\delta -17.71$ , and at  $\delta -10.20$  [q,  $J(BH) = 65$  Hz] for the  $B-H \rightarrow Ru$  group. The  $^{11}B\{^1H\}$  NMR spectrum is diagnostic for a  $\sigma$ -bonded  $B-Ru$  group with a resonance at

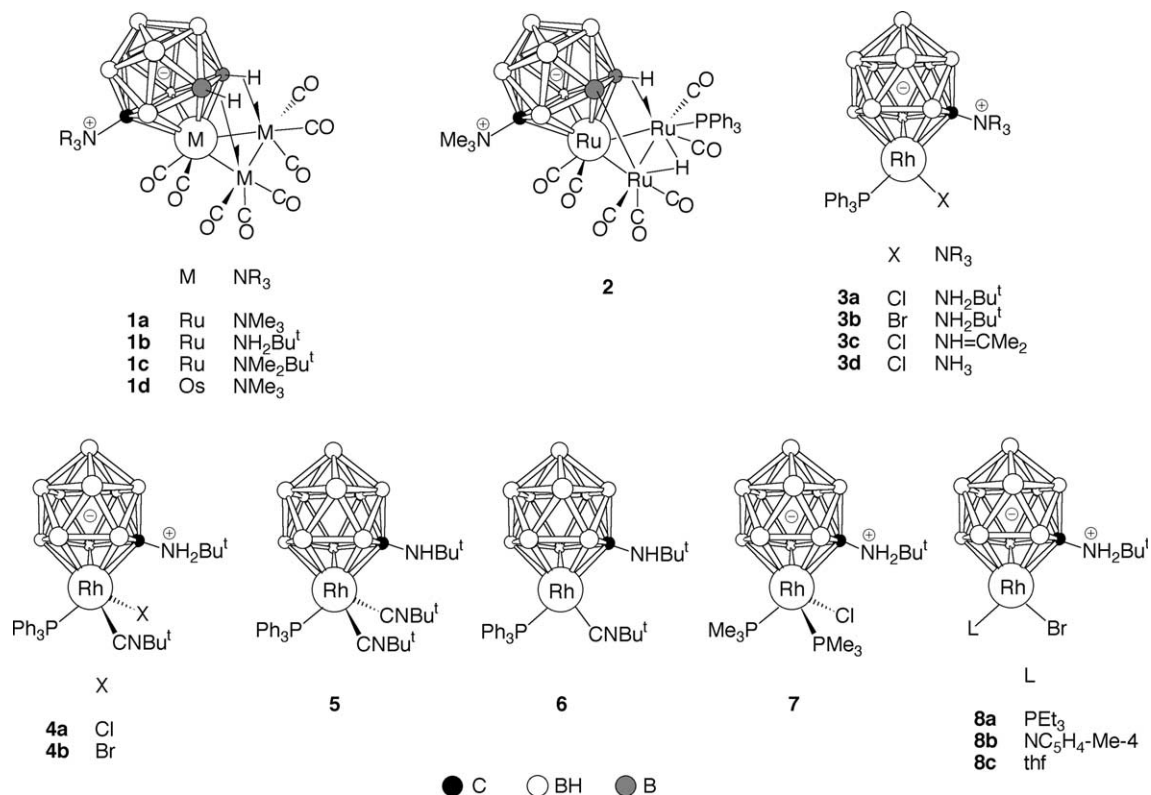
$\delta$  53.3 that remains a singlet in the  $^{11}\text{B}$  NMR spectrum, indicating that no proton is attached to the boron atom. Interestingly,  $\text{CNBu}^t$  reacts with **1a** with replacement of one CO ligand to give  $[1\text{-NMe}_3\text{-}2,2\text{-(CO)}_2\text{-}7,11\text{-}(\mu\text{-H})_2\text{-}2,7,11\text{-}\{\text{Ru}_2(\text{CNBu}^t)(\text{CO})_5\}\text{-}closo\text{-}2,1\text{-RuCB}_{10}\text{H}_8]$ , with no disruption of a  $\text{B-H}\rightarrow\text{Ru}$  bond.

It is interesting to compare these results with the products obtained from reactions between  $[\text{M}_3(\text{CO})_{12}]$  ( $\text{M}=\text{Ru}$  or  $\text{Os}$ ) and the carboranes  $7,8\text{-R}_2\text{-}nido\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}$  ( $\text{R}=\text{H}$  or  $\text{Me}$ ) or  $[\text{X}][nido\text{-}7\text{-CB}_{10}\text{H}_{13}]$  [ $\text{X}=\text{NHMe}_3$  or  $\text{N}(\text{PPh}_3)_2$ ]. As mentioned above,  $nido\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{13}$  with  $[\text{Ru}_3(\text{CO})_{12}]$  yields only the mononuclear ruthenium species  $[3,3,3\text{-(CO)}_3\text{-}closo\text{-}3,1,2\text{-RuC}_2\text{B}_9\text{H}_{11}]$ . In contrast  $7,8\text{-Me}_2\text{-}nido\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}$  affords a mixture of the mononuclear ruthenium compound  $[3,3,3\text{-(CO)}_3\text{-}1,2\text{-Me}_2\text{-}closo\text{-}3,1,2\text{-RuC}_2\text{B}_9\text{H}_9]$  and the trinuclear ruthenium compound  $[3,3\text{-(CO)}_2\text{-}4,8\text{-(}\mu\text{-H)}_2\text{-}3,4,8\text{-}\{\text{Ru}_2(\text{CO})_6\}\text{-}1,2\text{-Me}_2\text{-}closo\text{-}3,1,2\text{-RuC}_2\text{B}_9\text{H}_7]$  [13], while  $[\text{NHMe}_3][nido\text{-}7\text{-CB}_{10}\text{H}_{13}]$  gives almost exclusively the anionic trinuclear ruthenium complex  $[2,2\text{-(CO)}_2\text{-}7,11\text{-(}\mu\text{-H)}_2\text{-}2,7,11\text{-}\{\text{Ru}_2(\text{CO})_6\}\text{-}closo\text{-}2,1\text{-RuCB}_{10}\text{H}_9]^-$  and only traces of the mononuclear species  $[2,2,2\text{-(CO)}_3\text{-}closo\text{-}2,1\text{-RuCB}_{10}\text{H}_{11}]^-$  [14,15]. Moreover,  $[\text{Os}_3(\text{CO})_{12}]$  and  $[\text{N}(\text{PPh}_3)_2][nido\text{-}7\text{-CB}_{10}\text{H}_{13}]$  yield a mixture of  $[2,2\text{-(CO)}_2\text{-}7,11\text{-(}\mu\text{-H)}_2\text{-}2,7,11\text{-}\{\text{Os}_2(\text{CO})_6\}\text{-}closo\text{-}2,1\text{-OsCB}_{10}\text{H}_9]^-$  and

$[2,2,2\text{-(CO)}_3\text{-}closo\text{-}2,1\text{-OsCB}_{10}\text{H}_{11}]^-$  in approximately equal proportions [15], whereas with  $[\text{NHMe}_3][nido\text{-}7\text{-CB}_{10}\text{H}_{13}]$  the unusual boron substituted mononuclear species  $[12\text{-NMe}_3\text{-}2,2,2\text{-(CO)}_3\text{-}closo\text{-}2,1\text{-OsCB}_{10}\text{H}_{10}]$  is obtained [15]. There was no evidence for the formation of mononuclear ruthenium or osmium products in the reactions of the carbonyls  $[\text{M}_3(\text{CO})_{12}]$  ( $\text{M}=\text{Ru}$  or  $\text{Os}$ ) with  $7\text{-NMe}_3\text{-}nido\text{-}7\text{-CB}_{10}\text{H}_{12}$ .

### 3. Rhodium compounds

Several complexes have been prepared with rhodium a vertex in a  $\{1\text{-L-}closo\text{-}2,1\text{-RhCB}_{10}\text{H}_{10}\}$  ( $\text{L}=\text{NR}_3$ ,  $\text{NR}_2$ ) cage system. Thus the compounds  $[\text{RhX}(\text{PPh}_3)_3]$  react with  $7\text{-NH}_2\text{Bu}^t\text{-}nido\text{-}7\text{-CB}_{10}\text{H}_{12}$  in toluene to give the 16-electron zwitterionic  $\text{Rh}^{\text{III}}$  complexes  $[1\text{-NH}_2\text{Bu}^t\text{-}2\text{-X-}2\text{-PPh}_3\text{-}closo\text{-}2,1\text{-RhCB}_{10}\text{H}_{10}]$  (**3a**,  $\text{X}=\text{Cl}$ ; **3b**,  $\text{X}=\text{Br}$ ) [16]. The structure of **3b** was confirmed by X-ray diffraction analysis, which showed that the rhodium is coordinated on one side by  $\text{Br}$  and  $\text{PPh}_3$  groups and on the other in the pentahapto manner by the open  $\overline{\text{CBBBB}}$  face of the carborane ligand. The complexes **3a** and **3b** are related in an isolobal manner to the rhodium-dicarbollide species  $[2\text{-Cl-}2\text{-PPh}_3\text{-}closo\text{-}2,1,7\text{-RhC}_2\text{B}_9\text{H}_{11}]$  [17].

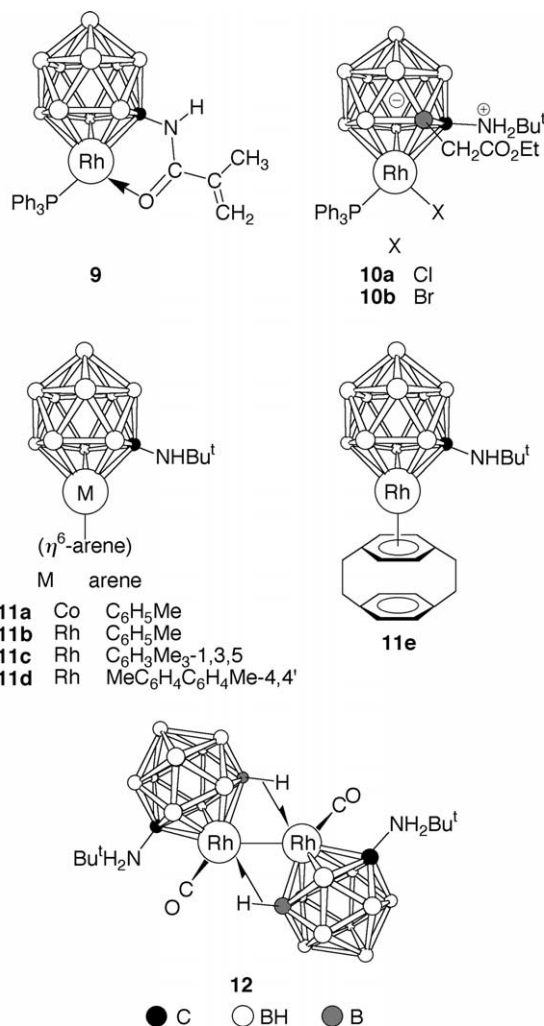


Some years ago, in related chemistry, it was shown that the carborane 7-NH<sub>3</sub>-*nido*-7-CB<sub>10</sub>H<sub>12</sub> reacted with [RhCl(PPh<sub>3</sub>)<sub>3</sub>] in methanolic solution to give [1-NH<sub>2</sub>-2,2-(PPh<sub>3</sub>)<sub>2</sub>-2-H-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>]<sup>-</sup>, which in refluxing methanol was converted to the dimeric anionic [2,2'-μ-H-{1,2'-μ-NH<sub>2</sub>-2-PPh<sub>3</sub>-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>}<sub>2</sub>]<sup>-</sup> [18]. In contrast, the carborane 7-NMe<sub>3</sub>-*nido*-7-CB<sub>10</sub>H<sub>12</sub> in refluxing methanol with the same rhodium reagent yields primarily 18-electron [1-NMe<sub>3</sub>-2-H-2-Cl-2,7-(PPh<sub>3</sub>)<sub>2</sub>-*closo*-2,1-RhCB<sub>10</sub>H<sub>9</sub>], together with the 16-electron complex [1-NMe<sub>3</sub>-2-Cl-2-PPh<sub>3</sub>-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>] [19]. The latter is an analogue of the species **3**.

Other studies in our laboratory have involved the carborane 7-NH=CMe<sub>2</sub>-*nido*-7-CB<sub>10</sub>H<sub>12</sub>, where the N atom of the *C*-amine carries a functional group. It was anticipated that the *exo*-polyhedral imine group could interact with the rhodium center, or alternatively would allow for the possibility of derivatization [20]. In toluene at reflux temperatures, [RhCl(PPh<sub>3</sub>)<sub>2</sub>] and 7-NH=CMe<sub>2</sub>-*nido*-7-CB<sub>10</sub>H<sub>12</sub> afford [1-NH=CMe<sub>2</sub>-2-Cl-2-PPh<sub>3</sub>-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>] (**3c**) structurally akin to **3a,b**. The compounds **3a–c** all undergo a variety of reactions.

Complexes **3a,b** react with several different donor molecules. With CNBu<sup>t</sup>, by changing the stoichiometry either the 18-electron complexes [1-NH<sub>2</sub>Bu<sup>t</sup>-2-X-2-CNBU<sup>t</sup>-2-PPh<sub>3</sub>-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>] (**4a**, X=Cl; **4b**, X=Br) together with [1-NHBu<sup>t</sup>-2,2-(CNBU<sup>t</sup>)<sub>2</sub>-2-PPh<sub>3</sub>-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>] (**5**) are obtained, or the 16-electron complex [1-NHBu<sup>t</sup>-2-CNBU<sup>t</sup>-2-PPh<sub>3</sub>-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>] (**6**) is formed. The formation of **5** and **6** results from loss of HX from the precursors **3a,b**, giving products in which a {7-NHBu<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>} cage, formally a three π-electron donor, ligates the rhodium. Reactions between the compounds **3a,b** and the donors PMe<sub>3</sub>, PET<sub>3</sub>, NC<sub>5</sub>H<sub>4</sub>Me-4, and thf (tetrahydrofuran) affords the complexes [1-NH<sub>2</sub>Bu<sup>t</sup>-2-Cl-2,2-(PMe<sub>3</sub>)<sub>2</sub>-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>] (**7**) and [1-NH<sub>2</sub>Bu<sup>t</sup>-2-Br-2-L-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>] (**8a**, L=PEt<sub>3</sub>; **8b**, L=NC<sub>5</sub>H<sub>4</sub>Me-4; **8c**, L=thf), respectively.

Upon methanolysis, **3c** yields [1-NH<sub>3</sub>-2-Cl-2-PPh<sub>3</sub>-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>] (**3d**). At room temperature, in the presence of Na<sub>2</sub>CO<sub>3</sub> the latter reacts with acetic, methacrylic, and crotonic anhydrides to give the complexes [1,2-μ-{NHC(R)=O}-2-PPh<sub>3</sub>-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>] [R=Me, CMe=CH<sub>2</sub>, and (*E*)-CH=CHMe, respectively] [20]. An X-ray diffraction study of [1,2-μ-{NHC(CMe=CH<sub>2</sub>)=O}-2-PPh<sub>3</sub>-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>] (**9**) established that the acyl group is coordinated to the rhodium through the oxygen. In the crystal the molecules lie pair-wise, linked by an intermolecular B–H→Rh bridge so that in one molecule the rhodium has a 16-electron shell and in the other an 18-electron configuration.



It was of interest to determine whether a B–H group of any of the complexes **3** could be functionalized and hence reactions of the species **3a,b** with the diazoalkane N<sub>2</sub>C(H)CO<sub>2</sub>Et were investigated [21]. In these reactions the compounds **3** readily afforded the complexes [1-NH<sub>2</sub>Bu<sup>t</sup>-2-X-2-PPh<sub>3</sub>-3-CH<sub>2</sub>CO<sub>2</sub>Et-*closo*-2,1-RhCB<sub>10</sub>H<sub>9</sub>] (**10a**, X=Cl; **10b**, X=Br). An X-ray diffraction study of **10b** revealed that the CH<sub>2</sub>CO<sub>2</sub>Et substituent was attached to one of the two α boron atoms adjacent to the carbon in the  $\overline{CBBBB}$  ring that ligates the Rh atom. Evidently insertion of the CH<sub>2</sub>CO<sub>2</sub>Et moiety occurs preferentially at one or other of the B<sub>α</sub> sites, either of which would yield enantiomers of the same product. The pathway for these reactions presumably involves formation of coordinatively and electronically saturated intermediate complexes [1-NH<sub>2</sub>Bu<sup>t</sup>-2-X-2-PPh<sub>3</sub>-2-{C(H)CO<sub>2</sub>Et}-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>] followed by insertion of the alkylidene ligand into an adjacent BH bond of the {*closo*-2,1-RhCB<sub>10</sub>} framework. There is ample precedent for such a step both from earlier work [22] and from studies with aminocarborane–rhenium complexes described below.

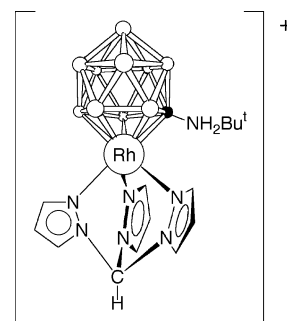
In contrast with the reactions of the compounds  $[\text{RhX}(\text{PPh}_3)_3]$  with 7-NH<sub>2</sub>Bu<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>12</sub> that yielded **3a,b**, the cobalt reagent  $[\text{CoCl}(\text{PPh}_3)_3]$  only reacted after prolonged refluxing for several hours in toluene, unexpectedly yielding the 18-electron arene-cobalt complex  $[1\text{-NHBU}^t\text{-2-(}\eta^6\text{-C}_6\text{H}_5\text{Me)-}closo\text{-2,1-CoCB}_{10}\text{H}_{10}]$  (**11a**) [16]. Formation of **11a** prompted an investigation as to whether other structurally similar arene-rhodium compounds could be obtained from the reagent **3a**.

The rhodium sandwich compounds  $[1\text{-NHBU}^t\text{-2-(}\eta^6\text{-arene)-}closo\text{-2,1-RhCB}_{10}\text{H}_{10}]$  (**11b**, arene = C<sub>6</sub>H<sub>5</sub>Me; **11c**, arene = C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>-1,3,5; **11d**, arene = MeC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Me-4,4'; **11e**, arene = [2<sub>2</sub>](1,4)-C<sub>16</sub>H<sub>16</sub>) were prepared from reactions between 1:1 mol mixtures of the arenes and **3a** in CH<sub>2</sub>Cl<sub>2</sub> in the presence of Ag[BF<sub>4</sub>] [23]. Evidently AgCl and [PPh<sub>3</sub>][BF<sub>4</sub>] are other reaction products. X-ray diffraction studies of **11c** and **11e** confirmed that in these species the rhodium is pentahapto coordinated on one side by the three-electron donor {7-NHBU<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>} ligand and on the other in the hexahapto manner by a mesitylene molecule and one C<sub>6</sub>H<sub>4</sub> ring of the cyclophane, respectively. The molecules **11** are the first mixed sandwich complexes of rhodium with arenes and a monocarbollide ligand, and are isolobal with many cationic cyclopentadienide complexes  $[\text{Rh}(\eta^6\text{-arene})(\eta^5\text{-C}_5\text{R}_5)]^+$ . The mode of formation of **11** demonstrates the readiness of the {7-NH<sub>2</sub>Bu<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>} unit to deprotonate at the *exo*-polyhedral N atom [24], a feature that will be of greater significance in the compounds of molybdenum, tungsten and rhenium described later.

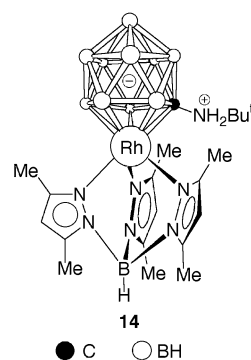
A major objective of the synthesis of compounds **11d** and **11e** was to establish whether the arene rings in these species which are not coordinated to the rhodium would bind another metal-ligand fragment. Accordingly **11e** was treated with **3a** and Ag[BF<sub>4</sub>] in an attempt to obtain a product in which both C<sub>6</sub>H<sub>4</sub> rings of the cyclophane formed a bridge between two {1-NHBU<sup>t</sup>-*closo*-2,1-RhCB<sub>10</sub>H<sub>10</sub>} moieties. In practice the desired reaction did not occur. In an attempt to add a metal-ligand fragment to **11d**, the latter was treated with [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>] in thf. A reaction occurred but a product in which both C<sub>6</sub>H<sub>4</sub> rings are hexahapto bonded to rhodium and molybdenum, respectively, was not isolated. Instead the dirhodium compound [ $\{7,2'\text{-}\mu\text{-H-1-NH}_2\text{Bu}^t\text{-2-CO-}closo\text{-2,1-RhCB}_{10}\text{H}_9\}_2$  (*Rh-Rh*)] (**12**) was obtained but only fully identified after an X-ray diffraction study [23]. Complex **12** has two B-H→Rh bonds bridging the Rh-Rh bond, a structural feature found in several other dimetal complexes formed by dimerization of the fragments {1,2-R<sub>2</sub>-3-L-*closo*-3,1,2-MC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>} (R = H or Me, L = CO or PR<sub>3</sub>, M = Co [25], Rh [26], or Ni [27]). However, **12** appears to be the first

monocarbollide complex of this type. The X-ray study revealed that in **12** both B-H→Rh bonds involve boron atoms β to the carbon atom in the  $\overline{\text{CB}}\overline{\text{BB}}$  rings ligating the rhodium centers [23].

Isolation of the compounds **11** raised the possibility as to whether structurally related molecules could be prepared from **3a** with tris(pyrazolyl)methane or hydrotris(3,5-dimethylpyrazolyl)borate groups. Of special interest was whether any sandwich complexes formed contained the three-electron donor {7-NHBU<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>} or the charge-compensated four-electron donor {7-NH<sub>2</sub>Bu<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>} group. A thf solution of **3a** and HC(pz)<sub>3</sub> after addition of Ti[PF<sub>6</sub>] gave the cationic complex  $[1\text{-NH}_2\text{Bu}^t\text{-2-}\{\kappa^3\text{-HC(pz)}_3\}\text{-}closo\text{-2,1-RhCB}_{10}\text{H}_{10}]^+$  (**13**). The tris(pyrazolyl)methane ligand is coordinated to the rhodium via three nitrogen atoms in the usual tridentate manner for this group. The reaction between **3a** and K[HB(pzMe<sub>2</sub>-3,5)<sub>3</sub>] in thf yielded the neutral complex  $[1\text{-NH}_2\text{Bu}^t\text{-2-}\{\kappa^3\text{-HB(pzMe}_2\text{-3,5)}_3\}\text{-}closo\text{-2,1-RhCB}_{10}\text{H}_{10}]$  (**14**). A similar methodology has been used previously to prepare the isolobal molecule  $[3\text{-}\{\kappa^3\text{-HB(pz)}_3\}\text{-}closo\text{-3,1,2-RhC}_2\text{B}_9\text{H}_{11}]$  [28].



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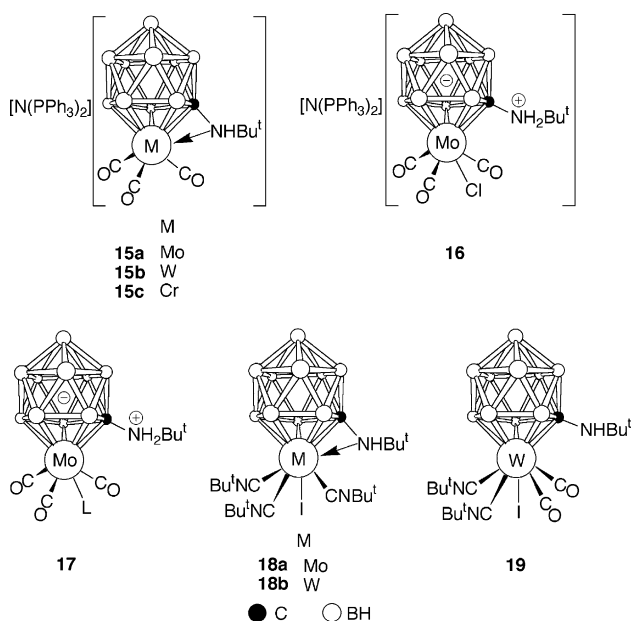


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#### 4. Molybdenum and tungsten compounds

Some years ago we prepared a useful allylmolybdenum dicarbollide reagent  $[\text{NEt}_4][3\text{-}(\eta^3\text{-C}_3\text{H}_5)\text{-3,3-(CO)}_2\text{-}closo\text{-3,1,2-MoC}_2\text{B}_9\text{H}_{11}]$  by treating  $\text{Ti}_2[3,3,3\text{-}$

(CO)<sub>3</sub>-*closo*-3,1,2-MoC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] with CH<sub>2</sub>=CHCH<sub>2</sub>Br, followed by addition of [NEt<sub>4</sub>]Cl [29]. We anticipated that we might prepare an analogous dianionic monocarbollide species [1-NHBu<sup>t</sup>-2-(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)-2,2-(CO)<sub>2</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> by deprotonating 7-NHBu<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>12</sub> [30] with 3 equivalents of LiBu<sup>n</sup> to generate [7-NHBu<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup>, following which the addition of [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>] would afford the trianion [1-NHBu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup> in situ. Treatment of the latter with CH<sub>2</sub>=CHCH<sub>2</sub>Br and [N(PPh<sub>3</sub>)<sub>2</sub>]Cl was then expected to give [N(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[1-NHBu<sup>t</sup>-2-(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)-2,2-(CO)<sub>2</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>]. Instead the trianion was merely oxidized by the allyl bromide and the final product isolated was [N(PPh<sub>3</sub>)<sub>2</sub>]-[1,2-μ-NHBu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>] (**15a**) [31].



It was subsequently found that **15a** could be more straightforwardly prepared and in better yield by the interaction of the lithium salt of the monoanionic species [7-NHBu<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>12</sub>]<sup>-</sup> [24] with [Mo(CO)<sub>6</sub>] in refluxing NCMe, followed by addition of [N(PPh<sub>3</sub>)<sub>2</sub>]Cl [31]. In the synthesis the two face-bridging protons of the carborane are reduced and eliminated as dihydrogen with a concomitant two-electron oxidation of the molybdenum. The tungsten (**15b**) and chromium (**15c**) analogues may be similarly prepared, but the chromium compound is relatively unstable. An X-ray diffraction study of the tungsten complex **15b** confirmed that in these products the NHBu<sup>t</sup> group forms a bridge between the cage-carbon atom and the metal atoms. Thus formally the [7-NHBu<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup> group contributes eight electrons (6π + 2σ) to the metal and the CO molecules

six electrons giving the metal (M<sup>II</sup>, d<sup>4</sup>) an 18-electron configuration.

The intramolecular N → Mo donor bond in **15a** may be lifted upon protonation. Thus, with HCl the salt [N(PPh<sub>3</sub>)<sub>2</sub>][1-NH<sub>2</sub>Bu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-2-Cl-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>] (**16**) is obtained, whereas treatment with donor molecules L (L = CO, PPh<sub>3</sub>, PMe<sub>3</sub>, PEt<sub>3</sub>, PMe<sub>2</sub>Ph) in the presence of H[BF<sub>4</sub>]·OEt<sub>2</sub> yielded zwitterionic compounds [1-NH<sub>2</sub>Bu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-2-L-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>] (**17**) [31]. Iodine oxidizes **15a** in the presence of CNBu<sup>t</sup> to give the Mo<sup>IV</sup> compound [1,2-μ-NHBu<sup>t</sup>-2,2,2-(CNBu<sup>t</sup>)<sub>3</sub>-2-I-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>] (**18a**). A similar reaction of **15b**, however, gave a mixture of [1,2-μ-NHBu<sup>t</sup>-2,2,2-(CNBu<sup>t</sup>)<sub>3</sub>-2-I-*closo*-2,1-WCB<sub>10</sub>H<sub>10</sub>] (**18b**) and [1-NHBu<sup>t</sup>-2,2-(CNBu<sup>t</sup>)<sub>2</sub>-2,2-(CO)<sub>2</sub>-2-I-*closo*-2,1-WCB<sub>10</sub>H<sub>10</sub>] (**19**). Interestingly, in the latter compound the trianionic carborane unit formally donates only 6 electrons to the tungsten because there is no μ-NHBu<sup>t</sup> group. Instead four ligands, two carbonyls and two isocyanide molecules, are bound to the metal center in addition to the iodide and carborane groups. Evidently the CO molecules are sufficiently strongly bound to the W<sup>IV</sup> atom that they are not displaced by the pendant NHBu<sup>t</sup> group.

Compound **15a** readily adds {M(PPh<sub>3</sub>)<sub>3</sub>}<sup>+</sup> (M = Cu or Au) groups [31]. Treatment of **15a** with [CuCl(PPh<sub>3</sub>)<sub>3</sub>]<sub>4</sub> in the presence of Tl[PF<sub>6</sub>] affords the bimetallic compound [1,2-μ-NHBu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-7,8,12-(μ-H)<sub>3</sub>-7,8,12-{Cu(PPh<sub>3</sub>)<sub>3</sub>}-*closo*-2,1-MoCB<sub>10</sub>H<sub>7</sub>] (**20**). Reaction between [AuCl(PPh<sub>3</sub>)<sub>3</sub>] and **15a**, in the presence of Tl[PF<sub>6</sub>], yields a mixture of [2-{Au(PPh<sub>3</sub>)<sub>3</sub>}-1,2-μ-NHBu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>] (**21**) and [Au(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[2,2'-μ-Au-{1,2-μ-NHBu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>}]<sub>2</sub> (**22a**) (Fig. 1).

Unfortunately suitable crystals of the copper compound **20** were not available for an X-ray diffraction study, nor did <sup>1</sup>H NMR studies reveal the presence of B-H → Cu bonds. However, this is not unusual in such systems where dynamic behavior in solution is fast on the NMR time scale. Nevertheless, it is reasonable to assume that the copper atom is bonded to a triangular B<sub>3</sub> face via three agostic-type B-H → Cu linkages. This is by analogy with the closely related species [2,2,2-(CO)<sub>3</sub>-2-PPh<sub>3</sub>-7,8,12-(μ-H)<sub>3</sub>-7,8,12-{Cu(PPh<sub>3</sub>)<sub>3</sub>}-*closo*-2,1-MoCB<sub>10</sub>H<sub>8</sub>] characterized by X-ray diffraction, which is obtained similarly from salts of the [2,2,2-(CO)<sub>3</sub>-2-PPh<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>11</sub>]<sup>-</sup> anion, and also does not reveal signals for the B-H → Cu linkages in its <sup>1</sup>H NMR spectrum [32].

Although the gold compounds **21** and **22a** could be separated by column chromatography it became clear that, following separation, the two products disproportionate in solution to form an equilibrium mixture of the two. Evidently two molecules of the neutral complex **21** may disproportionate into an [Au(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation and the anion [2,2'-μ-Au-{1,2-μ-NHBu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>}]<sup>-</sup>. Indeed, the latter can be

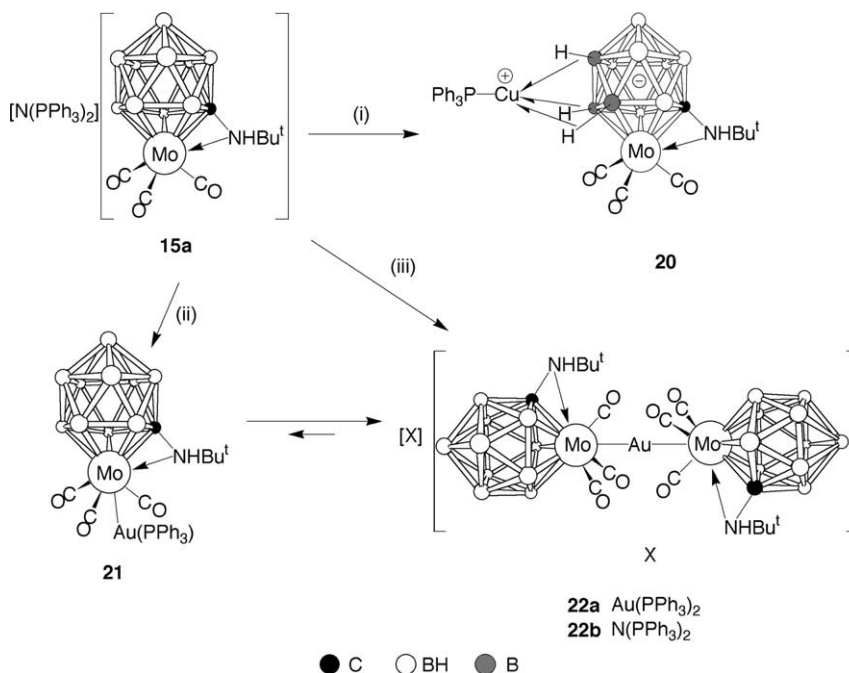
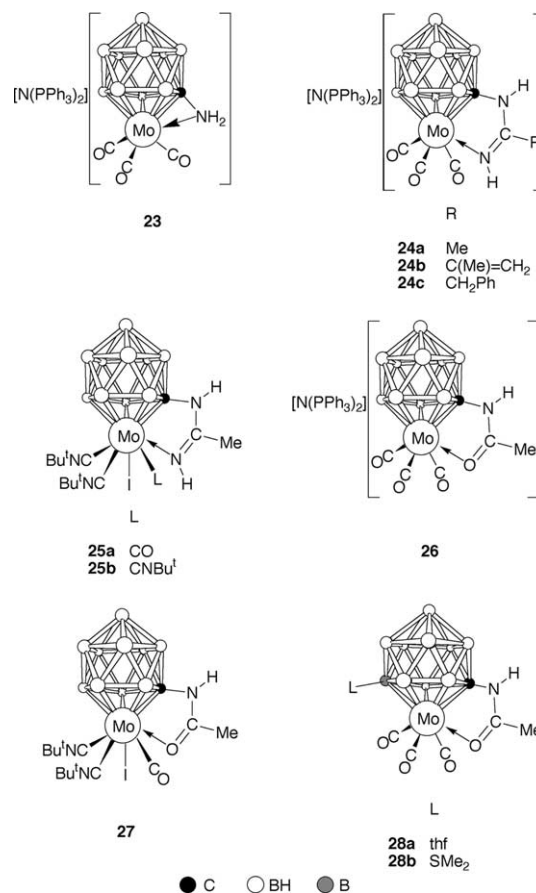


Fig. 1. Synthesis of compounds **20–22** from **15a**. (i) [CuCl(PPh<sub>3</sub>)<sub>4</sub>] and Tl[PF<sub>6</sub>]. (ii) [AuCl(PPh<sub>3</sub>)] and Tl[PF<sub>6</sub>]. (iii) [AuCl(tht)] and Tl[PF<sub>6</sub>]; X=N(PPh<sub>3</sub>)<sub>2</sub>.

isolated as its [N(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> salt by treating two mol equivalents of **15a** with one mol equivalent of [AuCl(tht)] (tht=tetrahydrothiophene) in the presence of Tl[PF<sub>6</sub>]. The product [N(PPh<sub>3</sub>)<sub>2</sub>][2,2'-μ-Au-{1,2-μ-NHBu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-closo-2,1-MoCB<sub>10</sub>H<sub>10</sub>}<sub>2</sub>] (**22b**) was identified by NMR spectroscopy and by X-ray diffraction analysis. In the anion the two {1,2-μ-NHBu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-closo-2,1-MoCB<sub>10</sub>H<sub>10</sub>} units are coordinated to the central Au atom in an approximately linear manner [Mo–Au–Mo=170.80(2)°]. The structure of the anion is related to those of the isolobal cyclopentadienyl anionic complexes [μ-Au-{M(CO)<sub>3</sub>-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>}]<sup>-</sup> (M=Cr, Mo, W) [33].

Similar methods to those that afforded **15a** but employing the carbaborane anions [7-NH<sub>2</sub>-nido-7-CB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup> or [7-NH<sub>2</sub>-nido-7-CB<sub>10</sub>H<sub>12</sub>]<sup>-</sup>, respectively, failed to yield [N(PPh<sub>3</sub>)<sub>2</sub>][1,2-μ-NH<sub>2</sub>-2,2,2-(CO)<sub>3</sub>-closo-2,1-MoCB<sub>10</sub>H<sub>10</sub>] (**23**). Instead the product obtained was [N(PPh<sub>3</sub>)<sub>2</sub>][1,2-μ-{NHC(Me)=NH}-2,2,2-(CO)<sub>3</sub>-closo-2,1-MoCB<sub>10</sub>H<sub>10</sub>] (**24a**) [34]. This and the related species **24b,c** arise from a coupling of the cage-carbon bound NH<sub>2</sub> group with a nitrile molecule NCR. An alternative route to **23** is available which avoids nitriles. It involves treating the carbaborane trianion [7-NH<sub>2</sub>-nido-7-CB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup> with [Mo(CO)<sub>4</sub>{NH(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub>] in thf when the trianionic molybdenocarbaborane species [1-NH<sub>2</sub>-2,2,2-(CO)<sub>3</sub>-closo-2,1-MoCB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup> is formed in situ. Addition to this of CH<sub>2</sub>=CHCH<sub>2</sub>Br as oxidant, followed by [N(PPh<sub>3</sub>)<sub>2</sub>]Cl, gives **23**.



The compound **24a** can be obtained by two different routes. It can be isolated either from the reaction between the carborane trianion  $[7\text{-NH}_2\text{-nido-7-CB}_{10}\text{H}_{10}]^{3-}$  and  $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$  in thf/NCMe at room temperature, followed by oxidation with  $\text{CH}_2=\text{CHCH}_2\text{Br}$ , or from the reaction between the monoanionic carborane  $[7\text{-NH}_2\text{-nido-7-CB}_{10}\text{H}_{12}]^-$  with  $[\text{Mo}(\text{CO})_6]$  in refluxing NCMe. In both cases  $[\text{N}(\text{PPh}_3)_2]\text{Cl}$  is added to isolate the salt. An X-ray diffraction study confirmed that in **24a** an acetamidine moiety is linked both to the cage-carbon atom and to the molybdenum vertex to form a five-membered ring. Mechanistically, formation of the acetamidine moiety appears straightforward. The intermediate  $[1\text{-NH}_2\text{-2,2,2-(CO)}_3\text{-closo-2,1-MoCB}_{10}\text{H}_{10}]^{3-}$  upon oxidation gains a vacant metal coordination site, which becomes occupied by an NCMe molecule to give transient  $[1\text{-NH}_2\text{-2,2,2-(CO)}_3\text{-2-NCMe-closo-2,1-MoCB}_{10}\text{H}_{10}]^-$ . Intramolecular attack by the amino group upon the metal activated nitrile followed by a redistribution of H atoms then gives the observed anion. Interestingly, in the synthesis of **15a** no relative of **24a** is formed. Arguably, an intermediate of the form  $[1\text{-NHBu}^t\text{-2,2,2-(CO)}_3\text{-2-NCMe-closo-2,1-MoCB}_{10}\text{H}_{10}]^-$  would be disfavored on steric and electronic grounds. The larger and more basic  $\text{NHBu}^t$  group could compete with NCMe more successfully than  $\text{NH}_2$  to fill the vacant site produced on the metal upon oxidation.

As mentioned above **15a** reacts with  $\text{CNBu}^t$  and  $\text{I}_2$  to give the  $\text{Mo}^{\text{IV}}$  species **18**. It was of interest to determine how **24a** would behave with the same reagents [34]. Two neutral  $\text{Mo}^{\text{IV}}$  products were obtained:  $[1,2\text{-}\mu\text{-}\{\text{NHC}(\text{Me})=\text{NH}\}\text{-2,2-(CNBu}^t)_2\text{-2-L-2-I-closo-2,1-MoCB}_{10}\text{H}_{10}]$  (**25a**,  $\text{L}=\text{CO}$ ; **25b**,  $\text{L}=\text{CNBu}^t$ ). In both complexes the amidine linkage remains intact, confirmed by an X-ray diffraction study of **25b**. The formally eight-coordinated Mo atom is pentahapto bonded by the  $\overline{\text{CBBBB}}$  face of the carborane cage with, in addition, bonds to an amidine nitrogen, three isocyanide molecules, and an iodide. The  $\text{Mo}^{\text{IV}}$  ( $d^2$ ) center receives six electrons from the isocyanide molecules, two from the iodide ligand and eight ( $6\pi+2\sigma$ ) from the  $\{7\text{-}\{\text{NHC}(\text{Me})=\text{NH}\}\text{-nido-7-CB}_{10}\text{H}_{10}\}$  group.

Intramolecular five-membered rings are also formed in reactions involving the carborane  $7\text{-NH}_2\text{C}(\text{O})\text{Me-nido-7-CB}_{10}\text{H}_{12}$ . Deprotonation of the latter with NaH in thf, adding NCMe and  $[\text{Mo}(\text{CO})_6]$  and refluxing the mixture, with final addition of  $[\text{N}(\text{PPh}_3)_2]\text{Cl}$  affords  $[\text{N}(\text{PPh}_3)_2][1,2\text{-}\mu\text{-}\{\text{NHC}(\text{Me})=\text{O}\}\text{-2,2,2-(CO)}_3\text{-closo-2,1-MoCB}_{10}\text{H}_{10}]$  (**26**) [35]. This complex, closely related to **24a**, undergoes a number of reactions. Thus it is oxidized with iodine in  $\text{CNBu}^t$  to yield the  $\text{Mo}^{\text{IV}}$  compound  $[1,2\text{-}\mu\text{-}\{\text{NHC}(\text{Me})=\text{O}\}\text{-2,2-(CNBu}^t)_2\text{-2-CO-2-I-closo-2,1-MoCB}_{10}\text{H}_{10}]$  (**27**), akin to complex **25a**. Compound **26** also reacts with electrophilic reagents

with removal of  $\text{H}^-$  from a BH vertex and its replacement by an electron pair donor molecule. Treatment of **26** with  $\text{CF}_3\text{SO}_3\text{Me}$  in a  $\text{CH}_2\text{Cl}_2\text{-thf}$  solvent mixture, or with  $\text{H}_2\text{SO}_4$  and  $\text{SMe}_2$ , affords the charge-compensated complexes  $[1,2\text{-}\mu\text{-}\{\text{NHC}(\text{Me})=\text{O}\}\text{-2,2,2-(CO)}_3\text{-7-L-closo-2,1-MoCB}_{10}\text{H}_9]$  (**28a**,  $\text{L}=\text{thf}$ ; **28b**,  $\text{L}=\text{SMe}_2$ ), respectively. In reactions of this kind the donor L is attached to the boron in a  $\beta$  site with respect to the carbon in the  $\overline{\text{CBBBB}}$  ring coordinated to the metal [22b,33]. This is because the  $\text{B}_\beta\text{-H}$  hydrogens are the most hydridic in the  $\overline{\text{CBBBB}}$  face of the cage and therefore the most easily removed by an electrophile.

Our unsuccessful attempt to prepare an allylmolybdenum monocarbollide complex  $[\text{NEt}_4]_2[1\text{-NHBu}^t\text{-2-(}\eta^3\text{-C}_3\text{H}_5\text{)-2,2-(CO)}_2\text{-closo-2,1-MoCB}_{10}\text{H}_{10}]$ , analogous to the dicarbollide species  $[\text{NEt}_4][3\text{-}(\eta^3\text{-C}_3\text{H}_5)\text{-3,3-(CO)}_2\text{-closo-3,1,2-MoC}_2\text{B}_9\text{H}_{11}]$  [29], was mentioned above. The sequence of reactions designed to give the desired allyl complex yielded instead compound **15a**, because the allyl bromide oxidized the intermediate trianion

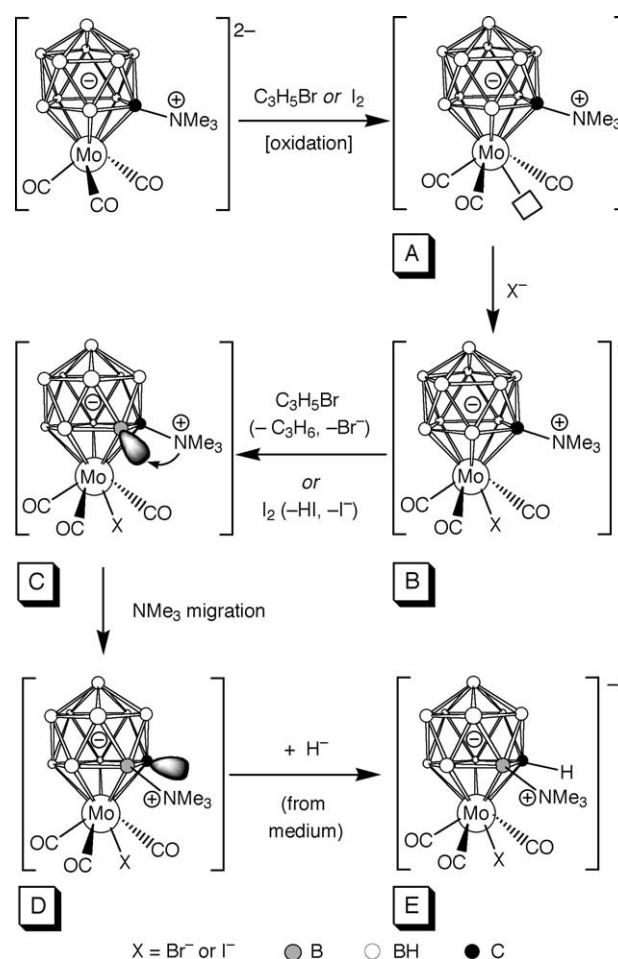
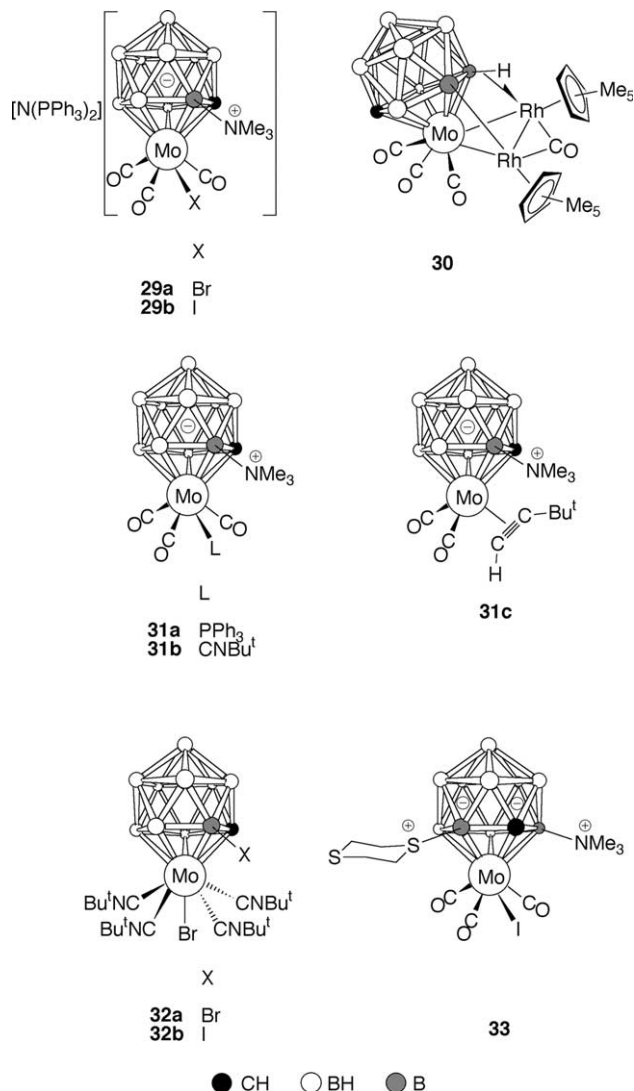


Fig. 2. Proposed pathway for the formation of the anions of compounds **29**. Reproduced from reference [37] by permission of The American Chemical Society.



[1-NHBu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup> instead of forming the target species.

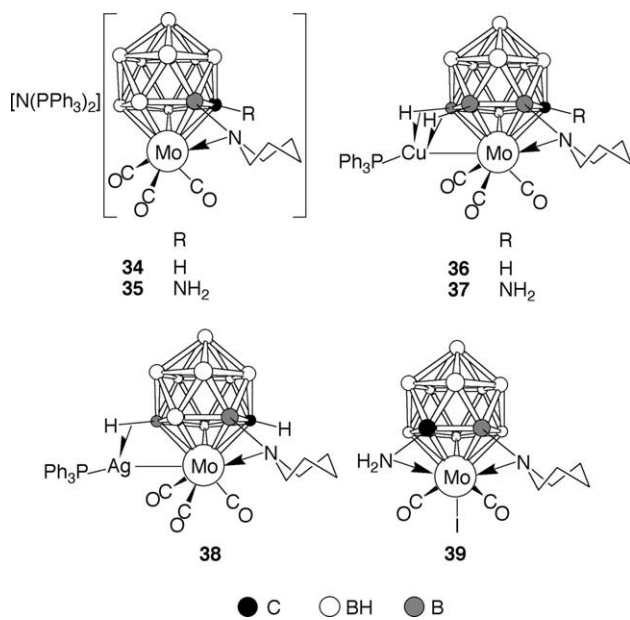
In a similar synthesis the dianion [2,2,2-(CO)<sub>3</sub>-1-NMe<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> was prepared in situ by treating the reagent Li<sub>2</sub>[7-NMe<sub>3</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> with [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>]. Upon addition of CH<sub>2</sub>=CHCH<sub>2</sub>Br or I<sub>2</sub> the intermediate [2,2,2-(CO)<sub>3</sub>-1-NMe<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> was oxidized giving the anionic complexes [2,2,2-(CO)<sub>3</sub>-2-X-3-NMe<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>]<sup>-</sup>, isolated as their [N(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> salts (**29a**, X=Br; **29b**, X=I) [37]. Surprisingly in these salts X-ray diffraction and NMR studies revealed that the NMe<sub>3</sub> group had transferred from the carbon vertex in the precursor to an adjacent  $\alpha$  boron atom in the CBBBB belt that ligates the molybdenum vertex. The transfer of an NMe<sub>3</sub> group in this manner is unprecedented and the pathway by which it occurs is unknown but a plausible route is indicated in Fig. 2. Several interesting reactions stemmed from this study.



When [Rh(NCMe)<sub>3</sub>( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)] [BF<sub>4</sub>] is used to oxidize the dianion [2,2,2-(CO)<sub>3</sub>-1-NMe<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> the trimetallic compound [2,2,2-(CO)<sub>3</sub>-7- $\mu$ -H-2,7,11- $\{Rh_2(\mu-CO)(\eta^5-C_5Me_5)_2\}$ -*closo*-2,1-MoCB<sub>10</sub>H<sub>9</sub>] (**30**) is formed, the NMe<sub>3</sub> group being lost. Reaction of **29a** in CH<sub>2</sub>Cl<sub>2</sub> with Tl[PF<sub>6</sub>] in the presence of donor ligands L affords neutral zwitterionic compounds [2,2,2-(CO)<sub>3</sub>-2-L-3-NMe<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>] for L=PPh<sub>3</sub> (**31a**), or CNBu<sup>t</sup> (**31b**), and [2-Bu<sup>t</sup>C $\equiv$ CH-2,2-(CO)<sub>2</sub>-3-NMe<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>] (**31c**) when L=Bu<sup>t</sup>C $\equiv$ CH. When **29a** is treated with CNBu<sup>t</sup> and X<sub>2</sub>, the metal center is oxidized and in the products obtained, [2,2,2,2-(CNBu<sup>t</sup>)<sub>4</sub>-2-Br-3-X-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>] (**32a**, X=Br; **32b**, X=I), the B-NMe<sub>3</sub> bond is replaced by B-X. In contrast, treatment of **29b** with I<sub>2</sub> and *cyclo*-1,4-S<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> results in oxidative substitution of the cluster and retention of the NMe<sub>3</sub> group, giving [2,2,2-(CO)<sub>3</sub>-2-I-3-NMe<sub>3</sub>-6- $\{cyclo$ -1,4-S<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>}-*closo*-2,1-MoCB<sub>10</sub>H<sub>9</sub>] (**33**). The structures of several of these complexes were confirmed by X-ray diffraction since they are without precedent in metallacarborane chemistry [37].

The difference in reactivity towards [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>] displayed by the various anions [7-NHR-*nido*-7-CB<sub>10</sub>H<sub>12</sub>]<sup>-</sup> (R=Bu<sup>t</sup> or H), [7-NMe<sub>3</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>2-</sup>, and [7-NHR-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup>, derived by deprotonating amine-carboranes, prompted investigation of reactions with [Mo(CO)<sub>4</sub>{NH(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub>] [NH(CH<sub>2</sub>)<sub>5</sub>=piperidine] [38]. In this way several new complexes were discovered containing one or two intramolecular amino groups bridging between cage vertices and the molybdenum center.

Thus, the room temperature reaction of Li<sub>2</sub>[7-NMe<sub>3</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>] with [Mo(CO)<sub>4</sub>{NH(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub>] in thf, followed by oxidation with CF<sub>3</sub>SO<sub>3</sub>Me or CH<sub>2</sub>=CHCH<sub>2</sub>Br, gave the anion [2,3- $\mu$ -{N(CH<sub>2</sub>)<sub>5</sub>}-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>]<sup>-</sup>, which can be isolated as its [N(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> salt (**34**). The same anion may be obtained from the direct reaction of 7-NMe<sub>3</sub>-*nido*-7-CB<sub>10</sub>H<sub>12</sub> with [Mo(CO)<sub>4</sub>{NH(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub>] in refluxing thf. The NMe<sub>3</sub> group is lost in these reactions. The molecular structure of **34**, with an intramolecular piperidynyl bridge between molybdenum and boron, is similar to that in complexes **15** and **23** described above, save that in **34** the intramolecular bridge involves a cage-boron, rather than cage-carbon, atom. In a related reaction, namely treatment of the same molybdenum reagent with the carborane anion [7-NH<sub>2</sub>-*nido*-7-CB<sub>10</sub>H<sub>12</sub>]<sup>-</sup> in refluxing thf, the product obtained after addition of [N(PPh<sub>3</sub>)<sub>2</sub>]Cl was [N(PPh<sub>3</sub>)<sub>2</sub>][1-NH<sub>2</sub>-2,3- $\mu$ -{N(CH<sub>2</sub>)<sub>5</sub>}-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>9</sub>] (**35**). In this product the NH<sub>2</sub> group remains attached to the cage-carbon atom.



A possible reaction pathway to compound **34** is indicated in Fig. 3. Oxidation of the Mo<sup>0</sup> dianion **A** with CH<sub>2</sub>=CHCH<sub>2</sub>Br or CF<sub>3</sub>SO<sub>3</sub>Me would give the neutral

Mo<sup>II</sup> complex **B** with a vacant coordination site on the metal, which then acquires a piperidine ligand from solution to form the electronically saturated compound **C**. The C–NMe<sub>3</sub> unit in **C** is then converted to C–H by loss of NMe<sub>3</sub> via **D** and gain of H<sup>−</sup> from the medium giving the anion **E**. The acidic N–H of the piperidine then abstracts H<sup>−</sup> from an α<sup>δ+</sup>B–H<sup>δ−</sup> vertex of the cage to eliminate H<sub>2</sub> and form the intramolecular B–N–Mo piperidynyl bridge in **F**, the anion of compound **34**.

In parallel with the synthesis of **34**, the formation of the anion of **35** (Fig. 4) likely proceeds via initial formation of an intermediate **G** (R=H). Elimination of H<sub>2</sub> from **G** again produces a piperidynyl group bridging between a cage α-boron and the molybdenum center, as seen in **H**, which is the anion of **35**. In contrast the reaction between [7-NHBu<sup>t</sup>-nido-7-CB<sub>10</sub>H<sub>12</sub>]<sup>−</sup> and [Mo(CO)<sub>4</sub>{NH(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub>] gives **15a** and it seems likely that the anion of the latter forms via a related intermediate **G** (with R=Bu<sup>t</sup>) from which the molybdenum bound piperidine is simply displaced by an intramolecular donor bond from the NHBu<sup>t</sup> group attached to the cage-carbon.

Treatment of **34** and **35** with {M(PPh<sub>3</sub>)<sup>+</sup>} (M=Cu, Ag) yields the heterobimetallic complexes [1-R-2,7,11-{Cu(PPh<sub>3</sub>)<sup>+</sup>}-7,11-(μ-H)<sub>2</sub>-2,3,μ-{N(CH<sub>2</sub>)<sub>5</sub>}-2,2,2-(CO)<sub>3</sub>-

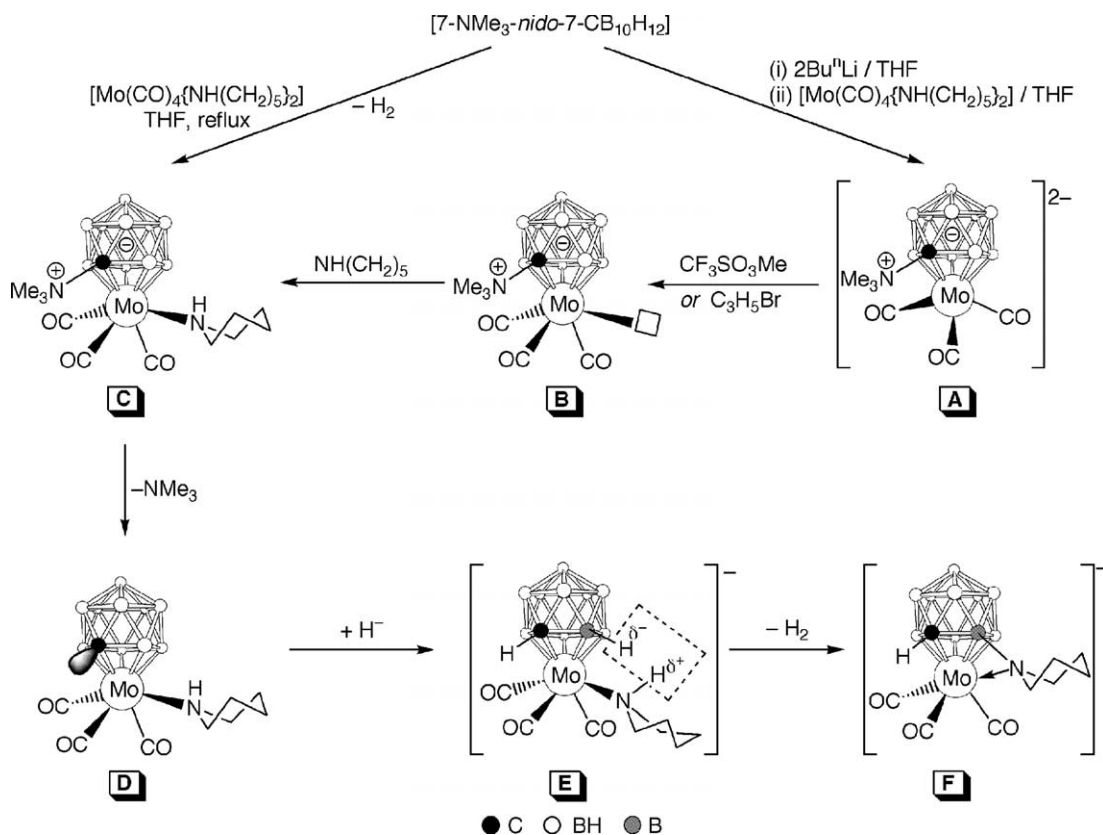


Fig. 3. Proposed pathway for the formation of the anion of compound **34**. Reproduced from reference [46] by permission of The Royal Society of Chemistry.

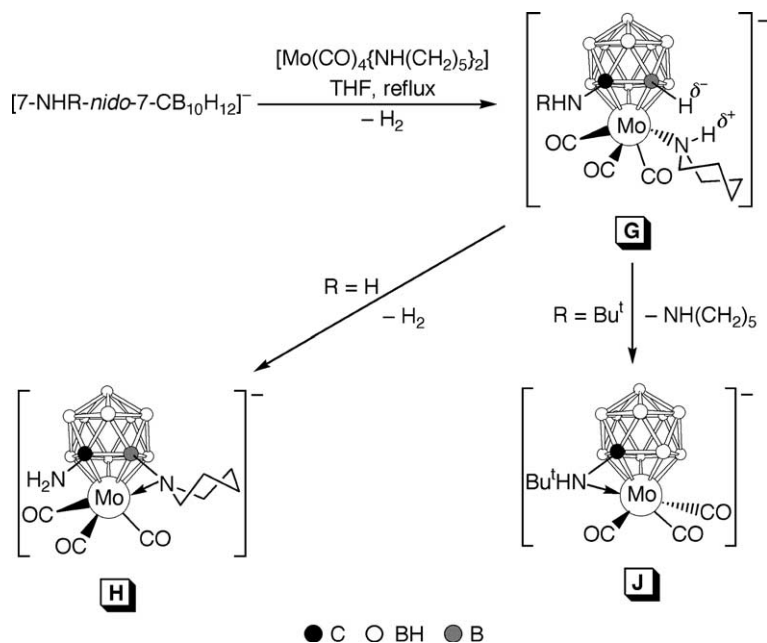


Fig. 4. Proposed pathway for the formation of the anions of compounds **15a** and **35**. Reproduced from reference [46] by permission of The Royal Society of Chemistry.

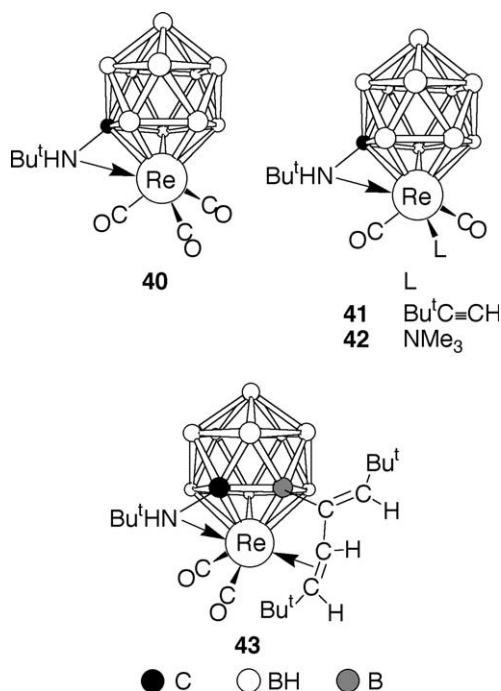
*closo*-2,1-MoCB<sub>10</sub>H<sub>7</sub>] (R = H, **36**; R = NH<sub>2</sub>, **37**) and [2,11-{Ag(PPh<sub>3</sub>)}-11-μ-H-2,3-μ-{N(CH<sub>2</sub>)<sub>5</sub>}-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>9</sub>] (**38**), respectively [38]. An X-ray diffraction analysis of **36** confirmed its molecular structure.

With I<sub>2</sub> in thf, complex **35** is oxidized giving the Mo<sup>IV</sup> complex [1,2-μ-NH<sub>2</sub>-2,3-μ-{N(CH<sub>2</sub>)<sub>5</sub>}-2,2-(CO)<sub>2</sub>-2-I-*closo*-2,1-MoCB<sub>10</sub>H<sub>9</sub>] (**39**). An X-ray diffraction study confirmed that in this iodo derivative there are two intramolecular amino bridges between cage vertices and the molybdenum [38]. Interestingly, on reaction with PEt<sub>3</sub> in refluxing thf a CO molecule in **39** is substituted by the phosphine, rather than an amino bridge being lifted, with formation of an {MoI(CO)<sub>2</sub>(PEt<sub>3</sub>)} group. More significantly, the {7-NH<sub>2</sub>-8-{N(CH<sub>2</sub>)<sub>5</sub>}-*nido*-7-CB<sub>10</sub>H<sub>9</sub>} ligand in **39** formally donates 10 electrons (6π + 2 × 2σ) to the Mo center, a feature unprecedented in metallocarborane chemistry.

## 5. Rhenium compounds

In preliminary studies aimed at preparing amino-substituted monocarbollide rhenium compounds, the neutral complex **40**, structurally similar to the anion of the molybdenum species **15a**, has been prepared [39]. Treatment of 7-NH<sub>2</sub>Bu<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>12</sub> with LiBu<sup>n</sup> (3

equiv) to generate [7-NHBu<sup>t</sup>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup> in situ followed by addition of [ReBr(thf)<sub>2</sub>(CO)<sub>3</sub>] ostensibly gives the dianionic rhenacarborane [1,2-μ-NHBu<sup>t</sup>-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-ReCB<sub>10</sub>H<sub>10</sub>]<sup>2-</sup>. Oxidation of the latter with iodine affords **40**. At room temperature in CH<sub>2</sub>Cl<sub>2</sub>, complex **40** reacts with a 1:1 mixture of Bu<sup>t</sup>C≡CH and Me<sub>3</sub>NO to give the monoalkyne complex [1,2-μ-NHBu<sup>t</sup>-2-Bu<sup>t</sup>C≡CH-2,2-(CO)<sub>2</sub>-*closo*-2,1-ReCB<sub>10</sub>H<sub>10</sub>] (**41**), a small amount of the amine complex [1,2-μ-NHBu<sup>t</sup>-2-NMe<sub>3</sub>-2,2-(CO)<sub>2</sub>-*closo*-2,1-ReCB<sub>10</sub>H<sub>10</sub>] (**42**), and a third product [1,2-μ-NHBu<sup>t</sup>-2,2-(CO)<sub>2</sub>-3,2-σ,η<sup>2</sup>-{C(=CH Bu<sup>t</sup>)-CH=CHBu<sup>t</sup>}-*closo*-2,1-ReCB<sub>10</sub>H<sub>9</sub>] (**43**) formed in larger yield. The latter contains a dienyl moiety that is bound both to the rhenium center and to a boron vertex ligating the metal. Treatment of the monoalkyne complex **41** with Me<sub>3</sub>NO and one further equivalent of Bu<sup>t</sup>C≡CH also affords **43**. In the pathway to **43** a bis(alkyne) complex is probably formed from [1,2-μ-NHBu<sup>t</sup>-2-Bu<sup>t</sup>C≡CH-2,2-(CO)<sub>2</sub>-*closo*-2,1-ReCB<sub>10</sub>H<sub>10</sub>]. One alkyne then rearranges to a vinylidene group which inserts into a B–H bond following which the second alkyne also transforms to a rhenium bound vinylidene group which inserts into the nearby C–H bond at the boron-bound terminus of the B–C(H)=C(H)Bu<sup>t</sup> group to yield **43**. Vinylidene-metal species have been implicated in the chemistry of molybdena- and ruthena-dicarbollide systems where alkynes RC≡CH insert into cage B–H bonds [29,40–42].



## 6. Conclusion

Our studies on monocarbollide metal complexes in which the carbon atom of a  $\{nido-7-CB_{10}\}$  fragment carries an *exo*-polyhedral  $-\text{NR}_3$  or an  $-\text{NR}_2$  group have so far been restricted to compounds of six metals: ruthenium, osmium, rhodium, molybdenum, tungsten and rhenium, with investigation of all but the rhodium and molybdenum species being relatively limited in scope. However, a very extensive amount of new chemistry has been developed. We have discovered many complexes having structures new to the metallocarborane field, and have shown that it is possible to introduce functional groups into the  $\{nido-7-CB_{10}\}$  framework in many different ways. There can be little doubt that it will be profitable to extend this area of investigation both to other metals, particularly the early transition metals, and to further develop the chemistry of the species described in this review.

## References

[1] Compounds described herein are based upon *closo*-1-carba-2-metalladodecaborane fragments, and all bear *exo*-polyhedral substituents. It should be noted that, although many contain chiral centers, those species are formed as racemates. Substituted boron atoms located at cage positions 3, 7, 11 or 6 could equally be labeled 6, 11, 7 and 3, respectively. In each case the former is used, in accordance with IUPAC convention.

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