

# Metal Complexes of Monocarbon Carboranes: A Neglected Area of Study?

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## I

### INTRODUCTION

The first metallacarboranes were isolated in M. F. Hawthorne's laboratory and contained a metal ion, two carbon and nine boron atoms forming an icosahedral {*closo*-MC<sub>2</sub>B<sub>9</sub>} cage structure.<sup>1,2</sup> It was immediately recognized that these species may be viewed as having metal ions coordinated 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. This was a useful formalism since it emphasized an isolobal relationship between the carborane dianion and the ubiquitous [C<sub>5</sub>H<sub>5</sub>]<sup>-</sup> ligand. Following isolation of metal dicarbollides 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 way to afford monocarbon metallacarboranes also with icosahedral frameworks. Indeed, a few complexes of this kind were isolated<sup>3</sup> soon after the first dicarbon analogues were discovered. Importantly in the early work, two types of monocarbollide metal compound were characterized. In the first a metal ion is sandwiched between [*nido*-7-CB<sub>10</sub>H<sub>11</sub>]<sup>3-</sup> ligands, as in the Fe<sup>III</sup> complex [*commo*-2,2'-Fe-(*closo*-2,1-FeCB<sub>10</sub>H<sub>11</sub>)<sub>2</sub>]<sup>3-</sup> (**1**) (Chart 1). In the second the cage-carbon atom carries an NR<sub>3</sub> or an NR<sub>2</sub> group, with the metal ion sandwiched between [7-NR<sub>3</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> groups, as in the Fe<sup>III</sup> complex [*commo*-2,2'-Fe-(1-NH<sub>3</sub>-*closo*-2,1-FeCB<sub>10</sub>H<sub>10</sub>)<sub>2</sub>]<sup>3-</sup> (**2**), or [7-NR<sub>2</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup>

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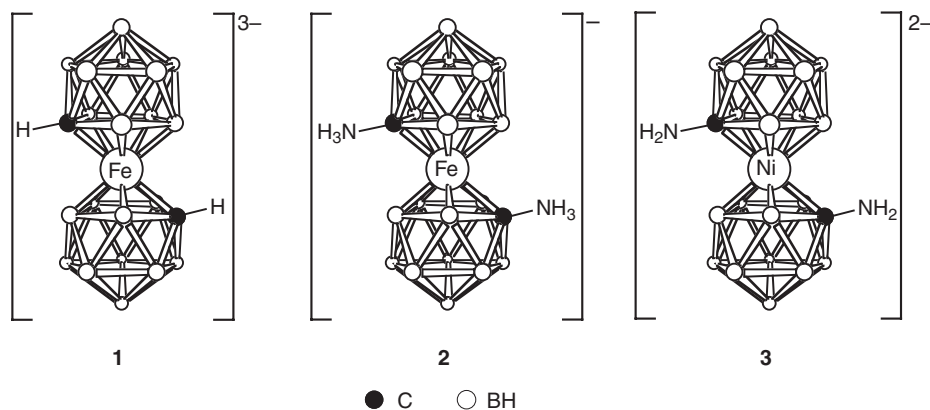


CHART 1.

groups as in [*commo*-2,2'-Ni-(1-NH<sub>2</sub>-*closo*-2,1-NiCB<sub>10</sub>H<sub>10</sub>)<sub>2</sub>]<sup>2-</sup> (3). The zwitterionic ligands [*7-NR*<sub>3</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> are isolobal with the dicarbollide anion [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup>, whereas the trianions [*7-NR*<sub>2</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup> are isolobal with [*nido*-7-CB<sub>10</sub>H<sub>11</sub>]<sup>3-</sup>.

In what has become a very large field of study during the past 40 years, metal-carborane chemistry has primarily focused on species with cages containing two or more carbon atoms,<sup>4,5</sup> whereas monocarbollide metal complexes have received very little attention.<sup>4,6,7</sup> The neglect of this area is somewhat surprising because monocarbollide metal complexes having [*nido*-7-CB<sub>10</sub>H<sub>11</sub>]<sup>3-</sup>, [*7-NR*<sub>3</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>2-</sup>, or [*7-NR*<sub>2</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup> groups would be expected to display reactivity patterns different from those of the corresponding dicarbollide species. In particular, the higher formal negative charge associated with the trianions [*nido*-7-CB<sub>10</sub>H<sub>11</sub>]<sup>3-</sup> and [*7-NR*<sub>2</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>]<sup>3-</sup>, compared with the dianion [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup>, renders metal complexes of the trianions more reactive towards electrophiles. As will be described later this feature provides avenues for introducing functional groups into a carborane cage, a topic of growing interest.

In metallacarborane chemistry it can be argued that it is more profitable to study molecules having half-sandwich 'piano-stool' structures than those with 'full-sandwich' structures. This is because in the piano-stool complexes the metal is ligated on one side by the carborane cage systems [*{7,8-R*<sub>2</sub>-*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>} (R = H or Me), *{nido*-7-CB<sub>10</sub>H<sub>11</sub>}, *{7-NR*<sub>2</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>}, or *{7-NR*<sub>3</sub>-*nido*-7-CB<sub>10</sub>H<sub>10</sub>}] and on the other side by the conventional ligands (CO, PR<sub>3</sub>, CNR, alkynes, etc.) of coordination chemistry. With a combination of different coordinated groups within the coordination sphere of the metal there is the probability of reactions occurring between the ligands and other substrate molecules, and also with the carborane cage itself, with the latter thus adopting a non-spectator role in the chemistry derived.<sup>8</sup> Both mono- and di-carbollide metal carbonyl half-sandwich complexes are especially desirable as synthons. They have isolobal relationships with cyclopentadienide metal carbonyls that are known to function as precursors to numerous other species through the lability of their carbonyl groups. Dicarbollide metal

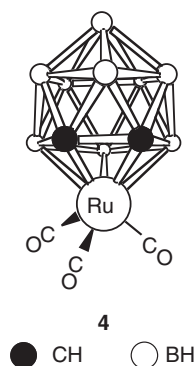


CHART 2.

carbonyls display a very extensive chemistry, as shown by  $[3,3,3\text{-}(\text{CO})_3\text{-}closo\text{-}3,1,2\text{-RuC}_2\text{B}_9\text{H}_{11}]$  (**4**),<sup>9</sup> thereby pointing to the desirability of obtaining related monocarbollide metal carbonyl species for use in synthesis (Chart 2).

In an attempt to redress the imbalance between studies on the dicarbollide and monocarbollide metal compounds we began a comprehensive study of the latter, concentrating our studies on the piano-stool-type complexes for the reasons given above. Our progress to date in this area will be the subject of this review. So far, most of the work has involved compounds in which the metal is one of the 12 vertices in a  $\{closo\text{-}2,1\text{-MCB}_{10}\}$  cage system, thereby complementing the host of studies made on their  $\{closo\text{-}3,1,2\text{-MC}_2\text{B}_9\}$  counterparts. However, as will also be described, preliminary investigation of 11-vertex  $\{closo\text{-}1,2\text{-MCB}_9\}$  systems is revealing the existence of unprecedented molecular structures in the metallacarborane field. We do not review in this chapter recent developments in the chemistry of monocarbollide–metal complexes in which the cage-carbon carries an  $\text{NR}_3$  or  $\text{NR}_2$  group because we have recently given an account of such species.<sup>10</sup>

## II

### SYNTHESIS

#### A. *Triruthenium and Triosmium Complexes*

The methodologies used to prepare monocarbollide metal carbonyls resemble those used to obtain cyclopentadienide metal carbonyls. The latter are generally obtained by one of two methods: heating cyclopentadiene or a substituted cyclopentadiene with a metal carbonyl or a metal carbonyl anion, or treating the carbonyl or a halo derivative of it with a salt of the cyclopentadienide ion. Similarly, procedures involving either heating a *nido*-carborane with a metal carbonyl or treating a metal carbonyl or a carbonyl-metal halide with the salt obtained by deprotonating a *nido*-carborane have afforded monocarbollide metal carbonyl complexes.

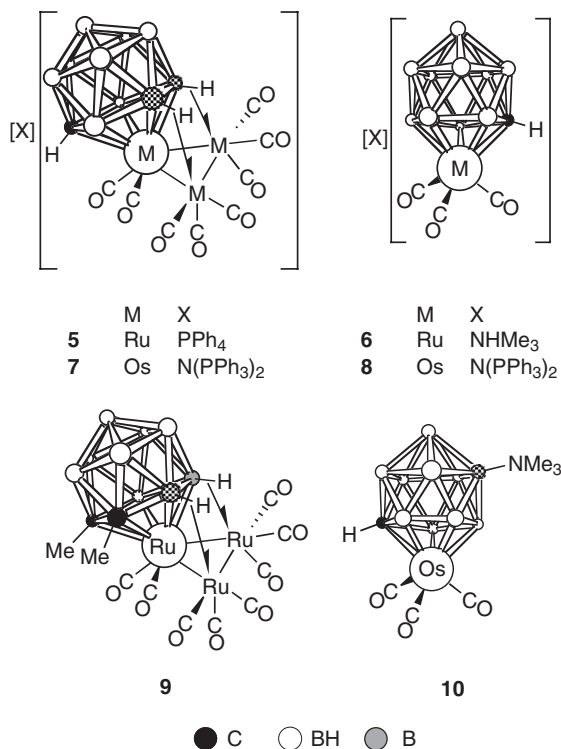


CHART 3.

Thus, in tetrahydrofuran (THF) at reflux temperatures  $[\text{Ru}_3(\text{CO})_{12}]$  and  $[\text{NHMe}_3][\text{nido-7-CB}_{10}\text{H}_{13}]$  react to give an anionic trinuclear ruthenium complex  $[\text{PPh}_4][2,2-(\text{CO})_2-7,11-(\mu\text{-H})_{2-2,7,11}\{\text{Ru}_2(\text{CO})_6\}\text{-closo-2,1-RuCB}_{10}\text{H}_9]$  (**5**)\* (Chart 3) following the addition of  $[\text{PPh}_4]\text{Cl}$ .<sup>11</sup> Subsequent analysis of this system revealed evidence for traces of the mononuclear species  $[\text{NHMe}_3][2,2,2-(\text{CO})_3\text{-closo-2,1-RuCB}_{10}\text{H}_{11}]$  (**6**) in the initial product mixture, but its isolation in a pure form proved impossible.<sup>12</sup> In contrast, the corresponding reaction between  $[\text{Os}_3(\text{CO})_{12}]$  and  $[\text{N}(\text{PPh}_3)_2][\text{nido-7-CB}_{10}\text{H}_{13}]$  in refluxing bromobenzene affords an approximately equimolar mixture of the analogous triosmium cluster  $[\text{N}(\text{PPh}_3)_2][2,2-(\text{CO})_2-7,11-(\mu\text{-H})_{2-2,7,11}\{\text{Os}_2(\text{CO})_6\}\text{-closo-2,1-OsCB}_{10}\text{H}_9]$  (**7**) and the monoosmium complex  $[\text{N}(\text{PPh}_3)_2][2,2,2-(\text{CO})_3\text{-closo-2,1-OsCB}_{10}\text{H}_{11}]$  (**8**).<sup>12</sup> The structures of the anions of **5** and **7** are similar to that of neutral  $[3,3-(\text{CO})_2-1,2\text{-Me}_2-4,8-(\mu\text{-H})_{2-3,4,8}\{\text{Ru}_2(\text{CO})_6\}\text{-closo-3,1,2-Ru}_2\text{C}_2\text{B}_9\text{H}_7]$  (**9**) obtained from the reaction between

\*The compounds described in Sections II and III are based upon *closo*-1-carba-2-metalladodecaborane fragments, with many bearing exo-polyhedral substituents. It should be noted that, although many contain chiral centers, the species are formed as racemates. Substituted boron atoms at 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. Likewise, compounds in Section IV are based upon *closo*-1-metalla-2-carbaundecaborane fragments and several are chiral. Boron atoms bearing substituents at the 4, 5, 6, or 7 positions could equally be labeled 5, 4, 7, and 6, respectively, but again the former is used by convention.

[Ru<sub>3</sub>(CO)<sub>12</sub>] and 7,8-Me<sub>2</sub>-*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>.<sup>13</sup> In all the trimetal species a {*nido*-CB<sub>10</sub>} or {*nido*-C<sub>2</sub>B<sub>9</sub>} framework bridges a triangular arrangement of ruthenium or osmium atoms with the open  $\overline{\text{CBBBB}}$  or  $\overline{\text{CCBBB}}$  faces, respectively, coordinated in a pentahapto fashion to one metal atom while the carborane cage forms two exopolyhedral B-H→M bonds with the other two metal atoms.

Surprisingly, instead of affording a mixture containing the anions of the cluster compound **7** and the mononuclear species **8**, the complex [12-NMe<sub>3</sub>-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-OsCB<sub>10</sub>H<sub>10</sub>] (**10**) is obtained by heating [Os<sub>3</sub>(CO)<sub>12</sub>] with [NHMe<sub>3</sub>][*nido*-7-CB<sub>10</sub>H<sub>13</sub>] in refluxing bromobenzene. The NMe<sub>3</sub> group is attached to a boron atom in the pentagonal belt lying above that of the  $\overline{\text{CBBBB}}$  ring η<sup>5</sup>-coordinated to the metal.<sup>12</sup> The source of the trimethylamine group must be the cation [NHMe<sub>3</sub>]<sup>+</sup>, but the pathway by which its NMe<sub>3</sub> fragment migrates to the cage is not clear.

### B. Mononuclear Compounds of Iron, Molybdenum, Tungsten, Rhenium, Platinum, Nickel and Cobalt

Reactions between salts of [*nido*-7-CB<sub>10</sub>H<sub>13</sub>]<sup>-</sup> and [Fe<sub>3</sub>(CO)<sub>12</sub>] afford the mononuclear anionic iron compound [2,2,2-(CO)<sub>3</sub>-*closo*-2,1-FeCB<sub>10</sub>H<sub>11</sub>]<sup>-</sup>, typically isolated as its [N(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> salt (**11**) (Chart 4).<sup>14</sup> No anionic triiron complex analogous to **5** and **7** is formed in this reaction. The anionic mononuclear iron, ruthenium and osmium complexes and the previously mentioned neutral mononuclear ruthenium dicarbollide complex **4**, obtained from [Ru<sub>3</sub>(CO)<sub>12</sub>] and *nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>13</sub>, are isolobal with the cyclopentadienide species [Mn(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] and [Fe(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)]<sup>+</sup>.

In an attempt to prepare a molybdenum complex related to compound **11**, [Mo(NCMe)<sub>3</sub>(CO)<sub>3</sub>] was treated with [NHMe<sub>3</sub>][*nido*-7-CB<sub>10</sub>H<sub>13</sub>] followed by [N(PPh<sub>3</sub>)<sub>2</sub>]Cl but the desired complex [N(PPh<sub>3</sub>)<sub>2</sub>][2,2,2,2-(CO)<sub>4</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>] (**12**) was obtained only in poor yield.<sup>14</sup> This complex was also formed in the reaction between Na<sub>3</sub>[*nido*-7-CB<sub>10</sub>H<sub>11</sub>] and [Mo(NCMe)<sub>3</sub>(CO)<sub>3</sub>] presumably *via* an intermediate species [2,2,2-(CO)<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>11</sub>]<sup>3-</sup>, isolobal with the long-known [3,3,3-(CO)<sub>3</sub>-*closo*-3,1,2-MoC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup> dianion.<sup>2</sup> Evidently any salt of [2,2,2-(CO)<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>11</sub>]<sup>3-</sup> is readily oxidized, scavenging a CO molecule to afford the final product. It was possible to prepare **12** by adding [Mo(NCMe)<sub>3</sub>(CO)<sub>3</sub>] in NCMe to a THF suspension of Na<sub>3</sub>[*nido*-7-CB<sub>10</sub>H<sub>11</sub>] at low temperatures while bubbling CO through the mixture, followed by addition of H[BF<sub>4</sub>]·OEt<sub>2</sub> and [N(PPh<sub>3</sub>)<sub>2</sub>]Cl.<sup>14</sup> It seems likely that in this reaction sequence, **12** is formed *via* a pathway involving the unstable hydrido species [2,2,2-(CO)<sub>3</sub>-2-H-*closo*-2,1-MoCB<sub>10</sub>H<sub>11</sub>]<sup>2-</sup> and [2,2,2-(CO)<sub>3</sub>-2,2-(H)<sub>2</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>11</sub>]<sup>-</sup> with the latter eliminating hydrogen and capturing a CO molecule to yield the observed product. The tungsten compound **13**, an analogue of **12**, can be prepared similarly using [W(NCET)<sub>3</sub>(CO)<sub>3</sub>] as the tungsten source.<sup>15a</sup>

Salts of [*nido*-7-CB<sub>10</sub>H<sub>11</sub>]<sup>3-</sup> have not been extensively employed as yet to obtain half-sandwich compounds {2-(ligand)<sub>n</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>11</sub>}, but their potential as precursors is demonstrated in the synthesis of rhenium and platinum compounds. Thus salts of the dianion [2,2,2-(CO)<sub>3</sub>-*closo*-2,1-ReCB<sub>10</sub>H<sub>11</sub>]<sup>2-</sup> have been prepared by

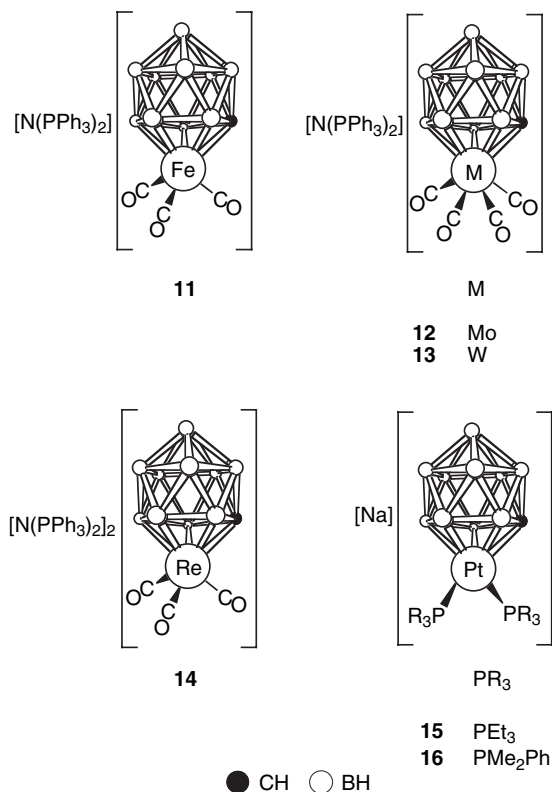


CHART 4.

treating  $[\text{ReBr}(\text{THF})_2(\text{CO})_3]$  with  $\text{Na}_3[\text{nido-7-CB}_{10}\text{H}_{11}]$  followed by addition of the appropriate cation, with the bis- $[\text{N}(\text{PPh}_3)_2]^+$  salt **14** typically isolated.<sup>16</sup> The dianion of **14** is isolobal with the long-known species  $[3,3,3\text{-}(\text{CO})_3\text{-}closo\text{-}3,1,2\text{-ReC}_2\text{B}_9\text{H}_{11}]^-$  and  $[\text{Re}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ , and displays an extensive chemistry discussed further below. Interestingly, mention was made of a species  $[2,2,2\text{-}(\text{CO})_3\text{-}closo\text{-}2,1\text{-MnCB}_{10}\text{H}_{11}]^{2-}$ , a manganese analogue of the dianion of **14**, in the original report of monocarbollide metal complexes, but without information on its properties.<sup>3a</sup>

Monocarbollide platinum complexes have also been prepared from  $\text{Na}_3[\text{nido-7-CB}_{10}\text{H}_{11}]$ . The latter in THF with  $[\text{PtCl}_2(\text{PR}_3)_2]$  affords  $\text{Na}[2,2\text{-}(\text{PR}_3)_2\text{-}closo\text{-}2,1\text{-PtCB}_{10}\text{H}_{11}]$  [ $\text{PR}_3 = \text{PEt}_3$  (**15**),<sup>17</sup>  $\text{PMe}_2\text{Ph}$  (**16**)<sup>18</sup>], species which as described later provide entry into a range of other compounds with similar  $\{closo\text{-}2,1\text{-PtCB}_{10}\}$  frameworks.<sup>17-19</sup> The  $[\text{NMe}_4]^+$  salt of the platinacarborane anion in **15** had been prepared much earlier by a 'polyhedral expansion' reaction involving treatment of  $[\text{NMe}_4][closo\text{-}2\text{-CB}_{10}\text{H}_{11}]$  with  $[\text{Pt}(\text{trans}\text{-stilbene})(\text{PEt}_3)_2]$ .<sup>7a</sup> Several related complexes were similarly obtained by treating this carborane anion with  $\text{Ni}^0$ ,  $\text{Pd}^0$  or  $\text{Pt}^0$  reagents, and as such rank among the earliest of monocarbollide metal complexes to be described.

Contemporary studies with the nickel system have extended the series of known nickel-monocarbollide anions (Chart 5). The salt  $[\text{NMe}_4][2,2\text{-}(\text{CNBu}^t)_2\text{-}closo\text{-}2,1\text{-NiCB}_{10}\text{H}_{11}]$  (**17a**) was prepared in the original study, using  $[\text{Ni}(\text{CNBu}^t)_2(\text{cod})]$

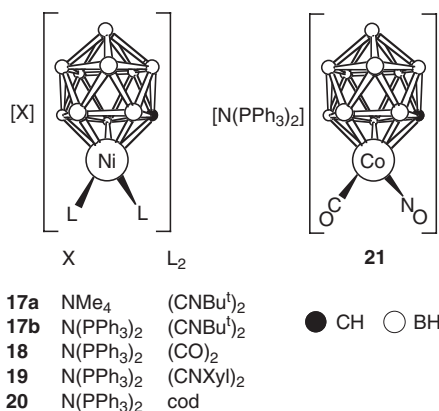


CHART 5.

(cod = 1,5-cyclooctadiene) as the Ni<sup>0</sup> reagent.<sup>7a</sup> Use of [Ni(CO)<sub>4</sub>], [Ni(CNXyl)<sub>2</sub> (cod)] (Xyl = C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6), or [Ni(cod)<sub>2</sub>] as the nickel source afforded the corresponding {NiCB<sub>10</sub>} species, isolated as the salts [N(PPh<sub>3</sub>)<sub>2</sub>][2,2-L<sub>2</sub>-*closo*-2,1-NiCB<sub>10</sub>H<sub>11</sub>] [L = CO (**18**), CNXyl (**19**); L<sub>2</sub> = cod (**20**)] following addition of [N(PPh<sub>3</sub>)<sub>2</sub>]Cl.<sup>20</sup> Indeed, this polyhedral expansion route remains an attractive possibility for preparing other monocarbollide metal compounds, as demonstrated by the recent synthesis of the cobalt compound [N(PPh<sub>3</sub>)<sub>2</sub>][2-CO-2-NO-*closo*-2,1-CoCB<sub>10</sub>H<sub>11</sub>] (**21**), formally isoelectronic with **18**, by reacting [*closo*-2-CB<sub>10</sub>H<sub>11</sub>]<sup>-</sup> with [Co(CO)<sub>3</sub>(NO)] in THF, followed by addition of [N(PPh<sub>3</sub>)<sub>2</sub>]Cl.<sup>21</sup> Complex **21** belongs to a rare class of nitrosyl substituted metallacarboranes and as far as we are aware is the first involving a monocarbollide metal species.<sup>22</sup>

As has been described, the ‘parent’ monocarbollide-metal carbonyl piano-stool species [2-(CO)<sub>n</sub>-*closo*-2,1-MCB<sub>10</sub>H<sub>11</sub>]<sup>x-</sup> are now known for all of the metals M = Mo (**12**), W (**13**), Re (**14**), Fe (**11**), Ru (**6**), Os (**8**), and Ni (**18**). Evidence also exists for a dicarbonyl-platinum analogue of compound **18**,<sup>20</sup> and as mentioned earlier, the manganese analogue of **14** has also briefly been reported.<sup>3a</sup> A notable absence from this list, however, is any representative of the Group 9 metals. The carbonyl nitrosyl-cobalt complex **21** is very closely related to the hitherto unknown dicarbonyl-cobalt dianion [2,2-(CO)<sub>2</sub>-*closo*-2,1-CoCB<sub>10</sub>H<sub>11</sub>]<sup>2-</sup> and this species remains an attractive synthetic target.

### III

## REACTIONS

### A. Ruthenium and Osmium Cluster Compounds

On protonation with H[BF<sub>4</sub>]·OEt<sub>2</sub> in THF the anionic trinuclear metal complexes **5** and **7** afford the neutral hydrido compounds [2,2-(CO)<sub>2</sub>-7,11-(μ-H)-2,2,7,

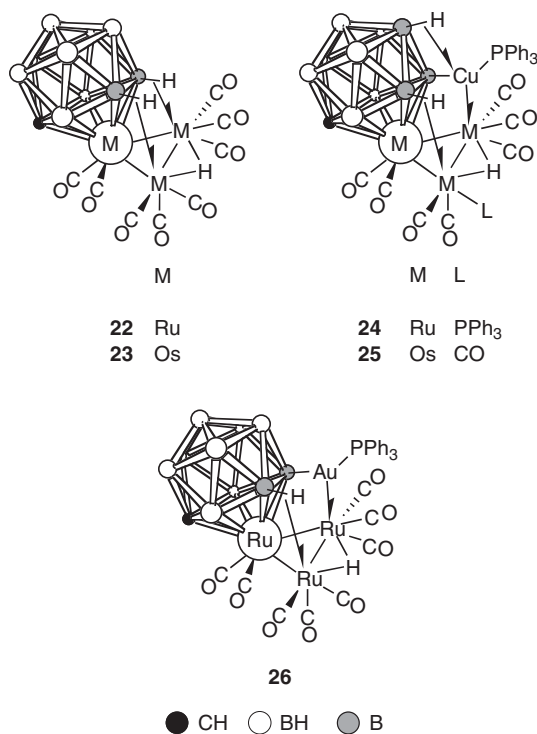


CHART 6.

11- $\{M_2(\mu-H)(CO)_6\}$ -*closo*-2,1- $MCB_{10}H_9$  [ $M = Ru$  (**22**) and  $Os$  (**23**)], respectively (Chart 6).<sup>11,12</sup> An X-ray diffraction study upon **22** revealed that in these species the hydrido ligand bridges the M–M bonding unit that is attached to the cage *via* the two B–H→M bonds. The bridging hydride reveals itself in the  $^1H$  NMR spectrum with diagnostic peaks at  $\delta -19.03$  (**22**) and  $\delta -18.65$  (**23**). The B–H→M linkages are also readily identified from the NMR spectra, in the  $^1H$  spectra by quartet resonances at  $\delta -10.31$  [ $J(BH) = 56$  Hz] (**22**) and  $\delta -13.50$  [ $J(BH) = 45$  Hz] (**23**), and in their fully coupled  $^{11}B$  spectra with doublets at  $\delta 23.4$  [ $J(BH) = 52$  Hz] (**22**) and at  $\delta 13.1$  [ $J(BH) = 45$  Hz] (**23**).

Both **5** and **7** undergo an interesting reaction in THF with  $[CuCl(PPh_3)_3]$  or  $[CuCl(PPh_3)_4]$ , respectively, in the presence of  $Tl[PF_6]$ , affording the neutral cluster compounds **24** and **25**, respectively. In the formation of these species one of the hydrides of a B–H→M bond ( $M = Ru, Os$ ) has migrated to a bridging M( $\mu$ -H)M site, being replaced by an isolobal  $\{Cu(PPh_3)\}^+$  fragment. A B–H→Cu bond, involving a BH unit in the  $B_5$  pentagonal belt lying above the  $\overline{CBBBB}$  ring pentahapto coordinated to the metal vertex, further attaches the copper to the cage. In the ruthenium compound a  $PPh_3$  molecule derived from the copper reagent substitutes for one of the CO ligands on the  $Ru_3$  triangle. Salts of the anion **5** react with  $[AuCl(PPh_3)]$  to yield **26** which has structural features similar to **24**, except that the gold atom has only a single B–Au  $\sigma$ -bonding attachment to the cage. The difference



in the bonding of Cu and Au atoms to the cage in **24** and **26** no doubt relates to the tendency of copper to seek a higher coordination number than gold, as discussed further below.

## B. Mononuclear Metal Compounds

### 1. Formation of Charge-Compensated Complexes with Donor Ligands

#### a. Complexes of Iron

Salts of the mononuclear iron anion of **11** undergo a variety of reactions (Chart 7).<sup>14,23</sup> The CO groups in **11** are not readily substituted by donor ligands. However, in the presence of  $\text{Me}_3\text{NO}$ , one CO group is readily replaced by donor molecules to yield  $[\text{N}(\text{PPh}_3)_2][2,2,2\text{-(CO)}_2\text{-2-L-closo-2,1-FeCB}_{10}\text{H}_{11}]$  [ $\text{L} = \text{PPh}_3$  (**27**),  $\text{CNBu}^t$  (**28**),  $\text{SMe}_2$  (**29**)]. More interestingly, **11** reacts with electrophiles ( $\text{NO}^+$ ,  $\text{Ph}_3\text{C}^+$ ,  $\text{H}^+$ ) in the presence of certain solvents L to give the species  $[2,2,2\text{-(CO)}_3\text{-7-L-closo-2,}$

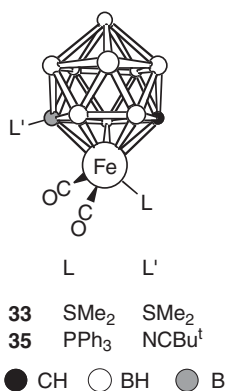
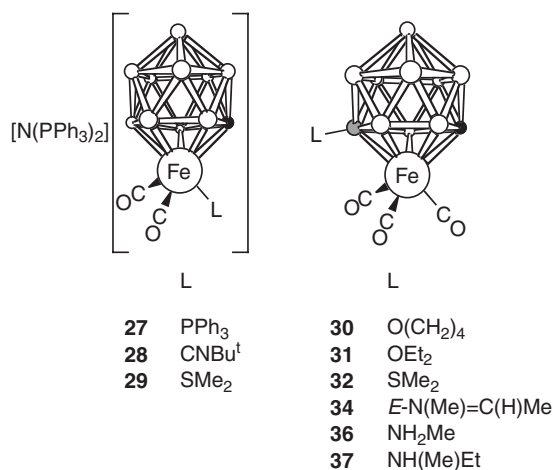


CHART 7.

1-FeCB<sub>10</sub>H<sub>10</sub>] [L = O(CH<sub>2</sub>)<sub>4</sub> (**30**), OEt<sub>2</sub> (**31**), SMe<sub>2</sub> (**32**)], in which a donor molecule L is bonded to a boron atom that is in a β site with respect to the carbon in the  $\overline{\text{CBBBB}}$  ring coordinated to the iron atom.<sup>14</sup> Apart from the use of X-ray crystallography to confirm the structures, NMR spectra leave no doubt about the presence of the {B-L<sup>+</sup>} groups in these charge-compensated products. Thus, for example, in the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of **30** there is a resonance at δ 20.4 which remains a singlet in a fully coupled <sup>11</sup>B spectrum while the other peaks, corresponding in total intensity to nine boron nuclei, display <sup>11</sup>B-<sup>1</sup>H coupling (ca. 130 Hz).

If compound **29** is treated with SMe<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> the zwitterionic complex [2,2-(CO)<sub>2</sub>-2,7-(SMe<sub>2</sub>)<sub>2</sub>-*closo*-2,1-FeCB<sub>10</sub>H<sub>10</sub>] (**33**) is obtained in which an SMe<sub>2</sub> group is attached both to the metal vertex and to a boron atom situated in one of the β sites in the  $\overline{\text{CBBBB}}$  ring coordinated to the iron, a result confirmed by X-ray diffraction.<sup>23</sup> In reactions of this kind the β rather than the α sites are favored for substitution by a donor molecule because the H atoms of their BH groups are the more hydridic and therefore are more susceptible to attack by electrophiles.

When complex **11** in NCMe is treated with CF<sub>3</sub>SO<sub>3</sub>Me, the product obtained is [2,2,2-(CO)<sub>3</sub>-7-{*E*-N(Me)=C(H)Me}-*closo*-2,1-FeCB<sub>10</sub>H<sub>10</sub>] (**34**) in which an iminium group {*E*-N(Me)=C(H)Me} is attached to a β-boron in the pentagonal  $\overline{\text{CBBBB}}$  ring ligating the iron.<sup>23</sup> The mode of formation of the iminium group present in **34**, and related complexes derived from other nitriles, involves CF<sub>3</sub>SO<sub>3</sub>Me reacting with NCMe to give an *N*-methylnitrilium cation [MeN≡CMe]<sup>+</sup> which itself then abstracts H<sup>-</sup> from the cage BH vertex to give an imine molecule. This then coordinates *via* the nitrogen atom to the naked site created at the boron vertex. The *E*-forms of imines are more stable than the *Z*-configurations and this must favor a facile rearrangement of initially formed *Z*-N(Me)=C(H)Me into *E*-N(Me)=C(H)Me in the reaction.<sup>23</sup> It is interesting that if a similar reaction is carried out with compound **27** as substrate, and employing the more bulky NCBu<sup>t</sup> instead of NCMe, a typical charge-compensated product [2,2-(CO)<sub>2</sub>-2-PPh<sub>3</sub>-7-NCBu<sup>t</sup>-*closo*-2,1-FeCB<sub>10</sub>H<sub>10</sub>] (**35**) is formed.

Introducing a functional imine group into the cage system in this manner opens the possibility of further syntheses with the substituent group. Several reactions have been studied.<sup>23</sup> Formally, the β-boron appended {N(Me)=C(H)Me}<sup>+</sup> group in **34** carries a positive charge, with two canonical forms for the fragment, one with the charge residing on the N atom and the other with the charge residing on the C atom of the C(H)Me terminus. The former is favored and thus it would be anticipated that the imine group would react with nucleophiles such as OH<sup>-</sup> or H<sup>-</sup>. Accordingly, treatment of **34** in THF with water yields the complex [2,2,2-(CO)<sub>3</sub>-7-NH<sub>2</sub>Me-*closo*-2,1-FeCB<sub>10</sub>H<sub>10</sub>] (**36**), a process catalyzed by PMe<sub>3</sub>. The {N(Me)=C(H)Me}<sup>+</sup> group may also be reduced by Na[BH<sub>3</sub>CN] to give [2,2,2-(CO)<sub>3</sub>-7-NH(Me)Et-*closo*-2,1-FeCB<sub>10</sub>H<sub>10</sub>] (**37**).

Treatment of **11** in THF with Bu<sup>t</sup>C≡CH in the presence of Me<sub>3</sub>NO, to facilitate removal of CO, yielded a single isomer of a species [N(PPh<sub>3</sub>)<sub>2</sub>][2,2-(CO)<sub>2</sub>-2,3-η<sup>2</sup>:σ-{{*E*}-CH=C(H)Bu<sup>t</sup>}-*closo*-2,1-FeCB<sub>10</sub>H<sub>10</sub>] (**38**), resulting from insertion of an alkyne molecule into a cage B-H bond (Chart 8). While the gross features of the molecular structure could be deduced from NMR data, the site of attachment of the

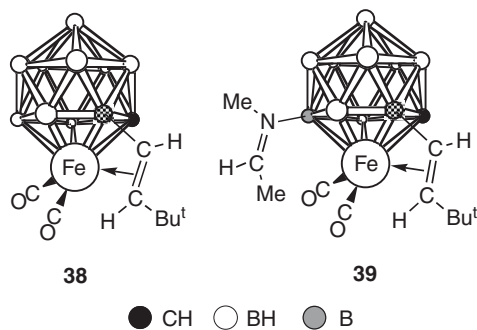


CHART 8.

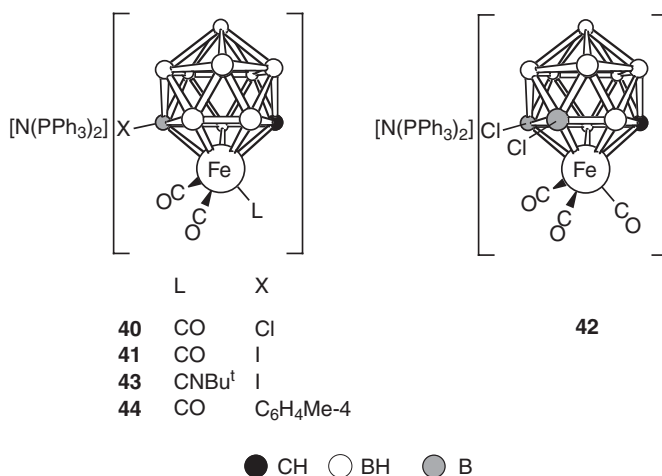


CHART 9.

*E*-C(H)=C(H)Bu<sup>t</sup> moiety to the cage could not be resolved with certainty. Crystals suitable for an X-ray diffraction study could not be obtained so **38** was reacted in NCMe with CF<sub>3</sub>SO<sub>3</sub>Me to give the imine derivative [2,2-(CO)<sub>2</sub>-2,3-η<sup>2</sup>:σ-*{E}*-CH=C(H)Bu<sup>t</sup>}-11-*{E}*-N(Me)=C(H)Me}-*closo*-2,1-FeCB<sub>10</sub>H<sub>9</sub>] (**39**). The latter did provide good quality crystals and its structure was fully resolved by X-ray diffraction. The *{E}*-C(H)=C(H)Bu<sup>t</sup> group is attached to a boron atom α to the carbon in the  $\overline{CBBBB}$  ring bonded to the iron while the C(H)=C(H) double bond is η<sup>2</sup> coordinated to the metal atom. The *{N*(Me)=C(H)Me} group occupies the site on the  $\overline{CBBBB}$  ring which is β with respect to the carbon atom and is more remote from the α-bound vinyl group.

Treatment of complex **11** in NCMe with H<sub>2</sub>SO<sub>4</sub> and dihalogen equivalents results in hydride abstraction and formation of *B*-halogenated anions (Chart 9).<sup>24</sup> Thus, with *N*-chlorosuccinimide (2 equiv) or iodine (1 equiv), the species [N(PPh<sub>3</sub>)<sub>2</sub>][7-*X*-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-FeCB<sub>10</sub>H<sub>10</sub>] [X = Cl (**40**), I (**41**)] are formed. Use of 4 equiv of

*N*-chlorosuccinimide yields dichloro-substituted  $[N(PPh_3)_2][7,11-Cl_2-2,2,2-(CO)_3-closo-2,1-FeCB_{10}H_9]$  (**42**). In each of these products, hydride replacement again occurs at boron atoms that are  $\beta$  with respect to the carbon atom in the iron-bound  $\overline{CBBBB}$  face, a feature confirmed by an X-ray diffraction study upon complex **42**. This site of substitution was also verified by treatment of **41** with  $Ag[BF_4]$  in the presence of THF, which afforded compound **30** *via*  $AgI$  elimination.

The potential of complexes **40–42** as precursors to further iron-monocarbollide species is also demonstrated<sup>24</sup> by the conversion of **41** to  $[N(PPh_3)_2][7-I-2,2-(CO)_2-2-CN Bu^t-closo-2,1-FeCB_{10}H_{10}]$  (**43**), parallel to the synthesis of **28** from **11**. Moreover, the utility of species such as **41** for the introduction of cluster organyl substituents was shown by its reaction with  $[MgBr(C_6H_4Me-4)]$  in THF, which gave  $[N(PPh_3)_2][7-(C_6H_4Me-4')-2,2,2-(CO)_3-closo-2,1-FeCB_{10}H_{10}]$  (**44**) *via* a cross-coupling reaction. Derivatives of the manganese dicarbollide anion  $[3,3,3-(CO)_3-closo-3,1,2-MnC_2B_9H_{11}]^-$ , isolobal with the anion of **11**, have recently also been demonstrated to possess an extensive cage substitution chemistry,<sup>22e</sup> with many parallels evident between the two systems. Compounds such as **40–44** would be expected to undergo many of the reactions observed for the corresponding  $\{MnC_2B_9\}$  species, leading to complexes bearing multiple cage-boron substituents.

## b. Complexes of Molybdenum and Tungsten

The monocarbollide-molybdenum and -tungsten carbonyl complexes **12** and **13** in many ways show a similar chemistry to that of **11** (Chart 10). Because the earlier mentioned molybdenum salt **12** in solution is somewhat unstable, the derivatives  $[N(PPh_3)_2][2,2,2-(CO)_3-2-PPh_3-closo-2,1-MCB_{10}H_{11}]$  [ $M = Mo$  (**45**),  $W$  (**46**)] were usually employed in further synthesis.<sup>14,15a</sup> These reagents, along with other  $M$ -substituted species  $[N(PPh_3)_2][2,2,2-(CO)_3-2-CN Bu^t-closo-2,1-MCB_{10}H_{11}]$  [ $M = Mo$  (**47**),  $W$  (**48**)], were prepared by reaction of **12** or **13** with the donor ligand in the presence of  $Me_3NO$ . When  $Bu^tC\equiv CH$  is the added ligand in the latter reaction, two carbonyl molecules are substituted and the alkyne behaves as a four-electron donor in the products  $[N(PPh_3)_2][2,2-(CO)_2-2-(Bu^tC\equiv CH)-closo-2,1-MCB_{10}H_{11}]$  [ $M = Mo$  (**49**),  $W$  (**50**)].<sup>14,15a</sup> A series of charge-compensated complexes  $[2,2,2-(CO)_3-2-PPh_3-7-L-closo-2,1-MCB_{10}H_{10}]$  has been prepared by treating mixtures of either the molybdenum **45** or the tungsten **46** precursors with a donor molecule  $L$  and either  $CF_3SO_3Me$  or concentrated  $H_2SO_4$  [ $L = OEt_2$ ,  $M = Mo$  (**51**),  $M = W$  (**52**);  $L = O(CH_2)_4$ ,  $M = Mo$  (**53**),  $M = W$  (**54**);  $L = SMe_2$ ,  $M = Mo$  (**55**);  $L = S(CH_2)_4$ ,  $M = Mo$  (**56**),  $M = W$  (**57**);  $L = CN Bu^t$ ,  $M = Mo$  (**58**),  $M = W$  (**59**);  $L = CNXyl$ ,  $M = Mo$  (**60**),  $M = W$  (**61**)].<sup>14,15a</sup>

As noted earlier, reactivity at the exo-polyhedral groups  $L$  without degradation of the cage system is of interest because functionalization of cage boron atoms opens the way to further new chemistry. If the donor atom is the oxygen of an ether molecule it carries a formal positive charge rendering an adjacent atom susceptible to attack by nucleophiles. Thus, treatment of **52** in THF with  $Me_3NO$ , followed by addition of  $[PPh_4]Br$ , affords  $[PPh_4][2,2,2-(CO)_3-2-PPh_3-7-OEt-closo-WCB_{10}H_{10}]$  (**62**), resulting from cleavage of an  $Et$  group from the precursor. The potential of

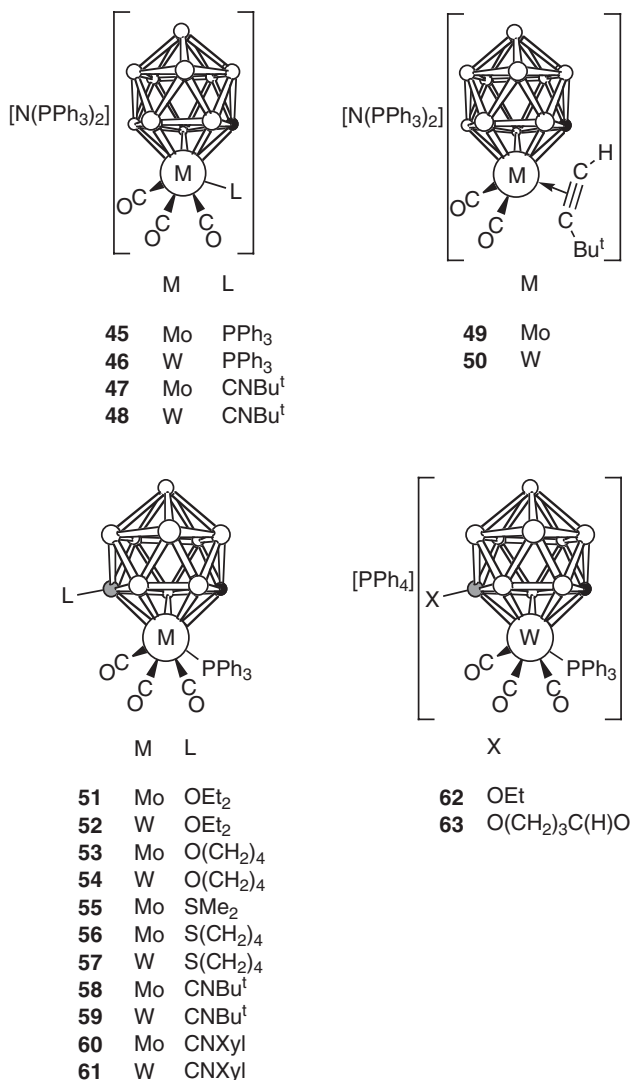


CHART 10.

this methodology to introduce functional groups on the cage is well illustrated by a similar reaction with **54**. In the latter, the CH<sub>2</sub> group to be displaced is anchored to the boron-bound oxygen by the CH<sub>2</sub> chain. Treatment with Me<sub>3</sub>NO followed by [PPh<sub>4</sub>]Br allowed the isolation of the compound [PPh<sub>4</sub>][2,2,2-(CO)<sub>3</sub>-2-PPh<sub>3</sub>-7-{O(CH<sub>2</sub>)<sub>3</sub>C(H)O}-*closo*-2,1-WCB<sub>10</sub>H<sub>10</sub>] (**63**) with a pendant aldehyde group attached to the cage.<sup>15a</sup>

The high anionic charge of the ligand [*nido*-7-CB<sub>10</sub>H<sub>11</sub>]<sup>3-</sup> is capable of stabilizing metals in higher oxidation states than the formal + II state of the molybdenum and

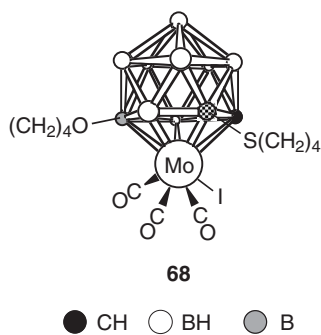
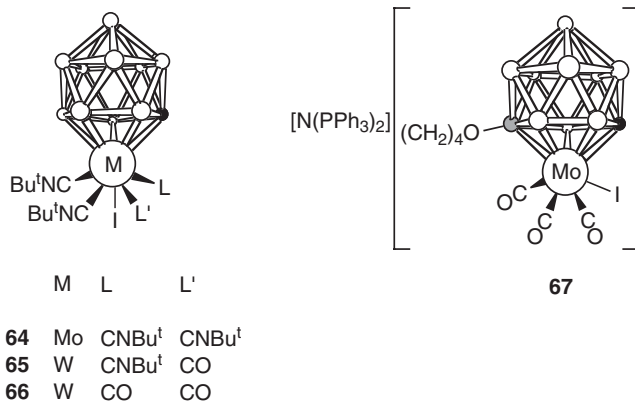


CHART 11.

tungsten found in the complexes discussed above. Since these two metals are capable of having oxidation states above  $M^{II}$ , oxidation rather than cage substitution can occur when the species **12** and **13** are treated with some reagents.<sup>15b</sup> However, there was a perceived need in such reactions for donors other than CO to be present, since in the higher oxidation state stabilization by the  $\pi$  bonding of CO molecules to the metal would be less effective. Thus when **12** in  $CH_2Cl_2$  is treated with iodine in the presence of excess CN<sup>t</sup>Bu the neutral Mo<sup>IV</sup> compound [2,2,2,2-(CN<sup>t</sup>Bu<sup>t</sup>)<sub>4</sub>-2-I-*closo*-2,1-MoCB<sub>10</sub>H<sub>11</sub>] (**64**) is produced in high yield (Chart 11). A similar reaction with **13** affords a mixture of the tungsten compounds [2,2,2,2-(CN<sup>t</sup>Bu<sup>t</sup>)<sub>3</sub>-2-CO-2-I-*closo*-2,1-WCB<sub>10</sub>H<sub>11</sub>] (**65**) and [2,2-(CN<sup>t</sup>Bu<sup>t</sup>)<sub>2</sub>-2,2-(CO)<sub>2</sub>-2-I-*closo*-2,1-WCB<sub>10</sub>H<sub>11</sub>] (**66**).

Compound **12** displays an altogether different reactivity pattern upon treatment with iodine in the presence of an ether or a thioether.<sup>15b</sup> Thus, the sole product of the reaction of **12** in THF with iodine was the anionic Mo<sup>II</sup> complex [N(PPh<sub>3</sub>)<sub>2</sub>][2,2,2-(CO)<sub>3</sub>-2-I-7-O(CH<sub>2</sub>)<sub>4</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>10</sub>] (**67**), with the carborane cage having undergone a substitution at a boron vertex. The substitution occurs at a  $\beta$  boron atom in the  $\overline{CBBBB}$  face that ligates the molybdenum atom. When **67** is treated with further iodine in THF no reaction occurs. However, treatment with iodine using

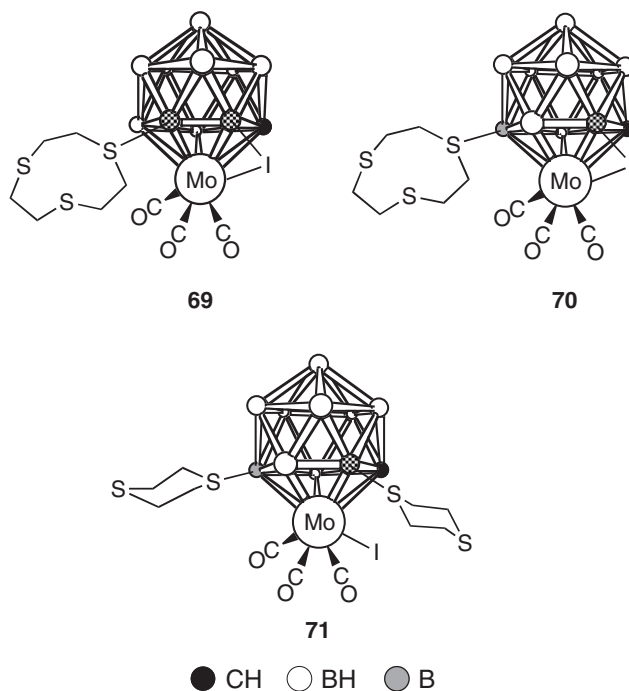


CHART 12.

$\text{S}(\text{CH}_2)_4$  as solvent results in a second cage substitution to give  $[2,2,2\text{-(CO)}_3\text{-2-I-3-S}(\text{CH}_2)_4\text{-11-O}(\text{CH}_2)_4\text{-}closo\text{-2,1-MoCB}_{10}\text{H}_9]$  (**68**), suggesting that iodine is more reactive in this medium. Notably, this second boron-bound substituent becomes attached to a boron atom in an  $\alpha$  site in the molybdenum-coordinated  $\overline{\text{CBBBB}}$  face.

With thioether ligands and iodine, compound **12** also reacts to yield cage-substituted species, but the situation is more complicated than that with THF.<sup>15b</sup> With equimolar amounts of iodine and thioethers L [L =  $\text{S}(\text{CH}_2)_4$ , *cyclo*-1,4- $\text{S}_2(\text{CH}_2)_4$ , *cyclo*-1,4,7- $\text{S}_3(\text{CH}_2)_6$ , *cyclo*-1,4,7,10- $\text{S}_4(\text{CH}_2)_8$ ] two distinct product types are formed (Chart 12). The members of the first series have the general formulation  $[2,2,2\text{-(CO)}_3\text{-2,3-(}\mu\text{-I)-}n\text{-L-}closo\text{-2,1-MoCB}_{10}\text{H}_9]$  and for each L they are formed as a mixture of two isomers ( $n = 7$  or 11). An X-ray crystallographic study on one isomer of the species  $[2,2,2\text{-(CO)}_3\text{-2,3-(}\mu\text{-I)-}n\text{-}\{cyclo\text{-1,4,7-}\text{S}_3(\text{CH}_2)_6\}\text{-}closo\text{-2,1-MoCB}_{10}\text{H}_9]$  established that the iodide ligand bridges between the metal atom and an  $\alpha$  boron atom in the coordinating  $\overline{\text{CBBBB}}$  face of the carborane cage. The trithiacyclononane ligand is bonded to a boron atom in a site that is  $\beta$  with respect to the cage-carbon atom in the open  $\overline{\text{CBBBB}}$  face of the cage. This isomer is thus formulated as  $[2,2,2\text{-(CO)}_3\text{-2,3-(}\mu\text{-I)-7-}\{cyclo\text{-1,4,7-}\text{S}_3(\text{CH}_2)_6\}\text{-}closo\text{-2,1-MoCB}_{10}\text{H}_9]$  (**69**) with the iodine atom and the thioether attached to adjacent sites,  $\alpha$  and  $\beta$  respectively, in the pentahapto  $\overline{\text{CBBBB}}$  face. The other isomer is of formulation  $[2,2,2\text{-(CO)}_3\text{-2,3-(}\mu\text{-I)-11-}\{cyclo\text{-1,4,7-}\text{S}_3(\text{CH}_2)_6\}\text{-}closo\text{-2,1-MoCB}_{10}\text{H}_9]$  (**70**) with the two substituents located at non-adjacent  $\alpha$  and  $\beta'$  boron atoms of the  $\overline{\text{CBBBB}}$  belt. The iodine-promoted replacement of boron-bound hydrides

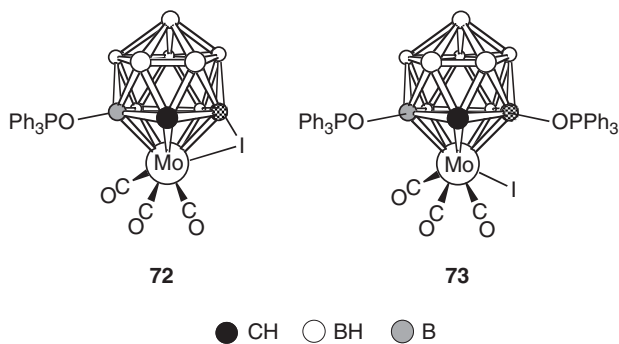


CHART 13.

by the two electron donor thioether molecules may formally be regarded as an oxidative-substitution reaction, as discussed in more detail elsewhere.<sup>15b</sup>

In the second series of compounds formed in the reaction between **12** and  $I_2$  and thioethers, two thiane molecules are attached to the cage in non-adjacent  $\alpha$  and  $\beta'$  sites with respect to the carbon in the  $\overline{CBBBB}$  ring. These products are formed as single isomers and the structure of [2,2,2-(CO)<sub>3</sub>-2-I-3,11-{*cyclo*-1,4-S<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>}<sub>2</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>9</sub>] (**71**) was confirmed by X-ray diffraction.

In contrast to the above reactions of **12** with  $I_2$ , compound **45** in  $CH_2Cl_2$  with the interhalogen ICl (1 equiv) gave a mixture of [2,2,2-(CO)<sub>3</sub>-2,3-( $\mu$ -I)-6-OPPh<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>9</sub>] (**72**) and [2,2,2-(CO)<sub>3</sub>-2-I-3,6-(OPPh<sub>3</sub>)<sub>2</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>9</sub>] (**73**), both identified with the aid of X-ray diffraction studies (Chart 13).<sup>25</sup> The bridging iodide in **72** is similar to that found in compounds **69** and **70** and related species, and is bonded to both the molybdenum vertex and an  $\alpha$  boron atom in the Mo-bound  $\overline{CBBBB}$  belt; the second boron-bound substituent, an OPPh<sub>3</sub> molecule, is bonded to the other  $\alpha$  boron atom. In **73** there are two OPPh<sub>3</sub> substituents, both of which are bound to  $\alpha$  boron atoms in the  $\overline{CBBBB}$  ring; the iodide is terminal to the molybdenum. Arguably, complexes **72** and **73** could both be formed from a common intermediate, similarly to the scheme proposed for the formation of compounds **69**–**71**.<sup>15b</sup> However, the reaction here must be considerably more complex: although the OPPh<sub>3</sub> molecules are believed to originate from the Mo-bound PPh<sub>3</sub> ligand of the precursor **45**, it is not clear how they are oxidized and then become attached to the cluster.

### c. Complexes of Nickel and Cobalt

In common with the molybdenum (**12**) and tungsten (**13**) species discussed earlier, the nickel-bound CO ligands in **18** are somewhat labile and hence phosphine-substituted derivatives [N(PPh<sub>3</sub>)<sub>2</sub>][2-CO-2-PR<sub>3</sub>-*closo*-2,1-NiCB<sub>10</sub>H<sub>11</sub>] [R = Et (**74**), Ph (**75**)] were again prepared and used in further studies (Chart 14).<sup>20</sup> Protonation of **74** or **75** with H[BF<sub>4</sub>] OEt<sub>2</sub> in  $CH_2Cl_2$ –OEt<sub>2</sub> then afforded zwitterionic species, with **74** giving as expected [7-OEt<sub>2</sub>-2-CO-2-PEt<sub>3</sub>-*closo*-2,1-NiCB<sub>10</sub>H<sub>10</sub>] (**76**).<sup>20</sup> However,



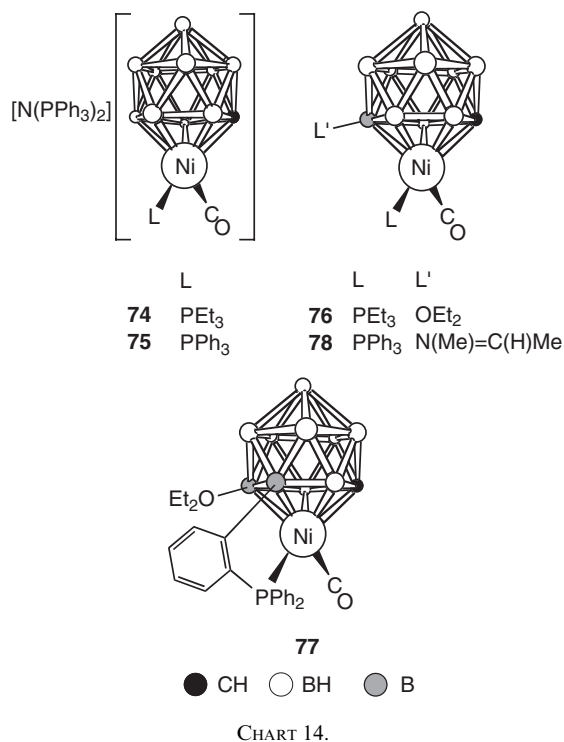
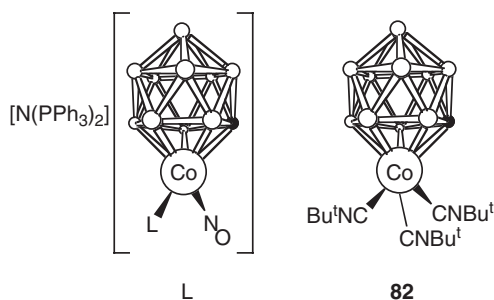


CHART 14.

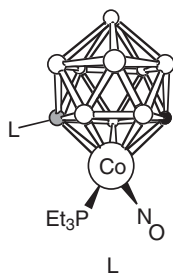
the analogous product was not obtained from **75**, which instead yielded [7-OEt<sub>2</sub>-2-CO-2,11-PPh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>-2'-B)-*closo*-2,1-NiCB<sub>10</sub>H<sub>9</sub>] (**77**) in which an additional *ortho*-cycloboronation of a phosphine phenyl ring has occurred. Compound **75**, like complexes **11** and **38** (and **45** and **46**<sup>15a</sup>), also reacts with NCMc and CF<sub>3</sub>SO<sub>3</sub>Me to afford a product, [7-{N(Me)=C(H)Me}-2-CO-2-PPh<sub>3</sub>-*closo*-2,1-NiCB<sub>10</sub>H<sub>10</sub>] (**78**), with a boron-bound iminium group. However, **78** is formed as a mixture of both *E* and *Z* isomers, a feature confirmed by NMR spectroscopy and X-ray diffraction analyses.<sup>20</sup>

Treatment of the cobalt complex **21** with PEt<sub>3</sub> or CNBu<sup>t</sup>, or with PPh<sub>3</sub> in the presence of Me<sub>3</sub>NO, affords [N(PPh<sub>3</sub>)<sub>2</sub>][2-NO-2-L-*closo*-2,1-CoCB<sub>10</sub>H<sub>11</sub>] [L = PEt<sub>3</sub> (**79**), CNBu<sup>t</sup> (**80**), PPh<sub>3</sub> (**81**)] (Chart 15).<sup>21</sup> Surprisingly, with an excess of CNBu<sup>t</sup> compound **21** reacts to give the Co<sup>III</sup> species [2,2,2-(CNBu<sup>t</sup>)<sub>3</sub>-2,1-*closo*-CoCB<sub>10</sub>H<sub>11</sub>] (**82**).

Compound **79** reacts with O(CH<sub>2</sub>)<sub>4</sub> and NCMc in the presence of CF<sub>3</sub>SO<sub>3</sub>Me, like the iron complex **11** and the molybdenum and tungsten complexes **45** and **46**, to give zwitterionic compounds [2-NO-2-PEt<sub>3</sub>-7-L-*closo*-2,1-CoCB<sub>10</sub>H<sub>10</sub>] [L = O(CH<sub>2</sub>)<sub>4</sub> (**83**), NCMc (**84**)].<sup>21</sup> Interestingly, the acetonitrile reaction gave in addition to **84** small amounts of the imine complex [7-{N(Me)=C(H)Me}-2-NO-2-PEt<sub>3</sub>-*closo*-2,1-CoCB<sub>10</sub>H<sub>10</sub>] (**85**), a product related to the iron and nickel compounds **34** and **78**, respectively. The latter pair were the only products when **11** and **75**, respectively, were



- 79**  $\text{PEt}_3$   
**80**  $\text{CNBu}^t$   
**81**  $\text{PPh}_3$



- 83**  $\text{O}(\text{CH}_2)_4$   
**84**  $\text{NCMe}$   
**85**  $\text{N}(\text{Me})=\text{C}(\text{H})\text{Me}$



CHART 15.

treated with  $\text{NCMe}$  in the presence of  $\text{CF}_3\text{SO}_3\text{Me}$ . It was thought that in the reaction with the iron and nickel compounds the acetonitrile was preferentially methylated to give  $[\text{MeC}\equiv\text{NMe}]^+$ , and that this species then reacts with hydride from a cage  $\text{B-H}^{\delta-}$  to yield the  $\text{B-N}(\text{Me})=\text{C}(\text{H})\text{Me}$  group. That the same reaction with the cobalt complex **74** proceeds to give only small amounts of **85**, with **84** as the major product, is probably due to the  $\beta\text{-B-H}^{\delta-}$  group in the  $\text{Co}^I$  compound having enhanced hydride character due to the presence of the  $\text{PEt}_3$  ligand contributing electron density to the cage system. Hence, the electrophile  $\text{Me}^+$  preferentially reacts with the  $\beta\text{-B-H}$  group, rather than the nitrogen of the  $:\text{NCMe}$  reagent.

## 2. Protonation and Related Reactions of Platinum Complexes

It is apparent from the reactions described above that in the anionic monocarbonyl metal carbonyls the negative charge is delocalized over the icosahedral framework and not localized on the metal center. Thus protonation of **11** in THF



Protonation of compound **16** with HCl in Et<sub>2</sub>O afforded three products. The anticipated hydrido species [2,2-(PMe<sub>2</sub>Ph)<sub>2</sub>-2-H-*closo*-2,1-PtCB<sub>10</sub>H<sub>11</sub>] (**87**) was formed in about 15% yield, along with the chloride complex [2,2-(PMe<sub>2</sub>Ph)<sub>2</sub>-2-Cl-*closo*-2,1-PtCB<sub>10</sub>H<sub>11</sub>] (**88**) in yields of about 10%.<sup>18</sup> Formation of the latter is understandable because it is a characteristic of transition metal hydrides such as **87** to react with Cl<sup>-</sup> to give chloro complexes. The reaction product formed in highest yield (ca. 20%), however, was the diplatinum species **89**. An X-ray diffraction study showed the molecule to consist of two {*closo*-2,1-PtCB<sub>10</sub>} cage frameworks, conjoined by a B–B connectivity [1.726(8) Å] and by two relatively long Pt–B connectivities [2.660(6) and 2.632(6) Å]. The B–B link is formed between a boron atom that is in a β site in the platinum-bound  $\overline{\text{CBBBB}}$  ring of one sub-cluster and one in an α site in the other  $\overline{\text{CBBBB}}$  ring. Each of these two boron atoms is also involved in a B–Pt linkage to the adjacent {PtCB<sub>10</sub>} moiety. Thus the PtBPtB unit forms a ‘butterfly’ arrangement, with the platinum atoms at the wing-tips, similar to the four boron atoms which join together two {*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>} cage systems in the ‘macropolyhedral’ carborane C<sub>4</sub>B<sub>18</sub>H<sub>22</sub>.<sup>26</sup>

The pathway by which **89** is formed is not known but appears to involve oxidation of the anion in **16** followed by a combination of two {2,2-(PMe<sub>2</sub>Ph)<sub>2</sub>-*closo*-2,1-PtCB<sub>10</sub>H<sub>11</sub>} fragments with loss of molecular hydrogen. Interestingly, C<sub>4</sub>B<sub>18</sub>H<sub>22</sub> is also formed by loss of hydrogen upon oxidation of the anion [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup>.

The results obtained by protonating **16** with HCl in Et<sub>2</sub>O prompted an investigation of products formed by treating **15** with the same acid. The reaction afforded a complex mixture among which was the hydrido complex **86** formed in only ca. 10–15% yield. The carborane anion [*nido*-7-CB<sub>10</sub>H<sub>13</sub>]<sup>-</sup> was detected by <sup>11</sup>B{<sup>1</sup>H} NMR spectroscopy among the products and this led to the addition of [NEt<sub>4</sub>]I to the mixture in an attempt to obtain anions of any other carborane species present. This permitted the isolation of the very unusual green crystalline compound [7,7'-μ-{I(H)}]-{2,2-(PEt<sub>3</sub>)<sub>2</sub>-*closo*-2,1-PtCB<sub>10</sub>H<sub>10</sub>}<sub>2</sub>] (**90**). An X-ray diffraction study revealed that the molecule has two {2,2-(PEt<sub>3</sub>)<sub>2</sub>-*closo*-2,1-PtCB<sub>10</sub>H<sub>10</sub>} units bridged by an iodine atom. Although the H atom of the HI group was not unambiguously located, a weak residual peak was found in the final electron density map. Thus formally the compound results from replacement of a cage hydride in each of two anions of **15** by iodine. Moreover, in both halves of the molecule the boron atoms linked to the iodine are in a β site with respect to the carbons in the  $\overline{\text{CBBBB}}$  rings ligating the metal atoms. There is precedent for a structure in which two carborane cages are joined by a halide bridge. Thus in the compound [9,9'-(μ-Br)-(*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)<sub>2</sub>][BF<sub>4</sub>], two {*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>} cages are linked by a bridging Br ligand.<sup>27</sup> Moreover, the B–Br–B angle therein (111.7°) is remarkably similar to the B–I–B angle [112.1(3)°] in **90**. The attachment of the H atom to the iodine in the latter allows a satisfactory explanation for the valence electron count in **90** that would not be possible if it were absent. The HI group *via* its iodine atom can be regarded as formally donating an electron pair to each {*closo*-2,1-PtCB<sub>10</sub>H<sub>10</sub>} unit. In this manner, the icosahedral {PtCB<sub>10</sub>H<sub>10</sub>I} moieties each attain the necessary 13 skeletal electron pairs for a filled orbital description, it being noted that a {Pt(PEt<sub>3</sub>)<sub>2</sub>} group is isolobal with a BH vertex contributing two electrons for

cluster bonding, and an  $\{I: \rightarrow B\}$  vertex would contribute three electrons behaving like a CH unit.

During the course of studies with compound **15** reactions with PhSeCl and PhTeI were investigated to determine if simple metathetical reactions would occur to give species  $[2,2-(PEt_3)_2-2-XPh-closo-2,1-PtCB_{10}H_{11}]$  ( $X = Se, Te$ ). It had previously been shown that a mercury compound  $[2,2-(PEt_3)_2-2-HgPh-closo-2,1-PtCB_{10}H_{11}]$  (**91**) can be prepared by treating **15** with PhHgCl.<sup>17</sup> With the selenium and tellurium reagents in THF, however, complex mixtures of products were obtained *via* pathways not established.<sup>19</sup> From PhSeCl the compounds  $[2-PEt_3-2,n-(SePh)_2-closo-2,1-PtCB_{10}H_{10}]$  [ $n = 3$  (**92**) or 7 (**93**)] and  $[2-PEt_3-2-SePh-3-\{O(CH_2)_4Cl\}-closo-2,1-PtCB_{10}H_{10}]$  (**94**) were characterized (Chart 17). From reactions described earlier in this chapter, it seems very likely that **94** results from nucleophilic attack of  $Cl^-$  on an intermediate having an  $O(CH_2)_4$  molecule coordinated to a boron located in an  $\alpha$  site in the metal-ligating  $CBBBB$  ring. With PhTeI, a product of formulation  $[2,2-(PEt_3)_2-7-\{Te(Ph)CH_2Cl\}-closo-2,1-PtCB_{10}H_{10}]$  (**95**) was obtained, along with the poly-tellurium species **96**. The  $\{CH_2Cl\}$  moiety in **95** was presumably derived from dichloromethane used in workup procedures.

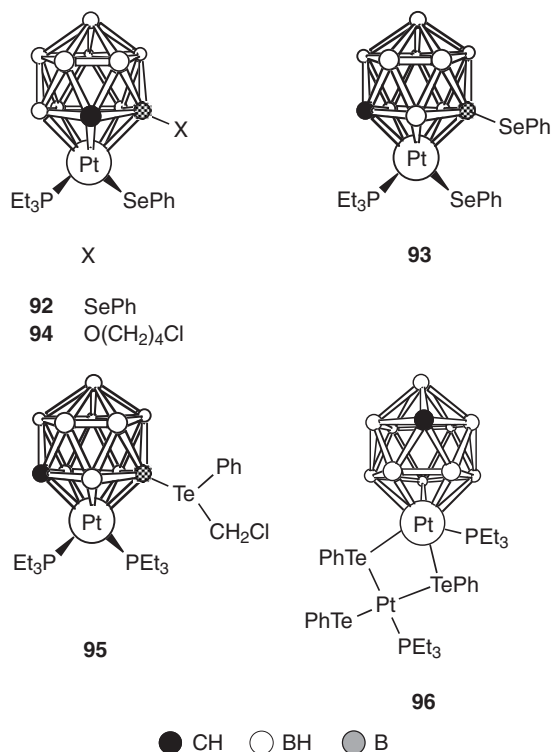


CHART 17.

### C. Zwitterionic Bimetallic Compounds<sup>†</sup>

Although the monocarbollide metal carbonyl complexes do not yield neutral hydrido compounds when they are protonated they do, in common with the platinum (**15**), cobalt (**81**) and nickel (**17**, **19**, **20**, **75**) monocarbollide compounds, often afford stable bimetal complexes on reaction with sources of the fragments  $\{M(PPh_3)\}^+$  ( $M = Cu, Ag, Au$ ) which are isolobal with the proton. Thus, the platinum compound **15** reacts with the reagents  $[CuCl(PPh_3)]_4$  and  $[AuCl(PPh_3)]$  to give  $[2,7,11-\{Cu(PPh_3)\}-7,11-(\mu-H)_2-2,2-(PEt_3)_2-closo-2,1-PtCB_{10}H_9]$  (**97**) and  $[2-\{Au(PPh_3)\}-2,2-(PEt_3)_2-closo-2,1-PtCB_{10}H_{11}]$  (**98**), respectively (Chart 18).<sup>17</sup> The cobalt compound **81** also reacts with  $[CuCl(PPh_3)]_4$  and  $[AuCl(PPh_3)]$ , in the presence of  $Tl[PF_6]$ , to form  $[2,7,11-\{Cu(PPh_3)\}-7,11-(\mu-H)_2-2-NO-2-PPh_3-closo-2,1-CoB_{10}H_9]$  (**99**) and  $[2-\{Au(PPh_3)\}-2-NO-2-PPh_3-closo-2,1-CoCB_{10}H_{11}]$  (**100**), and with  $Ag[BF_4]$  and  $PPh_3$  to yield  $[2,7-\{Ag(PPh_3)\}-7-(\mu-H)-2-NO-2-PPh_3-closo-2,1-CoCB_{10}H_{10}]$  (**101**).<sup>21</sup> It should be noted that in the copper and silver complexes the direct metal–metal bond is supported by agostic  $B-H \rightarrow M$  ( $M = Cu$  or  $Ag$ ) interactions whereas in the gold species it is believed that only a direct metal–metal bond is present.

Similarly to the platinum and cobalt systems, treatment of the nickel complexes **17b**, **19**, and **75** with  $[CuCl(PPh_3)]_4$  and  $Tl[PF_6]$  affords the respective bimetallic species<sup>28</sup>  $[2,7,11-\{Cu(PPh_3)\}-7,11-(\mu-H)_2-2-L-2-L'-closo-2,1-NiCB_{10}H_9]$  [ $L = L' = CNBu^t$  (**102**);  $L = L' = CNXyl$  (**103**);  $L = CO, L' = PPh_3$  (**104**)]. In addition, a species with  $L = CNBu^t$  and  $L' = PPh_3$  (**105**) was surprisingly formed along with **102**. With  $Ag[BF_4]$  and  $PPh_3$ , complex **75** gave  $[2,7-\{Ag(PPh_3)\}-7-(\mu-H)-2-CO-2-PPh_3-closo-2,1-NiCB_{10}H_{10}]$  (**106**), directly analogous to **101**. However, when **75** was treated with  $Ag[BF_4]$  alone, the same Ni–Ag species **106** was also obtained in modest yields *via*  $PPh_3$  scavenging, and was accompanied by small quantities of the full-sandwich species  $[Ag(PPh_3)_3][commo-2,2'-Ni\{closo-2,1-NiCB_{10}H_{11}\}\{7'-O(CH_2)_4-closo-2',1'-NiCB_{10}H_{10}\}]$  (**107**).<sup>28</sup> Formation of the latter may be rationalized in terms of a coming together of  $\{closo-2,1-NiCB_{10}\}$  and  $\{nido-7-CB_{10}\}$  fragments that are formed when  $PPh_3$  is scavenged from the precursor. An  $Ag^+$ -promoted oxidative substitution<sup>15b</sup> of a boron-bound hydride by a THF molecule has also occurred during the reaction. Treatment of compounds **19** and **75** with  $[AuCl(PPh_3)]$  in the presence of  $Tl[PF_6]$  also gave bimetallic species  $[2,7-\{Au(PPh_3)\}-7-(\mu-H)-2-L-2-L'-closo-2,1-NiCB_{10}H_{10}]$  [ $L = L' = CNXyl$  (**108**);  $L = CO, L' = PPh_3$  (**109**)]. Of these, an X-ray diffraction study upon **108** showed the presence of an Ni–Au bond that was supplemented by a  $B-H \rightarrow Au$  agostic-type interaction, so that the structure is similar to **106**, rather than **98**.

In contrast with the bimetallic nickel-monocarbollide derivatives **102–106**, **108**, and **109**, the  $\{Cu(PPh_3)\}^+$  adduct  $[7,8,12-\{Cu(PPh_3)\}-7,8,12-(\mu-H)_3-2,2-(cod)-closo-2,1-NiCB_{10}H_8]$  (**110**) formed from **20** lacks an Ni–Cu bond and the exo-polyhedral

<sup>†</sup>In structural formulae, metal–metal bonds are drawn for simplicity as a single line, but this need not imply a conventional single bond. This depiction is only used to indicate the presence of a connectivity between the two atoms, and does not necessarily denote a particular distribution of electrons in these zwitterionic compounds.

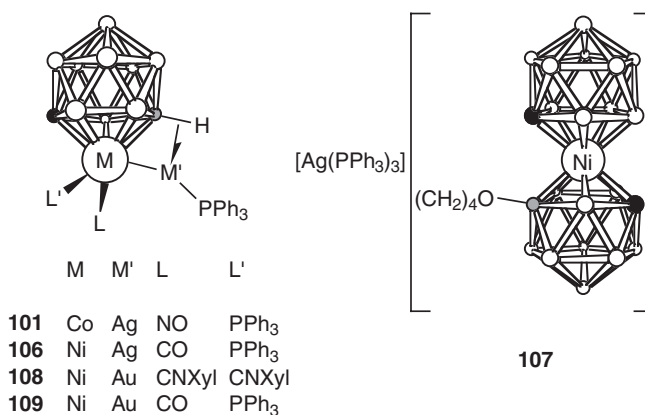
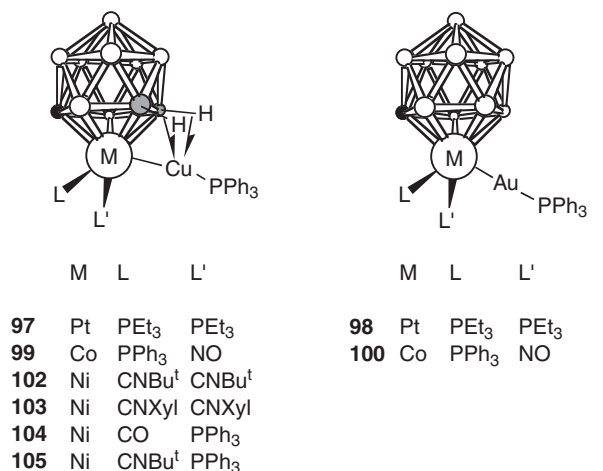


CHART 18.

metal fragment is supported only by three B–H→Cu interactions (Chart 19).<sup>28</sup> The reasons for this preference are not clear, but might be related to the differing donor properties of the nickel-bound ligands and the consequent effect on charge distribution within the cluster.

Several other species are also known where there are no metal–metal bonds and {M(PPh<sub>3</sub>)}<sup>+</sup> (M = Cu or Ag) fragments are attached to the cage in an exo-polyhedral manner, namely [7,8,12-{Cu(PPh<sub>3</sub>)}-7,8,12-(μ-H)<sub>3</sub>-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-FeCB<sub>10</sub>H<sub>8</sub>] (**111**), [7,12-{Ag(PPh<sub>3</sub>)}-7,12-(μ-H)<sub>2</sub>-2,2,2-(CO)<sub>3</sub>-*closo*-2,1-FeCB<sub>10</sub>H<sub>9</sub>] (**112**), [7,8,12-{Cu(PPh<sub>3</sub>)}-7,8,12-(μ-H)<sub>3</sub>-2,2,2-(CO)<sub>3</sub>-2-PPh<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>8</sub>] (**113**) and [7,12-{Ag(PPh<sub>3</sub>)}-7,12-(μ-H)<sub>2</sub>-2,2,2-(CO)<sub>3</sub>-2-PPh<sub>3</sub>-*closo*-2,1-MoCB<sub>10</sub>H<sub>9</sub>] (**114**).<sup>29</sup> These charge-compensated products are formed in reactions between **11** and **45**, respectively, with {M(PPh<sub>3</sub>)}<sup>+</sup>. It is noteworthy that the {Au(PPh<sub>3</sub>)}<sup>+</sup> moiety does not bond with either **11** or **45** perhaps because it is less electrophilic

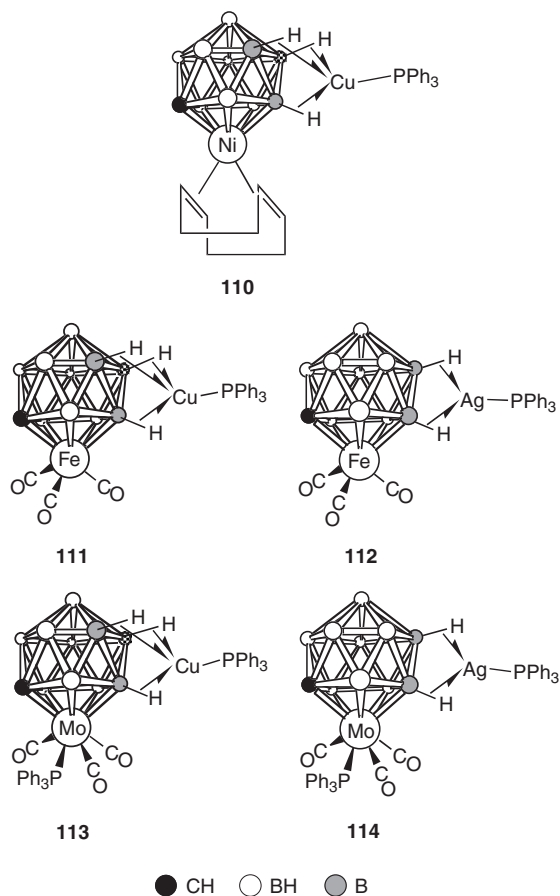


CHART 19.

than the copper and silver fragments and is not stabilized by a single B-H→Au bond. Moreover, the negative charges associated with the anions of **11** and **45** are evidently insufficiently metal centered for direct Fe-Au and Mo-Au bonds to be formed as occurs in the corresponding reactions with the reagents **15**, **19**, **75**, and **81**. An interesting feature of the complexes formed by  $\{\text{Cu}(\text{PPh}_3)\}^+$  is the propensity for copper to use four valence orbitals in bonding so that there are three attachments to the cage system, as shown by the X-ray diffraction studies upon **97**, **99**, **104**, **110**, and **113**. The difference in geometries in bonding of the  $\{\text{M}(\text{PPh}_3)\}^+$  (M = Cu or Ag) group may be the consequence of the valence hybrid  $sp_z$  and the degenerate pair of  $p_x$  and  $p_y$  orbitals for copper being sufficiently close to make all three orbitals valence orbitals, whereas with gold the  $p_x$  and  $p_y$  orbitals are of much higher energy and therefore less accessible for bonding.<sup>30</sup>

The mode of attachment of the  $\{\text{M}(\text{PPh}_3)\}^+$  fragments (M = Cu, Ag) to the cage via only B-H→M bonds is not limited to the complexes **110**–**114**, as evidenced by the structures of  $[\text{12-}\{\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)\}\text{-12-}(\mu\text{-H})\text{-2,2,2-}(\text{CO})_3\text{-2-PPh}_3\text{-}closo\text{-2,1-MoCB}_{10}\text{H}_{10}]$  (**115**) and  $[\text{7,8,12-}\{\text{RuCl}(\text{PPh}_3)_2\}\text{-7,8,12-}(\mu\text{-H})_3\text{-2,2,2-}(\text{CO})_3\text{-2-PPh}_3\text{-}$



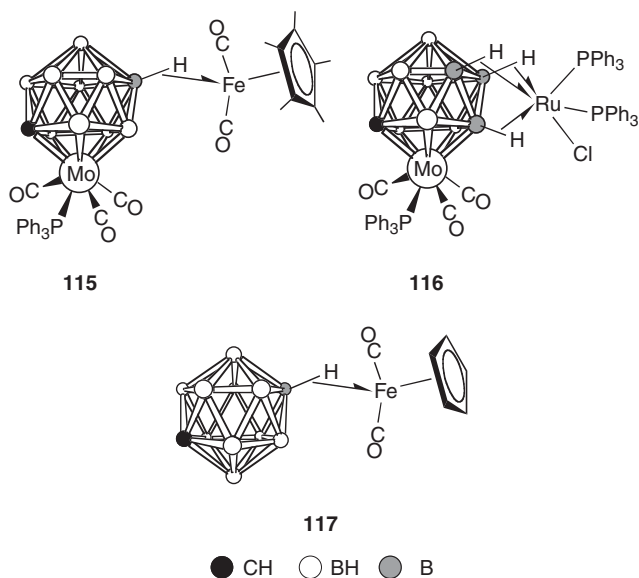


CHART 20.

*closo*-2,1-MoCB<sub>10</sub>H<sub>8</sub>] (**116**) in which the electrophilic metal–ligand groups are bonded to the cage frameworks *via* one and three agostic B–H→ML<sub>n</sub> bonds, respectively (Chart 20).<sup>29</sup> The various bimetal compounds formed from **11** and **45** illustrate the ability of the mononuclear iron and molybdenum anions to function as mono-, bi-, or tri-dentate ligands to the transition metal–ligand fragments. It is noteworthy that in the adduct **115** formed with the iron moiety {Fe(CO)<sub>2</sub>(η-C<sub>5</sub>Me<sub>5</sub>)}<sup>+</sup> the latter group is coordinated by a single agostic-type B–H→Fe bond involving a boron atom that is situated in the B<sub>5</sub> belt above the metal ligating CBBBB ring and which is antipodal to the cage carbon atom. There is a striking similarity between the structure of compound **115** and that of [12-{Fe(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)}-12-(μ-H)-*closo*-1-CB<sub>11</sub>H<sub>11</sub>] (**117**). The latter complex was prepared as part of a study using carborane anions as weakly coordinating anions.<sup>31</sup> The {Mo(CO)<sub>3</sub>(PPh<sub>3</sub>)} vertex in **115** is notionally replaced by the isolobal BH vertex in **117**.

It has been determined for the anion [*closo*-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> that the B–H vertex antipodal to the cage carbon atom is the most electron-rich site, thus rationalizing the location of the *exo*-{Fe(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)}<sup>+</sup> fragment in compound **117**. For metallocarboranes there is an accumulation of extra electron density at sites adjacent to the metal. Indeed, for dicarbollide complexes {3-L<sub>n</sub>-1,2-R<sub>2</sub>-*closo*-3,1,2-MC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>} (R = H or Me) activation of vertexes not in the coordinating CCBBB ring is quite rare. It might seem plausible that in **115**, with a bulky PPh<sub>3</sub> ligand and an {Fe(CO)<sub>2</sub>(η-C<sub>5</sub>Me<sub>5</sub>)} group in play, the CBBBB sites in the metallocarborane fragment are not as readily accessible. However, the species [*n*-{Fe(CO)<sub>2</sub>(η-C<sub>5</sub>Me<sub>5</sub>)}-*n*-(μ-H)-3,3,3-(CO)<sub>3</sub>-*closo*-3,1,2-ReC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>], derived from [3,3,3-(CO)<sub>3</sub>-*closo*-3,1,2-ReC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>-</sup> and {Fe(CO)<sub>2</sub>(η-C<sub>5</sub>Me<sub>5</sub>)}<sup>+</sup>, is formed as an equimolar mixture of two



fragment is attached to the  $\{closo-2,1-ReCB_{10}\}$  framework by an Re–Rh bond and two B–H→Rh linkages. The latter involve boron atoms in  $\alpha$  and  $\beta$  sites with respect to the carbon atom of the  $\overline{CB BBB}$  face of the cage ligating the rhenium atom. The complex is highly dynamic in solution with different processes in play. One involves heterolytic fission of the Re–Rh bond and migration of the  $\{Rh(\eta-C_5Me_5)\}$  fragment about the polyhedral  $\{closo-2,1-ReCB_{10}\}$  framework. This occurs *via* multiple exchanges of B–H bonds, employing a maximum of three B–H→Rh bonds and involving BH vertexes in both the Re-coordinating lower  $CB_4$  and the upper  $B_5$  pentagonal belts. A very similar dynamic exchange process, in which a  $\{Rh(PPh_3)_2\}$  fragment traverses the B–H vertexes in an exo-polyhedral manner, occurs for the complexes [*exo*-5,10- $\{Rh(PPh_3)_2\}$ ]-5,10-( $\mu-H$ )<sub>2</sub>-*endo*-10-X-7,8-*Me*<sub>2</sub>-*nido*-7,8- $C_2B_9H_7$ ] [X = H (**124**),<sup>34</sup> Au(PPh<sub>3</sub>) (**125**)<sup>35</sup>] and [8,9- $\{Rh(PPh_3)_2\}$ ]-8,9-( $\mu-H$ )<sub>2</sub>-3,3,3-(CO)<sub>3</sub>-*closo*-3,1,2- $ReC_2B_9H_9$ ]. The latter forms by treating Cs[3,3,3-(CO)<sub>3</sub>-*closo*-3,1,2- $ReC_2B_9H_{11}$ ] with  $[RhCl(PPh_3)_3]$ , and indeed the dicarbollide anion [3,3,3-(CO)<sub>3</sub>-*closo*-3,1,2- $ReC_2B_9H_{11}$ ]<sup>−</sup>, like **14**, affords a range of zwitterionic complexes on treatment with electrophilic metal-ligand fragments.<sup>32</sup>

Compounds **122** and **123** react with phosphines  $PR_3$  to give species in which one of the B–H→M interactions in the precursors (M = Rh, Ir) is replaced by an M– $PR_3$  bond. These species are often formed as mixtures of isomers, of which the structural types are exemplified by the complexes [2,3-*anti*- $\{Rh(PMe_2Ph)(\eta-C_5Me_5)\}$ ]-3-( $\mu-H$ )-2,2,2-(CO)<sub>3</sub>-*closo*-2,1- $ReCB_{10}H_{10}$ ] (**126**) and [2,7-*syn*- $\{Ir(PMe_2Ph)(\eta-C_5Me_5)\}$ ]-7-( $\mu-H$ )-2,2,2-(CO)<sub>3</sub>-*closo*-2,1- $ReCB_{10}H_{10}$ ] (**127**) which were characterized by X-ray diffraction (Chart 22).<sup>33</sup> The nature of the isomerism derives from whether the B–H→M bridge involves an  $\alpha$ -BH (as in **126**) or a  $\beta$ -BH (as in **127**) in the rhenium-bonded  $\overline{CB BBB}$  face, in combination with the relative disposition (*anti* or *syn*) of the phosphine with respect to this hydride. A more detailed discussion of this system is presented elsewhere.<sup>33</sup>

The formation of the bimetallic complexes **118–123** involves combination of dicationic transition metal fragments with the dianion of compound **14**. A further possibility exists, scarcely studied for 12-vertex  $\{closo-2,1-ReCB_{10}\}$  species but more extensively exploited in the analogous 11-vertex  $\{closo-1,2-MCB_9\}$  system (M = Mn, Re) discussed in Section IV. Treatment of the dianion of **14** with two

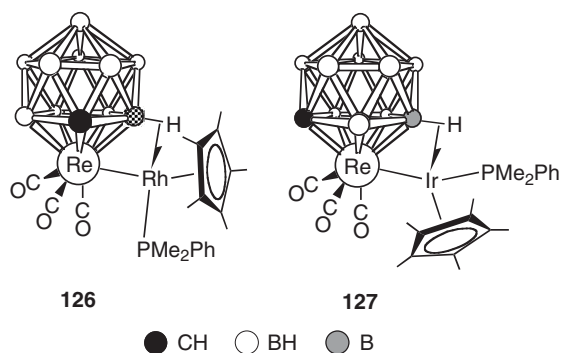


CHART 22.

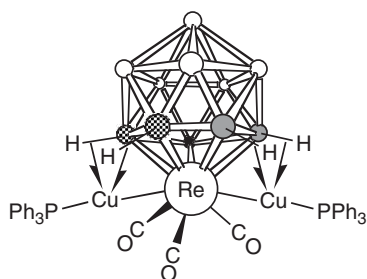
**128**

CHART 23.

equivalents of suitable monocationic fragments should give access to trimetallic species. Thus, **14** with  $[\text{CuCl}(\text{PPh}_3)]_4$  and  $\text{Ti}[\text{PF}_6]$  gave  $[2,3,7\text{-}\{\text{Cu}(\text{PPh}_3)\}\text{-}2,6,11\text{-}\{\text{Cu}(\text{PPh}_3)\}\text{-}3,6,7,11\text{-}(\mu\text{-H})_4\text{-}2,2,2\text{-}(\text{CO})_3\text{-}closo\text{-}2,1\text{-ReCB}_{10}\text{H}_7]$  (**128**) (Chart 23).<sup>36</sup> An X-ray diffraction experiment upon **128** revealed a V-shaped Cu–Re–Cu unit [ $\text{Cu}\text{-Re} = 2.6500(11), 2.6658(12) \text{ \AA}$ ;  $\text{Cu}\text{-Re}\text{-Cu} = 124.65(4)^\circ$ ], with each  $\{\text{Cu}(\text{PPh}_3)\}$  fragment attached *via* an Re–Cu bond and two B–H→Cu agostic-type linkages. Each pair of B–H→Cu interactions uses one  $\alpha\text{-B-H}$  and one  $\beta\text{-B-H}$  in the Re-bound  $\overline{\text{CBBBB}}$  face.

## IV

### MONOCARBOLLIDE–METAL COMPLEXES WITH NON-ICOSAHEDRAL CORE FRAMEWORKS

The material reviewed in this Chapter hitherto has focused on metallocarboranes in which the metal atom is a vertex in an icosahedral cage framework. Until recently, monocarbollide metal compounds with core structures other than 12 vertices were very rare since suitable carborane precursors were not readily available.<sup>4</sup> However, Brelloch's recent development of the reaction of decaborane with aldehydes to give 10-vertex monocarboranes<sup>37</sup> permits a considerable expansion in this area of boron cluster chemistry. As a consequence, several intermediate-sized monocarboranes are now easily accessible and we have recently begun to exploit the opportunities that these present. In particular, we have focused thus far on complexes derived from the *C*-phenyl-substituted species  $[6\text{-Ph-}nido\text{-}6\text{-CB}_9\text{H}_{11}]^-$ .<sup>38</sup> It is clear from these initial studies that a wealth of new chemistry remains to be discovered in this area, not only from among the metal derivatives of  $\{\text{PhCB}_9\}$  carboranes such as those discussed in this section, but also in the metal complexes of other newly available carboranes.

### A. Chemistry of the 11-Vertex Dianions [1,1,1-(CO)<sub>3</sub>-2-Ph-closo-1,2-MCB<sub>9</sub>H<sub>9</sub>]<sup>2-</sup> (M = Mn, Re)

Treatment of [NEt<sub>4</sub>][6-Ph-*nido*-6-CB<sub>9</sub>H<sub>11</sub>] in THF with Bu<sup>n</sup>Li (2 equiv) followed by [Mn(NCMe)<sub>3</sub>(CO)<sub>3</sub>][PF<sub>6</sub>] or [ReBr(THF)<sub>2</sub>(CO)<sub>3</sub>] gives the respective metal-lacarborane dianions, isolated as the mixed salts [NEt<sub>4</sub>][N(PPh<sub>3</sub>)<sub>2</sub>][1,1,1-(CO)<sub>3</sub>-2-Ph-*closo*-1,2-MCB<sub>9</sub>H<sub>9</sub>] [M = Mn (**129**),<sup>39</sup> Re (**130**)<sup>40</sup>], after addition of [N(PPh<sub>3</sub>)<sub>2</sub>]Cl (Chart 24). The actual existence during the synthesis of the trianion [6-Ph-*nido*-6-CB<sub>9</sub>H<sub>9</sub>]<sup>3-</sup> can only be inferred. X-ray diffraction studies of both salts confirmed that in their dianions the {M(CO)<sub>3</sub>} group is η<sup>6</sup>-coordinated by the  $\overline{\text{CBBBBB}}$  face of the {6-Ph-*nido*-6-CB<sub>9</sub>H<sub>9</sub>} ligand, the metal vertex being closer to the two 'prow' atoms of the boat-shaped ligating face [Mn–C 2.125(7) and Mn–B 2.118(8) Å in **129**; Re–C 2.226(8) and Re–B 2.210(12) Å in **130**] than to the other four coordinating boron atoms [2.354(8)–2.424(9) Å in **129**; 2.477(11)–2.525(10) Å in **130**], a feature typical of such *closo*-11-vertex 1-metalla(hetero)boranes.<sup>4,41</sup>

The dianions of **129** and **130** show contrasting behavior upon treatment with oxidizing agents. Thus, complex **129** in CH<sub>2</sub>Cl<sub>2</sub> with HgCl<sub>2</sub> gives [N(PPh<sub>3</sub>)<sub>2</sub>][1,1,1-(CO)<sub>3</sub>-2-Ph-*closo*-1,2-MnCB<sub>9</sub>H<sub>9</sub>] (**131**) by a one-electron oxidation process.<sup>39</sup> Conversely, solutions of **130** in CH<sub>2</sub>Cl<sub>2</sub> with HgCl<sub>2</sub> or I<sub>2</sub> give monoanionic complexes [N(PPh<sub>3</sub>)<sub>2</sub>][1,1-(CO)<sub>2</sub>-1-X-2-Ph-*hypercloso*-1,2-ReCB<sub>9</sub>H<sub>9</sub>] [X = Cl (**132**), I (**133**)], respectively,<sup>‡</sup> that formally are products of two-electron oxidation reactions. The latter oxidations appear reversible, as treatment of **132** with Na[C<sub>10</sub>H<sub>8</sub>] (2 equiv) and CO at low temperatures regenerated the dianion of **130**.<sup>42</sup>

The anion of **131** is paramagnetic, formally Mn<sup>II</sup>, and is surprisingly stable. A room temperature EPR (Electron Paramagnetic Resonance) study showed a six line pattern characteristic for a paramagnetic Mn<sup>II</sup> complex with coupling to the <sup>55</sup>Mn nucleus, indicating significant localization of the unpaired electron onto the manganese. Additional coupling to the cage hydrogen and boron atoms observed at low temperature provided evidence that the radical center is also distributed over the whole cluster, a conclusion supported by DFT (Density Functional Theory) calculations. This delocalization is likely a contributor to the stability of **131**.

Unlike those in **130**, the CO groups in **132** and **133** are readily substituted by donor ligands and treatment with, for example, PEt<sub>3</sub> gave near-quantitative conversion to [N(PPh<sub>3</sub>)<sub>2</sub>][1-CO-1-PEt<sub>3</sub>-1-X-2-Ph-*hypercloso*-1,2-ReCB<sub>9</sub>H<sub>9</sub>] [X = Cl (**134**), I (**135**)]. The rhenium-bound halide in these products may also be replaced upon reaction with donors L (1 equiv) in the presence of Tl[PF<sub>6</sub>]. Thus, compound **134** with L = PEt<sub>3</sub> gave [1-CO-1,1-(PEt<sub>3</sub>)<sub>2</sub>-2-Ph-*hypercloso*-1,2-ReCB<sub>9</sub>H<sub>9</sub>] (**136**); while with L = CNBu<sup>t</sup> it gave a mixture containing the species [1-L-1-L'-1-PEt<sub>3</sub>-2-Ph-*hypercloso*-1,2-ReCB<sub>9</sub>H<sub>9</sub>] [L = CO, L' = CNBu<sup>t</sup> (**137**); L = L' = CNBu<sup>t</sup> (**138**)], along with small quantities of **136**, and with **138** being the major product.<sup>42</sup>

As with the icosahedral monocarbollide-metal species reviewed in the preceding sections, the boron-bound hydrides of **129** and **130** may be abstracted by Me<sup>+</sup> and

<sup>‡</sup>The descriptor *hypercloso* is used here for clusters whose shapes are closed triangulated polyhedra, but which have one less electron pair available for skeletal bonding than do conventional *closo* species, according to traditional electron counting methods.

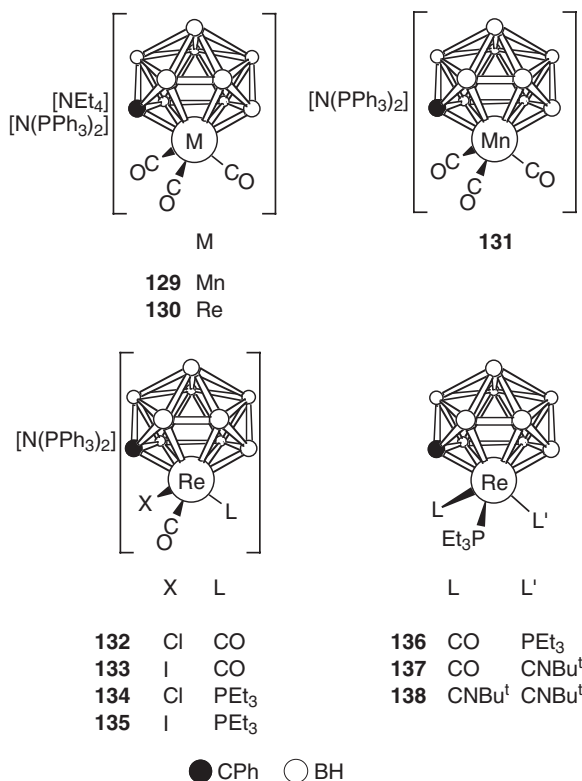


CHART 24.

replaced by donor ligands L.<sup>42</sup> Thus, treatment of **129** or **130** with CF<sub>3</sub>SO<sub>3</sub>Me in the presence of OEt<sub>2</sub> or NCMe gave, respectively, [6,7-L<sub>2</sub>-1,1,1-(CO)<sub>3</sub>-2-Ph-*closo*-1,2-MCB<sub>9</sub>H<sub>7</sub>] [M = Mn, L = OEt<sub>2</sub> (**139**); M = Mn, L = NCMe (**140**); M = Re, L = OEt<sub>2</sub> (**141**); M = Re, L = NCMe (**142**)] (Chart 25). The dianionic nature of the metallacarboranes in the precursors **129** and **130** allows for double hydride replacement to give neutral species, with both ligands L becoming bound to β boron atoms in the metal-bound  $\overline{\text{CBBBBB}}$  face. It is notable that in the formation of **140** and **142** boron-bound hydrides are replaced by NCMe molecules, similar to that in compound **84**, rather than imine moieties as was generally observed in other monoanionic icosahedral metallacarboranes such as **38** and **78**.

The neutral double zwitterions **139**–**142** are also susceptible to oxidation and treatment of **141** with I<sub>2</sub> (1 equiv) gave a surprising result.<sup>42</sup> In the product, [3,4-(OEt)<sub>2</sub>-1,1,1-(CO)<sub>3</sub>-2-Ph-*hypercloso*-1,2-ReCB<sub>8</sub>H<sub>6</sub>] (**143**), the rhenium center may be considered to be in the +III oxidation state, as in **132**–**138**, but the cluster in **143** has also lost one {BH} vertex. It is known<sup>43</sup> that oxidation of [6-Ph-*nido*-6-CB<sub>9</sub>H<sub>11</sub>]<sup>-</sup>, the 10-vertex carborane parent of **129** and **130**, with FeCl<sub>3</sub> affords 9-vertex [4-Ph-*arachno*-4-CB<sub>8</sub>H<sub>13</sub>] and indeed the carborane subunit of **143** also has the {*arachno*-4-CB<sub>8</sub>} geometry. In addition, two I<sup>-</sup> ions would be liberated following the oxidation reaction and nucleophilic attack of these upon the positively

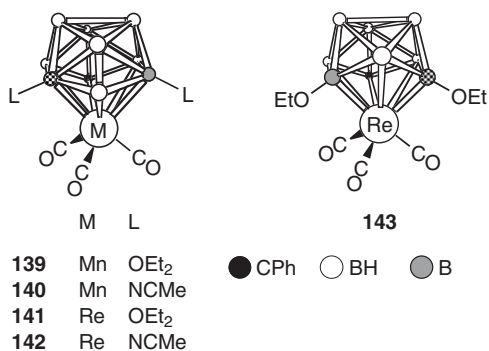


CHART 25.

charged B–OEt<sub>2</sub> moieties would remove one Et group from each – akin to the conversion of **52** to **62** – and yield the observed B–OEt substituents.

As does the dianion of **14**, the *closo*-11-vertex manganese- and rhenium-carborane dianions **129** and **130** react readily with cationic transition metal–ligand fragments, affording bimetallic products with novel structures in which the electrophilic metal–ligand groups {M'L<sub>n</sub>} are attached exo-polyhedrally to the {*closo*-1,2-MCB<sub>9</sub>} cage framework by rhenium–metal bonds supported by three-center two-electron B–H→M' linkages.<sup>40,44</sup> Thus treatment of **129** or **130** with [M'Cl<sub>2</sub>(dppe)] (M' = Ni, Pd or Pt), in the presence of Tl[PF<sub>6</sub>], gives the neutral complexes [1,3-{M'(dppe)}-3-μ-H-1,1,1-(CO)<sub>3</sub>-2-Ph-*closo*-1,2-MCB<sub>9</sub>H<sub>8</sub>] [M = Mn, M' = Ni (**144**); M = Mn, M' = Pd (**145**); M = Mn, M' = Pt (**146**); M = Re, M' = Ni (**147**); M = Re, M' = Pd (**148**); M = Re, M' = Pt (**149**)] (Chart 26).<sup>40,44</sup> An X-ray diffraction study for **149** established that a {Pt(dppe)} fragment is located at a site exo-polyhedral to the rhenacarborane cluster, and is bonded *via* a Re–Pt linkage and a three-center two-electron B–H→Pt bond. The latter involves the boron at the γ-BH vertex in the six-membered ring ligating the rhenium.<sup>40</sup> In contrast, in the solid-state structure determined for **146** by X-ray diffraction there was no Mn–Pt bond present and the exo-polyhedral {Pt(dppe)} fragment was instead anchored only by two B–H→Pt linkages (structure **146a**).<sup>44</sup> In solution, however, it is thought that these species are fluxional between the two structural types observed crystallographically.

More remarkably, the reaction forming the Mn–Pt species is unique among the compounds **144**–**149** in that three other metallocarborane products were also isolated from this system alone. These are two 12-vertex species, [1-Ph-2,2,2-(CO)<sub>3</sub>-7-X-8,8-dppe-*hypercloso*-8,2,1-PtMnCB<sub>9</sub>H<sub>8</sub>] [X = H (**150**), OEt (**151**)], and the complex [3,6,7-{Mn(CO)<sub>3</sub>}-3,7-(μ-H)<sub>2</sub>-1-Ph-6,6-dppe-*closo*-6,1-PtCB<sub>8</sub>H<sub>6</sub>] (**152**) formed by cluster contraction. Subsequent studies confirmed that the ethoxylated compound **151** is formed by reaction of **146** with adventitious EtOH present in the precursor **129**. Indeed, treatment of **146** with other alcohols ROH afforded similar species [1-Ph-2,2,2-(CO)<sub>3</sub>-7-OR-8,8-dppe-*hypercloso*-8,2,1-PtMnCB<sub>9</sub>H<sub>8</sub>] [R = Me (**153**), (CH<sub>2</sub>)<sub>2</sub>OH (**154**), (CH<sub>2</sub>)<sub>4</sub>OH (**155**)] with, surprisingly, only mono-cage products observed when diols were used as substrates. All of the alkoxy-substituted compounds **151** and **153**–**155** are relatively stable and do not react further, whereas





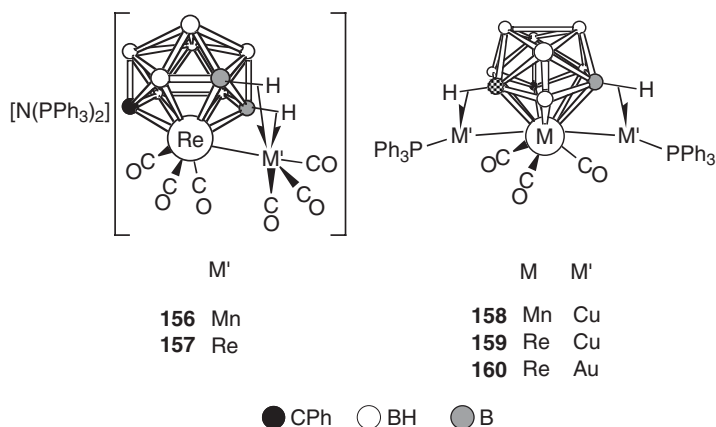


CHART 27.

the coordination sphere. Although an X-ray diffraction study was not possible to establish unambiguously the molecular structures, the  $^1\text{H}$  NMR spectra revealed signals for the  $\text{B-H}\rightarrow\text{M}'$  groups, for **156** at  $\delta -5.2$  and  $-9.6$ , and for **157** at  $\delta -3.5$  and  $-7.9$ . The molecular asymmetry is evidenced by signals for nine non-equivalent boron atoms in each of the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra and six separate resonances for the six CO ligands in their respective  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra.

Interestingly, treatment of **130** with an excess of the manganese and rhenium reagents did not afford neutral trimetallic species and only **156** and **157** were isolated.<sup>40</sup> Moreover, neither **156** or **157** reacted with the cations  $\{\text{M}'(\text{PPh}_3)\}^+$  ( $\text{M}' = \text{Cu}, \text{Au}$ ). However, these same cations did react with **129** and **130**. When the two latter species are treated with 1 equivalent of an  $\{\text{M}'(\text{PPh}_3)\}^+$  cation {from  $[\text{CuCl}(\text{PPh}_3)]_4$  or  $[\text{AuCl}(\text{PPh}_3)]$ , respectively, in the presence of  $\text{Ti}[\text{PF}_6]$ , the sole products isolated were the neutral trimetal compounds  $[1,6-\{\text{M}'(\text{PPh}_3)\}-1,7-\{\text{M}'(\text{PPh}_3)\}-6,7-(\mu\text{-H})_2-1,1,1-(\text{CO})_3-2\text{-Ph-closo-1,2-MCB}_9\text{H}_7]$  [ $\text{M} = \text{Mn}$ ,  $\text{M}' = \text{Cu}$  (**158**);  $\text{M} = \text{Re}$ ,  $\text{M}' = \text{Cu}$  (**159**);  $\text{M} = \text{Re}$ ,  $\text{M}' = \text{Au}$  (**160**)], respectively. The corresponding  $\text{MnAu}_2$  derivative has hitherto proved elusive. These products were obtained in higher yield when two equivalents of the copper or gold fragments were supplied. An X-ray diffraction study of **159** showed the molecule to consist of a central rhenacarborane moiety, with two  $\{\text{Cu}(\text{PPh}_3)\}$  groups each attached to the cluster surface *via* an  $\text{Re-Cu}$  bond and a  $\text{B-H}\rightarrow\text{Cu}$  interaction, the latter involving a  $\beta$ -boron atom in the rhenium-ligating  $\overline{\text{CBBBB}}$  face. Importantly, the two copper atoms are too far apart ( $\sim 4 \text{ \AA}$ ) to form a  $\text{Cu-Cu}$  bond so the trimetallic unit is V-shaped [ $\text{Cu-Re-Cu} = 93.89(2)^\circ$ ]. The structure of complex **159** resembles that of compound **128**, although in the latter species each  $\text{Re-Cu}$  bond is augmented by two  $\text{B-H}\rightarrow\text{Cu}$  linkages. Moreover, the different geometric demands of the rhenacarborane in **128** force the  $\text{Cu-Re-Cu}$  angle to be some  $30^\circ$  larger than in **159**. Whereas the trimetal unit in **158-160** is not a closed triangle in the solid state, such an arrangement may occur in solution during the fluxional behavior observed in the NMR data for these complexes.<sup>40</sup>

In seeking further to add two different monocationic metal fragments to the dianion of **130** in a stepwise fashion, the latter was treated with  $[\text{IrCl}(\text{CO})_2(\text{NH}_2\text{C}_6\text{H}_4\text{Me-1,4})]$  and  $\text{Tl}[\text{PF}_6]$ , in the hope of appending an  $\{\text{Ir}(\text{CO})_2\}^+$  fragment to the cluster. An anionic rhenium–iridium complex was indeed formed with its anion initially formulated<sup>45</sup> as an  $[\textit{exo}\text{-}\{\text{Ir}(\text{CO})_3\}\text{-}\textit{endo}\text{-}\{\text{Re}(\text{CO})_2\}\text{-}\{\text{CB}_9\text{H}_9\text{Ph}\}]^-$  species on the basis of spectroscopic data and X-ray structural analysis of several derivatives. Subsequent studies, however, revealed the true identity of the product to be  $[\text{N}(\text{PPh}_3)_2][1,3,6\text{-}\{\text{Re}(\text{CO})_3\}\text{-}3,6\text{-}(\mu\text{-H})_2\text{-}1,1\text{-}(\text{CO})_2\text{-}2\text{-Ph-}\textit{closo}\text{-}1,2\text{-IrCB}_9\text{H}_7]$  (**161**) (Chart 28).<sup>46,8</sup> The original incorrect formulation arose from the difficulty of distinguishing between Re and Ir in X-ray diffraction studies of derivatives of **161**, and it was thought that one CO ligand had simply been transferred from the supposed endo-polyhedral Re vertex to the exo-polyhedral Ir center. No such ambiguity arises, however, when the two metal centers are from different rows of the Periodic Table. Thus, treatment of **130** with  $[\text{Rh}(\mu\text{-Cl})(\text{CO})_2]_2$  and  $\text{Tl}[\text{PF}_6]$  afforded the Re–Rh analogue (**162**) of complex **161**, of which an X-ray diffraction analysis confirmed the anion to contain a rhodacarborane cluster with an exopolyhedral rhenium fragment.<sup>46</sup> The Mn–Ir (**163**) and Mn–Rh (**164**) analogues were prepared similarly from **129**.

It is not clear how the anions of **161–164** are formed, although it seems reasonable that the  $\{\text{M}'(\text{CO})_2\}^+$  fragments ( $\text{M}' = \text{Rh}, \text{Ir}$ ) do initially become attached in exo-polyhedral sites prior to internal reorganization. In this connection the conversion of **146** to **152** might be relevant, as that process also involves assimilation of an  $\{\text{M}'\text{L}_2\}$  fragment as a cluster vertex and extrusion of  $\{\text{Mn}(\text{CO})_3\}$ , albeit with concomitant loss of a boron vertex. That the formation of **152** appears to proceed *via* a 12-vertex  $\{\text{PtMnCB}_9\}$  intermediate might point to similar  $\{\text{MM}'\text{CB}_9\}$  intermediates ( $\text{M} = \text{Mn}, \text{Re}; \text{M}' = \text{Rh}, \text{Ir}$ ) being involved in the pathway leading to **161–164**. All of compounds **161–164** are somewhat unstable in solution, and the manganese species particularly so. They undergo mutual CO scavenging to give, respectively, the complexes  $[\text{N}(\text{PPh}_3)_2][1,3\text{-}\{\text{M}(\text{CO})_4\}\text{-}3\text{-}\mu\text{-H-}1,1\text{-}(\text{CO})_2\text{-}2\text{-Ph-}\textit{closo}\text{-}1,2\text{-M}'\text{CB}_9\text{H}_8]$  [ $\text{M} = \text{Re}, \text{M}' = \text{Ir}$  (**165**);  $\text{M} = \text{Re}, \text{M}' = \text{Rh}$  (**166**);  $\text{M} = \text{Mn}, \text{M}' = \text{Ir}$  (**167**);  $\text{M} = \text{Mn}, \text{M}' = \text{Rh}$  (**168**)], with no other metallocarborane products formed.<sup>46</sup>

The single negative charge retained by **161–164** makes them attractive substrates to which a further different cationic metal fragment could be added. In the case of the manganese species **163** and **164**, their rather facile conversion to **167** and **168**, respectively, appeared to compromise their ability to accommodate a second exopolyhedral moiety. However, this was not the case for the rhenium species **161** and **162** which, upon treatment with  $[\text{CuCl}(\text{PPh}_3)]_4$  or  $[\text{AuCl}(\text{PPh}_3)]$  in the presence of  $\text{Tl}[\text{PF}_6]$ , each unexpectedly give rise to two products.<sup>45,46</sup>

In the copper system, trimetallic Re–M'–Cu species  $[1,4,7\text{-}\{\text{Cu}(\text{PPh}_3)\}\text{-}1,5,6\text{-}\{\text{Re}(\text{CO})_3\}\text{-}4,5,6,7\text{-}(\mu\text{-H})_4\text{-}1,1\text{-}(\text{CO})_2\text{-}2\text{-Ph-}\textit{closo}\text{-}1,2\text{-M}'\text{CB}_9\text{H}_5]$  [ $\text{M}' = \text{Ir}$  (**169**), Rh

<sup>8</sup>Note that in all of the compounds (**161**, **169**, **171**, **173**, **175**) reported in the initial communication in this area,<sup>45</sup> the endo-polyhedral iridium vertex was erroneously assigned as being rhenium whilst the exopolyhedral  $\{\text{Re}(\text{CO})_3\}$  fragment in complexes **161**, **169**, and **175** was wrongly identified as  $\{\text{Ir}(\text{CO})_3\}$ . The assignments herein are correct.

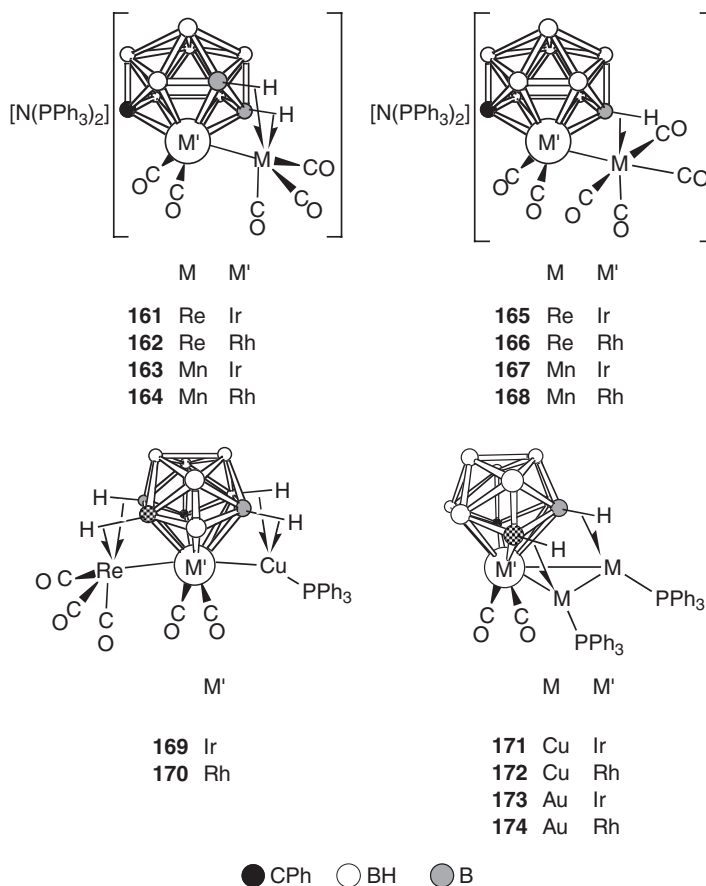


CHART 28.

(**170**) were indeed obtained, as anticipated. The exo-polyhedral  $\{\text{Cu}(\text{PPh}_3)\}$  and  $\{\text{Re}(\text{CO})_3\}$  units therein are bonded to the cluster surface by  $\text{Cu}-\text{M}'$  and  $\text{Re}-\text{M}'$  bonds, respectively, each of which is supplemented by two agostic-type interactions that employ  $\alpha$ - and  $\beta$ -B-H units in the  $\overline{\text{CBBBBB}}$  face ligating the cluster vertex  $\text{M}'$ . The major products in this system, however, were  $\text{M}'\text{Cu}_2$  species [ $1,3\text{-}\{\text{Cu}(\text{PPh}_3)\}\text{-}1,6\text{-}\{\text{Cu}(\text{PPh}_3)\}\text{-}(\text{Cu}-\text{Cu})\text{-}3,6\text{-}(\mu\text{-H})_2\text{-}1,1\text{-}(\text{CO})_2\text{-}2\text{-Ph-closo-}1,2\text{-M}'\text{CB}_9\text{H}_7$ ] [ $\text{M}' = \text{Ir}$  (**171**),  $\text{Rh}$  (**172**)]. These species merit comparison to the rhenium- and manganese-copper species **158** and **159**, which have molecular mirror symmetry and a V-shaped trimetal unit that lacks a  $\text{Cu}-\text{Cu}$  bond. Although **171** and **172** appear symmetric in solution on the NMR time scale due to fluxional processes, in the solid state the two copper centers are clearly inequivalent and a  $\text{Cu}-\text{Cu}$  bond is present. The metal triangle is supported by two  $\text{B}-\text{H}\rightarrow\text{Cu}$  linkages, one to each Cu center, involving  $\beta$ - and  $\gamma$ -B-H vertexes in the  $\text{M}'$ -bound  $\overline{\text{CBBBBB}}$  belt.

With a source of  $\{\text{Au}(\text{PPh}_3)\}^+$  the complexes **161** and **162** also give two products, but no  $\text{Re}-\text{M}'\text{-Au}$  analogues of compounds **169** and **170** were observed. The major

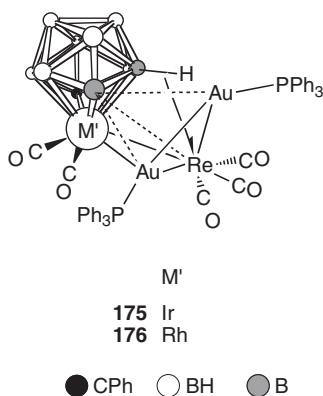


CHART 29.

products are the  $M'Au_2$  derivatives  $[1,3-\{Au(PPh_3)\}-1,6-\{Au(PPh_3)\}(Au-Au)-3,6-(\mu-H)_2-1,1-(CO)_2-2-Ph-closo-1,2-M'CB_9H_7]$  [ $M' = Ir$  (**173**),  $Rh$  (**174**)], analogous to **171** and **172** described above.

The second product type in the gold system, although isolated in lesser amounts, is of great interest. In these species, compounds **175** and **176**,  $\{Re(CO)_3\}$  and  $\{Au(PPh_3)\}$  moieties are bonded to the cluster  $\{M'(CO)_2\}$  vertex ( $M' = Ir, Rh$ ) and to each other (Chart 29). The  $Au-Re$  vector is bridged by a second  $\{Au(PPh_3)\}$  fragment, so that overall  $\{M'ReAu_2\}$  'butterflies' have been assembled starting from the rhenacarborane **130**. The rhenium center further interacts with the carbaborane *via* an additional  $B-H \rightarrow Re$  linkage and one boron vertex lacks a terminal hydrogen atom. It is notable that this naked boron vertex [B(3)] is in contact with all four metal centers, so that the  $M_4B$  core resembles that in transition-metal boride clusters. Despite this, this boron atom resonates at  $\delta$  37.9 in its  $^{11}B\{^1H\}$  NMR spectrum, substantially to higher field than in genuine borides. The mechanism by which the butterfly species **175** and **176** are formed is not clear, although it may reasonably be speculated that they are formed from  $Re-M'-Au$  species akin to **169** and **170**.

### B. Chemistry of the 11-Vertex Trianions $[1,3,6-\{M(CO)_3\}-3,6-(\mu-H)_2-1,1,1-(CO)_3-2-Ph-closo-1,2-MCB_9H_7]^{3-}$ ( $M = Mo, W$ )

Treatment of  $[NEt_4][6-Ph-nido-6-CB_9H_{11}]$  in THF with  $Bu^uLi$  (2 equiv), followed by 2 equivalents of  $[Mo(NCMe)_3(CO)_3]$  or  $[W(NCET)_3(CO)_3]$ , and then  $[NEt_4]I$  gives the salts  $[NEt_4]_3[1,3,6-\{M(CO)_3\}-3,6-(\mu-H)_2-1,1,1-(CO)_3-2-Ph-closo-1,2-MCB_9H_7]$  [ $M = Mo$  (**177**),  $W$  (**178**)] (Chart 30).<sup>47</sup> An X-ray diffraction study of the dimolybdenum species showed that in these trianions one  $\{M(CO)_3\}$  group is bonded exo-polyhedrally to a  $\{closo-1,2-MCB_9\}$  cage system by a dative  $M \rightarrow M$  bond supported by two three-center two-electron  $B-H \rightarrow M$  linkages. These two species can be compared with the rhenium-manganese and dirhenium species **156** and **157** discussed earlier.

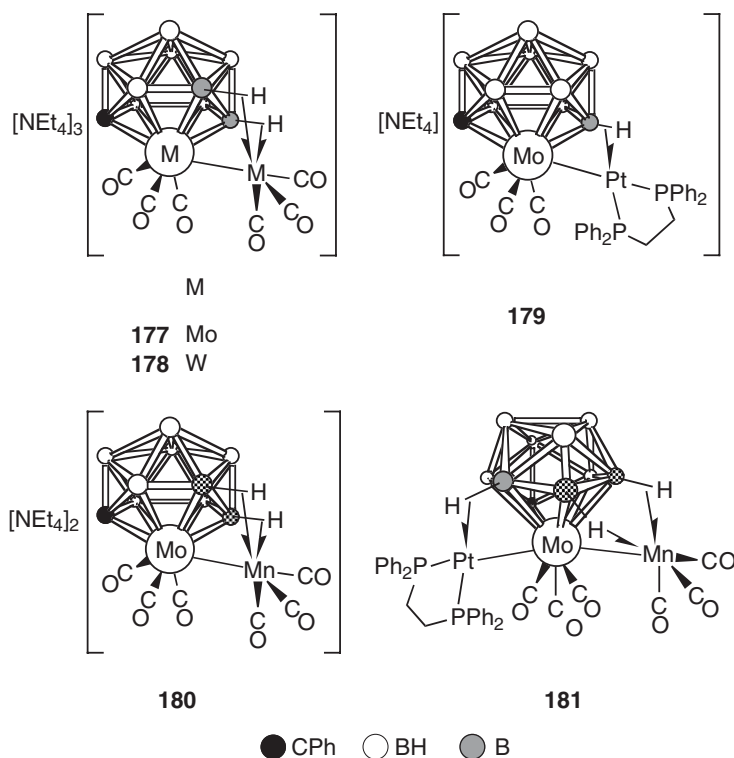


CHART 30.

Salts of the dimolybdenum trianion react<sup>47a</sup> readily with several cationic transition metal–ligand fragments with substitution of the exo-polyhedrally bonded  $\{\text{Mo}(\text{CO})_3\}$  group by a cationic fragment. Species prepared include  $[\text{NEt}_4][1,3\text{-}\{\text{Pt}(\text{dppe})\}\text{-}3\text{-}\mu\text{-H-}1,1,1\text{-}(\text{CO})_3\text{-}2\text{-Ph-}closo\text{-}1,2\text{-MoCB}_9\text{H}_8]$  (**179**) by the reaction of **177** with  $[\text{PtCl}_2(\text{dppe})]$  and  $\text{Ti}[\text{PF}_6]$ , and  $[\text{NEt}_4]_2[1,3,6\text{-}\{\text{Mn}(\text{CO})_3\}\text{-}3,6\text{-}(\mu\text{-H})_2\text{-}1,1,1\text{-}(\text{CO})_3\text{-}2\text{-Ph-}closo\text{-}1,2\text{-MoCB}_9\text{H}_7]$  (**180**) by reaction with  $[\text{Mn}(\text{NCMe})_3(\text{CO})_3][\text{PF}_6]$ , respectively. Structural studies reveal the anion of **179** to be essentially isostructural with the corresponding  $\{\text{ReCB}_9\}$  cluster **149**. The structure of complex **180** may also be compared with that of **177** and **178**, and with the  $\text{ReCB}_9$  species **156** and **157**. However, unlike the two latter compounds, it was shown that a further metal fragment could be added to compound **180**. Thus, treatment with  $[\text{PtCl}_2(\text{dppe})]$  and  $\text{Ti}[\text{PF}_6]$  gave a species that was characterized as  $[1,3,7\text{-}\{\text{Mn}(\text{CO})_3\}\text{-}1,6\text{-}\{\text{Pt}(\text{dppe})\}\text{-}3,6,7\text{-}(\mu\text{-H})_3\text{-}1,1,1\text{-}(\text{CO})_3\text{-}2\text{-Ph-}closo\text{-}1,2\text{-MoCB}_9\text{H}_6]$  (**181**) by a preliminary X-ray diffraction study.

Compound **177** reacts with  $\text{H}[\text{BF}_4] \cdot \text{OEt}_2$  (2 equiv) in the presence of CO and  $[\text{NEt}_4]\text{I}$  with oxidation of the metal center and formation of an unusual cage expansion species,  $[\text{NEt}_4][2,2,2\text{-}(\text{CO})_3\text{-}2\text{-I-}1\text{-Ph-}8\text{-OH-}closo\text{-}2,1,8\text{-MoC}_2\text{B}_9\text{H}_9]$  (**182**) (Chart 31).<sup>47b</sup> With  $\text{Ph}_2\text{S}_2$  as oxidizing agent, the dimolybdenum species  $[\text{N}(\text{PPh}_3)_2][1\text{-}\{\text{Mo}(\mu\text{-SPh}_2)(\text{CO})_4\}\text{-}2\text{-Ph-}hypercloso\text{-}1,2\text{-MoCB}_9\text{H}_9(\text{Mo-Mo})]$  (**183**) was isolated following addition of  $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ . Reaction of **177** with excess

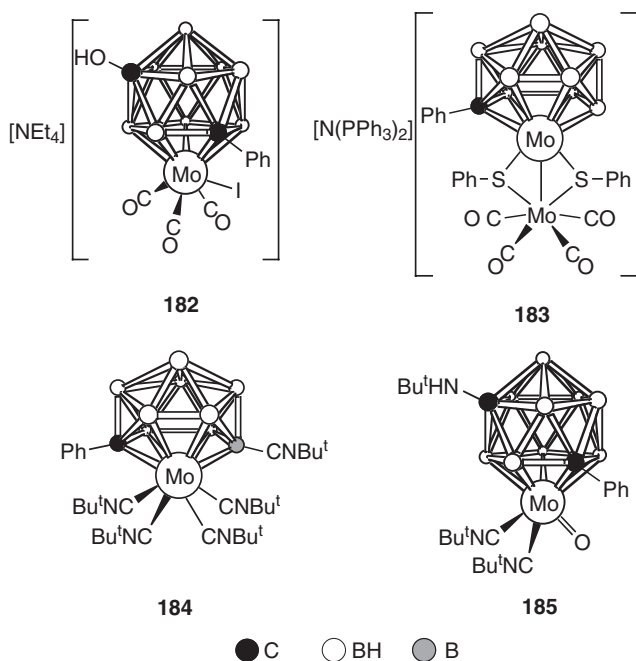


CHART 31.

CNBu<sup>t</sup> and Ag[PF<sub>6</sub>] (4 equiv) in MeCN gives the zwitterionic monomeric Mo<sup>II</sup> complex [1,1,1,1,3-(CNBu<sup>t</sup>)<sub>5</sub>-2-Ph-*closo*-1,2-MoCB<sub>9</sub>H<sub>8</sub>] (**184**), along with another cage expansion product, [2,2-(CNBu<sup>t</sup>)<sub>2</sub>-2-(=O)-1-Ph-8-NHBu<sup>t</sup>-*closo*-2,1,8-MoC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>] (**185**). It is notable that in both **182** and **185** the 'additional' {CX} vertex (X = OH, NHBu<sup>t</sup>) has inserted at the same site with respect to the {CPh} vertex from the precursor **177** and, moreover, that this site is the same as that occupied by the platinum vertex in the 12-vertex cluster-expanded species **150**, **151** and **153–155** derived from **146**. These {CX} vertexes may formally be considered as being formed by cage-promoted hydroboration of CO and CNBu<sup>t</sup> groups.

## ACKNOWLEDGEMENTS

The dedication and expertise of the coworkers cited in the references is gratefully acknowledged. We thank the Robert A. Welch Foundation for support of the research and Dr. Bruce E. Hodson for helpful comments during the preparation of this Chapter.

## REFERENCES

- (1) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818.
- (2) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.
- (3) (a) Hyatt, D. E.; Little, J. L.; Moran, J. T.; Scholer, F. R.; Todd, L. J. *J. Am. Chem. Soc.* **1967**, *89*, 3342. (b) Knoth, W. H. *J. Am. Chem. Soc.* **1967**, *89*, 3342. (c) Knoth, W. H. *Inorg. Chem.* **1971**, *10*, 598. (d) Hyatt, D. E.; Scholer, F. R.; Todd, L. J.; Warner, J. L. *Inorg. Chem.* **1967**, *6*, 2229. (e) Knoth, W. H.; Little, J. L.; Todd, L. J. *Inorg. Synth.* **1968**, *11*, 41.

- (4) (a) Grimes, R. N. (G. Wilkinson; E. W. Abel; F. G. A. Stone, Eds.), *Comprehensive Organometallic Chemistry*, **1982**, Vol. 1, Pergamon Press, Oxford, Section 5.5. (b) Grimes, R. N. (E. W. Abel; F. G. A. Stone; G. Wilkinson, Eds.), *Comprehensive Organometallic Chemistry II*, **1995**, Vol. 1, Pergamon Press, Oxford, (C. E. Housecroft, Ed.), Chapter 9. (c) Grimes, R. N. *Coord. Chem. Rev.* **2000**, *200–202*, 773.
- (5) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081.
- (6) (a) Wegner, P. A.; Guggenberger, L. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1970**, *92*, 3473. (b) Rietz, R. R.; Dustin, D. F.; Hawthorne, M. F. *Inorg. Chem.* **1974**, *13*, 1580. (c) Salentine, C. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 6382. (d) Alcock, N. W.; Taylor, J. G.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1168. (e) Stibr, B.; Janousek, Z.; Base, K.; Plesek, J.; Solntsev, K. A.; Butman, L. A.; Kuznetsov, I. I.; Kuznetsov, N. T. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1660. (f) Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; MacKinnon, P. I.; Macpherson, I. *J. Chem. Soc., Dalton Trans.* **1987**, 2385. (g) Alcock, N. W.; Jaszal, M. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1987**, 2793. (h) Fontaine, X. L. R.; Kennedy, J. D.; Thornton-Pett, M.; Nestor, K.; Stibr, B.; Jelinek, T.; Base, K. *J. Chem. Soc., Dalton Trans.* **1990**, 2887. (i) Stibr, B.; Jelinek, T.; Kennedy, J. D.; Fontaine, X. L. R.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1993**, 1261. (j) Jones, J. H.; Stibr, B.; Kennedy, J. D.; Lawrence, A. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1993**, 1269. (k) Pisareva, I. V.; Chizhevsky, I. T.; Petrovskii, P. V.; Bregadze, V. I.; Dolgushin, F. M.; Yanovsky, A. I. *Organometallics* **1997**, *16*, 5598. (l) Pisareva, I. V.; Dolgushin, F. M.; Yanovsky, A. I.; Balagurova, E. V.; Petrovskii, P. V.; Chizhevsky, I. T. *Inorg. Chem.* **2001**, *40*, 5318. (m) Konoplev, V. E.; Pisareva, I. V.; Vorontsov, E. V.; Dolgushin, F. M.; Franken, A.; Kennedy, J. D.; Chizhevsky, I. T. *Inorg. Chem. Commun.* **2003**, *6*, 1454.
- (7) (a) Carroll, W. E.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2263. (b) Stone, F. G. A. *J. Organomet. Chem.* **1975**, *100*, 257.
- (8) Jelliss, P. A.; Stone, F. G. A. *J. Organomet. Chem.* **1995**, *500*, 307.
- (9) (a) Anderson, S.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1995**, *14*, 3516. (b) Anderson, S.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1996**, *15*, 1676. (c) Anderson, S.; Jeffery, J. C.; Liao, Y.-H.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1997**, *16*, 958. (d) Jeffery, J. C.; Jelliss, P. A.; Rudd, G. E. A.; Sakanishi, S.; Stone, F. G. A.; Whitehead, J. *J. Organomet. Chem.* **1999**, *582*, 90.
- (10) McGrath, T. D.; Stone, F. G. A. *J. Organomet. Chem.* **2004**, *689*, 3891.
- (11) Ellis, D. D.; Franken, A.; Stone, F. G. A. *Organometallics* **1999**, *18*, 2362.
- (12) Ellis, D. D.; Franken, A.; McGrath, T. D.; Stone, F. G. A. *J. Organomet. Chem.* **2000**, *614–615*, 208.
- (13) Liao, Y.-H.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1996**, *15*, 5103.
- (14) Ellis, D. D.; Franken, A.; Jelliss, P. A.; Stone, F. G. A.; Yu, P.-Y. *Organometallics* **2000**, *19*, 1993.
- (15) (a) Du, S.; Franken, A.; Jelliss, P. A.; Kautz, J. A.; Stone, F. G. A.; Yu, P.-Y. *J. Chem. Soc., Dalton Trans.* **2001**, 1846. (b) Du, S.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **2001**, 2791.
- (16) Blandford, I.; Jeffery, J. C.; Jelliss, P. A.; Stone, F. G. A. *Organometallics* **1998**, *17*, 1402.
- (17) Batten, S. A.; Jeffery, J. C.; Jones, P. L.; Mullica, D. F.; Rudd, M. D.; Sappenfield, E. L.; Stone, F. G. A.; Wolf, A. *Inorg. Chem.* **1997**, *36*, 2570.
- (18) Blandford, I.; Jeffery, J. C.; Redfearn, H.; Rees, L. H.; Rudd, M. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1998**, 1669.
- (19) Batten, S. A.; Jeffery, J. C.; Rees, L. H.; Rudd, M. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1998**, 2839.
- (20) Franken, A.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. Unpublished results.
- (21) Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. *Polyhedron* **2003**, *22*, 109.
- (22) (a) Jeffery, J. C.; Stone, F. G. A.; Topaloglu, I. *J. Organomet. Chem.* **1993**, *451*, 205. (b) Dossett, S. J.; Li, S.; Stone, F. G. A. *Polyhedron* **1994**, *13*, 1773. (c) Ellis, D. D.; Jelliss, P. A.; Stone, F. G. A. *Chem. Commun.* **1999**, 2385. (d) Bitterwolf, T. E.; Scallorn, W. B.; Weiss, C. A.; Jelliss, P. A. *Organometallics* **2002**, *21*, 1856. (e) Hata, M.; Kautz, J. A.; Lu, X. L.; McGrath, T. D.; Stone, F. G. A. *Organometallics* **2004**, *23*, 3590.
- (23) Franken, A.; Du, S.; Jelliss, P. A.; Kautz, J. A.; Stone, F. G. A. *Organometallics* **2001**, *20*, 1597.
- (24) Ellis, D. D.; Franken, A.; Stone, F. G. A. Unpublished results.

- (25) Kautz, J. A.; Stone, F. G. A.; Yu, P.-Y. Unpublished results.
- (26) Janousek, Z.; Stibr, B.; Fontaine, X. L. R.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1996**, 3813.
- (27) Yanovskii, A. I.; Struchkov, Yu. T.; Grushin, V. V.; Tolstaya, T. P.; Demkina, I. I. *Zh. Strukt. Khim.* **1988**, 29, 89.
- (28) Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. Unpublished results.
- (29) Ellis, D. D.; Franken, A.; Jelliss, P. A.; Kautz, J. A.; Stone, F. G. A.; Yu, P.-Y. *J. Chem. Soc., Dalton Trans.* **2000**, 2509.
- (30) Hamilton, E. J. M.; Welch, A. J. *Polyhedron* **1990**, 9, 2407.
- (31) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1987**, 26, 2739.
- (32) Ellis, D. D.; Jelliss, P. A.; Stone, F. G. A. *Organometallics* **1999**, 18, 4982.
- (33) Jeffery, J. C.; Jelliss, P. A.; Rees, L. H.; Stone, F. G. A. *Organometallics* **1998**, 17, 2258.
- (34) Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, 106, 2979.
- (35) Jeffery, J. C.; Jelliss, P. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1993**, 1073.
- (36) Hodson, B. E.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. Unpublished work.
- (37) Brellocks, B. (M. G. Davidson, A. K. Hughes, T. B. Marder, K. Wade, Eds.), *Contemporary Boron Chemistry*, Royal Society of Chemistry, Cambridge, UK, **2000**, pp. 212–214.
- (38) (a) Jelinek, T.; Kilner, C. A.; Thornton-Pett, M.; Kennedy, J. D. *Chem. Commun.* **2001**, 1790.  
(b) Jelinek, T.; Thornton-Pett, M.; Kennedy, J. D. *Collect. Czech. Chem. Commun.* **2002**, 67, 1035.
- (39) Du, S.; Farley, R. D.; Harvey, J. N.; Jeffery, J. C.; Kautz, J. A.; Maher, J. P.; McGrath, T. D.; Murphy, D. M.; Riis-Johannessen, T.; Stone, F. G. A. *Chem. Commun.* **2003**, 1846.
- (40) Du, S.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. *Organometallics* **2003**, 22, 2842.
- (41) (a) Kennedy, J. D. *Prog. Inorg. Chem.* **1986**, 34, 211. (b) Barton, L.; Srivastava, D. K. (E. W. Abel; F. G. A. Stone; G. Wilkinson, Eds.), *Comprehensive Organometallic Chemistry II*, **1995**, Vol. 1, Pergamon Press, Oxford, UK, (C. E. Housecroft, Ed.), Chapter 8.
- (42) Du, S.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. Unpublished work.
- (43) Franken, A.; Kilner, C. A.; Thornton-Pett, M.; Kennedy, J. D. *Collect. Czech. Chem. Commun.* **2002**, 67, 869.
- (44) Du, S.; Jeffery, J. C.; Kautz, J. A.; Lu, X. L.; McGrath, T. D.; Miller T.A.; Riis-Johannessen, T.; Stone, F. G. A. *Inorg. Chem.* **2005**, 44, 2815.
- (45) Du, S.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. *Angew. Chem. Int. Ed.* **2003**, 42, 5728.
- (46) Du, S.; Hodson, B. E.; Kautz, J. A.; Lu, X. L.; McGrath, T. D.; Stone, F. G. A. Unpublished work.
- (47) (a) Lei, P.; McGrath, T. D.; Stone, F. G. A. *Chem. Commun.* **2005**, 3706. (b) Lei, P.; McGrath, T.D.; Stone, F.G.A. unpublished work.