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Invited review

Non-spectator behavior of carborane ligands in icosahedral metallacarboranes

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Abstract

Icosahedral metallacarboranes with *closo*-3,1,2-MC_2B_9 frameworks are formally derived by η^5 coordination of the open face of a *nido*-7,8-C_2B_9 cage to a metal atom. Recent work has established that the boron vertices of these $\overline{\text{CCBBB}}$ faces readily form *exo*-polyhedral bonds of various kinds. These include linkages to other metal–ligand systems via either three-center two-electron B–H $\rightharpoonup$ metal or two-center B-metal σ interactions, as well as attachments to organic groups via B–C or B–O bonds. Many new types of molecular structure have been identified, thereby opening a new domain of metallacarborane chemistry which merits further study.

Keywords: Boron; Carborane; Metallacarboranes

1. Introduction

In 1968 Hawthorne and his coworkers [1] reported the syntheses of the isomeric anionic carborane species $[7,n\text{-}R'_2\text{-}nido\text{-}7,n\text{-}C_2B_9H_9]^{2-}$ ($n = 8$ or 9, R′ = H or Me) and showed how the open pentagonal faces of these *nido* icosahedral fragments could function as pentahapto ligands towards transition metal ions, as in for example $[NMe_4]_2[Fe(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})_2]$. A formal analogy between the ligating properties of the anions $[7,n\text{-}R'_2\text{-}nido\text{-}7,n\text{-}C_2B_9H_9]^{2-}$ and the cyclopentadienyl groups $[\eta^5\text{-}C_5R'_5]^-$ thus became apparent, [1] leading to the preparation of numerous icosahedral metallacarboranes during the past 25 years, particularly by Hawthorne and his coworkers (Fig. 1) [2].

A continuing interest [3] in employing Fischer alkylidyne metal complexes, e.g. $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_5H_5)]$ (R = alkyl, aryl, or alkynyl), as synthons in metal cluster chemistry, led us to prepare salts of a family of anionic complexes $[M(\equiv CR)(CO)_2(\eta^5\text{-}7,8\text{-}R'_2\text{-}7,8\text{-}C_2B_9H_9)]^-$ (**I**, M = W or Mo, R′ = Me or H) and then to use these species to prepare complexes with heteronuclear metal–metal bonds [4a]. The metal atoms in the complexes **I** are vertices in the framework of a *closo* icosahedral structure but are also bonded to a reactive alkylidyne group which is *exo*-polyhedral to the cage. The chemistry of the species **I** is therefore of considerable interest because of the presence within the same complex of both reactive $[\eta^5\text{-}7,8\text{-}R'_2\text{-}7,8\text{-}C_2B_9H_9]$ cages and alkylidyne groups.

During work using the donor properties of the M≡C bonds of **I** to prepare di- and tri-metal compounds, it was discovered that the $[\eta^5\text{-}7,8\text{-}R'_2\text{-}7,8\text{-}C_2B_9H_9]$ ligands often adopt a non-spectator role. From these results, as well as other studies, it became evident that the B–H vertices in metallacarborane cages are more prone to activation than had been previously appreciated, and that this feature could be exploited to afford products with novel molecular structures [5]. This article reviews progress in this area.

2. Alkylidyne(carborane)metal complexes

2.1. Addition of metal–ligand groups to form metal–metal bonds

The first examples of the non-innocent behavior of $[\eta^5\text{-}7,8\text{-}R'_2\text{-}7,8\text{-}C_2B_9H_9]$ ligands were observed in our

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[1] With the anions $[7,n\text{-}R'_2\text{-}nido\text{-}7,n\text{-}C_2B_9H_9]^{2-}$ ($n = 8$ or 9, R′ = H or Me) metal atoms form icosahedral frameworks with *closo*-1,2-dicarba-3-metalla- or *closo*-1,7-dicarba-2-metalla-dodecaborane structures. However, in the formulae in this article we represent the cages as *nido* 11-vertex ligands with numbering as for an icosahedron from which the twelfth vertex has been removed. This emphasizes the pentahapto ligating character of these groups, with the cages acting formally as four electron donors to the metal centers, being thus related to the five electron donors $[\eta^5\text{-}C_5R'_5]$.

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laboratory while we were studying reactions between the reagents **I** and low valent rhodium complexes. Treatment of $[\mathrm{Rh(nbd)(PPh_3)_2}][\mathrm{PF_6}]$ (nbd = norbornadiene) with the salt **Ia** affords the dimetal compound $[\mathrm{WRh}(\mu\text{-}\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_2(\mathrm{PPh_3})_2(\eta^5\text{-}7,8\text{-}\mathrm{Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}C_7H_9})]$ (**II**, $\mathrm{C_7H_9}$ = tricyclo[2.2.1.0]heptane), while reaction with the salt **Ii** yields a mixture of the compounds $[\mathrm{WRh}(\mu\text{-}\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_2(\mathrm{PPh_3})_2(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_{10}}\text{-}n\text{-}\mathrm{C_7H_9})]$ (**IIIa**, n = 10; **IIIb**, n = 9) [6]. Since in the products a nortricyclene substituent is attached to the cage, these syntheses involve an unprecedented hydroboration of the nbd ligand of the rhodium precursor by cage B–H bonds, accompanied by C–C bond formation within this fragment. The boron atom to which the $\mathrm{C_7H_9}$ moiety is attached in **II** is in the β site with respect to the two carbons in the open pentagonal $\overline{\mathrm{CCB}\mathit{B}\mathrm{B}}$ face of the *nido*-$\mathrm{C_2B_9}$ cage ligating the tungsten atom [7]. With relatively few exceptions, it is the $\mathrm{B_\beta}$–H group which is activated if reaction occurs at a B–H vertex in a $\mathrm{M}(\eta^5\text{-}7,8\text{-}\mathrm{Me_2\text{-}7,8\text{-}C_2B_9H_9})$ system, unless this pathway is blocked by the β-boron carrying another group. This feature is believed to be due to the steric and electronic control exerted by the CMe substituents in the $\overline{\mathrm{CCBBB}}$ ring. In contrast, either the $\mathrm{B_\alpha}$–H or $\mathrm{B_\beta}$–H sites may be activated in reactions involving $\mathrm{M}(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})$ systems, as illustrated by the formation of **III** as a 1:1 mixture of the two isomers **IIIa** and **IIIb**.

It seems likely that the formation of **II** and **III** proceeds with retention of the $\mathrm{C_7H_8}$ ligand at the dimetal center, prior to insertion into a B–H bond. The latter is probably activated by formation of a B–H $\rightharpoonup$ Rh bond along the reaction pathway, an idea supported by the existence of numerous di- and tri-metal species with *exo*-polyhedral B–H $\rightharpoonup$ M groups, including $[\mathrm{Rh_2(PPh_3)_2}(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})_2]$ (**IV**) [8]. The latter complex

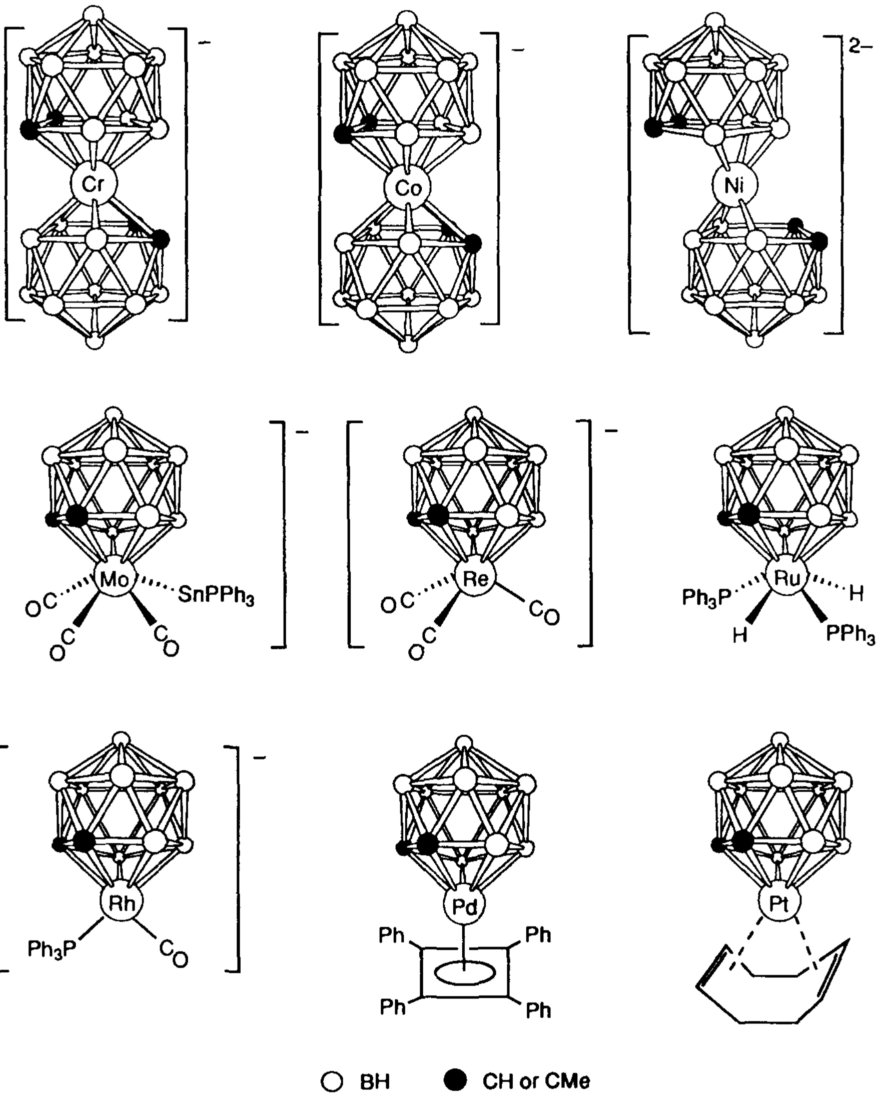
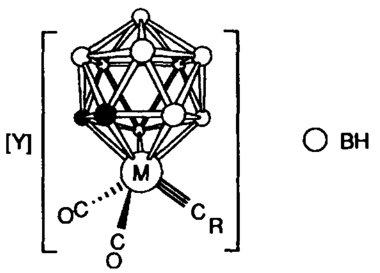


Fig. 1. Examples of metallacarborane complexes of the $[7,8\text{-}\mathrm{R'_2}\text{-}nido\text{-}7,8\text{-}\mathrm{C_2B_9H_9}]^{2-}$ (R′ = H or Me) ligands characterized by Hawthorne and coworkers [1,2]. In all these species the *nido* cage adopts a spectator role.

was isolated during studies on the use of mononuclear rhodacarborane complexes as homogeneous hydrogenation catalysts [9], and would appear to be the first reported example of a dimetallacarborane species in which a metal–metal bond is bridged by three-center two-electron B–H ⇀ M linkages. It is noteworthy in the context of the above mentioned existence of isomers of **III**, that the structure of **IV**, as found in the crystal by X-ray diffraction, is asymmetric with one cage having an *exo*-polyhedral B_α–H ⇀ Rh linkage and the other a B_β–H ⇀ Rh unit.

Addition of unsaturated metal–ligand fragments to the M≡C bonds of the reagents **I** has produced many compounds with metal–metal bonds bridged by B–H ⇀ M groups. A few examples of such species are shown in Figs. 2 and 3 [4a]. The B–H ⇀ M groups in these complexes represent an incipient oxidative-addition of agostic B–H groups at *exo*-polyhedral metal centers. Not surprisingly, therefore, these B–H ⇀ M linkages are often activated for further reaction as in the following examples.

Treatment of [MoW(μ-CC_6H_4Me-4)$(CO)_3$(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)(η^5-C_9H_7)] (C_9H_7 = indenyl), which has a B–H ⇀ Mo group (Fig. 2), with hex-3-yne gives [MoW{μ-σ,η^3-7,8-Me_2-7,8-$C_2B_9H_8$-10-C(H)C_6H_4-Me-4}(μ-CO)$(CO)_2$(EtC_2Et)(η^5-C_9H_7)] (**V**). This product results from addition of the alkyne to the tungsten center of the precursor, accompanied by insertion of the μ-CC_6H_4Me-4 ligand into the B–H ⇀ Mo bridge [10]. The cage in **V** is η^3 bonded to the tungsten, having slipped away from the two carbons towards the three boron atoms in the open pentagonal face of the ligating $\overline{\mathrm{CCBBB}}$ ring. The Mo–W distance [2.604(1) Å] is very short.



	M	R	●
Ia	W	C_6H_4Me-4	CMe
Ib	W	Me	CMe
Ic	W	C_6H_4Me-2	CMe
Id	W	$C_6H_3Me_2$-2,6	CMe
Ie	W	Ph	CMe
If	W	C_6H_4OMe-2	CMe
Ig	W	$C_6H_4CH_2$OMe-2	CMe
Ih	W	C≡CBu^t	CMe
Ii	W	C_6H_4Me-4	CH
Ij	W	Me	CH
Ik	W	C≡CBu^t	CH
Il	Mo	C_6H_4Me-4	CH
Im	Mo	C_6H_4Me-4	CMe

Y = NEt_4, PPh_4, $AsPh_4$, NMe_3Ph, $N(PPh_3)_2$, *etc.*

The reaction in THF (THF = tetrahydrofuran) between [MoW(μ-CC_6H_4Me-4)$(CO)_2$(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)(η^7-C_7H_7)] (Fig. 2) and excess MeC≡CMe initially yields the alkyne complex [MoW(μ-CC_6H_4Me-4)(CO)(MeC≡CMe)(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)(η^7-C_7H_7)] at approx. 65 °C but at higher temperatures (approx. 100 °C) further reaction takes place to give [MoW(μ-C_4Me_4){σ,η^5-7,8-Me_2-7,8-$C_2B_9H_8$-10-C(H)C_6H_4Me-4}(η^7-C_7H_7)] (**VI**) [11]. Clearly the C(H)C_6H_4Me-4 group in **VI** results from insertion of the alkylidyne group into a B_β–H bond.

In CH_2Cl_2 the MeCN groups in [Ru(CO)$(NCMe)_2$(η^5-C_5H_5)][BF_4] are readily replaced by **Ia** affording the dimetal complex [WRu(μ-CC_6H_4Me-4)$(CO)_3$(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)(η^5-C_5H_5)] (Fig. 2) [12]. Reaction of the latter with PMe_3 gives [WRu{μ-σ,η^5-7,8-Me_2-7,8-$C_2B_9H_8$-10-C(H)C_6H_4Me-4}$(CO)_3$(PMe_3)(η^5-C_5H_5)] (**VII**), the μ-CC_6H_4Me-4 group having inserted into the B_β–H ⇀ Ru bond of the precursor in a similar manner to the formation of **V**. Interestingly the B_β–H ⇀ Ru group in [WRu(μ-CC_6H_4Me-4)$(CO)_3$(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)(η^5-C_5H_5)] may be deprotonated with Bu^nLi to give, after addition of [$N(PPh_3)_2$]Cl, the salt [$N(PPh_3)_2$][WRu(μ-CC_6H_4Me-4)(μ-σ,η^5-7,8-Me_2-7,8-$C_2B_9H_8$)$(CO)_3$(η^5-C_5H_5)] (**VIII**) with a B_β–Ru σ bond.

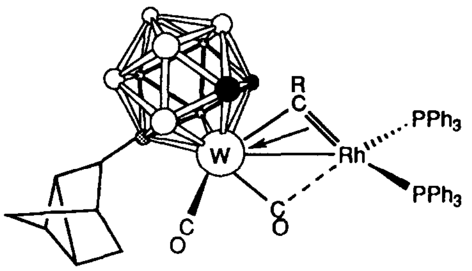
The reaction between [$Fe_2(CO)_9$] and **Ia** affords a mixture of the di- and tri-metal complexes [NEt_4]-[WFe{μ-C(H)C_6H_4Me-4}(μ-σ,η^5-7,8-Me_2-7,8-C_2B_9-H_8)(μ-CO)$(CO)_5$] (**IX**) and [NEt_4][WFe_2(μ_3-CC_6H_4Me-4)(μ-σ,σ',η^5-7,8-Me_2-7,8-$C_2B_9H_7$)$(CO)_8$] (**X**) [13]. Complex **IX** must result from insertion of a μ-CC_6H_4Me-4 group into the B–H ⇀ Fe bond present in an intermediate adduct [NEt_4][WFe(μ-CC_6H_4Me-4)$(CO)_5$(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)]. Unusually, a B_α–H ⇀ Fe rather than a B_β–H ⇀ Fe bridge must be involved in the reaction pathway because in **IX** the B–Fe σ bond involves a boron atom α to the carbons in the η^5-C_2B_3 ring of the cage. The pathway to the trimetal compound **X**, having two B–Fe *exo*-polyhedral σ bonds, probably involves addition of a second iron carbonyl fragment to [NEt_4][WFe(μ-CC_6H_4Me-4)$(CO)_5$(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)]. This would then be followed by loss of CO, accompanied by formation of two *exo*-polyhedral B–H ⇀ Fe bridges (as in the tungsten–dicobalt complex shown in Fig. 3).

Reductive elimination of hydrogen at the iron centers would then yield **X**.

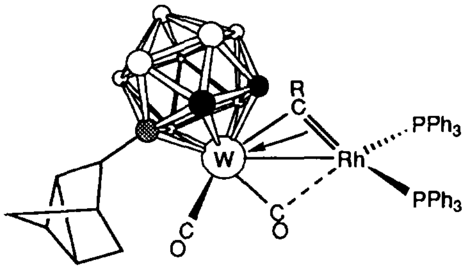
The intermediacy of three-center $B{-}H \rightharpoonup M$ linkages in the formation of two-center B–M σ bonds is well illustrated by the facile decomposition of $[WPtH(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PEt_3)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (Fig. 2) to yield a mixture of the complexes $[WPt(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}\sigma,\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8)(CO)_2(PEt_3)]$ (**XI**, two isomers) and $[WPt(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}\sigma,\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8)(CO)_3(PEt_3)]$ (**XII**). The major products are **XIa** and **XII** (approx. 50%) and result from elimination of H_2 from Pt–H and $B_\beta{-}H \rightharpoonup Pt$ groups in the precursor [14]. Isomer **XIb** is evidently derived from an isomer of $[WPtH(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PEt_3)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ having a $B_\alpha{-}H \rightharpoonup Pt$ linkage, but it is formed in only approx. 5% yield. This illustrates again the propensity of B_β–H groups to be more active than B_α–H bonds in the $[\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9]$ systems. Other examples of metallacarboranes with *exo*-polyhedral $B{-}H \rightharpoonup M$ or B–M linkages are mentioned below.

2.2. Protonation studies

Protonation of the salts **I** with one or more equivalents of $HBF_4 \cdot Et_2O$ in the presence of donor molecules L (CO, PPh_3, RC_2R) affords products resulting from initial formation of an alkylidene–metal species, following which the alkylidene inserts into the B_β–H bond of the ligating face of the cage [4b,15]. Thus CH_2Cl_2 solutions of **Ia** saturated with CO and treated with $HBF_4 \cdot Et_2O$ give $[W(CO)_4(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}CH_2C_6H_4Me\text{-}4)]$ (**XIII**). In contrast, if HCl or HI are the proton source, anionic complexes are formed with no connectivity between the carbon atoms of the cage, e.g. $[NEt_4][WI(CO)_3(\eta^5\text{-}2,8\text{-}Me_2\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}CH_2C_6H_4Me\text{-}4)]$ (**XIV**). Experiments with the molybdenum reagent **Im** established that the polytopal rearrangement of the cage framework occurs after insertion of the $C(H)C_6H_4Me$-4 moiety into the B–H bond. Thus treatment of a CO saturated solution of **Im** with aqueous HI gives, initially, the complex $[NEt_4][MoI(CO)_3(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}CH_2C_6H_4Me\text{-}4)]$ (**XVa**), which rearranges in solution after several hours

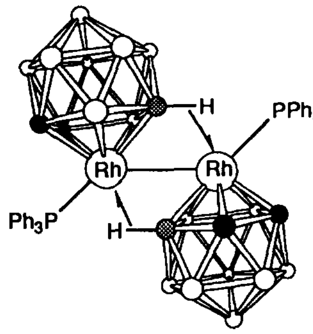


●
II CMe
IIIa CH



○ BH ◍ B
R = C_6H_4Me-4

IIIb ● CH



IV

○ BH ◍ B ● CH

to the *closo*-2,1,8-MoC$_2$B$_9$ isomer **XVb** [16]. The different behavior of HBF$_4$ · Et$_2$O and aqueous HI towards the compounds **I** may be used to prepare polytopal isomers of dimetal complexes. Thus treatment of **Ia** with HBF$_4$ · Et$_2$O in the presence of [Mo(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_5$H$_5$)] yields [MoW(μ-CR)(CO)$_3$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_8$-10-CH$_2$R)(η^5-C$_5$H$_5$)] (**XVIa**, R = C$_6$H$_4$Me-4) [17a], while the isomer [MoW(μ-CR)(CO)$_3$(η^5-2,8-Me$_2$-2,8-C$_2$B$_9$H$_8$-10-CH$_2$R)(η^5-C$_5$H$_5$)] (**XVIb**, R = C$_6$H$_4$Me-4) may be prepared by adding AgBF$_4$ to a mixture of **XIV** and [Mo(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_5$H$_5$)] in CH$_2$Cl$_2$ [17b].

A novel reaction occurs if **Ia** is 'protonated' with [PtH(OCMe$_2$)(PEt$_3$)$_2$][BF$_4$], the product being [WPt(CO)$_2$(PEt$_3$)$_2$(η^6-7,8-Me$_2$-7,8-C$_2$B$_9$H$_8$-10-CH$_2$C$_6$H$_4$-Me-4)] (**XVIIa**). This molecule contains a *hyper-closo*-3,1,2-WC$_2$B$_9$ cage with no connectivity between the cage carbon atoms (2.88 Å apart), and having six atoms $\overline{\mathrm{CBCBBB}}$ ligating the tungsten atom, rather than the five in the precursor **Ia**. In addition **XVIIa** has a very short W–Pt bond [2.602(1) Å] [18a]. The platinum reagent evidently supplies a proton to the alkylidyne group in **Ia** generating along the reaction pathway a W=C(H)C$_6$H$_4$Me-4 group, which then inserts into the nearby B$_\beta$–H bond to give a CH$_2$C$_6$H$_4$Me-4 substituent on the cage. Use of [PtD(OCMe$_2$)(PEt$_3$)$_2$][BF$_4$] in this reaction affords a BCH(D)C$_6$H$_4$Me-4 group on the cage. The reaction between the molybdenum reagent **Im** and [PtH(Cl)(PEt$_3$)$_2$] in THF in the presence of TlBF$_4$ gives the complex **XVIIb** but this product de-

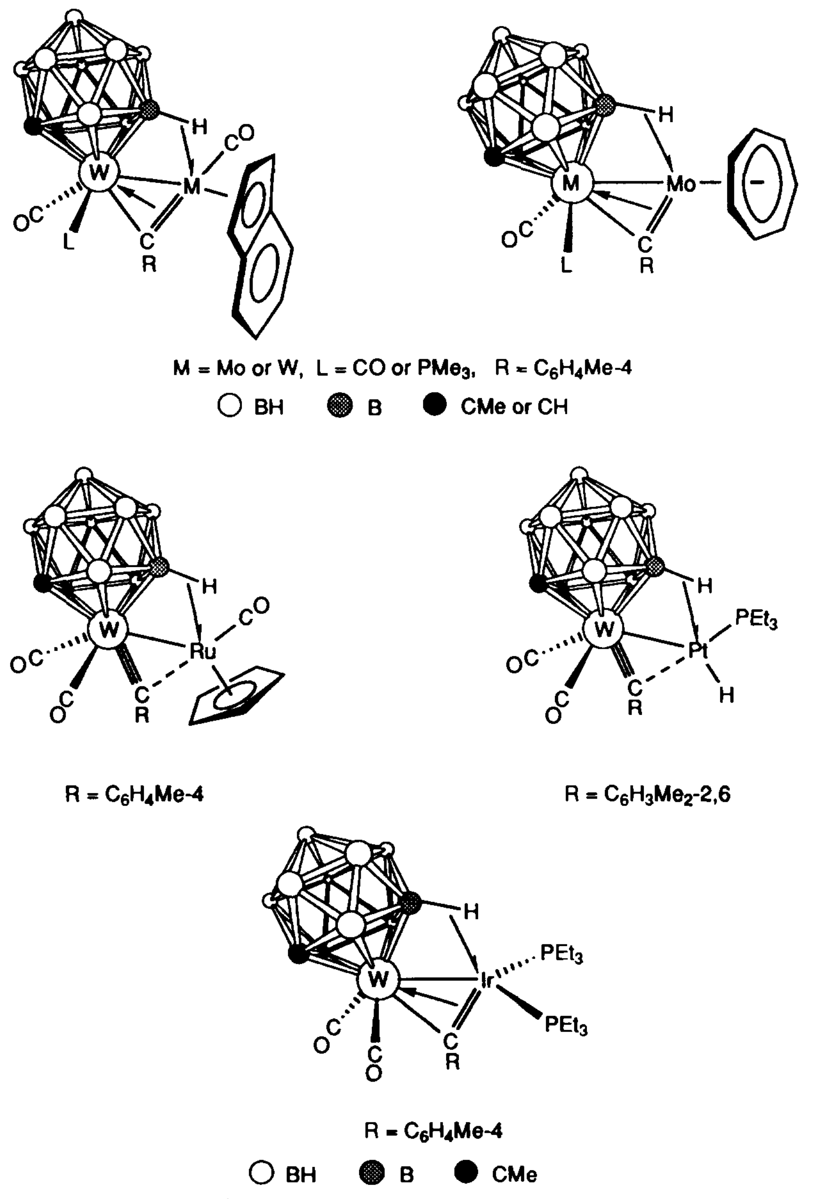
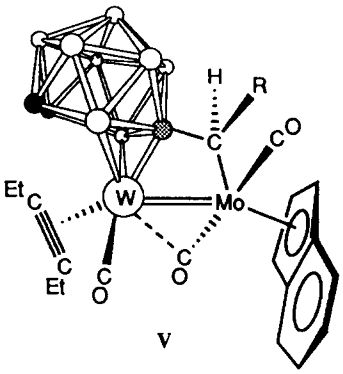


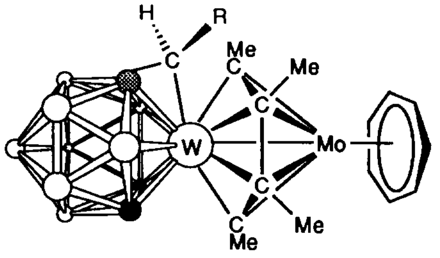
Fig. 2. Examples of alkylidyne(carborane)dimetal complexes with *exo*-polyhedral B–H → M bonds.

composes at approx. 0 °C [18b]. Both of the unsaturated 30 valence electron dimetal complexes **XVII** readily react with electron pair donors such as CO or PEt_3. Thus with CO the complexes $[MPt(\mu\text{-}H)(\mu\text{-}\sigma,\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_7\text{-}10\text{-}CH_2C_6H_4Me\text{-}4)(CO)_3(PEt_3)_2]$ (**XVIII**, M = Mo or W) are formed which have *closo*-3,1,2-WC_2B_9 cages. The *exo*-polyhedral B–Pt bonds and the μ-H groups in these products arise from oxidative-addition of a B–H bond in the open face of the cage of an intermediate species $[MPt(CO)_3(PEt_3)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}CH_2C_6H_4Me\text{-}4)]$, but the B–H group is necessarily α to the carbons because there is no B_β–H site available in the $\overline{CCBBB}$ ring.

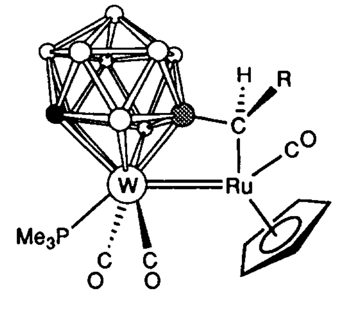
Structures with *hyper-closo* cage frameworks have been observed in other reactions of the species **I**. Treatment of **Ia** with approx. 0.5 mol equivalent of $HBF_4 \cdot Et_2O$ gives the ditungsten compound $[NEt_4][W_2(\mu\text{-}CR)(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)(\eta^6\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}CH_2R)]$ (**XIX**, R = C_6H_4Me-4) [19]. In the anion, the WC_2B_9 cage carrying the $CH_2C_6H_4Me$-4 substituent has a *hyper-closo* structure, with the carbon vertices separated by 2.917 Å and the C_2B_9 group η^6 coordinated to the tungsten atom. The other cage has a *closo*-3,1,2-WC_2B_9 framework but forms an *exo*-polyhedral B–H → W bridge across the short W–W bond [2.683(1) Å]. The species **XIX** is formed via the intermediacy of the thermally unstable η^2 ketenyl complex **XX**. The *hyper-closo* cage in **XIX** is transformed to a



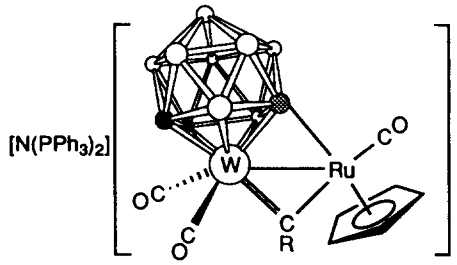
V



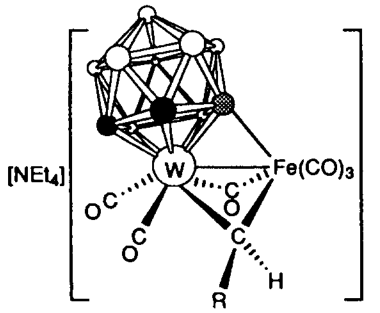
VI



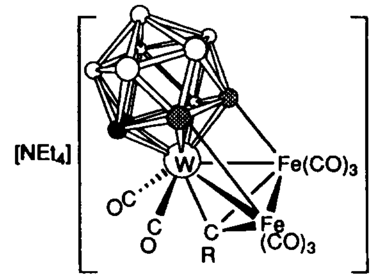
VII



VIII



IX



X

○ BH ◍ B ● CMe

R = C_6H_4Me-4

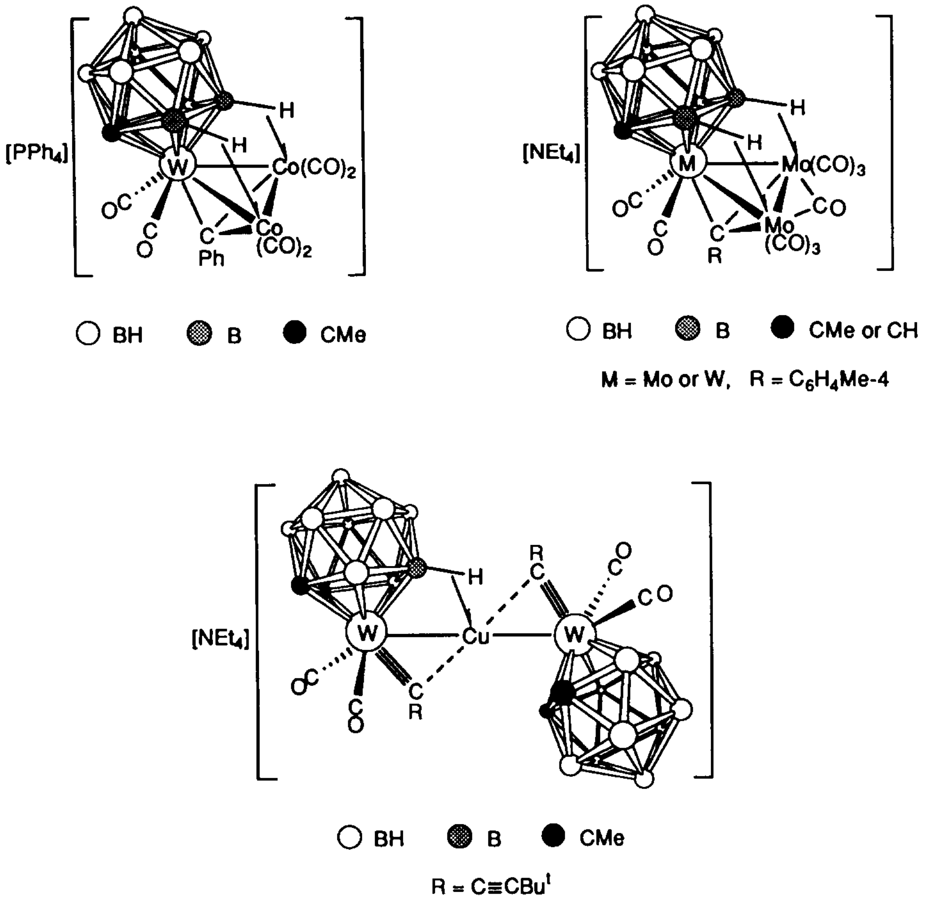
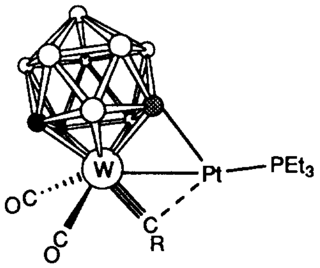
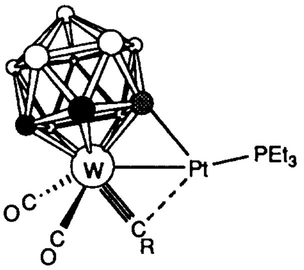


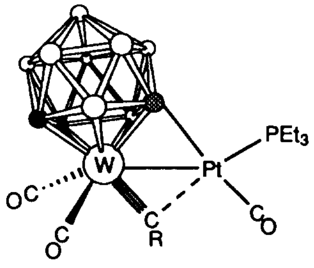
Fig. 3. Examples of alkylidyne(carborane)trimetal complexes with *exo*-polyhedral B–H → M bonds.



XIa



XIb



XII

○ BH ▨ B ● CMe

R = $C_6H_3Me_2$-2,6

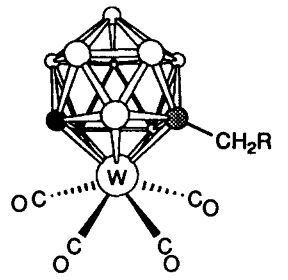
closo geometry upon treatment with CNBu^t, affording the species $[NEt_4][W_2(\mu\text{-}CR)(CO)_2CNBu^t)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}CH_2R)]$ (**XXI**).

Novel structures associated with non-innocent behavior of the carborane cage result from protonation reactions of **Ig** in the presence of various donor molecules [20]. Solutions of **Ig** which have been saturated with CO upon treatment with $HBF_4 \cdot Et_2O$ or aqueous HI afford, respectively, the complexes $[W(CO)_4(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_7\text{-}5,10\text{-}CH_2C_6H_4CH_2\text{-}2)]$ (**XXII**) and $[NEt_4][WI(CO)_3(\eta^5\text{-}2,8\text{-}Me_2\text{-}2,8\text{-}C_2B_9H_7\text{-}5,10\text{-}CH_2C_6H_4\text{-}CH_2\text{-}2)]$ (**XXIII**). It is thus apparent from these studies that protonation of the reagents **I** in the presence of substrate molecules can produce a variety of products in which the $[\eta^5\text{-}7,8\text{-}R'_2\text{-}7,8\text{-}C_2B_9H_9]$ ligands in the starting reagents play a non-spectator role [4b].

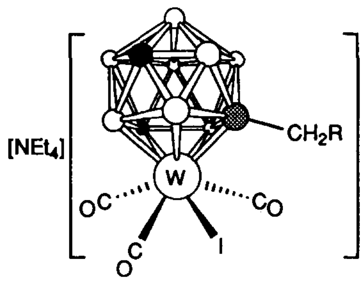
3. Allyl(carborane)metal complexes

Exploration of the reactivity of salts of the anionic allyl(carborane)metal complexes $[M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}R'_2\text{-}7,8\text{-}C_2B_9H_9)]^-$ (**XXIV**, M = W, R′ = Me; M = Mo, R′ = Me or H) [21] and $[M(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]^-$ (**XXV**, M = Ni, Pd, or Pt) [22] has uncovered several instances where B–H vertices of the carborane cages are activated to produce products wherein the cage has adopted a non-spectator role.

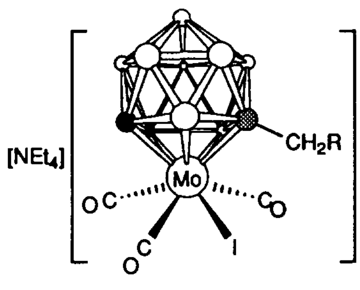
Protonation of the species **XXIV** with $HBF_4 \cdot Et_2O$



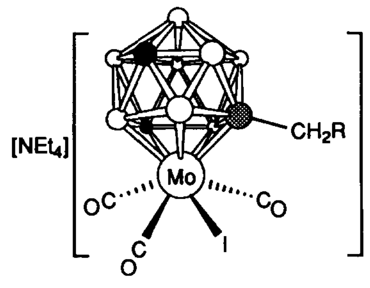
XIII



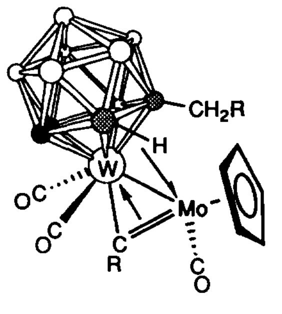
XIV



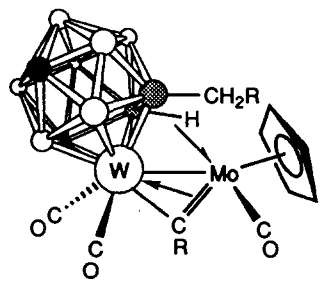
XVa



XVb



XVIa



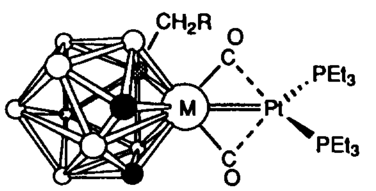
XVIb

○ BH ◍ B ● CMe

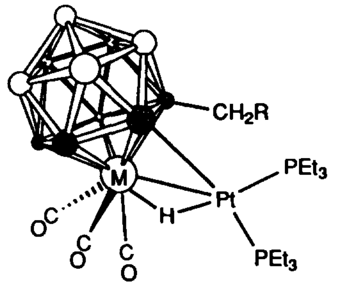
R = $C_6H_4Me\text{-}4$

generates the reactive fragments $[M(CO)_2(\eta^5\text{-}7,8\text{-}R'_2\text{-}7,8\text{-}C_2B_9H_9)]$ which react with suitable donor molecules. In this manner bis(alkyne) complexes $[M(CO)(RC_2R)_2(\eta^5\text{-}7,8\text{-}R'_2\text{-}7,8\text{-}C_2B_9H_9)]$ (R = Me, Ph, $SiMe_3$) may be obtained by protonating the reagents **XXIV** in the presence of alkynes [21]. However, if the $[N(PPh_3)_2]^+$ salt of **XXIVb** is protonated in the presence of $Me_3SiC{\equiv}CH$, the initially formed complex $[Mo(CO)(Me_3SiC_2H)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ rearranges in solution after several hours to yield the compound $[Mo(CO)(Me_3SiC_2H)\{\eta^2,\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}C(H){=}C(H)SiMe_3\}]$ (**XXVI**) in which one of the alkyne ligands has inserted into the B_β–H bond of the $\overline{\mathrm{CCB}\mathit{B}\mathrm{B}}$ ring ligating the molybdenum.

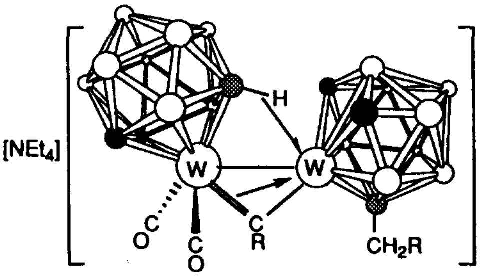
Treatment of CO saturated solutions of the complexes **XXIV** with the hydride abstracting reagent $[CPh_3][BF_4]$, in the presence of donor molecules L (OEt_2, THF, PPh_3, NC_5H_5, SMe_2), affords compounds with B_β–L groups [23]. Thus CO saturated CH_2Cl_2 solutions of the salt **XXIVb** with OEt_2 yield the zwitterionic species $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}OEt_2)]$ (**XXVII**). Treatment of the latter with $K[BH\{C(H)(Me)(Et)\}_3]$ cleaves a C–O bond to give an anionic complex $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}OEt)]^-$, isolated as the $[NEt_4]^+$ salt **XXVIII** following addition of $[NEt_4]Cl$. Protonation of CO saturated CH_2Cl_2 solutions of **XXVIII** with $HBF_4 \cdot Et_2O$ affords $[Mo(CO)_4(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}OEt)]$



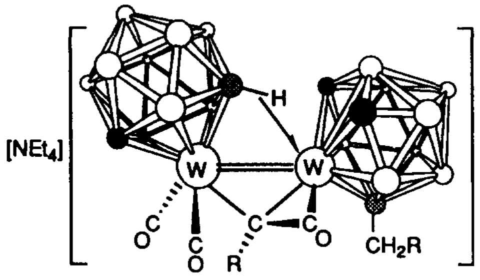
M
XVIIa W
XVIIb Mo



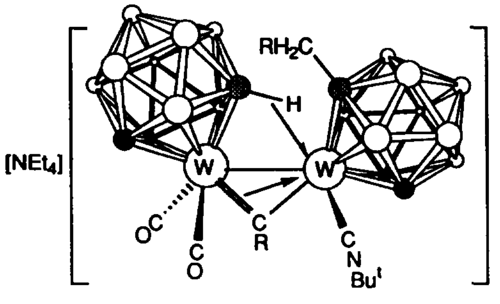
XVIII
M = W or Mo



XIX



XX



XXI

○ BH ● B ● CMe

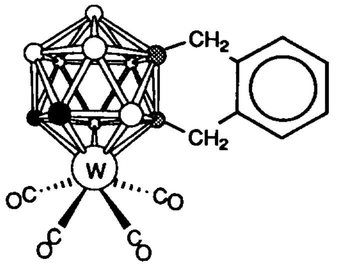
R = C_6H_4Me-4

(XXIXa). The latter isomerizes slowly in solution to give its polytopal isomer [Mo(CO)$_4$(η^5-2,8-Me$_2$-2,8-C$_2$B$_9$H$_8$-10-OEt)] **(XXIXb)**. Treatment of either of the species **XXIX** with [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_5$H$_5$)] yields dimetal compounds which are also polytopal isomers. Thus **XXIXa** and **XXIXb** yield [MoW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η^5-n,8-Me$_2$-n,8-C$_2$B$_9$H$_8$-10-OEt)(η^5-C$_5$H$_5$)] (**XXXa**, $n = 7$; **XXXb**, $n = 2$, respectively). Comparison of the structures of the isomers **XXX** with those of the isomers **XVI** is of interest. Both isomeric pairs have *exo*-polyhedral B–H ⇀ M bonds, but these involve a B$_\alpha$–H bond in the η^5-C$_2$B$_3$ ring since the generally more reactive B$_\beta$ site is not available.

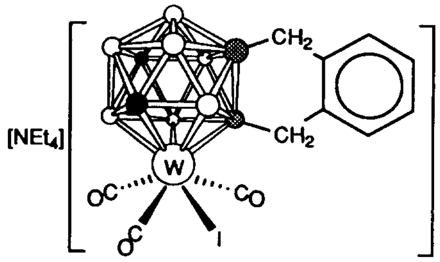
Protonation (HBF$_4$ · Et$_2$O) of CO saturated solutions of the complexes **XXV** affords very labile dicarbonyl species [M(CO)$_2$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] [22]. Cage B–H groups of the nickel dicarbonyl compound readily form agostic B–H ⇀ Ni linkages. Thus CH$_2$Cl$_2$ solutions of [Ni(CO)$_2$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] slowly release CO to give a mixture of three isomers [Ni$_2$(CO)$_2$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)$_2$] **(XXXIa)**, [Ni$_2$(CO)$_2$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)(η^5-2,7-Me$_2$-2,7-C$_2$B$_9$H$_9$)] **(XXXIb)**, and [Ni$_2$(CO)$_2$(η^5-2,7-Me$_2$-2,7-C$_2$B$_9$H$_9$)$_2$] **(XXXIc)**. In these complexes the unrearranged *closo*-3,1,2-NiC$_2$B$_9$ cages employ B$_\alpha$–H bonds to bridge the Ni–Ni connectivity, while the rearranged *closo*-2,1,4-NiC$_2$B$_9$ systems use one of two available B$_\beta$–H bonds in the CB*BB*B face to form the agostic linkage. The nickel dicarbonyl compound forms B–H ⇀ Co bonds in its reaction with [Co$_2$(CO)$_8$] which yields [Co$_2$Ni(μ-CO)(CO)$_5$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] **(XXXII)**. The structure of the latter is very similar to that of the tungsten–dicobalt compound depicted in Fig. 3.

4. The anionic complexes [M(CO)$_3$(η^5-7,8-R'$_2$-7,8-C$_2$B$_9$H$_9$)]$^{2-}$ (R' = H or Me)

Salts of the anionic complexes [M(CO)$_3$(η^5-7,8-R'$_2$-7,8-C$_2$B$_9$H$_9$)]$^{2-}$ (M = Mo or W, R' = H or Me) were first reported by Hawthorne and coworkers [1], and although they are isolobal with the well established cyclopentadienyl–metal anionic complexes [M(CO)$_3$(η^5-C$_5$H$_5$)]$^-$ their chemistry has been much less thoroughly studied. The cyclopentadienyl species are relatively nucleophilic and for many years this property has been employed to prepare compounds with metal–metal

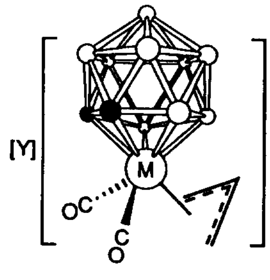


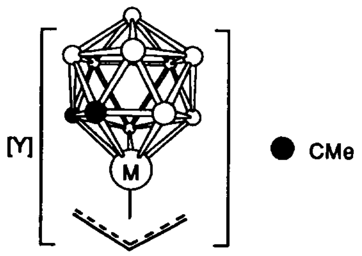
XXII



XXIII

○ BH ◉ B ● CMe





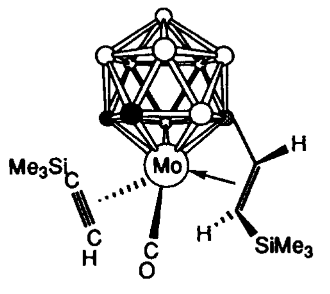
○ BH ◉ B

Y = NEt$_4$ or N(PPh$_3$)$_2$

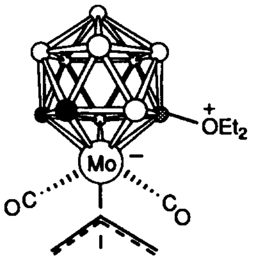
	M	●
XXIVa	W	CMe
XXIVb	Mo	CMe
XXIVc	Mo	CH

	M
XXVa	Ni
XXVb	Pd
XXVc	Pt

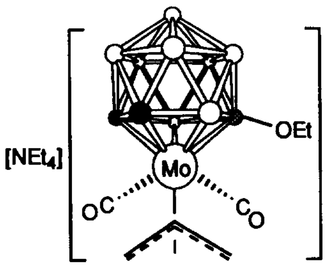
bonds in reactions with complex metal halides, e.g. the synthesis of [MoFe(CO)$_5$(η^5-C$_5$H$_5$)$_2$] from Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)] and [FeI(CO)$_2$(η^5-C$_5$H$_5$)] was reported as early as 1961 [24]. The anions [M(CO)$_3$(η^5-7,8-R'$_2$-7,8-C$_2$B$_9$H$_9$)]$^{2-}$ are less nucleophilic when used in related syntheses but the thallium salts Tl$_2$[M(CO)$_3$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] react with the platinum halides [PtCl$_2$(PR$_3$)$_2$] (R = Et or Ph) to give bimetal compounds of formulation [MPt(CO)$_3$(PR$_3$)$_2$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] (**XXXIII**, M = Mo or W, R = Et or Ph) [25]. These species in the crystalline state adopt structure **XXXIIIa** with the metal–metal bonds supported by three-center two-electron B–H → Pt bridge systems of the kind seen in many other compounds described in this survey. However, NMR studies on the tungsten complexes in CD$_2$Cl$_2$ solutions reveal the existence of an isomeric mixture (approx. 1:1) of molecules with structures **XXXIIIa** and **XXXIIIb**. This interconversion requires the making and breaking of B$_\beta$–H → Pt and B$_\alpha$–Pt linkages via the intermediacy of a B$_\alpha$–H → Pt system. This in turn necessitates rotation of the *nido*-C$_2$B$_9$ cage at some stage in the dynamic process. There is precedent for the latter step in the previously mentioned formation of **XIb** from [WPtH(μ-CC$_6$H$_3$Me$_2$-2,6)(CO)$_2$(PEt$_3$)(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)], the former having a B$_\alpha$–Pt bond and the latter (Fig. 2) a B$_\beta$–H → Pt group. There is also evidence for rapid interchange on the NMR time scale between structures with B$_\beta$–H → Ir and B$_\alpha$–H → Ir bridge systems in solutions of the complex [WIr(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PEt$_3$)$_2$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] even though in the solid state an X-ray diffraction analysis showed that only the isomer with a B$_\beta$–H → Ir bridge is present (Fig. 2) [26]. The latter is thus the thermodynamically preferred structure in this tungsten–iridium complex, in agreement with B$_\beta$–H → M bridges being generally pre-



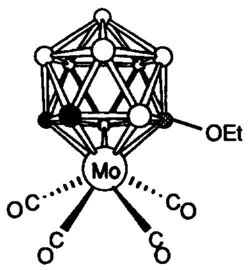
XXVI



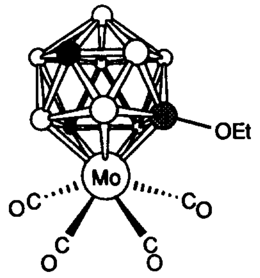
XXVII



XXVIII



XXIXa

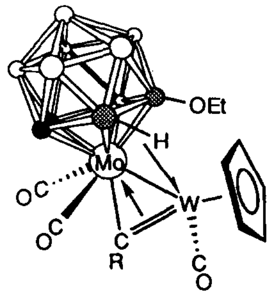


XXIXb

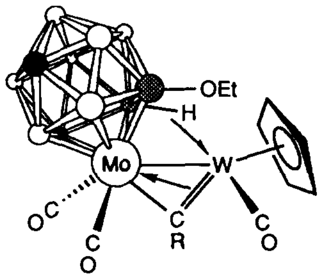
○ BH ◍ B ● CMe

ferred, although evidently in some systems the energy barrier between this and the B$_\alpha$–H $\rightharpoonup$ M bridge bonding mode is low.

A redox reaction occurs between the salts Na$_2$-[M(CO)$_3$(η^5-7,8-R'$_2$-7,8-C$_2$B$_9$H$_9$)] (M = Mo or W, R' = H or Me) and [Rh(NCMe)$_3$(η^5-C$_5$Me$_5$)][BF$_4$]$_2$ in THF to give [Rh(CO)$_2$(η^5-C$_5$Me$_5$)] and the trimetal complexes [MRh$_2$(μ-H)(μ-σ,η^5-7,8-R'$_2$-7,8-C$_2$B$_9$H$_8$)(μ-CO)(CO)$_2$(η^5-C$_5$Me$_5$)$_2$] (**XXXIVa**) [27]. In the crystalline state these complexes adopt a structure with the cage bridging the metal triangle via B$_\beta$–H $\rightharpoonup$ Rh and B$_\alpha$–Rh bonds. NMR studies show that while this structure persists in solution for [WRh$_2$(μ-H)(μ-σ,η^5-7,8-C$_2$B$_9$H$_{10}$)(μ-CO)(CO)$_2$(η^5-C$_5$Me$_5$)$_2$] from ambient temperatures down to −60 °C, the other species all display dynamic behavior over this temperature range. At −60 °C, limiting low temperature spectra are observed for these remaining complexes corresponding to the presence of a single isomer of type **XXXIVa**. However, as the temperature is raised, new resonances appear indicating conversion into isomers of structural type **XXXIVb**. At ambient temperatures only the latter structure appears to be present, although a second dynamic process persists involving exchange of the hydrido ligands between Rh(μ–H)Rh and Rh(μ–H)M sites.



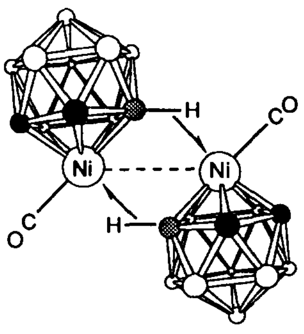
XXXa



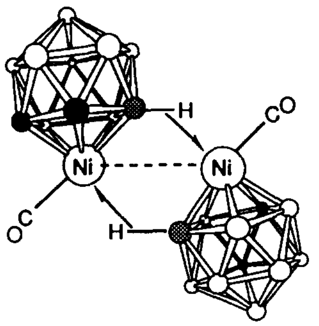
XXXb

○ BH ◍ B ● CMe

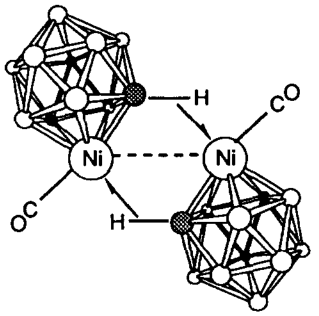
R = C$_6$H$_4$Me-4



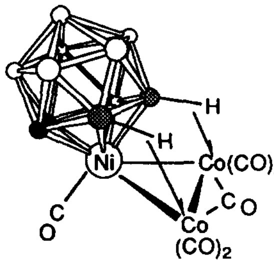
XXXIa



XXXIb



XXXIc



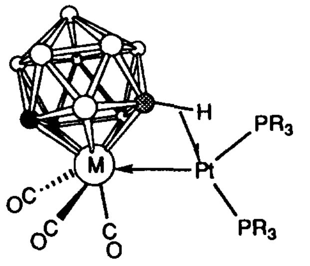
XXXII

○ BH ◍ B ● CMe

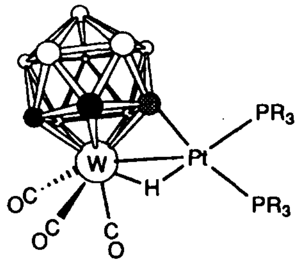
5. The anionic complexes [10-*endo*-{Au(PPh_3)}-7,8-R′-*nido*-7,8-$C_2B_9H_9$]$^-$ (R′ = H or Me)

The anions [10-*endo*-H-7,8-R'_2-*nido*-7,8-$C_2B_9H_9$]$^-$ and [10-*endo*-{Au(PPh_3)}-7,8-R'_2-*nido*-7,8-$C_2B_9H_9$]$^-$ (R′ = H or Me) are isolobal, and X-ray diffraction studies have demonstrated the close structural relationship between these species [28]. The former have been used extensively as starting reagents for preparing metallacarboranes via reactions with metal halides [1,2]. Recent work has shown that the gold anions also react readily with metal halides, frequently affording products with novel structures.

Treatment of [NEt_4][10-*endo*-{Au(PPh_3)}-7,8-Me_2-*nido*-7,8-$C_2B_9H_9$] with [RhCl(CO)(PPh_3)$_2$] in THF yields [RhAu(CO)(PPh_3)$_2$(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)] **(XXXVa)** [29a]. The significance of this reaction, in the context of work described below, is the complete transfer of the carborane cage from gold to rhodium. In contrast with these results, the corresponding reaction between [RhCl(PPh_3)$_3$] and the auracarborane reagent gives solutions containing an equilibrium mixture of the isomers [5,10-*exo*-{Rh(PPh_3)$_2$}-5,10-(μ-H)$_2$-10-*endo*-{Au(PPh_3)}-7,8-Me_2-*nido*-7,8-$C_2B_9H_7$] **(XXXVIa)** and [RhAu(PPh_3)$_3$(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)] **(XXXVIIa)**. The former predominates in solution (approx. 6:1) and crystals obtained from these solutions have been shown by X-ray diffraction to be exclusively of structure **XXXVIa** with an *exo*-polyhedral [Rh(PPh_3)$_2$]$^+$ fragment attached to a [10-*endo*-{Au(PPh_3)}-7,8-Me_2-*nido*-7,8-$C_2B_9H_7$]$^-$ cage by two agostic B–H ⇀ Rh bonds. The structure is thus zwitterionic and bears a striking resemblance to a family of *exo*-phosphinerhoda-*nido*-carboranes [5,10-*exo*-{Rh(PPh_3)$_2$}-5,10-(μ-H)$_2$-10-*endo*-H-7,8-R'_2-*nido*-7,8-$C_2B_9H_7$] (R′ = alkyl or aryl) studied by Hawthorne and coworkers [30]. For example, the species [5,10-*exo*-{Rh(PPh_3)$_2$}-5,10-(μ-H)$_2$-10-*endo*-H-7,8-Me_2-*nido*-7,8-$C_2B_9H_7$] **(XXXVIb)** exists in solution in equilibrium with a small amount of its isomer [RhH(PPh_3)$_2$(η^5-7,8-Me_2-7,8-$C_2B_9H_9$)]



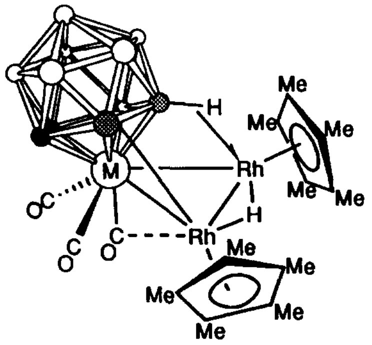
XXXIIIa
M = Mo or W



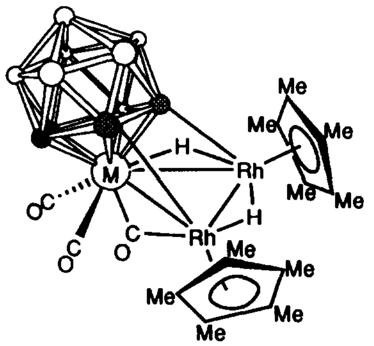
XXXIIIb

○ BH ● B ● CMe

R = Et or Ph



XXXIVa



XXXIVb

○ BH ● B ● CH or CMe

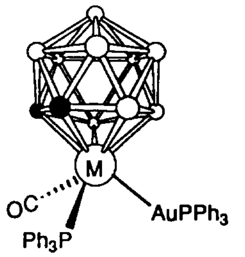
M = Mo or W

(**XXXVIIb**). The isomeric pairs **XXXVIa** and **XXXVIIa**, and **XXXVIb** and **XXXVIIb** clearly illustrate the isolobal relationship between H and Au(PPh$_3$) groups.

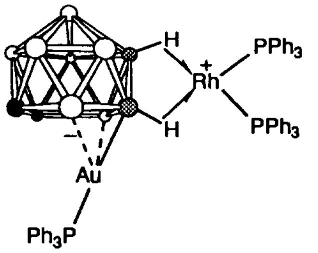
The reaction between [Rh(cod)(PPh$_3$)$_2$][PF$_6$] (cod = cycloocta-1,5-diene) and [NEt$_4$][10-*endo*-{Au(PPh$_3$)}-7,8-Me$_2$-*nido*-7,8-C$_2$B$_9$H$_9$] in the presence of H$_2$ yields a mixture of the rhodium–digold compound [RhAu$_2$(μ-H)(PPh$_3$)$_3$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] (**XXXVIII**), in which the cage plays a spectator role, and **XXXVIa**, in which it does not.

Treatment of [IrCl(CO)(PPh$_3$)$_2$] with [NEt$_4$][10-*endo*-{Au(PPh$_3$)}-7,8-Me$_2$-*nido*-7,8-C$_2$B$_9$H$_9$] gives [IrAu(CO)(PPh$_3$)$_2$(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] (**XXXVb**), while a similar reaction using [IrCl(CO)$_2$(NH$_2$C$_6$H$_4$Me-4)] yields [IrAu(CO)$_2$(PPh$_3$)(η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] (**XXXIX**) [29b]. In both **XXXVb** and **XXXIX** the carborane group is η^5 coordinated to the metal in the classical manner. However, in the synthesis of **XXXIX** small quantities of the hexanuclear metal cluster compound [Ir$_2$Au$_4$(μ-σ,η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_8$)(CO)$_3$(PPh$_3$)$_4$][7,8-Me$_2$-*nido*-7,8-C$_2$B$_9$H$_{10}$] (**XL**) are produced. In the cation the carborane unit bridges the Ir–Ir bond in a manner similar to that found in several other structures, e.g. **VIII**, **XI** or **XII**. In contrast with the results from the reaction between [NEt$_4$][10-*endo*-{Au(PPh$_3$)}-7,8-Me$_2$-*nido*-7,8-C$_2$B$_9$H$_9$] and [RhCl(PPh$_3$)$_3$], which gives **XXXVIa**, the gold reagent with [IrCl(PPh$_3$)$_3$] affords [IrAuH(μ-σ,η^3-7,8-Me$_2$-7,8-C$_2$B$_9$H$_8$)(PPh$_3$)$_3$] (**XLI**). In the latter the carborane group is both trihapto bonded to the iridium in an apparently borallylic interaction, and also σ bonded to the *exo*-gold atom.

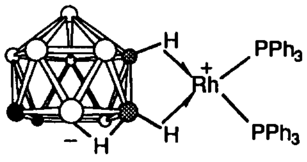
In reactions with the complex platinum halides [PtCl(R)L$_2$] (R = H, L = PEt$_3$; R = Me, L = PMe$_2$Ph) the gold reagents [NEt$_4$][10-*endo*-{Au(PPh$_3$)}-7,8-R′$_2$-



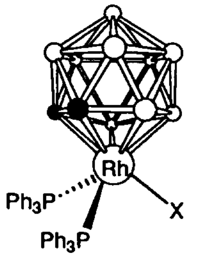
	M
XXXVa	Rh
XXXVb	Ir



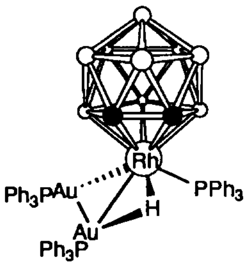
XXXVIa



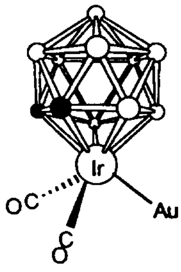
XXXVIb



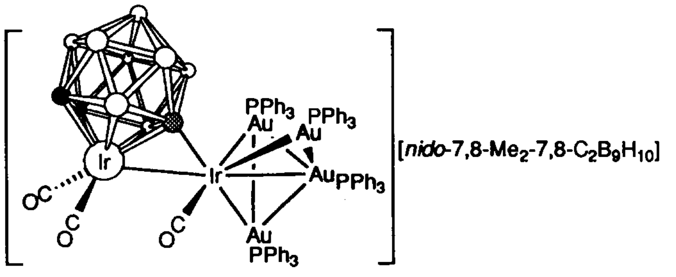
	X
XXXVIIa	Au(PPh$_3$)
XXXVIIb	H



XXXVIII



XXXIX



XL

○ BH ▨ B ● CMe

nido-7,8-$C_2B_9H_9$] give the dimetal species [10-*exo*-{Pt(R)L_2}-10-(μ-H)-10-*endo*-{Au(PPh_3)}-7,8-R'_2-*nido*-7,8-$C_2B_9H_8$] (**XLII**) in which the carborane ligand displays a non-spectator role [31]. These products are zwitterionic in character comprising cationic $[Pt(R)L_2]^+$ fragments linked to the anions [10-*endo*-{Au(PPh_3)}-7,8-R'_2-*nido*-7,8-$C_2B_9H_9$]$^-$ (R′ = H or Me) by a B_β–H ⇀ Pt bridge and further anchored by a long Au–Pt contact [3.000(1) Å in **XLIIa**].

The novel complex [9-*exo*-{Au(PPh_3)}-9-(μ-H)-10-*endo*-{Au(PPh_3)}-7,8-Me_2-*nido*-7,8-$C_2B_9H_8$] (**XLIII**) is formed in the reaction between [NEt_4][10-*endo*-{Au(PPh_3)}-7,8-Me_2-*nido*-7,8-$C_2B_9H_9$] and [AuCl(PPh_3)] in CH_2Cl_2 [32]. This product may be deprotonated in THF with NaH to generate in situ a digold–carborane monoanion, which upon treatment with [AuCl(PPh_3)] affords the trigold compound [10-*exo*-{$Au_2(PPh_3)_2$}-10-*endo*-{Au(PPh_3)}-7,8-Me_2-*nido*-7,8-$C_2B_9H_8$] (**XLIV**). The latter has a remarkable structure in which the boron atom β to the cage carbons asymmetrically caps [B_β–Au 2.192(9), 2.227(7), 2.307(8) Å] an isosceles triangle [Au–Au 2.691(1), 2.922(1), 3.010(1) Å] of gold atoms. The molecule displays dynamic behavior on the NMR time scale, fluxionality occurring via the mechanism indicated in Fig. 4. Rota-

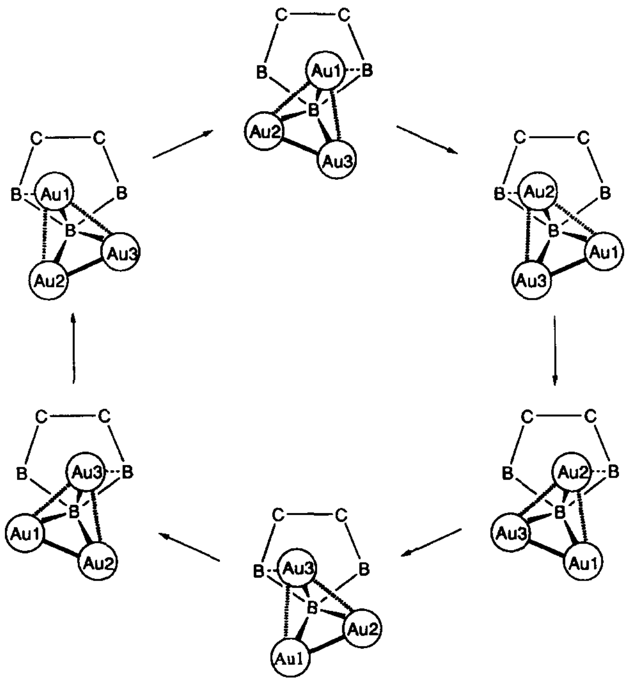
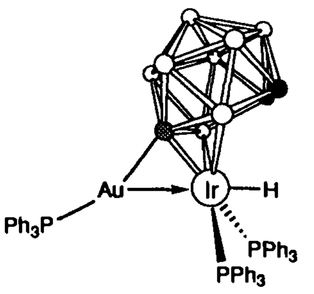
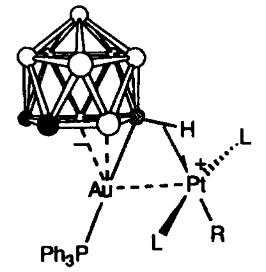


Fig. 4. Dynamic behavior of the complex **XLIV** in solution. ——— denotes short Au–Au separation, ,,,,,,,, longer Au–Au separation. Reproduced with the permission of the Royal Society of Chemistry (Ref. [32]).



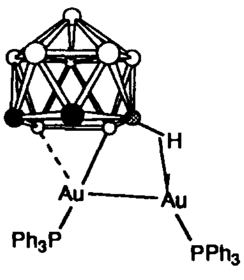
XLI

○ BH ◍ B ● CMe

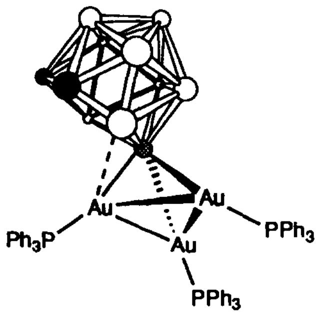


○ BH ◍ B

	L	R	●
XLIIa	PEt_3	H	CMe
XLIIb	PEt_3	H	CH
XLIIc	PMe_2Ph	Me	CMe
XLIId	PMe_2Ph	Me	CH



XLIII



XLIV

○ BH ◍ B ● CMe

tion of the cage above the Au_3 triangle would be accompanied by a breaking and reformation of the weak connectivity between a boron atom α to the two cage carbons and the *endo*-gold atom, as well as concomitant contraction and expansion of the long and short Au–Au bonds.

6. Conclusion

The reactions reviewed in this article amply demonstrate that the anions $[7,8\text{-}R'_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_9]^{2-}$ (R' = H or Me) are more versatile ligands than previously recognized, and are thus able to afford many complexes with molecular structures not previously encountered. The cage systems react via several different pathways, and the discoveries made so far suggest that further research is likely to add to this new domain of metallacarborane chemistry [33].

Acknowledgment

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[33] We have not discussed in this article many related reactions of the 13 atom *closo*-4,1,6-MC_2B_{10} cage systems, the [η^6-7,9-

Me_2-7,9-$C_2B_{10}H_{10}$] ligands of which often undergo reactions at their B–H vertices, including loss of a boron vertex with formation of M(η^5-7,9-Me_2-7,9-$C_2B_9H_9$) groups. See N. Carr, D.F. Mullica, E.L. Sappenfield, F.G.A. Stone and M.J. Went, *Organometallics, 12* (1993) 4350, and S. Li and F.G.A. Stone, *J. Organomet. Chem., 467* (1994) 95, and refs. listed therein. We have also omitted reviewing our work using the anions $[Rh(CO)(L)(\eta^5\text{-}7,n\text{-}R'_2\text{-}7,n\text{-}C_2B_9H_9)]^-$ ($n = 8$ or 9, R′ = H or Me, L = CO or PPh_3) to prepare complexes with metal–metal bonds, studies which have afforded many products with the cage systems forming *exo*-polyhedral bonds to adjacent groups. See M.U. Pilotti, I. Topaloğlu and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.,* (1991) 1355; J.E. Goldberg, D.F. Mullica, E.L. Sappenfield and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.,* (1992) 2693; J.E. Goldberg, J.C. Jeffery and F.G.A. Stone, *J. Organomet. Chem., 462* (1993) 353, and refs. listed therein.