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Advances in
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Metal Complexes of Monocarbon Carboranes: A Neglected Area of Study?

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I

INTRODUCTION

The first metallocarboranes were isolated in M. F. Hawthorne's laboratory and contained a metal ion, two carbon and nine boron atoms forming an icosahedral $\{closo-MC_2B_9\}$ cage structure.^{1,2} 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 $[nido-7,8-C_2B_9H_{11}]^{2-}$ dianion. This was a useful formalism since it emphasized an isolobal relationship between the carborane dianion and the ubiquitous $[C_5H_5]^-$ ligand. Following isolation of metal dicarbollides from reactions between metal salts and salts of $[nido-7,8-C_2B_9H_{11}]^{2-}$, it was logical that the monocarbon trianion $[nido-7-CB_{10}H_{11}]^{3-}$ would react in a similar way to afford monocarbon metallocarboranes also with icosahedral frameworks. Indeed, a few complexes of this kind were isolated³ 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 $[nido-7-CB_{10}H_{11}]^{3-}$ ligands, as in the Fe^{III} complex $[commo-2,2'-Fe-(closo-2,1-FeCB_{10}H_{11})_2]^{3-}$ (**1**) (Chart 1). In the second the cage-carbon atom carries an NR_3 or an NR_2 group, with the metal ion sandwiched between $[7-NR_3-nido-7-CB_{10}H_{10}]^{2-}$ groups, as in the Fe^{III} complex $[commo-2,2'-Fe-(1-NH_3-closo-2,1-FeCB_{10}H_{10})_2]^-$ (**2**), or $[7-NR_2-nido-7-CB_{10}H_{10}]^{3-}$

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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 [$\{7,8\text{-R}_2\text{-nido-7,8-C}_2\text{B}_9\text{H}_9\}$ ($\text{R} = \text{H}$ or Me), $\{\text{nido-7-CB}_{10}\text{H}_{11}\}$, $\{7\text{-NR}_2\text{-nido-7-CB}_{10}\text{H}_{10}\}$, or $\{7\text{-NR}_3\text{-nido-7-CB}_{10}\text{H}_{10}\}$] and on the other side by the conventional ligands (CO , PR_3 , 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.⁸ 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

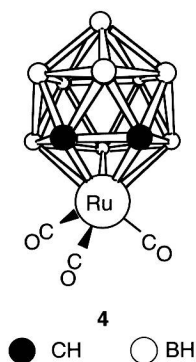


CHART 2.

carbonyls display a very extensive chemistry, as shown by $[3,3,3-(\text{CO})_3\text{-}closo\text{-}3,1,2\text{-RuC}_2\text{B}_9\text{H}_{11}]$ (**4**),⁹ 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 vertexes 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 NR_3 or NR_2 group because we have recently given an account of such species.¹⁰

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.

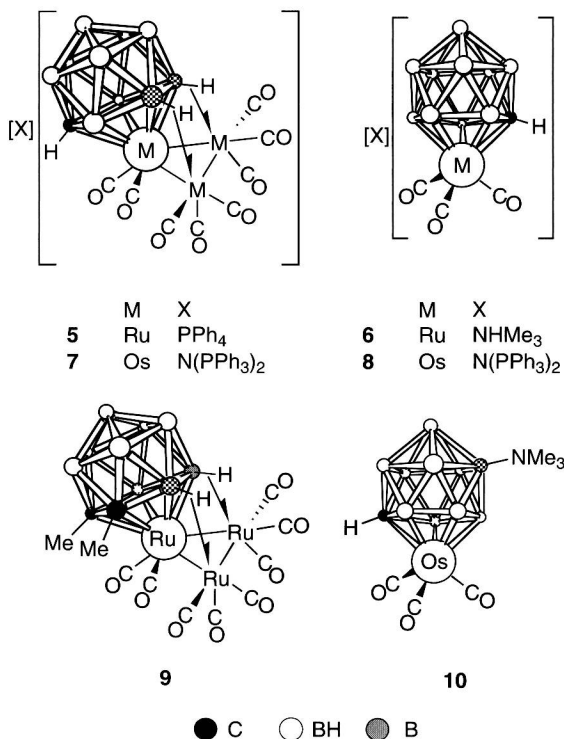


CHART 3.

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 $[\text{PPh}_4][2,2-(\text{CO})_2-7,11-(\mu\text{-H})_2-2,7,11-\{\text{Ru}_2(\text{CO})_6\}\text{-}closo\text{-}2,1\text{-RuCB}_{10}\text{H}_9]$ (**5**)* (Chart 3) following the addition of $[\text{PPh}_4]\text{Cl}$.¹¹ Subsequent analysis of this system revealed evidence for traces of the mononuclear species $[\text{NHMe}_3][2,2,2-(\text{CO})_3\text{-}closo\text{-}2,1\text{-RuCB}_{10}\text{H}_{11}]$ (**6**) in the initial product mixture, but its isolation in a pure form proved impossible.¹² 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 $[\text{N}(\text{PPh}_3)_2][2,2-(\text{CO})_2-7,11-(\mu\text{-H})_2-2,7,11-\{\text{Os}_2(\text{CO})_6\}\text{-}closo\text{-}2,1\text{-OsCB}_{10}\text{H}_9]$ (**7**) and the monoosmium complex $[\text{N}(\text{PPh}_3)_2][2,2,2-(\text{CO})_3\text{-}closo\text{-}2,1\text{-OsCB}_{10}\text{H}_{11}]$ (**8**).¹² The structures of the anions of **5** and **7** are similar to that of neutral $[3,3-(\text{CO})_2-1,2\text{-Me}_2-4,8-(\mu\text{-H})_2-3,4,8-\{\text{Ru}_2(\text{CO})_6\}\text{-}closo\text{-}3,1,2\text{-RuC}_2\text{B}_9\text{H}_7]$ (**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.

[Ru₃(CO)₁₂] and 7,8-Me₂-*nido*-7,8-C₂B₉H₁₁.¹³ In all the trimetal species a {*nido*-CB₁₀} or {*nido*-C₂B₉} 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-NMe₃-2,2,2-(CO)₃-*closo*-2,1-OsCB₁₀H₁₀] (**10**) is obtained by heating [Os₃(CO)₁₂] with [NHMe₃][*nido*-7-CB₁₀H₁₃] in refluxing bromobenzene. The NMe₃ group is attached to a boron atom in the pentagonal belt lying above that of the $\overline{\text{CBBBB}}$ ring η⁵-coordinated to the metal.¹² The source of the trimethylamine group must be the cation [NHMe₃]⁺, but the pathway by which its NMe₃ 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-CB₁₀H₁₃][−] and [Fe₃(CO)₁₂] afford the mononuclear anionic iron compound [2,2,2-(CO)₃-*closo*-2,1-FeCB₁₀H₁₁][−], typically isolated as its [N(PPh₃)₂]⁺ salt (**11**) (Chart 4).¹⁴ 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 [Ru₃(CO)₁₂] and *nido*-7,8-C₂B₉H₁₃, are isolobal with the cyclopentadienide species [Mn(CO)₃(η-C₅H₅)] and [Fe(CO)₃(η-C₅H₅)]⁺.

In an attempt to prepare a molybdenum complex related to compound **11**, [Mo(NCMe)₃(CO)₃] was treated with [NHMe₃][*nido*-7-CB₁₀H₁₃] followed by [N(PPh₃)₂]Cl but the desired complex [N(PPh₃)₂][2,2,2,2-(CO)₄-*closo*-2,1-MoCB₁₀H₁₀] (**12**) was obtained only in poor yield.¹⁴ This complex was also formed in the reaction between Na₃[*nido*-7-CB₁₀H₁₁] and [Mo(NCMe)₃(CO)₃] presumably *via* an intermediate species [2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₁]^{3−}, isolobal with the long-known [3,3,3-(CO)₃-*closo*-3,1,2-MoC₂B₉H₁₁]^{2−} dianion.² Evidently any salt of [2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₁]^{3−} is readily oxidized, scavenging a CO molecule to afford the final product. It was possible to prepare **12** by adding [Mo(NCMe)₃(CO)₃] in NCMe to a THF suspension of Na₃[*nido*-7-CB₁₀H₁₁] at low temperatures while bubbling CO through the mixture, followed by addition of H[BF₄]·OEt₂ and [N(PPh₃)₂]Cl.¹⁴ It seems likely that in this reaction sequence, **12** is formed *via* a pathway involving the unstable hydrido species [2,2,2-(CO)₃-2-H-*closo*-2,1-MoCB₁₀H₁₁]^{2−} and [2,2,2-(CO)₃-2,2-(H)₂-*closo*-2,1-MoCB₁₀H₁₁][−] 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(NCt)₃(CO)₃] as the tungsten source.^{15a}

Salts of [*nido*-7-CB₁₀H₁₁]^{3−} have not been extensively employed as yet to obtain half-sandwich compounds {2-(ligand)_{*n*}-*closo*-2,1-MCB₁₀H₁₁}, but their potential as precursors is demonstrated in the synthesis of rhenium and platinum compounds. Thus salts of the dianion [2,2,2-(CO)₃-*closo*-2,1-ReCB₁₀H₁₁]^{2−} have been prepared by

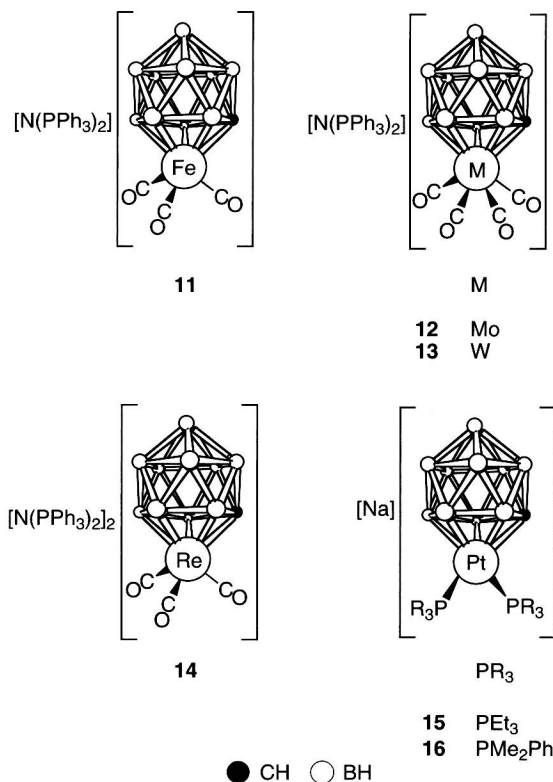


CHART 4.

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.¹⁶ The dianion of **14** is isolobal with the long-known species $[\text{3,3,3-(CO)}_3\text{-}closo\text{-3,1,2-ReC}_2\text{B}_9\text{H}_{11}]^-$ 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 $[\text{2,2,2-(CO)}_3\text{-}closo\text{-2,1-MnCB}_{10}\text{H}_{11}]^{2-}$, a manganese analogue of the dianion of **14**, in the original report of monocarbollide metal complexes, but without information on its properties.^{3a}

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 $\text{Na}[2,2\text{-(PR}_3)_2\text{-}closo\text{-2,1-PtCB}_{10}\text{H}_{11}]$ [$\text{PR}_3 = \text{PEt}_3$ (**15**),¹⁷ PMe_2Ph (**16**)¹⁸], species which as described later provide entry into a range of other compounds with similar $\{closo\text{-2,1-PtCB}_{10}\}$ frameworks.¹⁷⁻¹⁹ The $[\text{NMe}_4]^+$ salt of the platinacarborane anion in **15** had been prepared much earlier by a 'polyhedral expansion' reaction involving treatment of $[\text{NMe}_4][closo\text{-2-CB}_{10}\text{H}_{11}]$ with $[\text{Pt}(\text{trans-stilbene})(\text{PEt}_3)_2]$.^{7a} Several related complexes were similarly obtained by treating this carborane anion with Ni^0 , Pd^0 or 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 $[\text{NMe}_4][2,2\text{-(CNBu}^t)_2\text{-}closo\text{-2,1-NiCB}_{10}\text{H}_{11}]$ (**17a**) was prepared in the original study, using $[\text{Ni}(\text{CNBu}^t)_2(\text{cod})]$

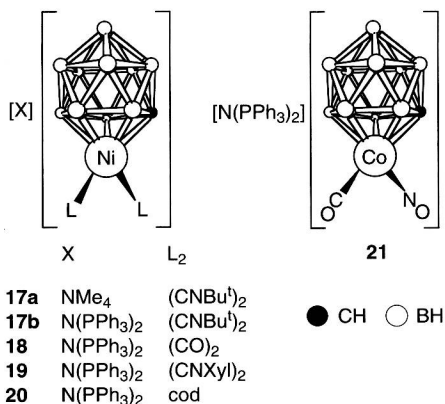


CHART 5.

($cod = 1,5$ -cyclooctadiene) as the Ni^0 reagent.^{7a} Use of $[Ni(CO)_4]$, $[Ni(CNXyl)_2(cod)]$ ($Xyl = C_6H_3Me_2-2,6$), or $[Ni(cod)_2]$ as the nickel source afforded the corresponding $\{NiCB_{10}\}$ species, isolated as the salts $[N(PPh_3)_2][2,2-L_2-closo-2,1-NiCB_{10}H_{11}]$ [$L = CO$ (**18**), $CNXyl$ (**19**); $L_2 = cod$ (**20**)] following addition of $[N(PPh_3)_2]Cl$.²⁰ 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 $[N(PPh_3)_2][2-CO-2-NO-closo-2,1-CoCB_{10}H_{11}]$ (**21**), formally isoelectronic with **18**, by reacting $[closo-2-CB_{10}H_{11}]^-$ with $[Co(CO)_3(NO)]$ in THF, followed by addition of $[N(PPh_3)_2]Cl$.²¹ 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.²²

As has been described, the 'parent' monocarbollide-metal carbonyl piano-stool species $[2-(CO)_n-closo-2,1-MCB_{10}H_{11}]^{x-}$ 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**,²⁰ and as mentioned earlier, the manganese analogue of **14** has also briefly been reported.^{3a} 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 $[2,2-(CO)_2-closo-2,1-CoCB_{10}H_{11}]^{2-}$ and this species remains an attractive synthetic target.

III

REACTIONS

A. Ruthenium and Osmium Cluster Compounds

On protonation with $H[BF_4] \cdot OEt_2$ in THF the anionic trinuclear metal complexes **5** and **7** afford the neutral hydrido compounds $[2,2-(CO)_2-7,11-(\mu-H)_2-2,7,$

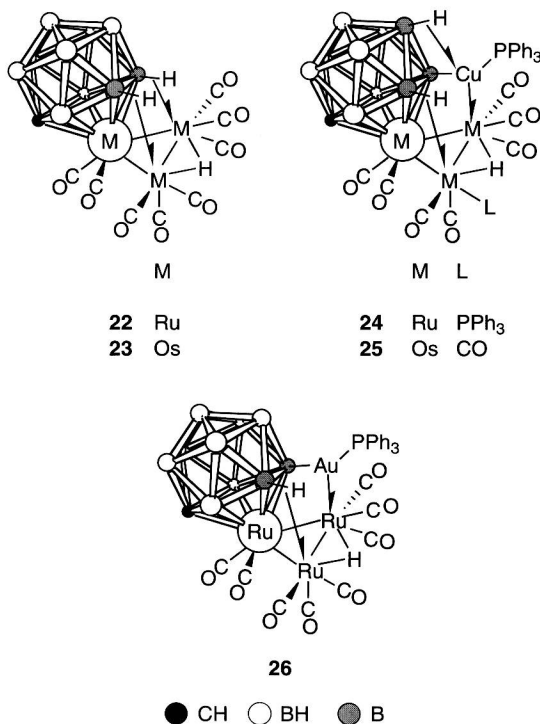


CHART 6.

11- $\{M_2(\mu-H)(CO)_6\}$ -*closo*-2,1-MCB₁₀H₉ [M = Ru (**22**) and Os (**23**)], respectively (Chart 6).^{11,12} 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 δ –19.03 (**22**) and δ –18.65 (**23**). The B–H→M linkages are also readily identified from the NMR spectra, in the ¹H spectra by quartet resonances at δ –10.31 [$J(BH) = 56$ Hz] (**22**) and δ –13.50 [$J(BH) = 45$ Hz] (**23**), and in their fully coupled ¹¹B spectra with doublets at δ 23.4 [$J(BH) = 52$ Hz] (**22**) and at δ 13.1 [$J(BH) = 45$ Hz] (**23**).

Both **5** and **7** undergo an interesting reaction in THF with [CuCl(PPh₃)₃] or [CuCl(PPh₃)₄], respectively, in the presence of Tl[PF₆], 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(μ-H)M site, being replaced by an isolobal {Cu(PPh₃)₃}⁺ fragment. A B–H→Cu bond, involving a BH unit in the B₅ pentagonal belt lying above the $\overline{CBBB\overline{B}}$ ring pentahapto coordinated to the metal vertex, further attaches the copper to the cage. In the ruthenium compound a PPh₃ molecule derived from the copper reagent substitutes for one of the CO ligands on the Ru₃ triangle. Salts of the anion **5** react with [AuCl(PPh₃)] to yield **26** which has structural features similar to **24**, except that the gold atom has only a single B–Au σ-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).^{14,23} The CO groups in **11** are not readily substituted by donor ligands. However, in the presence of Me_3NO , one CO group is readily replaced by donor molecules to yield $[\text{N}(\text{PPh}_3)_2][2,2-(\text{CO})_2-2\text{-L-closo-2,1-FeCB}_{10}\text{H}_{11}]$ [$\text{L} = \text{PPh}_3$ (**27**), CNBu^t (**28**), SMe_2 (**29**)]. More interestingly, **11** reacts with electrophiles (NO^+ , Ph_3C^+ , H^+) in the presence of certain solvents L to give the species $[2,2,2-(\text{CO})_3-7\text{-L-closo-2,1-FeCB}_{10}\text{H}_{11}]$.

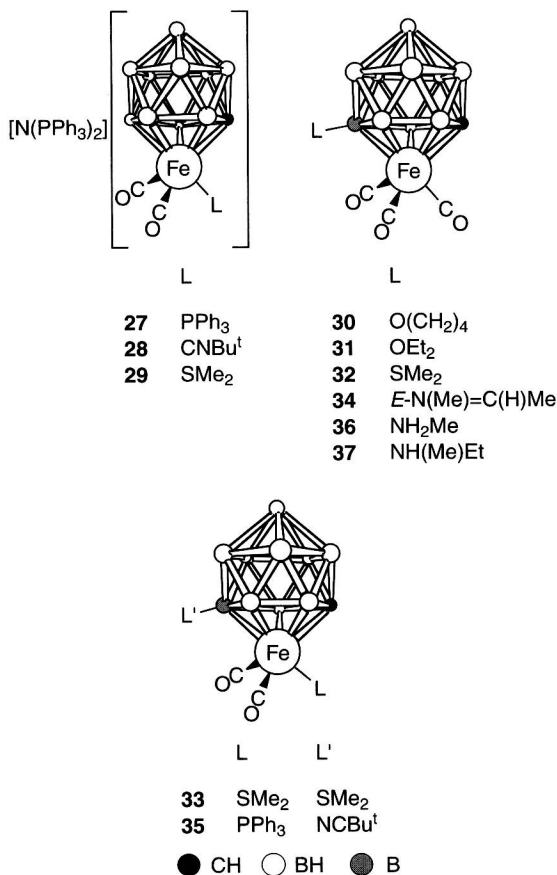


CHART 7.

1-FeCB₁₀H₁₀] [L = O(CH₂)₄ (**30**), OEt₂ (**31**), SMe₂ (**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.¹⁴ Apart from the use of X-ray crystallography to confirm the structures, NMR spectra leave no doubt about the presence of the {B-L⁺} groups in these charge-compensated products. Thus, for example, in the ¹¹B{¹H} NMR spectrum of **30** there is a resonance at δ 20.4 which remains a singlet in a fully coupled ¹¹B spectrum while the other peaks, corresponding in total intensity to nine boron nuclei, display ¹¹B-¹H coupling (ca. 130 Hz).

If compound **29** is treated with SMe₂ and H₂SO₄ the zwitterionic complex [2,2-(CO)₂-2,7-(SMe₂)₂-*closo*-2,1-FeCB₁₀H₁₀] (**33**) is obtained in which an SMe₂ 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.²³ 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 CF₃SO₃Me, the product obtained is [2,2,2-(CO)₃-7-{(*E*)-N(Me)=C(H)Me}-*closo*-2,1-FeCB₁₀H₁₀] (**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.²³ The mode of formation of the iminium group present in **34**, and related complexes derived from other nitriles, involves CF₃SO₃Me reacting with NCMe to give an *N*-methylnitrilium cation [MeN \equiv CMe]⁺ which itself then abstracts H⁻ 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.²³ It is interesting that if a similar reaction is carried out with compound **27** as substrate, and employing the more bulky NCBu^t instead of NCMe, a typical charge-compensated product [2,2-(CO)₂-2-PPh₃-7-NCBu^t-*closo*-2,1-FeCB₁₀H₁₀] (**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.²³ Formally, the β -boron appended {N(Me)=C(H)Me}⁺ 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⁻ or H⁻. Accordingly, treatment of **34** in THF with water yields the complex [2,2,2-(CO)₃-7-NH₂Me-*closo*-2,1-FeCB₁₀H₁₀] (**36**), a process catalyzed by PMe₃. The {N(Me)=C(H)Me}⁺ group may also be reduced by Na[BH₃CN] to give [2,2,2-(CO)₃-7-NH(Me)Et-*closo*-2,1-FeCB₁₀H₁₀] (**37**).

Treatment of **11** in THF with Bu^tC \equiv CH in the presence of Me₃NO, to facilitate removal of CO, yielded a single isomer of a species [N(PPh₃)₂][2,2-(CO)₂-2,3- η^2 : σ -{(*E*)-CH=C(H)Bu^t}-*closo*-2,1-FeCB₁₀H₁₀] (**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