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METAL SANDWICH COMPLEXES OF CYCLIC PLANAR AND PYRAMIDAL LIGANDS CONTAINING BORON

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CONTENTS

A. INTRODUCTION

The large, extraordinarily varied family of metal—boron cage and cluster compounds [1] includes, among others, a class of molecules that are direct structural and electronic analogues of the metallocenes and the metal—arene π-complexes. The distinguishing feature of these species is the presence of one or more cyclic planar borane or heteroborane ligands which are face-bound to metal atoms. Some of these ligands have an independent existence in the uncomplexed state, such as borazine ($B_3N_3H_6$), while others ($C_2B_3H_5^{4-}$ and $C_2B_3H_7^{2-}$, for example) are known only in complexed form. Furthermore, they include homocyclic systems such as $B_4H_8^{2-}$ as well as heterocyclic rings in which the heteroatom(s) may be carbon, nitrogen, sulfur, or even a transition metal.

All such ligands have in common a planar, or nearly planar, geometry (exclusive of bridging hydrogen atoms) and a significant degree of electron delocalization, and hence aromatic character. They are thus electronic counterparts of the prototype hydrocarbon arenes, $C_4H_4^{2-}$, $C_5H_5^-$, and C_6H_6, but there are some important differences. Metal complexes of the boron ligands (1) are frequently more stable than their metallocene relatives (in some cases the corresponding metallocene is not even known), (2) exhibit structural isomerism and thermal migration of metal atoms in the molecular framework (virtually unknown in metallocene chemistry), as well as other kinds of novel stereochemistry, and (3) include numerous extended sandwich systems, such as triple-decked complexes, in which the cyclic planar ligand is fully face-bonded to two metal atoms simultaneously; again, such systems are almost without precedent in the metallocenes, the only known example being $(\eta^5\text{-}C_5H_5)_3Ni_2^+$ [2].

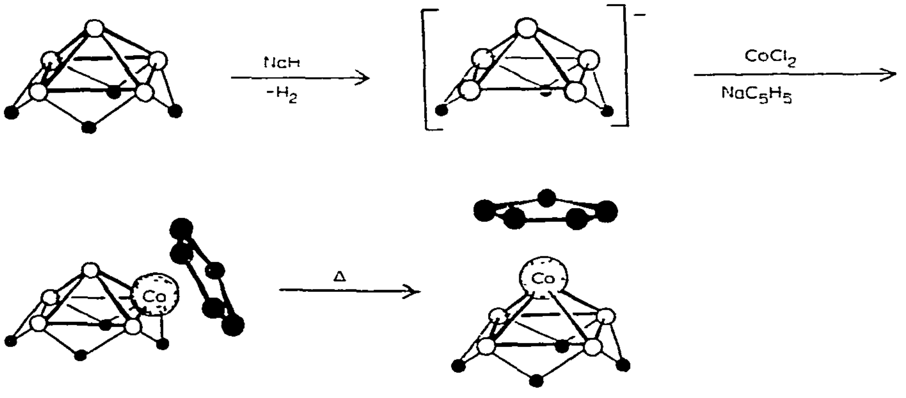
The first well-established π-complexes of transition metals with boron-containing ligands were icosahedral metallocarboranes of the types $(\eta^5\text{-}C_5H_5)MC_2B_9H_{11}$ and $(C_2B_9H_{11})_2M^{n-}$, where M is most frequently iron, cobalt or nickel [3]. In such systems, the metal interacts with an essentially planar C_2B_3 face on the $C_2B_9H_{11}^{2-}$ ligand, and hence an electronic analogy with ferrocene and other metallocenes was recognized; structural, spectroscopic and theoretical studies gave further support to this picture [1b,f]. Subsequently, many other metallocarboranes and metalloboranes of widely varying polyhedral shapes, sizes, and compositions were prepared [1]. Many of these, like the icosahedral species just mentioned, have no direct structural analogues among the metallocenes or other metal—hydrocarbon π-complexes, and hence will not be covered in this review. However, all metallocarboranes and metalloboranes which contain a planar (e.g. $C_2B_3H_5^{4-}$) or pyramidal (e.g. $C_2B_4H_6^{2-}$) ligand will be included (the latter species are formally generated from the planar systems by addition of BH^{2+}).

The types of compounds to be treated here vary rather widely in composition, synthesis and chemistry, and range from metalloboranes and metallocarboranes to complexes of boron—nitrogen and boron—sulfur ligands, as well as those of substituted diborolene and borabenzene rings. To my knowledge, there has been no previous review in which all these varieties of metal—boron complexes have been discussed from a common structural and electronic viewpoint; this reflects, no doubt, the very different synthetic origins of species such as the metalloboranes and the thiadiborolene complexes. A major purpose of this article, therefore, is to draw together a number of areas of metal—boron chemistry which have evolved separately, but which share metallocene-like molecular (and presumably electronic) structures.

B. SOME CONSIDERATIONS OF STRUCTURE AND BONDING IN METALLOBORON COMPLEXES

The compounds to be discussed in this article can be viewed both as metal—ligand π-complexes, in which a metal ion is considered to be face-bonded to an anionic carborane or borane ligand, or as polyhedral cages in which the metal atoms occupy vertices in the framework. The distinction is only conceptual, and each viewpoint has its virtues depending on the context of discussion; thus, the "metal-complex" approach is useful in comparing metalloboron compounds to metallocenes and other hydrocarbon sandwich complexes, while the polyhedral cage description emphasizes the relationship between the various kinds of cluster molecules — boranes, heteroboranes, metal clusters and the pyramidal carbocations. For example, one can describe 1-(η^5-C_5H_5)CoB_4H_8 (Fig. 1) either as an analogue of B_5H_9 in which the apical BH unit has been replaced by a (η^5-C_5H_5)Co group, or as a sandwich complex wherein a Co^{3+} ion is bonded to planar $(\eta^5\text{-}C_5H_5)^-$ and $(\eta^4\text{-}B_4H_8)^{2-}$ ligands [4]. In the latter sense, the molecule is seen to be directly analogous to (η^5-C_5H_5)Co(η^4-C_4H_4), since $C_4H_4^{2-}$ is isoelectronic with $B_4H_8^{2-}$.

The polyhedral borane description does have the considerable advantage that it facilitates discussion of cage structures in terms of the polyhedral electron-count theory [5—7]. In this widely used scheme, each vertex atom in an n-vertex *closo* system (a polyhedron in which all faces are triangular) is considered to utilize three valence orbitals in bonding to the cage framework.



1 2

Fig. 1. Conversion of B_5H_9 to the $B_5H_8^-$ ion and 2-(η^5-C_5H_5)CoB_4H_8 (1), and rearrangement to 1-(η^5-C_5H_5)CoB_4H_8 (2). ● CH; ○ BH; • H.

This normally produces $n + 1$ bonding molecular orbitals in the polyhedron, and hence a capacity of $2n + 2$ skeletal bonding electrons; an excess of electrons beyond that number induces cage-opening to form a *nido* ($2n + 4$ electrons) or *arachno* ($2n + 6$ electrons) system, where the terms *nido* and *arachno* refer to *closo* polyhedra with one and two vacant vertices, respectively. Since electrons used in bonding to external ligands are not included in the framework count, a BH unit contributes two electrons and a CH group three, to framework bonding. With first-row transition metals, it is normally assumed that of the nine valence orbitals, three are utilized for bonding to the remainder of the cage while the other six are employed in metal—external ligand bonding and for storage of non-bonding electron pairs. Many transition metal groups such as $Co(\eta^5\text{-}C_5H_5)$ and $Fe(CO)_3$ are formal two-electron donors and hence "equivalent" to BH, while others such as $Ni(\eta^5\text{-}C_5H_5)$ are three-electron donors analogous to CH. The electrons of bridging hydrogen atoms are included in the skeletal electron count but do not affect the value of n, since they do not affect the number of bonding MO's.

As an illustration of these rules, the cobaltaborane isomers in Fig. 1 are 14-electron systems ($2e^-$ from $(\eta^5\text{-}C_5H_5)Co$, $2e^-$ from each BH group and $1e^-$ from each of the four bridging hydrogens), and hence are $(2n + 4)$-electron cages with $n = 5$. This corresponds to a *nido* structure, in agreement with the observed square-pyramidal shapes of both isomers.

Despite some limitations [1a,5,8], the skeletal electron-count theory has enjoyed considerable success in dealing not only with boron cage structures but also with many metal clusters and other types of polyhedral systems. I shall use it with some frequency in this review, both to demonstrate how molecular structures can be correctly predicted and rationalized, and to emphasize structural and electronic relationships that might otherwise have been missed. At the same time, I shall also be describing these systems in the "metal-complex" format. Hopefully, it will be clear that there is no inconsistency in using both concepts in parallel, and indeed, that in doing so one's concept of these molecular structures is usefully extended.

C. SYNTHETIC ROUTES

Boron-containing metal sandwich complexes have been prepared by five principal methods:

(1) direct addition of the metal group to the free ligand, with the ligand undergoing little or no structural change;

(2) addition of the metal to a boron-containing substrate, producing major alterations in the substrate;

(3) rearrangement or partial degradation of an existing complex species;

(4) addition of boron to a metal—hydrocarbon π-complex;

(5) addition of carbon to a metal—borane π-complex.

The first route is, of course, the standard method of synthesis for metal—hydrocarbon sandwich complexes. Accordingly, it is the procedure most commonly employed to prepare complexes of the planar heterocyclic ligands such as borole, diborolene, thiadiborolene and borazine, which are direct analogues of the cyclic hydrocarbon ligands. In addition, a large number of metallocarboranes have been obtained in this manner, as illustrated by the following:

$$Co^{2+} + C_2B_9H_{11}^{2-} + C_5H_5^- \rightarrow (C_2B_9H_{11})Co(C_5H_5)^- \xrightarrow{[O]} (C_2B_9H_{11})Co(C_5H_5)$$

$$Fe^{2+} + 2(CH_3)_2C_2B_4H_5^- \rightarrow [(CH_3)_2C_2B_4H_4]_2FeH_2$$

Method (2) is frequently employed in metalloborane and metallocarborane synthesis, and involves, in effect, creation of π-complexes whose ligands are not available as free species; an example is the preparation of the triple-decked complex $(\eta^5\text{-}C_5H_5)Co(C_2B_3H_5)Co(\eta^5\text{-}C_5H_5)$ from $CoCl_2$, $Na^+C_5H_5^-$, and the 2,3-$C_2B_4H_7^-$ ion (Section E(ii)). The planar $C_2B_3H_5^{4-}$ ligand, like nearly all cyclic planar borane and carborane ligands, is known only in complexed form and has never been observed in the free state.

The third route is common in metallocarborane chemistry, and takes advantage of the nearly unique ability of these cage molecules to undergo thermal isomerization or removal of a BH group, e.g.

$$1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_4H_6 \rightarrow 1,2,4\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$$

$$\xrightarrow{O_2,\ H_2O} 1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$$

Such rearrangements or partial degradations (that is, removal of one or more cage atoms while retaining the basic cage structure) are extremely rare among hydrocarbon sandwich complexes or their boron-heterocycle counterparts.

Method (4) has been extensively employed in the preparation of η^6-borabenzene sandwich complexes from cobaltocene, as described in Section F. Finally, the fifth route has been utilized in a few instances such as the reactions of alkynes with 2-$(\eta^5\text{-}C_5H_5)CoB_4H_8$ to generate metallocarborane sandwich complexes of the planar $R_2C_2B_3H_5^{2-}$ ion (Section E(ii)). Methods (4) and (5) would seem to have considerable potential for extension to many other systems which have yet to be investigated.

Further discussion of each of these synthetic procedures appears in the Sections which follow.

D. SQUARE PLANAR AND SQUARE PYRAMIDAL LIGANDS: ANALOGUES OF $C_4H_4^{2-}$

(i) $B_4H_8^{2-}$ *complexes*

The direct tetraboron counterpart of the cyclobutadienide ion, $C_4H_4^{2-}$, would be square planar $B_4H_4^{6-}$. Such an entity is not known in the free state but can be said to exist in the octahedral molecules $B_6H_6^{2-}$ and 1, 6-$C_2B_4H_6$ if one views those molecules formally as complexes of $B_4H_4^{6-}$ face-bonded to two BH^{2+} and two CH^{3+} units, respectively [9]. A transition metal analogue of these systems, not yet prepared but almost certainly capable of existence, would be 1,6-$(\eta^5\text{-}C_5H_5)_2Ni_2B_4H_4$ (several isoelectronic cobaltaboranes are known [4b], although these lack a planar B_4 array).

The insertion (in a formal sense) of four protons as bridging hydrogens into the B—B bonds of square planar $B_4H_4^{6-}$ generates $B_4H_8^{2-}$, which again is unknown as a free ion but does form η^4-complexes with BH^{2+} (to give the square pyramidal borane B_5H_9) and with transition metal groups. Two such metal complexes of cyclic planar * $B_4H_8^{2-}$ have been isolated and characterized. In 1973 Miller and Grimes [4a] obtained the red, crystalline metalloborane 2-$(\eta^5\text{-}C_5H_5)CoB_4H_8$, **1** (Fig. 1), as the principal product of the reaction of $Na^+B_5H_8^-$ with $CoCl_2$ and $Na^+C_5H_5^-$ in cold tetrahydrofuran (THF) (other cobaltaboranes isolated from the reaction will be described later in this review). The structure of **1** was deduced from ^1H and ^{11}B NMR spectra [4a], and was later confirmed in a crystallographic study [10]. On heating at 200° in the vapor phase, **1** rearranged to 1-$(\eta^5\text{-}C_5H_5)CoB_4H_8$, **2**, a yellow solid whose square-planar geometry was clearly shown from NMR data.

Isomers **1** and **2** are both isoelectronic counterparts of B_5H_9, with a $Co(\eta^5\text{-}C_5H_5)^{2+}$ group replacing a BH^{2+} unit in each case (the Wade formalism [5—7], discussed in Section B, invokes neutral BH and $Co(\eta^5\text{-}C_5H_5)$ moieties as two-electron donors to skeletal framework bonding; in either language the equivalence between B_5H_9 and the cobaltaboranes is preserved). Isomer **2** contains the cyclic planar $B_4H_8^{2-}$ ligand, isoelectronic with $C_4H_4^{2-}$, and was the first such complex to be prepared. Thus, **2** is directly analogous to the sandwich compound $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4H_4)$ [11]. It is useful to consider both the $C_4H_4^{2-}$ and the $B_4H_8^{2-}$ ligands as formal dinegative units, if only because this is consistent with the common designation of cyclopentadienide ($C_5H_5^-$) as an ionic ligand. Moreover, the formal metal oxidation states that are implied by these ionic ligand assignments (e.g. usually +2 for iron and +3 for cobalt) are highly compatible with the chemical and spectroscopic properties of the compounds.

The only other known complex of planar $B_4H_8^{2-}$ is 1-$(CO)_3FeB_4H_8$, **3**, an orange liquid which has been assigned the structure in Fig. 2 [12]. Again, this species can be viewed as both a cage compound (analogous to B_5H_9 in terms of skeletal electron-count) and as a sandwich complex which is a counterpart of the known molecule [13] $(CO)_3Fe(\eta^4\text{-}C_4H_4)$. Fehlner and co-workers [14] have examined the He(I) and Ne(I) photoelectron spectra of the latter complex as well as **3** and concluded that there is greater metal—ring interaction in the borane complex than in $(CO)_3Fe(\eta^4\text{-}C_4H_4)$: that is, the iron is more "cage-like" in **3**. Given the higher electronegativity of carbon compared to boron, it is not surprising that the hydrocarbon ligand appears to

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* The term "planar" throughout this review denotes an approximate planarity of the non-hydrogen atoms in the ligand, and excludes bridging hydrogens.

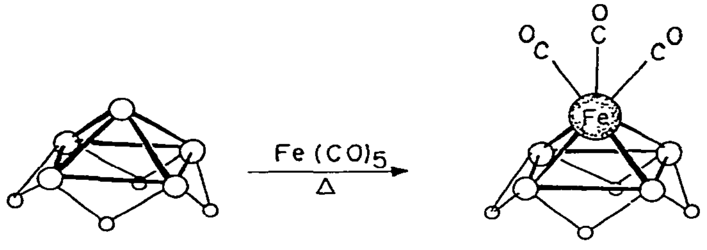

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Fig. 2. Synthesis of 1-$(CO)_3FeB_4H_8$ (3) from B_5H_9.

exhibit more ionic character than does the square planar tetraboron ligand.

The chemistry of 1-(η^5-C_5H_5)CoB_4H_8 and 1-$(CO)_3FeB_4H_8$ has been little studied, but an intriguing reaction of the iron species which may have considerable synthetic significance is the displacement of iron by two molecules of 2-butyne [15]:

$$\underset{3}{(CO)_3FeB_4H_8} + 2\ CH_3C{\equiv}CCH_3 \xrightarrow{h\nu} \underset{4}{(CH_3)_4C_4B_4H_4}$$

The product 4 has been formulated from NMR data as a carborane with a fluxional cage structure [15], but it should be noted that an electronically analogous tetranickel complex, $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$, has been shown to have a *closo*, non-fluxional, dodecahedral shape [16].

(ii) Complexes of square pyramidal ligands

Metal—hydrocarbon sandwich complexes incorporating square pyramidal C_5 ligands are unknown; however, the synthesis of derivatives of the square pyramidal carbocation $C_5H_5^+$ [17] suggests that such complexes might be prepared eventually. The prototype square pyramidal borane ligand is the hypothetical $B_5H_5^{4-}$ ion (formally generated by removal of the four bridging protons from B_5H_9), and the analogous square pyramidal carborane ligand (which is part of an isoelectronic sequence with $C_5H_5^+$ and $B_5H_5^{4-}$) is $C_2B_3H_5^{2-}$. Salts of this ion have not been prepared, but its diprotonated derivative, the carborane $C_2B_3H_7$, has been well characterized and is indeed pyramidal [18]. Two metal complexes of $C_2B_3H_5^{2-}$ were synthesized in our laboratory several years ago (Fig. 3), and were the first known examples of octahedral boron cage species containing metal atoms [19]. The orange liquid 1, 2, 4-$(CO)_3FeC_2B_3H_5$, 4, and yellow-orange solid 1, 2, 4-(η^5-C_5H_5)$CoC_2B_3H_5$, 5, were prepared by metal insertion into *closo*-1,5-$C_2B_3H_5$ as shown, and characterized from ^{11}B and ^1H NMR data. Once again, these species can be formulated either as η^4-complexes of the $C_2B_3H_5^{2-}$ ligand or as *closo*-metallocarboranes; in the latter approach one counts in each case 14 skeletal electrons (two from each BH, Co(η^5-C_5H_5), or $Fe(CO)_3$ group and three from each CH), as expected for

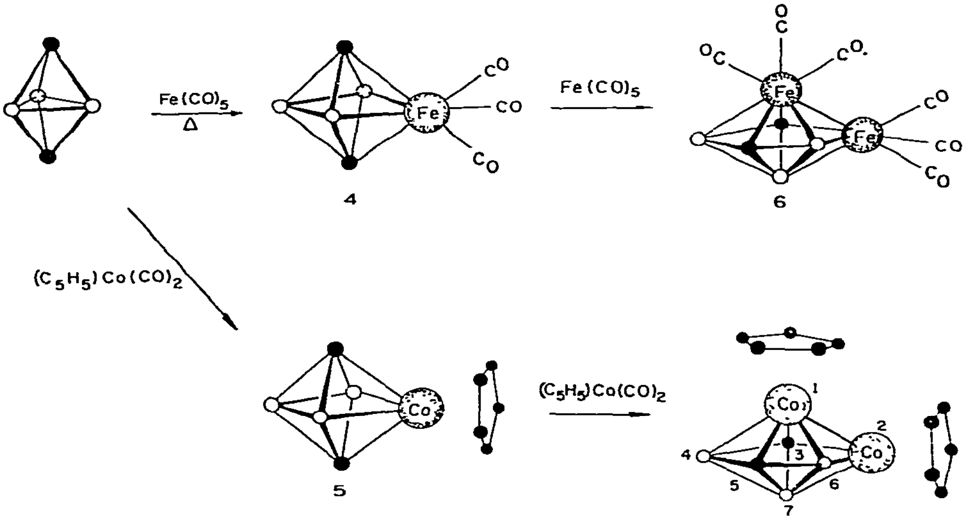

Fig. 3. Synthesis of 1,2,4-$(CO)_3FeC_2B_3H_5$ (**4**), 1,2,3,5-$[(CO)_3Fe]_2C_2B_3H_5$ (**6**), 1,2,4-$(\eta^5\text{-}C_5H_5)CoC_2B_3H_5$ (**5**) and 1,2,3,5-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ (**7**) from 1,5-$C_2B_3H_5$. ● CH; ○ BH.

6-vertex *closo* structures (see Section B). In the metal-complex description, the overlap of orbitals on the metal and ligand atoms is qualitatively identical to that in square planar metal sandwich compounds; that is, three bonding MOs on the ligand are combined with three suitable metal orbitals to generate a set of bonding MOs which accommodate the six electrons supplied by the dinegative ligand.

Both **4** and **5** can be converted to dimetallic, 7-vertex cages (**6** and **7**) by reaction with appropriate metal reagents [19], as illustrated in Fig. 3. These processes are examples of polyhedral expansion by direct metal insertion, a method which has been successfully applied to many different cage systems.

A ferraborane analogue of **4** and **5**, $(CO)_3FeB_5H_3(CO)_2$, **8**, has been reported by Ulman and Fehlner [20] who proposed the structure shown in Fig. 4. This compound, the first example of an MB_5 octahedral cluster, was obtained in the reaction of B_5H_9 with $Fe(CO)_5$ at 30—280°C in daylight.

Three other octahedral metalloboranes which are isoelectronic analogues of **4**, **5**, and **8** are violet 1,2-$(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$, **9**, brown 1, 2, 3-$(\eta^5\text{-}C_5H_5)Co_3B_3H_5$, **10**, and yellow 1, 2, 3-$(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$, **11**, all of which were originally isolated [4,21] as minor products of the synthesis of **1** from $B_5H_8^-$, $CoCl_2$, and NaC_5H_5 (Fig. 1); recently, work in our group has demonstrated [22] that **9**, **10** and **11** form by addition of cobalt to the anion of **1**, as shown in Fig. 5. The octahedral cage structures shown have been established crystallographically [23,24], with the face-bridging protons precisely

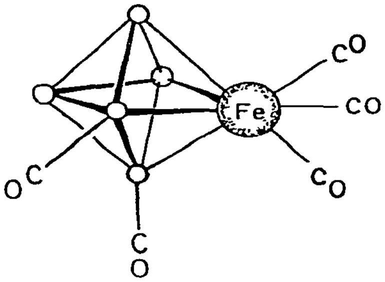

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Fig. 4. Proposed structure of $(CO)_3FeB_5H_3(CO)_2$.

located in **9**. In addition to being 6-vertex, 14-electron *closo* systems * directly analogous to $B_6H_6^{2-}$ as well as **4**, **5** and **8**, both **9** and **10** can be considered as η^4-complexes of a $Co(\eta^5\text{-}C_5H_5)^{2+}$ unit with square pyramidal $(\eta^5\text{-}C_5H_5)CoB_4H_6^{2-}$ and $(\eta^5\text{-}C_5H_5)_2Co_2B_3H_5^{2-}$ ligands, respectively. Both ligands are analogues of $B_5H_7^{2-}$, which of course is simply a diprotonated derivative of $B_5H_5^{4-}$. The capped-octahedral species **11** is structurally unique in the boron cage family, but is electronically related to several heavy-metal clusters such as $Os_7(CO)_{21}$ [25]; it can be formally generated from **10** by replacing the two "extra" hydrogen atoms with an electronically equivalent :BH group.

At the time of writing, one other octahedral metalloboron complex, the mixed-metal species $(CO)_4Fe(\eta^5\text{-}C_5H_5)_2Co_2B_3H_3$, **12**, has been characterized. This brown compound (Fig. 6) was isolated from the reaction of $Fe(CO)_5$ with **1**, and the structure shown was proposed from NMR evidence [22]. Again, the framework electron count of 14 (which takes into account the presence of four carbonyl groups) is identical to that in the octahedral species mentioned above, and a description in terms of a metal ion—square planar ligand complex similar to that given for **9** and **10** is also possible.

Table 1 summarizes the known complexes of square planar and pyramidal boron-containing ligands.

(iii) *Other complexes involving metal—square planar face interactions*

A few larger metallocarboranes and metalloboranes are known in which the metal atom is η^4-bonded to a cyclobutadiene-like square planar face, although the ligand as a whole is neither planar nor pyramidal. These complexes are not strictly within the scope of this review, but will be mentioned inasmuch as this type of metal—ligand interaction is qualitatively similar to that discussed above. The assigned cage geometry in most of these molecules is either a 9-vertex tricapped trigonal prism or a 10-vertex bicapped square antiprism,

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* It should be recalled that the electrons supplied by the bridging hydrogens are included in the total framework count.

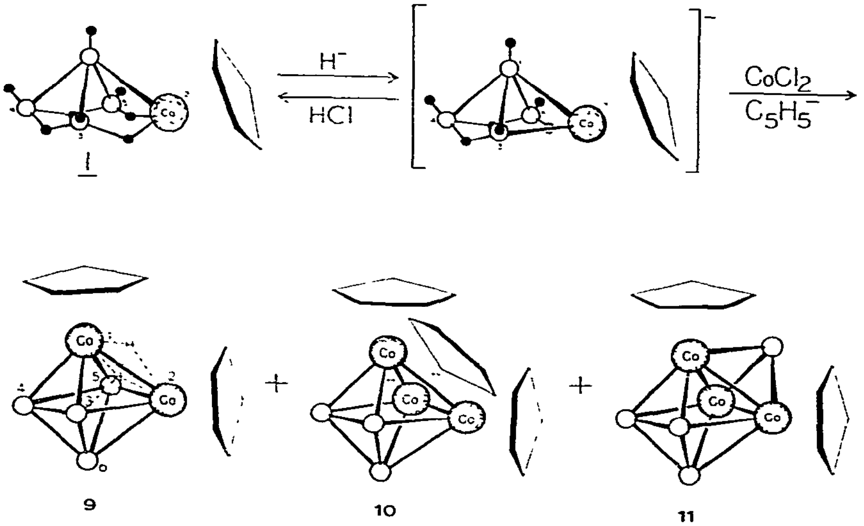


Fig. 5. Synthesis of 1,2-(η^5-C_5H_5)$_2$$Co_2B_4H_6$ (**9**), 1,2,3-(η^5-C_5H_5)$_3$$Co_3B_3H_5$ (**10**) and (η^5-C_5H_5)$_3$$Co_3B_4H_4$ (**11**) from the [2-(η^5-C_5H_5)CoB_4H_7]$^-$ ion. One C_5H_5 ring has been omitted for clarity in **10**. Structures of **9**, **10** and **11** have been crystallographically established. ○ B or BH; • H.

TABLE 1

Complexes of square planar and square pyramidal ligands

Complex[a]	Color	M.p. (°C)	Data[b]	Ref.
	Square planar ligands			
1-$CpCoB_4H_8$	yellow		B, H, IR, MS	4
1-$(CO)_3FeB_4H_8$	orange	5	B, H, IR, MS; UVP	12; 14
	Square pyramidal ligands			
1,2,4-$(CO)_3FeC_2B_3H_5$	orange		B, H, IR, MS; UVP	19; 14
1-$(CO)_3FeB_5H_3(CO)_2$	red	~5	B, H, IR, MS, E; UVP	20; 14
1,2,4-$CpCoC_2B_3H_5$	yellow-orange		B, H, IR, MS, E	19
1,2-$Cp_2Co_2B_4H_6$	violet		B, H, IR, MS; X	4b, 21; 24
3-σ-C_5H_9-1,2-$Cp_2Co_2B_4H_5$	violet		B, H, IR, MS	4b, 21
4-σ-C_5H_9-1,2-$Cp_2Co_2B_4H_5$	violet		B, H, IR, MS	4b, 21
1,2,3-$Cp_3Co_3B_3H_5$	brown		B, H, IR, MS; X	4b, 21; 23
1,2,3-$Cp_2Co_2(CO)_4FeB_3H_3$	brown		B, H, MS	22

[a] Cp = (η^5-C_5H_5). [b] B = ^{11}B NMR; H = ^{1}H NMR; IR = infrared data; MS = mass spectroscopic data; X = X-ray crystallographic data; UVP = ultraviolet photoelectron spectroscopic data; E = electronic spectral data.

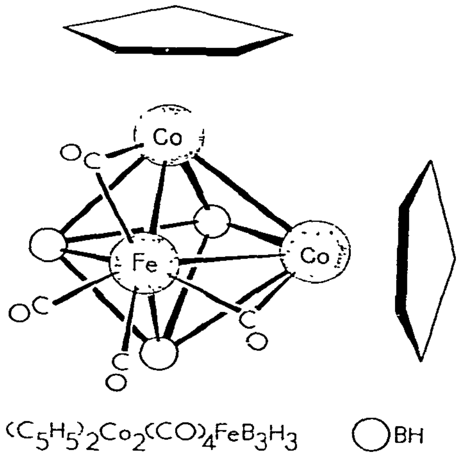


Fig. 6. Proposed structure of $(CO)_4Fe(\eta^5\text{-}C_5H_5)_2Co_2B_3H_3$ (12).

the metal in each case occupying a capping vertex (Fig. 7). Of the reported 9-vertex structures, the only ones that have been crystallographically verified are $4,5,6\text{-}[(CH_3)_3P]_2PtC_2B_6H_8$ and its C,C′-dimethyl derivative [26,27]. Other molecules of this class, whose structures were proposed from NMR evidence, include $4,1,8\text{-}(\eta^5\text{-}C_5H_5)FeC_2B_6H_8$ [28] and $4,1,9,2,8\text{-}[(CO)_3Fe]_2(\eta^5\text{-}C_5H_5)\text{-}Co(CH_3)_2C_2B_4H_4$ [29]. A *nido* 9-vertex species (monocapped square antiprism), $(\eta^5\text{-}C_5H_5)_4Ni_4B_5H_5$, is proposed to have one nickel atom in the capping vertex bonded to an NiB_3 "square" face [16].

Ten-vertex systems which have been assigned structures containing metal—square planar face interactions are $1,10\text{-}(\eta^5\text{-}C_5H_5)_2NiCoCB_7H_8$ [30], 10,1,2- and $10,1,6\text{-}(\eta^5\text{-}C_5H_5)_2Co_2CB_7H_8$ [31], $10,1\text{-}(\eta^5\text{-}C_5H_5)NiCB_8H_9$ [32], and $1\text{-}(\eta^5\text{-}C_5H_5)NiB_9H_9^-$ and its B-perchloro derivative [33].

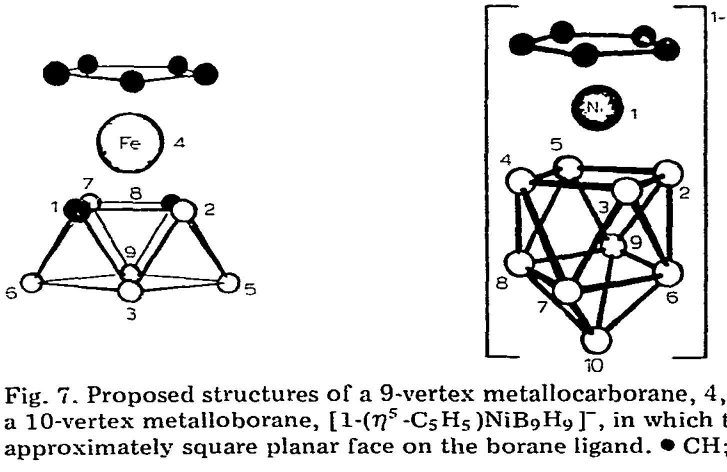


Fig. 7. Proposed structures of a 9-vertex metallocarborane, $4,1,8\text{-}(\eta^5\text{-}C_5H_5)FeC_2B_6H_8$, and a 10-vertex metalloborane, $[1\text{-}(\eta^5\text{-}C_5H_5)NiB_9H_9]^-$, in which the metal ion is bonded to an approximately square planar face on the borane ligand. ● CH; ○ BH.

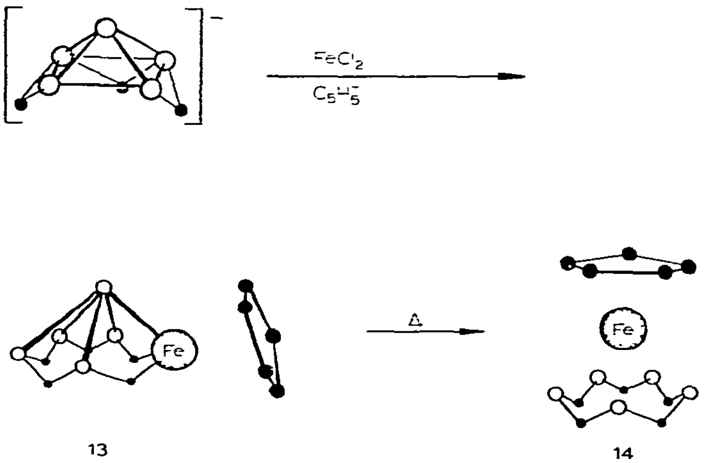
E. PENTAGONAL PLANAR AND PENTAGONAL PYRAMIDAL LIGANDS: ANALOGUES OF $C_5H_5^-$

(i) Systems with one η^5-bonded metal atom

(1) Complexes of cyclic planar $B_5H_{10}^-$

Following a similar approach to that used in dealing with square-planar borane ligands (see above), I begin this section by observing that the simple borane counterpart of the cyclopentadienide system would be cyclic planar $B_5H_5^{6-}$. As might be expected for such a highly charged species, the free ligand has not been found, nor have any metal π-complexes been prepared (however, planar $B_5H_5^{6-}$ could be said to exist as a formal complex with two BH^{2+} groups in the pentagonal bipyramidal $B_7H_7^{2-}$ ion [9,34]).

The pentaprotonated derivative of $B_5H_5^{6-}$, i.e. $B_5H_{10}^-$, does exist in one known metal complex which was recently prepared in our laboratory [35a]. As shown in Fig. 8, addition of $FeCl_2$ and NaC_5H_5 to a solution of $Na^+B_5H_8^-$ in THF at 25° gave violet 2-(η^5-C_5H_5)FeB_5H_{10}, **13**, which in turn rearranged at 175—180°C to the 1-isomer, **14**. From ^{11}B and ^1H NMR spectra the structures depicted were assigned [35a], both being electronic and structural analogues of B_6H_{10}. The structure of **14**, which is strongly indicated by the high (C_{5v}) symmetry evident from NMR data, is a direct isoelectronic and isostructural analogue of $(\eta^5\text{-}C_5H_5)_2Fe$ (ferrocene). Compounds **14** and 1-(η^5-C_5H_5)CoB_5H_9 [35b] are the only known examples of complexes containing a planar B_5 borane ligand. However, several metal complexes of nonplanar B_5 ligands have been prepared, e.g. $(CO)_3FeB_5H_9$ and the $(CO)_3FeB_5H_8^-$ ion [36], $[(C_6H_5)_3P]_2CuB_5H_8$ [37] and $B_5H_{10}BeBH_4$ and $(B_5H_{10})_2Be$ [38,39]; it is possible that some of these might be induced to iso-



13 14

Fig. 8. Synthesis and proposed structures of 2-(η^5-C_5H_5)FeB_5H_{10} (**13**) and 1-(η^5-C_5H_5)FeB_5H_{10} (**14**). ● CH; ○ BH; • H.

merize to sandwich-like complexes with cyclic planar borane ligands analogous to **14**.

(2) Complexes of cyclic planar $C_2B_3H_7^{2-}$

A hypothetical series of cyclic planar carborane anions which are isoelectronic with $C_5H_5^-$ and $B_5H_5^{6-}$ would consist of $C_4BH_5^{2-}$, $C_3B_2H_5^{3-}$, $C_2B_3H_5^{4-}$ and $CB_4H_5^{5-}$. Of this group, metal complexes are presently known for C-substituted derivatives of $C_4BH_5^{2-}$ and $C_3B_2H_5^{3-}$, and for the parent $C_2B_3H_5^{4-}$ ion and several of its derivatives. In addition, heterocyclic analogues of these ligands containing sulfur or nitrogen also form complexes with metals, as described in later sections. The $C_2B_3H_5^{4-}$ system, though nonexistent as a free species, is important in metallocarborane chemistry in three ways [1a,40,41a]: (a) planar $C_2B_3H_5^{4-}$ forms "triple-decked sandwich" complexes by simultaneous η^5-bonding to two metal atoms (discussed in Section E(ii), below); (b) the pyramidal $C_2B_4H_6^{2-}$ ligand (which may be regarded as a π-complex of a BH^{2+} group with $C_2B_3H_5^{4-}$) forms numerous η^5-complexes with metal atoms; (c) the planar $C_2B_3H_7^{2-}$ ion, which is simply $C_2B_3H_5^{4-}$ with two B—H—B bridging protons added, is also a common η^5 ligand in metal complexes.

Most of the known species containing $C_2B_3H_7^{2-}$ or its C-substituted derivatives have been obtained from complexes of $C_2B_4H_6^{2-}$ (or its derivatives) by removal of the apical BH group. The first synthesis of a metal complex of $C_2B_3H_7^{2-}$ involved the reaction of the *nido*-carborane 2,3-$C_2B_4H_8$ with $Fe(CO)_5$ at 240° in a hot—cold reactor [42,43], which gave both pale yellow liquid 1-$(CO)_3FeC_2B_3H_7$, **15**, and yellow-orange liquid 1,2,3-$(CO)_3FeC_2B_4H_6$, **16** (Fig. 9); it was shown that **15**, the more stable of the two species, forms on thermal degradation of **16**. The structure of **15** was assigned from NMR spectra and later confirmed in an X-ray study [44], which disclosed that the C_2B_3 ring is planar and symmetrically bonded to the iron atom (all Fe—B and Fe—C distances are identical within one standard deviation).

Complex **15** is an isoelectronic analogue of the well-known $(\eta^5\text{-}C_5H_5)Fe(CO)_3^+$ ion and of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ (cymantrene), and is at the same time directly related to its carborane precursor $C_2B_4H_8$ (Fig. 9) by replacement of BH^{2+} with an $Fe(CO)_3^{2+}$ group. Ab initio molecular orbital calculations on **15** suggested that the metal—ligand bonding is mainly ionic [45], a conclusion which seems at variance with the volatile, stable, covalent-like nature of the

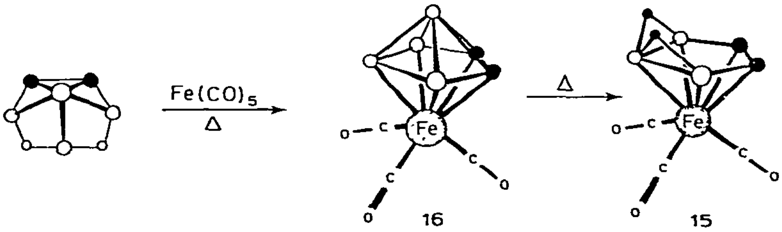


Fig. 9. Synthesis of 1-$(CO)_3FeC_2B_4H_6$ (**16**) and 1-$(CO)_3FeC_2B_3H_7$ (**15**). ● CH; ○ BH; • H. The structure of **15** has been crystallographically established.

molecule, and with the Fe—B and Fe—C bond distances [44] (2.11—2.14 Å), which are typical of covalent interactions. Recent measurements of its ultraviolet photoelectron spectrum [14] also cast doubt on the ionic-bonding model.

In addition to the study of **15** mentioned above, one other metal complex of a $C_2B_3H_7^{2-}$ derivative has been examined crystallographically [46], this being the red, solid, zwitterionic cobaltocenium—carborane species 5-[(η^5-C_5H_5)Co(η^5-C_5H_4)]-[2,3-$(CH_3)_2C_2B_3H_5$]Co[2,3-$(CH_3)_2C_2B_4H_3$], **17**, shown in Fig. 10. This molecule contains a Co^{3+} ion η^5-bonded to a pyramidal $(CH_3)_2C_2B_4H_4^{2-}$ ligand and a $(CH_3)_2C_2B_3H_5^{2-}$ cyclic planar ligand, with a terminal hydrogen on the former replaced by a [(η^5-C_5H_5)Co(η^5-C_5H_4)]$^+$ (cobaltocenium) substituent. There are several interesting structural features, but of primary concern here is the $(CH_3)_2C_2B_3H_5^{2-}$ ligand. The C_2B_3 ring is completely planar within experimental error, and as in complex **15**, is symmetrically bonded to the metal atom. A further similarity between **15** and **17** is the short carbon—carbon bond in the C_2B_3 ligand in each complex (1.410(4) and 1.418(9) Å, respectively), which is also a feature of pyramidal carboranes containing adjacent carbon atoms (e.g. $C_2B_4H_8$ [47]); the shortness of these interactions has been interpreted as evidence of localized multiple bonding between the carbons [47,48].

A number of other metal η^5-complexes of the $C_2B_3H_7^{2-}$ ligand or its C-substituted derivatives have been prepared in our laboratory (Table 2), and one sequence is illustrated in Fig. 11. The bridging protons in most of these compounds are acidic toward hydride ion in ethereal solvents; thus, reaction of **19** with NaH in THF generates the conjugate base anion **20** and releases hydrogen [49] (Fig. 11). Only one bridging proton per molecule can be removed

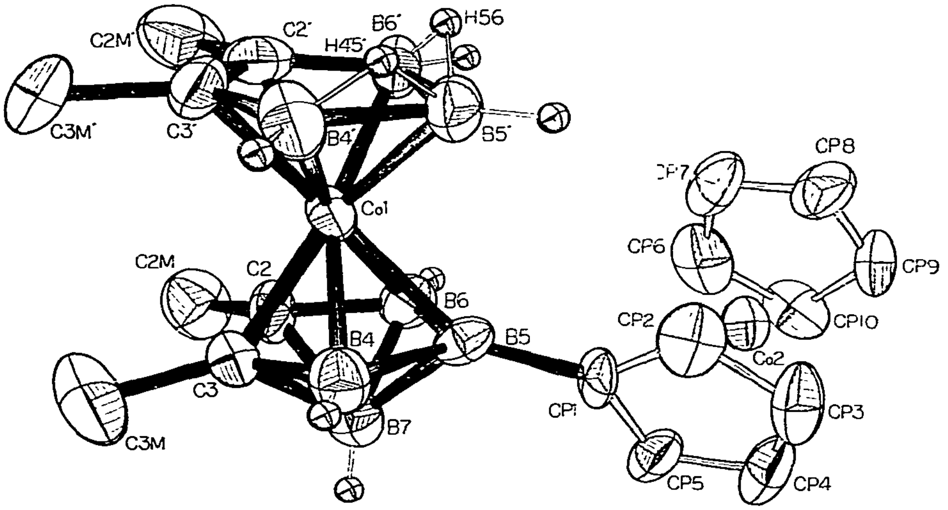


Fig. 10. Structure of 5-[(η^5-C_5H_5)Co(η^5-C_5H_4)]-[2,3-$(CH_3)_2C_2B_3H_5$]Co[2,3-$(CH_3)_2C_2B_4H_3$], **17**.

TABLE 2

Complexes of pentagonal planar ligands

Complex [a]	Color	M.p. (°C)	Data [b]	Ref.
	Complexes with one η^5-bonded metal atom			
B_5 ring systems				
1-$CpFeB_5H_{10}$	violet		B, H, MS	35a
1-$CpCoB_5H_9$			B, H, MS	35b
C_2B_3 ring systems				
1,2,3-$(CO)_3FeC_2B_3H_7$	pale yellow	~−15	B, H, IR, MS; X	42, 43; 44
1,2,3-$CpCoC_2B_3H_7$	pale yellow		B, H, IR, MS	49
2-CH_3-1,2,3-$CpCoC_2B_3H_6$	yellow		B, H, IR, MS	49
2,3-$(CH_3)_2$-1,2,3-$CpCoC_2B_3H_5$	yellow		B, H, MS	22
[2,3-$(CH_3)_2C_2B_4H_4$]CoH[2,3-$(CH_3)_2C_2B_3H_5$]	yellow		B, H, IR, MS	51
$(CH_3)_4N^+$[2,3-$(CH_3)_2C_2B_4H_4$]Co[2,3-$(CH_3)_2C_2B_3H_5$]$^-$	yellow	259—262	B, H, IR, MS	51
5-[CpCo(C_5H_4)]-[2,3-$(CH_3)_2C_2B_4H_3$]Co[2,3-$(CH_3)_2C_2B_3H_5$]	red-brown		B, MS, X	46
σ-$(CH_2)_4$O-[2,3-$(CH_3)_2C_2B_4H_3$]Co[2,3-$(CH_3)_2C_2B_3H_5$]	yellow		B, H, IR, MS	46
[CpCo$(CH_3)_2C_2B_3H_3$]CoH[2,3-$(CH_3)_2C_2B_3H_5$]	red-brown		B, H, IR, MS	51
C_4B (borole) ring systems				
$(CO)_3FeC_4B(C_6H_5)_5$	pale yellow	218—220	IR, MS	77
2-C_2H_5-6-C_6H_5-$(CO)_3FeC_4BH_3$	amber	<−30	H, IR, MS	77
$(CO)_2NiC_4B(C_6H_5)_5$	wine-red	214—216	IR, MS	77
C_3B_2 (diborolene) ring system				
$CpNiC_3(C_2H_5)_2(CH_3)B_2(C_2H_5)_2$	orange-red	46	B, H, MS	80
C_2B_2S (thiadiborolene) ring systems				
$(CO)_4CrC_2(C_2H_5)_2B_2(CH_3)_2S$	yellow-green liquid		B, H, IR, MS	82
$(CO)_2Cr[C_2(C_2H_5)_2B_2(CH_3)_2S]_2$	yellow	169—170	B, H, IR, MS	82
$(CO)_4MoC_2(C_2H_5)_2B_2(CH_3)_2S$	yellow-green liquid		B, H, IR, MS	82
$(CO)_2Mo[C_2(C_5H_5)_2B_2(CH_3)_2S]_2$	yellow	159—160	B, H, IR, MS	82
$(CO)_3FeC_2(C_2H_5)_2B_2(R)_2S$				81
R = I	red-orange	96—98	B, H, IR, MS	
R = Br	yellow-orange	59—60	B, H, IR, MS	
R = Cl	yellow-red		B, H, IR, MS	

TABLE 2 (continued)

Complex [a]	Color	M.p. (°C)	Data [b]	Ref.
R = CH_3	yellow-orange	23—25	B, H, IR, MS	
R = $N(CH_3)_2$	dark red	101—102	B, H, IR, MS, X	
R = OC_2H_5	dark red	45—46	B, H, IR, MS	
R = SCH_3	dark red	125—126	B, H, IR, MS	
R = H	yellow		B, H, IR, MS	
R = F, I	yellow-red		B, H, IR, MS	
R = OC_2H_5, I	dark red		B, H, IR, MS	
R = CH_3, I	red	68—70	B, H, MS	
C_2N_2B (diazaboroline) ring systems				
$(CO)_3CrC_2H_2N_2[C(CH_3)_3]_2BCH_3$	yellow	170 dec	B, H, IR, MS	83
Complexes with two η^5-bonded metal atoms (triple-decked sandwiches)				
2,3-C_2B_3 ring systems (adjacent carbon atoms)				
1,7,2,3-$Cp_2Co_2C_2B_3H_5$	red-brown		B, H, IR, MS; E	49, 84; 53
2-R-3-R′-1,7,2,3-$Cp_2Co_2C_2B_3H_3$				
R = CH_3, R′ = H	red-brown		B, H, IR, MS; X	49; 84
R = R′ = CH_3	red-brown		B, H, IR, MS	49
R = $(CH_3)_3Si$, R′ = H	red		B, H, MS	41a
R = C_6H_5, R′ = H	red		B, H, MS	41a
RR′ = C_3H_4	red		B, H, IR, MS; X	4b; 48
5-Br-1,7,2,3-$Cp_2Co_2C_2B_3H_4$	red		B, H, MS	41a
5-I-1,7,2,3-$Cp_2Co_2C_2B_3H_4$	red		B, H, MS	41a
1,7,2,3-$(CH_3C_5H_4)CpCo_2C_2B_3H_5$	red		B, H, MS	41a

1,7,2,3-$(C_2H_5C_5H_4)CpCo_2C_2B_3H_5$	red		B, H, MS	41a
1,7,2,3-$[(CH_3)Si\text{-}C_5H_4]CpCo_2C_2B_3H_5$	red		B, H, MS	41a
$CpCo[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_3H_3]CoCp$	black		B, H, IR, MS	51
$CpCo(CH_3)_2C_2B_3H_3Fe(CO)_3$	red-brown		B, H, IR, MS	52
2,4-C_2B_3 ring systems (nonadjacent carbon atoms)				
1,7,2,4-$Cp_2Co_2C_2B_3H_5$	dark green		B, H, IR, MS; E	49, 84; 19
2-R-1,7,2,4-$Cp_2Co_2C_2B_3H_4$				
R = CH_3	dark green		B, H, IR, MS; X	53; 88
R = $(CH_3)_3Si$	green		B, H, MS	41a
R = C_6H_5	green		B, H, MS	41a
1,7,2,4-$(CH_3C_5H_4)CpCo_2C_2B_3H_5$	green		B, H, MS	41a
1,7,2,4-$(C_2H_5C_5H_4)CpCo_2C_2B_3H_5$	green		B, H, MS	41a
1,7,2,4-$[(CH_3)_3Si\text{-}C_5H_4]CpCo_2C_2B_3H_5$	green		B, H, MS	41a
C_4B (borole) ring systems				
2-C_2H_5-6-C_6H_5-$(CO)_6Mn_2C_4BH_3$	brown-red	119—120	B, H, IR, MS, X	90
C_3B_2 (diborolene) ring system				
$Cp_2FeCoC_3(C_2H_5)_2(CH_3)B_2(C_2H_5)_2$	green	>270 dec	B, H, MS	91
$Cp_2Ni_2C_3(C_2H_5)_2(CH_3)B_2(C_2H_5)_2$	deep green		MS, MAG	80b
$Cp_2CoNiC_3(C_2H_5)_2(CH_3)B_2(C_2H_5)_2$	green		MS	80b
$Cp_2Co_2C_3(C_2H_5)_2(CH_3)B_2(C_2H_5)_2$	yellow-green		MS	80b
C_2B_2S (thiadiborolene) ring systems				
$(CO)_6Mn_2C_2(C_2H_5)_2B_2(CH_3)_2S$	orange-red	183—184	B, H, IR, MS, X	92
$Cp_2Fe_2C_2(C_2H_5)_2B_2(CH_3)_2S$	dark green	230 dec	B, H, MS, X	93
$[C_2(C_2H_5)_2B_2(CH_3)_2S]_3Co_2$	shiny black	172—173	B, H, MS	94

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[a] Cp = (η^5-C_5H_5). Within each ligand class, complexes are grouped by metals. [b] B = ^{11}B NMR; ^{1}H = ^{1}H NMR; IR = infrared data; MS = mass spectroscopic data; X = X-ray crystallographic data; E = electronic spectral data; MAG = magnetic susceptibility.

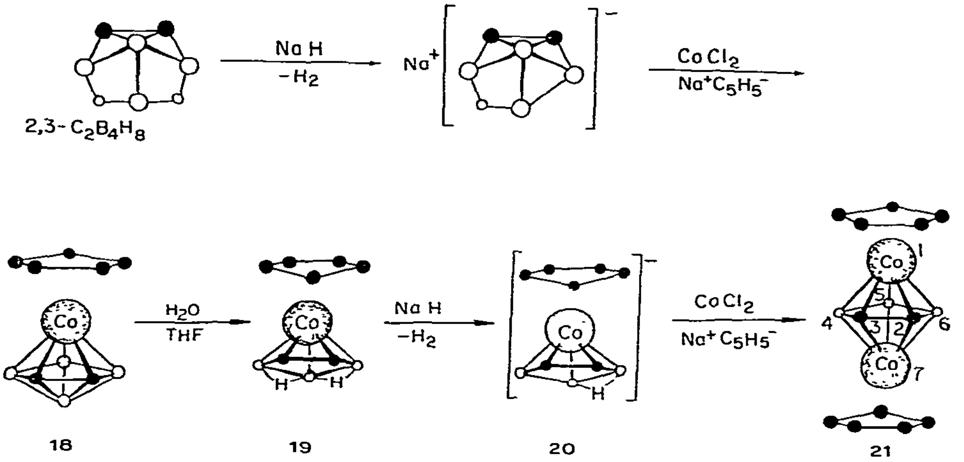

Fig. 11. Synthesis of Co^{3+} complexes of $C_2B_4H_6^{2-}$, $C_2B_3H_7^{2-}$, $C_2B_3H_6^-$ and $C_2B_3H_5^{4-}$ (**18**, **19**, **20**, **21**). ● CH; ○ BH.

by hydride attack; this is identical to the behavior of the corresponding carborane, 2,3-$C_2B_4H_8$ [50], also shown in Fig. 11. Treatment of the cobaltacarborane anion **20** with $CoCl_2$ and NaC_5H_5, followed by workup in aqueous media yields the triple-decked complex 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, **21** (Fig. 11); in this process the remaining bridge proton in **20** is lost, but its fate has not been determined [49]. The triple-decked species will be discussed in detail in Section E(ii) below.

In one type of $C_2B_3H_7^{2-}$ (or $(CH_3)_2C_2B_3H_5^{2-}$) complex, the B—H—B bridges are not reactive toward NaH. These compounds contain a metal-bound proton which is preferentially attacked by hydride ion in THF, leaving the bridging hydrogens unaffected [51]. As shown in Fig. 12, the removal of the Co—H proton in **23** is reversible (it should be noted that the cobaltocenium-substituted species **17**, depicted in Fig. 10, is a derivative of **23**). The conversion of **22** to **23** is another example of the degradation of a pyramidal C_2B_4 to a planar C_2B_3 ligand, in effect similar to the formation of **15** from **16** although the experimental conditions are different. (However, in contrast to the sequences in Figs. 11 and 12, iron complexes of $(CH_3)_2C_2B_4H_4^{2-}$ are not degraded to the analogous C_2B_3 complexes by base hydrolysis [52].)

(3) Complexes containing one pyramidal $C_2B_4H_4R_2^{2-}$ ligand

Metallocarboranes incorporating $C_2B_4H_6^{2-}$ ligands of two isomeric types have been prepared, their structures differing in the location of cage carbon atoms (Table 3). Complexes of 2,3-$C_2B_4H_6^{2-}$ contain adjacent carbons in the equatorial ring, and are prepared from 2,3-$C_2B_4H_8$ as illustrated in Figs. 9, 11, and 12; complexes of 2,4-$C_2B_4H_6^{2-}$ have non-adjacent carbons in the equatorial ring, and are obtained either by thermal isomerization of 2,3-$C_2B_4H_6^{2-}$ complexes[53] or by direct synthesis from a carborane containing nonvicinal

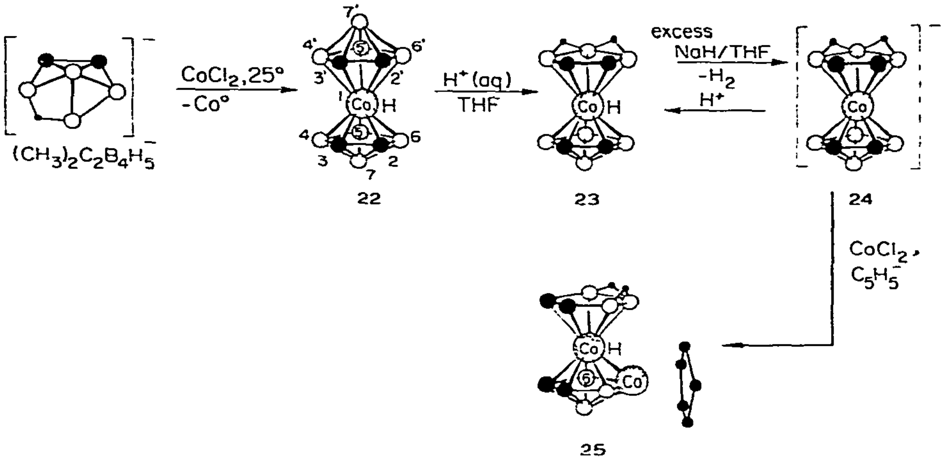

Fig. 12. Synthesis of bis(carboranyl) complexes of Co^{3+} involving the planar [2,3-(CH$_3$)$_2$C$_2$B$_3$H$_5$]$^{2-}$, pyramidal [2,3-(CH$_3$)$_2$C$_2$B$_4$H$_4$]$^{2-}$ and pyramidal [2,4,5-(η^5-C$_5$H$_5$)Co-(CH$_3$)$_2$C$_2$B$_3$H$_3$]$^{2-}$ ligands (**22**, **23**, **24**, **25**). ● CCH$_3$; ○ BH.

carbons, such as octahedral 1,6-C$_2$B$_4$H$_6$ or 2,4-C$_2$B$_5$H$_7$ [49,54]. C-substituted derivatives of both isomeric types can be synthesized from the appropriate C-substituted carborane.

Direct synthesis of 2,3-C$_2$B$_4$H$_6^{2-}$ complexes by reaction of 2,3-C$_2$B$_4$H$_8$ with metal reagents has been accomplished in a few cases, such as the insertion of iron [42,43] (Fig. 9), gallium [55,56] and indium [56]:

$$\mathrm{M(CH_3)_3} + 2,3\text{-}\mathrm{C_2B_4H_8} \xrightarrow{\Delta} \mathrm{CH_3MC_2B_4H_6} \qquad \mathrm{M = Ga,\ In}$$

However, the treatment of the C$_2$B$_4$H$_7^-$ ion or its derivatives with metal reagents has been much more generally successful, yielding numerous 2,3-R$_2$C$_2$B$_4$H$_4^{2-}$ complexes of iron, cobalt, nickel, tin and lead [49,57a] (Table 3). X-ray crystallographic studies have been conducted on several of these compounds, including 1-CH$_3$-1,2,3-GaC$_2$B$_4$H$_6$, **26** [56], shown in Fig. 13; 1,2,3-(η^5-C$_5$H$_5$)Co(CH$_3$)$_3$C$_2$B$_4$H$_4$(a C,C′-dimethyl derivative of **18**) (see Fig. 11) [58], and the cobaltocenium—metallocarborane species shown in Fig. 10 [46]. The structural parameters of the C$_2$B$_4$H$_6^{2-}$ ligands are similar in these complexes, except that the gallium atom in **26** is displaced from the centroid of the C$_2$B$_3$ ring and is ~0.2 Å closer to the boron than to the carbon atoms [56]. The effect is proposed to be of electronic origin, and resembles the slip-distortions observed in certain electron-rich transition metal complexes of the C$_2$B$_9$H$_{11}^{2-}$ ion [59]. In all three structures the carboranyl C—C link is short (1.46—1.49 Å), though not as short as in the C$_2$B$_3$H$_7^{2-}$ and (CH$_3$)$_2$C$_2$B$_3$H$_5^{2-}$ complexes referred to earlier (1.41—1.42 Å); as in the latter species, some degree of carbon—carbon multiple bonding is apparent in the complexes of C$_2$B$_4$ ligands.

TABLE 3

Complexes of pentagonal pyramidal ligands

Complex[a]	Color	M.p. (°C)	Data[b]	Ref.
	Complexes with one pyramidal ligand			
C_2B_4 pyramidal ligands				
$1,2,3\text{-}(CO)_3FeC_2B_4H_6$	orange	<20	B, H, IR, MS	42, 43
$1,2,4\text{-}(CO)_3FeC_2B_4H_6$	orange		B, H, IR, MS	43
$1,2,3\text{-}CpFe^{III}C_2B_4H_6$	brown		B, H, IR, MS MAG[c], PR[d]	43
$1,2,4\text{-}CpFe^{III}C_2B_4H_6$	brown		MS	43
$\sigma\text{-}C_{10}H_7\text{-}1,2,4\text{-}CpFe^{III}C_2B_4H_5$	green		B, H, MS	43
$5\text{-}[2'\text{-}(2',4'\text{-}C_2B_5H_6)]\text{-}1,2,4\text{-}CpFeC_2B_4H_5$	lime green		B, H, IR, MS	43
$1,2,3\text{-}CpFe(H)C_2B_4H_6$	red-orange		B, H, IR, MS	43
$1,2,4\text{-}CpFe(H)C_2B_4H_6$	red-orange		B, H, IR, MS	43
$\sigma\text{-}(2',4'\text{-}C_2B_5H_6)\text{-}1,2,4\text{-}CpFe(H)C_2B_4H_5$			MS	43
$1,2,3\text{-}CpCoC_2B_4H_6$	orange		B, H, IR, MS	49
$2\text{-}CH_3\text{-}1,2,3\text{-}CpCoC_2B_4H_5$	orange		B, H, IR, MS	49
$2,3\text{-}(CH_3)_2\text{-}1,2,3\text{-}CpCoC_2B_4H_4$	dark orange		B, H, IR, MS; X	49; 58
$2\text{-}[(CH_3)_3Si]\text{-}1,2,3\text{-}CpCoC_2B_4H_5$	orange		B, H, IR, MS	41b
$B\text{-}[(CH_3)_3Si]\text{-}1,2,3\text{-}CpCoC_2B_4H_5$	orange		B, H, IR, MS	41b
$B\text{-}Br\text{-}1,2,3\text{-}CpCoC_2B_4H_5$	orange		B, H, IR, MS	41b
$1,2,4\text{-}CpCoC_2B_4H_6$	yellow		B, H, IR, MS	54
$3\text{-}(2\text{-}C_{10}H_7)\text{-}1,2,4\text{-}CpCoC_2B_4H_5$	yellow		B, H, IR, MS	54
$5\text{-}(1\text{-}C_{10}H_7)\text{-}1,2,4\text{-}CpCoC_2B_4H_5$	yellow		B, H, IR, MS	49
$3\text{-}(2',4'\text{-}C_2B_5H_6)\text{-}1,2,4\text{-}CpCoC_2B_4H_5$	yellow		B, H, IR, MS	54
$[2,3\text{-}(CH_3)_2C_2B_4H_4]CoH[2,3\text{-}(CH_3)_2C_2B_3H_5]$	yellow		B, H, IR, MS	51
$(CH_3)_4N^+[2,3\text{-}(CH_3)_2C_2B_4H_4]Co[2,3\text{-}(CH_3)_2C_2B_3H_5]^-$	yellow	259–262	B, H, IR, MS	51
$5\text{-}[CpCo(C_5H_4)]\text{-}[2,3\text{-}(CH_3)_2C_2B_4H_3]Co[2,3\text{-}(CH_3)_2C_2B_3H_5]$	red-brown		B, MS, X	46
$\sigma\text{-}(CH_2)_4O\text{-}[2,3\text{-}(CH_3)_2C_2B_4H_3]Co[2,3\text{-}(CH_3)_2C_2B_3H_5]$	yellow		B, H, IR, MS	46
$1,2,4\text{-}[(C_6H_5)_3P]_2NiC_2B_4H_6$	red-orange		B, H, IR, MS, E	19

1,2,3-$[(C_6H_5)_2PCH_2]_2NiC_2B_4H_6$	brown		B, H, IR, MS	49
1-CH_3-1,2,3-$GaC_2B_4H_6$	white	33.5—34.5	B, H, IR, MS, X	55, 56
1-CH_3-2,3-$(CH_3)_2$-1,2,3-$GaC_2B_4H_4$	white		B, H, IR, MS	57b
1-CH_3-1,2,3-$InC_2B_4H_6$	white		B, H, IR, MS	56
1,2,3-$SnC_2B_4H_6$	white		B, H, IR, MS	57a
2,3-$(CH_3)_2$-1,2,3-$SnC_2B_4H_4$	white		B, H, IR, MS	57a
1,2,3-$PbC_2B_4H_6$	white		B, H, IR, MS	57a
2,3-$(CH_3)_2$-1,2,3-$PbC_2B_4H_4$	white		B, H, IR, MS	57a
C_3B_3 pyramidal ligands				
2-CH_3-1,2,3,4-$(CO)_3MnC_3B_3H_5$	yellow	<20	B, H, IR, MS	74
2,3-$(CH_3)_2$-1,2,3,4-$(CO)_3MnC_3B_3H_5$	yellow-orange	<20	MS	74
C_2B_3M pyramidal ligands				
1,2,3,5-$(CO)_6Fe_2C_2B_3H_5$	orange		B, H, IR, MS	19
1,2,3,5-$Cp_2Co_2C_2B_3H_5$	dark green		B, H, IR, MS, E	19
1,2,4,5-$Cp_2Co_2C_2B_3H_5$	dark green		B, H, IR, MS, E	53
4,5-$(CH_3)_2$-1,2,4,5-$Cp_2Co_2C_2B_3H_5$	green		B, H, IR, MS	51
$[CpCo(CH_3)_2C_2B_3H_3]CoH[2,3\text{-}(CH_3)_2C_2B_3H_5]$	red-brown		B, H, IR, MS	51
$CpCoFeH(CH_3)_2C_2B_3H_3$	brown		B, H, IR, MS	67
Complexes with two pyramidal ligands				
$[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$	red		B, H, IR, MS	52
$(CH_3)_4N^+\{[2,3\text{-}(CH_3)_2C_2B_4H_4]_2Fe^{III}\}^-$	red-orange	243—246 dec	B, H, IR, MS	52
$[2,3\text{-}(CH_3)_2C_2B_4H_4]FeBH[2,3\text{-}(CH_3)_2C_2B_3H_3CoCp]$	dark green		B, H, IR, MS, X	52,72
$[2,3\text{-}(CH_3)_2C_2B_4]_2FeGe$	red-brown		B, H, IR, MS	67
$[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeSn$	dull red		B, H, IR, MS	67
$[2,3\text{-}(CH_3)_2C_2B_4H_4]FeH_2[2,3\text{-}(CH_3)_2C_2B_3H_3CoCp]$	brown-violet		B, H, IR, MS	67
$(CH_3)_4N^+[(2,4\text{-}C_2B_4H_6)_2Co]^-$	golden		B, H, IR, MS	49
$[2,3\text{-}(CH_3)_2C_2B_4H_4]_2CoH$	bright red		B, H, IR, MS	51
$CpCo[(CH_3)_2C_2B_3H_3]CoH[(CH_3)_2C_2B_3H_3]CoCp$	black		B, H, IR, MS	51

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[a] Cp = (η^5-C_5H_5). Within each ligand class, compounds are grouped by metals. [b] See footnote in Table 1. [c] Magnetic susceptibility.
[d] Paramagnetic resonance data.

Insertion of metal atoms into the open face of a $C_2B_4H_7^-$ ion probably occurs via initial linkage at the vacant (non-protonated) B--B edge on the base of the pyramid, from which position the metal can move to the center of the face and adopt full η^5-coordination with the ligand. In one case, a transition-metal bridged intermediate has actually been isolated, and subsequently converted to *closo*-metallocarboranes incorporating the $2,3\text{-}C_2B_4H_6^{2-}$ ligands [43] (Fig. 14). The species 28 and 29 can be reversibly interconverted via acid--base and redox chemistry:

$$\underset{\textbf{28}\text{ red-orange}}{1,2,3\text{-}(\eta^5\text{-}C_5H_5)Fe^{II}(H)C_2B_4H_6} \underset{HCl}{\overset{NaH}{\rightleftharpoons}} \underset{\textbf{30}\text{ orange}}{(\eta^5\text{-}C_5H_5)Fe^{II}C_2B_4H_6^-} \underset{Na/Hg}{\overset{O_2}{\rightleftharpoons}}$$

$$\underset{\textbf{29}\text{ brown}}{1,2,3\text{-}(\eta^5\text{-}C_5H_5)Fe^{III}C_2B_4H_6}$$

Other B—M—B bridged complexes analogous to 27 have been prepared, where M = Si, Ge, Sn, Pb, B, Al, Ga, Rh, Au and Hg [60—63], but in no case was

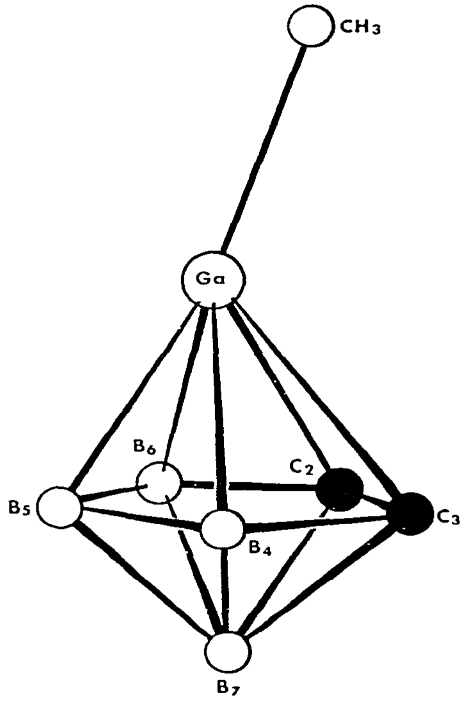


Fig. 13. Established structure of $1\text{-}CH_3\text{-}1,2,3\text{-}GaC_2B_4H_6$ (26). ● CH; ○ BH.

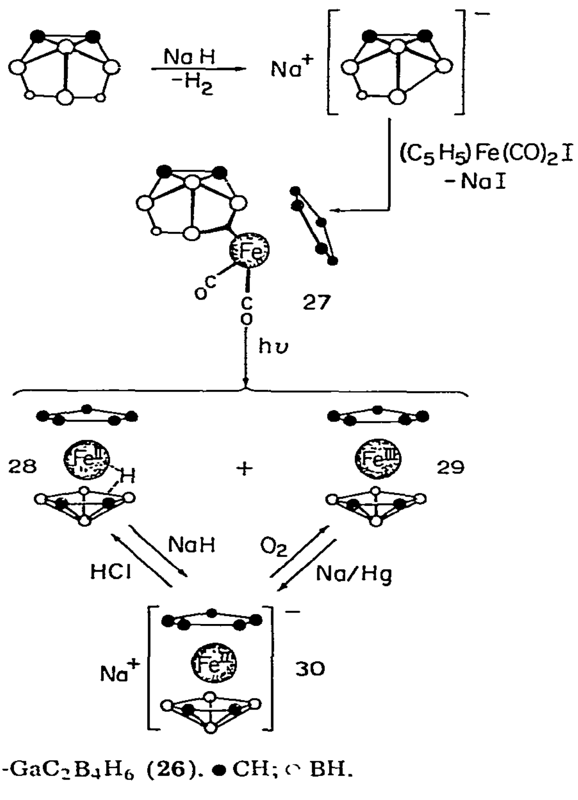


Fig. 14. Synthesis of $\mu\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]\text{-}2,3\text{-}C_2B_4H_7$ (27) and its conversion to Fe(II) and Fe(III) *closo*-ferracarboranes (28, 29, 30). ● CH; ○ BH.

conversion to the corresponding *closo*-metallocarborane observed, probably because the metal-bound ligands in these compounds (usually CH_3, C_6H_5 or $P(C_6H_5)_3$) are less easily displaced than are the CO groups in **27**.

The insertion of cobalt into $C_2B_4H_7^-$ occurs readily, as shown in Figs. 11 and 12, and nickel(II) complexes form similarly [49]. The same anion, as well as its C,C′-dimethyl derivative $(CH_3)_2C_2B_4H_5^-$, reacts with $SnCl_2$ and with $PbBr_2$ to give $:MR_2C_2B_4H_4$ species (M = Sn, Pb; R = H, CH_3) which have been characterized as pentagonal bipyramidal *closo* cages containing a "bare" tin or lead atom [57a]. (Higher homologues with the composition $MC_2B_9H_{11}$ have also been reported [64,65].)

When the orange compound 1,2,3-(η^5-C_5H_5)$CoC_2B_4H_6$ (**18**, Fig. 11), or its C,C′-dimethyl derivative, is heated to 400°, a clean isomerization to the yellow 1,2,4 isomer **31** (or its derivative) takes place [53] (Fig. 15). The same complex, **31**, is also produced in the reaction of 2,4-$C_2B_5H_7$ with sodium naphthalide in THF with subsequent addition of $CoCl_2$ and NaC_5H_5 [54]; although other mono- and dicobaltaboranes are obtained, **31** is the major product (20—25% yield). Still another route to **31** is the reaction of 1,6-$C_2B_4H_6$ with (η^5-C_5H_5)$Co(CO)_2$ at 230°/60°C in a hot—cold reactor [19]. Complexes of the 2,4-$C_2B_4H_6^{2-}$ ligand with iron and nickel have been similarly prepared [19]:

$$1,6\text{-}C_2B_4H_6 \xrightarrow{Fe(CO)_5} 1,2,4\text{-}(CO)_3FeC_2B_4H_6$$

32 orange liquid

$$1,6\text{-}C_2B_4H_6 \xrightarrow{(\pi\text{-}C_2H_4)Ni[P(C_6H_5)_3]_2} [1,2,4\text{-}(C_6H_5)_3P]_2NiC_2B_4H_6$$

33 red-orange plates

The reaction of 2,4-$C_2B_5H_7$ with sodium naphthalide, $FeCl_2$, and NaC_5H_5 is complex [43], generating both iron(II) and iron(III) species incorporating the 2,4-$C_2B_4H_6^{2-}$ ligand; the major product is a linked-cage complex, 1,2,4-(η^5-C_5H_5)$Fe^{III}C_2B_4H_5$-(2,4-$C_2B_5H_6$), **34**.

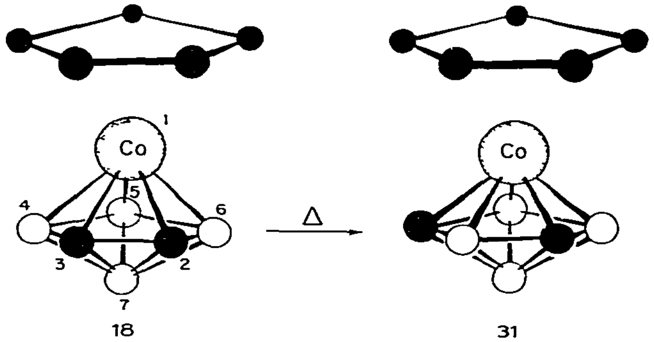


Fig. 15. Thermal rearrangement of 1,2,3-(η^5-C_5H_5)$CoC_2B_4H_6$ (**18**) to 1,2,4-(η^5-C_5H_5)$CoC_2B_4H_6$ (**31**). ● CH; ○BH.

(4) Complexes containing two $C_2B_4H_4R_2^{2-}$ ligands. The oxidative ligand fusion reaction

The reaction of the $(CH_3)_2C_2B_4H_4^{2-}$ ion with $CoCl_2$ or FeH_2 in THF *in the absence of $C_5H_5^-$* yields, respectively, the red solid bis-carboranyl complexes $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2Co^{III}H$, **22** (Fig. 12) and $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2Fe^{II}H_2$, **35**. Both complexes are air-sensitive (highly unusual for metallocarboranes) and are readily oxidized by air or other agents, yielding the novel tetracarbon carborane $(CH_3)_4C_4B_8H_8$, **36**, a colorless, air-stable solid [51,52,66,67]. Figure 16 illustrates the sequence for the iron system. These reactions occur in high yield at room temperature, and involve the oxidative fusion of two $(CH_3)_2C_2B_4H_4^{2-}$ ligands with excision of the metal (the metallic product may be an oxide, hydroxide, free metal, or mixture of these depending on the experimental circumstances). The net process is therefore

$$2[(CH_3)_2C_2B_4H_4]^{2-} \xrightarrow{[O]} \underset{\mathbf{36}}{(CH_3)_4C_4B_8H_8}$$

and can be envisioned as occurring via face-to-face merger of the two pyramidal units. The structures of **36** and its iron complex precursor **35** (Fig. 16) have been established crystallographically [68,69], and the fusion process is easy to visualize from a comparison of the two.

Recent work has shown that conversion of small cages to large cages via oxidative fusion occurs in other systems as well [67,70,71]. For example, if one subjects the cobaltacarborane **19** or its anion **20** (Fig. 11) to strongly basic conditions, "fused" cobaltacarboranes containing $Co_2C_4B_6$ frameworks are formed [71] (Fig. 17). In this case the fusion occurs in at least two different ways to give the products shown (a third, unidentified product isomeric with **37** and **38** is also obtained). When the dimethyl-substituted anion $[1,2,3\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_4]^-$ is treated in the same way, a single isomer, corre-

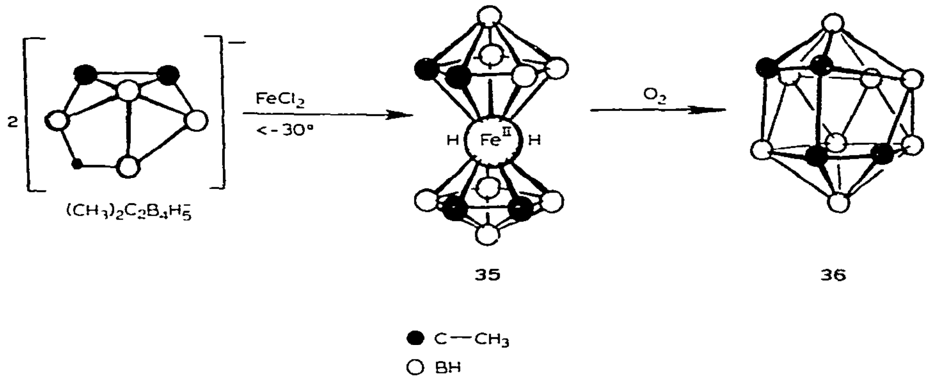


Fig. 16. Synthesis of $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH$ (**35**) and oxidative fusion to form $(CH_3)_4C_4B_8H_8$ (**36**). Structures of **35** and **36** are established.

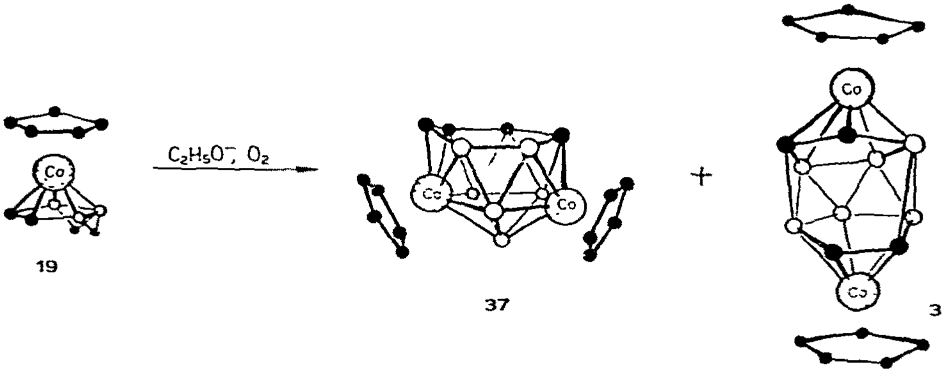


Fig. 17. Oxidative fusion of 1,2,3-$(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$ (**19**) to isomers of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ (**37** and **38**). Established structures of **37** and **38** are shown. ● CH; ○ BH; • H.

sponding to the C-tetramethyl derivative of **38**, is formed [71]. It will be noted that **38** (and its C-tetramethyl derivative) is structurally analogous to the carborane **36**, with the important difference that the central C—C distance corresponds to a strongly bonding interaction in **36** (1.53(1) Å) but is distinctly non-bonding in **38** (2.791(5) Å). Thus, the cobalt atoms appear to play a significant role in dictating the gross structure of the fused product; a simple rationale is that the skeletal bonding in **36** is more delocalized than in **38**, due to metal—carborane bonding interactions in the latter species.

The bis-carboranyl iron complex **35** exhibits other novel chemistry in addition to the air-oxidation to **36** described above; for example, the treatment of **35** with $(\eta^5\text{-}C_5H_5)Co(CO)_2$, or of its conjugate base anion with germanium or tin halides, generates the peculiar complexes shown in Fig. 18, in which a boron or metal atom occupies a "wedging" location between the pyramidal ligands [67]. The structure of **39a** was determined crystallographically [72]: those of **39b** and **39c** were proposed from NMR data [67] and by analogy with the known geometry of **39a**. These structures can be rationalized in terms of skeletal electron-counting arguments (Section B), since in each case there is a deficiency of two electrons (relative to a normal system which would have 7- and 8-vertex *closo* cages linked at the iron atom), resulting in capped polyhedral geometry [5—7]. Complex **39a** (and perhaps **39b** and **39c**) can be regarded as "partially fused" systems whose formation involves an incomplete oxidative fusion process; thus, it may be that an intermediate something like **39a** is involved in the conversion of **22** and **35** to the tetracarbon system **36** (Fig. 16).

(5) Complexes of pyramidal $C_3B_3H_6^-$ derivatives

The three-carbon carborane 2,3,4-$C_3B_3H_7$, a pyramidal system isoelectronic with 2,3-$C_2B_4H_8$, has been characterized in the form of several C-alkyl

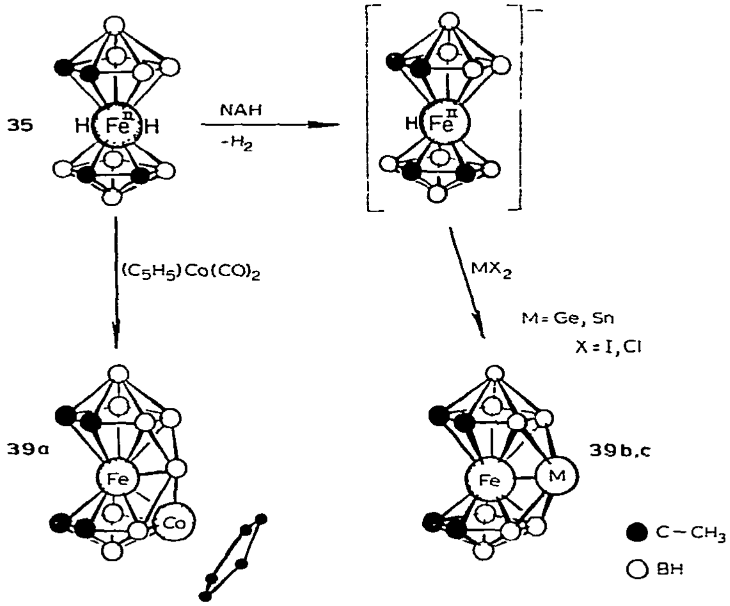
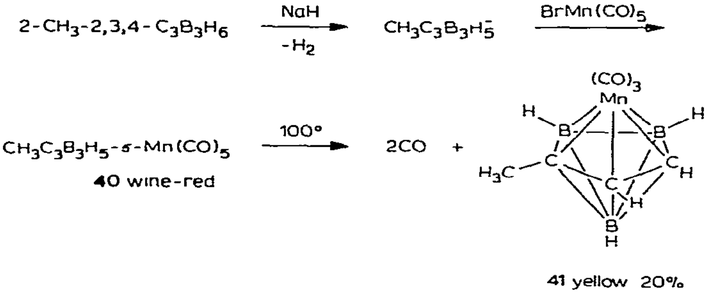


Fig. 18. Insertion of metals into $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$ (**35**) and its conjugate base anion. The structure of **39a** is known from a crystallographic study; those of **39b** (M = Ge) and **39c** (M = Sn) are proposed from NMR data.

derivatives (the parent species has never been isolated) [73]. Removal of the lone bridging proton by treatment with NaH in THF generates the monoanion, which contains a planar C_3B_2 face capable of η^5-bonding to a transition metal atom; thus, reaction of the anion with $BrMn(CO)_5$ in diglyme produces a red intermediate **40**, which in turn is converted at 100°C to a yellow η^5-complex, **41**, with loss of carbon monoxide [74].

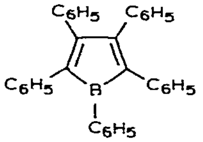


The $Mn(CO)_5$ group in **40** is presumably linked to the cage via a 3-center B—Mn—B bond analogous to the structure of **27** (Fig. 14), but this species has not been characterized. The *closo*-metallocarborane **41**, an analogue of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ (cymantrene), is proposed to have a pentagonal bipyramidal structure with Mn in one apex and three adjacent carbon atoms in the equator; the same compound has also been obtained in 85—90% yield by direct reaction of the neutral carborane 2-CH$_3$-2,3,4-C$_3$B$_3$H$_6$ with Mn$_2$(CO)$_{10}$ at 175—200° [74].

Although C$_3$B$_3$H$_6^-$ and its derivatives are attractive ligands for sandwich-bonding to metals (in that the bonding face is unencumbered by bridge hydrogens) no other complexes have been prepared in the seven years since **41** and its C,C'-dimethyl derivative were first reported. This reflects the difficulty of preparing the tricarbon carboranes, for which the reaction of the unstable boranes B$_4$H$_{10}$ or B$_5$H$_{11}$ with alkynes [73] is the only known synthesis. Similar difficulties have discouraged the preparation of metal complexes of 2,3,4,5-C$_4$B$_2$H$_6$ [75], a pyramidal carborane which is analogous to C$_3$B$_3$H$_7$ and C$_2$B$_4$H$_8$; though C$_4$B$_2$H$_6$ has a planar face which should readily accept η^5-complexation with metal atoms, no such compounds have been reported. However, a number of complexes derived from the closely related C$_4$BH$_5^{2-}$ ion are known, as described in the following section.

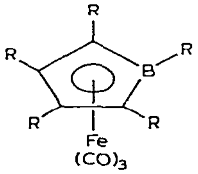
(6) Complexes of cyclic planar $C_4BH_5^{2-}$ derivatives

The neutral ring compound borole (C$_4$BH$_5$) is unknown, but its pentaphenyl derivative, **42**, has been characterized as a reactive green solid [76]. This compound is a 4π-electron, "antiaromatic" cyclic system which is isoelectronic

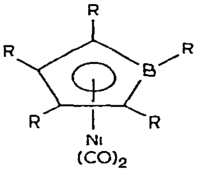


42

with (C$_6$H$_5$)$_5$C$_5^+$, and accordingly can be stabilized by η^5-complexation with metals or other donors capable of supplying two electrons. Thus, reaction of Fe$_2$(CO)$_9$ or Ni(CO)$_4$ in toluene affords complexes **43** and **44** respectively [77]. These complexes incorporate the formal C$_4$B(C$_6$H$_5$)$_5^{2-}$ cyclic planar anion,



43 pale yellow

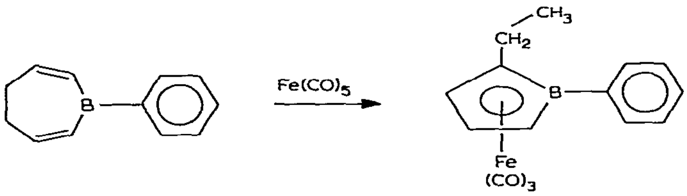


44 wine-red

R = C$_6$H$_5$

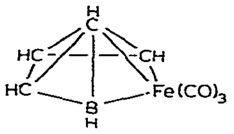
a 6π-electron ligand which is, of course, analogous to C$_5$(C$_6$H$_5$)$_5^-$ and C$_5$H$_5^-$. The parent species, C$_4$BH$_5^{2-}$, is directly related to the pyramidal carborane series C$_n$B$_{6-n}$H$_{10-n}$ which includes CB$_5$H$_9$, C$_2$B$_4$H$_8$, C$_3$B$_3$H$_7$ and C$_4$B$_2$H$_6$ [78]; for example, C$_4$B$_2$H$_6$ can be viewed as an η^5-complex of BH^{2+} with planar C$_4$BH$_5^{2-}$.

An alternative route to metal—borole complexes [77] utilizes 1-phenyl-4,5-dihydroborepin, **45**, which on treatment with Fe(CO)$_5$ in boiling mesitylene undergoes ring contraction to give the iron tricarbonyl species **46**. A structurally different complex formulated as 2,1,3,4,5-(CO)$_3$FeC$_4$BH$_5$, **47**, has



45 **46**

been prepared photolytically from (η^4-C_4H_4)Fe(CO)$_3$ and B_5H_9 [79]. The structure shown was assigned from NMR data; conceivably, it might undergo thermal rearrangement to place the iron atom in the apical position, thus



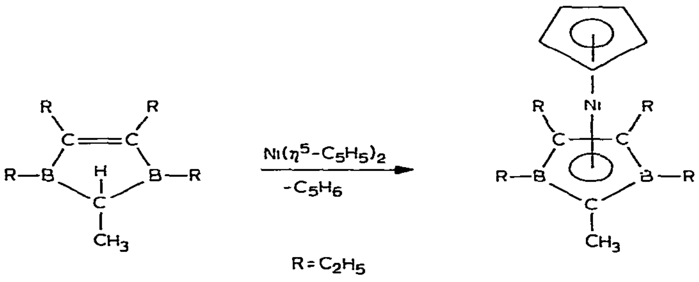
47

forming the parent species of **46**. It is useful to note that complexes **43**, **44**, **46**, and **47** are all 16-skeletal electron, 6-vertex *nido* cages, in agreement with the electron-counting rules outlined in Section B. If the number of skeletal electrons in any of these molecules is reduced by two, closure to an octahedral ($2n + 2$)-electron system is expected. One way to remove two electrons is to replace two carbons by two borons; if this is done in **47**, the result is the known complex $(CO)_3FeC_2B_3H_5$, **4**, whose apparent structure [19] is indeed octahedral, as shown in Fig. 3.

The borole ring system is capable of η^5-bonding to two metals simultaneously to form triple-decked sandwich species, as described in Section E(ii).

(7) Complexes of cyclic planar $C_3B_2H_5^{3-}$ derivatives

Metal sandwich compounds derived from the 1,3-diborolene system have been reported [80a, b]. The reaction of 2-methyl-1,3,4,5-tetraethyl-1,3-diborolene, **48**, with nickelocene at 180° produced brownish-red **49**, the structure of which was deduced from NMR and mass-spectroscopic data. Again,

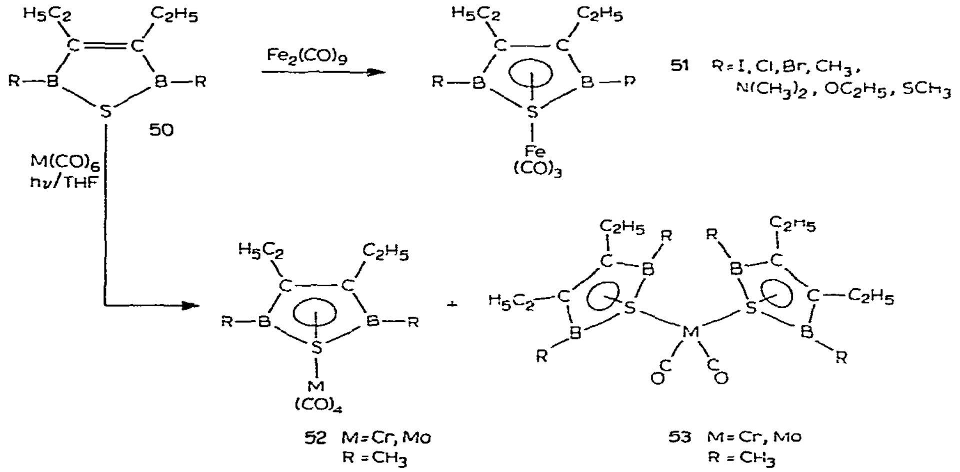


48 **49**

the 16-electron NiC_3B_2 *nido* cage system satisfies the electron-count rules since (η^5-C_5H_5)Ni, C and B are respectively 3-, 3- and 2-electron donors.

(8) Complexes of cyclic planar $C_2B_2SH_4^{2-}$ derivatives

The thiadiborolene ring system, isoelectronic with 1,3-diborolene, has been shown to form transition metal η^5-complexes readily. The majority of those reported are dimetallic triple-decked species, described below, but a few mononometallic *nido*-type complexes have been prepared. Substituted 1,2,5-thiadiborolenes, **50**, reacted with $Fe_2(CO)_9$ to give stable thiadiborolenetricarbonyl iron complexes, **51**; the unstable 2,5-dihydro- and 2-fluoro-5-iodo derivatives of **51** were also prepared [81]. Reaction of the same substrate with chromium or molybdenum hexacarbonyls under UV light [82] generated complexes **52** and **53**. X-ray structural studies of the ligand **50** (R = $N(CH_3)_2$) and of complex **51** (R = $N(CH_3)_2$) revealed that the B—C distances in the ligand are shortened substantially (by 0.04 Å) upon complexation; at the same time, the C—C distance is lengthened by 0.09 Å [81]. These observations reflect the effects of electron donation from the $Fe(CO)_3$ unit to the ring (as well as back-donation into metal orbitals from the ligand), producing significant electron-delocalization within the ligand itself. Here again the structures of **51**, **52**, and **53** obey the Wade electron-counting formalism.



50

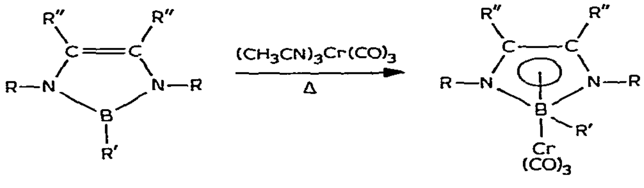
51 R=I, Cl, Br, CH_3, $N(CH_3)_2$, OC_2H_5, SCH_3

52 M=Cr, Mo
R = CH_3

53 M=Cr, Mo
R = CH_3

(9) Complexes of cyclic planar $C_2BN_2H_5$ derivatives

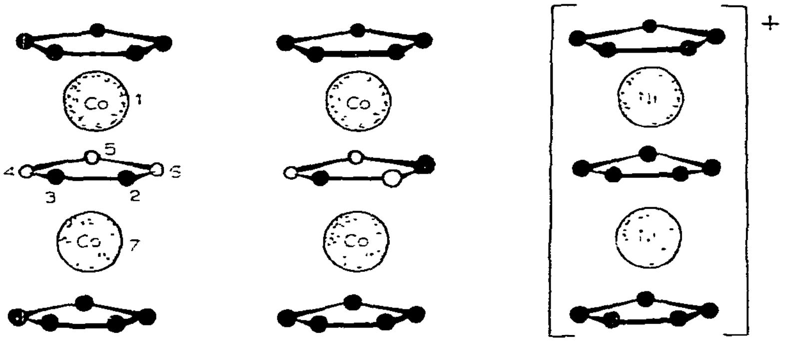
A further example of a heterocyclic ring isoelectronic with $C_5H_5^-$ is the diazaboroline system, **54**. One example of a metal η^5-complex has been prepared from reaction of the N,N'-bis(t-butyl)-B-methyl-diazaboroline with $(CH_3CN)_3Cr(CO)_3$ at 85° in dioxane [83].



54

55

R=$C(CH_3)_3$, R'=CH_3, R''=H



21(56) 57 58

Fig. 19. Triple-decked sandwich complexes, **21**, **57** and **58**, containing the 2,3-$C_2B_3H_5^{4-}$, 2,4-$C_2B_3H_5^{4-}$ and $C_5H_5^-$ central ligands. Complex **56** is a 2-methyl derivative of **21**. ● CH; ○ BH.

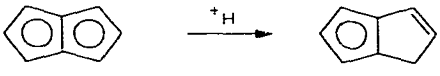
With a framework electron count of 16 (B, C, N and $Cr(CO)_3$ being 2-, 3-, 4- and 0-electron donors respectively), complex **55** is a 16-electronic *nido* system as expected.

(ii) Systems with two η⁵-bonded metal atoms (triple-decked sandwiches)

(1) Complexes of the cyclic planar 2,3-$C_2B_3H_5^{4-}$ ligands and derivatives

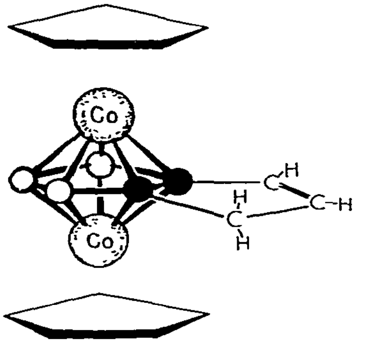
Two isomeric forms of the $C_2B_3H_5^{4-}$ system are possible, having the skeletal carbon atoms adjacent to each other in one isomer and non-adjacent in the other (in the $C_2B_3H_7^{2-}$ ring system, described above, only the adjacent-carbon (2,3-) isomer is possible because of the presence of two bridging protons, which can span B—B but not B—C or C—C interactions). Both $C_2B_3H_5^{4-}$ ligands are bifunctional and can form pentahapto links with two metal atoms simultaneously, creating triple-decked sandwich structures. The first complexes of the 2,3- and 2,4-$C_2B_3H_5^{4-}$ system (Fig. 19) were prepared in our laboratory in 1972, and the initial report of these compounds [84] included X-ray structural confirmation of the triple-decked sandwich geometry of **56** (a C-methyl derivative of **21**, Fig. 11) by Palenik and Mathew. Complex **56** was the first structurally established example of a true triple-decked sandwich compound; a triple-decked structure had been postulated earlier for the $(C_5H_5)_3Ni_2^+$ ion **58** by Werner and Salzer [2,85] and this was subsequently proved correct in an X-ray study by Dubler et al. [86]. Since then, numerous other triple-decked complexes incorporating 2,3- and 2,4-$C_2B_3H_5^{4-}$ and other ligands have been prepared (see following sections), but the dinickel species **58** remains the only characterized example of a triple-decker with $C_5H_5^-$ as the central ligand.

Complexes of 2,3-$C_2B_3H_5^{4-}$ and its derivatives have been prepared [41,49, 84] from the corresponding complexes of $C_2B_3H_7^{2-}$ (Fig. 11). A very different synthetic route produced the red, C,C′-(1,3-propenylene)-disubstituted derivative, **59**, shown in Fig. 20; a small quantity of **59** was isolated from the reaction of $B_5H_8^-$ with $CoCl_2$ and NaC_5H_5 in cold THF and characterized from ^{11}B and ^1H NMR data [4b] and an X-ray structural study [48]. This synthesis represents the only known instance of insertion of a cyclopentadienyl ring into a borane cage system, and is also one of the few known cases of metallocarborane synthesis from a metalloborane. The crystallographically determined structural parameters for 59 [48] and the C-monomethyl derivative 56 [84] are nearly identical except for a slightly longer (by 0.04 Å) C—C bond distance in the central ring of 59; this probably reflects the fact that the ring carbon atoms in 59 participate not only in the electron-delocalized C_2B_3 ring, but also in a C_5 ring which is partially delocalized, thus lowering the C—C bond order relative to 56. In both 56 and 59, the central C_2B_3 ring is planar and symmetrically bonded to the metal, with cobalt—ring vectors of 1.568(1) and 1.570(1) Å, respectively. In 59, the C_3 propenylene chain is coplanar with the C_2B_3 ring, so that the entire central ligand may be regarded as planar $C_5B_3H_7^{4-}$, isoelectronic with $C_8H_7^-$, a species related to the pentalenide dianion $C_8H_6^{2-}$ by addition of a proton [48]. Each of the $C_5H_5^-$ rings in both 56 and 59 is titled with respect to the central C_2B_3 plane by 5.0 and 5.2°, respectively, a phenomenon which has not been explained but is evidently of electronic origin.



$C_8H_6^{2-}$ $C_8H_7^-$

Measurements of ^{11}B and ^1H NMR chemical shifts in a series of C- and B-substituted derivatives of **21**, together with the structural findings described above, indicate that the carbon—carbon bond in the C_2B_3 ring has multiple-bond character, and that there is substantial local π-interaction between each metal atom and the central C—C link; there is evidently also a strong metal—



59

Fig. 20. Crystallographically determined structure of 2,3-(1,3-C_3H_4)-1,7,2,3-(η^5-C_5H_5)$_2C_2B_3H_3$ (**59**). ● C; ○ BH.

central boron interaction [41a]. This model contrasts sharply with the corresponding 1,7,2,4 system (**57**), which is considered to have greater electron delocalization in the C_2B_3 ring and more uniform metal—ring atom bonding. In both **21** and **57**, there is some NMR evidence of direct through-cage electronic interaction between the cobalt atoms [41a], although this has not yet been established. Both NMR and electrochemical studies [87] indicate a high degree of electron delocalization over the polyhedral surface, not only in **21** and **57** but also in their metal—metal bonded isomers (discussed below).

(2) Complexes of the cyclic planar 2,4-$C_2B_3H_5^{4-}$ ligand and derivatives. Rearrangement of 2,3- to 2,4-$C_2B_3H_5^{4-}$ complexes

The planar 2,4-$C_2B_3H_5^{4-}$ ligand lacks a carbon—carbon bond, and as mentioned above, its dicobalt triple-decked η^5-complexes are clearly different, in electronic terms, from its 2,3-$C_2B_3H_5^{4-}$ counterparts. The differences are manifested in their colors and UV spectra (**21** is red and has a major band at 776 μm [53] while **57** is green and has no significant bands above 555 μm [19]), and in the more uniform environments of the boron nuclei in the complexes of the 2,4 system, as measured by ^{11}B NMR spectroscopy [41a,49]. However, **21** and **57** are structurally similar, as shown by X-ray studies of their respective C-monomethyl derivatives [84,88] and of the 1,3-propenylene derivative of **56**, mentioned above. Moreover, there do not appear to be major differences in chemical stability; thus, isomers **21** and **57** are both air- and water-stable.

Triple-decked dimetallic complexes of the 2,4-$C_2B_3H_5^{4-}$ system have been prepared by insertion of metal atoms into carboranes having nonadjacent carbon atoms (e.g. 1,6-$C_2B_4H_6$) [49], and have also been obtained by thermal rearrangement of the 2,3 (adjacent-carbon) isomers [53]. The latter route is usually preferable since cage isomerizations normally proceed in high yield [53,89]; thus, **21** can be converted to **57** quantitatively by heating above 300°C in the vapor phase [53]. When this isomerization was conducted under milder conditions (200—250°C) it was possible to isolate and characterize two intermediate species, as shown in Fig. 21. The structures of **60** and **61** were assigned from ^{11}B and ^{1}H NMR spectra of the pure compounds. From the observed rearrangement sequence it was possible to identify the main driving force as separation of the cage carbon atoms en route to the thermodynamically favored isomer **57**. The actual mechanism is not known (as is the case for most boron cage rearrangements) but a possible pathway involving cooperative rotation of CoB_2 and Co_2B triangles has been proposed [53]. The metal atoms in **60** and **61** occupy adjacent vertices in the polyhedron, an arrangement that seemed unusual at the time of discovery but has recently been observed in many metallocarboranes, as described below. Both **60** and **61** are stable to heat, air and water, requiring temperatures above 200° for rearrangement to **57** [53].

(3) Metal—metal bonded isomers of $M_2C_2B_3$ triple-decked complexes

In addition to **60** and **61** (Fig. 21), numerous other pentagonal bipyramidal

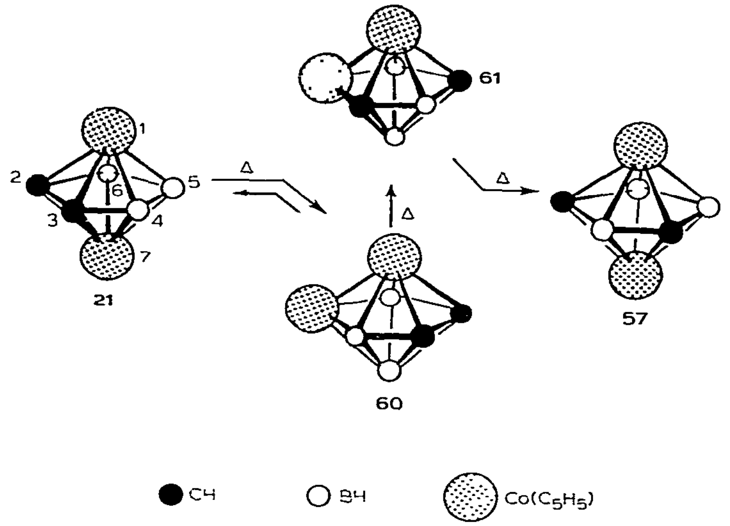


Fig. 21. Thermal rearrangement of 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ (**21**) to 1,7,2,4-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ (**57**) via intermediate isomers **60** and **61**.

clusters containing adjacent metal atoms have been prepared [19,51,52,67]. Several of these are shown in Fig. 22. Although the formal $C_2B_3H_5^{4-}$ ligand in this type of complex is nonplanar, these species are isomers of the triple-decked sandwich complexes such as **21** and **57**; presumably clusters such as **62** will undergo thermal rearrangements of the type shown in Fig. 21, yielding triple-decked sandwich complexes. (In the case of **63**, isomerization should produce a quadruple-decked complex containing two planar $(CH_3)_2C_2B_3H_3^{4-}$ ligands.)

It is also possible to view species of the type **60**—**65** as sandwich complexes containing a roughly planar metallocyclic MC_2B_2 central ligand; thus, **60** would be described as a $(\eta^5\text{-}C_5H_5)CoC_2B_2H_4^{4-}$ ring (isoelectronic with $C_2B_3H_5^{4-}$) which is η^5-coordinated to a BH^{2+} unit on one side and a $Co(\eta^5\text{-}C_5H_5)^{2+}$ group on the other.

The adjacent-metal complexes shown in Fig. 22 were prepared [51,67] by insertion of a second metal atom into a bis-carborane complex $[(CH_3)_2C_2B_4H_4]_2M$, where M = $Fe^{II}H_2$ or $Co^{III}H$ (see **22** and **35**, Figs. 12 and 16). Treatment of **22** with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ under UV light in THF yielded green **62**, black **63** and a product which decomposed to give the previously mentioned species **25** (see Fig. 12). The addition of $CoCl_2$ and C_5H_6 to **35** in ethanolic KOH produced numerous compounds, including brown-violet **64** and brown **65** (complexes **62**—**65** were characterized from their ^{11}B and ^1H NMR and mass spectra [51,67]. Other examples of adjacent-metal insertion have been presented earlier (see Fig. 18)).

The fact that the entry of a second metal atom so frequently occurs at a vertex adjacent to the first metal atom clearly represents a kinetic effect of central boron interaction [41a]. This model contrasts sharply with the corresponding 1,7,2,4 system (**57**), which is considered to have greater electron delocalization in the C_2B_3 ring and more uniform metal—ring atom bonding. In both **21** and **57**, there is some NMR evidence of direct through-cage electronic interaction between the cobalt atoms [41a], although this has not yet been established. Both NMR and electrochemical studies [87] indicate a high degree of electron delocalization over the polyhedral surface, not only in **21** and **57** but also in their metal—metal bonded isomers (discussed below).

(2) Complexes of the cyclic planar $2,4\text{-}C_2B_3H_5^{4-}$ ligand and derivatives. Rearrangement of 2,3- to $2,4\text{-}C_2B_3H_5^{4-}$ complexes

The planar $2,4\text{-}C_2B_3H_5^{4-}$ ligand lacks a carbon—carbon bond, and as mentioned above, its dicobalt triple-decked η^5-complexes are clearly different, in electronic terms, from its $2,3\text{-}C_2B_3H_5^{4-}$ counterparts. The differences are manifested in their colors and UV spectra (**21** is red and has a major band at 776 μm [53] while **57** is green and has no significant bands above 555 μm [19]), and in the more uniform environments of the boron nuclei in the complexes of the 2,4 system, as measured by ^{11}B NMR spectroscopy [41a,49]. However, **21** and **57** are structurally similar, as shown by X-ray studies of their respective C-monomethyl derivatives [84,88] and of the 1,3-propenylene derivative of **56**, mentioned above. Moreover, there do not appear to be major differences in chemical stability; thus, isomers **21** and **57** are both air- and water-stable.

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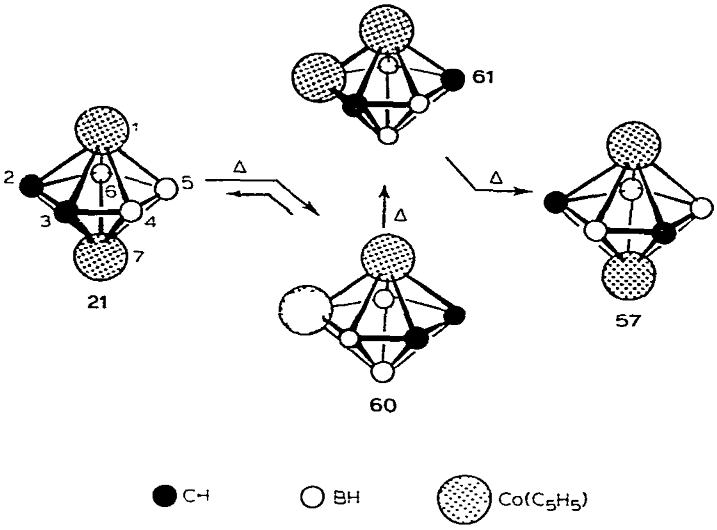

Fig. 21. Thermal rearrangement of 1,7,2,3-(η^5-C_5H_5)$_2$$Co_2C_2B_3H_5$ (**21**) to 1,7,2,4-(η^5-C_5H_5)$_2$$Co_2C_2B_3H_5$ (**57**) via intermediate isomers **60** and **61**.

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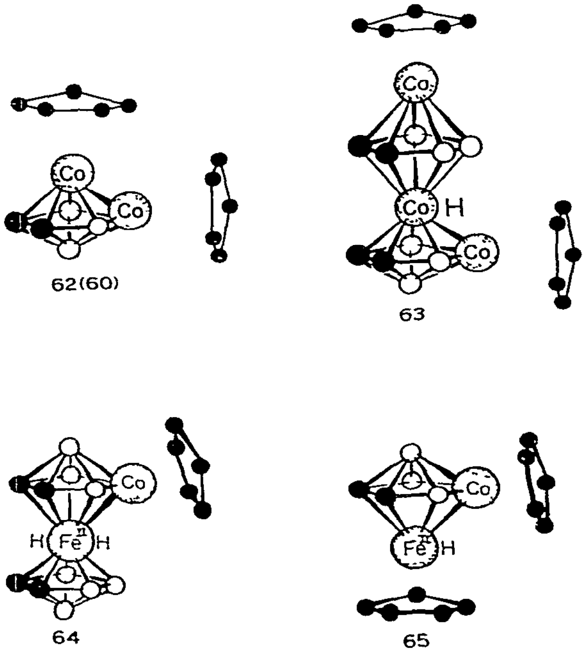


Fig. 22. Proposed structures of metal η^5-complexes containing MC_2B_2 planar ring systems. Complex **62** is a C,C-dimethyl derivative of **60** (Fig. 21). ● CH or CCH_3; ○ BH.

considerable scope; even non-carborane substrates such as $B_5H_8^-$ undergo reactions with Co^{2+} or Ni^{2+} ions to generate metal—metal bonded products (for example, see Fig. 5).

The precise nature of the metal—metal interactions in these systems is only now being investigated. Preliminary electrochemical results on the dicobalt species **56**, **57**, **60**, and **61** indicate a remarkable similarity in all four isomers, implying a high degree of electron delocalization in each polyhedral system [87]; thus, it may turn out that the electronic structure of the system is not greatly dependent on the presence or absence of a direct metal—metal link.

(4) Complexes of cyclic planar $C_4BH_5^{2-}$ and $C_3B_2H_5^{3-}$ derivatives

In Section E(i), the monometallic complexes derived from planar C_4B and C_3B_2 ligands were described. These ring systems can also function as dimetallic ligands, forming triple-decked sandwich compounds; thus, the reaction of 1-phenyl-4,5-dihydroborepin (**45**) with $Mn_2(CO)_{10}$ at 165°C yields **66** as brown-red needles (Fig. 23) [90]. The product was fully characterized by X-ray diffraction data, which disclosed a typical 7-vertex metallocarborane structure obeying the electron-counting formalism discussed earlier; since each $Mn(CO)_3$ group supplies one electron to framework bonding, the total is 16 as expected for the Mn_2C_4B *closo* system.

In similar fashion, the 1,3-diborolene derivative **48** reacts with

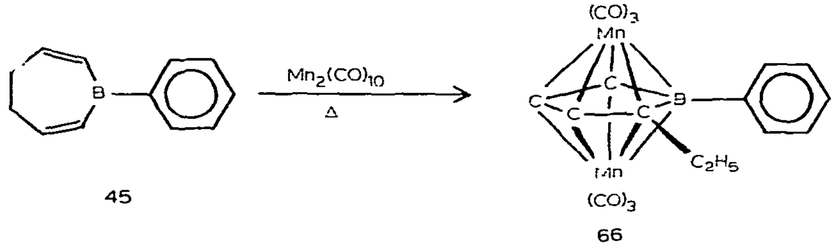


Fig. 23. Synthesis of 2-C_2H_5-6-C_6H_5-1,7,2,3,4,5-$[(CO)_3Mn]_2C_4BH_3$ (**66**). Hydrogen atoms on carbon are omitted for clarity.

(η^5-C_5H_5)Co$(CO)_2$ and $[(\eta^5$-$C_5H_5)Fe(CO)_2]_2$ together at 180—200°C under N_2, yielding the green mixed-metal complex **67** (Fig. 24) which was structurally identified from its ^{11}B and ^1H NMR and mass spectra; again, the skeletal valence electron population is 16, in accord with the proposed structure [91]. Several paramagnetic triple-decker sandwiches derived from 1,3-diborolene have recently been described [80b, c].

(5) Complexes of cyclic planar $C_2B_2SH_4^{2-}$ derivatives

The 1,2,5-thiadiborolene ring system, like its counterparts $C_4BH_5^{2-}$ and $C_3B_2H_5^{3-}$ just discussed, can form both mono- and dimetallic η^5-complexes. Several monometallic species were described earlier; in each of these compounds (**51**, **52**, **53**) the metallic group (e.g. $Fe(CO)_3$ or $Cr(CO)_4$) is a formal two-electron donor, [5—7] so that the total skeletal electron count is 16 and the 6-vertex complex is a *nido* system with pyramidal shape. One would expect that complexation of a thiadiborolene ring with a one-electron donor such as $Mn(CO)_3$ or Fe(η^5-C_5H_5) would introduce two metal atoms, producing 7-vertex triple-decked complexes. This is in fact observed in the reactions shown in Fig. 25 [92,93]. The structures shown were deduced from NMR and

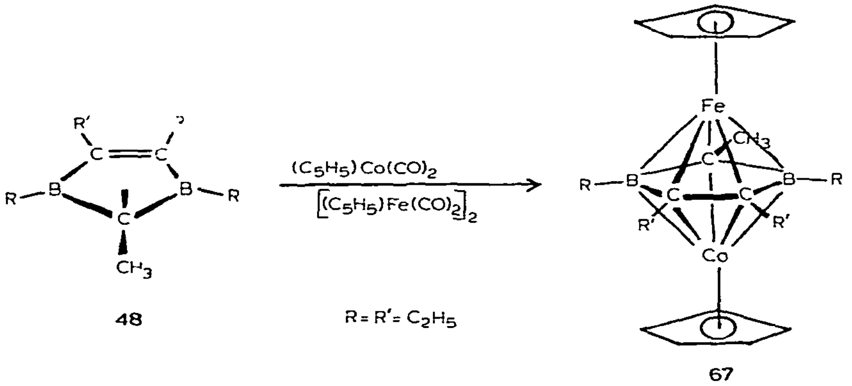


Fig. 24. Synthesis of 2-CH_3-3,4,5,6-$(C_2H_5)_4$-1,7,2,4,5-$(\eta^5$-$C_5H_5)_2FeCoC_3B_2$ (**67**).

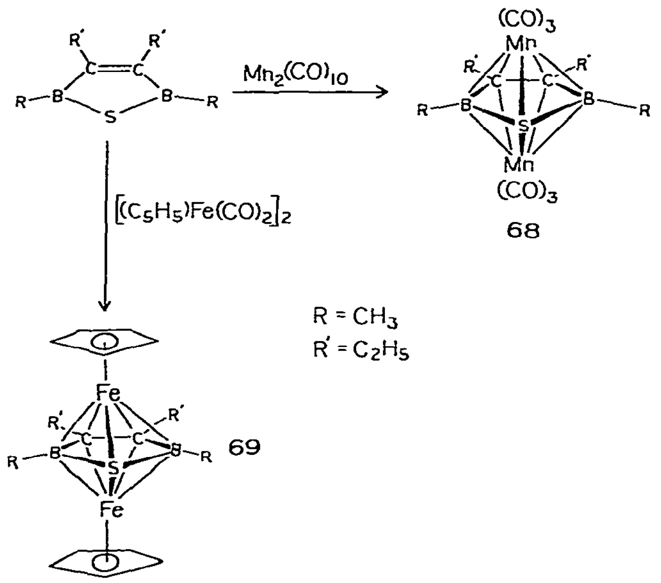
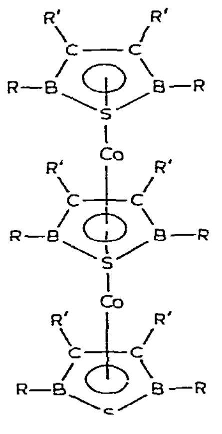


Fig. 25. Synthesis of 2,3-$(C_2H_5)_2$-4,6-$(CH_3)_2$-1,7,2,3,5-$[(CO)_3Mn]_2C_2B_2S$ (**68**) and 2,3-$(C_2H_5)_2$-4,6-$(CH_3)_2$-1,7,2,3,5-$(\eta^5\text{-}C_5H_5)_2Fe_2C_2B_2S$ (**69**).

mass spectra, supported by X-ray diffraction studies of both compounds [92, 93]. In **69** (and presumably in **68** also, though this is not stated), the central ring is planar. The metal—metal distance in **69** is much shorter than in **68** (3.236(1) Å vs. 3.506(1) Å), for reasons not yet clear; however, both are much shorter than the metal—metal distance in **58** $[(\eta^5\text{-}C_5H_5)_3Ni_2^+]$ (3.576 Å), a result accountable in the fact that the dinickel species has four more electrons than **68** and **69**. Both thiadiborolene species are electronic analogues of the $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ triple-deckers **56**, **57**, and **59** (Figs. 19 and 20), in which, for comparison, the average Co—Co distance is 3.138(2) Å [48,84,88].

The same thiadiborolene derivative reacts with $Co_2(CO)_8$ to yield a black complex, **70**, in which the three rings are identical [94].

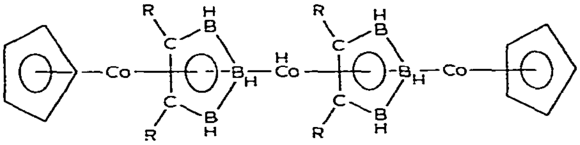


70
R = CH_3, R' = C_2H_5

The skeletal electron count in the central $Co_2C_2B_2S$ pentagonal bipyramid is 16, corresponding to a 7-vertex *closo* cage, while in each "end" CoC_2B_2S system it is also 16, corresponding to a 6-vertex *nido* framework. (In this analysis one assigns 6 "nonbonding" electrons to each metal atom, as usual. Of the remaining 3 electrons, each cobalt donates two to its end ring and one to the central ligand; C, B and S atoms supply 3, 2 and 4 electrons each.) Thus, **70** is analogous to all of the heteroborane triple-decked complexes previously discussed in this review.

(iii) Systems with three η^5-bonded metal atoms (quadruple-decked sandwiches)

At the time of writing there is only one example of a true quadruple-decked complex containing four planar π-bonded rings covalently linked by three metal atoms [132]. The reaction of 1,2,3-$(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_4^-$ (**20**) with $CoCl_2$ yields black, neutral $\{(\eta^5\text{-}C_5H_5)Co^{III}[(CH_3)_2C_2B_3H_3]\}_2Co^{III}H$, **71**. The structural characterization of **71** is based on ^{11}B and NMR and mass spectra [95a], but confirmation by X-ray diffraction has not yet been possible. A



71 R = CH_3

species derived from the thiadiborolene ligand, $[(CO)_3Mn \cdot (C_2H_5C)_2(CH_3B)_2S]_2Fe$, has been reported by Siebert et al.; this can be considered a type of quadruple-decker if one considers the end $(CO)_3$ groups to be equivalent to ring ligands [131].

No quadruple-decked complex based on $C_5H_5^-$ central ligands has been characterized, and in view of the low stability of the known triple-decked species $(\eta^5\text{-}C_5H_5)_3Ni_2^+$ [2,85] it appears unlikely that any such species will prove sufficiently stable to be isolated.

(iv) Other complexes involving metal—pentagonal planar face interactions

A large number of icosahedral metallocarboranes [3,1b] and metalloboranes [33] have been prepared and characterized, in all of which the metal atom(s) is coordinated to an essentially planar five-membered (usually C_2B_3) face (see Section B). The metal—cage ligand bonding in these species has been described [3] in the same qualitative terms as that between the metal and the $C_5H_5^-$ ligands in ferrocene and other metallocenes. Structural and Mössbauer studies [1b] have tended to bear out this view in a general way, although recent MO calculations [95b] suggest that there are significant differences between the metal—ligand interactions in $(\eta^5\text{-}C_5H_5)FeC_2H_9H_{11}$ and $(\eta^5\text{-}C_5H_5)_2Fe$.

TABLE 4

Complexes of hexagonal planar ligands

Complex [a]	Color	M.p. (°C)	Data [b]	Ref.
C_5B (borabenzene) ring systems				
$(C_5H_5BCH_3)_2Cr$	red-orange	81.5—82.0	IR, MS, MAG	108
$(C_5H_5BC_6H_5)_2Cr$	wine-red	176.5—178.5	IR, MS, MAG	108
$(CO)_3Mn(C_5H_5BC_6H_5)$	pale yellow	85.5— 86.5	B, H, IR, MS; X	101; 103
$(CO)_3Mn(4\text{-}CH_3\text{-}C_5H_4BC_6H_5$	pale yellow	73 — 75	B, H, IR, MS	109
$(CO)_3Re(4\text{-}CH_3\text{-}C_5H_4BC_6H_5)$	white	115.5	B, H, IR, MS	109
$CpFe(C_5H_5BCH_3)$	bright red	56 — 57	B, H, MS	110a
$CpFe(C_5H_5BC_6H_5)$	red	77.5— 78.5	B, H, MS	110a
$(C_5H_5BCH_3)_2Fe$		44 — 45	B, H, MS, E, IP [c]	106, 102
$(C_5H_5BC_6H_5)_2Fe$	red-orange	156 —157.5	B, H, MS, E, IP [c], MB [d]	106, 102
$[C_5H_5BC(CH_3)_3]_2Fe$		144 —145	B, H, MS, E, IP [c]	106
$[CH_3CO\text{-}C_5H_4BCH_3]Fe[C_5H_5BCH_3]$			H, MS	106
$[4\text{-}CH_3C_5H_4BC_6H_5]_2Fe$	red-orange	172	B, H, MS	109
$[3,4\text{-}(CH_3)_2\text{-}C_5H_3BC_6H_5]_2Fe$	brown	133	B, H, MS	109
$[(C_5H_5BCH_3)Fe(CO)_2]_2$	violet	130 dec.	IR, MS; X	102; 103
$[(C_5H_5BC_6H_5)Fe(CO)_2]_2$	violet	150 dec.	B, H, IR, MS	102
$(C_5H_5BCH_3)_2Ru$	pale yellow	64 — 65	B, H, MS	107
$(C_5H_5BC_6H_5)_2Ru$	white	136 —136.5	B, H, MS	107
$(C_5H_5BC_6H_5)_2Os$	white	146	B, H, MS	107
$CpCo(C_5H_5BCH_3)^+PF_6^-$	red-orange	180	B, H	99
$CpCo(C_5H_5BC_6H_5)^+PF_6^-$	red	139	B, H	97, 99
$CpCo(C_5H_5BC_6H_5)$	dark brown	70 — 71	MS, IP	98, 99
$CpCo(C_5H_5BCH_3)$	dark red	28	MS, IP	98, 99

$[(C_6H_5)_4C_4]Co(C_5H_5BCH_3)$	deep yellow	183 —184	H, IR, MS	110b
$(C_2B_9H_{11})Co(C_5H_5BC_6H_5)$	red	201	B, H, IR, MS	111
$(C_8H_{12})Co(C_5H_5BC_6H_5)$	pale yellow	161 —162	B, H, MS	104
$(CO)_2Co(C_5H_5BC_6H_5)$	brown	79.5— 80.0	B, H, IR, MS	110c
$(C_5H_5BC_6H_5)_2Co$	dark red	190 —191	MS, IP	98, 99
$(C_5H_5BCH_3)_2Co$	dark red	98	MS, IP; X	98, 99; 100a
$(C_5H_5BOH)_2Co$			MS	98
$(C_5H_5BOCH_3)_2Co$		98	MS, IP, MAG[e]; X	98; 100
$(C_5H_5BC_6H_5)_2Co^+I_3^-$	black		H	105
$(C_5H_5BC_6H_5)_2Co^+PF_6^-$	dark orange-red		H	105
$(C_5H_5BC_6H_5)Rh(C_8H_{12})$	bright yellow	161 —162	B, H, MS	107
$(C_5H_5BCH_3)Rh(C_8H_{12})$	honey-yellow	76.5— 78	B, H, MS	107
$(C_5H_5BC_6H_5)Pt(CH_3)_3$	white	37 — 38	B, H, MS	107
$C_2B_2N_2$ (diazadiboracyclohexene) ring system				
$(CO)_3Cr[C_2(C_2H_5)_2B_2(CH_3)_2N_2(CH_3)_2]$	red	111 —112	B, H, IR, MS	113
B_3N_3 (borazine) ring systems				
$(CO)_3Cr[B_3(CH_3)_3N_3(C_2H_5)_3]$	orange	110 —150 dec	H, IR, MS, E	119
$(CO)_3Cr[B_3(CH_3)_3N_3(CH_3)_3]$	orange-yellow	141 dec	H, ^{14}N[f], IR, MS, E, D[g]	115, 116, 119
$(CO)_3Cr[B_3(C_2H_5)_3N_3(CH_3)_3]$	orange	150 dec	H, ^{14}N, IR, D	116
$(CO)_3Cr[B_3(C_2H_5)_3N_3(C_2H_5)_3]$	orange		X	118
$(CO)_3Cr[B_3(C_6H_5)(CH_3)_2N_3(CH_3)_3]$	orange	110 —150 dec	H, IR, MS, E	119
$(CO)_3Cr[B_3(C_2H_5)(CH_3)_2N_3(CH_3)_3]$	orange	110 —150 dec	H, IR, MS, E	119
$(CO)_3Mo[B_3(CH_3)_3N_3(C_2H_5)_3]$	yellow	110 —120 dec	H, IR, MS	117
$(CO)_3Mo[B_3(C_2H_5)_3N_3(CH_3)_3]$	yellow	110 —120 dec	H, IR, MS	117

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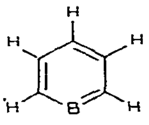
[a] Cp = (η^5-C_5H_5). Within each ligand class, complexes are grouped by metals. [b] See footnote b in Table 1. [c] IP = ionization potential. [d] MB = Mössbauer data. [e] MAG = magnetic susceptibility. [f] ^{14}N NMR data. [g] D = dipole moment measurements.

The icosahedral complexes do not fall within the scope of this review, but their chemistry has been extensively reviewed elsewhere [1b, 1e, 1f, and references cited therein].

F. HEXAGONAL PLANAR LIGANDS: ANALOGUES OF C_6H_6

(i) Complexes of $C_5H_5BR^-$ (borabenzene) ligands [95c]

The planar heterocycles borabenzene (C_5H_5B), **72**, and the borabenzenide anion, **73**, are both unknown, but B-substituted derivatives of the latter have been prepared as alkali metal salts [96,104,106—108] and as transition metal η^6-complexes [97—110c]. The anion **73** is isoelectronic with benzene, and NMR evidence on its B-phenyl derivative [96] indicates substantial aromatic character; this is further supported by NMR and X-ray structural data on several sandwich complexes of B-substituted derivatives. Table 4 lists the characterized borabenzene complexes as well as those derived from other η^6 planar ligands.



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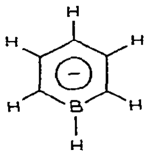
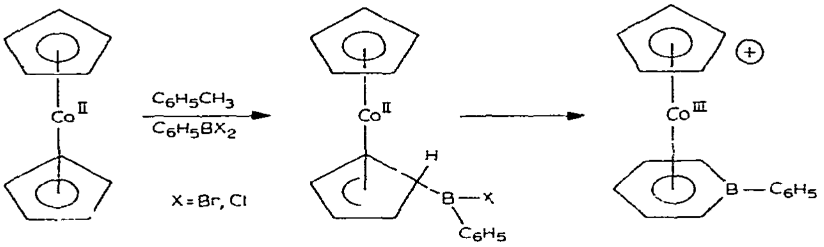


73

The original synthesis of borabenzene sandwich complexes by Herberich and co-workers involved a two-step boron insertion into one C_5H_5 ring in cobaltocene [97]:



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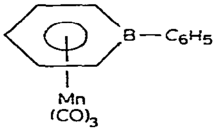
75

The presumed intermediate **74** has not been isolated, but on treatment with $SnBr_4$, hydrolysis, and addition of NH_4PF_6, the diamagnetic cation **75** is obtained as a red-orange salt. Subsequently, it was found that paramagnetic neutral cobalt(II) complexes containing one or two borabenzene ligands could be obtained (Fig. 26) [98,99]. The paramagnetic mixed-ligand Co(II) complex **76** can be oxidized to the corresponding diamagnetic Co(III) species (e.g., **75**) by treatment with Fe^{3+} ion. Derivatives of **77** with R = OH and R = OCH_3 have also been isolated and characterized [98].

Crystal structure determinations on the bis(1-methoxyborinate) and bis(1-methylborinate) complexes of cobalt(II) have confirmed the centrosymmetric structure of 77 shown in Fig. 26 [100]. In both species the rings are nearly planar and are parallel to each other, and the cobalt atom is further from boron than from the *para* carbon atom (~1.6 vs. 1.3 Å). This unsymmetrical ring—ligand bonding has been cited as evidence of cyclic conjugation [100]; since very similar effects are seen in the related structures of iron carbonyl and manganese carbonyl complexes to be described below, these structural patterns are evidently typical of borabenzene—metal complexes as a class.

In a reaction very similar to those discussed above, the icosahedral metallocarborane 3,1,2-(η^5-C_5H_5)$CoC_2B_9H_{11}$ was reduced with sodium and treated with $C_6H_5BCl_2$ in an attempt to introduce a phenylboron unit into the metallocarborane cage [111]. Instead, however, C_6H_5B insertion took place selectively on the C_5H_5 ring, yielding the borabenzene—cobaltacarborane complex 78 (Fig. 27).

Borabenzene sandwich complexes of other transition metals have also been prepared. Compound 79 was obtained [101] by treatment of 77 (R = C_6H_5) with $Mn_2(CO)_{10}$ in boiling toluene, and was structurally characterized from NMR data and from an X-ray structure determination [103]. The metal—ligand geometry in 79 is very similar to that in the 77 complexes that have



79

been structurally investigated; the C_5B ring is planar, but the Mn—B distance is 0.34 Å greater than the Mn—C (*para*) vector. A similar ligand-insertion reaction of 77 (R = C_6H_5, CH_3) with $Fe_2(CO)_9$ or $Fe(CO)_5$ at 70—120°C gave 80, which on heating at 230°C gave 81 [102]. The structure of 80 was determined crystallographically and the metal was found to be 0.22 Å further from boron

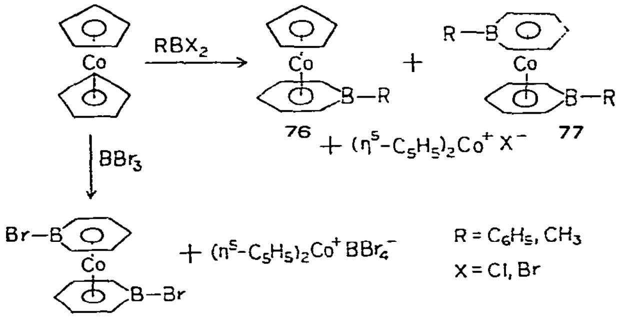
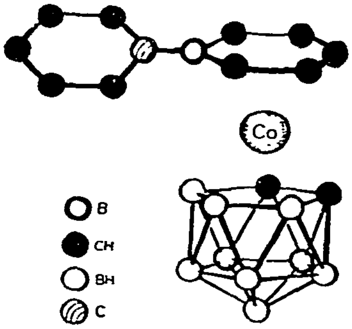


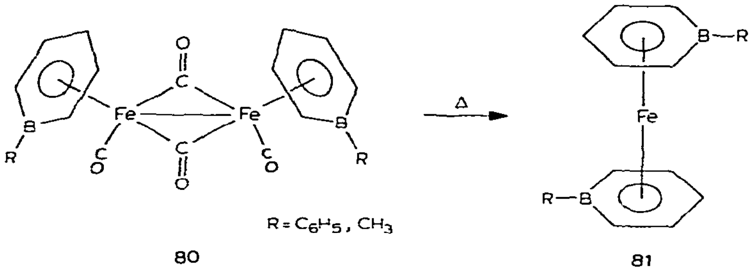
Fig. 26. Synthesis of B-substituted borabenzene complexes from cobaltocene.



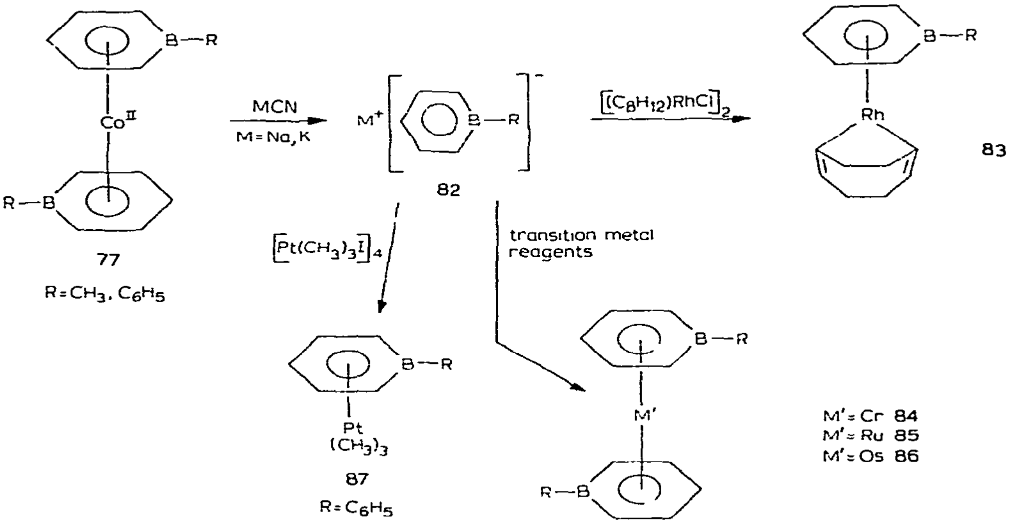
78

Fig. 27. Proposed structure of 1,2,3-$(1\text{-}C_6H_5BC_5H_5)CoC_2B_9H_{11}$ (**78**).

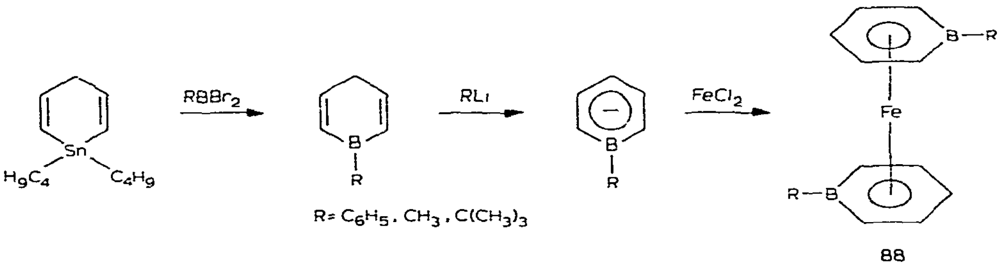
than from the *para* carbon atom in the ring [103], consistent with other compounds of this class as discussed above.



All of the above borabenzene complexes were derived from an initial boron insertion into one or both C_5 rings in cobaltocene. Recently, Herberich and co-workers have shown that bis(borabenzene) cobalt complexes, **77**, on heating with KCN or NaCN in acetonitrile are degraded to the alkali metal borinates, from which other transition metal sandwich complexes can be generated [104,107,108].

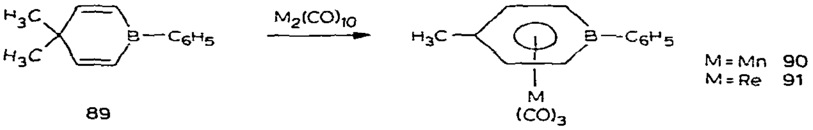


Ashe and co-workers [96,106] have prepared free B-substituted borabenzene anions from 1,1-dibutyl-1,4-dihydrostannabenzene and treated these with $FeCl_2$ to produce bis(borabenzene) iron complexes:

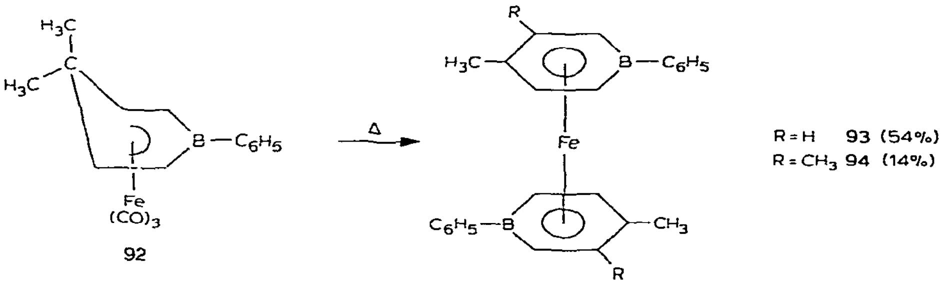


Friedel-Crafts acylation of **88** (R = CH_3) and acid-catalyzed exchange of deuterium occur at the α position on one ring only. Mössbauer spectra of **88** (R = C_6H_5) suggest that the borabenzene ring ligand is more strongly electron withdrawing, with respect to iron, than are the cyclopentadienyl rings of ferrocene [106]. At present, it is difficult to evaluate such findings in the absence of corroborative evidence such as detailed NMR studies.

Another route to borabenzene complexes involves the thermal reactions of 4,4-dimethyl-1-phenyl-1-bora-2,5-cyclohexadiene (**89**) with $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ [109]:

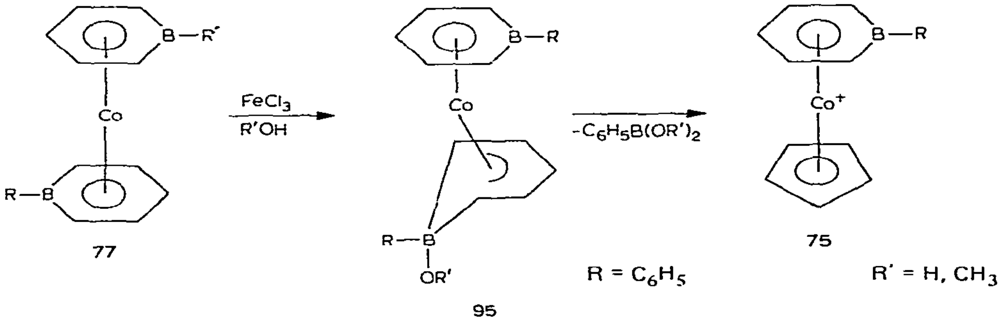


Compound **89** forms an η^5-complex with iron (**92**) [112], which on pyrolysis generates bis(borabenzene) sandwich products [109]. The structure of the

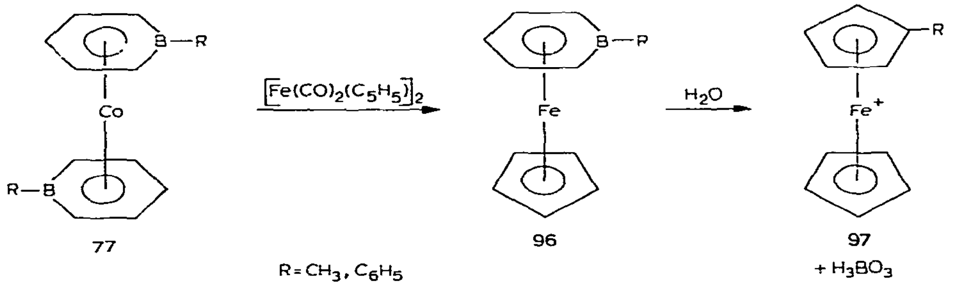


dimethylsilylene analogue of **92** has been determined crystallographically [112] and the silicon atom was found to be bent away from the plane of the C_4B ring at a dihedral angle of 43.5°. Thus, compounds of the **92** type can be viewed as η^5 sandwich complexes of a planar C_4B ring in which one C—C interaction is bridged by an R_2C or R_2Si group.

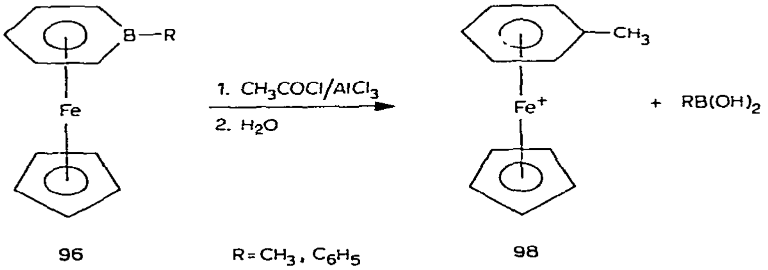
In the conversion of **92** to **93** and **94**, the bridging carbon undergoes a change of hybridization from approximately sp^3 to sp^2 and becomes assimilated into the metal—ring sandwich system. It is possible to effect a conversion in the opposite direction, that is, to move a ring atom out of the plane and away from the metal, in this case involving boron rather than carbon [105]. Treatment of the bis(borabenzene) cobalt complex **77** with $FeCl_3$ generates a boron-bridged intermediate, **95** (analogous to **92**), which quantitatively eliminates boron to give **75**, a mixed-ligand sandwich species that has also been prepared directly from cobaltocene (see above).



A related type of ring-contraction occurs in the following sequence, which produces substituted ferrocenium species [110a]:



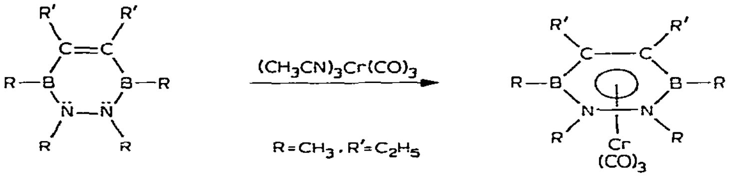
Remarkably, when Friedel-Crafts acetylation of **96** was attempted, the B—R group was replaced by C—CH_3, generating on hydrolysis the mixed-ligand complex **98**.



These boron-elimination reactions complete a closed circuit of synthetic operations wherein cyclopentadienyl sandwich complexes can be converted to borabenzene—metal species, from which cyclopentadienyl and benzene complexes can be obtained. With these preparative tools in hand, an enormous area of novel metal-sandwich chemistry appears ready for exploration.

(ii) Complexes of boron—nitrogen ligands

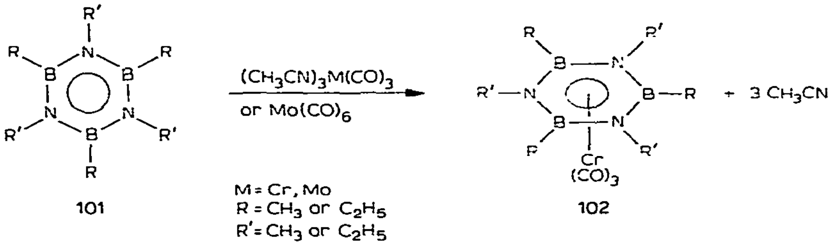
The cyclic molecule 1,2-diaza-3,6-diboracyclohexene, **99**, is isoelectronic with benzene, and its 4,5-diethyl-1,2,3,6-tetramethyl derivative forms a chromium η^6-complex, **100**, which is analogous to $C_6H_6Cr(CO)_3$ [113].



99

100

The best known cyclic planar boron—nitrogen system is, of course, borazine ($B_3N_3H_6$), also isoelectronic with benzene [114]. Several η^6-complexes of substituted borazines with transition metals have been prepared by reaction of the ligand with chromium or molybdenum carbonyls [114—119]. Other derivatives of **102** with phenyl, methyl and/or ethyl substituents have also



101

102

been prepared [119]. A crystallographic study of **102** ($R = R' = C_2H_5$) revealed that the borazine ring is slightly bent into a chair conformation but is centric with respect to the $Cr(CO)_3$ group [120]. The near-planarity of the ring, and the fact that the Cr—B and Cr—N distances are similar save for the difference in covalent radii of B and N, support the view that **102** is an η^6-complex analogous to $C_6H_6Cr(CO)_3$. The average B—N distance is 1.44 ± 0.02 Å, compared to 1.435 ± 0.002 Å in free borazine [121].

Complexes **100** and **102** obey the previously described electron-count formalism for cage structures. Thus, with nitrogen, carbon, boron and $Cr(CO)_3$ [or $Mo(CO)_3$] donating 4, 3, 2, and 0 electrons respectively to the hexagonal pyramidal framework, each complex is a 7-vertex, 18-electron $2n + 4$ system, in agreement with the observed *nido* geometry. If one were to introduce a second $Cr(CO)_3$ unit into the system, the number of skeletal electrons would be unchanged, resulting in an 18-electron, 8-vertex *closo* framework; the ob-

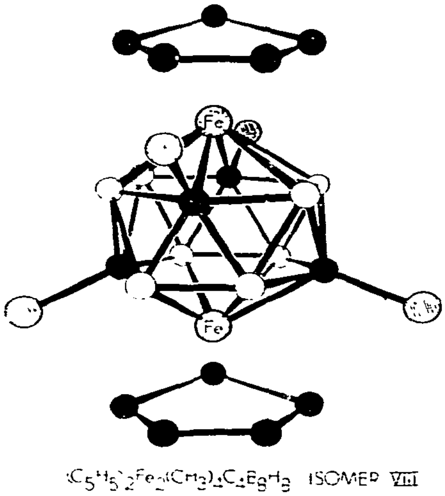


Fig. 28. Established structure of 1,14,2,5,9,12-(η^5-C_5H_5)$_2$$Fe_2(CH_3)_4C_4B_8H_8$. ● C or CH; ✲ CH_3; ○ BH.

vious geometry might seem to be a hexagonal bipyramid, but in fact this is unlikely since all known *closo* 8-vertex clusters (even including some 16- and 20-electron systems) are dodecahedral [122]. Consequently, it can be predicted that species such as $[(CO)_3Cr]_2B_3N_3R_6$ will also adopt *closo* dodecahedral structures.

(iii) Other complexes involving metal ion—hexagonal planar face interactions

The 14-vertex dicobalt metallocarborane (η^5-C_5H_5)$_2$$Co_2C_2B_{10}H_{12}$, prepared several years ago [128], is proposed from NMR data to have the geometry of a bicapped hexagonal antiprism with each cobalt occupying one of the capping vertices. This type of geometry has been crystallographically established for the first time [129] in the diiron tetracarbon species 1,14,2,5,9,12-(η^5-C_5H_5)$_2$$Fe_2(CH_3)_4C_4B_8H_8$, **103** (Fig. 28). In this molecule, prepared [130] by insertion of (η^5-C_5H_5)Fe^+ groups into the $(CH_3)_4C_4B_8H_8^{2-}$ ligand followed by thermal rearrangement through several intermediate isomers, each metal atom is symmetrically η^6-bonded to a C_2B_4 face. The two C_2B_4 rings are not quite planar, the carbon atoms being slightly out-of-plane due to the fact that the inter-ring B—C interactions are shorter than the B—B bonds. The carborane ligand is formally $(CH_3)_4C_4B_8H_8^{2-}$, whose parent species would be $C_4B_8H_{12}^{2-}$; the latter is an isoelectronic analogue of the hypothetical $C_{12}H_{12}^{6+}$ "barrel-shaped" cage which one can envisage as a pair of benzene rings fused face-to-face in a staggered conformation. Such a highly charged cation (or its boron counterpart $B_{12}H_{12}^{6-}$) would be unlikely, but neutral $C_6B_6H_{12}$, a hexagonal antiprism, could well exist; introduction of two zero-electron-donor metal groups such as $Cr(CO)_3$ or $Mn(\eta^5\text{-}C_5H_5)$ into the hexagonal open faces could produce an $M_2C_6B_6$ 14-vertex cage isoelectronic with **103**. Such speculations are, of course, easier to arrive at conceptually than to realise in the laboratory.

ACKNOWLEDGMENTS

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