RECENT STUDIES OF METALLOBORON CAGE COMPOUNDS DERIVED FROM THE SMALL CARBORANES

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ABSTRACT

The preparation, structural characterization, and chemistry of several families of small metallocarboranes which have a close structural and electronic relationship to the metal clusters and other organometallic cage systems, are reviewed with emphasis on recent developments. Reactions of *nido*-2,3-$C_2B_4H_8$, $Na^+C_2B_4H_7^-$, and the *closo*-carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ with metal salts and organometallic reagents in the gas phase or in solution generate a variety of open- and closed-cage mono-, di-, and tri-metallocarboranes having six or more framework atoms. Novel structural features and spectroscopic properties of several species are discussed, and the reactions, interconversions, thermal rearrangements, and other observations pertaining to the small metallocarboranes are described and correlated.

INTRODUCTION

A large class exists of boron cage molecules containing one or more metal atoms bound into an electron-delocalized framework. Most such species also contain skeletal carbon atoms and are described as metallocarboranes[1]. These compounds are not only interesting in their own right from a structural, electronic, and stereochemical viewpoint, but are of added significance as a consequence of their close relationship to many non-boron cage compounds such as the metallic and organometallic clusters. Recently, a number of workers[2-4] have described simple electron-counting rules which relate otherwise dissimilar classes and which supply the synthetic chemist with a highly useful predictive tool. The basic postulate, first pointed out explicitly by Wade[2a] and by Rudolph and Pretzer[3], states that a cage framework of n atoms will adopt a closed polyhedral geometry (all sides triangular) if the number of valence electrons (e) is $2n + 2$ and an open-cage (*nido*) structure if $e > 2n + 2$. The broad generality of these ideas is illustrated in *Figure 1*, which depicts the known or proposed structures of several molecules of different types, all of which are formal 14-electron, 5-atom cage systems in

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which $e = 2n + 4$ and the geometry is open*; in contrast, the 12-electron $(2n + 2)$ system $C_2B_3H_5$ is a closed trigonal bipyramid. Similarly, the species B_6H_{10}, $C_2B_4H_8$, $C_4B_2H_6$, $(\eta\text{-}C_5H_5)CoC_2B_3H_7$, $(CO)_3Fe(\eta\text{-}C_5H_5)^+$, and $(\eta\text{-}C_5H_5)_2Co^+$ all feature open pentagonal pyramidal frameworks having $2n + 4$ electrons (in the last example there are two such systems fused at the metal atom); the molecules $B_6H_6^{2-}$, $C_2B_4H_6$, $(\eta\text{-}C_5H_5)_2Co_2B_4H_6$, and $(C_2H_5)_2C_2Co_4(CO)_{10}$ contain $2n + 2$ skeletal electrons and are known or postulated to be closed octahedra.

B_5H_9 $C_2B_3H_7$ $C_5H_5{}^+$

$1\text{-}B_4H_8Co(C_5H_5)$ $1\text{-}B_4H_8Fe(CO)_3$ $(C_4H_4)Fe(CO)_3$
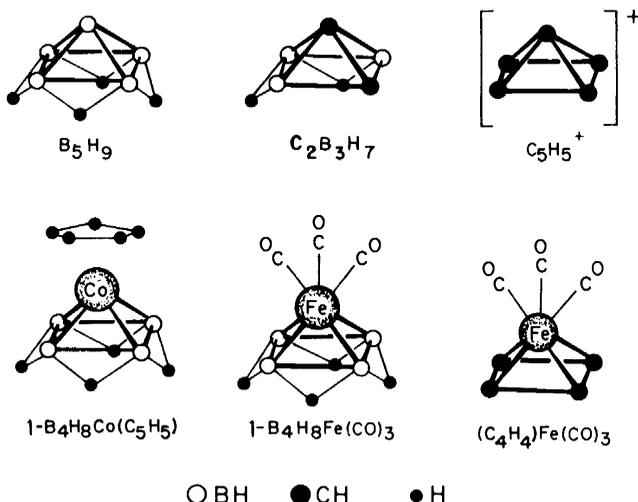
○ BH   ● CH   ● H

Figure 1. Established or proposed structures of several 5-vertex, square pyramidal cage molecules containing 14 framework electrons. The geometries shown have been established for B_5H_9, $C_2B_3H_7$, and $(C_4H_4)Fe(CO)_3$, and have been postulated from n.m.r. data and theory for the others. The connecting lines shown in these structures have no bonding significance

Although the synthetic origins of these molecules differ considerably, their electronic and geometric similarities suggest an underlying unity in the chemistry of the cage compounds which is well worth exploring. An example of similar behaviour of three such compounds in different classes (a borane[6], a carborane[7], and a metalloborane[8, 9]) is given in *Figure 2*. Among the various classes of cages and clusters, the boron compounds are particularly amenable to detailed investigation because of (1) the versatility of boron in accommodating hetero (non-boron) skeletal atoms of a wide variety of metals and non-metals, (2) the stability of the heteroboranes generated, and (3) the development of rational techniques for the preparation and interconversion of such compounds, which may in some degree prove applicable even to non-boron clusters.

The study of metallocarborane chemistry has proceeded rapidly in a number of laboratories, including that of Hawthorne and co-workers, who

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* The ground-state geometry of $C_5H_5^+$ is in dispute; the C_{4v} (square pyramidal) structure shown has been variously calculated to be either the most stable form[5a], or one of several stable structures[5b-5d]. However, experimental evidence for the square pyramidal geometry has been reported[5e, 5f].

● CH ○ BH • H
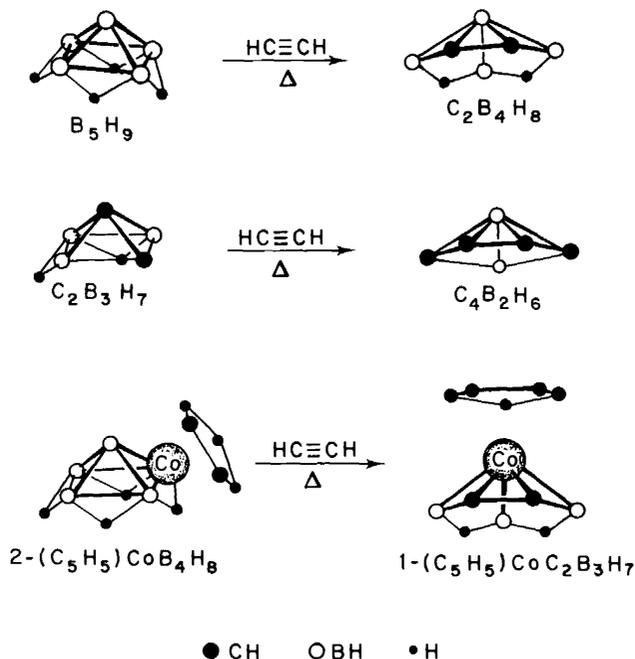
Figure 2. Reaction scheme for the insertion of C_2H_2 into B_5H_9[6], $C_2B_3H_7$[7], and 2-$(C_5H_5)CoB_4H_8$[8,9]. Other products formed in these reactions are not shown

discovered the field and have prepared many novel intermediate-to-large cage systems in which the number of framework atoms is nine or larger. The present paper describes work on small systems having as few as five cage atoms, which are direct structural and electronic analogues of various metal clusters and organometallic cage species.

SYNTHESIS OF METALLOCARBORANES FROM SMALL CARBORANES

The only significant routes to metallocarboranes at this time involve insertion of metals into a carborane framework, although other routes are possible, such as carbon insertion into metalloboranes (an example of the latter[9] is seen in *Figure 2*). Of the small carboranes[1c], the most accessible are *nido*-2,3-$C_2B_4H_8$ and the *closo* compounds 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$. Isolated instances of metal insertion into *nido*-1,2-$C_2B_3H_7$ (*Figure 2*) and *nido*-2-CH_3-2,3,4-$C_3B_3H_6$ are known[10,11] but these carboranes are much less readily available[1c].

Synthesis from 2,3-$C_2B_4H_8$

The carborane $C_2B_4H_8$ is particularly versatile and reacts with suitable metal reagents both directly in the gas phase (*Figure 3*) and via the conjugate-base $C_2B_4H_7^-$ ion in ethereal solvents. The gas phase reactions produce mainly 7-vertex pentagonal bipyramidal monometallocarboranes[12,13],

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although in the reaction with $Fe(CO)_5$ [13] a pale yellow *nido* species, 1,2,3-$(CO)_3FeC_2B_3H_7$*, is also formed by partial thermal degradation of the 1.2,3-$(CO)_3FeC_2B_4H_6$ produced initially (*Figure 3*). The structures of 1,2,3-$CH_3GaC_2B_4H_6$ [12] and 1,2,3-$(CO)_3FeC_2B_3H_7$ [14] have been established from x-ray diffraction studies.

(a)

(b)

M = Ga, In

CH_3

(c)
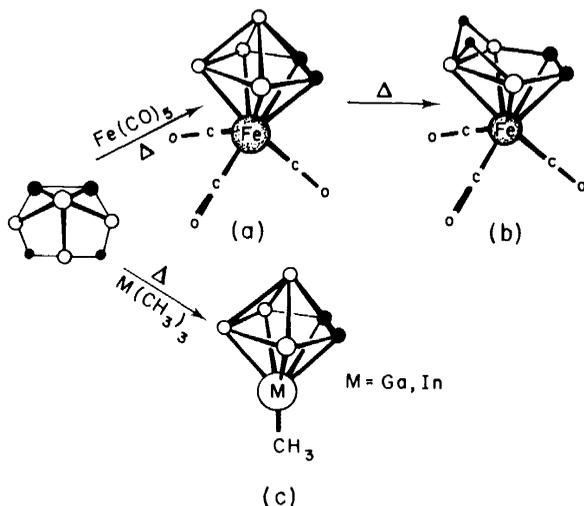
Figure 3. Reaction scheme for the direct insertion of metal atoms into $C_2B_4H_8$

The $C_2B_4H_7^-$ ion is readily formed by deprotonation of $C_2B_4H_8$ with sodium hydride in tetrahydrofuran (THF), and metal insertion into the resulting B—B bond on the base of the pyramid produces bridge-substituted derivatives[13,15-17] featuring a 3-centre, 2-electron B—M—B bond (*Figure 4*). The C,C'-dimethyl derivative, $(CH_3)_2C_2B_4H_5^-$, undergoes similar reactions[18]. The bridged structures are supported primarily by [11]B and [1]H n.m.r. spectra, which indicate that all terminal B—H and C—H bonds are retained and thus eliminate terminally-substituted isomers (a closely related bridged derivative of B_5H_9, $\mu-[(CH_3)_3Si]B_5H_8$ [19a], has been structurally characterized in an x-ray study[19b]). The Group IV-bridged species have not been found to convert to a closed metallocarborane cage, and on heating either rearrange to terminally B-substituted isomers or decompose to form $C_2B_4H_8$ [15,16].

$$\mu-(CH_3)_3SiC_2B_4H_7 \xrightarrow{\Delta} 4-(CH_3)_3SiC_2B_4H_7 \xrightarrow{\Delta} 2-(CH_3)_3SiC_2B_4H_7.$$
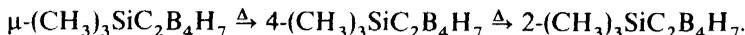
However, the yellow iron-bridged compound $\mu-[(\eta-C_5H_5)(CO)_2Fe]C_2B_4H_7$ does convert photolytically to two *closo*-metallocarborane species[13], red-orange diamagnetic 1,2,3-$(\eta-C_5H_5)Fe^{II}HC_2B_4H_6$ and brown paramagnetic 1,2,3-$(\eta-C_5H_5)Fe^{III}C_2B_4H_6$ (*Figure 5*). The initial product is evidently the iron(II) species which can form merely by loss of two CO groups from the bridged compound, with concomitant movement of the metal fully into the

* Numbers preceding metallocarborane formulas designate the cage locations of metal and carbon atoms in that order, using the IUPAC numbering scheme for boron polyhedra outlined in *Pure Appl. Chem.*, **30**, 683 (1972).
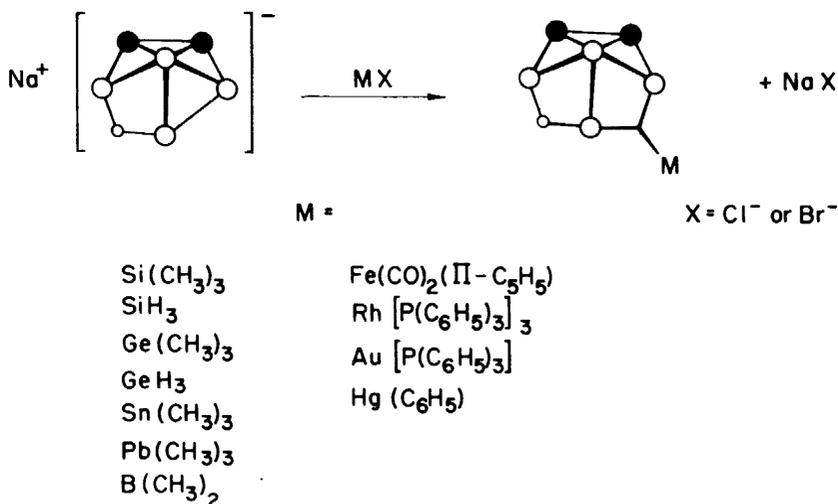
Figure 4. Bridge-insertion reactions of $C_2B_4H_7^-$ ion

cage. The bridging proton is retained and almost surely becomes associated with the iron atom, as indicated by the high-field ^1H n.m.r. signal at $\delta + 14.4$ relative to tetramethylsilane[13]. This proton is probably not present as a 'pure' Fe—H group, but as an Fe—H—B bridge or possibly an Fe—H—B_2 multicentre bond in which the proton tautomerizes between two equivalent FeB_2 triangular faces. The proton is acidic toward hydride ion and is reversibly removed to generate a $(\eta-C_5H_5)Fe^{II}C_2B_4H_6^-$ ion which can be oxidized, again reversibly, to neutral $(\eta-C_5H_5)Fe^{III}C_2B_4H_6$ (*Figure 5*). The indicated oxidation state of $+3$ in this species is supported by a variable-temperature magnetic susceptibility study which gave $\mu = 2.1$, corresponding to a low-spin d^5 configuration[13].

Both $1,2,3-(\eta-C_5H_5)Fe^{II}HC_2B_4H_6$ and $1,2,3-(\eta-C_5H_5)Fe^{III}C_2B_4H_6$ have 1,2,4 isomers in which the cage carbon atoms are equatorial but non-adjacent, prepared from *closo*-$2,4-C_2B_5H_7$ as mentioned below. The 1,2,3 isomers are likely to undergo thermal rearrangement to the corresponding 1,2,4 species; such isomerization has not been studied in these iron systems but occurs readily in the analogous cobalt species, $1,2,3-(\eta-C_5H_5)CoC_2B_4H_6$ [9].

The $C_2B_4H_7^-$ ion also affords a simple route to small cobaltacarboranes. Thus, treatment with $CoCl_2$ and NaC_5H_5 in the THF yields primarily the orange diamagnetic *closo* species $1,2,3-(\eta-C_5H_5)CoC_2B_4H_6$ (*Figure 6*)[20]. Two other products, *nido*-$1,2,3-(\eta-C_5H_5)CoC_2B_3H_7$ and *closo*-$1,7,2,3-(\eta-C_5H_5)_2Co_2C_2B_3H_5$ are obtained following work-up of the original reaction mixture in neutral or basic aqueous media, and are formed via base-degradation of the original CoC_2B_4 system (see below). This process is considerably retarded when the work-up is conducted in 1 M aqueous HCl.

The $1,2,3-(\eta-C_5H_5)Co^{III}C_2B_4H_6$ does not undergo protonation by aqueous HCl and is completely stable in this medium. However, the closely related species $[2,3-(CH_3)_2C_2B_4H_4]_2Co H^0$ and $[2,3-(CH_3)_2C_2B_4H_4]-$
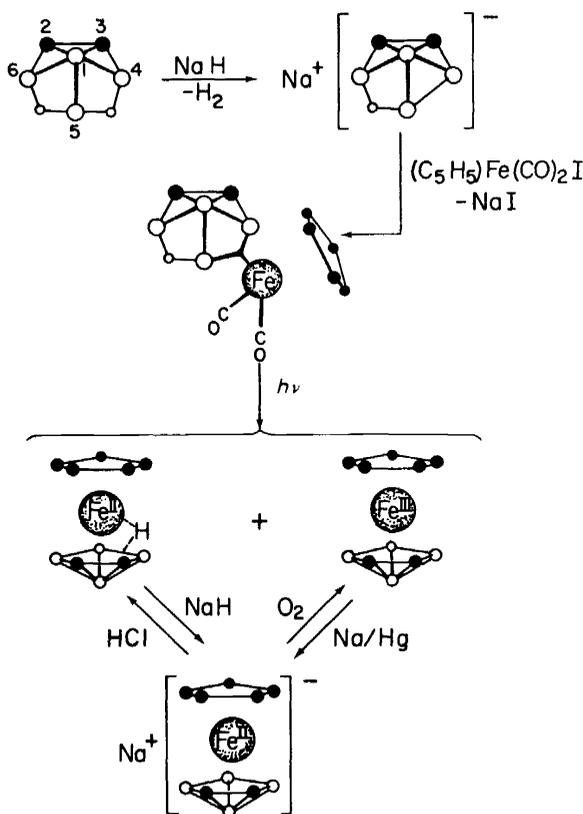
Figure 5. Reaction scheme for the synthesis of cyclopentadienyl iron metallocarboranes from $C_2B_4H_8$

$CoH[2,3-(CH_3)_2C_2B_3H_5]^0$ are formed from $Na^+[(CH_3)_2C_2B_4H_5]^-$ and $CoCl_2$ in the *absence* of NaC_5H_5 [21]. The former complex, a bright red solid, undergoes hydrolysis to give the latter yellow compound whose metal atom apparently resides in both a *nido* and a *closo* metallocarborane system (*Figure* 7). The ^1H n.m.r. spectrum contains only a single broad peak in the bridge-proton region, at $\delta + 6$, instead of the expected widely separated B—H—B and Co—H—B resonances, suggesting that the three bridging protons in the molecule undergo rapid exchange on the n.m.r. time scale between B—H—B and Co—H—B (or Co—H—B$_2$) locations.

The base-degradation of $1,2,3-(\eta-C_5H_5)CoC_2B_4H_6$, referred to above, has been examined in some detail and occurs with KOH in H_2O–THF or even in neutral H_2O–C_2H_5OH or H_2O–THF solutions[9]. The initial product, *nido*-$1,2,3-(\eta-C_5H_5)CoC_2B_3H_7$, is analogous to the previously mentioned species $1,2,3-(CO)_3FeC_2B_3H_7$ whose structure has been conclusively established[14]. Since $(\eta-C_5H_5)CoC_2B_3H_7$ can be regarded as $C_2B_4H_8$ with the apex BH group replaced by a $(\eta-C_5H_5)Co$ moiety, similar bridge-deprotonation by NaH was expected, and this occurs reversibly[20] as shown
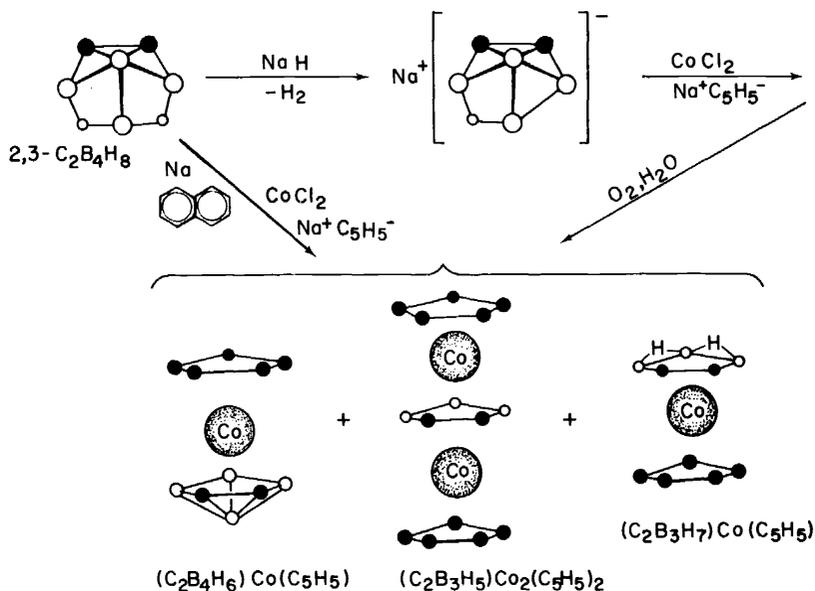
Figure 6. Reaction scheme for the synthesis of cobalt metallocarboranes from $C_2B_4H_8$

$\bigcirc$ BH   ● CH   • H
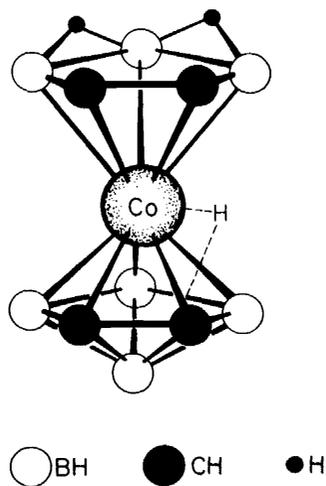
Figure 7. Proposed structure of $(2,3\text{-}C_2B_3H_7)CoH(2,3\text{-}C_2B_4H_6)$, obtained as bis(C,C′-dimethyl) derivative

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$(C_2B_3H_7)Co(C_5H_5)$
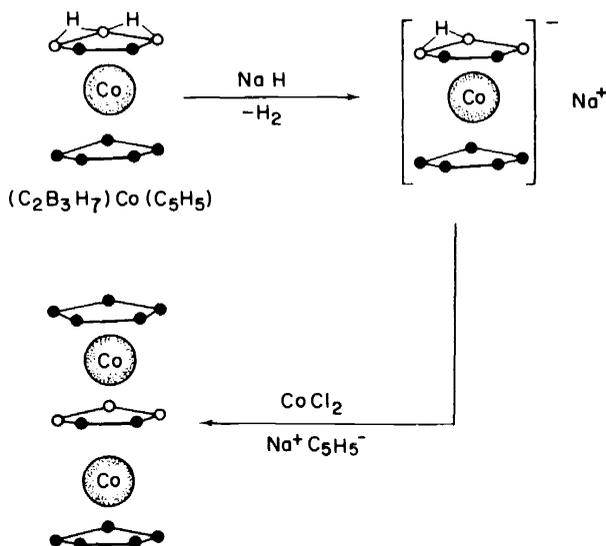
Figure 8. Reaction scheme for the conversion of $1,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_3H_7$ to $(\eta\text{-}C_5H_5)CoC_2B_3H_6^-$ ion and $1,7,2,3\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$

in *Figure 8.* Treatment of the resulting anion with $CoCl_2$ and NaC_5H_5 produces $1,7,2,3\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$[20, 22], a dimetallocarborane whose x-ray-determined structure, found for the C-methyl derivative[22], is given in *Figure 9.* Since the central ring is planar and can be formally represented
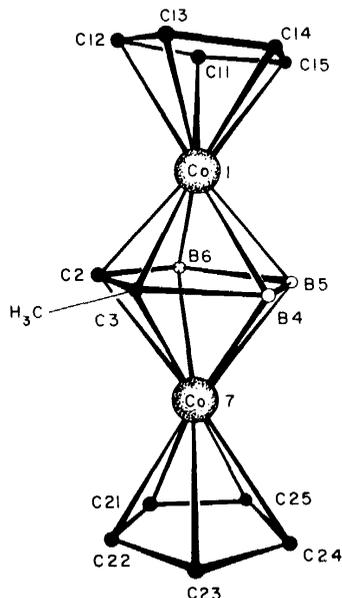

Figure 9. Structure of $C\text{-}CH_3\text{-}1,7,2,3\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_4$

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as $C_2B_3H_5^{4-}$, isoelectronic with $C_5H_5^-$, the molecule is analogous to a triple-decked metallocene [the $(\eta\text{-}C_5H_5)_3Co_2^{3+}$ ion is unknown, but a $(\eta\text{-}C_5H_5)_3Ni_2^+$ complex has been reported and a triple-decked structure postulated from ^1H n.m.r. and infra-red evidence[23]]. Both $(\eta\text{-}C_5H_5)$-$CoC_2B_3H_7$ and $1,7,2,3\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ are air-stable solids. Several other isomers of the $(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ system have been prepared and are described later in this paper. The C-methyl and C,C'-dimethyl derivatives of $1,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_6$ undergo analogous reactions[20].

The compound $1,2,3\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_6$ is thermally stable to at least $300°$, but at $400°$ undergoes rapid conversion to the 1,2,4 isomer in 90 per cent yield[9] (the latter species is also produced directly from $C_2B_5H_7$ as described below). No other isomers of this system have been detected in any reaction studied, and it is noteworthy that all other possible isomers with non-adjacent carbons, assuming pentagonal bipyramidal geometry, would have the metal in an equatorial location. Such an arrangement may well be unstable in *monometallic* 7-vertex metallocarboranes, but several dimetallic 7-vertex systems believed to have one equatorial iron or cobalt atom are described in a later section of this article.

The $1,2,4\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_6$ isomer, in contrast to the 1,2,3 species, is highly resistant to base attack and is not significantly reactive even toward ethoxide ion[9]. This observation is consistent with other data including ^{11}B and ^1H n.m.r. chemical shifts and thin layer chromatographic R_f values, which indicate that the 1,2,3 isomer is much more polar than the 1,2,4 system and hence would be expected to exhibit greater reactivity towards base attack.

The $C_2B_4H_7^-$ ion also undergoes insertion reactions with nickel reagents[20] as shown in *Figure 10*. The brown species $(\eta\text{-}C_5H_5)_2Ni_2C_2B_5H_7$ was
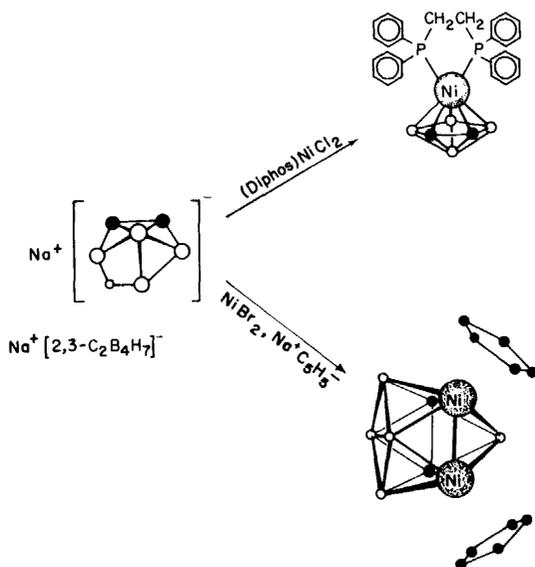
Figure 10. Reaction scheme for the synthesis of nickel metallocarboranes from $Na^+C_2B_4H_7^-$. The proposed structure of $(\eta\text{-}C_5H_5)_2Ni_2C_2B_5H_7$ is shown schematically, but distortion is expected (see text). Diphos denotes $[(C_6H_5)_2PCH_2]_2$

obtained in very low yield but is interesting in that the number of framework valence electrons is 22, two more than in the previously reported compound $(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$. The dinickel species is thus a $2n + 4$ system and might therefore be expected to undergo distortion of the normal 9-vertex polyhedron. Such a distortion might involve the usual cage-opening, which in this case would produce an unusual *nido* structure having no bridging hydrogens on the open face; a more attractive possibility is that the two 'extra' electrons occupy an antibonding orbital in the nickel–nickel bond, thereby producing a distorted polyhedron having an unusually long metal–metal distance[20, 24]. Such effects attributable to antibonding electrons have been found in organometallic clusters, for example the trigonal bipyramidal system $(\eta\text{-}C_5H_5)_3Ni_3S_2$[25]. If correct, this would suggest a general modification of the '$2n + 2$ rule' for metalloboron cages having adjacent metal atoms[24], to the effect that excess valence electrons may either occupy relatively low-lying antibonding orbitals in the region of the metals, or alternatively may be accommodated by opening the polyhedron. Presumably, only the latter mechanism is available in boron cages lacking metal atoms since suitable antibonding orbitals of low energy are not normally available.

Synthesis from small polyhedral carboranes via sodium reduction

The treatment of polyhedral carboranes of the $C_2B_{n-2}H_n$ series with sodium in the presence of naphthalene generates, in principle, an open-faced $C_2B_{n-2}H_n^{2-}$ dianion capable of accepting a metal atom to form an MC_2-$B_{n-2}H_n$ system which is a closed polyhedron one vertex larger than the original cage[26]. 'Polyhedral expansion' syntheses[26] of this sort in actual practice are often accompanied by complicating side reactions, and are not well understood; the presumed carborane dianions, for example. have been characterized in only two or three cases, e.g. $C_2B_9H_{11}^{2-}$[1]. The application of this method to $2,4\text{-}C_2B_5H_7$ with $FeCl_2$[13] or $CoCl_2$[27] and NaC_5H_5 gave a wealth of products, of which the major species were MC_2B_4 cages in which the metal, in net effect, replaced a boron atom instead of adding to the original cage. The main species formed on addition of sodium naphthalide to $C_2B_5H_7$ in THF does indeed appear to be a $C_2B_5H_7^{2-}$ anion, since oxidation with $SnCl_2$ regenerated $C_2B_5H_7$[28]. The addition of $CoCl_2$ and NaC_5H_5 to a THF solution of the $C_2B_5H_7^{2-}$ ion, and subsequent work-up of the metallo-carborane products in aqueous acetone, gave a series of monocobalt products, $(\eta\text{-}C_5H_5)CoC_2B_{n-2}H_n$ ($n = 6$–8) and a series of dicobalt species, $(\eta\text{-}C_5H_5)_2\text{-}Co_2C_2B_{n-2}H_n$ ($n = 6$–8) (*Figure 11*), but the predominant product (20 per cent yield) is the previously described $1,2,4\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_6$[27]. The 'expanded' cage species $(\eta\text{-}C_5H_5)CoC_2B_5H_7$ was formed only in low yield, which at the time suggested that this 8-vertex system might be unstable with respect to loss of boron and formation of $1,2,4\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_6$. However, later results have shown that this is not so, as discussed below. It now appears that the $C_2B_5H_7^{2-}$ ion itself is unstable and forms 7-vertex MC_2B_4 species directly, on reaction with metal reagents. Further evidence of this is given by the reaction of $C_2B_5H_7^{2-}$ ion with $CoCl_2$ in the *absence* of NaC_5H_5, which produced the bis(carboranyl)$(2,4\text{-}C_2B_4H_6)_2Co^-$ ion[20] (*Figure 12*). This complex is hydrolytically stable and was evidently not protonated by aqueous HCl, despite the fact that the isomeric $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2CoH$
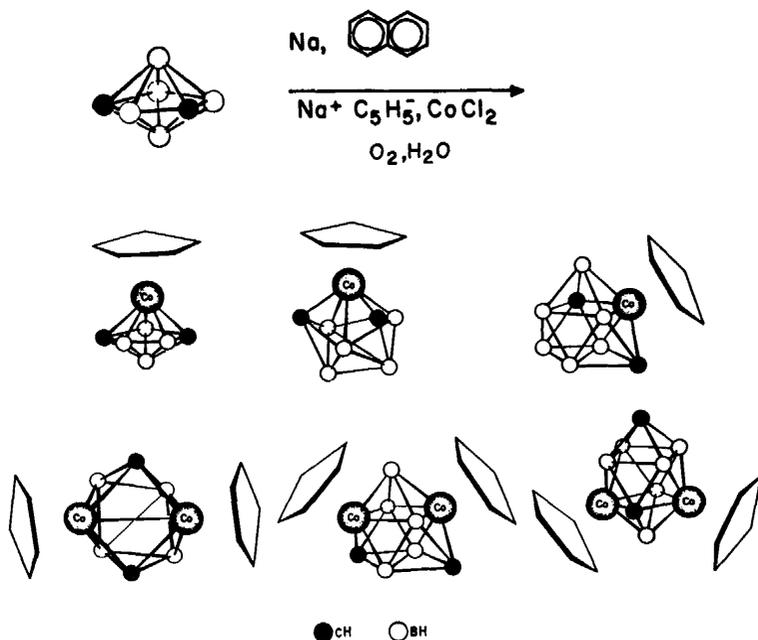
Figure 11. Proposed structures of metallocarboranes formed from 2,4-$C_2B_5H_7$, $CoCl_2$, and NaC_5H_5 via reduction of the carborane with sodium naphthalide in THF. Other products, not shown, include naphthyl- and $C_2B_5H_6$-substituted derivatives of 1,2,4-(η-C_5H_5)$CoC_2B_4H_6$
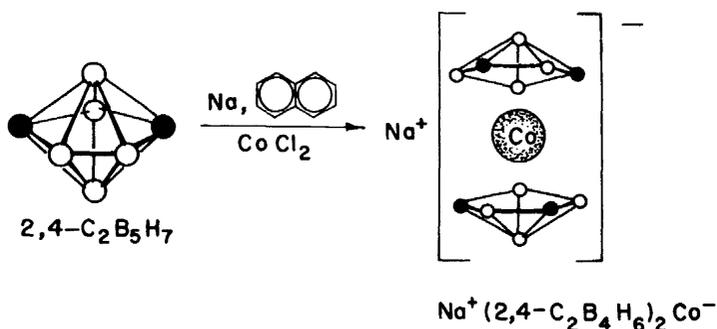
Figure 12. Preparation of the (2,4-$C_2B_4H_6$)$_2$Co$^-$ ion from $C_2B_5H_7$, showing proposed structure (orientation of ligand rings is arbitrary)

complex was obtained easily in the reaction of Na[(CH$_3$)$_2$C$_2$B$_4$H$_5$] with $CoCl_2$ (see above).

The reaction of $FeCl_2$ and NaC_5H_5 with $C_2B_5H_7^{2-}$ ion in THF followed by air-oxidation produced several 7-vertex FeC_2B_4 species including the linked-cage system 1,2,4-(η-C_5H_5)$FeC_2B_4H_5$-$C_2B_5H_6$; no expanded-cage products were obtained[13]. In this case the work-up was conducted entirely in non-aqueous media, so that the absence of expanded polyhedra cannot be attributed to hydrolytic degradation.

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The application of the same sodium-naphthalide–metal ion treatment to $1,6\text{-}C_2B_4H_6$ gave a mixture of products in poor yield, the major species being the 'triple-decked' dicobalt system $1,7,2,4\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$, isomeric with the 1,7,2,3 species mentioned earlier, and only a small amount of the expected $1,2,4\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_6{}^{20}$. Similar reactions of $1,5\text{-}C_2B_3H_5$ gave no isolatable metallocarboranes. It appeared, therefore, that the sodium naphthalide technique is too severe for the smallest polyhedral carboranes, and hence a new synthetic approach to the insertion of metals into the lower carboranes was sought.

Direct metal insertion into small polyhedral carboranes

In the course of our studies of small carboranes we had noted that $2,4\text{-}C_2B_5H_7$ reacts directly with $Fe(CO)_5$ in the vapour phase to form $(CO)_3FeC_2B_5H_7$ and $1,2,4\text{-}(CO)_3FeC_2B_4H_6{}^{13}$. Also, the reaction of the 11-vertex polyhedral cage $1,8\text{-}C_2B_9H_{11}$ with nickel group reagents in solution has been reported to give icosahedral metallocarboranes[29]. These observations led us to explore systematically the direct reactions of several polyhedral carboranes with organometallic reagents of iron, cobalt, and nickel[30], with emphasis on gas-phase experiments conducted in a sealed bulb or in a 'hot-cold' reactor described elsewhere[30]. The results indicate that the direct insertion method is a general, broadly applicable technique which is simple in execution and avoids many of the competing side reactions (e.g. metallocene formation) that frequently occur in syntheses involving metal ions and cyclopentadienide ion in solution. With this technique, metallocarboranes have been obtained in low to excellent yields from $1,5\text{-}C_2B_3H_5$, $1,6\text{-}C_2B_4H_6$, $2,4\text{-}C_2B_5H_7$, and $1,2\text{-}C_2B_{10}H_{12}$, and several of the products formed are structurally novel[30].

The reaction of $C_2B_3H_5$ with $(\eta\text{-}C_5H_5)Co(CO)_2$ or $Fe(CO)_5$ at 230° produced both 6-vertex monometallic and 7-vertex bimetallic species as shown in *Figure 13*. In addition to the compounds shown, the previously mentioned 'triple-decked' isomer, $1,7,2,4\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$, was also isolated from the cobalt reaction. The $(\eta\text{-}C_5H_5)CoC_2B_3H_5$ and $(CO)_3Fe\text{-}C_2B_3H_5$ are the smallest known polyhedral metallocarboranes and the first of octahedral geometry. They are 14-electron $2n + 2$ systems and are isoelectronic with $B_6H_6^{2-}$, $C_2B_4H_6$, octahedral metal clusters such as $(C_2H_5)_2C_2Co_4(CO)_{10}{}^{31}$, and the metalloborane $(\eta\text{-}C_5H_5)_2Co_2B_4H_6{}^{8}$. The dimetallic products shown are also novel, in that the two metal atoms evidently reside in adjacent 5- and 4-coordinate vertices in the 7-atom polyhedron[30]. Since each of these molecules is totally asymmetric and contains a metal atom in a low-coordinate equatorial position, their thermal stability is surprising and suggests possible stabilization by the direct metal–metal bonding interaction*.

The $1,2,3,5\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ species is a third isomer of the previously described 'triple-decked' compounds, 1,7,2,3- and $1,7,2,4\text{-}(\eta\text{-}C_5H_5)_2\text{-}Co_2C_2B_3H_5$. Since the 1,2,3,5 isomer was obtained at elevated temperature,

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* Metal atoms in metallocarboranes tend strongly to occupy high-coordinate vertices[1]. Except for the octahedral species mentioned here, in which no higher-coordinate vertex exists, only one previous instance of a metal apparently occupying a low-coordinate metallocarborane vertex has been reported[26].
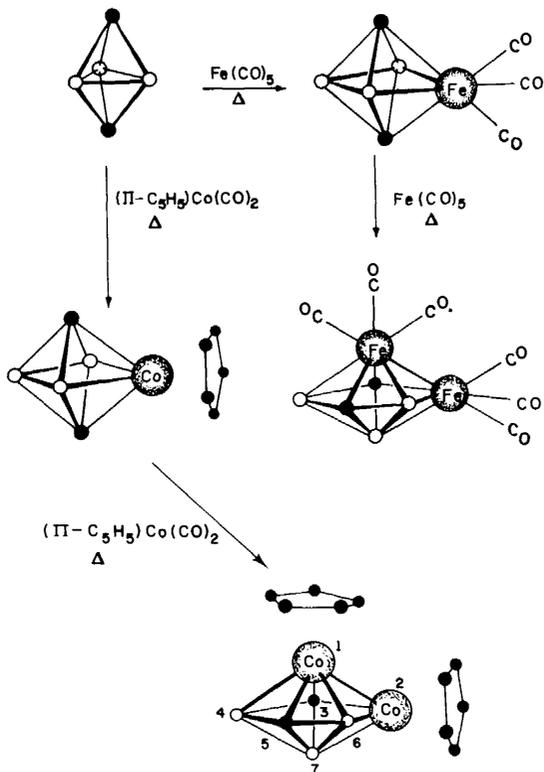
Figure 13. Reaction scheme for the synthesis of metallocarboranes from $1,5\text{-}C_2B_3H_5$ via direct metal insertion. An additional cobaltacarborane product, $1,7,2,4\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$, is not shown

it was suspected that it could have formed via rearrangement of thermally less stable isomers. Accordingly, it was found that mild (210°) heating of $1,7,2,3$-$(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ induces slow rearrangement to the 1,2,3,5 and 1,7,2,4 compounds, and in addition produces a small quantity of a fourth isomer, characterized as $1,2,4,5\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ (*Figure 14*). It appears that the 1,7,2,4 system is the most thermally stable $(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ system, and that the 1,2,3,5 and 1,2,4,5 isomers, which have one metal atom in the equator, are intermediates in the formation of the 1,7,2,4 from the 1,7,2,3 system. A more detailed discussion of this rearrangement will be given elsewhere[9], but it should be noted that the 1,2,3,5, 1,2,3,6 and 1,7,2,4 species are the only possible isomers having non-adjacent carbons and no more than one equatorial cobalt atom. The formation of species having adjacent framework carbon atoms is unlikely at elevated temperature[1], and placement of two cobalts in the equator of the pentagonal bipyramid would produce a severely distorted, flattened polyhedron. It is also noteworthy that the direct insertion of a second $(\eta\text{-}C_5H_5)Co$ unit into $1,2,4\text{-}(\eta\text{-}C_5H_5)CoC_2B_3H_5$ cannot lead directly to the $1,7,2,4\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ in one step, but
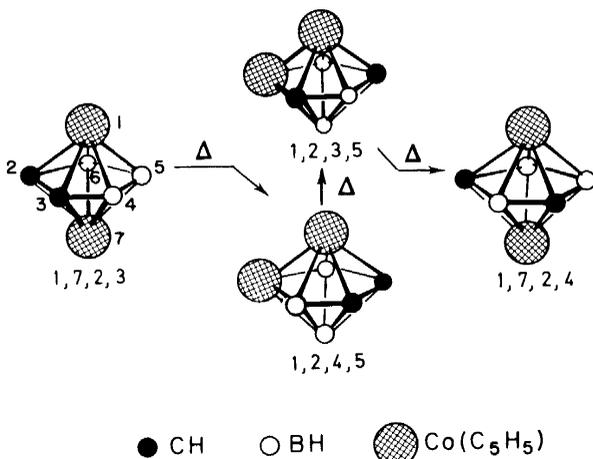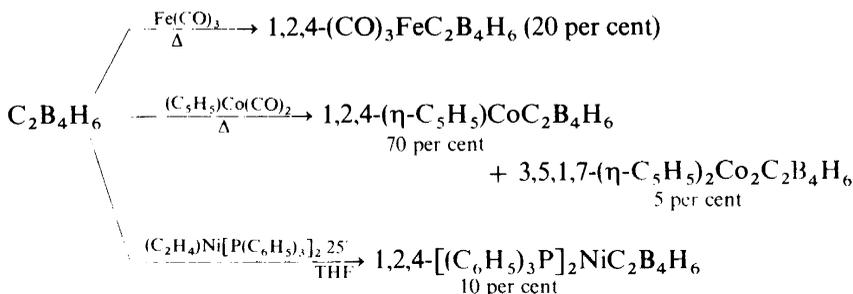
● CH   ○ BH   Co(C₅H₅)

Figure 14. Schematic diagram of the probable rearrangement route for $(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ isomers

must first form the 1,2,3,5 isomer if intermediates having two equatorial cobalts are assumed to be excluded.

The direct gas-phase metal insertion of $Fe(CO)_5$, $(\eta\text{-}C_5H_5)Co(CO)_2$, or $(\pi\text{-}C_2H_4)Ni[P(C_6H_5)_3]_2$ into $1,6\text{-}C_2B_4H_6$ gave primarily the expected $MC_2B_4H_6$ species[30].

$$C_2B_4H_6 \begin{cases} \xrightarrow[\Delta]{Fe(CO)_5} 1,2,4\text{-}(CO)_3FeC_2B_4H_6 \text{ (20 per cent)} \\[2ex] \xrightarrow[\Delta]{(C_5H_5)Co(CO)_2} 1,2,4\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_6 \\ \qquad\qquad\qquad \text{70 per cent} \\ \qquad\qquad\qquad + 3,5,1,7\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_4H_6 \\ \qquad\qquad\qquad\qquad \text{5 per cent} \\[2ex] \xrightarrow[THF]{(C_2H_4)Ni[P(C_6H_5)_3]_2\ 25^\circ} 1,2,4\text{-}[(C_6H_5)_3P]_2NiC_2B_4H_6 \\ \qquad\qquad\qquad \text{10 per cent} \end{cases}$$

The gas-phase reaction of $(\eta\text{-}C_5H_5)Co(CO)_2$ with $2,4\text{-}C_2B_5H_7$ at $260°$ in the hot-cold reactor gave an overall ~ 60 per cent yield of metallocarboranes as shown[30].

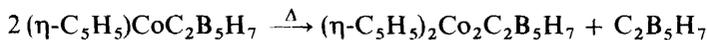$$C_2B_5H_7 + (\eta\text{-}C_5H_5)Co(CO)_2 \xrightarrow{\Delta}$$

	Per cent yield
$1,2,4\text{-}(\eta\text{-}C_5H_5)CoC_2B_4H_6$	3.6
$3,1,7\text{-}(\eta\text{-}C_5H_5)CoC_2B_5H_7$	25
$1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$	25
$1,7,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$	2.5
$2,3,8,1,6\text{-}(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7$	2.4*
$2,3,4,1,10\text{-}(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7$	0.3

* Obtained in substantially higher yield in sealed-bulb reactions at $300°$ (see text).

The $3,1,7$-$(\eta$-$C_5H_5)CoC_2B_5H_7$, a major product of the reaction, is identical to the species formed in low yield in the sodium naphthalide–metal ion procedure described above. This compound is both thermally and hydrolytically stable, and no other isomer of this system has been found; at $300°$ it undergoes very slow disproportionation to $1,8,5,6$- and $1,7,5,6$-$(\eta$-$C_5H_5)_2Co_2C_2$-B_5H_7 and $2,4$-$C_2B_5H_7$[9].

$$2\,(\eta\text{-}C_5H_5)CoC_2B_5H_7 \xrightarrow{\Delta} (\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7 + C_2B_5H_7$$

The two isomers of $(\eta$-$C_5H_5)_2Co_2C_2B_5H_7$ formed in this disproportionation were also obtained in the $(\eta$-$C_5H_5)Co(CO)_2$–$C_2B_5H_7$ reaction[30] (see above), and a study of their relative thermal stability revealed that the $1,8,5,6$ isomer (*Figure 15*) rearranges to the new $1,7,5,6$ species in high yield at $300°$. The $1,7,5,6$ isomer is proposed to have cobalt atoms in adjacent $(1,7)$ vertices, and the apparent movement of metal atoms toward each other is at least consistent with the observed formation of isolatable species containing adjacent metals in the $(\eta$-$C_5H_5)Co(CO)_2$–$C_2B_3H_5$ reaction described above.
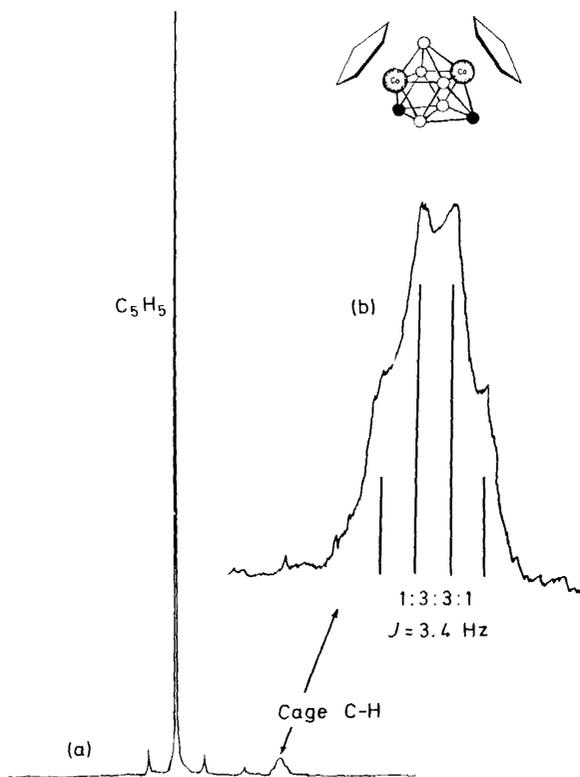

Figure 15. 100-MHz Fourier transform proton n.m.r. spectrum of $1,8,5,6$-$(\eta$-$C_5H_5)_2C_2B_5H_7$ in $CDCl_3$. (a) Complete spectrum. (b) Enlarged cage C—H resonance

The 100-MHz [1]H n.m.r. spectrum of the 1,8,5,6 isomer provides an interesting example of a phenomenon frequently observed in our laboratory[20, 22, 27, 30]: the cage C—H resonance contains fine structure which we attribute to H—B—C—H proton–proton spin coupling (*Figure 15*). In this particular case the resonance is an apparent quartet, indicative of coupling between each of two equivalent C—H protons and three adjacent B—H groups. This observation, obtained on a Fourier transform spectrometer[30], provides further support for the structure shown, which was formerly postulated[27] from continuous-wave [11]B and [1]H n.m.r. data (the earlier proton spectrum[27] failed to resolve the cage C—H resonance). Evidence of H—B—C—H spin coupling has apparently not been observed in icosahedral metallocarboranes, the cage C—H proton resonances typically being broad singlets, but Onak has detected this effect in several small 5- to 7-vertex polyhedral carboranes with the aid of [11]B decoupling[32]. In our work electronic boron decoupling was not employed, but the presence of one or more cobalt nuclei very probably induces partial boron-decoupling in certain favourable structural situations occurring in some of our compounds. Consequently, we have noted the effect in some metallocarboranes and not in others. A case in which this phenomenon proved particularly useful in structural assignment is that of the tricobalt compounds discussed below.
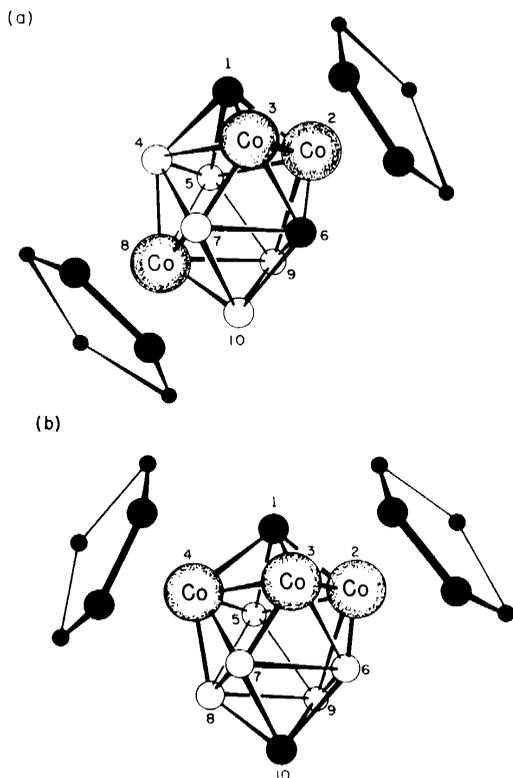

Figure 16. Proposed structures of $(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7$ isomers. (a) 2,3,8,1,6 isomer. (b) 2,3,4,1,10 isomer. In each structure the C_5H_5 ligand on the cobalt (3) atom is omitted for clarity

The trimetallic $(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7$ isomers were obtained only in low yield in the hot–cold reactor[30], but sealed-bulb experiments employing the same reactants have afforded ~ 20 per cent yields of the more abundant species[33]. The proposed structures of these compounds, which are the first sub-icosahedral boron cages having more than two metal atoms, are shown in *Figure 16* [one other trimetallic system, a 12-vertex $(\eta\text{-}C_5H_5)_3Co_3C_2B_7H_9$ species, has been reported by Hawthorne[34]]. The structures depicted are consistent with the ^{11}B and ^1H n.m.r. spectra; other possibilities cannot be excluded, but certain features of the spectra serve to increase the probability that the arrangements shown are the correct ones. First, the low-field $[\delta - 50$ p.p.m relative to $BF_3 \cdot O(C_2H_5)_2]$ doublet of area 1 in the ^{11}B n.m.r. spectrum of the 2,3,8,1,6 isomer (*Figure 17*) is indicative of a BH group in a low-coordinate (apex) position adjacent to cobalt, an effect noted frequently in our work and that of others[26,27]. The 2,3,4,1,10 isomer has no such
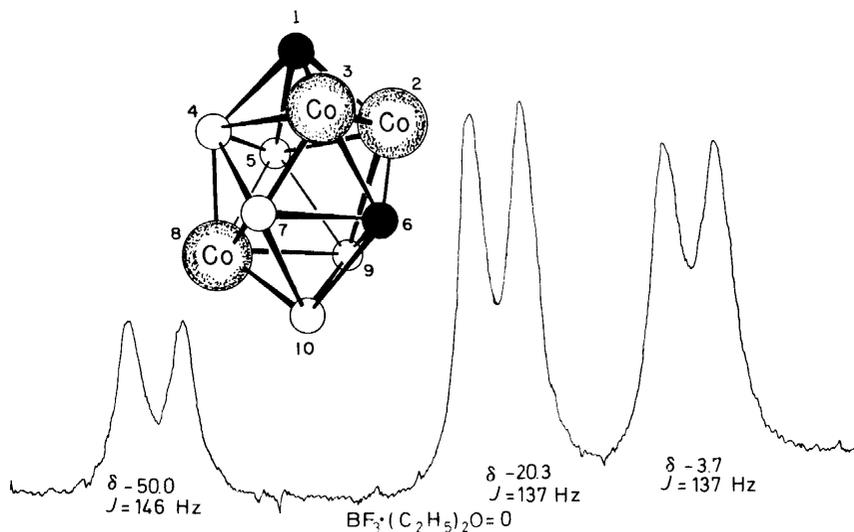
Figure 17. 32.1-MHz Fourier transform ^{11}B n.m.r. spectrum of 2,3,8,1,6-$(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7$ in $CDCl_3$. 6.1 mg (0.013 mmol)/0.2 ml

resonance at very low field. Second, the ^1H n.m.r. spectra of both isomers contain one exceptionally low-field cage C—H resonance and one at somewhat higher field. Thus, the 2,3,8,1,6 compound exhibits C—H peaks at $\delta - 10.65$ and -6.94 p.p.m. relative to $(CH_3)_4Si$ (*Figure 18*) while the other species has corresponding signals at $\delta - 15.81$ and -5.69. The two very low-field proton resonances are strongly suggestive of a CH group adjacent to several cobalt nuclei, as in the well-known cluster $HCCo_3(CO)_9$, which exhibits a ^1H n.m.r. signal at $\delta - 12.08$[35]. Furthermore, the C—H peaks in the spectrum of 2,3,8,1,6-$(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7$ are split into a triplet and quadruplet, respectively (*Figure 18*) indicating that one CH unit is adjacent to two BH groups while the other CH is directly attached to three BH. In the 2,3,4,1,10 isomer, the low-field C—H peak is split into a doublet, as expected
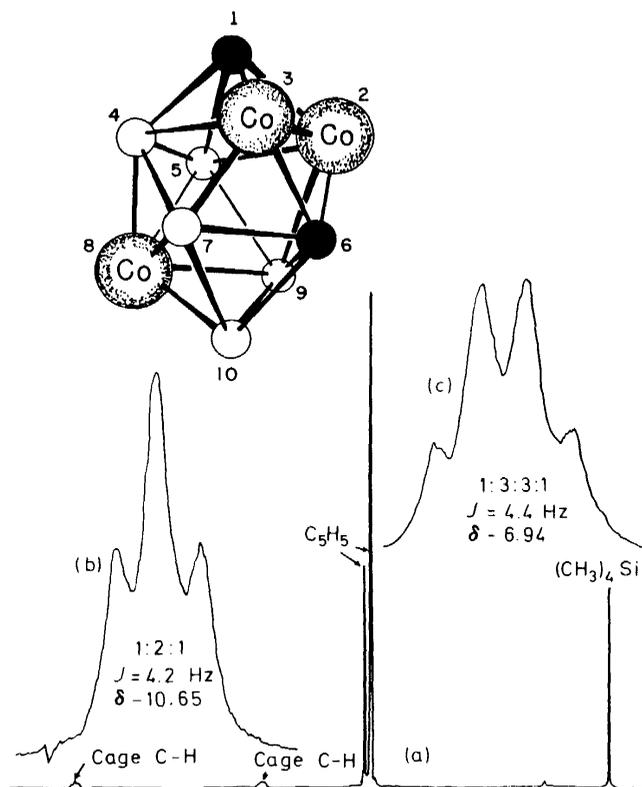
471

Figure 18. 100-MHz Fourier transform proton n.m.r. spectrum of 2,3,8,1,6-(η-C_5H_5)$_3$Co$_3$C$_2$B$_5$H$_7$ in CDCl$_3$. (a) Complete spectrum; (b) and (c) enlarged cage C—H resonances

for the structure shown in *Figure 16*(b) in which the carbon in position 1, adjacent to three cobalts, is directly linked to only one BH group[30].

Direct metal insertion into the extremely stable icosahedral system 1,2-$C_2B_{10}H_{12}$ (ortho-carborane) somewhat to our surprise was effected in the gas phase at 300° in a sealed bulb, producing a mixture of icosahedral (η-C_5H_5)CoC$_2$B$_9$H$_{11}$ isomers in a total yield of $\sim$50 per cent[30]. In this instance, the expanded 13-vertex species was not found, but presumably forms initially only to undergo thermal degradation with loss of boron to form the 12-atom products. This reaction represents the first reported instance of direct heteroatom insertion into a closed icosahedral carborane, and illustrates the potentially broad applicability of the method.

CONCLUDING REMARKS

The work described here demonstrates the existence of an extremely rich chemistry of small metallocarboranes based on the insertion of metals, by direct and indirect methods, into the lower *closo-* and *nido-*carboranes. Since many of the products are electronic and structural analogues of metallic and

organometallic clusters of five or more atoms, a direct and theoretically well-founded relation between the boron and non-boron cages exists, and appears ready for exploitation by synthetic chemists. Thus, metallocarboranes might be synthesized by insertion of boron into organometallic clusters; compounds of the latter type, conversely, might be found to undergo general cage-opening or cage-expansion reactions similar to the boron polyhedra; and the successive replacement of boron atoms by metal atoms could provide a new approach to metal cluster synthesis, as has been previously suggested[36].

Although three or four metal atoms might well represent an upper limit of stability in an icosahedral cage, the existence of many smaller polyhedra having up to six metal atoms (as in the metal clusters) implies that such a limitation may be less stringent in the lower metallocarborane series, and that 6- or 7-vertex cages in which the metal atoms outnumber boron are feasible. Such species would very likely exhibit properties intermediate between the metallocarboranes and the metal clusters and would establish an experimental bridge between these classes of compounds, augmenting the known electronic and structural analogies.

ACKNOWLEDGEMENTS

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