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Cluster forming and cage fusion in metallacarborane chemistry

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Contents

Abstract

Multidecker sandwich complexes in which transition metal centers are bridged by C_2B_3 carborane rings are organometallic species by definition, and are close electronic and structural relatives of metallocenes and metal–arene sandwiches. At the same time, these complexes can be described as 7-vertex MC_2B_3M' or MC_2B_4 metallacarborane clusters and manifest chemical properties typical of that class, such as cage rearrangement and metal insertions into the polyhedral framework. Their "boron cluster" character is particularly evident in metal-promoted oxidative fusion reactions in which two 6-vertex *nido*-MC_2B_3 cages are fused face to face to form a 12-vertex $M_2C_4B_6$ cluster. Such fusions often occur as competitive processes in the synthesis of multidecker sandwich complexes via metal stacking reactions. In this article we discuss the propensity of small metal–boron units to undergo clustering, centering on the factors that promote such reactions and strategies that can be employed to control and exploit them for synthetic purposes. Specific examples of unusual cluster geometries, some of them unique, that have been obtained via fusion will be treated from both synthetic and structural perspectives.

Keywords: Clusters; Cage fusion; Metallacarboranes; Cobaltacarboranes; Ferracarboranes; Multidecker sandwich complexes

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1. Introduction

Syntheses of large molecular clusters or cages from small building block units are typically uncontrolled and mechanistically undefined [1]. This is true of main group species (e.g. the formation of icosahedral $B_{12}H_{12}^{2-}$ from $NaBH_4^-$ and B_2H_6) as well as transition metal clusters (the conversion of $Rh_4(CO)_{12}$ to $[Rh_{13}(CO)_{25}H_3]^{2-}$, for example). As a general proposition, the designed assembly of clusters of specified geometry and composition from molecular synthons is a formidable synthetic challenge. A conceptually attractive approach is the metal-mediated face-to-face fusion of two substrate molecules (Fig. 1). This strategy has not, so far, found general application in the metal cluster field, possibly because of the paucity of suitable

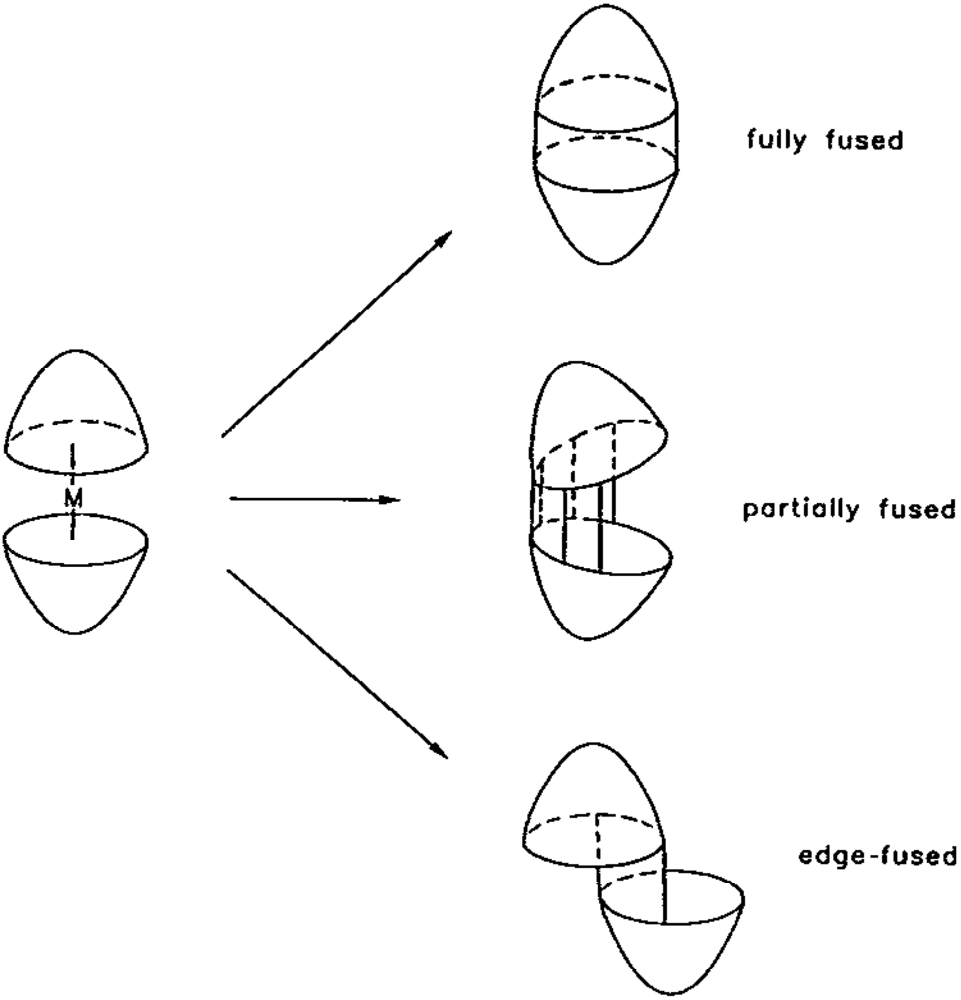


Fig. 1. Modes of metal-mediated ligand fusion.

building block complexes and the frequent presence of CO or other ligands that prevent close approach of the metal frameworks on the two units.

A very different story emerges in boron cage chemistry, where metal-promoted cage fusion is well established and in recent years has been developed into a useful synthetic tool. Our discovery in 1974 [2] of the extremely facile conversion, via rapid air oxidation in cold THF solutions, of $(Me_2C_2B_4H_4)_2MH_n$ sandwich complexes ($MH_n = Fe^{II}H_2$ or $Co^{III}H$) to 12-vertex $R_4C_4B_8H_8$ open-faced carboranes (vide infra) was followed by extensive investigation of this class of reactions [3]. During this work it became apparent that oxidative fusion is not a "freak" reaction limited to the original *nido*-carborane system, but can in fact be applied to a variety of small boron cluster substrates including binary boron hydrides as well as metallaborane and metallacarborane clusters. Consequently, the method furnishes a valuable and indeed powerful approach to the designed synthesis of boron-containing clusters, as will be demonstrated.

The earlier work in this area, involving the fusion reaction itself as well as the new subfield of carbon-rich carboranes and metallacarboranes that evolved from it, has been elaborated in previous reviews and papers [3]. The present article offers a current perspective on fusion as a workable synthetic strategy in cluster chemistry, with special attention to the emerging relationship between multidecker metal stacking and metal-mediated cage fusion.

2. Metal-promoted cage fusion as a synthetic tool

2.1. Directed synthesis of new boranes and carboranes

Of the two dozen or so known binary neutral boron hydrides (B_nH_m), almost all were first produced in high energy, uncontrolled reactions, often involving pyrolytic or gas phase electric discharge methods [1c]. A notable exception is $B_{12}H_{16}$, synthesized in high yield under mild conditions via the cobalt-promoted fusion of two $B_6H_9^-$ units with loss of H_2 (Fig. 2(a)) [3m].

This reaction was the first planned synthesis of a new binary borane of predesignated composition (the detailed molecular geometry was not, however, predicted in advance). As far as this author is aware, it remains unique in this regard. In analogous fashion, the fusion of two pentaborane anions, $B_5H_8^-$, via metal complexation with $RuCl_3$ or $FeCl_2$ followed by air oxidation, produces $B_{10}H_{14}$ in moderate yield under mild conditions (Fig. 2(b)) [3k]. Studies of this reaction involving apically substituted DB_5H_8 and MeB_5H_8 derivatives, together with analogous fusions of CoB_4 units to form Co_2B_8 clusters (vide infra), suggest the mechanistic scheme in Fig. 2(c), in which the apex atoms of the original 5-vertex clusters occupy vertices 2 and 4 in the 10-vertex fusion product [3k]. Given the availability of a multiton US Government stockpile of B_5H_9 (from which the anion is formed by removal of a B—H—B proton) and the low cost of ferrous chloride, this represents a potentially important route to decaborane(14) although it has not yet been explored on a large scale.

In related work, the previously characterized [4] hydride n-$B_{18}H_{22}$ was obtained

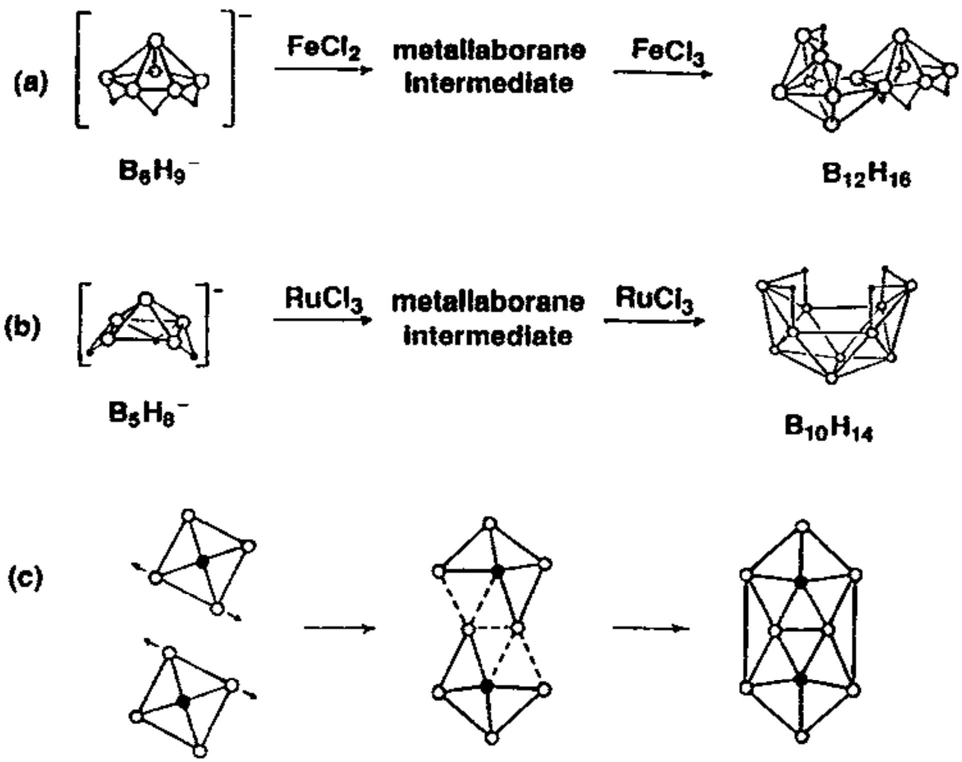


Fig. 2. (a) Synthesis of $B_{12}H_{16}$ via metal-promoted fusion of $B_6H_9^-$ [3m]. (b) Synthesis of $B_{10}H_{14}$ via metal-promoted fusion of $B_5H_8^-$ [3k]. (c) Proposed mechanism for fusion of two square pyramidal units to form a 10-vertex *nido* cluster [3k].

via oxidative edge fusion of $B_9H_{12}^-$ in the presence of H_9Br_2 [5]; similarly, the conjugate base anion $B_{18}H_{21}^-$ was obtained on treatment of $B_9H_{12}^-$ with $[Os(CO)_3Cl_2]_2$ [6]. It has not been established that these reactions do in fact involve metal–borane complex formation as opposed to an alternative (e.g. radical) mechanism, but there is no doubt that the metal reagents are involved. In any event, the degree of control achieved in these borane fusion syntheses is remarkable in view of the usual high reactivity of the lower boron hydrides and their tendency to generate multiple products even under mild conditions.

Application of oxidative fusion to the synthesis of carborane clusters has been far more extensively investigated, centering primarily on the metal sandwich complexes of *nido*-$(R_2C_2B_4H_4)^{2-}$ ligands as mentioned in the introduction. Fig. 3 depicts the fusion of two C_2B_4 pyramidal units to create a C_4B_8 cage, the precise geometry of the product depending on the nature of the carbon-bound R substituents [3a–3j, 3n–3s].

When R is CH_3 or C_2H_5, the $R_4C_4B_8H_8$ molecule in solution is fluxional, oscillating between the geometries shown. The solid state structures of these compounds, however, each consist of only one isomer: that of $(Me_4C_4B_8H_8)$ adopts the "closed" (A)

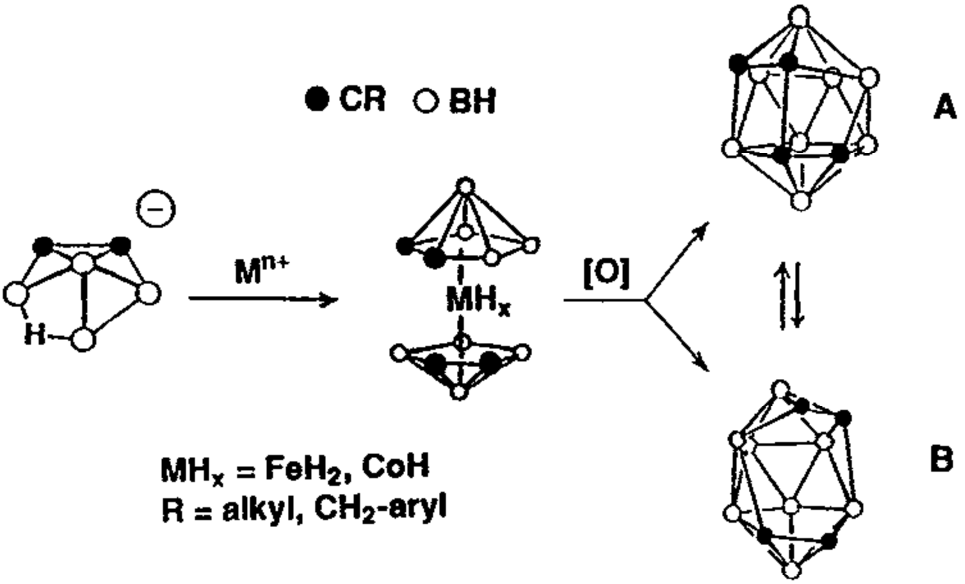


Fig. 3. Synthesis of $R_4C_4B_8H_8$ carboranes via oxidative fusion of $H_xM(R_2C_2B_4H_4)_2$ sandwich complexes.

geometry [7] while that of ($Et_4C_4B_8H_8$) has the "open" (B) form [3j]. Larger R substituents such as benzyl and hexyl force the open geometry exclusively, and no fluxionality is observed [8]. $(R_2C_2B_4H_4)^{2-}$ ligands in which both R groups are the very bulky indenylmethyl and fluorenylmethyl groups do not undergo fusion at all [3n,3p,3r].

In no case is a closed icosahedral C_4B_8 cage formed, a finding that conforms with the polyhedral skeletal electron-pair theory (PSEPT) [9]. The requirement for a closed n-vertex deltahedron (a cluster having all faces triangular) is $2n+2$ valence electrons exclusive of external B—H and C—R bonds, so that 12-vertex, 26-electron polyhedra such as $R_2C_2B_{10}H_{10}$ are icosahedral; "electron-rich" 28-electron $R_4C_4B_8H_8$ cages must adopt somewhat more open structures, although there are many ways to do this, discussed below [10,11].

The mechanisms of C_4B_8 cage formation and rearrangement have been investigated [3h,3i], and polyhedral expansion via the incorporation of metals to generate 13- and 14- vertex $M_nC_4B_m$ metallacarborane clusters has been described elsewhere [3a,12].

2.2. *Directed synthesis of dimetallic metallaboranes and metallacarboranes*

A large number of polyhedral metallaboranes (metal–boron clusters lacking skeletal carbon atoms) have been prepared, many of them in complex reactions involving metal salts and $B_nH_m^-$ anions [1,13,14]. Owing to the high reactivity of most borane anions and the presence of multiple sites for metal complexation on the boron framework, such processes typically generate mixtures of metallaborane products whose cage structures differ markedly from the original borane substrate. This approach has had spectacular success in yielding a profusion of structurally varied clusters [13,14], but is clearly not suitable for the designed synthesis of specific target compounds. For the latter purpose, metal-promoted fusion of metallaborane synthons is a useful approach that has been demonstrated in several systems. As shown in Fig. 4, the two isomers of *nido*-$CpCoB_4H_8$ (an electronic and structural analogue of B_5H_9) produce isomers of the dicobalt cluster *nido*-$Cp_2Co_2B_8H_{12}$, analogous to $B_{10}H_{14}$ [3k].

Significantly, the deprotonation and fusion of 1-$CpCoB_4H_8$ affords only 2,4-$Cp_2Co_2B_8H_{12}$, whereas the 2-isomer gives rise to three isomeric clusters as shown. These findings are entirely consistent with the proposed mechanism in Fig. 2(c), if one replaces an apex BH or basal BH in B_5H_9 with its electronic counterpart CpCo. No evidence is seen for the formation of other products, suggesting a relatively simple, clean process as would be anticipated for a metal-mediated fusion.

Oxidative fusion of a ferraborane moiety has been reported by Fehlner and his students, who found that the dilithio salt of the $(CO)_6Fe_2B_2H_4^{2-}$ dianion, on treatment with $FeCl_2$ at low temperature followed by oxidation with $FeCl_3$, yields B,Fe-

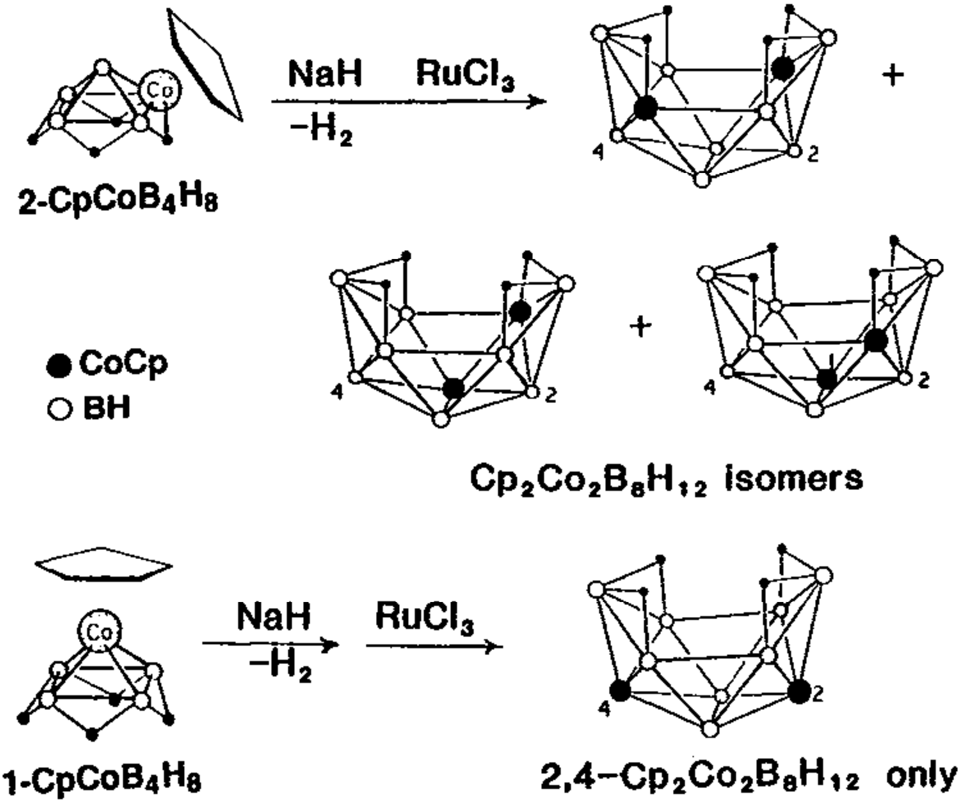


Fig. 4. Conversion of 1- and 2-$CpCoB_4H_8$ to $Cp_2Co_2B_8H_{12}$ isomers [3k].

conjuncto-$[(CO)_6Fe_2B_2H_4]_2$ (Fig. 5, isomer A) [15]. On heating in solution, a second isomer (B) having a B,B-*conjuncto* structure (Fig. 5) is formed and an equilibrium between the two species is established.

The solid state structure of isomer A is unchanged in solution, but that of B is present as three tautomers, the most abundant of which corresponds to the solid state geometry [15].

As noted earlier, the fusion approach has been extensively applied to small metallacarboranes, especially those of the pentagonal–pyramidal *nido*-MC_2B_3 class. Sandwich complexes of the type $LCo(R_2C_2B_3H_5)$ where L = Cp or Cp* (Cp* = η^5-C_5Me_5) are electronic and structural analogues of the previously discussed *nido*-2,3-$R_2C_2B_4H_6$ carborane family via formal replacement of BH by an electronically equivalent (two-electron donor) CoCp or CoCp* unit. In both families, there is a planar C_2B_3 face containing two B—H—B bridging protons, of which one or both can be easily removed to generate a monoanion or dianion respectively. Coordination of two such ligands to a common metal cation can occur in several ways, including (a) full face bridging (η^5 complexation), (b) partial face bridging, and (c) edge bridging, as depicted in Fig. 6.

Species of the first variety can be viewed as "double clusters" in which two pentagonal bipyramids share a common metal vertex; the LM-capped structures can also be described as tetradecker (quadruple-decker) sandwiches. Any of these types

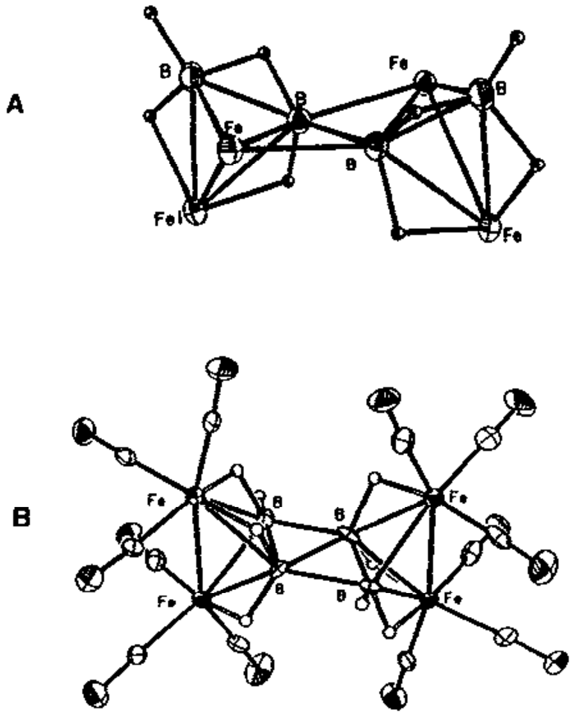


Fig. 5. Structures of B,Fe-*conjuncto*-$[(CO)_6Fe_2B_2H_4]_2$ (A) and B,B-*conjuncto*-$[(CO)_6Fe_2B_2H_4]_2$ (B) [15].

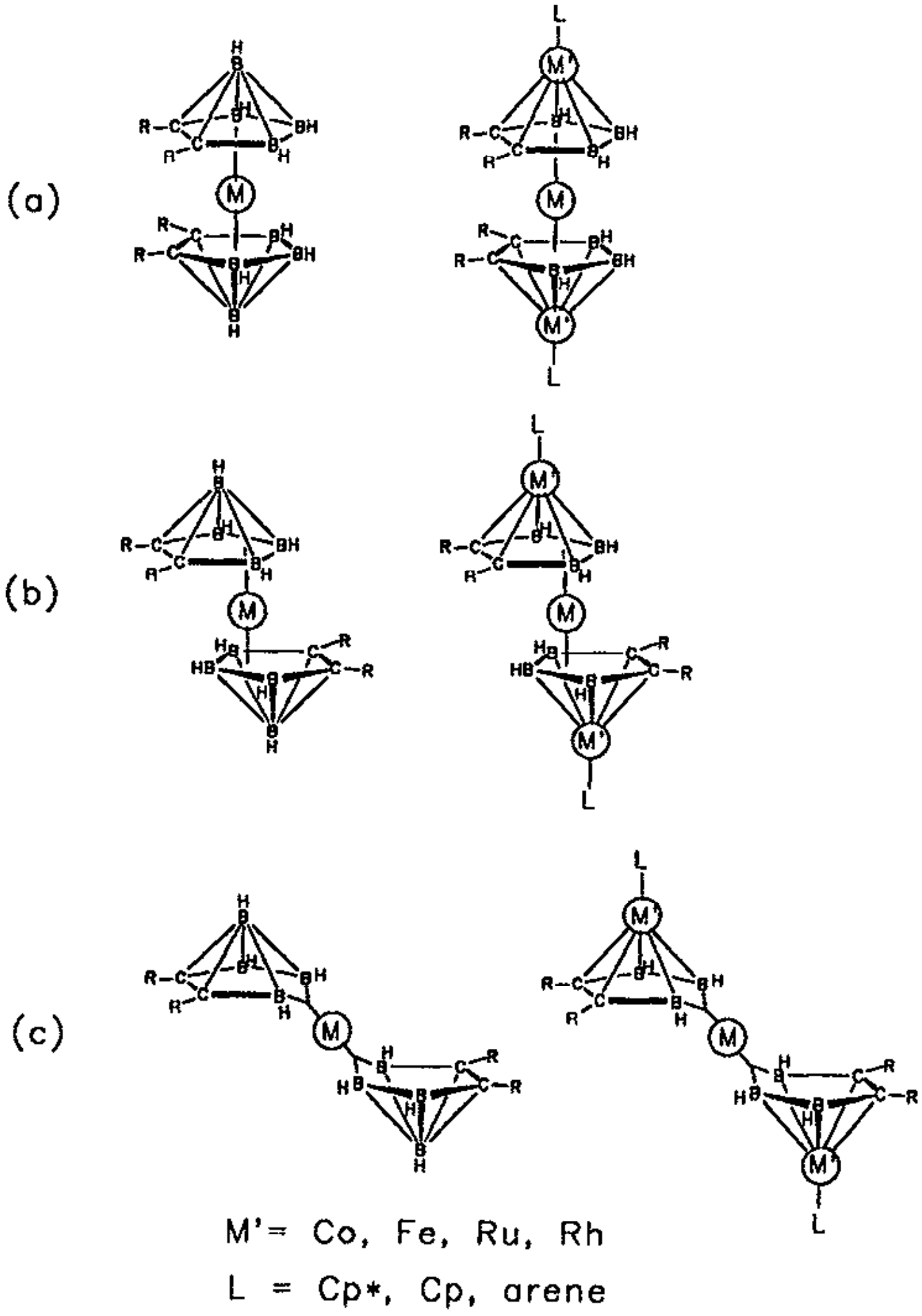


Fig. 6. Coordination of 6-vertex carborane or metallacarborane ligands to a central metal (M) via η^5, η^3, or η^2 coordination.

of metal-bridged complex can undergo fusion or B—B coupling, as will be shown. However, there is considerable variation in the ease with which fusion (or coupling) occurs: in some cases the metal-bridged species is stable to oxidation and does not fuse at all, while at the other extreme, the fusion may occur so rapidly that the intermediate metal complex is never observed. This variability reflects the choice of metal ion, the influence of substituents on the carborane ligands, and the experimental conditions, for example exposure to air or other oxidants, and can be used to advantage in synthesis.

3. Multidecker stacking and cluster fusion

3.1. Metal–ligand stacking reactions: formation of triple-decker metallacarborane sandwich complexes

Heterocyclic boron–carbon rings are well suited to the purpose of assembling multidecker sandwiches, much more so than are aromatic hydrocarbon ligands. Following the preparation of the very unstable $Cp_3Ni_2^+$ cation over 20 years ago in the classic work of Werner and Salzer [16], molecular triple-decker sandwich complexes bridged by C_5Me_5 or benzene rings were synthesized [17], but other C_5H_5-bridged species were unknown until the very recent work of Herberich et al. [18]. Triple-decker sandwiches containing cyclic planar P_n or As_n rings where $n = 3$, 4, 5, or 6 have also been prepared [19]. However, at present the area of multidecker sandwich chemistry is overwhelmingly dominated by complexes of boron–carbon ligands, especially those incorporating borole (C_4B), diborole (C_3B_2), carborane (C_2B_3), and diborabenzene (C_4B_2) rings. In addition to the hundreds of triple-decker complexes incorporating these ligands, all known examples of larger (tetra- or higher-decker) molecular sandwiches contain diborole or carborane rings, excluding species having staggered multilevel structures. The elegant pioneering work of Siebert and of Herberich and their groups in the area of organoboron (borole, diborole, and diborabenzene) metal sandwiches has been described in a number of reviews [20]. Ligand fusion has not been observed in organoboron complexes; such reactions are limited, evidently, to borane or carborane ligands having no more than two carbon atoms in the metal-coordinated rings, a fact that clearly has mechanistic implications. The present discussion is consequently centered on metal–small carborane complexes and the relationship between their multidecker stacking and fusion reactions.

Monometallic "double-decker" carborane sandwiches of the type $LM(RR'C_2B_4H_4)$ where L is an arene, Cp, or Cp*, M is a transition metal, and R and R′ are usually alkyl, arylalkyl, or $SiMe_3$ groups, are obtained via reaction of an LMX_n reagent (X = halogen) with the $RR'C_2B_4H_5^-$ monoanion or $RR'C_2B_4H_4^{2-}$ dianion (Fig. 7 [3c,21]).

Removal of the apex BH unit ("decapitation") is readily accomplished in most double-decker species via base attack, affording an open-faced *nido*-$LM(RR'C_2B_3H_5)$ complex where "*nido*" designates a cluster formally derived from a deltahedron via removal of one vertex (i.e. the MC_2B_3 cage is a fragment of a 7-vertex pentagonal

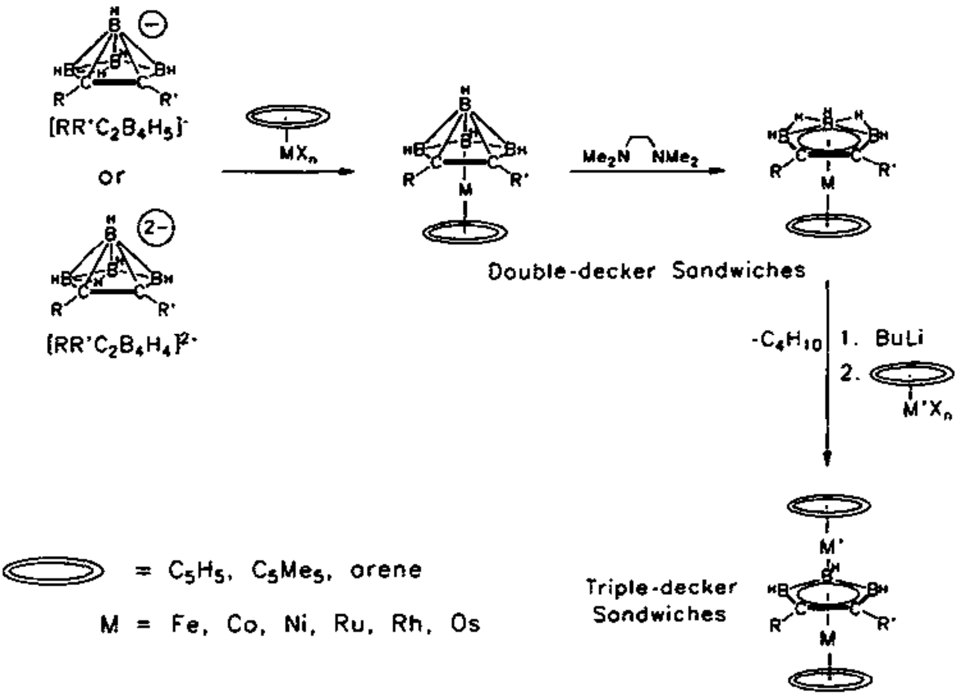


Fig. 7. Directed syntheses of double- and triple-decker metallacarborane sandwich complexes.

bipyramid). The *nido* complex, like the original ($RR'C_2B_4H_4$) carborane, has protonic B—H—B hydrogen atoms that can be removed and a second metal–ligand group inserted to form a triple-decker sandwich, as illustrated in Fig. 7. This approach was employed in the 1972 synthesis of $CpCo(RR'C_2B_3H_3)CoCp$ isomers [22], the first neutral, stable triple-decker sandwiches, and has been employed to generate a wide variety of homo- and heterobimetallic $(L)M(C_2B_3)M'(L)$ triple-deckers involving first-, second- and third-row transition metals, most of which are isolable as air-stable crystalline solids [21]. The end rings (L) can be arenes, Cp or Cp*, or even C_4X heterocycles such as phosphollyl and pyrrolyl [23]. Detailed electrochemical and spectroscopic studies on selected triple-decker sandwiches have established extensive electron delocalization between the metal centers; in Co—Ru and Ru—Ru cationic triple-deckers, the odd electron is fully delocalized over the two metals [24]. In related work, "hybrid" triple-decked sandwiches incorporating both carborane (C_2B_3 or C_2B_4) and borole (C_3B_2) ring ligands have been prepared [25].

3.2. *Directed synthesis of tetradecker metallacarborane sandwiches and oligomers*

A priori, a straightforward route to tetradecker (quadruple-decker) complexes appeared feasible via the via coordination of two $LM(RR'C_2B_3H_3)^{2-}$ units to a central metal as depicted in Fig. 6(a), representing a simple extension of the triple-decker synthesis just described. However, the formation of stable tetradecker sandwiches in this manner turned out to be highly sensitive to the electronic character of the open face on the double-decker substrate (Fig. 8).

We found that stable $Cp^*Co(Et_2C_2B_3H_2\text{-}X)M(Et_2C_2B_3H_2\text{-}X)CoCp^*$ tetradeckers (Co-M-Co) that can survive silica chromatography in air are readily prepared from $Cp^*Co(Et_2C_2B_3H_3\text{-}X)^-$ complexes in which the X substituent (located on the middle boron, B[5]) is strongly electron withdrawing; the Cl, Br, I, propargyl, and acetyl derivatives work well [26]. A quantitative measure of the electron density on the open face is found in the proton nuclear magnetic resonance (NMR) shift of the B—H—B hydrogen atoms in neutral $Cp^*Co(Et_2C_2B_3H_4\text{-}X)$ complexes: when δ_{BHB} is less negative than (i.e. to low field of) −5.24, stable tetradecker products are formed, whereas complexes exhibiting values at higher field either show no evidence of reaction with metal ions (e.g. the ethyl derivative) or give unstable products [26].

In accordance with this empirical rule, the complex in which X = Me (δ_{BHB} = −5.23) forms a tetradecker, while that in which X = Et (δ_{BHB} = −5.36) does not. The

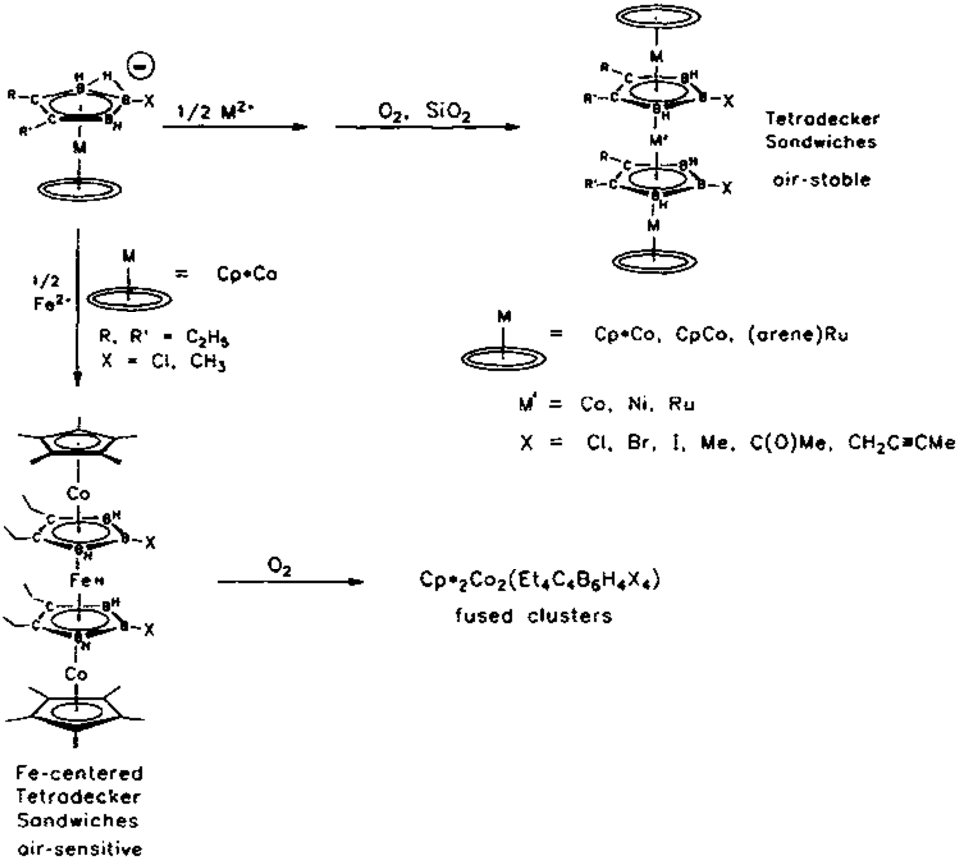


Fig. 8. Directed syntheses of tetradecker metallacarborane sandwich complexes.

parent species (X = H) represents a special case. The value of δ_{BHB} is highly shielded (−5.94), implying that a tetradecker should not form, and indeed none is found under the usual work-up conditions. If contact with silica or O_2 is avoided, however, the corresponding tetradecker complex can be isolated via fractional crystallization. Similarly, while no iron-centered tetradecker could be isolated using the usual work-up on silica gel, in recent work such complexes have been obtained under silica- and O_2-free conditions (Fig. 8) [27]. As is discussed in Section 3.4, the Co-Fe-Co tetradeckers on exposure to air undergo oxidative fusion.

The molecular and electronic structures of a number of the carborane-bridged tetradeckers have been investigated in detail via X-ray crystallographic, spectroscopic, and electrochemical studies [26,28]. The crystal structure of the Co-Ni-Co *B,B'*-diacetyl complex (Fig. 9(a)) reveals a moderately bent stack with a Co-Ni-Co angle of 171°; the corresponding angle in the Co-Ni-Co and Co-Co-Co *B,B'*-dichloro tetradecker complexes is 172°. However, a Co-Ru-Co trichloro sandwich (Fig. 9(b)) is more severely bent with a Co—Ru—Co angle of 165°, a finding that has been rationalized on electronic grounds [26].

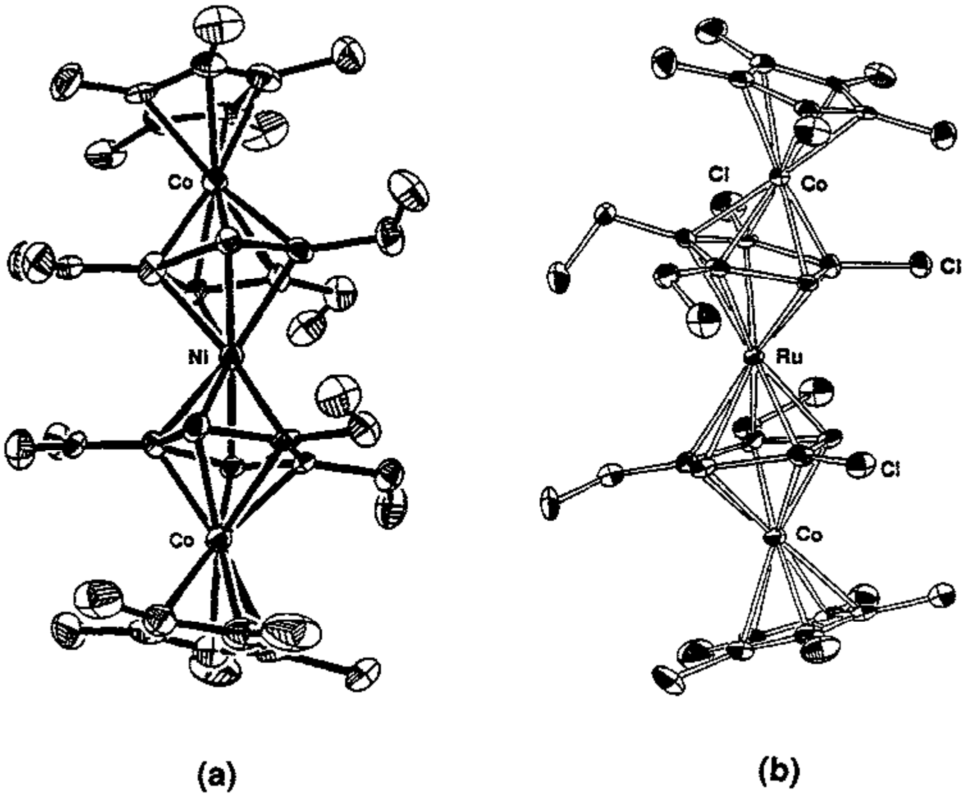


Fig. 9. Structures of (a) $[Cp^*Co(Et_2C_2B_3H_2\text{-}5\text{-}C(O)Me)]_2Ni$ and (b) $Cp^*Co(Et_2C_2B_3H_2\text{-}5\text{-}Cl)Ru(Et_2C_2B_3H\text{-}4,5\text{-}Cl_2)CoCp^*$ [26].

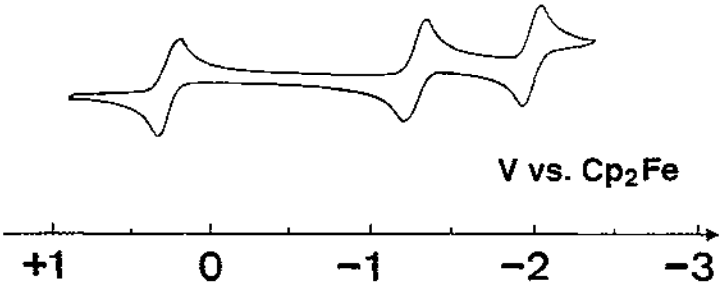


Fig. 10. Cyclic voltammogram of [Cp*Co(Et$_2$C$_2$B$_3$H-4,5-Cl$_2$)]$_2$Ni in 0.1 M Bu$_4$NPF$_6$–CH$_2$Cl$_2$ [28].

As in the case of the triple-deckers, there is strong evidence for extensive electron delocalization in paramagnetic Co-Co-Co and Co-Ni-Co tetradecker sandwiches. A characteristic feature of many of these compounds is their ability to undergo reversible, well-separated one- and two-electron reductions and one-electron oxidations [28], illustrated by the cyclic voltammogram of the Co-Ni-Co tetrachloro tetradecker shown in Fig. 10.

These properties, together with their general stability and solubility in organic solvents, suggest their use as synthons for constructing large multisandwich or multicluster arrays that could form a basis for new types of conducting or semiconducting polymeric materials [29]. As a step in this direction, stacking reactions have been employed in our laboratory to construct "staircase" oligomers in which individual tetradecker units are connected either by direct C—C bonds between Cp ligands (Fig. 11) or by linking phenylene rings (Fig. 12) [30].

As can be seen, the building-block units in these syntheses are "double ended", having open C_2B_3 rings that allow metal complexation at both ends of the molecule, making possible the stepwise assembly of oligomers and polymers. Electrochemical data [28] imply that interstack electron delocalization in the phenylene-linked oligomers is minimal, probably because steric constraints force the C_6H_4 rings to tilt out of the plane of the adjacent C_5Me_4 rings, thereby preventing π conjugation. In the directly linked $H_4C_5-C_5H_4$ (fulvalene) systems shown in Fig. 11, interstack communication between the metals is expected, and preliminary electrochemical evidence is consistent with such behavior [31].

3.3. *Directed synthesis of hexadecker metallacarborane sandwiches*

The construction of hexadecker complexes via sequential metal stacking, in a fashion analogous to the tetradecker synthesis, requires triple-decker synthons having an open C_2B_3 face that can coordinate to a metal ion. In recent work this strategy was employed as shown in Fig. 13 to prepare Co_5 hexadecker sandwiches that have been characterized via multinuclear NMR spectroscopy and X-ray crystallography on the cobalt-dihydrogenated species [32].

As is frequently observed in cobaltacarborane chemistry [2,21,29] some of the hexadecker metal centers have directly bound hydrogen ligands; invariably these

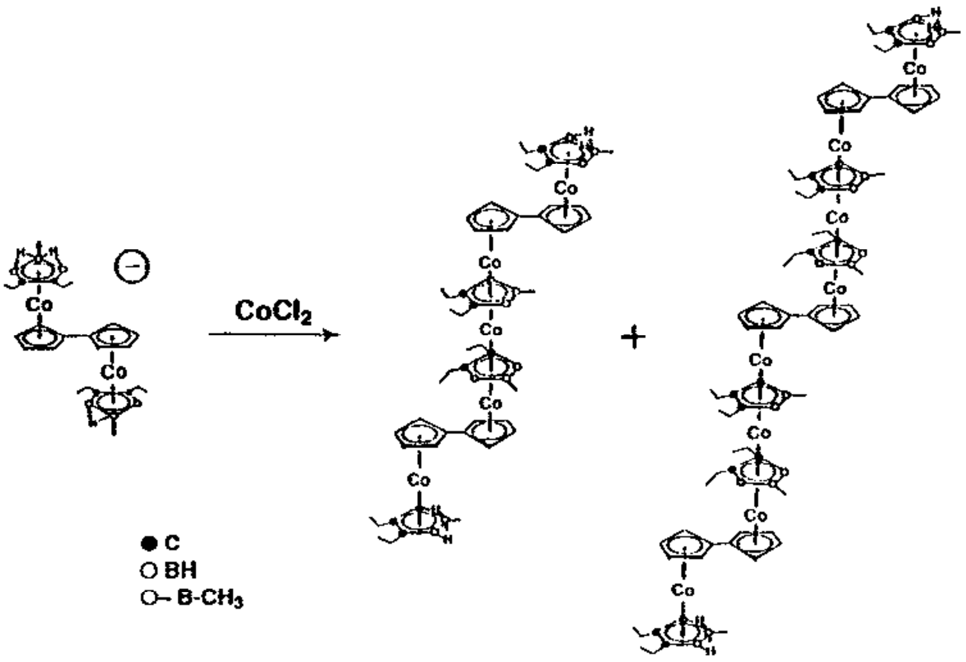


Fig. 11. Synthesis of fulvalene-bridged staircase cobaltacarborane sandwich oligomers via tetradecker stacking reactions, showing proposed structures based on NMR and mass spectroscopic data [30].

show acidic (H^+) character and are readily removed by nucleophiles such as butyllithium. In the case of the precursor triple-decker **3** (Fig. 13), which contains both CoH and B—H—B hydrogen atoms, deprotonation occurs preferentially at the CoH group to form the anion **4** whose B—H—B hydrogen atoms cannot be removed, thereby blocking metal complexation at the open face. The problem was circumvented by oxidizing the anion to form neutral, paramagnetic Co^{III}–Co^{IV} species **5**. This compound was bridge deprotonated and treated with $CoCl_2$ to give the black crystalline air-stable hexadeckers **6** and **7** which contain two and one cobalt-bound hydrogen atoms respectively. The crystal structure of **6** (the first obtained for any hexadecker sandwich), depicted in Fig. 14, revealed one of the two CoH protons; the other was disordered and could not be refined. A hexadecker structure has also been proposed for a diborole sandwich complex prepared earlier by Kuhlmann and Siebert [33].

The five-cobalt array is significantly bent, with Co—Co—Co angles of $168° \pm 1°$, possibly reflecting the presence of high formal oxidation state metals (Co^{III} and Co^{IV}). Electron spin resonance (ESR) data indicate that **6** and **7** are paramagnetic with one and two unpaired electrons respectively, consistent with the presence of one formal Co(IV) center in **6** and two such centers in **7**, the other metals being formal Co(III) in both species [32]. The question of electron delocalization in these sandwiches is currently under investigation.

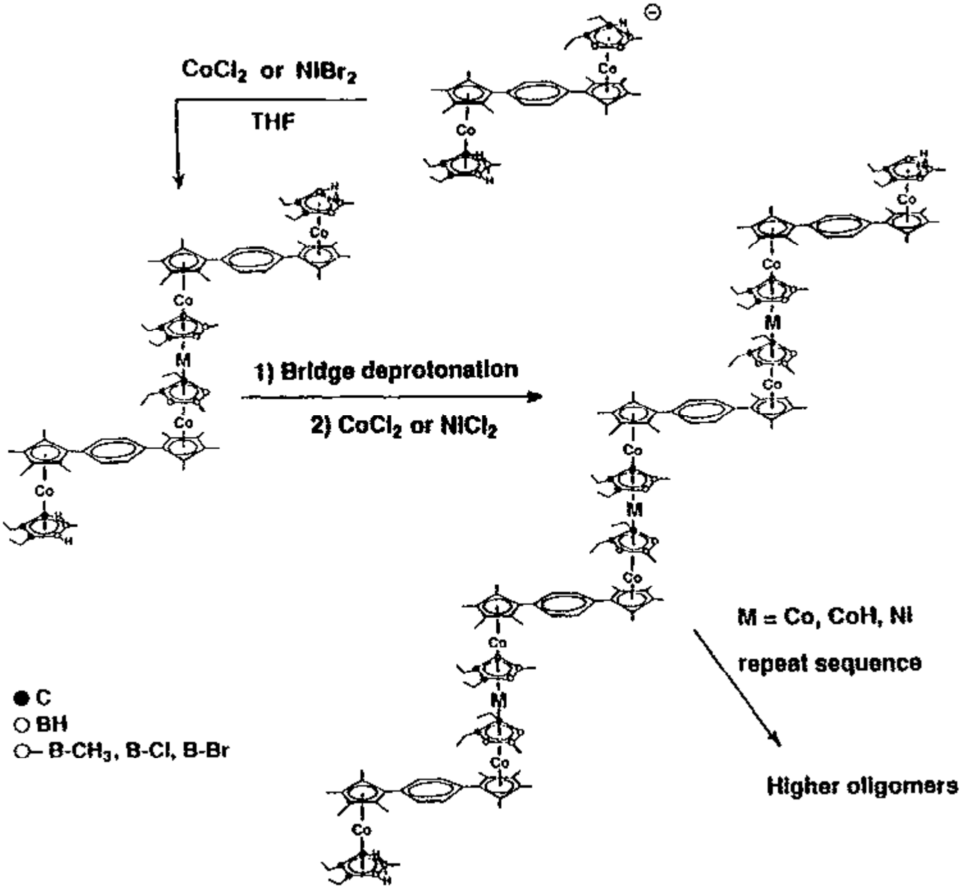


Fig. 12. Sequential tetradecker stacking to generate phenylene-linked oligomers. The pentacobalt (three-stack) species has been structurally characterized by X-ray crystallography [30].

3.4. *Metal-promoted fusion and stacking as competitive processes*

Given the propensity of *nido*-(RR′$C_2B_4H_4$)$^{2-}$ carborane anions to undergo metal-assisted oxidative fusion forming $R_2R'_2C_4B_8H_8$ as described earlier, it is not surprising that analogous *nido*-LM(RR′$C_2B_3H_3$)$^{2-}$ groups behave similarly, generating 12-vertex $L_2M_2(R_2R'_2C_4B_6H_6)$ tetracarbon dimetallacarborane clusters. Such reactions were observed as far back as 1978, in attempts to prepare a tricobalt tetradecker sandwich [3e]. Fusion of the *nido*-CpCo($Me_2C_2B_3H_4$)$^-$ anion gave the dicobalt cluster depicted in Fig. 15, whose structure was established crystallographically [3f].

Surprisingly, under similar conditions the parent complex *nido*-CpCo($H_2C_2B_3H_4$)$^-$ anion gave three isomeric $Cp_2Co_2(Et_4C_4B_6H_6)$ fusion products (Fig. 16, D–F) that exhibit sharply different cage geometries as shown by multinuclear NMR and supported by X-ray crystallography in the cases of D and E [3e,3f]. The presumed

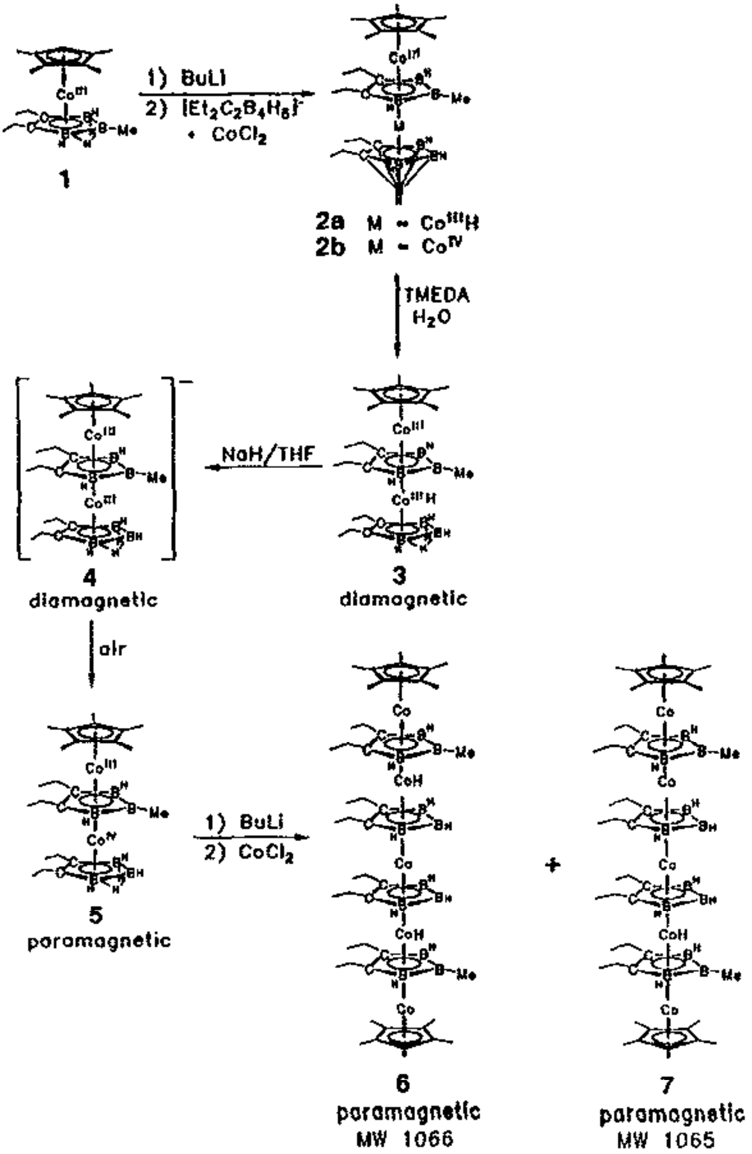


Fig. 13. Synthesis of cobaltacarborane hexadecker sandwich complexes via sequential metal stacking reactions [32].

tetradecker intermediate A was not isolated in this work although its presence was suggested by NMR evidence.

The scheme in Fig. 16 accounts for the formation of these clusters with a minimum of cage rearrangement, and invokes the proposed species B and C as reaction

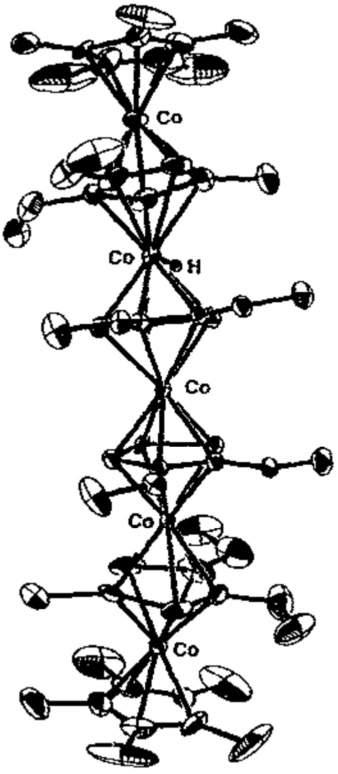


Fig. 14. Molecular structure of [Cp*Co(Et$_2$C$_2$B$_3$H$_2$-5-Me)CoH(Et$_2$C$_2$B$_3$H$_3$)]$_2$Co [32].

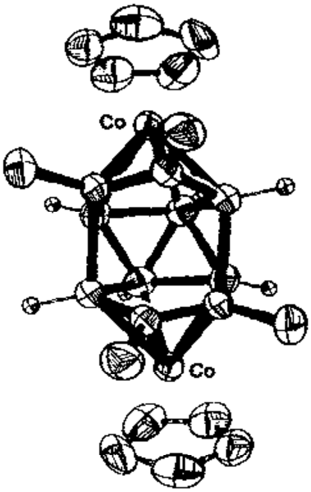
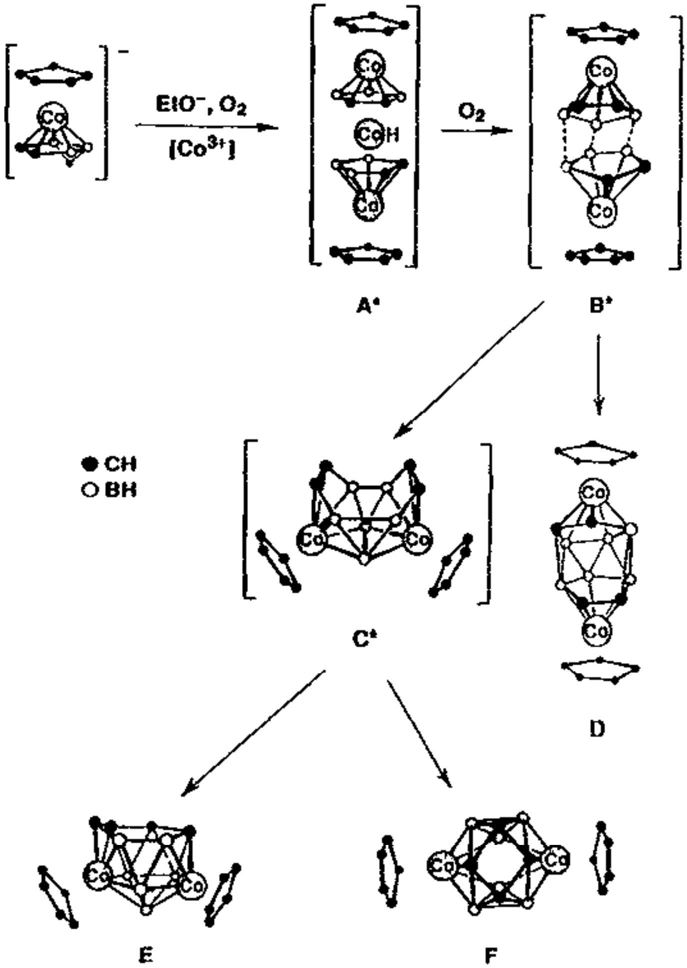


Fig. 15. Molecular structure of Cp$_2$Co$_2$(Me$_4$C$_4$B$_6$H$_6$) [3f].



*Postulated intermediate (not isolated)

Fig. 16. Proposed scheme for formation of $Cp_2Co_2(C_4B_6H_{10})$ isomers D, E, and F via metal-promoted fusion of the $CpCo(C_2B_3H_6)^-$ anion [3f]. The structures of D and E are established and that of F is proposed from NMR evidence; species in brackets are proposed intermediates.

intermediates [3f]. As will be seen, the postulated cluster C, unknown at the time, has turned up unexpectedly in the form of isolable complexes obtained in recent work.

The expected geometry for these 12-vertex, 28-valence electron clusters according to PSEPT is a 13-vertex *closo* polyhedron with one vacant vertex; clearly, E exhibits this structure but the others do not. Isomer D has the same cage geometry as its tetra-*C*-methyl derivative (Fig. 15), and closely matches the solid state structures of $R_4C_4B_8H_8$ for R = ethyl or benzyl [3j,8], in which the apical BH units in the latter species are formally replaced by electronically equivalent CpCo moieties. From this and related work, it is clear that boron cluster species obtained under low energy conditions are kinetically rather than thermodynamically determined products, and hence it is inappropriate to attempt to draw general conclusions about preferred cluster geometries based on such systems.

This point has been emphatically reinforced in some unexpected recent findings in our laboratory that came about during studies of tetradecker complex formation. As was noted earlier (Section 3.2), in attempting to apply stacking reactions of the type depicted in Fig. 8 to the synthesis of iron-centered Co-Fe-Co tetradecker sandwiches, no such complexes were isolated following chromatography on silica in air. Under these conditions, the treatment of *nido*-$Cp^{*}Co(Et_2C_2B_3H_3\text{-}X)^-$ monoanions with $FeCl_2$ in THF gave only clusters having the composition $Cp^{*}_{2}Co_2(Et_4C_4B_6H_4\text{-}X_2)$ (Fig. 17).

The cage geometry shown has been confirmed crystallographically for the cases in which X is H or Cl [11], and it is unusually interesting in that it is both unprecedented and perhaps the most flagrant violator of the PSEPT rules yet encountered. The basket framework is a 12-vertex fragment of a 16-vertex *closo* polyhedron of T_d symmetry (Fig. 17, bottom) that is unknown in molecular chemistry, although it has recently turned up as an In_{16} cluster in solid state $Na_7In_{11.8}$ [34]); additionally, it has been proposed by Lipscomb and co-workers for the still-unknown $B_{16}H_{16}$ borane cluster [35].

Remarkably, the geometry of this dicobaltacarborane is identical to that postulated

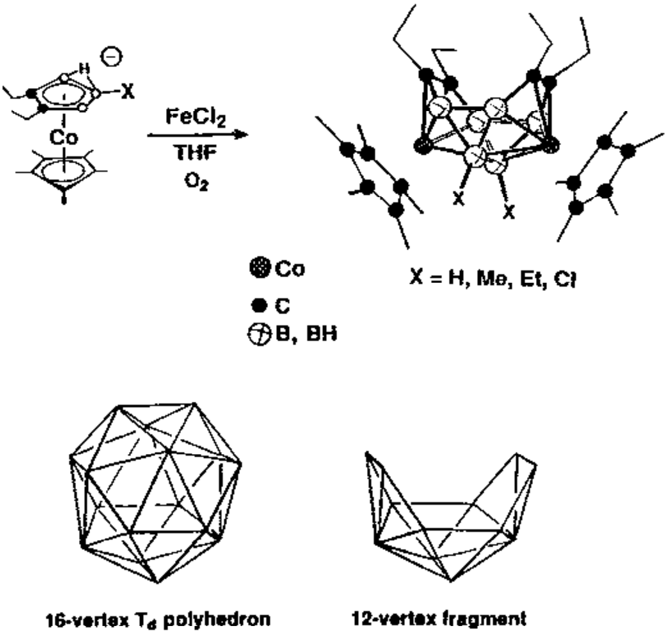


Fig. 17. Formation of 12-vertex $Cp^{*}_{2}Co_2(Et_4C_4B_6H_4X_2)$ clusters via fusion of $Cp^{*}Co(Et_2C_2B_3H_3\text{-}5\text{-}X)$ anions [11].

in 1979 by Pipal and Grimes [3f] for the intermediate species C in the formation of $Cp_2Co_2C_4B_6H_{10}$ isomers shown in Fig. 16. That it is indeed a fragment of the parent 16-vertex polyhedron is clear from the fact that the cobalt atoms occupy 6-coordinate vertices and that the four cage carbon atoms form two parallel C—C edges at the top of the basket, exactly corresponding to the parent geometry. If the PSEPT rules can be applied to clusters as large as 16 vertices (a debatable point), the electron requirement for such a cluster, and any fragment derived therefrom, would be 34, or 6 more than the 28 present in this molecule; hence this structure cannot be rationalized from simple electronic arguments. It is highly likely that the observed cage is a kinetically trapped product that is generated via metal-mediated fusion of a tetradecker-sandwich intermediate as suggested in Fig. 16. This finding serves to emphasize a point made earlier: great care should be exercised in attempting to draw conclusions about "preferred" structures and metal electron–orbital contributions, based on crystal structures of metallaboranes and metallacarboranes that are generated under mild conditions. In such circumstances, the observed product structures are more likely to reflect the reaction pathway than thermodynamic driving forces.

As the preceding discussion has shown, the bridge deprotonation of *nido*-$LM(R_2C_2B_3H_5)$ complexes followed by treatment with metal ions can lead to isolable

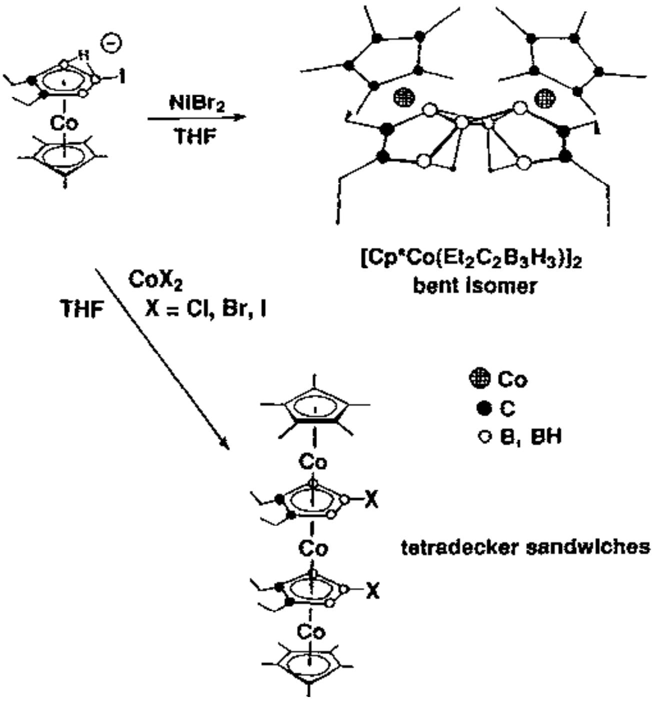


Fig. 18. Reactions of the $Cp^*Co(C_2B_3H_3I)^-$ anion with metal salts to generate edge-fused and tetradecker sandwich products [11].

tetradecker sandwiches or to $M_2C_4B_6$ clusters (Fig. 18). There is a third possible outcome, namely the formation of edge-fused (*conjuncto*) dimeric products. Fig. 18 depicts the reaction of a *B*-iodo substrate anion with metal salts in THF solution [11].

When cobalt(II) halides are employed, the corresponding *B,B'*-dihalo tetradecker sandwich was isolated; however, the reaction with $NiBr_2$ gave instead the dimer $[Cp^*Co(Et_2C_2B_3H_3)]_2$, whose two C_2B_3 rings are tilted away from each other by 100°, reflecting steric interaction between the Cp* groups. It is notable that each carborane ring has one B—H—B and two B—H units, and that the central boron atom in each ring has no terminal hydrogen atom (Fig. 19(a)).

An isomer of this dimer, having a centrosymmetric structure with coplanar C_2B_3 rings and the Cp*Co units on opposite sides of the ring plane (Fig. 19(b)), was isolated as a minor product of the reaction shown in Fig. 20 [11].

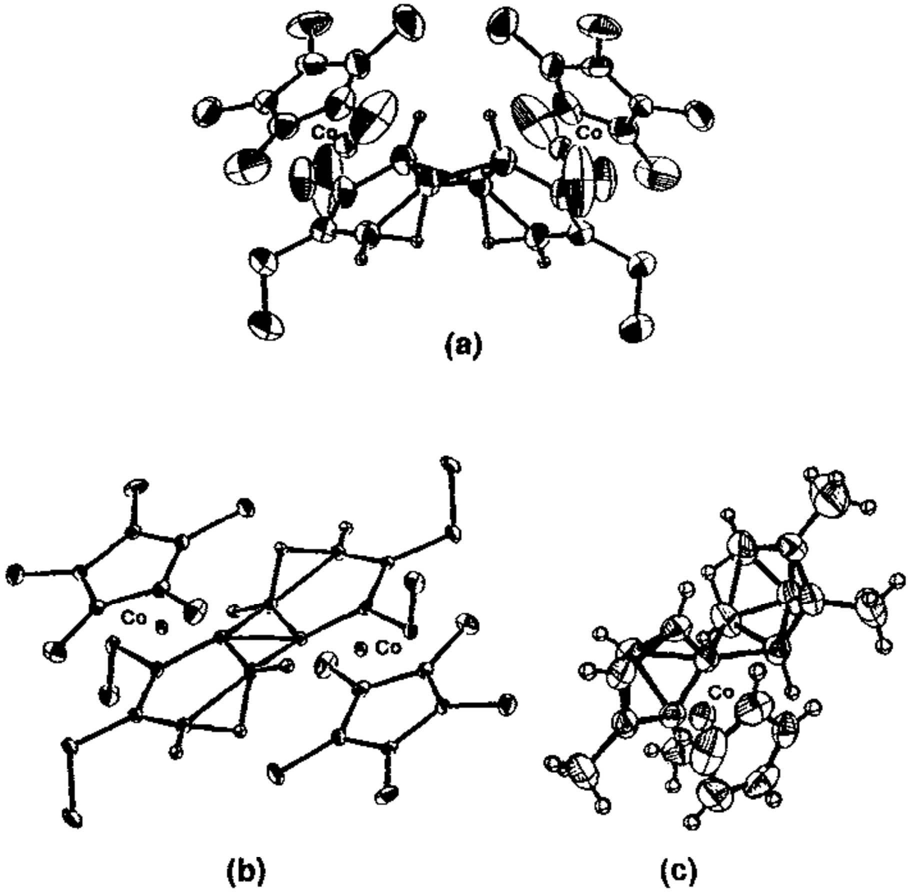


Fig. 19. Structures of (a) *nido*-$[Cp^*Co(Et_2C_2B_3H_3)]_2$ (bent isomer) [11], (b) *nido*-$[Cp^*Co(Et_2C_2B_3H_3)]_2$ ("planar" isomer) [11], and (c) *nido*-$CpCo(Me_2C_2B_4H_3)Me_2C_2B_4H_5$ [36].

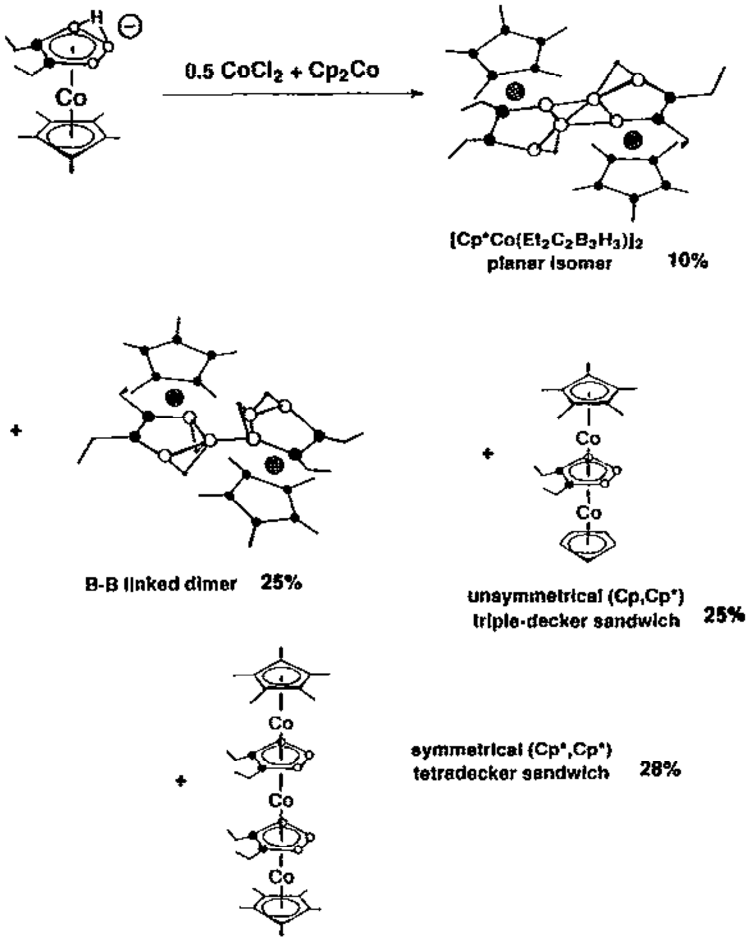


Fig. 20. Formation of fused, linked and multidecker-sandwich cobaltacarboranes from the $Cp^*Co(Et_2C_2B_3H_4)^-$ anion [11].

As shown, this reaction also produced a $[Cp^*Co(Et_2C_2B_3H_4)]_2$ dimer joined by a B—B single bond, as well as other products. The dimers pictured in Figs. 18–20 were obtained in mechanistically obscure processes, but the fact that all of these species were isolated as air-stable crystals further illustrates the importance of kinetic stabilization in cluster chemistry. The structures of these edge-fused dimers are reminiscent of the *conjuncto*-ferraborane complexes in Fig. 5, and the intramolecular linkage in both species can be formulated as two three-center two-electron B—B—B bonds. A related cobaltacarborane, shown in Fig. 19(c), contains $CpCo(Me_2C_2B_4H_3)$ and $Me_2C_2B_4H_5$ cage units that are joined by one B—B—B three-center bond [36].

The formation of bis(cobaltacarborane) dimers in the presence of transition metal ions competes with tetradecker formation, as is clearly evident in the reactions depicted in Figs. 18 and 20. The "partially fused" structures of these complexes may

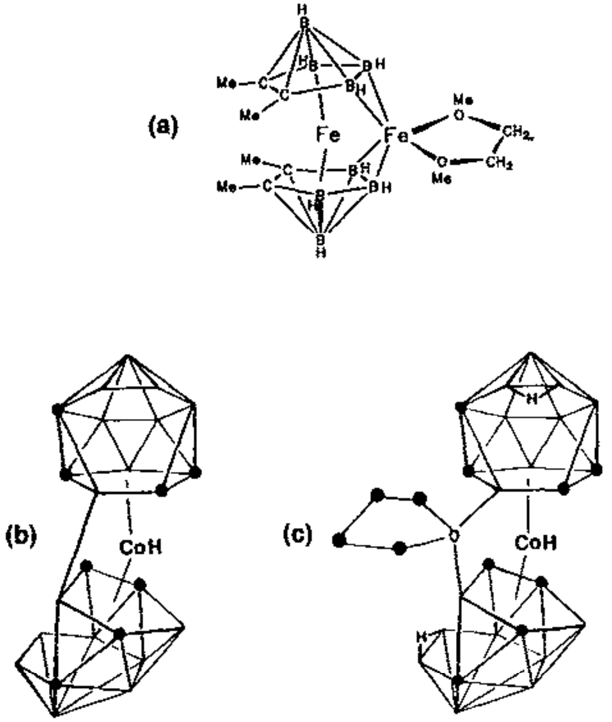


Fig. 21. (a) Structure of $C_2H_4(MeO)_2Fe_2(Me_2C_2B_4H_4)_2$ [3i]. (b) Proposed structure of *nido*-$CoH(Et_4C_4B_8H_7)_2$ [12b]. (c) Proposed structure of *nido*-$(Et_4C_4B_8H_8)CoH(Et_4C_4B_8H_8\text{–}OC_4H_8)$ [12b]. ●, carbon atoms.

represent an early stage in the process of full (face-to-face) oxidative fusion that generates, for example, the $Co_2C_4B_6$ clusters discussed above. In the case of the dimers, the fact that more complete fusion is not achieved may be associated with retention of two bridging hydrogen atoms (one on each CoC_2B_3 unit). When all four hydrogen atoms on the *nido*-$LM(R_2C_2B_3H_4)^-$ substrate anion are retained, cage fusion is precluded but oxidative coupling to form the B—B linked dimer can take place (Fig. 20) [11].

Metal-mediated fusion of carborane and metallacarborane units is presumed to involve, at an early stage, the joining of the two metal-bound ligands via either direct B—B bonding or a linking group which could be a solvent molecule. In most cases these linked intermediates have not been directly observed (much less isolated), but a solvated iron-bridged bis(carboranyl) ferracarborane is known to be an intermediate in the oxidative fusion of $H_2Fe(Me_2C_2B_4H_4)_2$ to form $Me_4C_4B_8H_8$, and has been isolated and characterized [3i]. This extremely air-sensitive purple complex is paramagnetic with four unpaired electrons, and has the structure shown in Fig. 21(a).

Mössbauer, magnetic, and ESR studies indicate that the *exo*-bridging metal is high spin Fe(II) with no apparent spin coupling to the low spin Fe(II) in the sandwich, despite a relatively short (2.414 Å) Fe–Fe distance. The diiron complex,

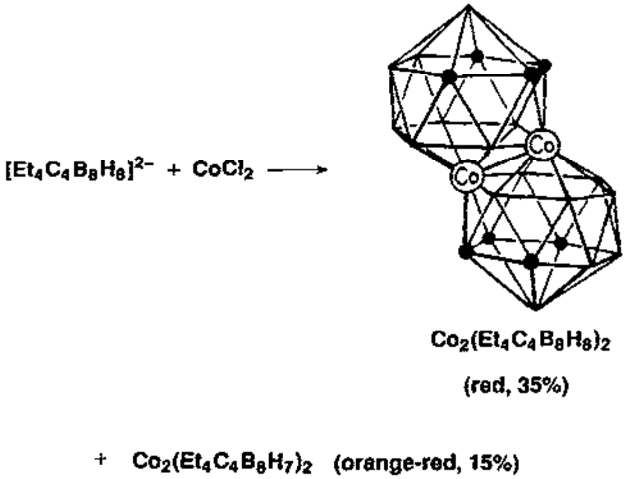


Fig. 22. Synthesis and proposed structure of an edge-fused bis(14-vertex) cluster, $Co_2(Et_4C_4B_8H_8)_2$ [12a]. ●, *C*-ethyl units.

which forms slowly from $H_2Fe(Me_2C_2B_4H_4)_2$ on exposure to air, ferric ion, or other oxidants, is rapidly converted to the fused C_4B_8 cluster, probably facilitated by solvent-assisted removal of the outer metal with concomitant formation of interligand boron-boron bonds, as discussed elsewhere [3h].

Other examples of biscarborane metal complexes having interligand B—B or B—X—B links are shown in Figs. 21(b) and 21(c) [12b]. In contrast to the diiron intermediate in Fig. 21(a), these cobaltacarboranes are stable to oxidants and do not undergo fusion, a fact that is very likely associated with the large cage size. They may well represent cases of "arrested fusion" in which interligand connections form but do not lead to further joining of the cages and expulsion of the metal. In any case, these structures do emphasize the ease with which interligand linkage is achieved in biscarborane complexes.

Cluster building involving a different type of cage fusion is encountered in the reaction of $CoCl_2$ with the $Et_4C_4B_8H_8^{2-}$ dianion, shown in Fig. 22. The structure of the main product, as deduced from COSY 2d ^{11}B NMR and other spectroscopic data [12a], consists of two 14-vertex *closo* polyhedra sharing an edge defined by a Co—Co bond. Its formation from two *arachno*-carborane dianions and two Co^{2+} cations can be described as a non-oxidative edge fusion in which no electrons are lost or gained. The minor product, with two fewer hydrogen atoms, is proposed to have a direct B—B linkage between the carborane ligands.

4. Summary

Reactions of small carborane and metallacarborane anions with transition metal ions can generate metal-centered sandwich complexes or fused clusters, depending on the substrate ions and the reaction conditions. Empirical observations on many such systems have provided some general guidelines on what to expect from specific combinations of metal reagents, substrates, and work-up method. Consequently, it has been possible to develop synthetic routes for constructing well-defined carborane-bridged multidecker sandwich complexes up to the level of hexadeckers, and to design and build linked-sandwich oligomers and polymers having desired electronic properties.

Achieving control of fusion for synthetic purposes is more difficult, although recent work on Fe-centered tetradecker sandwiches establishes the fact that such species are indeed intermediates in the fusion of CoC_2B_3 *nido* clusters, and that their fate in a given reaction, "to fuse, or not to fuse", can be regulated to some degree by the choice of reaction media and exposure to oxidants. Through continuing experimental work, coupled with rapid advances in molecular modeling approaches for transition metal complexes (for a brief overview of the state of the art and a comparison of different MO approaches to organometallic chemistry, see Ref. [37]), it is reasonable to expect that cluster synthesis via metal-promoted fusion involving borane or carborane building-block units will eventually be as controllable, and hence synthetically useful, as multidecker sandwich synthesis has already become.

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