

Designed synthesis of multi-functional carboranes and organotransition metal-carborane complexes

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Abstract - General synthetic routes to functionalized C- and B-substituted derivatives of nido- $C_2B_4H_8$, $C_4B_8H_{12}$, and $C_2B_3H_7^{2-}$ are described together with their use as building-block units in the planned construction of multidecker transition-metal sandwich complexes and related systems. Specifically discussed are (1) synthesis of C_2B_4 nido-carboranes containing sterically demanding and/or electronically active groups; (2) transition-metal π -complexation of the C_2B_4 derivatives at carboranyl and aryl sites; (3) controlled stepwise oxidative fusion of C_2B_4 -metal complexes to form asymmetrically substituted C_4B_8 clusters; and (4) current efforts in the author's laboratory directed toward the preparation of electron-delocalized polymers incorporating carboranes or metallacarboranes.

INTRODUCTION

Boron clusters, particularly the carboranes and their metal-containing derivatives, present intriguing possibilities for the construction of large electron-delocalized multilayer metal sandwich complexes, and, of particular interest, polymers exhibiting low-dimensional electrical conductivity. Following the synthesis of the first ionic (ref. 1) and electrically neutral (ref. 2) triple-decker sandwich complexes, a number of triple- to hexa-decker boron-containing sandwiches have been characterized (ref. 3, 4), and an electrically conducting nickel-diborolyl polymer has been reported (ref. 5). As a group, carboranes exhibit high chemical and thermal stability, substantial electron delocalization in the cage framework, ease of complexation with transition metals (for open-cage species), and relatively straightforward functionalization by organic groups at cage carbon locations. These properties have been extensively exploited, in the icosahedral $C_2B_{10}H_{12}$ carboranes (ref. 6), to prepare uniquely stable high polymers (ref. 7), metallacarborane-based catalysts (ref. 8), and agents for ^{10}B neutron capture therapy of tumors (ref. 9).

Until recently, $C_2B_{10}H_{12}$ derivatives were relatively accessible via the base-promoted reaction of alkynes with $B_{10}H_{14}$, but the once-large U.S. Government stockpile of that hydride has virtually disappeared. In contrast, a substantial quantity of B_5H_9 (ca. 10^5 kg) remains available for research and hence this borane is a convenient precursor to carboranes and other materials. Particularly useful are the organo derivatives of nido-2,3- $C_2B_4H_8$ (first prepared by Onak, Williams, and Weiss a quarter-century ago (ref. 10)), which can be directly and easily prepared from B_5H_9 (ref. 11) and which exhibit considerable synthetic versatility. This article describes our group's efforts to utilize nido- C_2B_4 units and their derivatives in the directed syntheses of multidecker (and eventually polydecker) sandwich complexes and other potentially novel materials.

PROPERTIES OF $C_2B_4H_6^{2-}$ AND $C_2B_3H_7^{2-}$ IONS IN METAL COMPLEXATION

The pentagonal pyramidal $C_2B_4H_6^{2-}$ ion (1, Fig. 1) and its C- and B-substituted derivatives are ideal ligands for the preparation of stable transition-metal organometallic complexes, especially stacked sandwich compounds. The planar C_2B_3 basal ring readily undergoes η^5 -metal coordination (ref. 4), particularly with d^6 ions such as Fe^{2+} and Co^{3+} ; like the $C_5H_5^-$ ion and neutral arenes, 1 is a formal 6-electron donor. The dinegative charge on 1 is advantageous in stabilizing high metal oxidation states (which is difficult to do with arene or cyclopentadienyl ligands). Moreover, owing to the lower electronegativity of boron vs. carbon, carborane-transition-metal bonds are more covalent and exhibit generally higher stability than their metal-hydrocarbon counterparts. In C_2B_4 -metal-hydrocarbon complexes, even the metal-hydrocarbon linkage is strengthened by the presence of the carborane ligand, as illustrated by the remarkably stable cyclooctatetraene complexes $(\eta^8-C_8H_8)M(Et_2C_2B_4H_4)$ [$M = Ti(IV), V(IV)$] (ref. 12) which are extremely rare if not unique examples of $\eta^8-C_8H_8$ -first row transition metal complexes that are unreactive toward atmospheric oxygen.

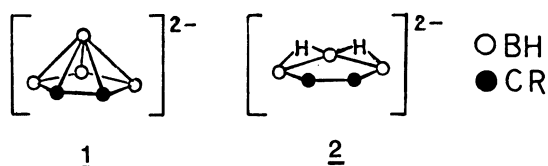


Fig. 1. Structures of nido-2,3- $R_2C_2B_4H_4^{2-}$ and arachno-2,3- $R_2C_2B_3H_5^{2-}$ ligands (lines depict connectivity only, not discrete electron-pair bonds). Both ligands are formal 6-electron donors to η^5 -bound metal atoms.

The utility of ligand 1 in metal coordination can be further extended by removal of the apex BH unit (in metal complexes of 1) to generate the formal $R_2C_2B_3H_5^{2-}$ ligand (2, Fig. 1) which can η^5 -coordinate to metal centers on both sides of the ring plane to form multiple-decker, multimetal sandwich systems (ref. 2, 4) as described below. Figure 2 illustrates schematically the main approaches we are currently investigating, all of which depend on the availability of specific "designed" carboranes and arene-metal-carborane complexes.

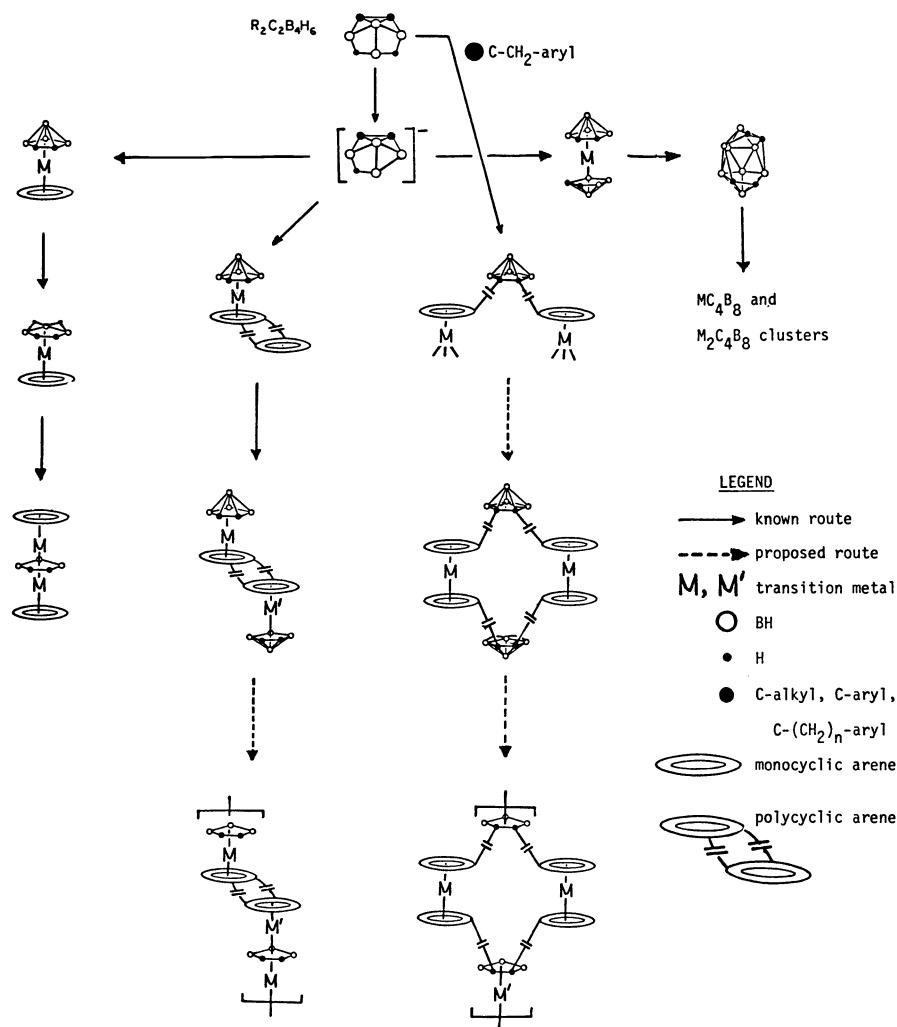


Fig. 2. $R_2C_2B_4H_6$ nido-carboranes as building blocks for construction of multi-decker sandwich arrays. Processes shown with solid arrows are known, although more than one step may be required (not all intermediate species are shown).

As shown, the principal pathways that have been established or are under study utilize nido-RR'C₂B₄H₆ derivatives whose R groups are attached to cage carbon atoms. However, the versatility in this chemistry can be further extended via introduction of functional groups at boron locations, as will be described below. For simplicity, only C-substituted carboranes are depicted in Fig. 2. Four general reaction types are illustrated, several of which start with bridge-deprotonation of the RR'C₂B₄H₆ substrate to form the RR'C₂B₄H₅⁻ anion:

(1) Formation of transition-metal mixed ligand (R₂C₂B₄H₄)M(arene) complexes in which the arene is monocyclic or polycyclic (ref. 13). In the latter case, a second metal can in some cases be coordinated to the arene to create a multidecker system (ref. 13c, 13e-13g).

(2) Conversion of metal-complexed R₂C₂B₄H₄²⁻ ligands to R₂C₂B₃H₅²⁻ via removal of the apex BH group ("decapitation") and subsequent complexation to a second metal to create triple- or multiple-decker sandwiches (ref. 2, 13b-13d, 13f).

(3) In carboranes in which R itself contains an aryl ring, complexation of metal(s) to one or more of these carborane-bonded aryls (ref. 14). Since the same metal center may also coordinate to another carborane or polyarene, this affords an alternative method for building multilayer arrays as suggested in Fig. 2.

(4) Metal-promoted oxidative fusion of R₂C₂B₄H₆ carboranes (ref. 14, 15) via deprotonation, to form R₄C₄B₈H₈ cages which in turn can be expanded to give 13- and 14-vertex metallacarboranes (ref. 15). Recent work, summarized below, has illuminated aspects of the fusion mechanism and extended the reaction to a variety of boron cage substrates.

SYNTHESIS OF C- AND B-SUBSTITUTED nido-C₂B₄H₈ DERIVATIVES

The reaction of an alkyne with B₅H₉ in the presence of triethylamine under mild conditions proceeds as shown in Fig. 3, affording the nido-RR'C₂B₄H₆ product which is isolated via vacuum-line fractionation (for the more volatile derivatives) or preparative plate or column chromatography (ref. 11-13).

The preparation of the C,C'-diphenyl derivative **3i** requires a modification of this approach, since the presence of amine promotes polymerization and the monomer is obtained only in very low yield. When diphenylacetylene and B₅H₉ are heated at 180° in a steel cylinder, **3i** is produced in quite acceptable (30%) isolated yield (ref. 16).

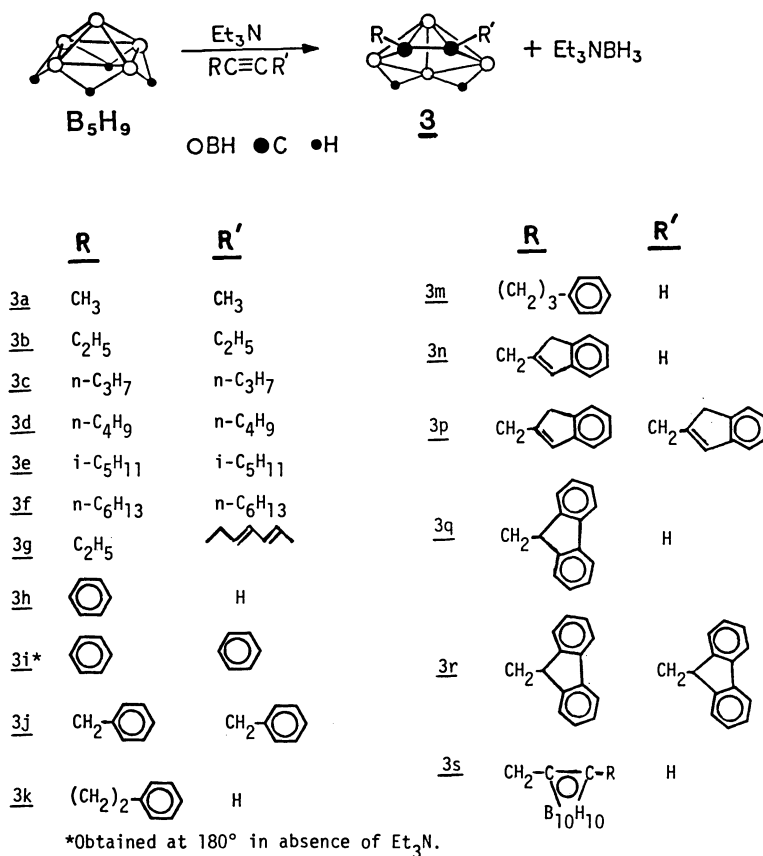


Fig. 3. Preparation of RR'C₂B₄H₆ Derivatives

Extension of the general method to dialkynes is straightforward, producing biscarboranes as shown in Fig. 4.; these compounds further extend the potential scope of carborane-based polymetallic sandwich systems. For most of the C,C'-disubstituted derivatives in Figs. 3 and 4, the alkyne reagents either are commercially available or can be prepared by literature methods, but in a few cases (e.g., the indenyl and fluorenyl species) it was necessary to devise our own alkyne syntheses.

The controlled functionalization of RR'C₂B₄H₆ carboranes at boron positions is an important aspect of planned synthesis in this area, since clearly the range of structural modes involving metal sandwich-building is thereby enhanced. Although Onak et al. obtained all possible B-monomethyl derivatives of R₂C₂B₄H₆ (R = H or Me) from the reaction of MeB₅H₈ with alkynes (ref. 17), no method has been reported for the introduction of organic substituents at specific boron locations on the nido-C₂B₄ skeleton. Wilczynski and Sneddon (ref. 18) have shown that the addition of 2-butyne to 2,3-C₂B₄H₈ (catalyzed by a cobalt carbonyl reagent) generates the 1-, 4-, and 5-cis-2-butenyl derivatives. Recently we have found (ref. 19) that reactions of benzyl or xylyl halides with RR'C₂B₄H₅⁻ anions give B-substituted products in good yield, evidently via initial formation of B-C-B bridged derivatives which rearrange to place the organic group at a terminal boron position on the base of the pyramid (Fig. 5). Such a mechanism would be analogous to known reactions of R₂C₂B₄H₅⁻ or B₅H₈⁻ ions with Group IV alkyl halides, which generate metal-bridged complexes whose bridging group in some cases exchanges places with a B-H terminal hydrogen (ref. 20, 21).

SYNTHESIS OF CARBORANE-MONOIRON- η^6 -ARENE SANDWICH COMPLEXES

Several icosahedral ferra- and ruthenacarboranes of the type (η^6 -arene)M(C₂B₉H₁₁) have been prepared via solution reactions (ref. 22), and a small amount of (η^6 -tolyl)Fe(Et₂C₂B₄H₄) was isolated from the interaction of iron vapor with Et₂C₂B₄H₆ and toluene (ref. 23). We sought simple, general routes affording bench-scale quantities of (η^6 -arene)Fe(R₂C₂B₄H₄) from any desired arene, and discovered that the readily available cyclooctatriene complexes (η^6 -C₈H₁₀)⁻Fe(R₂C₂B₄H₄) (ref. 13a) undergo facile displacement of the C₈H₁₀ ligand by arenes (ref. 13b-13g). The process can be conducted either via AlCl₃ catalysis or, better, by thermolysis without solvent (Fig. 6). Intramolecular displacement of C₈H₁₀ is also possible, as demonstrated by the synthesis and structural characterization of the "trashcan" complex 27 (Fig. 7), whose phenyl "lid" may be induced to flip on and off the metal reversibly, perhaps after partial hydrogenation of the aryl ligand (not yet observed) (ref. 13d).

Recently we have shown that the direct reaction of R₂C₂B₄H₅⁻ anions with FeCl₂ and arene anions such as naphthaleneide (C₁₀H₈²⁻) or fluoreneide (C₁₃H₁₀⁻) also produces (η^6 -arene)Fe-(R₂C₂B₄H₄) complexes in reasonable yield (ref. 13f). For arenes capable of reduction to an anion, this procedure conveniently bypasses the need for a cyclooctatriene-complex intermediate (11 in Fig. 6).

Using these methods we have prepared a wide variety of (η^6 -arene)Fe(RR'C₂B₄H₄) complexes which, in most cases, are air-stable, yellow to red-orange crystalline solids. As shown in Fig. 6, both the carboranyl substituents (R groups) and the arene ligands on the metal can be varied; at this writing, the latter include mono-, di-, and tricyclic hydrocarbons. Additionally, these complexes can be converted to open (η^6 -arene)Fe(RR'C₂B₃H₅) species (24, Fig. 6) via base-promoted decapitation as described above; addition of a second coordinating metal to 24, following deprotonation, gives triple-decked systems (Fig. 2). The next section describes the utilization of these compounds as building blocks in our attempts to assemble larger multidecker sandwich arrays.

SYNTHESIS OF CARBORANE-METAL-POLYCYCLIC ARENE SANDWICH COMPLEXES

As suggested in Fig. 2, the essential strategy involves linking arene-metal carborane complexes via strong multihapto (η^5 or η^6) covalent bonds. Depending on the substrates involved, such linkages can occur (i) at C₂B₃ faces, (ii) on polycyclic arene ligands already coordinated to metals, (iii) on arenes attached to the carborane framework, and on combinations of these. Figure 8 depicts several multidecker (or multilayer) sandwich complexes (ref. 13f, 13g) in which the linking arene is biphenyl (29), fluorene (30 and 31), or 9,10-dihydroanthracene (32). With the exception of the biphenyl system, electron-delocalization between the aromatic C₆ rings in these bicyclic arenes (as uncomplexed molecules) is significant and hence one expects their metallacarborane derivatives to exhibit similar delocalization. This is particularly true of complexes incorporating [2.2]paracyclophane (Figure 9) whose two decks interact to such an extent that they can be considered a single π -electron system. Boekelheide and co-workers have prepared metal complexes of [2_n]cyclophanes including several multilevel systems having Ru²⁺ centers coordinated to different cyclophane decks (ref. 24). The complexes depicted in Figure 8 are stable crystalline solids whose structures

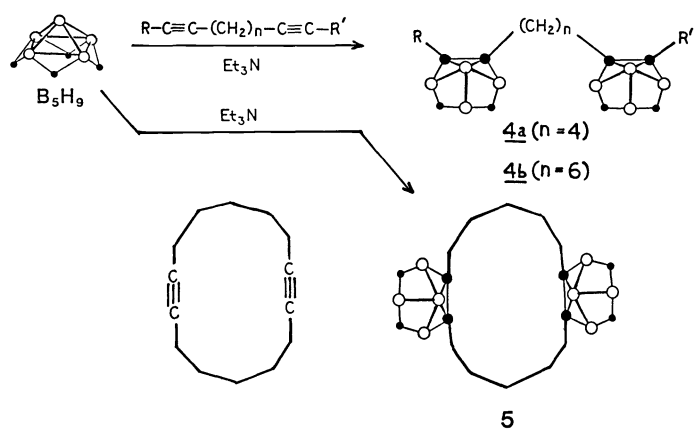


Fig. 4 (see ref. 16a)

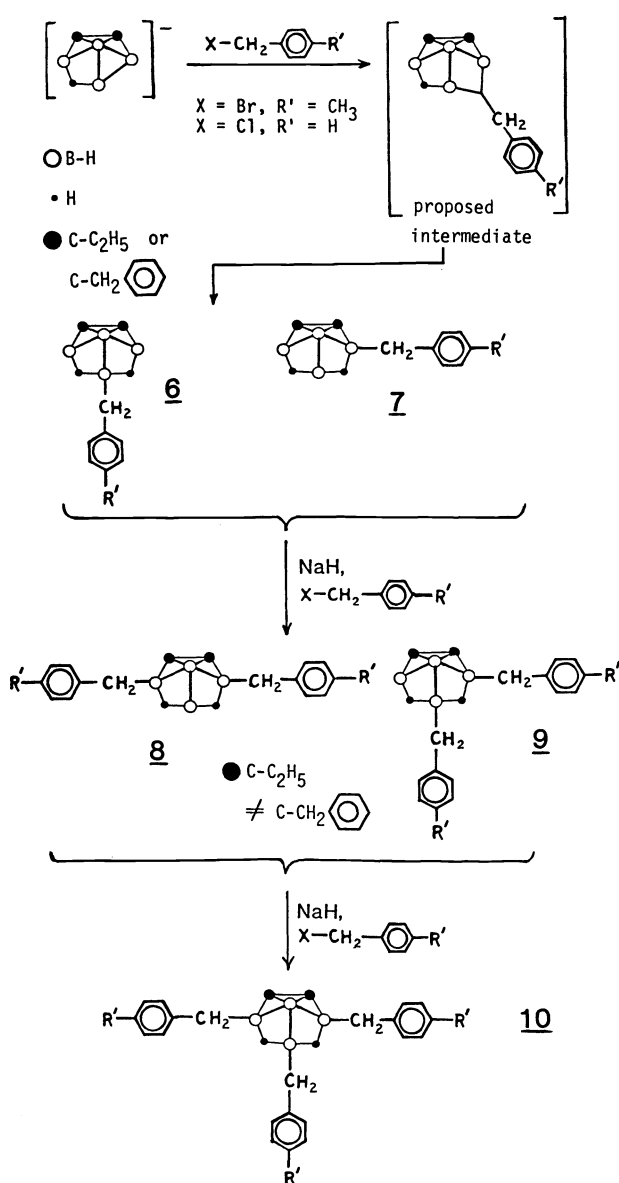
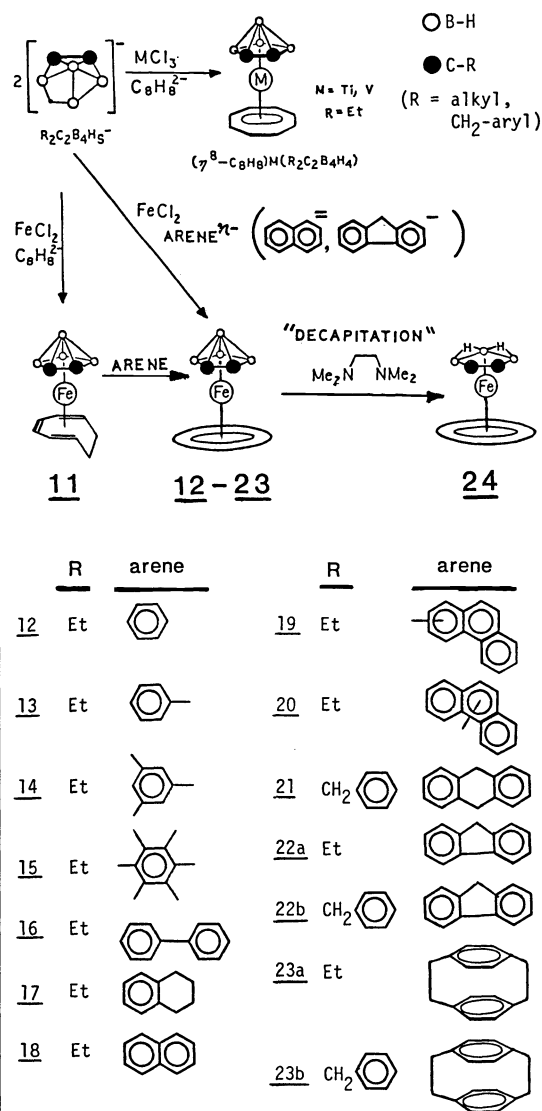


Fig. 5. Attachment of aryl substituents at boron positions


 Fig. 6. Controlled synthetic routes to $(\eta^6\text{-arene})Fe(RR'C_2B_4H_4)$ complexes

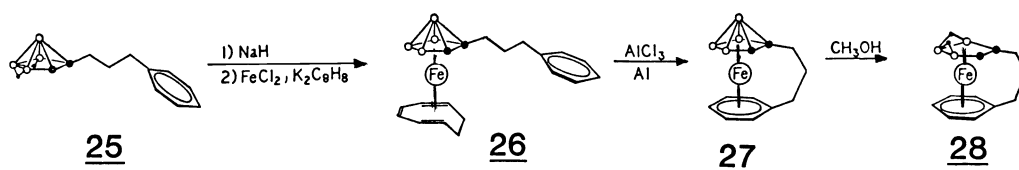
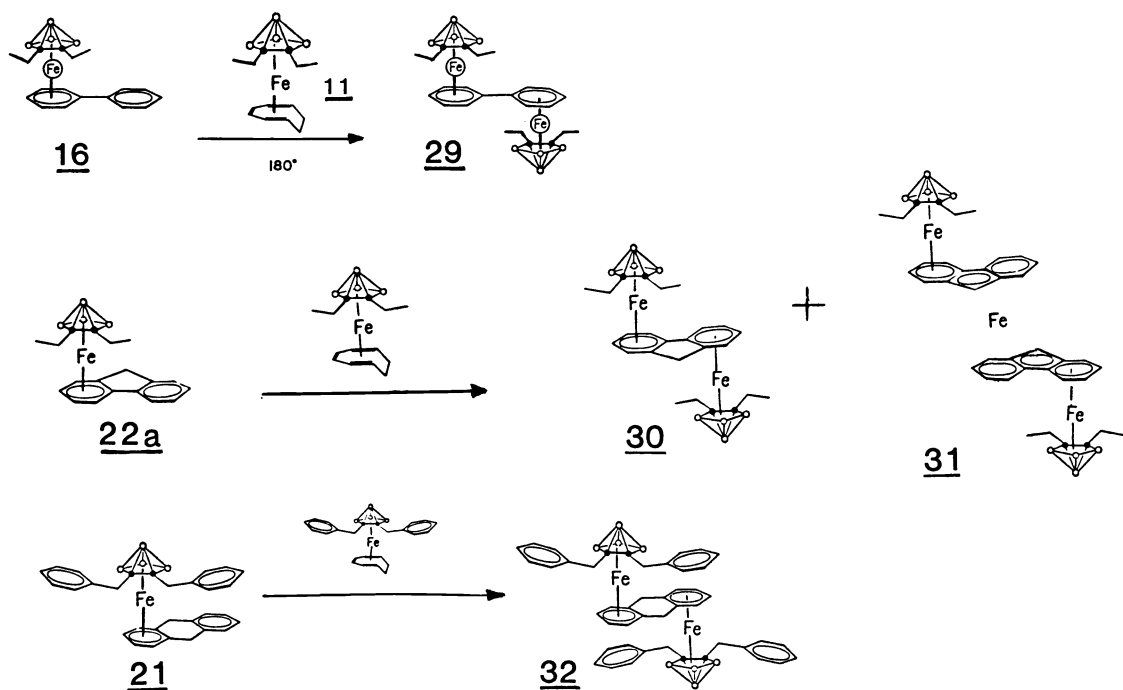
Fig. 7. Synthesis and decapitation of the "trashcan" complex 27 (ref. 13d)

Fig. 8. Synthesis of di- and trimetallic polycyclic arene complexes

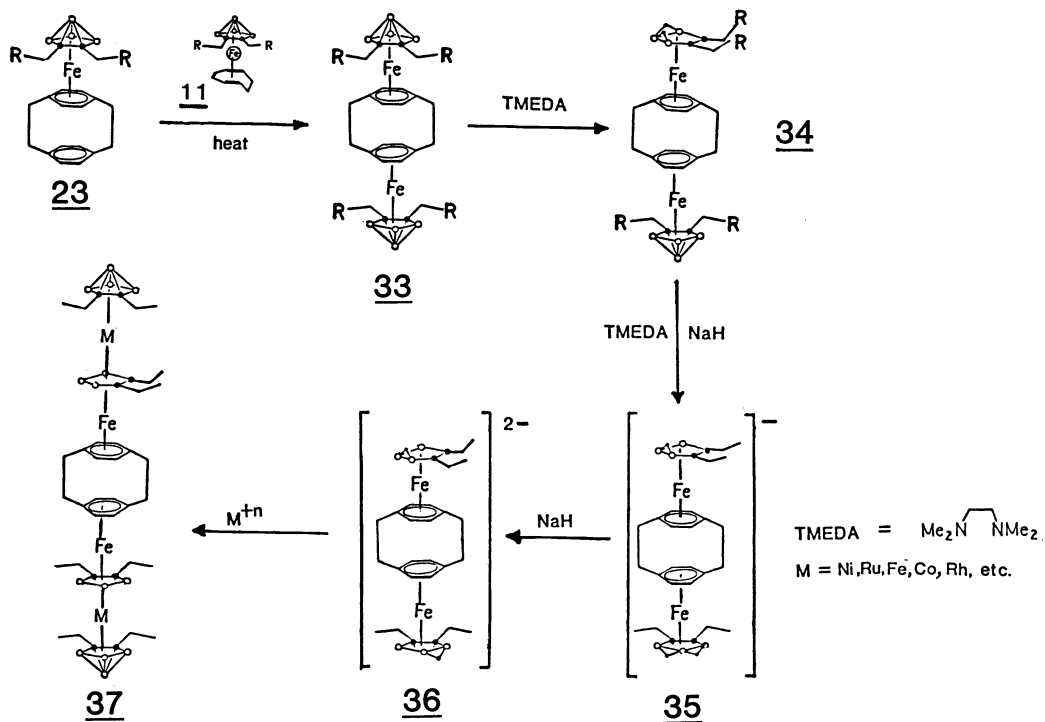


Fig. 9. Proposed route to multidecker [2.2]paracyclophane iron complexes

have been established by X-ray diffraction for **16**, **22a**, and **30** and are proposed from NMR and other spectroscopic data for the others (ref. 13c, 13f, 13g). In the minor product **31** the mode of binding of the central iron to the bridging fluorene ligands is uncertain at this writing. Figure 9 presents a proposed scheme for building on the known [2.2]paracyclophane complex **23** to create the hypothetical multidecker complexes **33** - **37**, utilizing general reactions already discussed.

By extension of these synthetic methods and structural principles, one can visualize even larger polydecker sandwich arrays. Ultimately, it may be possible to achieve stacks of truly polymeric size in which electrons are delocalized along the stacking axis, and which exhibit anisotropic electrical conductivity; undoubtedly this will require a mixed-valence system involving metal centers in different formal oxidation states (ref. 24). At present, this presents a formidable synthetic challenge, but as the chemistry of the smaller multidecker species is developed, more ambitious syntheses of larger stacks should become feasible.

METAL COMPLEXATION OF ARENE RINGS ATTACHED TO CARBORANES

A number of the metallacarborane derivatives described above have substituent groups containing aryl rings, which furnish additional sites for metal complexation. For this purpose the metals of choice are those of the chromium group (when diamagnetic 18-electron species are desired), and the treatment of the benzyl compound **3j** with Cr(CO)₆ easily generates mono- and dichromium complexes as shown in Fig. 10; similar reactions on the cyclooctatriene-iron-carborane complex **11** produce species **40** and **41**. The chromium complexes exhibit significant differences in reactivity from their uncomplexed counterparts (ref. 14), and help to illuminate further the correlation between structure and reactivity in this area. Sandwich complexes involving Cr atoms η^0 -bonded to two arene rings either intra- or intermolecularly might be preparable via reactions with chromium vapor. The intramolecular iron-difluorenyl sandwich **42** has been isolated in low yield (ref. 25) and tentatively identified as shown.

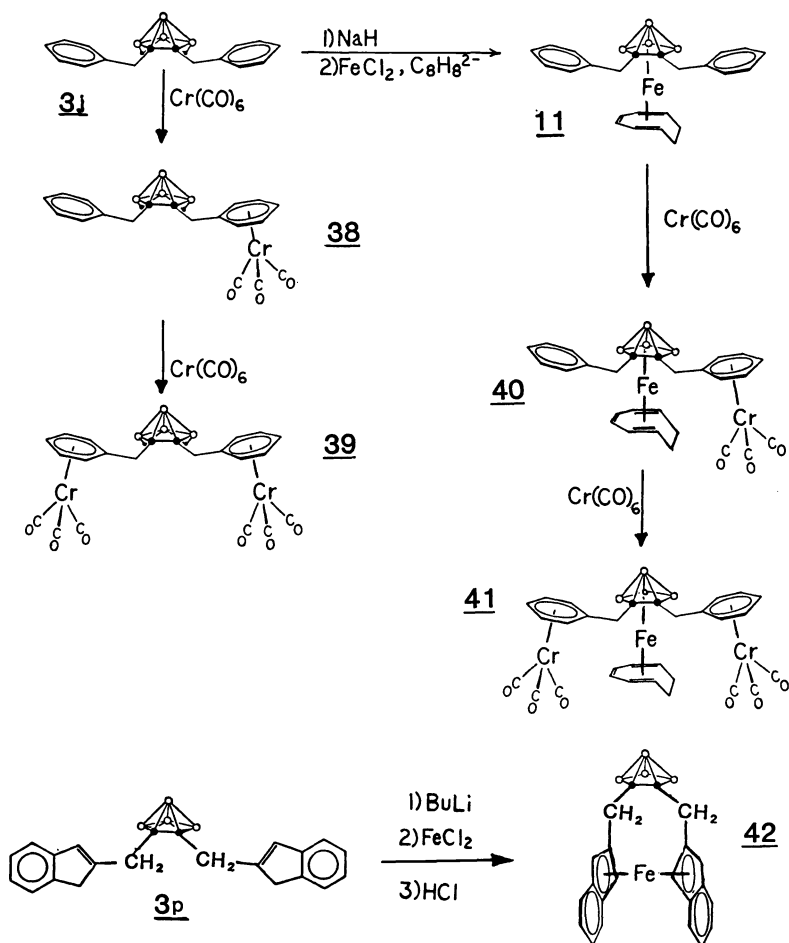


Fig. 10. Metal complexation at carboranyl arene rings

PROPERTIES OF $RR'C_2B_4H_4^{2-}$ LIGANDS WITH BULKY R GROUPS: STERIC CONTROL OF OXIDATIVE FUSION

The transition metal-promoted fusion of small carborane anions was discovered more than a decade ago in $(R_2C_2B_4H_4)_2MH_x$ complexes ($MH_x = FeH_2$ or CoH), which on air-oxidation in cold THF are quantitatively converted to $R_4C_4B_8H_8$ carboranes (ref. 26). Since then, the mechanism has been extensively probed (ref. 15, 27), revealing the existence of a paramagnetic diiron intermediate complex which contains both low-spin and high-spin Fe(II) (ref. 27). Metal-promoted fusion has also been demonstrated with metallacarboranes, metallaboranes, and binary boron hydrides (ref. 28-30). In the latter category, $B_5H_8^-$ salts have been converted to $B_{10}H_{14}$ in good yield, and the new borane $B_{12}H_{16}$ has been prepared from $B_6H_6^-$ ion, both reactions occurring via formation of metal complex intermediates under mild conditions (ref. 30).

Recently, the availability of $RR'C_2B_4H_6$ carboranes with sterically demanding R groups has led us to investigate the fusion behavior of these species via their $RR'C_2B_4H_5^-$ anions. As shown in Fig. 11, the dibenzylcarborane **3j** does form a biscarboranyl complex with Fe^{2+} and subsequently fuses (ref. 14), albeit slowly compared to the dialkyl $R_2C_2B_4H_6$ substrates. The monochromium tricarbonyl derivative **38** also fuses, even more slowly, to give the C_4B_8 product isomers **45**; however, the dichromium species **39** does not (ref. 31). Indeed, although **39** deprotonates normally to give the $[(CO)_3CrPhCH_2]_2C_2B_4H_5^-$ anion, we find no evidence of complexation with Fe^{2+} (there is reason to believe that electronic as well as steric factors play a role here).

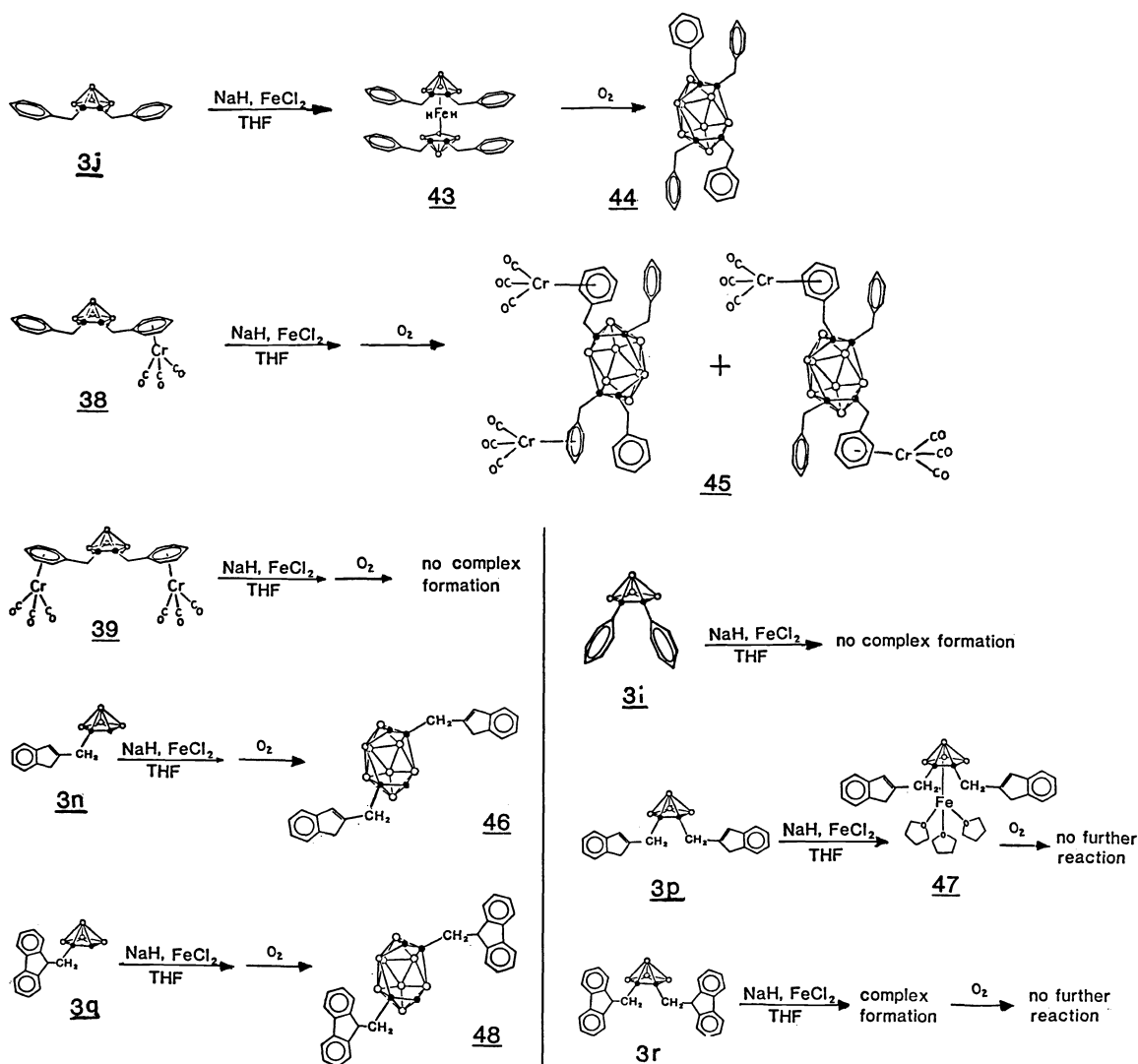


Fig. 11. Metal complexation and fusion properties of $RR'C_2B_4H_5^-$ anions having large R groups

The mono(fluorenylmethyl) and mono(indenylmethyl) derivatives **3n** and **3q** do undergo fusion as shown, there being apparently only one isomer formed in each case (ref. 32). Not surprisingly, considering the bulk of the organic ligands, the bis(fluorenylmethyl) and bis(indenylmethyl) carborane anions **3r** and **3p** do not exhibit fusion, although in the latter case there is evidence of formation of the iron "half-sandwich" **47** on addition of FeCl_2 . In all cases where fusion is not observed, substantial amounts of the $\text{RR}'\text{C}_2\text{B}_4\text{H}_6$ reagent are recovered, indicating reprotonation of the carborane anion in THF solution; as this is written, we are examining these systems in other solvents to determine whether this behavior can be repressed. Another general observation is that the C_4B_8 cages produced by fusion in the reactions depicted in Fig. 11 are all nonfluxional, exhibiting none of the tendency to undergo reversible cage rearrangement that is observed in the $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$ species having only alkyl R groups (ref. 15, 33).

These results suggest that by selective use of appropriate nido- $\text{RR}'\text{C}_2\text{B}_4\text{H}_6$ carboranes it should be possible to control the metal complexation/fusion sequence so as to allow the stepwise incorporation of two different C_2B_4 units into a C_4B_8 cage. While this can be done inefficiently via treatment of a mixed solution of $\text{R}_2\text{C}_2\text{B}_4\text{H}_5^-$ and $\text{R}'_2\text{C}_2\text{B}_4\text{H}_5^-$ anions with FeCl_2 and O_2 (which of course yields not only the desired heterosubstituted $\text{R}_2\text{R}'_2\text{C}_4\text{B}_8\text{H}_8$ product but also the homosubstituted $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$ and $\text{R}'_4\text{C}_4\text{B}_8\text{H}_8$ compounds), we have recently achieved directed mixed-ligand fusion via displacement of cyclooctatriene (Fig. 12) in a process analogous to the preparation of arene complexes described above (see Fig. 7). This type of reaction represents a significant extension of the C_8H_{10} -displacement approach to synthesis and suggests that its application may be quite broad indeed.

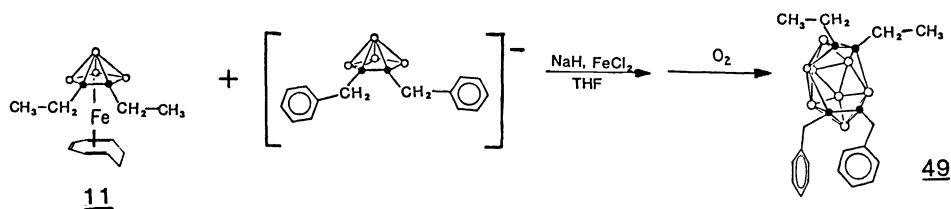


Fig. 12. Directed synthesis of $\text{Et}_2(\text{PhCH}_2)_2\text{C}_4\text{B}_8\text{H}_8$ (ref. 34)

SUMMARY

The nido-2,3- $\text{R}_2\text{C}_2\text{B}_4\text{H}_6$ carboranes, in combination with suitable organic π -ligands and transition metals, are highly versatile units from which both multilevel sandwich complexes and large polyhedral clusters can be synthesized in a controlled manner. To an increasing degree it is possible to prepare stacks and cages having desired functional groups at specified locations including carbon, boron, and metal centers, and to do it with reasonable efficiency. Eventually this may allow the construction of designed organotransition metal-carborane materials having specifically planned properties. This potential, and the relatively easy accessibility and intrinsic stability of these compounds are attractive features from the synthetic chemist's viewpoint and assure continuing interest in developing this borderline area which straddles organic, transition metal, and boron cluster chemistry.

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