Boron–Carbon Ring Ligands in Organometallic Synthesis

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Contents

Russell N. Grimes was born in Meridian, MS and raised in eastern Pennsylvania. He is a B.S. graduate of Lafayette College. He holds a Ph.D. degree from the University of Minnesota, but his thesis research was conducted at Harvard following the move of his advisor, William Lipscomb, to that institution. After postdoctoral work with Lipscomb and with M. F. Hawthorne, in 1963 he joined the faculty at the University of Virginia, where he served as department chairman from 1981 to 1984 and is currently Professor of Chemistry. He is a former Fulbright Scholar and a Fellow of the American Association for the Advancement of Science and has held Guest Professorships at the University of Canterbury (New Zealand) and at the University of Heidelberg, Germany. He serves on the Editorial Boards of *Inorganic Chemistry* and *Inorganic Syntheses* and is Editor-in-Chief of *Inorganic Syntheses*, Volume 29. His research interests are in the synthesis and structure of boron clusters and organometallic sandwich compounds, with particular focus on the interface between these areas.

I. Introduction

The enormous scope and diversity of boron cluster chemistry—from polyboranes to carboranes to metallaboranes, main-group heteroboranes, metallacarboranes, and metal sandwich complexes of organoboron ligands—is difficult for the nonspecialist to appreciate. In the rapid development of this field over the last 25 years, the profusion of exotic structures and reactions, while fascinating to read about, have understandably seemed to have little relation to the rest of chemistry. But this is changing, and fast. Major advances in theory and experiment have established the boranes as central players in a larger family of clusters which range from hydrocarbons to polymetallic cages to iron–sulfur protein cores. As several recent volumes[1–4] make abundantly clear, the boranes provide a foundation for understanding and drawing together areas as seemingly diverse as metal clusters and nonclassical carbocations: for example, the square pyramidal species $C_5Me_5^+$ and $(CO)_{15}Fe_5C$ are both isostructural and isoelectronic analogues of B_5H_9.

Practical applications are emerging, too. Siloxane-linked polymers containing *m*-carborane ($1,7$-$C_2B_{10}H_{10}$) icosahedral units having extraordinary chemical and thermal stability are commercially available. Recent advances in the areas of boron neutron capture therapy (BNCT) for tumors and medical imaging herald possibly important clinical roles for boron cluster compounds, especially (in the case of BNCT) derivatives of carboranes linked to monoclonal antibodies. Powerful metallacarborane catalysts for hydroformylation and hydrosilylation have been developed, and polyborane derivatives have shown promise as precursors to boron carbide and other ceramics. And there is increasing evidence that carborane and organoboron ligands are of value as ligands in organometallic synthesis, indeed allowing the creation of new kinds of stable structures and, potentially, new materials having novel electronic, magnetic, or optical properties. It is this area to which the present article is directed.

This review is an attempt to summarize an aspect of boron chemistry that evolved in recent years in our own

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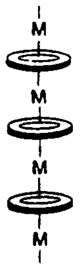
and other laboratories,[5-7] namely the systematic use of small boron–carbon ring ligands as synthons in the construction of extended (linked or multidecker sandwich) organometallic systems. In the experience of the author's research group, this idea was not preconceived but grew out of repeated observations[5,8] that small *nido*-carborane and metallacarborane cages (i) are readily prepared, (ii) form stable sandwich complexes in combination with a wide variety of transition metals and organic ring systems, (iii) have a direct isostructural relationship with aromatic hydrocarbon ligands (enabling the formal replacement of $C_5H_5^-$ by $C_2B_3H_7^{2-}$, for example), (iv) possess a remarkable, almost unique ability to stabilize organometallic systems that are otherwise unstable or even nonexistent, (v) can be manipulated and modified *in a controlled manner* using techniques drawn from organic, boron cluster, and metal chemistry, and (vi) are sufficiently robust that they undergo multiple changes in metal oxidation state without degradation. A further observation of interest is that studies of paramagnetic triple-decker sandwiches bridged by C_2B_3 carborane rings, to be discussed in section V, reveal extensive electron delocalization between metal centers.

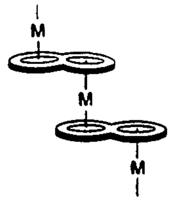
These findings, combined with developments emanating from other research groups,[9-11] clearly demonstrate that small carborane-based organometallic chemistry is an emerging area of very considerable scope and versatility. This effort rests on the elegant foundation created by Hawthorne, the discoverer of metallacarboranes,[12] who has pioneered the chemistry of the large metallaboron clusters for over a quarter of a century. Although the metal–small carborane ligand interactions dealt with in this article are similar to those of the 12-vertex metallacarboranes, and some of the chemical transformations are likewise related, the stereochemistry is markedly different. In the systems described in this review the boron-containing bridging ligands are planar, allowing the construction of multidecker arrays with parallel rings that are in fact stacked organometallic compounds; moreover, certain reactions of the small metal–borane clusters (e.g. metal-promoted oxidative fusion) have no known parallel in the icosahedral systems. Thus the chemistry to be described has evolved with distinct features, albeit with obvious relationships to other areas.

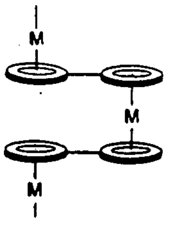
This article is concerned with the design and stepwise assembly of polymetallic sandwich complexes in which boron–carbon rings serve a multiple purpose: as binding faces for metal atoms, as electronic stabilizing agents, as conduits for electron delocalization between centers, and as frameworks to which external functional groups can be attached. Various aspects of this subject, including small carborane complexes of transition metals[5,8] and main-group elements,[9] and metal derivatives of organoboron ligands,[6,7,13,14] have been reviewed elsewhere; in addition, synthetic approaches employed in the author's research have been discussed in earlier articles and chapters.[5,8,15]

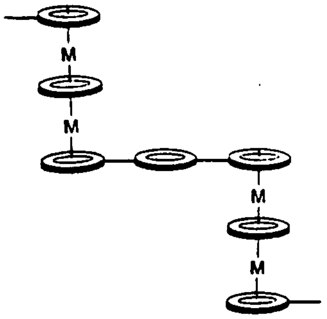
II. The Basic Building Blocks

The essential idea to be developed is that small carborane or organoboron ligands can be combined with metal ions and aromatic hydrocarbons or heterocycles to create a wide range of extended (linked or stacked) sandwich complexes of remarkable stability and chemical versatility. We are concerned here with *multiunit systems* which may be sandwich complexes having three or more decks, linked-sandwich oligomers, or polymers:









Although metal π-complexes can be prepared from many different boron-containing ligands, only a few have played a significant role in building multimetal arrays as defined above; thus, borabenzene (C_5B) rings, which readily form double-decker sandwiches,[13] are not known to form larger stacked complexes. The central function of the organoboron or carborane ligands is easily appreciated when it is realized that the scope of synthetic possibilities afforded by metals and hydrocarbons *alone* is quite limited if air-stable products are sought. For example, while a wide variety of bis(arene) transition-metal complexes can be prepared, most are oxygen-sensitive;[16] a recently reported naphthalene–chromium sandwich polymer[17] is typical. As a means of stabilization, the incorporation of boron is strikingly effective: the majority of the boron-containing structures discussed herein are unreactive to air over indefinite periods, and indeed are generally robust materials which can undergo reversible redox processes and survive chemical modification without structural disintegration.

A. Small Carborane and Organoborane Ligands

The boron–carbon units of interest here are depicted in Figure 1. For uniformity, these are shown as formal ligands with charges that render them 6π-electron donors to a face-bonded metal, so that all are electronically analogous to C_6H_6 and $C_5H_5^-$. Alternatively, they can be viewed as electrically neutral $n\pi$-donors where n is the difference between 6 and the charge shown; thus, neutral $C_2B_4H_6$ is a 4π-electron ligand. Some of these groups (e.g., $C_2B_3H_5^{4-}$ and $C_2B_3H_7^{2-}$) are known only in complexed form; for all ligands shown, B- and/or C-substituted derivatives are commonly employed in synthesis (in several cases the parent species are unknown).

The ligands shown possess, in general, two significant advantages over aromatic hydrocarbons: (1) the presence of boron, with lower electronegativity than carbon, promotes strong covalent binding to metal centers, and

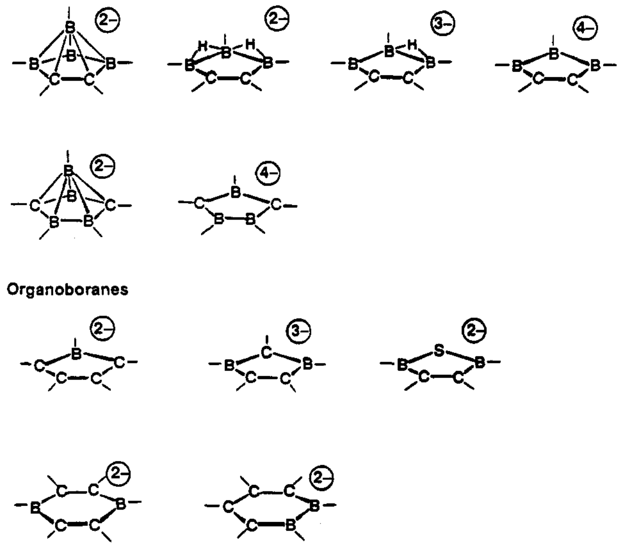


Figure 1. Boron–carbon 6π-aromatic bridging ligands in extended metal sandwich complexes, with formal charges indicated (except for the C_2B_4 carborane dianions, the species shown are not found as free ligands in solution). Substituents are usually alkyl or H.

(2) the planar groups readily form η^5 or η^6 bonds with *two metals simultaneously* on opposite sides of the ring plane, forming triple- or multiple-decker sandwiches. (This characteristic is shared even by the pyramidal C_2B_4 carborane, which can coordinate to two metals, generating an 8-vertex cluster.[18]) Planar hydrocarbon rings rarely exhibit this property, there being only a few known triple-decker complexes (and no larger ones) bridged by cyclic C_nR_n groups.[19–21] However, a number of triple-deckers with central P_n or As_n rings have been prepared.[22]

Synthetic routes to the ligands or ligand precursors in Figure 1 have been extensively described in the literature,[6–8,13,14] and a selection of typical procedures is presented in Figure 2. An unusual aspect of this chemistry is that investigations of the small dicarbon carboranes with metallacarboranes have been pursued mostly in the United States, while the study of organoboranes as ligands in multidecker metal sandwiches (defined here as triple-decker or larger) has been almost exclusively associated with German chemists. (Indeed, the two fields developed entirely separately over many years until a recent collaborative effort[18,23–25] produced the first "hybrid" complexes incorporating both types of ligands.) This peculiar history was shaped in large part by two fortuitous circumstances: the large stockpile (still over 10^5 kg) of B_5H_9 in the United States remaining from a rocket fuel development project of several decades ago, and the ready availability of boron trihalides in Germany. Pentaborane(9) is directly converted into lower carboranes as shown in Figure 2a, while boron halides are important in the preparation of cyclic organoboranes (Figure 2, parts b–e).

The reaction of B_5H_9 with alkynes in the absence of solvent is quite general, proving successful even with cyclic and polyalkynes,[26] and can be used to prepare both symmetric (R = R′) and unsymmetric (R ≠ R′) *nido*-2,3-RR′$C_2B_4H_6$ derivatives in which R and R′ are alkyl, arylalkyl, or trimethylsilyl groups.[5,8–10] Very recently, a major advance has been reported by Cendrowski-Guillaume and Spencer, who found that this synthesis can be conducted on a large scale and in high yield in tetrahydrofuran (THF) solution.[10] The B_5H_9–THF solutions are remarkably stable (degrading only slowly even on exposure to air) and can be employed as a bench reagent in a fashion analogous to the use of $BH_3{\cdot}OEt_2$ solution as a reagent in organic chemistry. (In the author's laboratory this method generated over 30 g of $Et_2C_2B_4H_6$ in 80% yield in a single preparation.)

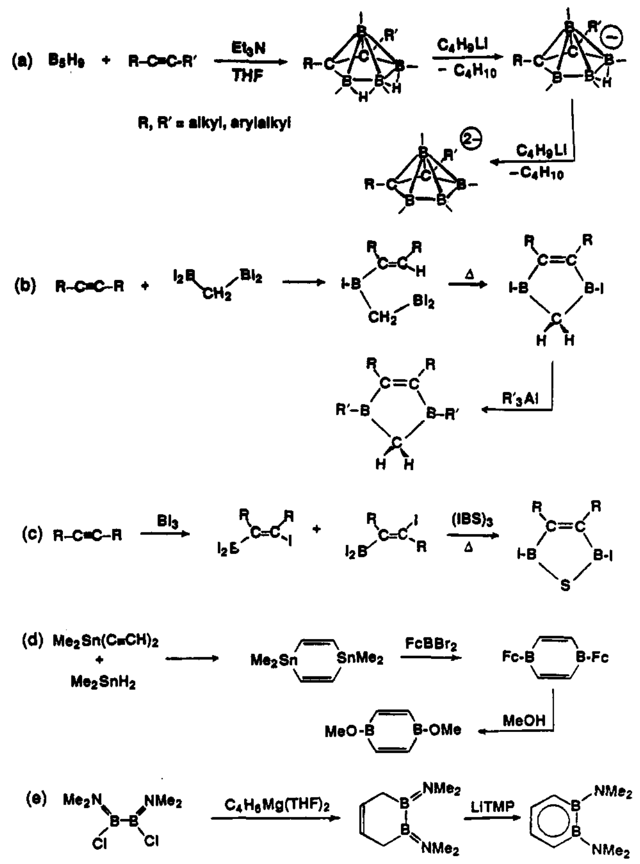


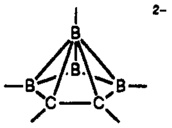
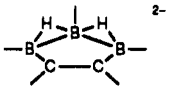
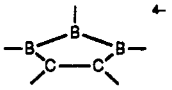
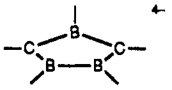
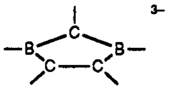
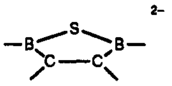
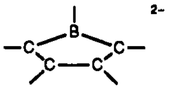
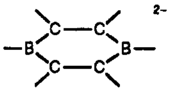
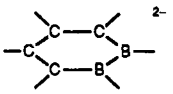
Figure 2. Some synthetic routes to ligands and ligand precursors commonly used in construction of extended metal sandwiches: (a) 2,3-*nido*-$R_2C_2B_4H_6$ (dicarbahexaborane) and its bridge-deprotonated mono- and dianions,[5,8,9] (b) 2,3-dihydro-1,3-diborolenyl derivatives,[6] (c) 2,5-dihydro-1,2,5-thiadiborolenyl derivatives,[6] (d) 1,4-dimethoxy-1,4-diboracyclohexadiene,[7] and (e) 1,2-bis(dimethylamino)-1,2-diboratabenzene.[28]

In another recent development, reported by Hosmane,[9] the mono- and bis(*C*-trimethylsilyl) derivatives were readily desilylated to give the corresponding C–H species. As described below, the RR′$C_2B_4H_6$ carboranes can be further tailored by regioselective introduction of organic substituents to the B(4) or equivalent B(6) locations on the open face (the borons adjacent to carbon) via treatment of the bridge-deprotonated monoanion with an alkyl halide.[27]

B. Metals

Many transition metals, as well as several main-group elements, form isolable sandwich complexes with carborane and/or organoborane ligands, as summarized in Table I. These species include both homoligand (L–M–L) and heteroligand (L–M–L) bonding situations and encompass double-, triple-, and higher-decker compounds. The metal reagents employed, given in the discussion of individual syntheses to follow, are commercially available or readily prepared via literature methods. In general, there is no chemically significant

TABLE I. Metals Forming η^5 or η^6 Sandwich Complexes

ligand	1st transition series	2nd transition series	3rd transition series	main-group metals
	Ti, V, Cr, Fe, Co, Ni	Zr, Ru, Rh	Os, Pt	Al, Ga, In, Si, Ge, Sn, Pb
	Fe, Co	Ru, Rh		
	Fe, Co, Ni	Ru, Rh	Os, Pt	
	Co			
	Cr, Mn, Fe, Co, Ni, Cu, Zn	Ru, Rh	Pt	Tl, Sn
	Mn, Fe, Co, Ni, Zn			
	V, Cr, Fe, Co, Ni	Nb, Mo, Ru, Rh	Ta, W, Re, Os, Ir	Li
	Fe, Ni	Rh	Pt	
		Rh		Li

pattern to be found in the particular metal–ligand combinations shown, which largely reflect experimental choice or convenience rather than thermodynamic stability. An updated version of this table a few years hence will undoubtedly have many more entries. Even at the present time, the extraordinary synthetic versatility in this family of complexes is apparent.

C. Aromatic Hydrocarbons and Heterocycles

In this chemistry, organic groups coordinated to metals are found in two roles: as end-capping sandwich ligands (e.g., $C_5Me_5^-$) and as agents for connecting two or more cluster or sandwich units. For the latter purpose one requires polyarenes or other ligands having more than one aromatic ring to which metals can be η^5- or η^6-coordinated. Figure 3 depicts a representative sample of both types of organic ligand found in characterized multidecker compounds. Most of these hydrocarbons are available from suppliers or can be prepared by published methods, but in some instances previously unknown ligands (e.g., Me_4C_5–CH_2–C_6H_5)[29] have been synthesized in our laboratory for use as linking groups.

D. Bonding Considerations

The molecular species of interest in this review can be described both as boron clusters and as metal sandwich complexes or ligands. Excellent discussions of bonding theory in polyboron cages, including the classic treatments of Lipscomb, Wade, and Mingos, are available elsewhere,[30] so only a brief summary of some useful principles will be given here. Although carboranes such as *nido*-$R_2C_2B_4H_6$ (Figure 2a) can be described in terms of three-center and two-center localized bonds,[31] such molecules are usually depicted as shown in Figures 1 and 2, in which the lines between atoms *depict connectivity only and do not imply electron*

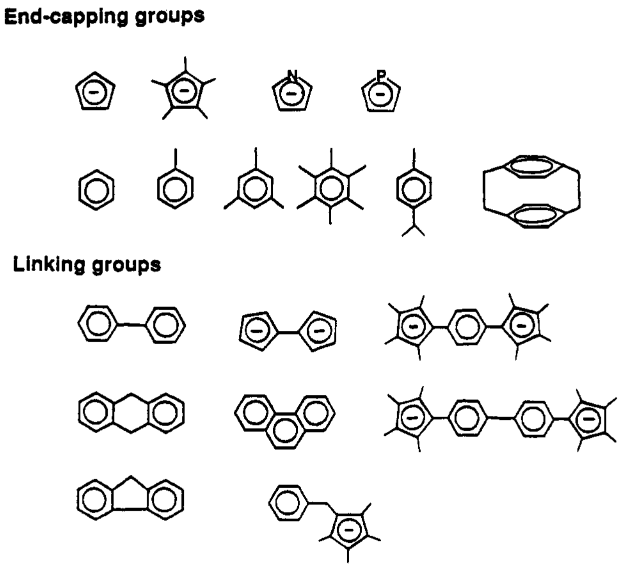


Figure 3. End-capping and bridging organic ligands in triple- and higher-decker metal sandwich complexes.

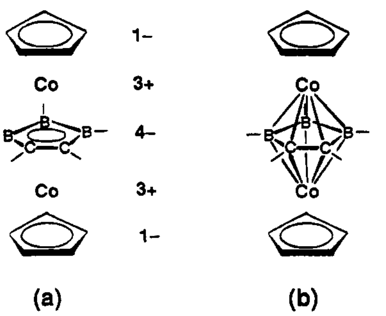


Figure 4. $CpCo(R_2C_2B_3H_3)CoCp$ depicted as a triple-decker sandwich complex with formal charges shown for each unit (left), and as a 16-electron 7-vertex $Co_2C_2B_3$ closo cluster (right).

bond pairs. This convention is followed throughout this review.

Triple-decker complexes involving bonding interactions between the end (capping) ligands, the central ring, and two metal atoms, usually generate 15–17 bonding molecular orbitals requiring 30–34 electrons for a filled-shell system.[32] The electron count observed varies depending on the metal–ligand combination, and in known triple-decker complexes ranges from 26 to 34. In triple-deckers bridged by carbon–boron rings, 30 is the usual "magic number" for stable, diamagnetic systems. In larger stacks, each additional metal–ligand unit adds 12 electrons, so that a closed-shell diamagnetic tetradecker sandwich is anticipated to have 42e, a pentadecker 54e, and so on (double-deckers, e.g. ferrocene, are 18e systems).

In the triple-decker sandwich $CpCo(C_2B_3H_5)CoCp$, for example (Figure 4a), the formal $C_2B_3H_5^{4-}$ bridging ligand supplies 6 electrons, each Co^{3+} center provides 6 more, and the end-capping $C_5H_5^-$ rings account for a total of 12, making a 30-electron diamagnetic system. (Obviously, this number is independent of the assignment of formal charges to the rings and metals; if one desires, each unit can be regarded as a neutral entity.) Species such as the dicobalt complex can also be regarded as 7-vertex closo polyhedra (Figure 4b) and treated by cluster electron-counting methods,[1,3] which require $n + 1$ electron pairs for a closo (deltahedral) cage system, in this case 16e for the $Co_2C_2B_3$ bipyramid; this number is achieved via 2e contributions from each BH and CoCp unit and 3e from each CH group. In the present context, the "sandwich" model is the more useful in that we are dealing with stacked and linked systems in which we consider the boron–carbon ring ligands to be electronically interchangeable with arene and cyclopentadienyl rings.

III. Methods for Designed Synthesis and Chemical Modification of Monomers

In this and the following sections, our focus will be on controlled synthetic methods having reasonably broad applicability in the construction of multimetallic systems. Alternative preparative routes which may be of interest but lack practicality (for example, affording unacceptably low product yields) will be omitted in the present discussion.

A. Assembly of Double-Decker Sandwiches

Coordination of metal ions or metal–ligand fragments to organoboron rings such as borolenyl (C_4B), diborolenyl (C_3B_2), or thiadiborolenyl (C_2B_2S) is usually accomplished by direct reaction of the organoborane or its deprotonated anion with a metal reagent. Thus, $CpCo(C_2H_4)_2$ and $Et_2MeHC_3B_2Et_2$ combine to generate **1** in high yield (Figure 5a); below room temperature, a cobalt hydride intermediate **2** is formed which rapidly converts to **1**.[6] Other transition-metal reagents can be used to produce double- and higher-decker sandwiches directly from the diborolenyl ligands.

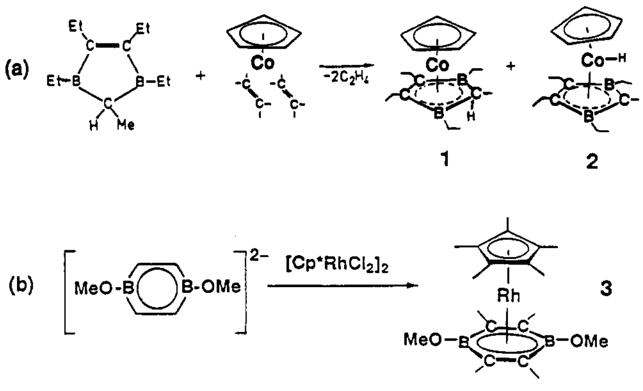


Figure 5. (a) Synthesis of dihydrodiborolyl cobalt complexes[6] and (b) synthesis of $Cp^*Rh[1,4\text{-}H_4C_4B_2(OMe)_2]$.[33]

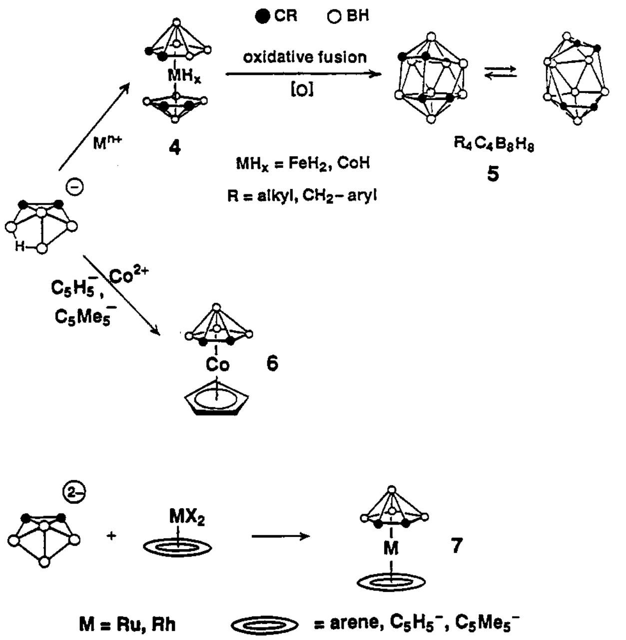


Figure 6. Synthetic routes to $LM(RR'C_2B_4H_4)$ complexes of Co,[35] Rh,[24] and Ru.[36]

1,4-Diborabenzene (C_4B_2) metal complexes can be prepared directly from the neutral ligand via reduction to the dianion and treatment with transition metal reagents, as illustrated by the synthesis of the rhodium species **3** (Figure 5b).[33] Complexes of 1,2-diborabenzene are obtained by similar methods.[34]

The synthesis of metal sandwiches containing C_2B_3 carborane rings is less direct, since cyclic carboranes are not available as free ligands. One must first coordinate a metal ion or metal–ligand unit to the open face of a pyramidal C_2B_4 anion or dianion with an appropriate metal reagent in cold THF. As shown in Figure 6, transition-metal dihalides ($FeCl_2$, $CoCl_2$) in the absence of other ligands give the biscarborane species **4**, which on exposure to air produce the fused C_4B_8 carboranes

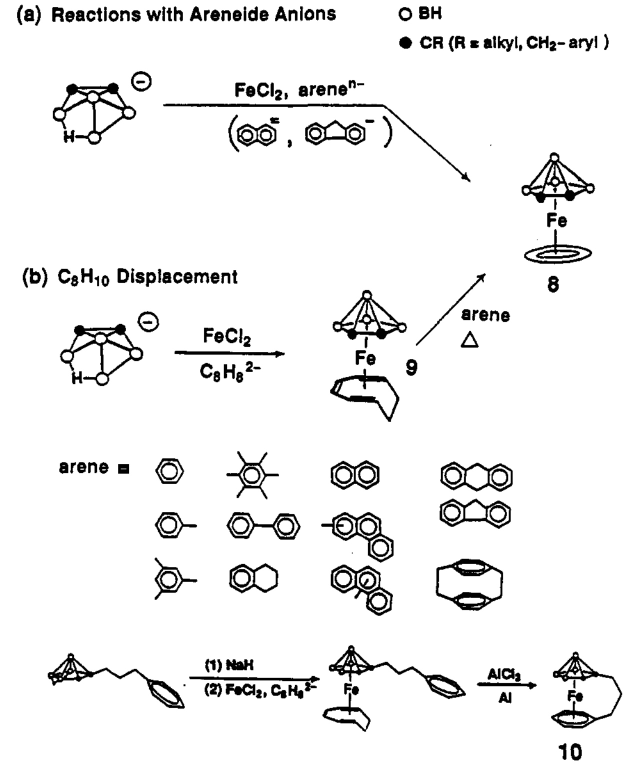


Figure 7. Synthetic routes to (arene)Fe($RR'C_2B_4H_4$) complexes.[40]

5 (vide infra). Three-component reactions involving a hydrocarbon anion, carborane ligand, and metal ion can generate mixed-ligand species of the type LM($RR'C_2B_4H_4$) (6). This method requires divalent metal reagents (which undergo a change in formal oxidation state from +2 to +3 in complex formation), and is most useful with $CoCl_2$ and Cp^- or Cp^{*-} ($Cp^* = C_5Me_5$).[35]

A problem that can arise with the $RR'C_2B_4H_5^-$ monoanions is that in THF and similar solvents, reprotonation to generate the neutral $RR'C_2B_4H_6$ species is often competitive with metal complexation. For this reason, MC_2B_4 complexes involving second- and third-row transition metals are not in general easily obtained from the carborane monoanions. However, this problem is overcome via use of $RR'C_2B_4H_4^{2-}$ *dianions*, which are more reactive toward metal reagents; examples are the syntheses of the ruthenium[36] and rhodium[24] complexes 7 (Figure 6). The discovery of the carborane dianions by Hosmane[37] was instrumental in the development of this chemistry in our group.

Carborane–iron–arene sandwiches (8) can be obtained in three-way reactions of the type described above provided the arene ligand can be reduced to an anion, as in the cases of naphthalene and fluorene (Figure 7a).[38] This method is not applicable to nonreducible arenes such as benzene and its methyl derivatives, but complexes of these ligands can be obtained by thermal displacement of cyclooctatriene from the readily available[39] ferracarborane (η^6-C_8H_{10})Fe($RR'C_2B_4H_6$) (9, Figure 7b).[40] The process can be conducted intramolecularly, as in the synthesis of "carboranophanes"[41] such as 10. The displacement reaction is very general, working with a wide variety of arenes, and furnishes a powerful synthetic route to arene–ferracarborane sandwiches which are of special interest because of their unusual stability and electrochemical versatility (see section V.A).

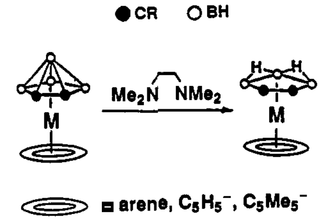


Figure 8. Base-promoted conversion of LM($RR'C_2B_4H_4$) to *nido*-LM($RR'C_2B_3H_5$) complexes.

B. Decapitation (Base-Catalyzed Apex BH Removal)

The methods outlined above can be employed to synthesize LM($RR'C_2B_4H_4$) sandwich complexes of most of the transition metals and many main-group elements as well. However, in order to use these species as building blocks for multidecker stacks, it is necessary to create an open C_2B_3 face via removal of the apical BH unit. This is readily accomplished by treatment with Lewis bases such as *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in the presence of a proton donor (water is often used) as shown in Figure 8.[5,8] Formally, this process converts the $RR'C_2B_4H_4^{2-}$ ligand to $RR'C_2B_3H_5^{2-}$ wherein the apical BH is replaced by an electronically equivalent pair of hydrogen atoms that bridge the two B–B edges (Figure 8). As with other synthetically useful reactions discussed here, decapitation is generally applicable and is employed routinely to convert *closo*-MC_2B_4 to *nido*-MC_2B_3 complexes which are the primary precursors to multidecker sandwiches.

C. Metal-Promoted Oxidative Fusion

The face-to-face consolidation of two pyramidal fragments or ligands into a single cluster would seem to be an unlikely, disfavored process under mild conditions, but in fact this reaction is well known in small boron clusters and is a useful synthetic tool. Following the discovery[42] that bis(carboranyl) metal complexes of the type $(R_2C_2B_4H_4)_2MH_x$ ($MH_x = FeH_2$ or CoH) on exposure to oxidants are converted to high yield to tetracarbon carboranes ($R_4C_4B_8H_8$) in cold THF (Figure 6, top), it was subsequently found that small metallacarboranes,[43] metallaboranes,[44] and even binary boron hydrides[44,45] ($B_5H_8^-$, $B_6H_9^-$) undergo similar fusions (Figure 9).

These reactions involve the net oxidation of a pair of anionic ligands to a neutral product, as in the formation of $R_4C_4B_8H_8$ from two $R_2C_2B_4H_4^{2-}$ units, and have been extensively studied.[43,46,47] Thus far, the fusion of two units into a single polyhedral cluster (or cluster fragment) has been observed only in 5- and 6-vertex nido substrates; efforts to fuse larger species such as icosahedral-fragment C_2B_9 anions have given linked or edge-joined products[48] rather than single cages.

Although some truly remarkable chemistry has been uncovered in studies of oxidative fusion (for example, an isolable intermediate in the formation of tetracarbon carboranes 5, Figure 6, is a diiron species having four unpaired electrons and containing both Fe^{II} and Fe^{IV} centers![49]), it is not yet clear how fusion might best be exploited as a useful synthetic method in constructing multicage networks. Some intriguing possibilities can be envisioned, such as the fusion of polymeric chains of *nido*-MC_2B_3 units to generate polycarborane prod-

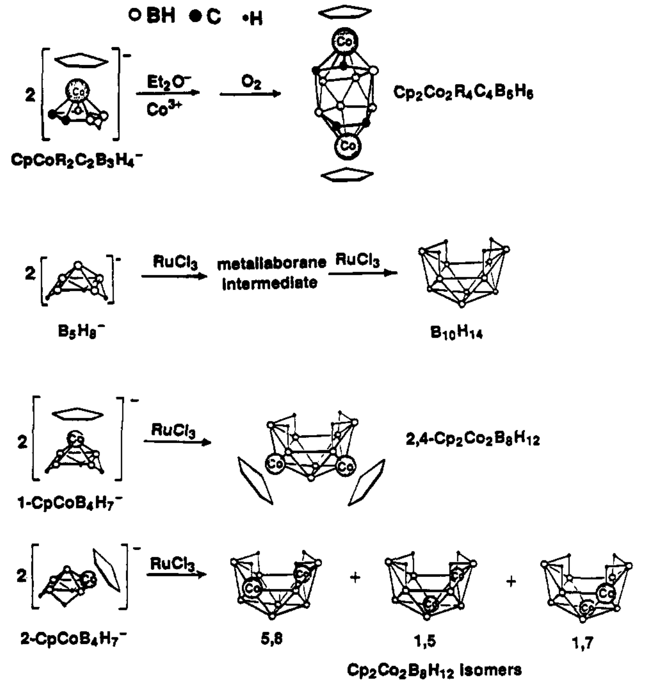


Figure 9. Examples of metal-promoted oxidative fusion of metallacarboranes,[43] metallaboranes,[44] and boron hydride anions.[44,45]

ucts, and such ideas are currently under study in the author's laboratory.

D. Controlled Introduction of Substituent Groups in *nido*-$LM(C_2B_3)$ Synthons

In the course of our development of synthetic routes to multiunit organometallic systems based on small carboranes, it was clear that methods were needed for attaching organic functional groups to the carborane ligands. This is important for three reasons: (1) to tailor the properties of the carborane groups and their complexes via electronic and/or steric effects, (2) to allow linkage of metallacarborane stacks or clusters via connecting groups, and (3) to conduct organic chemistry (e.g., condensation and polymerization reactions) on cage-bound substituents. These aspects are discussed in section IV below.

1. Substitution at Boron

Attachment of organic groups to boron on open C_2B_3 faces is carried out either on the *nido*-$RR'C_2B_4H_6$ carborane prior to metal complexation, or on *nido*-LM($RR'C_2B_3H_5$) metal complexes, in both cases via reactions of deprotonated anions. Removal of one[50] or both[37] of the acidic B–H–B protons by nucleophiles in THF generates, respectively, the carborane mono- or dianion as depicted in Figure 2a. Treatment of the monoanion with alkyl halides produces the B(4)- (and equivalent B(6)-) alkyl derivative in 99% regiospecificity (Figure 10).[27] The sequence cannot be repeated, however, so that only mono-B-alkylation is possible by this route.

Since the construction of linked and stacked complexes to be discussed utilizes double-decker sandwiches of the type LM($RR'C_2B_3H_5$) as building blocks, it is highly desirable to be able to place substituents directly on these species. Complexes in which LM is Cp*Co, (C_6Me_6)Fe, or (cymene)Ru have been explored;[51] as with the *nido*-carboranes, the B–H–B protons are acidic and can be removed to produce the mono- or dianions, which in turn are susceptible to attack by alkyl halides. In these metal complexes, however, the product usually obtained (typically in 100% regioselectivity) is the B(5)-substituted derivative (Figure 11), in sharp contrast to the B(4,6)-substitution observed with the C_2B_4 carboranes. It is synthetically fortuitous that the nonchiral B(5)–X derivative is the sole isomer produced in most cases, thereby avoiding complex product mixtures when these species are oligomerized as described below. Unlike the reactions of $RR'C_2B_4H_5^-$ ions with alkyl halides, the corresponding treatment of the metallacarborane substrates can be repeated through two or three deprotonation/substitution cycles, affording di- and tri-B-substituted products if desired.[51]

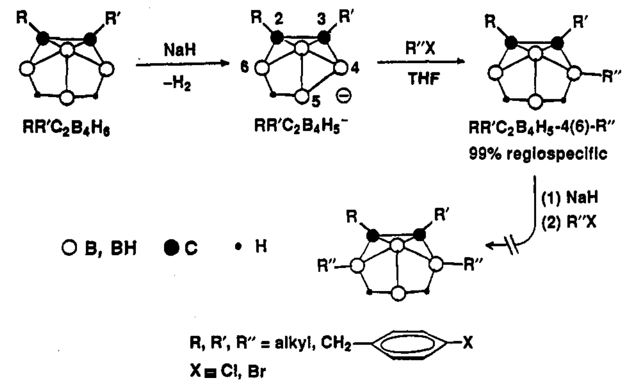


Figure 10. Preparation of B(4/6)-alkyl and -arylalkyl derivatives of *nido*-2,3-$RR'C_2B_4H_6$.[27]

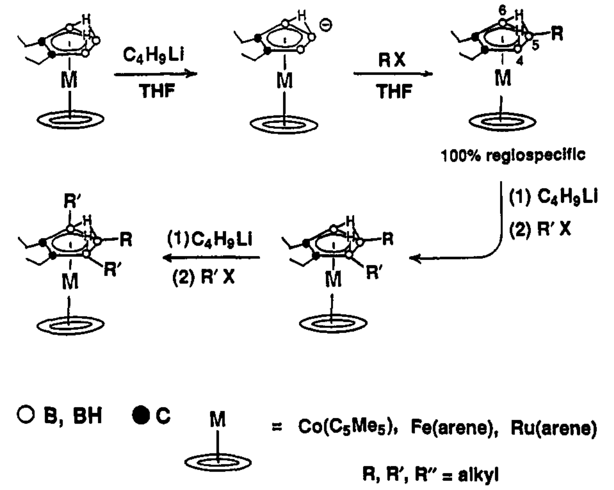


Figure 11. Preparation of B(5)-alkyl derivatives of *nido*-LM($RR'C_2B_3H_5$) complexes (L = aryl, Cp, Cp*).[51]

The derivatization of the *nido*-cobaltacarborane Cp*Co($Et_2C_2B_3H_5$) (11) has been extensively studied, and a variety of B-functionalized derivatives (12) has been prepared, in most cases via reactions of the anion (Figure 12).[52,53] The introduction of organic functional groups such as acyl, amino, and carboxylic acid clearly opens many new synthetic avenues in this area.

2. Substitution at Carbon

Until recently, the only means of varying the R and R' groups attached to the cage carbons in these systems was via the choice of alkyne in the preparation of the $RR'C_2B_4H_6$ carborane from B_5H_9 (Figure 2a). Moreo-

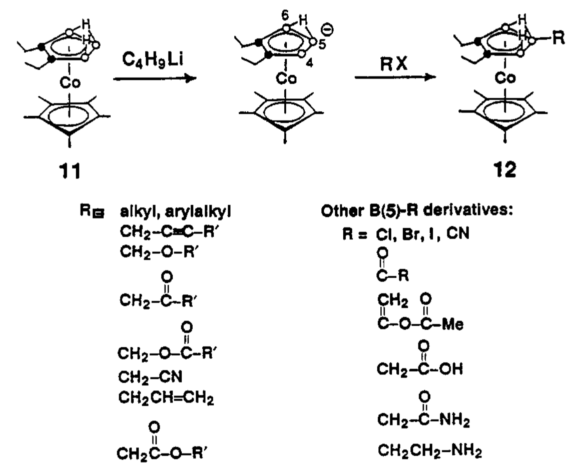


Figure 12. Preparation of B(5)-organo-substituted derivatives of *nido*-Cp*Co($Et_2C_2B_3H_5$).[52,53]

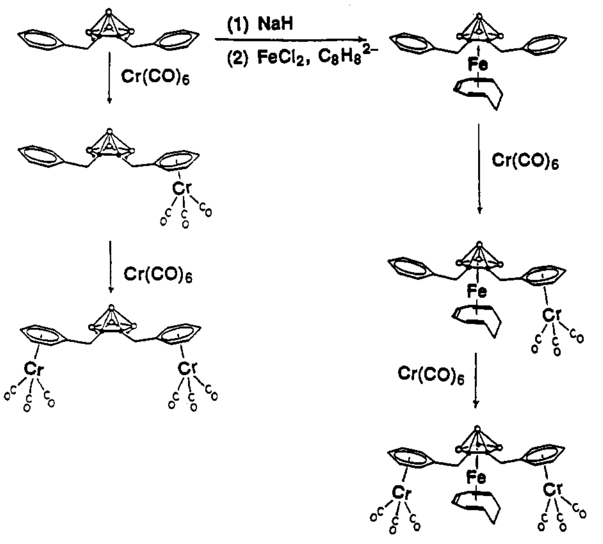


Figure 13. Chromium tricarbonyl complexation of $(PhCH_2)_2C_2B_4H_6$ and (η^6-C_8H_{10})Fe$(PhCH_2)_2C_2B_4H_6$.[54]

ver, these substituents (usually alkyl or arylalkyl) cannot readily be removed from the carborane or metallacarborane cage. Consequently, the role of carbon-bound groups in this chemistry was restricted to the metallation of aryl rings in the *C,C′*-dibenzylcarborane and its metallacarborane derivatives[54,55] as shown in Figure 13. However, recent work has shown that the *C,C′*-bis(trimethylsilyl)cobaltacarborane derivatives undergo *catalytic* desilylation on treatment with $Bu_4N^+F^-$ in wet THF to generate the corresponding C–H species (Figure 14).[56] The C–H protons in these products are sufficiently acidic to be removable on treatment with butyllithium, affording mono- or di-*C*-lithio derivatives which react with organohalides to place substituents on carbon, as shown. (Curiously, although trimethylsilyl *nido*-carboranes are desilylated by HCl gas,[57] this treatment is ineffective with the silylcobaltacarboranes.) This reaction sequence extends still further the range of possibilities for creative use of metallacarborane sandwiches in synthesis, since both boron and carbon framework locations are available for attachment of functional groups.

3. Substitution in B–X–B Bridging Positions

In addition to the terminally B- and C-substituted species, one other type of derivative is possible in

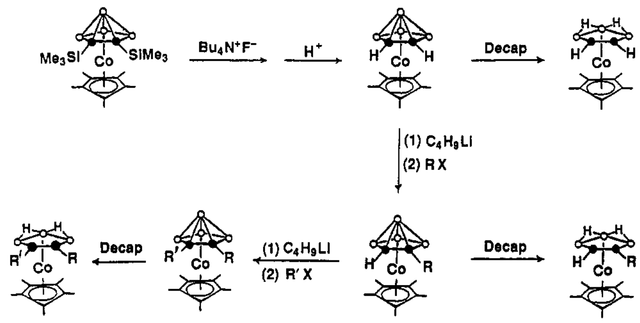


Figure 14. Synthesis of parent *nido*-Cp*Co($C_2B_3H_7$) and its *C*-alkyl and *C,C′*-dialkyl derivatives from the *C,C′*-bis(trimethylsilyl) complex.[56]

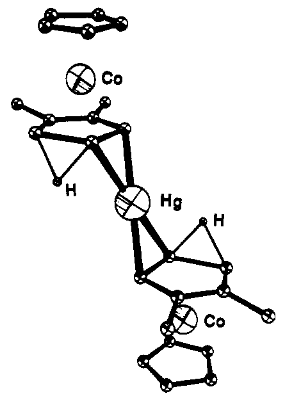


Figure 15. Crystallographyically determined structure of $[CpCo(Me_2C_2B_3H_4)]_2Hg$.[59]

nido-MC_2B_3 systems, namely, that in which a bridging group replaces a B–H–B proton. Both main-group- and transition-metal-bridged complexes of *nido*-RR′$C_2B_4H_6$ are well known,[58] but in the family of *nido*-MC_2B_3 compounds the only such characterized species are mercury- and silicon-bridged (refs 59 and 52, respectively) derivatives of $(C_5R_5)Co(R'_2C_2B_3H_5)$, an example of which is depicted in Figure 15. Extended structures based on bridge-linked small metallacarboranes can be visualized, but this principle has not yet been exploited in the synthesis of multiunit systems larger than dimers.

IV. Methods for Controlled Assembly of Multidecker and Linked Sandwiches

A variety of synthetic strategies can be envisioned for building multimetallic extended networks from small metal–carborane sandwich units, and Figure 16 depicts four approaches that are currently under investigation in our laboratory.

A. Multidecker Stacking

Boron-containing ring ligands have played a dominant role in the history of multidecker sandwich chemistry. The first stable and electrically neutral triple-decker compounds of any type (and the first to be structurally characterized by X-ray crystallography) incorporated C_2B_3 carborane rings,[60] and currently all known tetra- and higher-decker sandwiches utilize C_2B_3 and/or C_3B_2 bridging units. The basic synthetic approach to carborane triple-deckers entails the addition of metal–ligand units to double-decker substrates, which can be accomplished in several ways as shown in Figure 17.

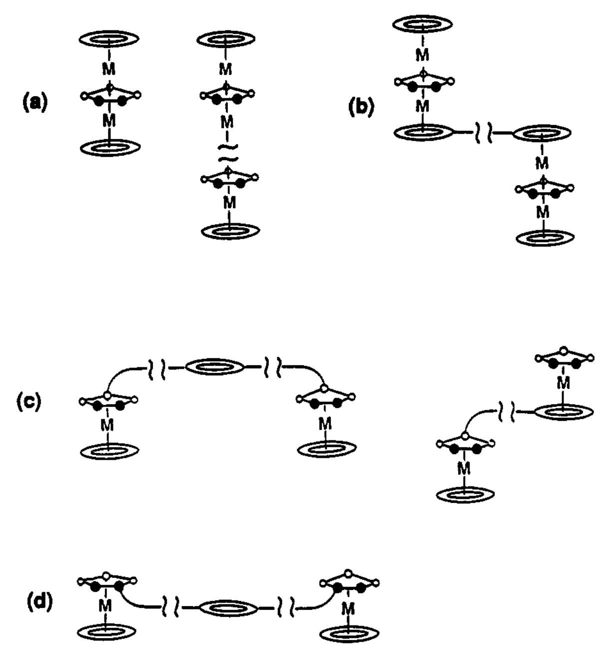


Figure 16. Modes of assembly of multiunit carborane sandwich systems: (a) multidecker stacking, (b) linkage via polycyclic ligands and metals, (c) linkage via organic groups on boron, and (d) linkage via organic groups on carbon.

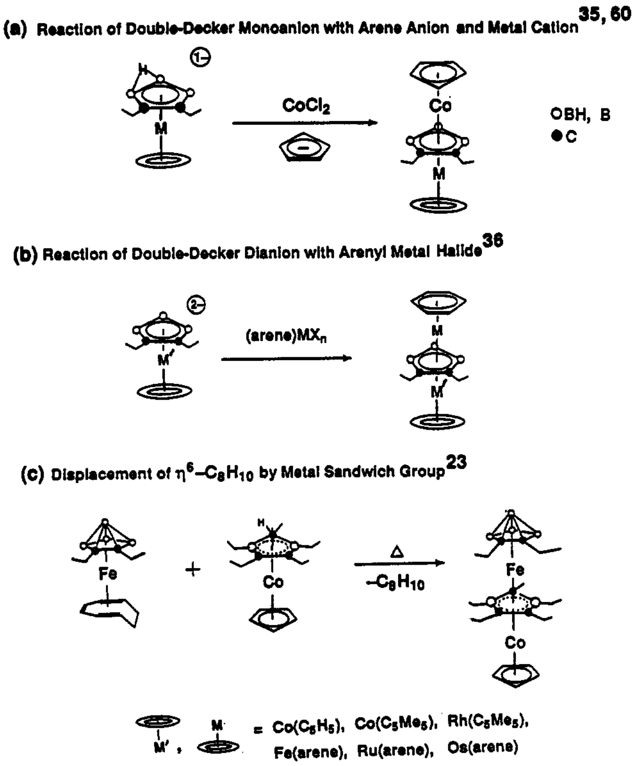


Figure 17. Methods for synthesis of carborane-containing triple-decker complexes.

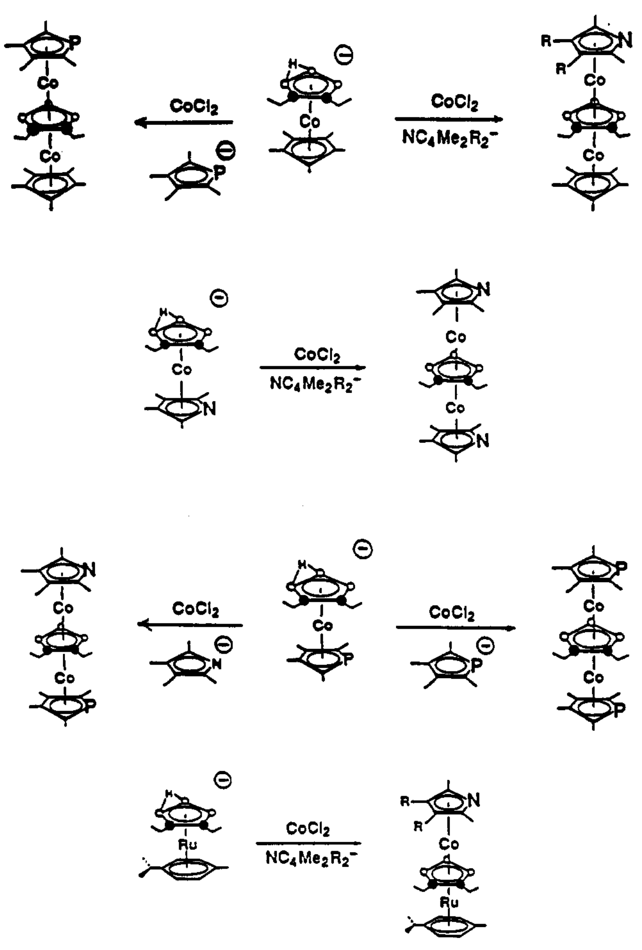


Figure 18. Synthesis of pyrrolyl- and phospholyl-capped triple-decker carborane sandwiches.[61]

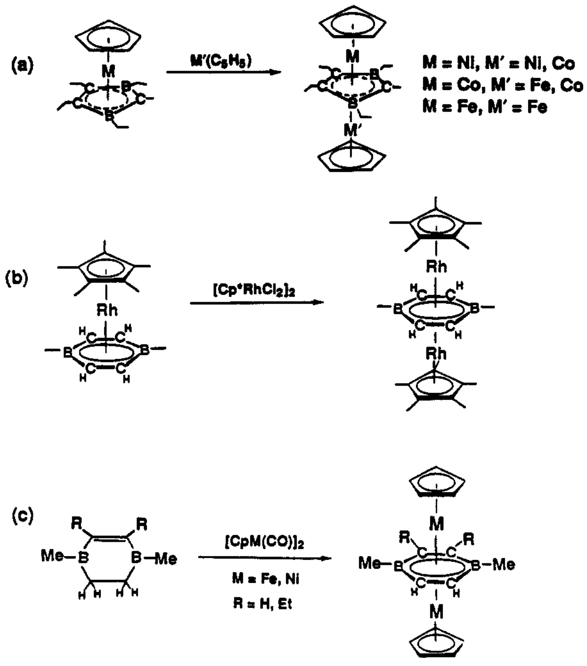


Figure 19. (a) A route to diborolenyl-bridged triple-decker sandwiches[6,62–66] and (b) and (c) syntheses of 1,4-diborabenzene-bridged triple-deckers.[67,68]

The synthetic methods outlined above have been extended to heterocyclic ligands, producing pyrrolyl- and phospholyl-capped carborane-bridged species such as those presented in Figure 18.[61] All of the products shown have been isolated as colored crystalline solids, and several have been characterized by X-ray diffraction.

Organoborane-based triple-decked complexes are prepared similarly,[6,62–68] as illustrated by the examples in Figure 19. Reactions a and b, as in the corresponding metal–carborane systems, proceed via coordination of a second metal to a double-decker species, but in c the bimetallic species is obtained directly from the 1,4-dibora-2-cyclohexene precursor. As mentioned

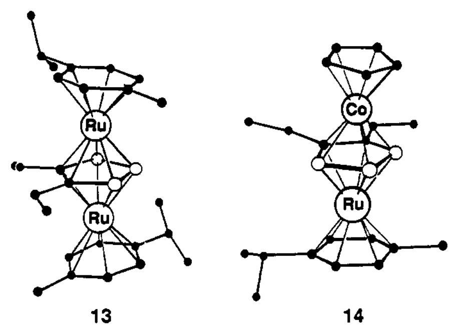


Figure 20. Molecular structures[36] of CyRu($Et_2C_2B_3H_3$)RuCy (**13**) and CyRu($Et_2C_2B_3H_3$)CoCp (**14**). (Cy = cymene [*p*-isopropyltoluene]).

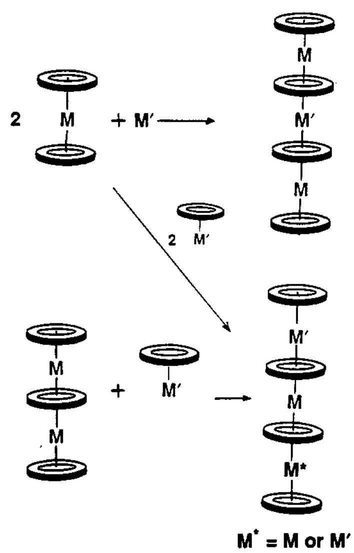


Figure 21. Approaches to multidecker synthesis from small sandwich units.

earlier, hybrid sandwiches comprised of both organoboron (C_3B_2) and carborane ligands have also been prepared by rational routes[18,23-25] and structurally characterized; an example is the iron–cobalt complex shown in Figure 17c. Tetradecker hybrid systems are discussed below.

The triple-decker sandwich geometry is well established from X-ray crystallographic studies of numerous complexes, of which those depicted in Figure 20 are typical.[36] In the C_2B_3-bridged species, the three rings are seldom parallel; tilts of 3 to 5 deg between the end ligand and central ring planes are normal and are ascribed to slight inequivalence between the metal–carbon and metal–boron binding in the heterocyclic carborane ring. When the bridging ligand is more symmetrical, as in complexes of 1,4-diborabenzene (Figure 19c), the end rings are nearly parallel with the central ring plane.[68]

The construction of higher-decker systems has been approached in two ways, i.e., by coordination of two small complexes to a central metal atom, and by stepwise addition of metal–ligand units to the end rings of an existing stack (Figure 21). Both methods have been employed by Siebert, Wadepohl, and co-workers, who prepared the first tetradeckers[6,66] as well as the only currently known pentadecker,[69] hexadecker,[70] and polydecker[71] sandwiches, all of which employ diborolenyl or thiadiborolenyl ligands (Figure 22). The polydecker nickel system **19** is an electrical semiconductor.

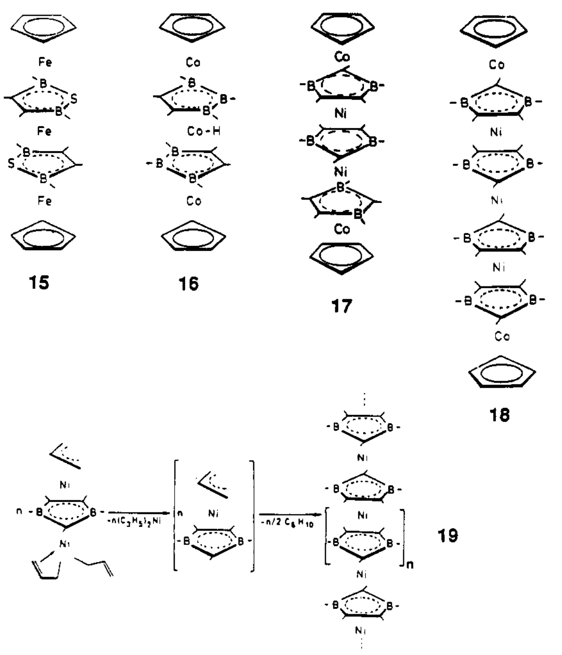


Figure 22. Examples of tetradecker, pentadecker, hexadecker, and polydecker diborolenyl-bridged complexes.[6,68-70]

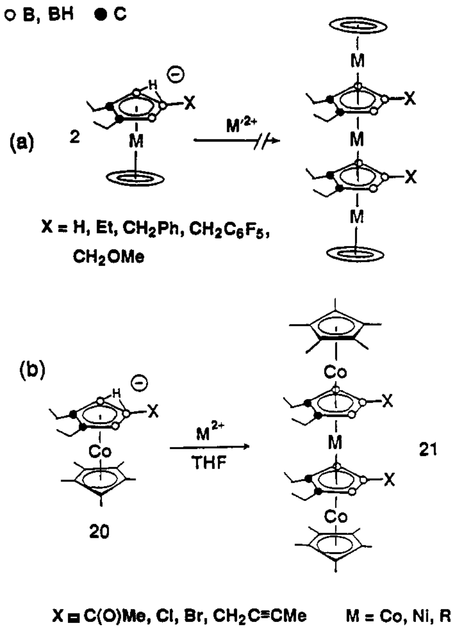


Figure 23. Synthesis of carborane-bridged tetradecker complexes: (a) unsuccessful and (b) successful.[72,73]

Carborane-bridged tetradecker (and larger) sandwiches were unknown until recently, as attempts in the author's group to stack two double-deckers around a third metal ion were unsuccessful (Figure 23a). However, we have found that this approach can be made to work with Cp*Co($Et_2C_2B_3H_3$)-5-X^- complexes (**20**) provided the electron density of the C_2B_3 ring is adjusted via choice of the X substituent.[72] Empirical observations show that when the electron donor/acceptor properties of X are such that the ^1H NMR chemical shift of the B–H–B proton in **20** is downfield of (less negative than) δ −5.25, tetradecker formation occurs as in Figure 23b. When the shift is more negative than δ −5.25 (as when X is H or Et, for example), no tetradecker is obtained. Electronic "fine tuning" in this manner has allowed the synthesis of a series of

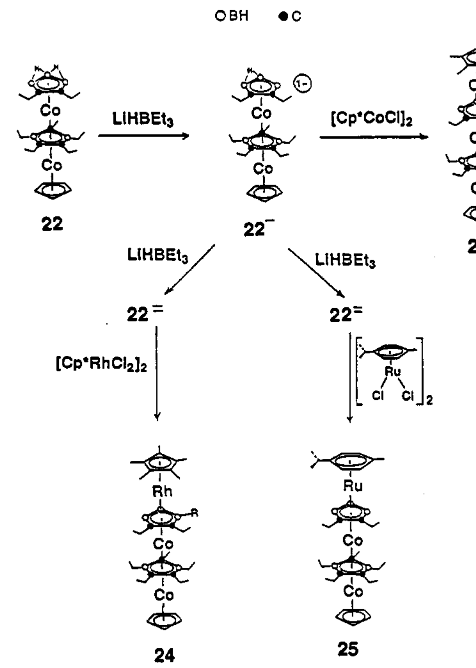


Figure 24. Synthesis of hybrid tetradecker complexes containing carborane and diborolenyl ring ligands.[25] The structure of 24 is established from X-ray diffraction[25] (see also Figure 35).

C_2B_3-bridged tetradeckers, as shown.[72,73]

Hybrid tetradecker complexes containing both C_2B_3 and C_3B_2 rings have been prepared as well (Figure 24).[25]

B. Assembly of Multilevel Polyarene-Bridged Complexes

Our group has been actively investigating the concept of linking stable sandwich modules via organic groups that could permit electronic communication between the metal centers. In the arrangement depicted in Figure 16b, the end metal atoms in different stacks are connected via polycyclic aromatic hydrocarbons. This approach has led to the synthesis of the first examples of linked multidecker sandwich complexes (Figure 25).[74,29] As shown, the characterized products utilize fulvalene $[(C_5H_4)_2]$ (28) and bis(tetramethylcyclopentadienyl)polyphenylene $[(Me_4C_5)_2(C_6H_4)_x, x = 1, 2]$ linking groups (26, 27). The structure of 26 has been crystallographically established (Figure 26).[74] A related class of complexes (e.g., 29 and 30, Figure 25) has been derived from benzyltetramethylcyclopentadiene.[29] Extension of this structural principle to larger oligomers and polymers is certainly possible, and approaches of the kind outlined in Figure 27 are being explored at this writing.[75] We have been able to isolate and structurally characterize oligomeric species such as 31, depicted in Figure 28, in which a tetradecker unit is linked to two double-deckers via phenylene rings. Complexes of this class have, in turn, been used as modules for constructing larger oligomers, in which two or more 31-type units are coordinated via additional metal atoms.[76]

C. Linkage via Carborane or Organoborane Boron Atoms

The method described in section III.D.1 for attachment of organic substituents to boron locations on *nido*-metallacarborane complexes can be used to link such units (Figure 16c) via reactions with bifunctional organic reagents, as illustrated in Figure 29.[29,77] When the bridging group contains aromatic rings, these can be metallated via the cyclooctatriene–ferracarborane displacement reaction (section III.A) to give species such as 35.

Very recently Herberich and co-workers have prepared the bis(borolenyl)nickel dimer 37 shown in Figure 30 and confirmed the structure via X-ray diffraction.[78] As indicated, an unspecified polymeric product is also produced.

D. Linkage via Carborane Carbon Atoms

Metal–carborane sandwich units can also be chained together via the ring carbon atoms, as depicted in Figure 16d. One way of accomplishing this is to prepare linked *nido*-carboranes of the type $(RC_2B_4H_4)$–$(CH_2)_n$–$(C_2B_4H_4)$–$(CH_2)_n$–$(RC_2B_4H_4)$ by reaction of polyalkynes with B_5H_9,[26] and subsequently metallate the C_2B_4 cages. A more generally useful approach, however, exploits the recent synthesis of *nido*-Cp*Co($C_2B_4H_6$) complexes whose cage C–H protons are displaceable on attack by alkyl halides (Figure 14).[56] As expected, we have found that alkyl dihalides readily attach to two cobaltacarborane moieties, connecting them through the cage carbon positions. Since a variety of organic substituents can be introduced at both boron and carbon locations in these complexes, additional modes of linkage, such as via condensation and polymerization reactions of appropriately functionalized derivatives, now appear feasible.

V. Physical and Chemical Properties and Trends

A. Chemical and Thermal Stability

A distinguishing characteristic of most carborane- and organoborane-based metal complexes is their high resistance to oxidative and thermal degradation, which allows them to survive a wide range of conditions and makes them attractive as synthetic building blocks. In the majority of cases these compounds are isolated as colored crystalline solids which are soluble in both polar and nonpolar organic solvents. The thermal stability of the carborane multideckers is illustrated by the dicobalt complex CpCo(2,3-$C_2B_3H_5$)CoCp (Figure 4), which undergoes rearrangements through several intermediates between 200 and 300 °C, finally producing the 2,4 isomer in which the carborane carbon atoms are separated; the latter product is stable to 400 °C![79]

The remarkably low reactivity of LM(RR′$C_2B_4H_4$) metal complexes toward O_2 is typified by the η^8-cyclooctatetraene sandwich complexes $(C_8H_8)M(Et_2C_2B_4H_4)$ in which M is Ti or V, and the chromium–tropylium species $(C_7H_7)Cr(Et_2C_2B_4H_4)$, all structurally characterized.[80] The titanium and vanadium compounds are rare (perhaps the only) examples of air-stable complexes in which first-row transition-metal atoms are η^8-coordinated to planar C_8 rings. Most LMC_2B_4 metallacarborane clusters do, however, undergo controlled degradation to *nido*-LMC_2B_3 species in the presence of Lewis bases, via the "decapitation" reaction discussed in section III.B. Significantly, and fortunately for synthetic purposes, only one boron is extracted and the remaining MC_2B_3 unit remains intact. The general stability of these metallaboron clusters is a major factor

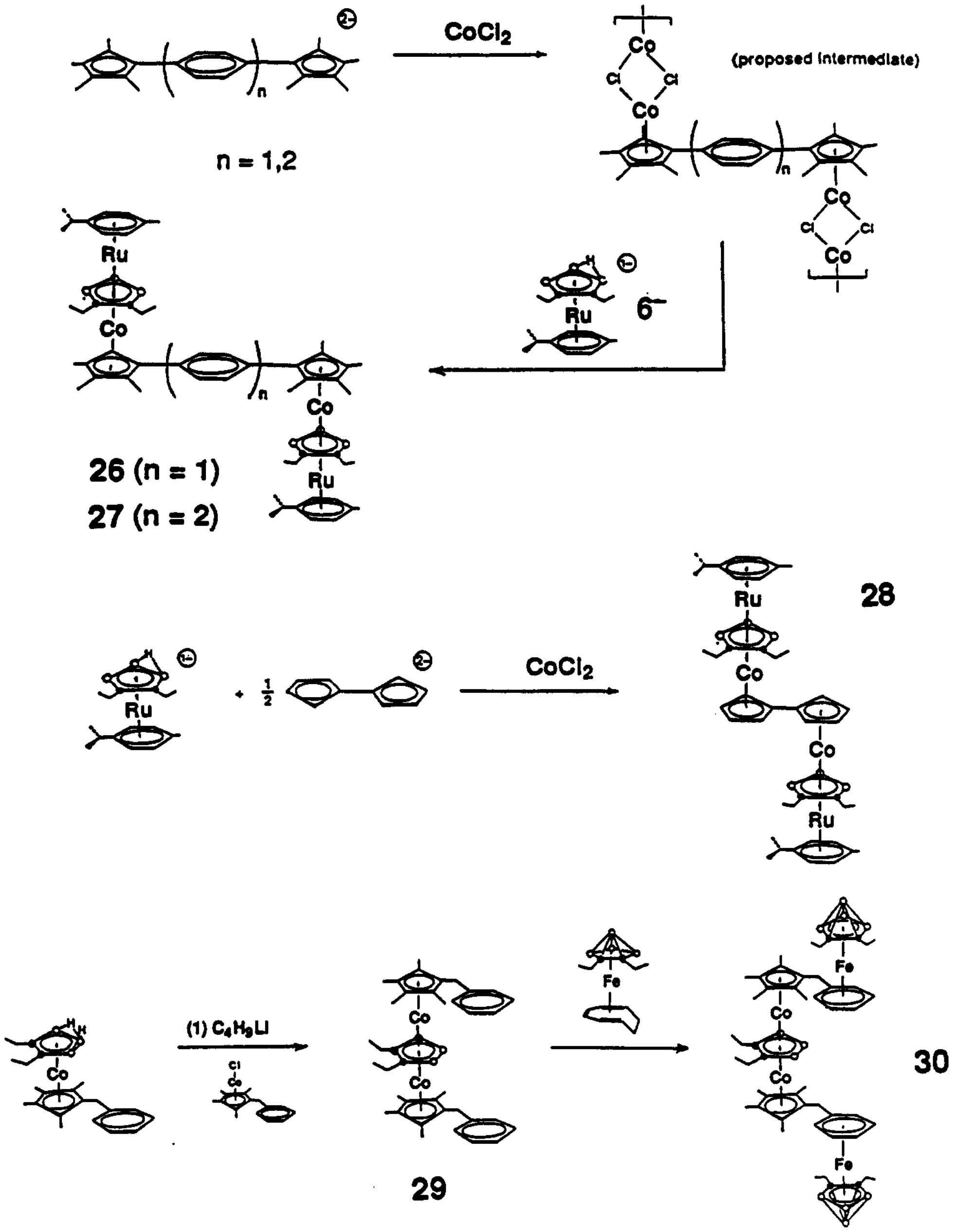


Figure 25. Synthesis of cyclic hydrocarbon-linked multidecker complexes.[74,29]

in their utility as synthons for larger systems as described above. The robust character of this class of complexes stands in contrast to the sensitivity of many transition-metal organometallics to air, heat, or moisture.

B. Electrochemical Properties

The resistance of metal–boron sandwiches to degradation carries over to their electrochemical behavior. Typically, transition metals in these species can be reversibly oxidized and/or reduced, often through several formal oxidation states, as illustrated in Figure 31 for the triple-deckers 38–40. That it is the metal centers, and not the ligands, that undergo the redox processes is clear from optical and ESR spectroscopy, as discussed below. As can be seen, the neutral diamagnetic species are readily converted to paramagnetic cations and anions, which in some cases have been studied in detail. The cyclic voltammograms for the dicobalt system 39,[24] presented in Figure 32, are representative of data obtained for such complexes. Similar observations, i.e., multiple reductions and oxidations generating stable anionic and/or cationic species, have been reported in multidecker borolenyl-, diborolenyl-, and diborabenzene-bridged compounds.[62,63,67,82,83]

In recent collaborative work of our group and that of W. E. Geiger, the diruthenium and cobalt–ruthenium triple-decker complexes 13 and 14 (Figure 20) have been reversibly oxidized electrochemically to give paramagnetic monocations. ESR and optical spectroscopy on these ions reveal them to be Class III mixed-valence systems having *complete electron delocalization between the metal centers*, which are consequently in a formal 5/2 oxidation state.[84] A bimetallic ferracarborane system exhibiting similar delocalization is the biphenyl-linked complex 41 shown in Figure 33,[85] which undergoes two reversible one-electron oxidations at $E°$ = +0.55 and +0.84 V vs ferrocene; the 290-mV separation of these values is slightly less than that reported

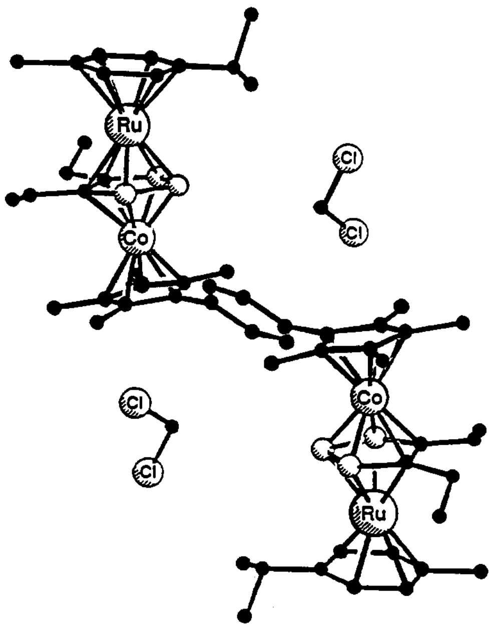


Figure 26. Crystal structure of $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Co}(\eta^5\text{-Me}_4\text{C}_5)]_2(\text{C}_6\text{H}_4)$ (**26**).[74]

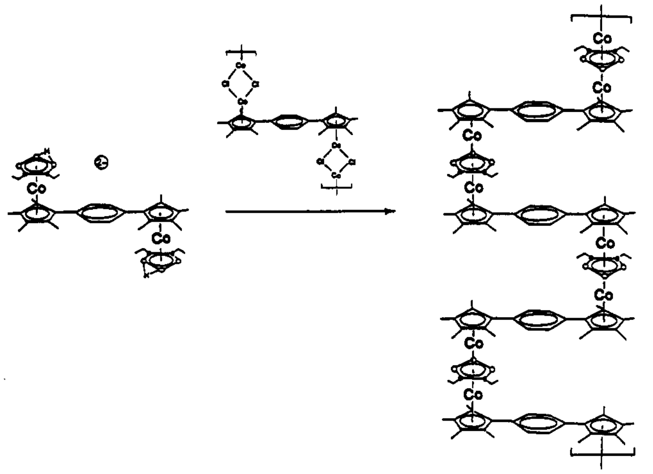


Figure 27. A synthetic route to a cobaltacarborane polymer.[75]

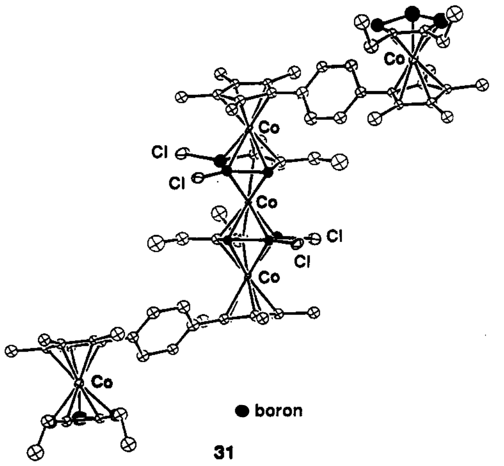


Figure 28. Molecular structure of a pentametallic linked sandwich complex.[76]

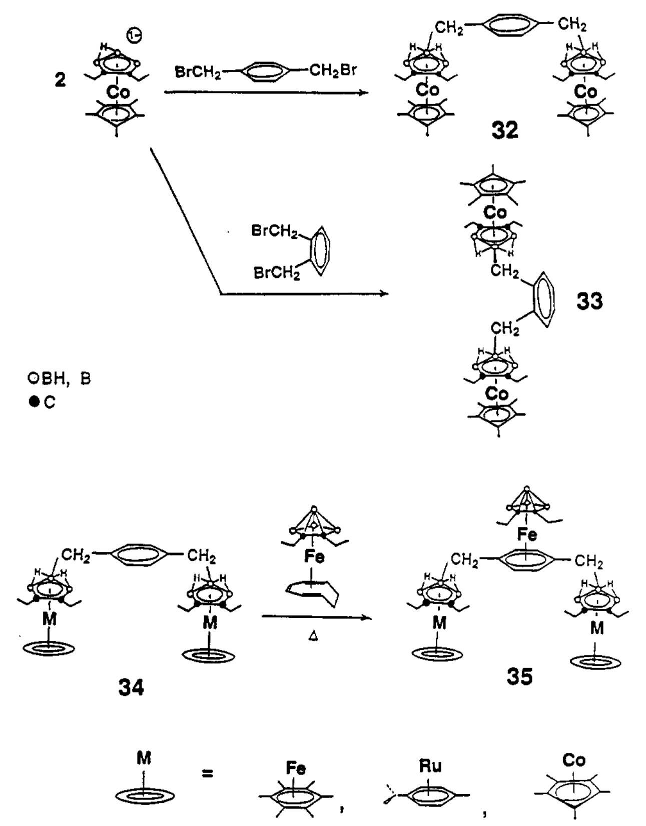


Figure 29. Synthesis of polymetallic complexes linked via boron-attached substituents.[77]

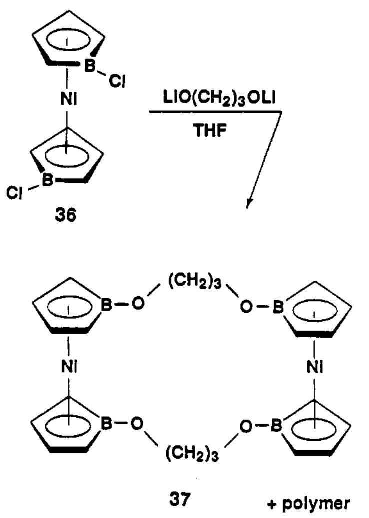


Figure 30. Synthesis of a linked bis(borolenyl)nickel sandwich dimer.[78]

for the successive oxidations of biferrocene[86] and indicates that the iron centers in 41 are, in fact, communicating. These findings offer some encouragement for the idea that polymers constructed from multidecker stacked and/or linked systems of the kind described in this review may, with proper choice of organic linking groups, exhibit high electron delocalization and hence low-dimensional conductivity.

The extraordinary ability of the *nido*-$\text{RR}'\text{C}_2\text{B}_4\text{H}_4{}^{2-}$ carborane ligand to stabilize organometallic complexes, discussed above, is highlighted in mixed-ligand species of the type $(\text{arene})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ (**8**, Figure 7a). The formal Fe(II) in these complexes is readily oxidized, chemically or electrochemically, generating *stable* $(\text{arene})\text{Fe}^{\text{III}}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)^+$ cations, as established in a recent electrochemical study of a series of such complexes.[85,87] These species represent, with just one exception,[88] the first examples of stable Fe(III)–arene sandwich com-

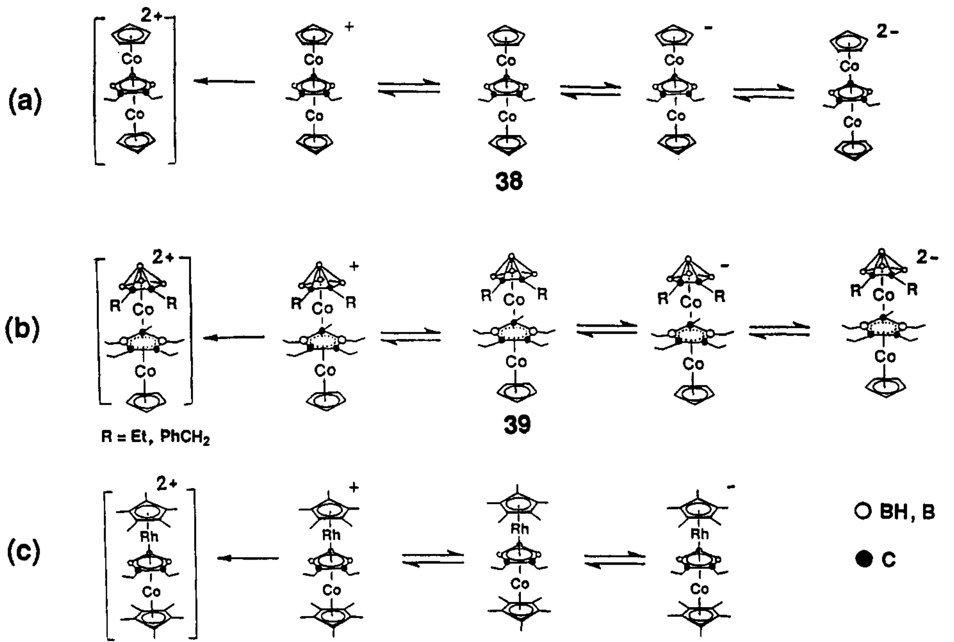


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Figure 31. Electrochemical interconversions of triple-decker complexes (species in brackets are irreversibly generated): (a) $Cp_2Co_2(Et_2C_2B_3H_3)$,[81] (b) $(R_2C_2B_4H_4)Co(Et_2MeC_3B_2Et_2)CoCp^*$,[24] and (c) $Cp^*Rh(Et_2C_2B_3H_3)CoCp^*$.[24]

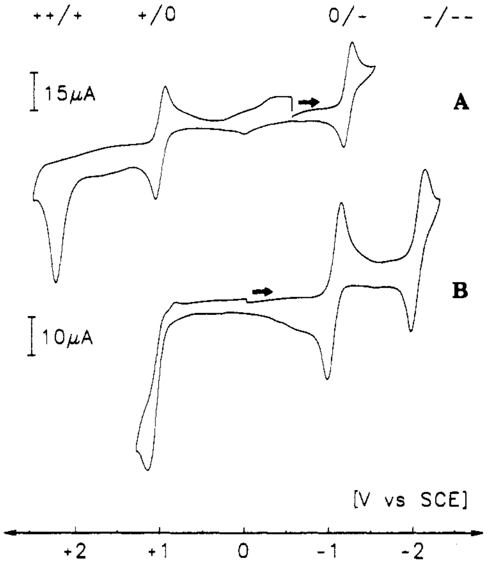

Figure 32. Cyclic voltammograms of **39** ($R = PhCH_2$) at Pt electrodes vs SCE at 20 °C ($\upsilon = 0.1\ V\ s^{-1}$): (A) in 0.1 M Bu_4NPF_6/CH_2Cl_2 and (B) in 0.1 M Bu_4NPF_6/DME.[24]

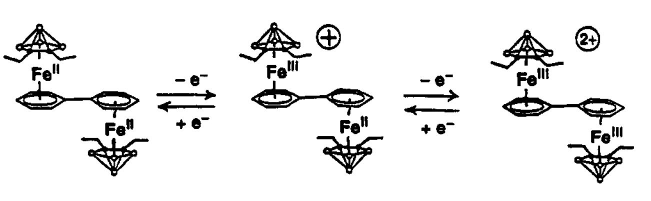

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Figure 33. Electrochemical interconversions of a bis(ferracarborane)biphenyl complex.[85]

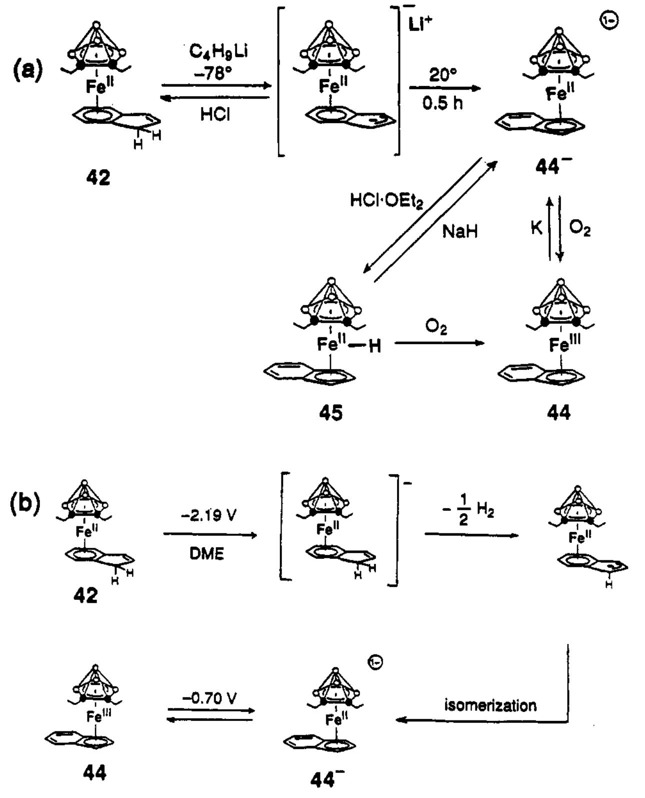

Figure 34. Chemical (a) and electrochemical (b) redox processes in indenylferracarborane complexes.[18]

plexes. The corresponding $(arene)Ru(Et_2C_2B_4H_4)$ sandwiches have similarly been found to undergo reversible electrochemical oxidation to the Ru(III) species.[85,87]

The indenylferracarborane **42**[18] provides a particularly interesting example of new chemistry which is opened up by carborane ligand stabilization. As diagrammed in Figure 34a, orange, air-stable **42** upon chemical reduction undergoes a haptotropic shift of Fe from the C_6 to the C_5 ring, and the anion **44**⁻ can be reversibly oxidized to the magenta paramagnetic **45**. These transformations are paralleled in the electrochemistry of this family of complexes,[18] a portion of which is depicted in Figure 34b.

Electrochemistry is similarly important in the physical characterization of multidecker and linked-sandwich systems such as the mixed-ligand tetradecker

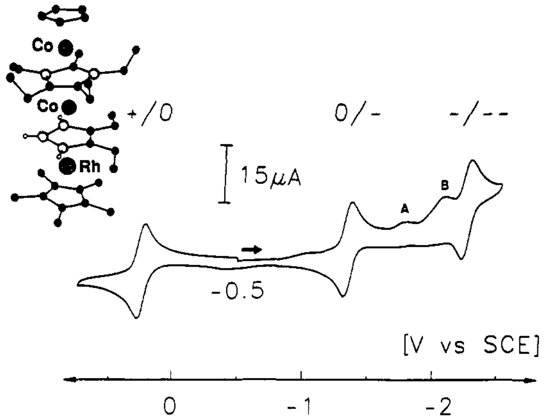

Figure 35. Cyclic voltammogram for **24** (R = H) at GC electrodes vs SCE at 20 °C in 0.1 M Bu_4NPF_6/DME, scan rate 0.1 V s^{-1}. Peaks A and B are due to impurities in the sample.[25]

complexes **23**–**25** (Figure 24) which exhibit reversible one- and two-electron reductions and one-electron oxidations. Figure 35 depicts the cyclic voltammogram of **24** (R = H).[25] Currently, probes of the electron transport and related properties of linked-sandwich systems, such as **31** (Figure 28) and its higher oligomers, are under investigation via cyclic voltammetry and controlled potential electrolysis.[89]

C. ESR Studies

The ease with which metal–organoborane and metal–carborane sandwich complexes can be reversibly oxidized and reduced gives access to many paramagnetic species incorporating C_3B_2 or C_2B_3 bridging rings, a number of which have been studied by ESR spectroscopy.[18,23,24,62,63,83,84] For several reasons, including rapid relaxation effects in solution,[62] definitive ESR information on some of these compounds has been difficult to obtain, but data on a variety of species have been reported. One of the clearer examples is provided by the cobalt–nickel diborolenyl comples **46**, whose radical anion and cation gave the spectra shown in Figure 36. Although the rhombic **g** tensor is observed, only very small cobalt hyperfine splitting is detected.[62]

A system in which ESR spectroscopy has given detailed information on redox processes is the paramagnetic hybrid triple-decker complex $[(PhCH_2)_2C_2B_4H_4]Fe(Et_2MeC_3B_2Et_2)CoCp$ (**47**), which can be reversibly reduced, via chemical or electrochemical methods, to give a diamagnetic monoanion and a paramagnetic dianion (the *C,C′*-diethylcarborane analogue exhibits virtually identical behavior).[23] The ESR spectrum of the neutral complex (Figure 37, top) shows no cobalt hyperfine structure, but that of the dianion clearly reveals such splitting. This indicates that the unpaired electron in the neutral species is *localized in the vicinity of the iron atom while that in the dianion is associated with the cobalt*, supporting the assignment of oxidation states in the bottom diagram.

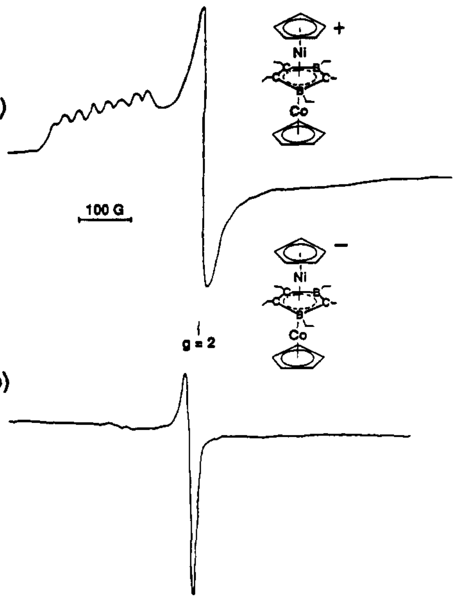

Figure 36. ESR spectra of the cation (obtained electrolytically) and anion (obtained via Na/K reduction) of $CpCo(Et_2MeC_3B_2Et_2)NiCp$ (**46**) at 77 K in THF.[62]

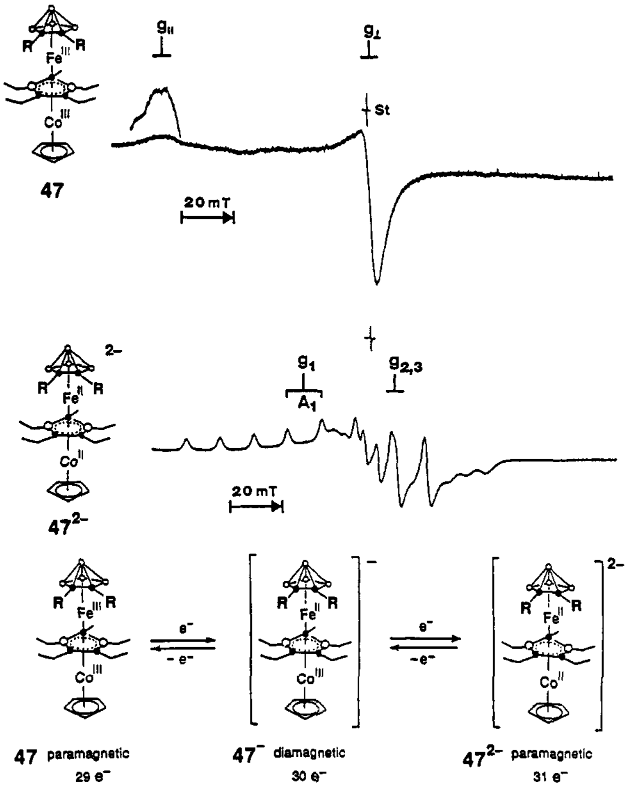

Figure 37. X-band ESR spectra in THF glass at −160 °C of **47** and 47^{2-} (obtained via reduction on a potassium mirror). (R = $PhCH_2$, St = Li(TCNQ), *g* = 2.0025.)

At this writing, only limited data are available on higher-decker stacks. The tricobalt tetradecker complex **21**, M = Co, X = Cl (Figure 23) is a paramagnetic species (formally a Co^{III}–Co^{IV}–Co^{III} system) whose low-temperature ESR spectrum is consistent with the presence of one unpaired electron, but shows no detectable cobalt hyperfine splitting.[89] This can be taken as evidence, albeit not conclusive, that the odd electron is delocalized over the three metal centers so that each cobalt assumes an oxidation state of 10/3; such behavior would be consistent with the observation of electron delocalization in dicobalt and cobalt–ruthenium triple-decker sandwiches discussed above.

X-band ESR spectra[90] of the nickel–diborolenyl polymer **19** (Figure 22) in the temperature range of 2–290 K display a broad signal (**g** = 2.25) at room temperature. An additional sharp band (**g** = 2.10) appearing below 50 K has been assigned to Ni^{2+}. These data, together with magnetic, NMR, electron micrography, and EXAFS investigations and measurements of electrical conductivity, have allowed a detailed characterization of this material as a Peirls distorted polydecker structure whose conductivity with no doping is in the range of highly doped polyacetylene.[90]

VI. Current and Future Directions: The Versatile Role of Boron

Clearly, the tools are now in hand to enable the planned synthesis of a variety of new types of extended organometallic structures stabilized by boron-containing rings, in a wide range of metal–ligand combinations. The synthetic approaches outlined in this review draw on the techniques and insights of boron, organic, and transition-metal chemistry, a powerful troika which has considerable potential for creating entirely new families of materials. The advantages in synthesis are formidable: one can design and construct stable multimetallic stacked and linked-sandwich systems with designated metals and ligands, attach desired organic functional groups to specific framework locations, and conduct organic transformations on these substituents, and chemically or electrochemically alter the oxidation states of metal centers.

Since these compounds (particularly the paramagnetic species) have an inherent tendency toward electron delocalization as a consequence of their nonclassical covalent bonding, it is natural to think in terms of creating electronically or magnetically novel materials, especially ones that can be chemically tailored to have specified combinations of properties. Among the possibilities that come to mind are polymers that can function alternately as electrical insulators, semiconductors, or conductors depending on the chemical or magnetic environment. Another line of speculation centers on the use of boron-containing multidecker sandwiches as precursors to electrically conducting ceramics, which could be generated by controlled partial degradation at high temperature; as the organic ligands are driven off, the remaining metal–carborane/organoborane cluster units might consolidate into extended solid-state networks. The operative word is "controlled", in that the end products of such treatments would likely bear a structural resemblance to their molecular precursors; in most ceramic syntheses, of course, this is not the case and there is effectively no control over the atomic arrangement in the product. If this concept can be made to work in the laboratory, it may provide an entry to an entirely new class of metal–boron–carbon solid-state materials.

Along with the continuing development of synthetic methods in this area, much remains to be learned about the electronic structures and behavior in these extended multimetal systems. We know that the attachment of substituents to carborane ligands, for example, can profoundly influence the metal coordination properties of building-block species such as $CpCo(RR'C_2B_3H_5)$ (vide supra), but we know very little about the nature of this effect. Much chemistry remains to be done, and also much physics, materials science, and engineering: there is no doubt that future progress in this area, including bringing to reality the kinds of new materials we have speculated about, will require intensive interdisciplinary efforts.

A serious limitation on the further development of this field has been the fact that the boron-containing ligands and ligand precursors are not available commercially, and their syntheses require expertise in the handling of volatile boranes or boron halides. Hence this chemistry has been limited to the relatively few laboratories equipped for such work. However, the recent discovery[10] of a high-yield route to $R_2C_2B_4H_6$ *nido*-carboranes which circumvents the use of gaseous pentaborane, described in section II.A, is a major step forward. Further breakthroughs in synthesis may eliminate entirely the need for B_5H_9 handling; indeed, a one-pot preparation of $Me_2C_2B_4H_6$ from $Et_4N^+B_3H_8^-$ (a benign salt easily obtained from $NaBH_4$) was reported by us several years ago.[91] Even better would be a method for directly generating *nido*-metallacarboranes of the $LM(R_2C_2B_3H_5)$ class from monoboron compounds. An indication that this may be possible is the recent preparation[92] of several metallaboron clusters having 4–10 boron atoms from the common laboratory reagent $THF{\cdot}BH_3$.

Boron-stabilized organometallic chemistry has reached a level of sophistication allowing true designed synthesis, where, as in organic chemistry, one can now build complex structures of preconceived architecture using known synthetic techniques. Consequently, the question now is shifting from "how to build" to "what to build", i.e., to determine which types of multimetal systems are most deserving of detailed study of their electronic properties and their promise for practical exploitation. Input from many branches of science and technology will be crucial in dealing intelligently with this challenge.

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