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REVIEW

Metal–Carborane Multidecker Sandwich Complexes as Building Blocks for New Materials

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Transition-metal sandwich complexes incorporating bifacially coordinated C_2B_3 planar carborane rings form a large and varied family of generally air-stable, highly robust compounds that feature multidecker stacking. As a group, these complexes offer a number of advantages that are potentially of interest in the development of new electronic, magnetic and/or optical materials. They are remarkably versatile, accommodating a wide range of metals and organic substituents; they are soluble in organic solvents and are typically resistant to air and moisture; they can be reversibly oxidized and reduced; in many cases they are paramagnetic, exhibiting substantial electron delocalization of the unpaired electrons between metal centers. Moreover, the small carborane starting materials can now be prepared in large (*ca* 100 g) quantities, making the complexes readily accessible. A brief overview of this area is presented with emphasis on the systematic utilization of metallacarborane sandwich complexes in the construction of large multimetallic systems and studies of their electronic and molecular structures.

Keywords: metal-carborane complexes; sandwich complexes; transition-metal complexes; metallacarboranes; multidecker complexes

INTRODUCTION

A prominent theme in current organometallic synthesis is the targeting of research toward specific goals, including the development of new types of 'smart' materials that will be required for the complex technologies of the 21st century.[1] Until very recently, breakthroughs in the development of new materials were typically achieved through serendipitous discovery or repetitive trial-and-error efforts; however, it is increasingly clear that more systematic and controlled approaches to synthesis are required. As many authors have observed recently, the demands of new technologies for materials having specified electronic, magnetic, optical or other, properties, and especially *combinations* of properties, make the traditional 'heat, beat and hope' strategy[1b] obsolete. An idea that is rapidly gathering momentum is the application of molecular science, i.e. chemistry, to the design and synthesis of materials in which one has some control over the composition and structure at the atomic/molecular level, and hence the physical characteristics, of the product. This approach has the powerful advantage of drawing on many decades of research in molecular synthesis, particularly in organic chemistry but more recently in inorganic as well. Not only does it permit the design and construction of large molecular assemblies in a controlled manner, but it also allows modification via straightforward synthetic techniques.

In order to be useful for such purposes, molecular compounds that are air-stable, soluble in common solvents, and generally robust are required; in addition, it is highly desirable that they may be capable of systematic modification so that their properties can be adjusted as needed. A class of organometallics that fits this prescription to a remarkable degree is the metallacarboranes or metal–carborane sandwich complexes,[2] which form an extraordinarily diverse field that began more than 30 years ago with the original investigations of Hawthorne *et al.* on the larger cage systems.[3] Work in our laboratory has led to the carborane-bridged multidecker sandwich complexes such as those shown in Fig. 1, which are particularly well-suited as building-block units for constructing large multimetallic arrays. Compounds of this class incorporate small planar or pyramidal carborane ligands of the types shown in Fig. 2 or their substituted derivatives, all of which utilize six π-electrons in binding to

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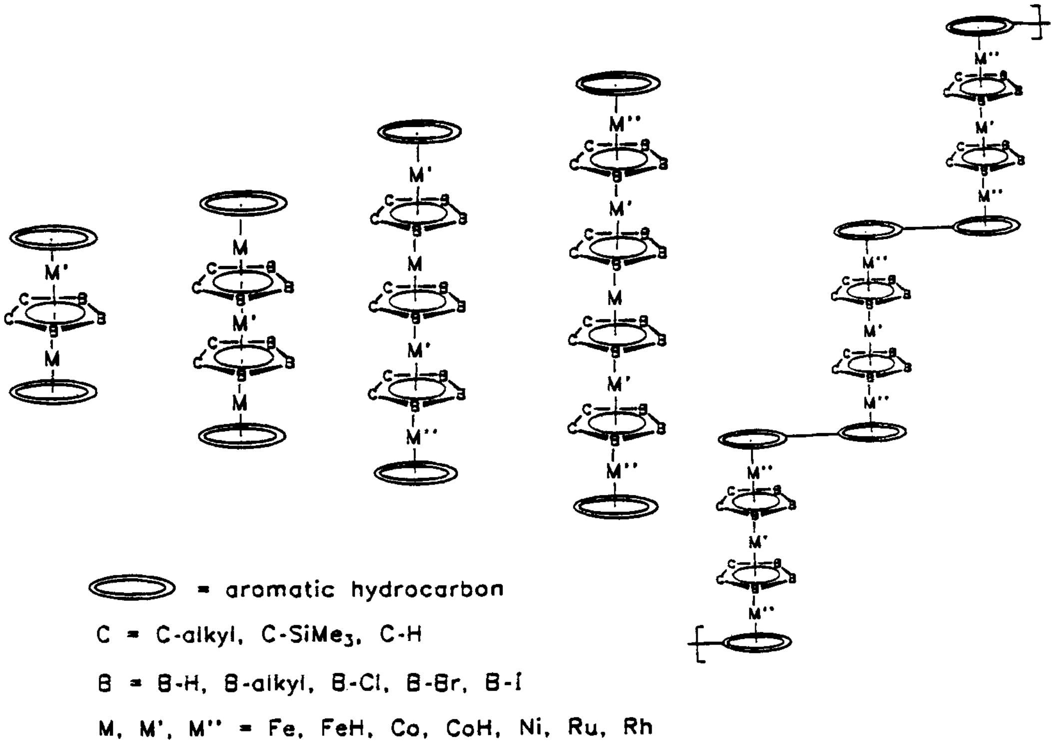


Figure 1 Examples of known and characterized carborane-bridged multidecker sandwich complexes.

metals and hence are electronic analogs of $C_5H_5^-$ and C_6H_6.

In general, the carborane ligands coordinate to metals much more tightly, and with greater versatility, than do hydrocarbon rings. The higher negative charge on the carborane units helps to stabilize high metal oxidation states [e.g., cobalt(III), cobalt(IV), nickel(IV)] and the lower electronegativity of boron in comparison with carbon tends to promote electron sharing (covalence) in metal–ligand binding.

In contrast to most neutral bis(cyclopentadienyl) and bis(arene) transition-metal sandwiches (ferrocene being the major exception), metallacarborane sandwich complexes are typically air-stable, survive a wide range of conditions, and undergo reversible oxidation and reduction at the metal centers. In addition to their exceptional stability and tailorability, many of these compounds exhibit other qualities, such as electron delocalization and paramagnetism, that are of interest from a materials perspective.[4]

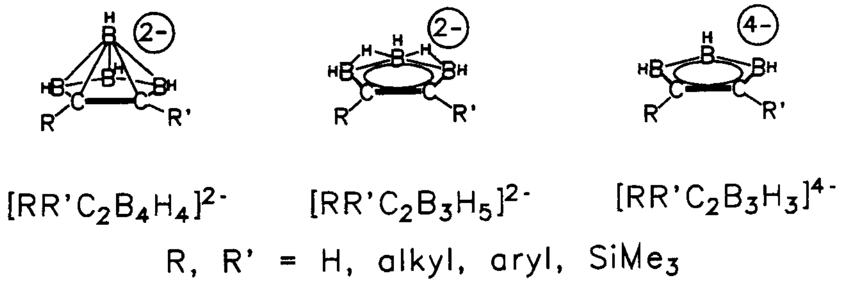
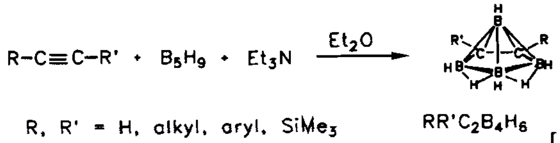


Figure 2 Small carborane ligands. Lines indicate connectivities, not electron bond pairs; these are electron-delocalized (nonclassical) species, analogous to $C_5H_5^-$, whose electronic structures are best described in molecular orbital (MO) terms. Of the ligands shown, only $RR'C_2B_4H_4^{2-}$ exists as a free species in solution; the others are known only in metal sandwich complexes.

Moreover, many of them are now accessible on a multigram scale—an important consideration in this context. This short review describes a program that has been under way in our laboratory in recent years, centered on the systematic exploitation of small metallacarboranes as synthons, or building blocks, for the construction of new materials that we believe are capable of being engineered to have desired combinations of electronic, magnetic and/or optical properties. This work is grounded in small-molecule research but increasingly emphasizes the assembly of larger systems, with recent characterization of soluble multisandwich species with molecular weights of several thousand daltons. In this paper the preparation of small metallacarborane synthon compounds, their modification via introduction of organic or inorganic substituent groups, their use in the construction of larger systems including multidecker sandwiches and linked-sandwich assemblies, and their relevant electronic and other physical properties are described, concluding with a discussion of future directions and possible aplications.

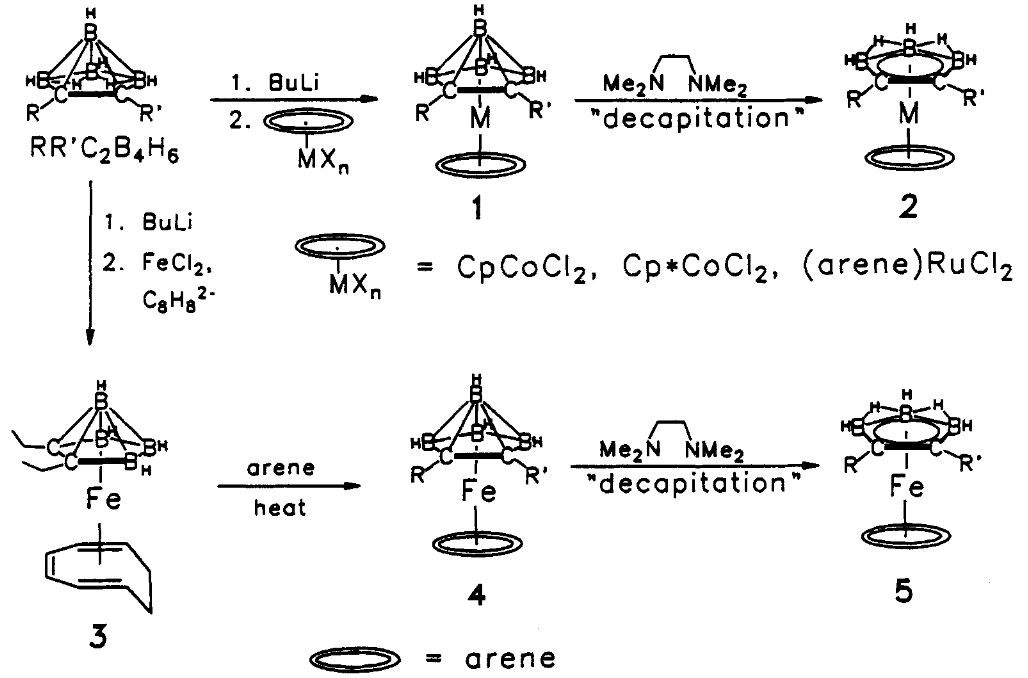
SYNTHESIS OF SMALL CARBORANES AND METALLACARBORANES

The starting point for this chemistry is the preparation of $RR'C_2B_4H_6$ *nido*-carboranes (where *nido* designates an open-cage structure) from B_5H_9 and alkynes, as shown in Eqn [1]. Our earlier synthetic procedure[5] has recently been modified[6] to permit the synthesis of up to 100 g of pure $Et_2C_2B_4H_6$ under mild conditions, using 3-hexyne and B_5H_9 drawn from the large (*ca* 100 000 kg) US Government stockpile of that borane. Other carborane derivatives, such as $(SiMe_3)_2C_2B_4H_6$,[7] can be similarly obtained by employing commercially available or readily prepared alkynes.



[1]

The neutral carboranes are bridge-



Scheme 1 Synthesis of $LM(RR'C_2B_4H_4)$ and *nido*-$LM(RR'C_2B_3H_5)$ metal sandwich complexes.

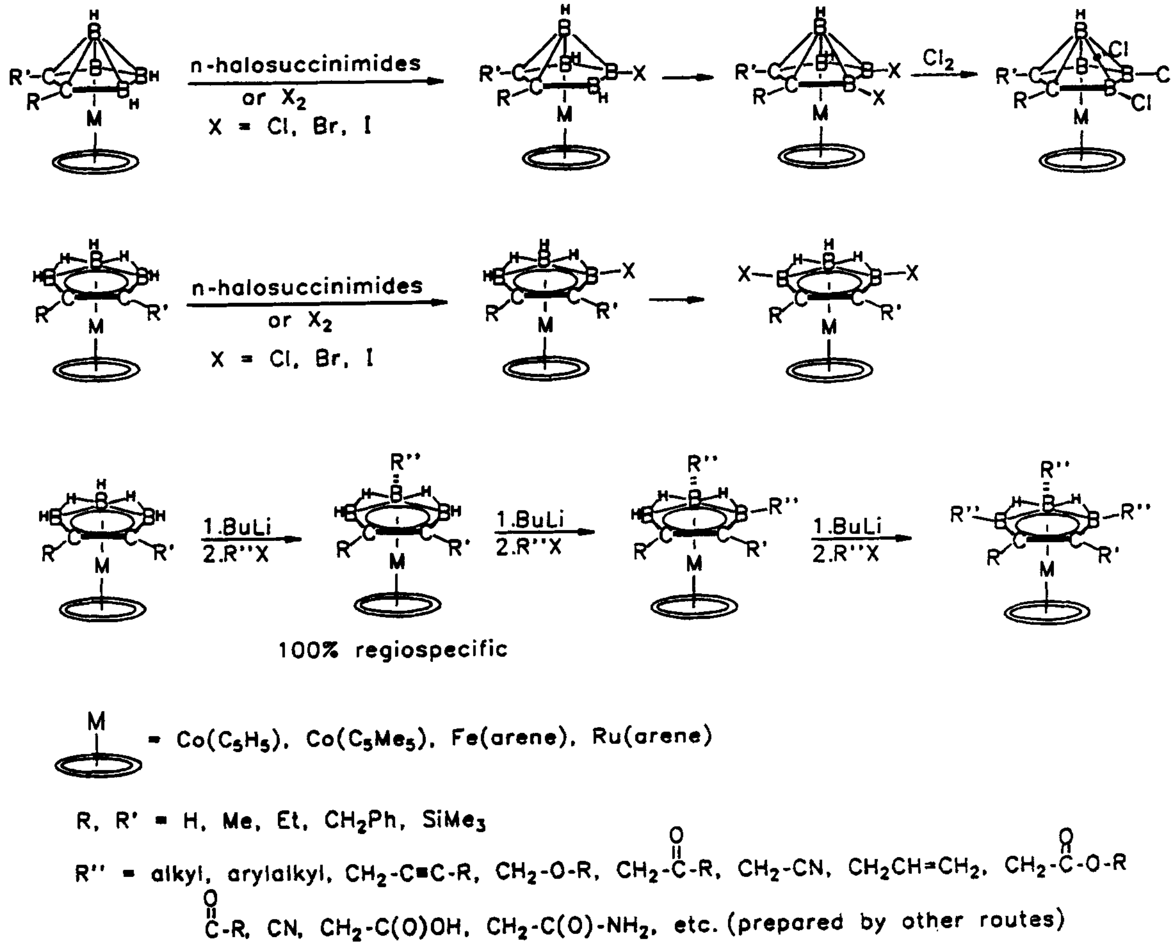
deprotonated via treatment with alkyl-lithium reagents in THF solution to form the mono- or dianions, which readily coordinate to transition metals to generate the double-decker sandwich metallacarborane complexes of types LM(RR'$C_2B_4H_4$) (**1**, **3**, and **4** in Scheme 1) and *nido*-LM(RR'$C_2B_3H_5$) (**2** and **5**).[8–10]

In general, these compounds are easily prepared and handled. For example, *nido*-Cp*Co($Et_2C_2B_3H_5$) (**2**, Cp* = C_5Me_5) is a yellow air-stable crystalline solid, soluble in organic solvents, routinely prepared in 10–20 g lots and readily derivatized via introduction of functional groups on the carborane ligand. Such complexes, in turn, are suitable precursors to multidecker sandwiches, linked-sandwich systems and related species, as will be described.

DERIVATIZATION OF SMALL METALLACARBORANE SYNTHONS

The development of systematic procedures for introducing a variety of organic and inorganic substituents at designated boron[11] and carbon[12] locations on the carborane ligands and on the metal centers[13] has considerably broadened the scope of synthetic possibilities for these compounds. Scheme 2 illustrates some routes employed for substitution at boron vertices on LM(RR'$C_2B_3H_5$) double-decker complexes.

The importance of substituents is twofold: their nature and location can markedly influence the reactivity of the metallacarborane complex via electronic and/or steric effects (e.g. in metal stacking reactions, to be discussed); secondly,



Scheme 2 Introduction of halogens and other substituents to small metal–carborane complexes.

many functional groups are useful in achieving coupling, linking, polymerization, metal complexation and other chemistry. Obviously, methods for regioselective substitution are crucial in controlled synthesis and in the construction of molecular systems tailored for specific purposes.

Although one can derivatize the neutral $RR'C_2B_4H_6$ carborane prior to formation of a metal complex,[14] the preferred method is to start with unsubstituted double-decker $LM(RR'C_2B_4H_4)$ or *nido*-$LM(RR'C_2B_3H_5)$ complexes and introduce substituents at that stage, as shown.[11] With this approach, one can effect substitution at one, two or all three boron atoms in the C_2B_3 ring. The substituents on the ring *carbons* can also be varied, as illustrated in Scheme 3, by desilylating $Cp^*Co(SiMe_3)_2C_2B_4H_4$ (**6**), lithiating the resulting parent (CH) species **8**, and displacing lithium via electrophilic attack to generate mono- or di-C-substituted species such as **10** and **11**, or decapitating to form the *nido* complex **9**.[12]

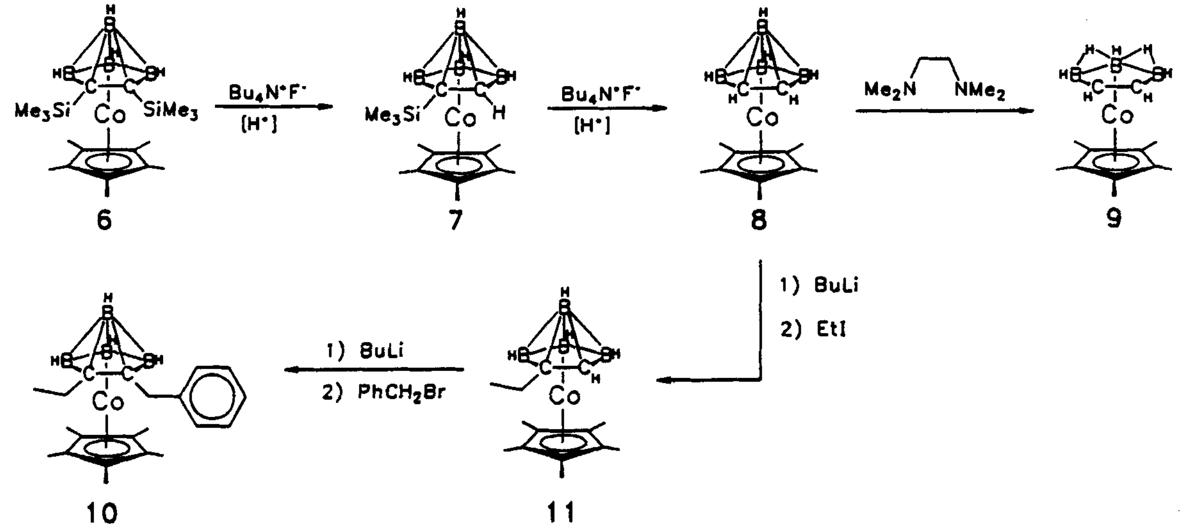
ASSEMBLY OF MULTIMETALLIC SYSTEMS

We have pursued two parallel strategies for building macromolecules from small metallacarborane synthons, namely multidecker stacking and connection of multiple sandwich units with organic linking groups. Both of these approaches, as well as combinations of the two, will be described.

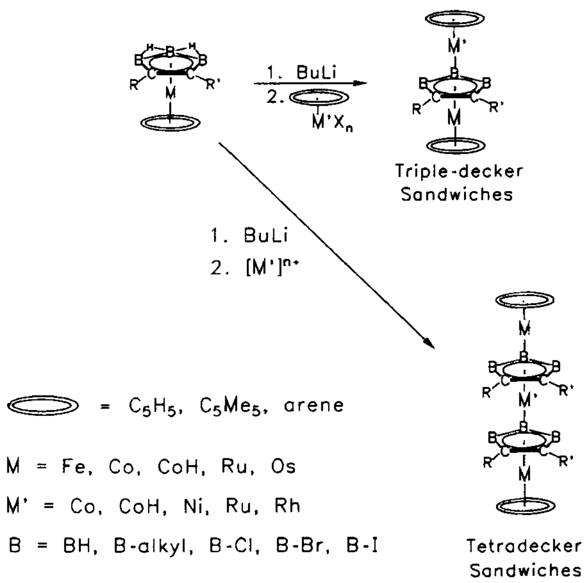
Multidecker stacking

Carborane-bridged multidecker sandwiches date back to our 1973 synthesis of several $CpCo(RR'C_2B_3H_3)CoCp$ (R,R' = H, Me) complexes—the first stable (and also the first neutral) triple-deckers[15]—following the classic preparation of the $Cp_3Ni_2^+$ triple-decker cation, a very air- and water-sensitive species, by Werner and Salzer.[16] Since that time, a few additional triple-decker sandwiches bridged by cyclic hydrocarbons have been prepared,[17] as have related species containing cyclic planar P_n or As_n rings.[18] However, at present the field of multidecker sandwich compounds is intensively boron-centered: most known and characterized triple-decker complexes, and *all* known true (nonstaggered) tetra- and higher-deckers, incorporate carborane or organoboron (e.g., C_3B_2, C_4B) bridging rings. In the latter category, a wide variety of organoboron-based multidecker sandwiches has been generated in the laboratories of Siebert[19] and Herberich.[20]

Carborane-bridged triple- and tetra-decker sandwiches are synthesized from *nido*-$LM(RR'C_2B_3H_5)$ complexes (obtained as in Scheme 1) by bridge-deprotonation with nucleophiles such as butyl-lithium, followed by complexation of the C_2B_3 face with a metal–hydrocarbon unit or metal cation, as illustrated in Scheme 4.



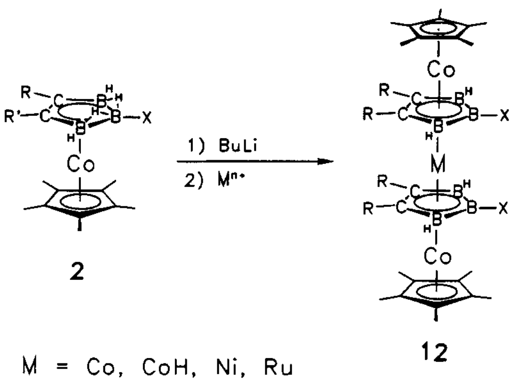
Scheme 3 Synthesis of the parent cobaltacarborane **8** and substitution at cage carbon atoms.



Scheme 4 Synthetic routes to triple- and tetra-decker metal–carborane sandwiches.

We have employed this approach to generate a wide variety of homo- and hetero-bimetallic (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.[9,21] In most cases, the end ligands (L) are arenes, Cp or Cp*, or C_4X heterocycles such as phospholyl and pyrrolyl,[21b] although carbonyl groups can also serve, as in the ruthenium tricarbonyl complex $(CO)_3Ru(Et_2C_2B_3H_2Cl)CoCp*$ from which a Fischer carbene was synthesized.[22] Closely related 'hybrid' triple- and tetra-decker sandwiches incorporating both carborane (C_2B_3 or C_2B_4) and diborole (C_3B_2) ring ligands have also been prepared.[23]

The most extensively studied class of tetradeckers, **12** in Eqn [2], contains Cp*Co^{III} end units and Co^{IV}, Co^{III}H, Ni^{IV} or Ru^{IV} metal centers (M).[24] Their preparation via 'stacking reactions' involving the coordination of two $LM(RR'C_2B_3H_3)^{2-}$ units (obtained via removal of both B–H–B protons from **2**) to a central metal ion, as shown in Eqn [2], is highly sensitive to the electronic character of the open face on the double-decker substrate. Tetradecker formation is favored when the X substituent [located on the middle boron, B5] is strongly electron-withdrawing, as in the Cl, Br, I, propargyl, and acetyl derivatives.[24a] Empirical observations show that the electron density on the open face is correlated with the proton NMR shift of the B–H–B hydrogens in neutral $Cp*Co(Et_2C_2B_3H_4X)$ complexes; those exhibiting high-field δ_{BHB} values either give no evidence of reaction with metal ions (e.g. the ethyl derivative) or give unstable products, while complexes showing relatively deshielded bridging protons, e.g. halo- or acyl-substituted derivatives, typically form tetradeckers readily.[24a]



M = Co, CoH, Ni, Ru
X = H, Cl, Br, I, Me, C(O)Me, $CH_2C{\equiv}CMe$
R = alkyl, $SiMe_3$ [2]

Other classes of C_2B_3-bridged tetradeckers

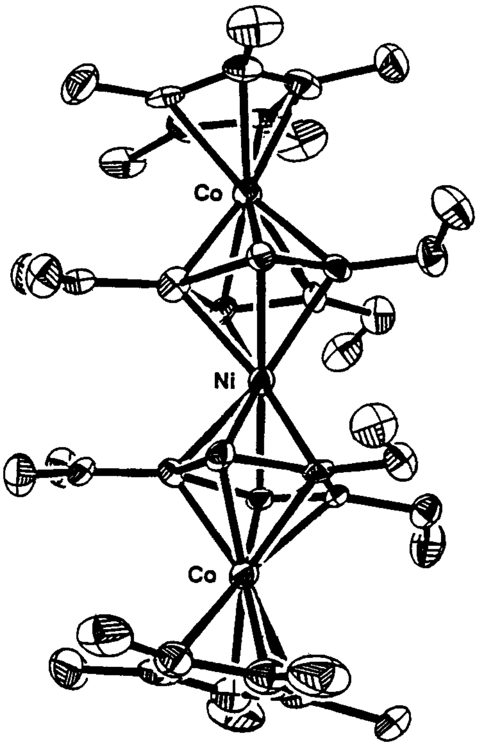
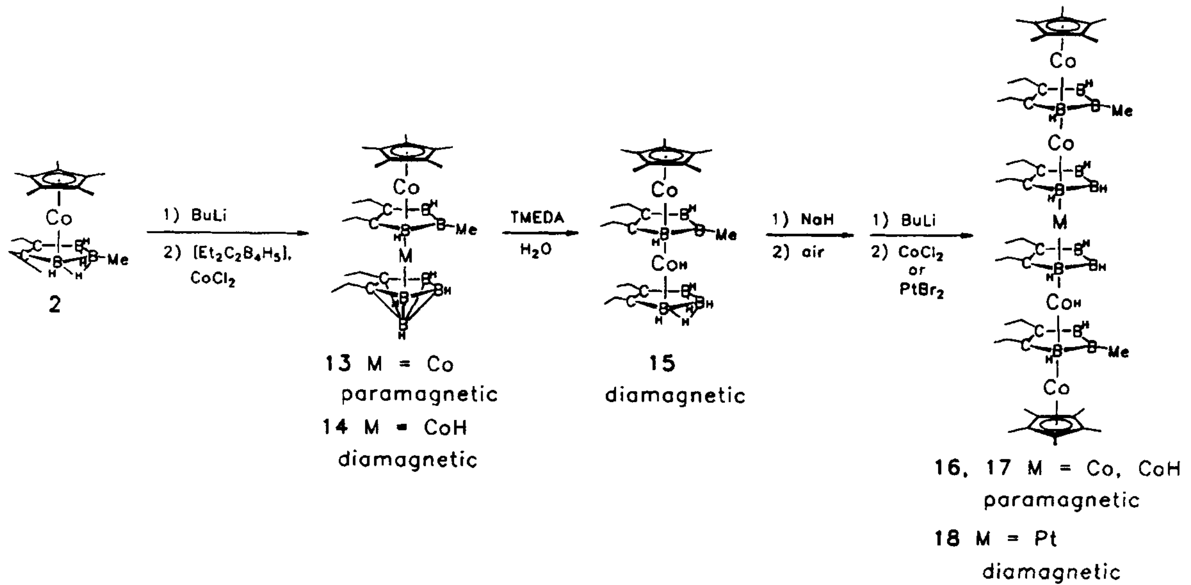


Figure 3 Structure of $[Cp*Co(2,3-Et_2C_2B_3H_2-5-C(O)Me)]_2Ni$.



Scheme 5 Synthesis of hexadecker sandwich complexes.

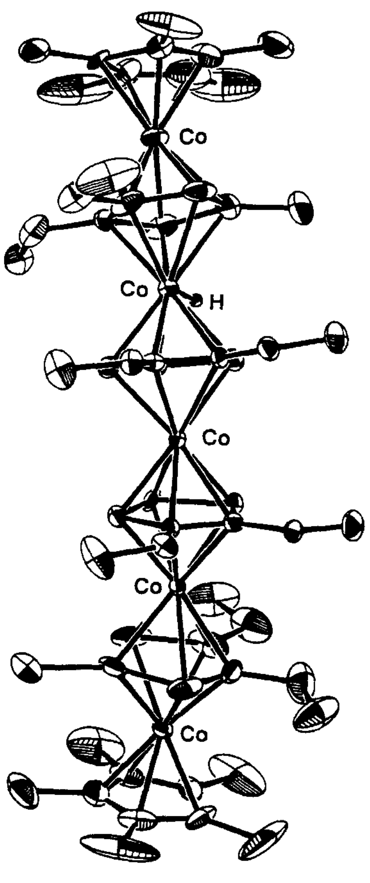
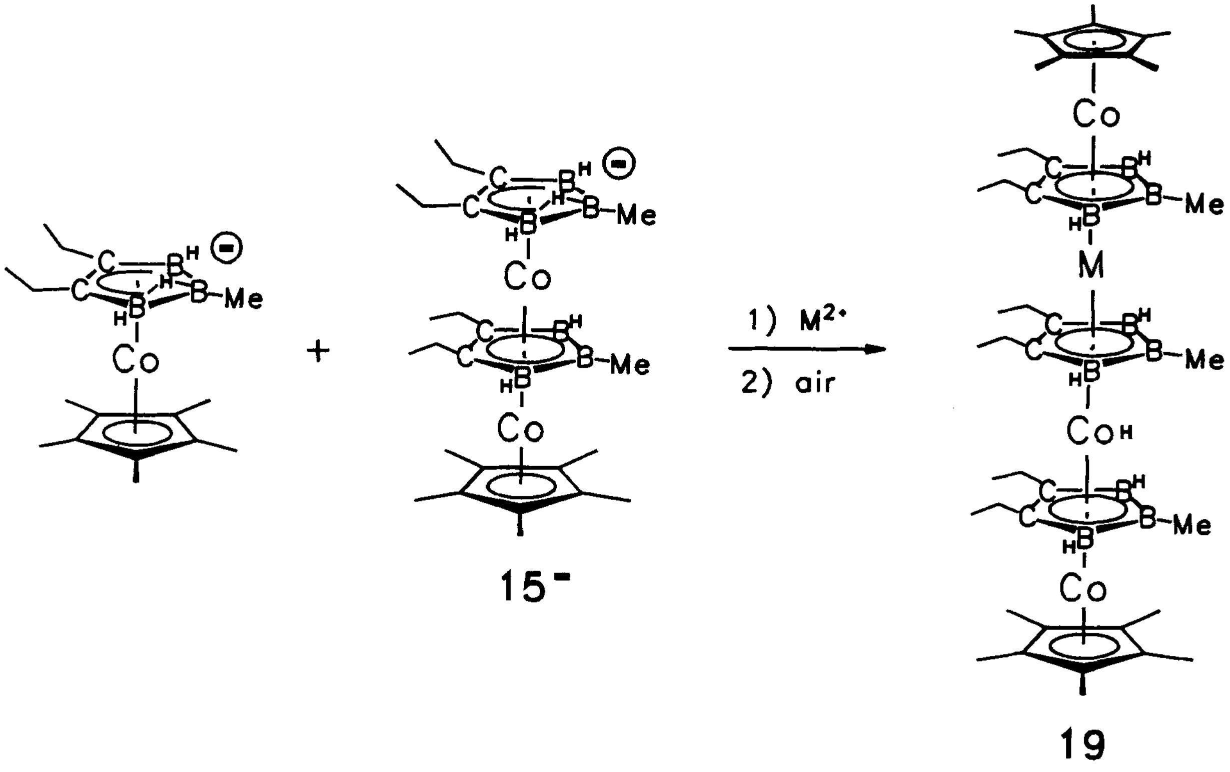


Figure 4 Structure of [Cp*Co($Et_2C_2B_3H_2Me$)CoH($Et_2C_2B_3H_3$)]$_2$Co (**17**).

have also been characterized, including a recently prepared series having *p*-[(Me_2CH)C_6H_4Me]Ru end units.[25] Iron-centered tetradecker sandwiches are more difficult to isolate, as they undergo oxidative fusion (a competing reaction,[26] beyond the scope of this review, that generates dimers or fused clusters) to form $M_2C_4B_6$ cages on exposure to silica in air; however, several C_2B_3-bridged Co–Fe–Co tetradeckers have been prepared.[27]

The molecular and electronic structures of a number of these complexes have been investigated in detail via X-ray crystallographic, spectroscopic and electrochemical studies.[24, 25] For example, the crystal structure of the Co-Ni-Co B,B′-diacetyl complex (Fig. 3) 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°.[24a] The electronic properties of these species, clearly relevant to their potential role in electronic applications, are discussed below.

In order to build complexes having more than four decks, e.g. pentadecker and hexadecker sandwiches, triple-decker synthons featuring open C_2B_3 end rings are required. As outlined in Scheme 5, compounds of this type (**15**) have been prepared and subsequently employed to make the hexadecker sandwiches **16**, **17** and **18**.[28] This strategy requires the attachment of a halogen or alkyl group on the C_2B_3 ring in the Cp*Co($Et_2C_2B_3H_4X$) starting complex **2** in order to inhibit fusion (see above) and promote forma-



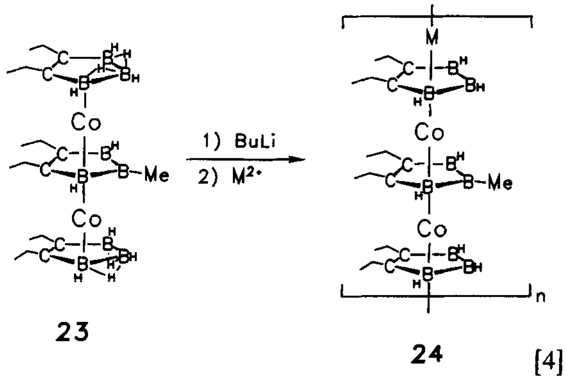
[3]

tion of the hexadecker products. In addition to the paramagnetic species **16** and **17**, which have respectively two and one unpaired electrons as shown by ESR measurements,[28] the diamagnetic Pt-centered hexadecker **18** has also been isolated.[29] The crystallographically established structure of **17**, revealing a slightly bent metal backbone, is illustrated in Fig. 4.

Very recently, pentadecker sandwiches (**19**) have been prepared via the process depicted in Eqn [3] in which triple- and double-decker units are stacked.[27b, 29] Although this is a mixed-ligand reaction and hence is susceptible to competitive formation of tetradecker and hexadecker by-products, the desired pentadecker is fortuitously obtained in highest yield.

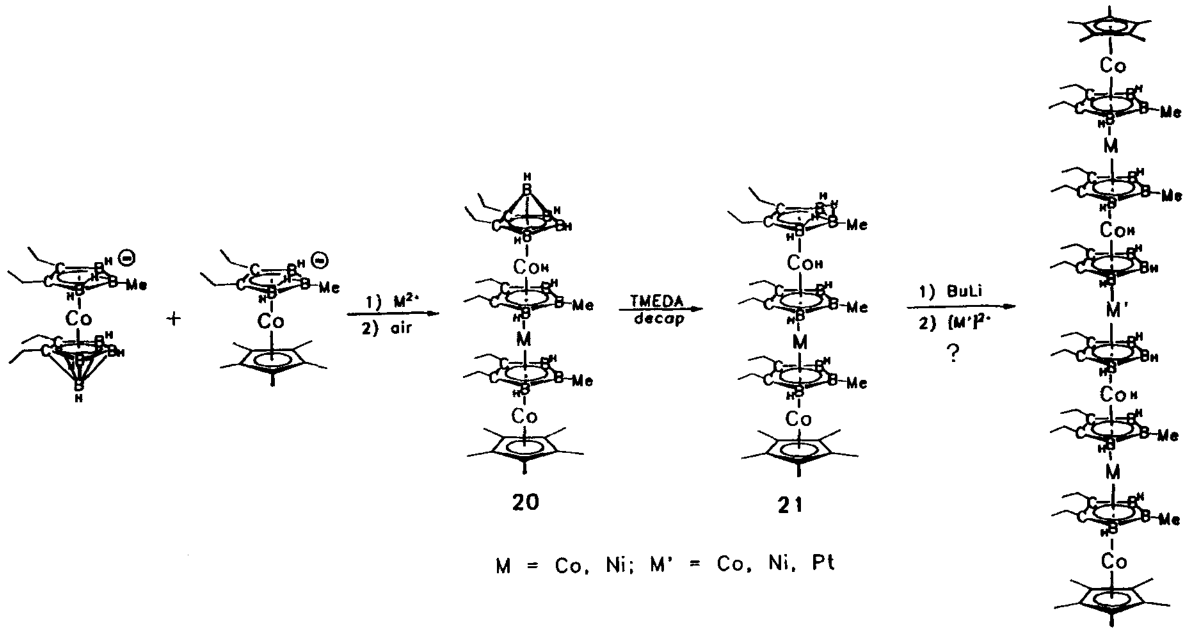
This approach seems likely to lead to still larger sandwiches, such as hepta- and octa-decker complexes (currently unknown genres) via metal stacking reactions with tetradecker species having open carborane end rings, as suggested in Scheme 6. At the time of writing, **21** has been prepared and characterized as shown[29] but octadeckers such as **22** have not yet been isolated.

Construction of even higher stacks, leading up to high-molecular-weight polydecker sandwiches can be envisioned. This will require synthons containing open carborane rings on both ends, e.g. **23**, that can be deprotonated and metal-complexed to form polymers similar to **24**, as suggested in Eqn [4].



[4]

Current efforts directed at the preparation of the precursor triple-decker species **23** have not yet succeeded. However, Siebert and co-workers



Scheme 6 Synthesis of carborane-endcapped tetradecker complexes **20** and **21** and proposed synthesis of octadecker sandwiches.

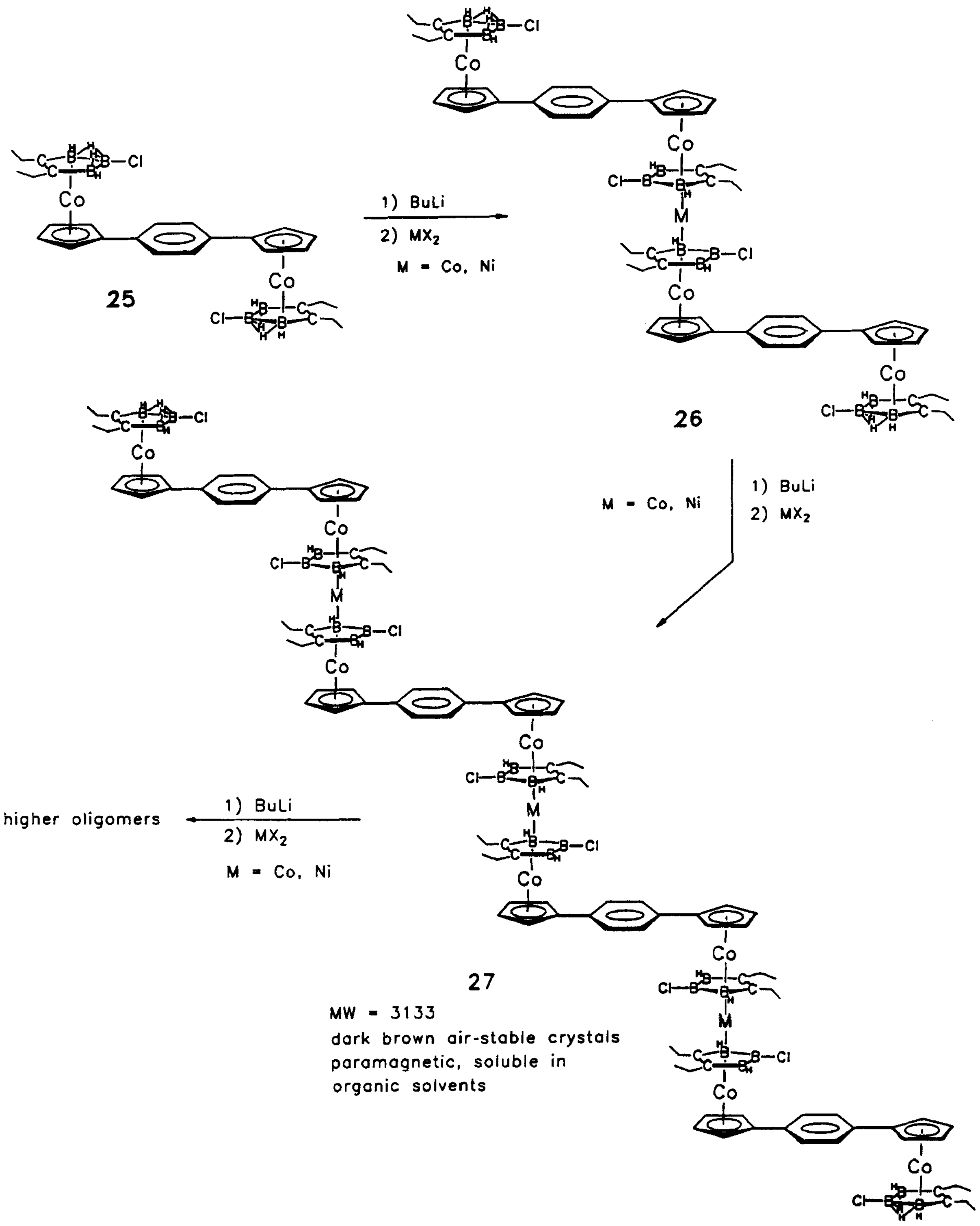
have synthesized and partially characterized a nickel–diborolyl sandwich polymer having C_3B_2 bridging rings that has been shown to be a semiconductor.[30]

A point worth emphasizing is the air-, thermal- and redox-stability of the known carborane-bridged multidecker sandwich systems, which represents a significant advantage over hydrocarbon-bridged sandwich polymers, many of which are air-sensitive and/or have low solubility.[31] For example, a recently reported pentalene–iron staggered tetradecker sandwich[31a] and an earlier chromium–naphthalene polymer[31b] manifest these problems. A different (nonsandwich) type of organometallic polymer, consisting of $Cp(Ph_3P)CoC_4$ cobaltacycle units connected by alkyne bridges, is reportedly air-stable.[31c] Our systems may in fact reflect the general observation,[1i] supported by recent theoretical studies,[32] that the incorporation of boron or other main-group heteroatoms into organic and organometallic polymers promotes stability as well as metallic behavior.

Construction of linked-sandwich systems

Scheme 7 outlines the synthesis of multisandwich oligomers linked by phenylene groups, via tetradecker stacking of the 'double-ended' bis(cobaltacarborane) complex **25** which has two C_2B_3 open faces for coordination to metal ions.[24b] Complexes **26** and **27** have been characterized from ^1H and ^{11}B NMR and mass spectra, supported by an X-ray diffraction study on **26** (Fig. 5). The phenylene-linked systems contain individual paramagnetic Co–M–Co tetradecker sandwich units in which there is extensive electron delocalization *within* each stack, but evidently little communication *between* them, as discussed in the following section. Consequently, polymers based on such units are unlikely to be conductors or semiconductors, although they may turn out to have interesting bulk magnetic properties if unpaired electrons are trapped within the individual sandwich units.

Directly linked complexes that incorporate $(C_5H_4)_2$ (fulvalene) units are more promising candidates for long-range electron delocalization between metal centers, and accordingly the fulvalene-linked oligomers **31** have been prepared from the dimetallic synthon **28**, as shown in Scheme 8.[24b] Preliminary electrochemical data (W. E. Geiger, private communication) on complexes of type **31** are consistent with interstack electron delocalization, and hence polymers constructed from such units may be prospects for 'molecular wire' one-dimensional conductors.



MW = 3133
dark brown air-stable crystals
paramagnetic, soluble in
organic solvents

Scheme 7 Synthesis of known and characterized phenylene-linked oligomers incorporating tetradecker sandwich units.

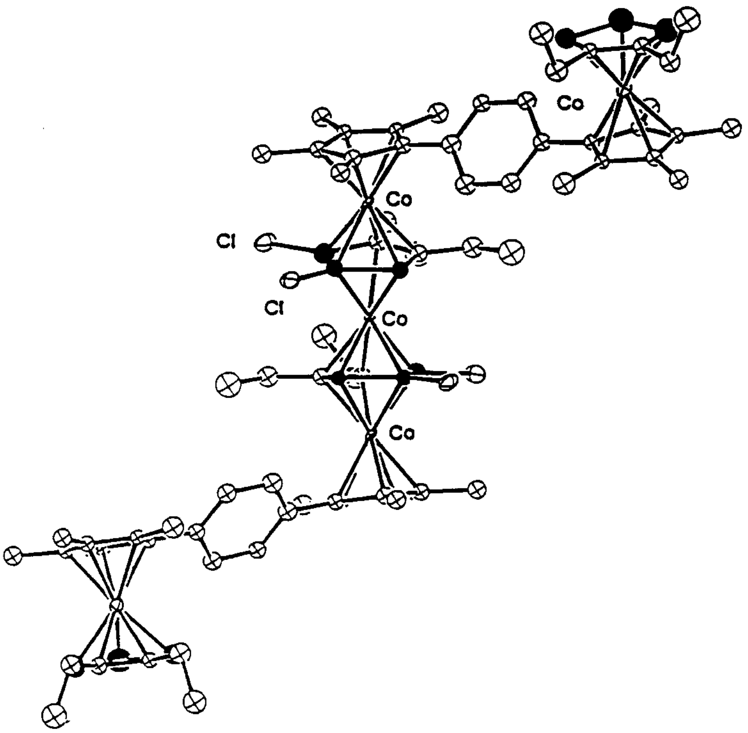


Figure 5 Structure of $[(Et_2C_2B_3H_5)Co(C_5Me_4)C_6H_4(C_5Me_4)Co(Et_2C_2B_3H\text{-}4,5\text{-}Cl_2)]_2Co$ (**26**).

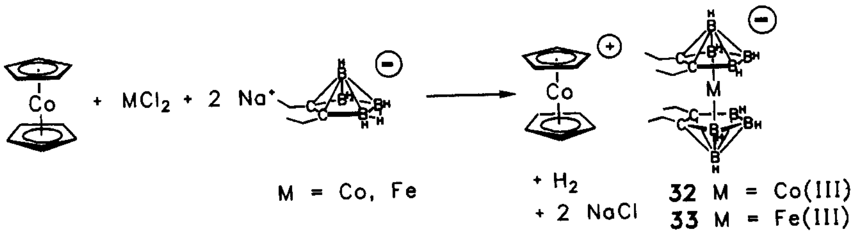
Metallocenium–metallacarboranide salts

The electronic analogy between carborane anions and $C_5H_5^-$ ions discussed earlier is augmented, in the case of small carboranes, by an *isosteric* relationship: that is, the two kinds of ligands have similar spatial requirements and hence are in principle interchangeable in a solid lattice. This isoelectronic/isosteric analogy creates possibilities for preparing mixed charge-transfer salts that incorporate both metallocenium and metallacarboranide ions, which may, with the proper choice of metals, ligands and substituents, crystallize in stacked arrays that allow low-dimensional electron delocalization. As a first step, we prepared and structurally characterized the cobaltocenium salts **32** and **33** (Eqn [5]).[33]

The orange-red, air-stable, diamagnetic cobaltocenium–cobaltacarboranide salt **32** gives evidence of cation–anion pairing in the gas phase (FAB mass spectra) and in the solid state (Fig. 6). Its iron(III) counterpart **33** is paramagnetic and exhibits an unusual crystal structure having a large unit cell (>35 Å along one axis), that has not yet been successfully refined.

STUDIES OF ELECTRONIC STRUCTURE AND PROPERTIES

Central to research in this area is the development of a detailed understanding of the electronic



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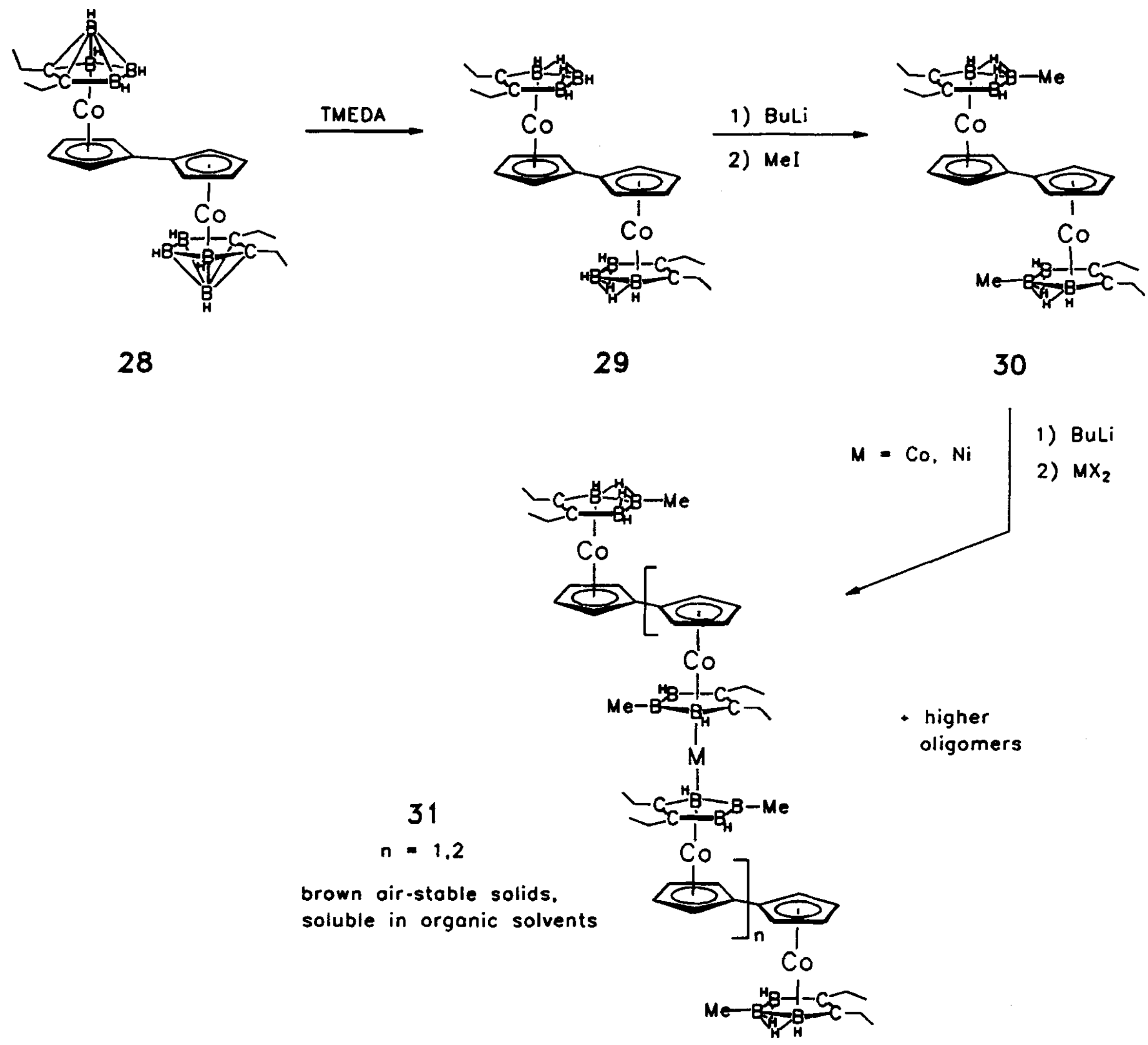


Scheme 8 Synthesis of fulvalene-bridged tetradecker sandwich oligomers. TMEDA, tetramethylethylenediamine.

character of the various families of monometallic and polymetallic species. The long-range goal of tailoring materials to exhibit specific combinations of electrical/magnetic/optical properties requires that we learn how these properties are influenced by the choices of metals, metal oxidation states, ligands, substituents and molecular or solid-state architecture. To this end, the main investigative tools have been X-ray crystallography, electrochemistry, multinuclear NMR, ESR and UV–visible spectroscopy, as well as Mössbauer spectroscopy and temperature-dependent magnetic measurements, often involving collaboration between our own and other laboratories, especially those of W. E. Geiger (University of Vermont), W. Siebert (University of Heidelberg), and U. Zenneck (University of Erlangen–Nürnberg).

As noted earlier, the question of electron-delocalization between metal centers in polymetallic species is of central interest, and electrochemical studies have been particularly useful. A spectroelectrochemical investigation of the paramagnetic triple-decker sandwich cations $CpCo(Et_2C_2B_3H_3)Ru(MeC_6H_4iPr)^+$ (**34**) and $(MeC_6H_4iPr)Ru(Et_2C_2B_3H_3)Ru(MeC_6H_4iPr)^+$(**35**)

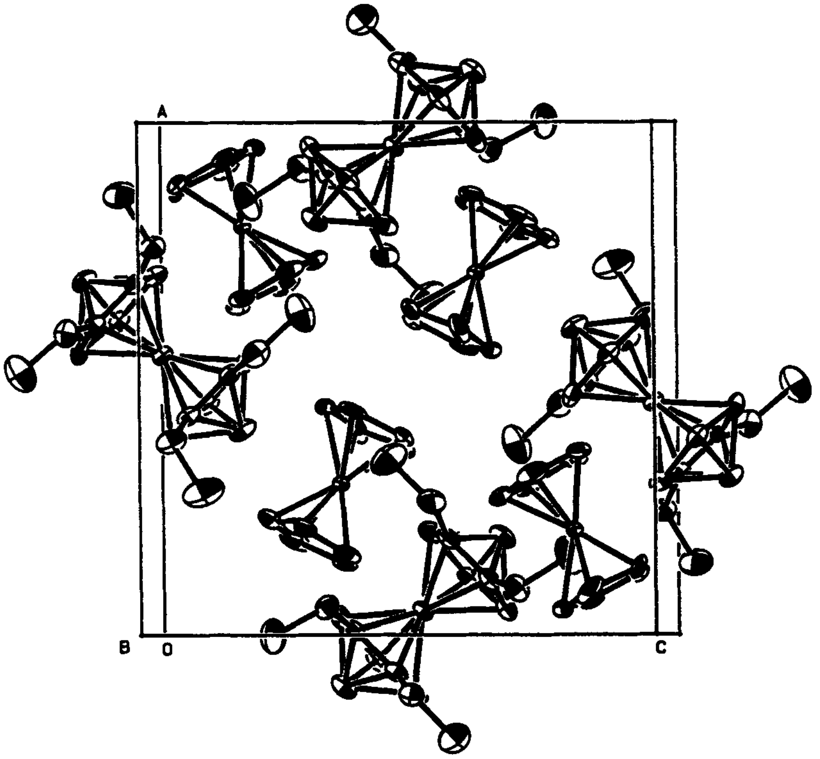
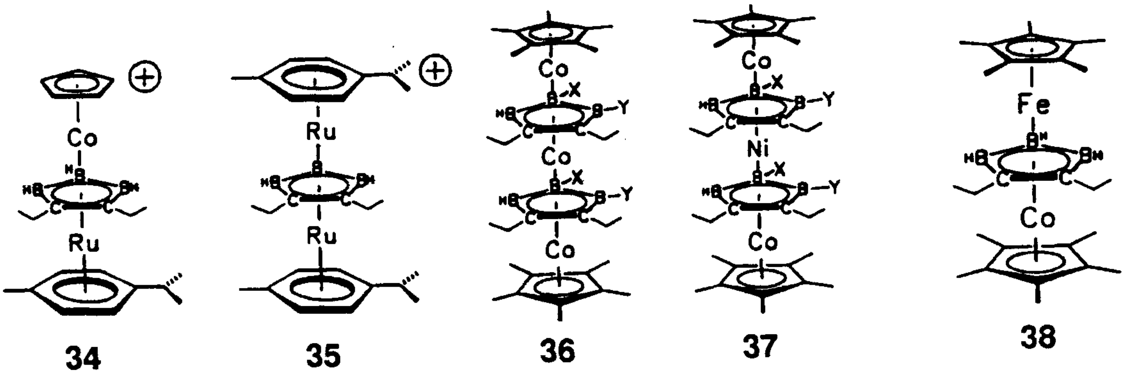


Figure 6 Structure of Cp_2Co^+ $(Et_2C_2B_4H_4)_2Co^{III}]^-$ (**32**).



X = Me, C(O)Me, Cl, Br, I, $CH_2C{\equiv}CMe$
Y = H, Cl

Figure 7 Examples of triple- and tetra-decker sandwich complexes exhibiting complete (**34**, **35**), extensive (**36**, **37**), and little or no electron delocalization (**38**) between metal centers, based on NMR, ESR, electrochemical and infrared data.

(Fig. 7) established that these are Class III (fully delocalized) mixed-valence species.[34] Similarly, cyclic voltammetry and controlled potential electrolysis on a series of Co–Co–Co and Co–Ni–Co tetradecker complexes (**36** and **37**) give a strong indication of extensive delocalization in these systems.[24c, d] On the other hand, ESR and paramagnetic correlated NMR (see below) studies on the iron–cobalt triple-decker complex **38** are consistent with highly *localized* electronic states;[21c] oxidation and reduction of the paramagnetic 29-electron neutral species occur exclusively at the iron center, while reduction of the diamagnetic 30-electron monoanion takes place on cobalt. The range of these findings, encompassing fully delocalized as well as localized systems, implies that it should be possible to synthesize multidecker species having intermediate levels of electron delocalization, via the proper choice of metal–ligand combinations.

Studies of the linked-sandwich multimetallic complexes show varying behavior. The absence of electronic communication *between* the sandwich units in phenylene-connected complexes such as

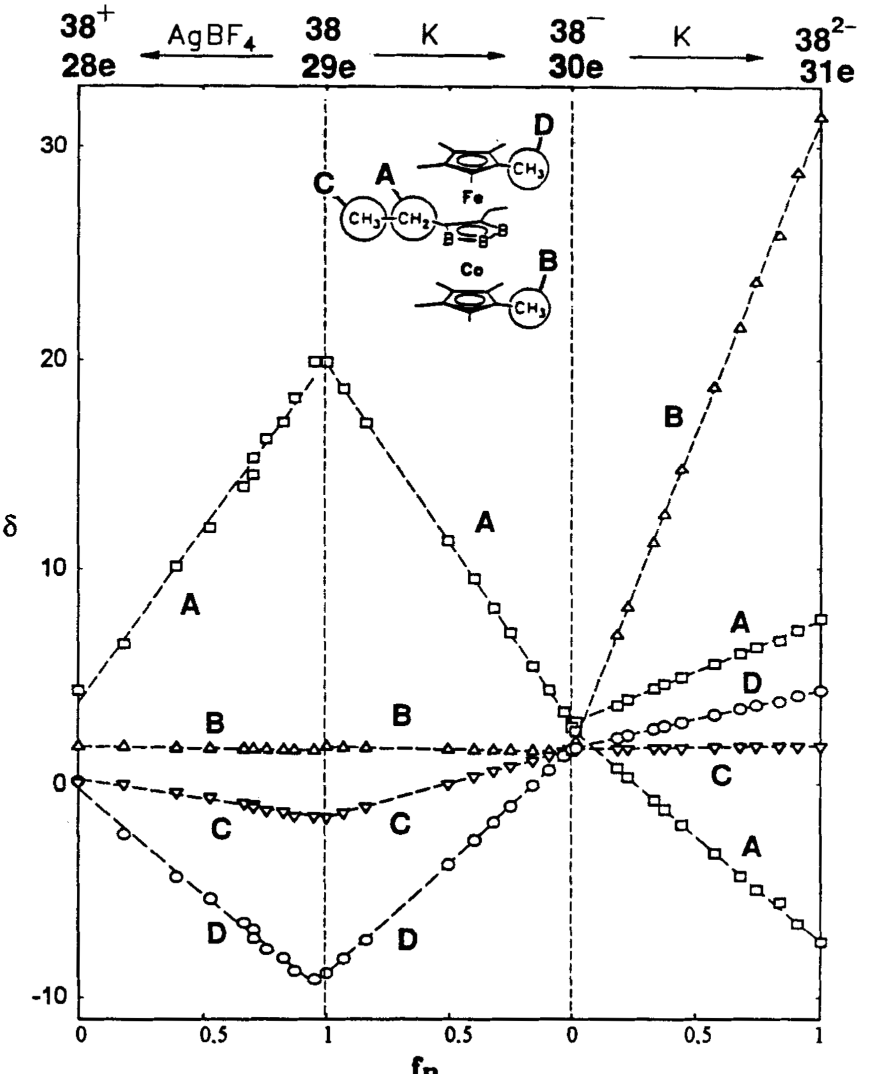


Figure 8 Correlation diagram for ^1H NMR spectra of the Fe–Co triple-decker complex **38**, its cation, and its mono- and dianions. The chemical shift δ is plotted vs. f_p, the mole fraction of paramagnetic component in each redox process.

27, mentioned earlier, is almost certainly a consequence of the tilt (*ca* 40°) between the phenylene ring and the adjacent cyclopentadienyl rings[24b] which prevents π-conjugation. However, when the sandwiches are directly linked, as in the fulvalene-based oligomers **31** (Scheme 8), intersandwich electron delocalization is promoted (W. E. Geiger, private communication). In very recent work on polymetallic complexes, a new technique, spectroelectrochemical infrared spectroscopy, has been added to the arsenal.[35] Collaborative studies with Geiger's laboratory on the dicobalt fulvalene complex **28** (Scheme 8) have demonstrated that successive one-electron reductions of the neutral species to the dianion produce a very large (80 cm^{-1}) total shift in the B–H stretching frequency, equally partitioned between the two steps and thus establishing a delocalized electronic structure. More generally, it has been demonstrated that the effect is a sensitive diagnostic tool for probing delocalization.[35]

In addition to cyclic voltammetry, ESR and UV–visible spectroscopy, another technique we have used to probe electronic structure is that of correlated NMR spectroscopy.[21c,36] In this method, ^{1}H or ^{13}C NMR spectra of paramagnetic species are completely assigned via stepwise reduction or oxidation of the initial species, with the spectrum recorded at each stage. This produces a linear plot for each signal as a function of f_p, the fraction of paramagnetic species in solution, and hence allows correlation with the diamagnetic spectrum (in which the assignment of resonances is usually straightforward). Figure 8 shows changes in the proton chemical shifts (δ) for the Fe–Co triple-decker complex **38**, a 29-electron paramagnetic neutral system, as it undergoes oxidation to the diamagnetic cation and reduction to a diamagnetic monoanion and a paramagnetic dianion.[21c]

Taken together with ESR and other data, the wealth of information generated in this way is very revealing with respect to electronic struc-

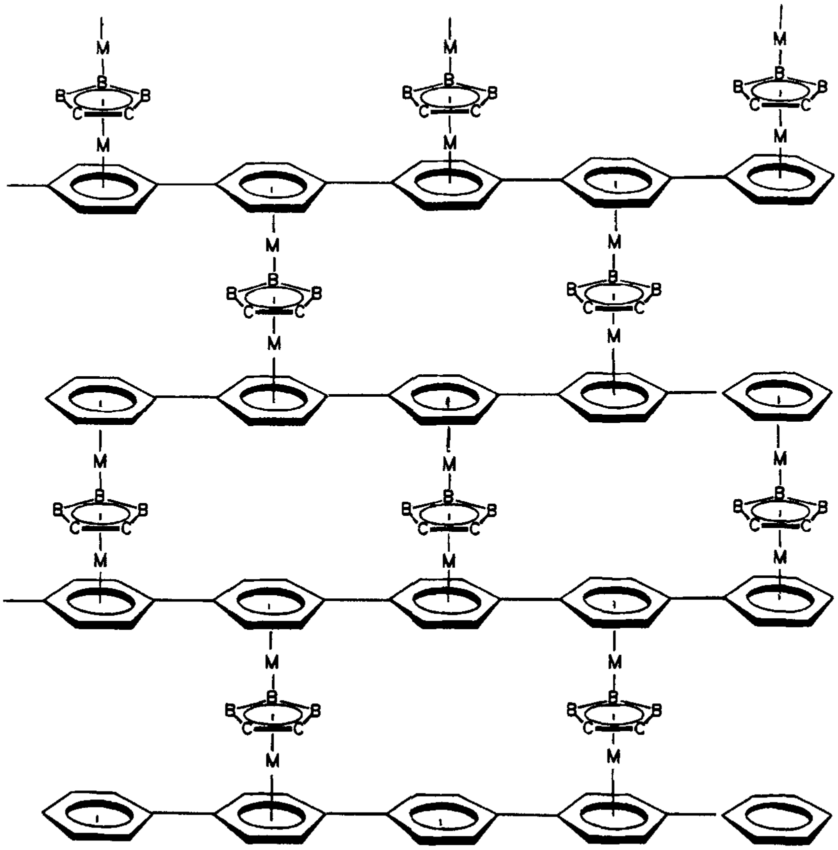


Figure 9 A proposed two-dimensional sheet polymer incorporating arene-capped triple-decker sandwich units.

ture; in this case, for example, the oxidation and reduction of the neutral complex are associated with the iron center, while reduction to the dianion takes place on cobalt. Consistently with electrochemical, ESR and Mössbauer observations, these data establish that this system has a localized structure (no metal–metal communication), in sharp contrast to the fully delocalized Co–Ru and Ru–Ru triple-deckers **34** and **35**.[34]

CURRENT AND FUTURE DIRECTIONS

Metallacarborane sandwich complexes offer a number of major advantages as building blocks for construction of new materials. The intrinsic stability, tailorability and versatility of these compounds allow wide-ranging studies that focus on families of systematically related complexes, as opposed to single isolated species. Moreover, the designed synthesis of new metallacarborane-centered materials fits in well with a strong current trend in materials science.[1] As Allcock[1i] puts it, 'The need for rational design in this field cannot be overemphasized. The unplanned discovery of new and valuable materials will always be one of the most exciting aspects of science; but the main need is to construct predictive schemes that allow molecular solid-state, or surface structural changes to be used predictably to generate tailored properties.' With respect to polymer synthesis, the same author has pointed out that the replacement of carbon as a skeletal element by inorganic elements increases the thermo-oxidative stability and leads to materials that are intermediate between polymers and ceramics or metals. A special strength of metallacarborane sandwich chemistry is its interdisciplinary nature, drawing heavily on both organic and inorganic methodology and concepts and featuring main-group, transition-metal, cluster and organometallic chemistry. This allows one to think in terms of a wide variety of synthetic targets having application in several fields, including conducting polymers, molecular magnets, nonlinear optical materials and solid-state electronic devices. For example, it should be possible to assemble one-, two- and three-dimensional solid-state materials such as that suggested in Fig. 9 that could be tailored for particular purposes via appropriate choice of substituents and metals.

Particularly intriguing is the prospect of ultimately designing and preparing multiproperty materials that combine two or more functions, e.g. magnetization and second-harmonic generation.[1d] It is likely that the applicability of this chemistry will prove more fruitful in some of these areas than in others, but clearly a wide range of possibilities is open for exploration.

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