

Small carboranes as building blocks in designed organometallic synthesis

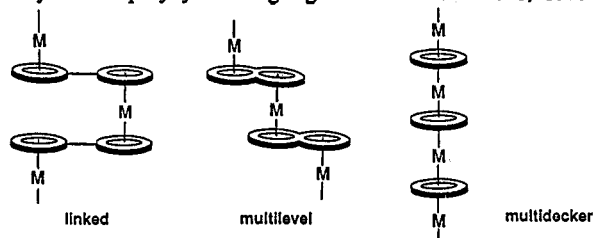
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Abstract. Methods are now at hand to permit the systematic construction of multidecker-, multilevel-, and linked-sandwich complexes from transition metals, aromatic hydrocarbon or heterocyclic ligands, and carborane (C_2B_3) rings. As a consequence of detailed studies of the electronic properties and chemistry of selected building-block complexes, especially those of the type $LM(R_2C_2B_3H_4R')$, where L is C_5R_5 or an arene and M is a first-, second-, or third-row transition element, the reactivity of such compounds can be adjusted, or "tuned", by attachment of appropriate R' substituents to boron; this allows the controlled synthesis of a variety of types of polymetallic systems which exhibit substantial electron-delocalization. These include triple- and tetradecker complexes, poly(sandwich) species linked via organic units attached at boron or carbon positions, and related systems. This chemistry in turn opens the way to the preparation of extended molecular solid or liquid materials which can be tailored to combine unusual or novel electronic properties with high thermal and oxidative stability.

INTRODUCTION

Interest in the controlled synthesis of new solid and liquid materials having specified electronic, optical, or other properties, is large and growing.¹ Among the more intensively studied areas are, of course, the preparation of ceramic semi- and superconductors via solid-state reactions at high temperature, and the creation of novel low-dimensional conducting materials ("organic metals") from organic ions. An alternative approach to the synthesis of new materials involves the stepwise construction of *covalently bonded* extended molecular systems from basic building-block units or synthons, as in the construction of organometallic conducting polymers from aromatic hydrocarbons and transition metals.² Such polymers are of interest in a variety of potential applications,³ e.g., as electromagnetic shields, antistatic agents, anti-lightning airframes, lightweight plastic batteries, and devices for controlled drug delivery into the skin. In principle, many types of electron-delocalized organometallic networks might be constructed from cyclic or polycyclic ring ligands and metal ions; several possibilities are shown conceptually:

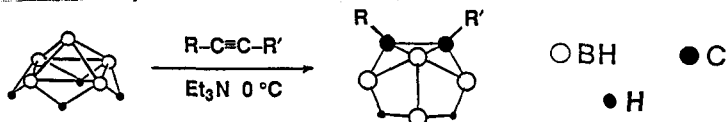


The linking units could be simple polyarenes, and in fact a multilevel-type naphthalene-chromium sandwich polymer has been prepared and partially characterized.⁴ However, the oxygen-sensitivity and autocatalytic disproportionation of this material makes it unsuitable for practical application. This exemplifies a general problem of instability in conductive organometallic polymers, which often arises when the material is oxidized in order to produce unpaired electrons on the metal centers and thus promote electrical conductivity.³ This situation is frequently encountered even in monomeric species, as in the fact that the oxidation of most Fe(II)-arene species proceeds irreversibly.

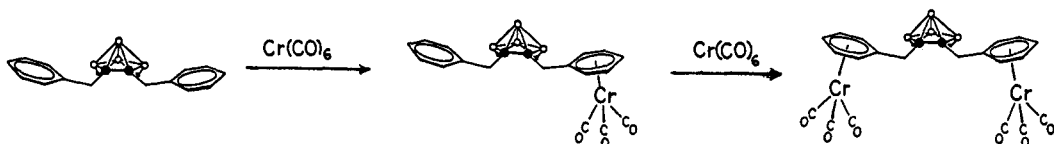
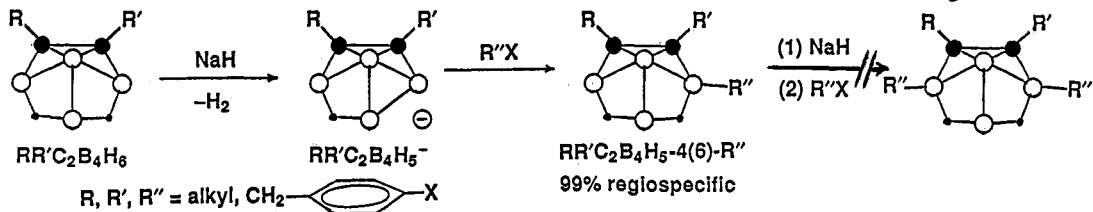
Such difficulties can be overcome by introducing appropriate stabilizing ligands, especially carborane or heteroboron units. The ability of nido-carborane moieties such as $C_2B_9H_{11}^{2-}$ and $R_2C_2B_4H_4^{2-}$ to stabilize metal-hydrocarbon systems has been long known and is well documented.⁵ Our research has concentrated on the C_2B_4 species⁶ because of their ready accessibility, broad synthetic versatility, and facile conversion to planar C_2B_3 ring ligands which can bridge two metals, thereby serving as a linchpin for construction of multidecker sandwich systems. In recent years, we have devoted considerable effort to making these small carborane ligands truly useful as reagents for organometallic synthesis, and to developing an integrated "organometallacarborane" chemistry which combines the principal advantages of both transition-metal organometallic and metal-carborane chemistry. A central point is that the planar C_2B_3 ring is isolobal and *essentially isosteric* with $C_5H_5^-$ and C_6H_6 , allowing the carborane ring to function as a steric replacement for cyclopentadienyl or arene rings in metallocene-like arrays. Given the versatility of the C_2B_3 ligands (*vide infra*), this allows the construction of progressively larger organotransition-metal oligomers from small units in a straightforward manner. Once assembled, the products are usually aerobically stable and typically can undergo reversible oxidation and/or reduction to generate paramagnetic species with high electron delocalization. This short paper will outline some of the principal synthetic routes and present selected recent examples of their application.

SYNTHESIS OF NIDO-CARBORANE STARTING MATERIALS

The base-promoted reaction of alkynes with B_5H_9 in the absence of solvent yields *nido*- $RR'C_2B_4H_6$ carboranes, in a process which could be described as "tetraboronation" (net addition of B_4H_6) of each $C\equiv C$ group.⁷ The reaction is quite general, working with nearly all alkynes thus far examined including cyclic and polyacetylenes,⁸ thereby providing access to a wide variety of C,C'-disubstituted derivatives.^{6a}

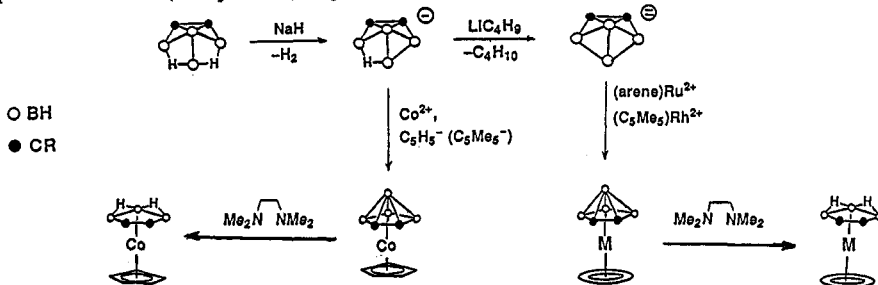


Still greater versatility is achieved through controlled, regiospecific addition of organic substituents at boron, which is accomplished via treatment of the bridge-deprotonated monoanion with alkyl or arylalkyl halides.⁹ The reaction affords only the B(4)- [and equivalent B(6)]- monosubstituted derivatives (similar treatment of the analogous *nido*-metallacarboranes proceeds differently, as will be described). Aryl rings can be metallated as shown,¹⁰ but most of our interest has centered on complexation at the C_2B_3 face, as summarized in the following sections.



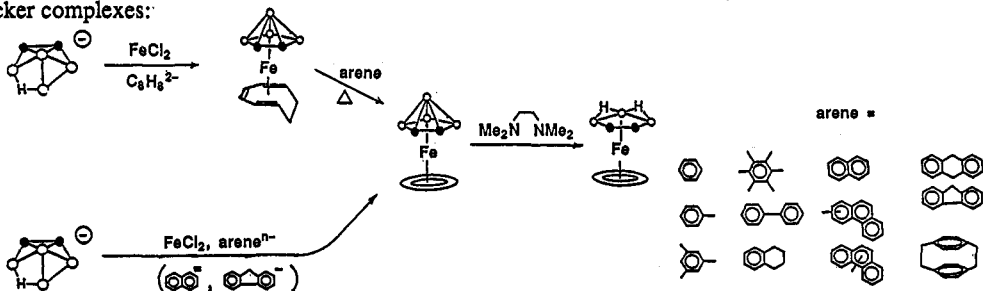
SYNTHESIS OF DOUBLE-DECKER METALLACARBORANE BUILDING BLOCKS

The removal of one or both bridge protons¹¹ generates the carborane mono- or dianion, respectively, whose C_2B_3 faces can coordinate to metals to give $LM(R_2C_2B_4H_4)$ *closo*-metallacarboranes.^{12,13} These species in turn readily undergo apex-BH removal (decapitation) to produce the desired double-decker building-block complexes:

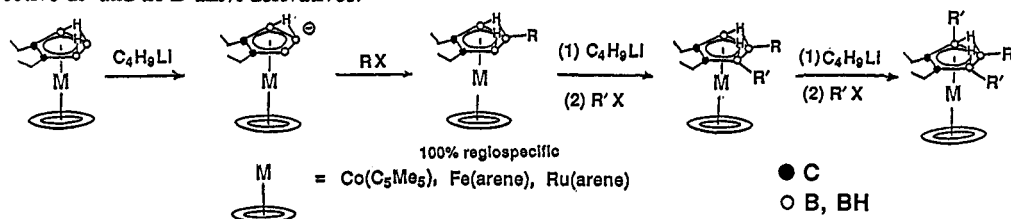


As shown, the cobalt species are prepared from the monoanion,¹² while those of ruthenium and rhodium are obtained from the dianion.¹³ Indeed, not until the carborane dianion became available^{11b} was it possible to develop a systematic route to $LM(C_2B_4)$ and $LM(C_2B_3)$ sandwich complexes of the heavier transition metals.

The synthesis of $(arene)Fe(R_2C_2B_4H_4)$ complexes presented a special problem, as the above methods are not applicable to iron (except in the case of polyarenes such as naphthalene or fluorene that can be reduced to aromatic anions). A viable route, discovered serendipitously in our laboratory, involves thermal displacement of cyclooctatriene from $(\eta^5-C_8H_{10})Fe(R_2C_2B_4H_4)$ (prepared as shown¹⁴) by arenes;¹⁵ as will be illustrated, this is a very general reaction and has proved extremely useful in synthesis. Subsequent decapitation affords the arene-iron double-decker complexes:



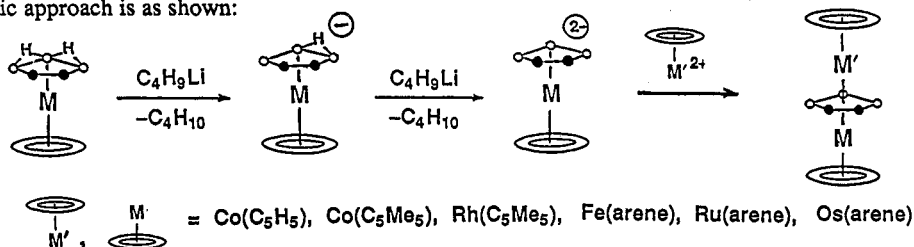
The synthetic utility of the double-decker complexes can be augmented by the selective introduction of substituents on the carborane framework. Boron-substitution via attack of one equivalent of an alkyl halide on the Co, Fe, or Ru double-decker anions affords exclusively the B(5)-R derivative, as shown;¹⁶ this contrasts sharply with the alkylation of the $R_2C_2B_4H_5^-$ species mentioned above. Further deprotonation/alkylation cycles yield the respective di- and tri-B-alkyl derivatives:



Effecting substitution at the cage carbon locations presents a different challenge, since our complexes usually contain non-displaceable C-alkyl groups. However, very recently we have found¹⁷ that the trimethylsilyl ligands in *closo*-(C_5Me_5)Co(Me_3Si) $_2$ C $_2$ B $_4$ H $_4$] can be displaced by fluoride to yield the parent complex *closo*-(C_5Me_5)Co(C $_2$ B $_4$ H $_6$), which can be lithiated and treated with organic halides to give desired C- and C,C'-derivatized complexes. The methods thus far described permit the tailored synthesis of small metallacarborane building-block reagents in which the metal, the B-substituents, and the C-substituents can be varied within broad limits. In the remainder of the paper, some selected examples will be presented in which this chemistry is applied to the assembly of several types of large multimetallic systems.

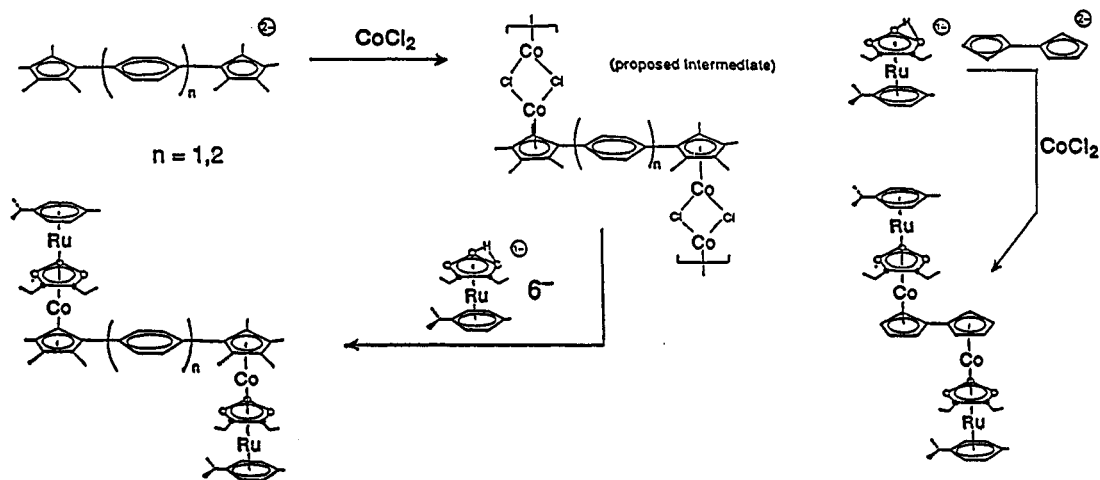
MOLECULAR ENGINEERING WITH METAL-CARBORANE COMPLEXES

Addition of a second metal to the open face of a double-decker species generates C $_2$ B $_3$ -bridged triple-decker complexes. Red CpCo(C $_2$ B $_3$)CoCp and its derivatives, the first neutral triple-deckers, were prepared in 1973¹⁸ but not until recently was this family of complexes extended to other metals^{13,19} (although many closely related triple- and higher-decker species bridged by organoboron rings have been prepared in the interim²⁰). Our general synthetic approach is as shown:

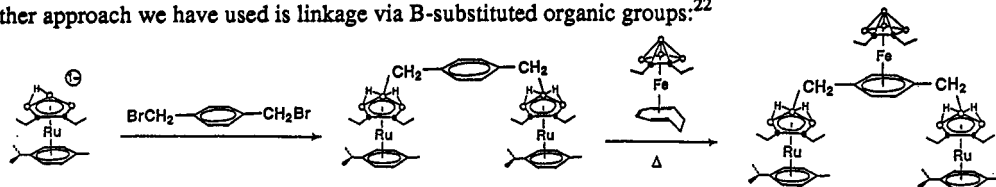


Detailed structural, spectroscopic, and electrochemical studies of many of these complexes^{13,19,21} have shown that although they are highly stable, tightly bound sandwiches, they can be oxidized or reduced to paramagnetic species which exhibit complete electron delocalization between metal centers, i.e., they are Class III mixed-valence complexes.²¹ This, in turn, suggests that extended networks of such stacks are promising candidates for low-dimensional electrical conductors or semiconductors.

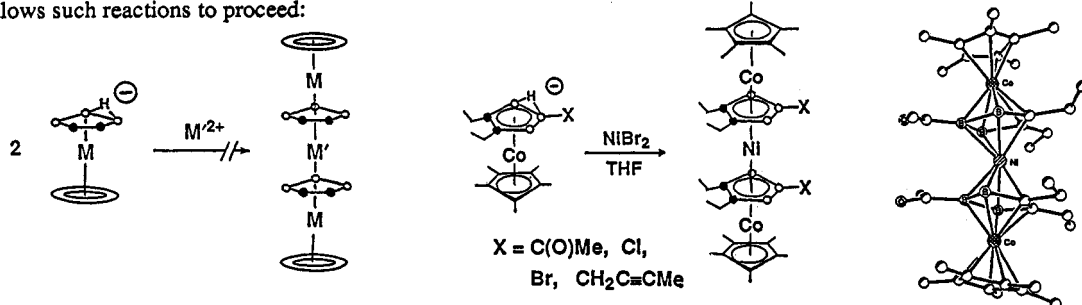
Several strategies are currently being employed in our laboratory to prepare multimetal linked systems. These include the use of polyaromatic hydrocarbon ligands, which afforded the first examples of linked triple-decker complexes:¹⁹



Another approach we have used is linkage via B-substituted organic groups.²²



A different structural concept is that of multidecker stacking, which Siebert and co-workers have used effectively to prepare C_3B_2 -bridged tetra-, penta-, and hexadecker complexes.^{20a} Attempts to synthesize carborane-bridged tetradeckers from double-decker complexes, as shown in the left diagram below, were unsuccessful until we made the unexpected discovery²³ that attachment of strongly electron-withdrawing groups (e.g., acetyl, Cl, Br) at boron allows such reactions to proceed:



This very recent finding has already led to the preparation of several tetradeckers, including the structurally characterized Co-Ni-Co species depicted, and may well open major new avenues in the designed synthesis of multidecker stacks.

Other related areas we are currently exploring, which space limitations prevent discussing here, include the use of heterocyclic ring ligands such as pyrrolyl (C_4N), phospholyl (C_4P), and thiophene (C_4S) in C_2B_3 -bridged sandwich complexes,²⁴ and the synthesis and study of "hybrid" carborane-metal-diborole triple- and tetradecker systems.²⁵

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