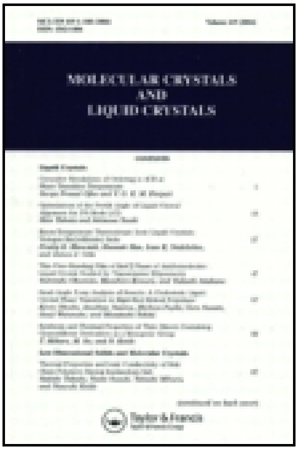

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Russell N. Grimes [a]

[a] Department of Chemistry, University of Virginia, Charlottesville, Virginia, 22901, U.S.A.

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Metal-Carborane Multidecker Sandwiches as Building Blocks for Metallopolymers and Nanostructured Materials

RUSSELL N. GRIMES

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, U.S.A.

The ability of cyclic planar $[RR'C_2B_3H_2X]^{4-}$ carborane ligands (R, R′ = alkyl, aryl, $SiMe_3$, H; X = alkyl, Cl, Br, I, H) to bind tightly to transition and main-group metals on both sides of the C_2B_3 ring plane allows the construction of a wide range of polymetallic multidecker sandwich complexes involving different metals, metal oxidation states, and molecular architectures. Although these ligands are isoelectronic and isosteric analogues of $C_5H_5^-$, they form stronger covalent bonds to metal centers, and can stabilize many robust, *isolable* structural types that are not readily accessible (or are completely unknown) in metallocene chemistry. Many of these metallacarborane sandwich complexes are paramagnetic and exhibit extensive electron-delocalization that can be "tuned" by redox action or by the introduction of appropriate substituents to the carborane ligands or the metal centers. This remarkable versatility suggests that there is considerable potential for the creation of novel polymeric and solid state materials that can be tailored to have desired electronic, optical, or other properties. This review summarizes recent efforts in the designed syntheses of oligomeric and polymeric systems and the systematic exploration of structure-property relationships.

Keywords: carboranes; metallacarboranes; multidecker sandwiches; metallopolymers; metallooligomers; metallaboranes

I. INTRODUCTION

The search for new classes of materials having useful electronic, magnetic, optical, or other properties based on small-molecule precursors has spurred interest in polyhedral boron compounds, especially those containing metal atoms bound into the skeletal framework.[1] The metallacarboranes in particular are attractive candidates for use as building-blocks in this area, because of their intrinsic stability and their ability to incorporate virtually all of the transition metals and most of the main-group metals.[1c-g] Of special interest are the small metallacarboranes – polyhedral cages having no more than 6 or 7 vertices – owing to their very close steric and electronic relationship to the metallocenes. While the larger metallacarborane systems typically feature cages of 12 or more vertices that have no structural counterparts in metal-hydrocarbon chemistry,[1c] the small metallacarboranes can function as direct subrogates of their metallocene analogues. In these compounds, pyramidal-shaped *nido*-$RR'C_2B_4H_4^{2-}$ or cyclic planar $RR'C_2B_3H_3^{4-}$ ligands (Figure 1) formally replace $C_5H_5^-$ or $C_5Me_5^-$ in transition metal sandwich and half-sandwich complexes, leading to substantially altered electronic and other properties.[1c-e,g,2] Largely owing to electron-delocalization within the cage, the metallacarboranes exhibit higher oxidative stability than their metallocene counterparts; they also show remarkable synthetic versa-

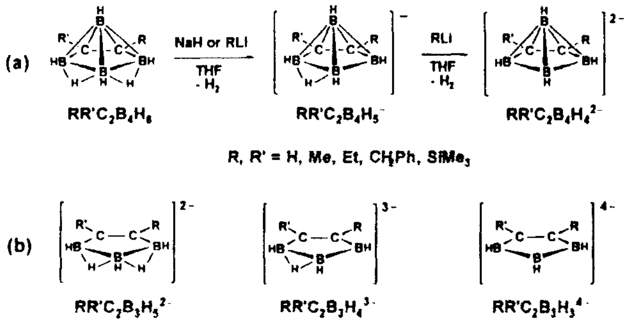


FIGURE 1. (a) Generation of small carborane ligands $RR'C_2B_4H_5^-$ and $RR'C_2B_4H_4^{2-}$ via deprotonation of *nido*-$RR'C_2B_4H_6$. (b) cyclic planar $RR'C_2B_3H_n^{n-7}$ ligands (n = 3-5). All of the C_2B_3 and C_2B_4 ligands are formal 6-electron donors to metals, analogous to $C_5H_5^-$.

tility, including an ability to form multidecker sandwiches and other extended metal sandwich structures.[1e,g]

The development of systematic methods for derivatizing, linking, and stacking small metallacarboranes[3] has opened possibilities for creating designed nanostructured molecular materials having specific desired properties.

II. MONONUCLEAR COMPLEXES

The synthesis of small monometallacarboranes containing C_2B_4 ligands may be accomplished in several ways, depicted in Figure 2. These include direct complexation of an anionic carborane ligand with a metal reagent and the preparation of iron complexes via displacement of a cyclooctatriene ligand from neutral $(\eta^6\text{-}C_8H_{10})Fe(RR'C_2B_4H_4)$ complexes.[3] Removal of the apex boron atom from C_2B_4 complexes via base attack ("decapitation") affords open-faced metal-C_2B_3 compounds that play a central role in the synthesis of multidecker and other extended systems.[1e,g]

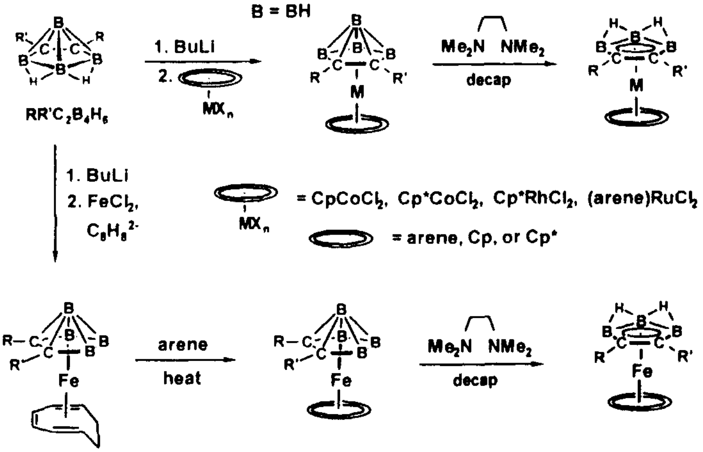


FIGURE 2. Synthesis of mononuclear metallacarborane complexes ($Cp = \eta^5\text{-}C_5H_5$; $Cp^* = \eta^5\text{-}C_5Me_5$).

The R and R' substituents on the carborane carbon atoms can be varied by methods described elsewhere,[1e,g] and the hydrogens attached to the equatorial boron vertices can be replaced by alkyl, aryl, or halo substituents using controlled, regiospecific reactions.[3] Placement of substituents at the apex boron is more difficult, but can be achieved via insertion of B-X monoboron fragments into the open faces of metal-C_2B_3 complexes[4] as shown in Figure 3.

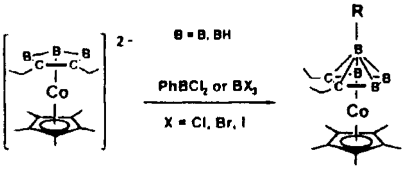
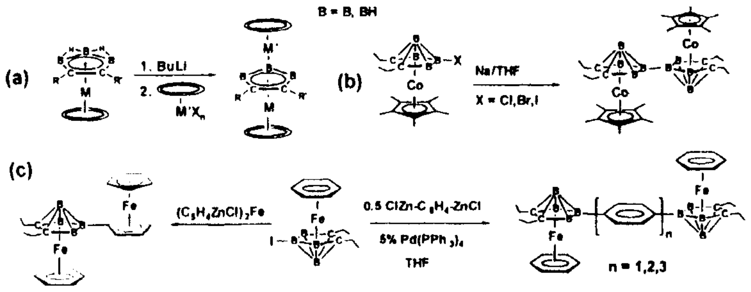


FIGURE 3. Synthesis of apically-substituted Cp*Co(2,3-$Et_2C_2B_4H_3$-7-R) derivatives via boron insertion (recapitation).[4]

III. DINUCLEAR COMPLEXES

A variety of structural classes of dimetallic metallacarboranes are accessible from mononuclear complexes, as illustrated in Figure 4. The main synthetic routes include (a) metal stacking reactions,[3,5] (b) Wurtz-type B-B linkage,[6] (c) metal-catalyzed B-B(C) coupling,[7] (d) boron insertion,[4] (e) metal-metal bond formation,[8] and linkage via metal-bound hydrocarbon ligands (f and g).[7,9] Oxidation or reduction of these systems generates mixed-valence species that serve as excellent probes for studying metal-metal communication;[2] in addition, the "double-ended" bifunctionality of some types (*e.g.*, e, f, g and their substituted derivatives), allows the construction of metallooligomers and polymers via metal stacking reactions.[1e,g,5,10]



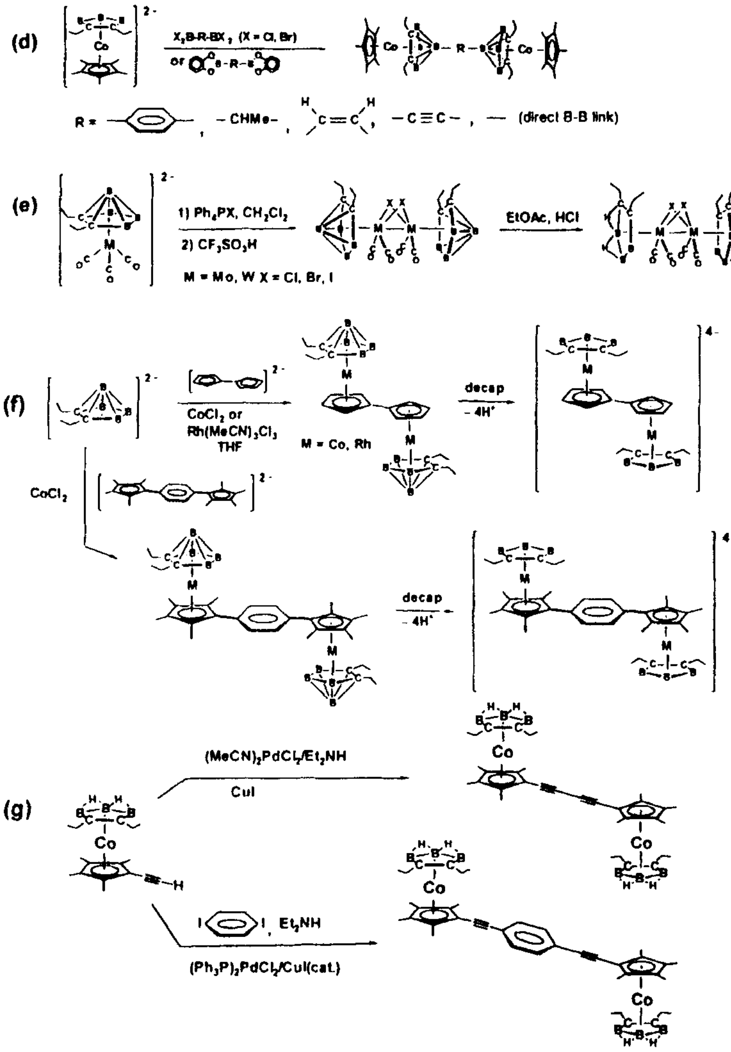


FIGURE 4. Synthesis of some classes of dinuclear metallacarboranes: (a) triple-decker sandwiches,[3] (b,c) linkage at equatorial borons,[6,7] (d) linkage at apical borons,[4] (e) linkage via bridged metal-metal bonds,[8] (f) fulvalene- and polycyclic hydrocarbon-linked complexes,[9] (g) alkynyl-linked complexes.[7]

IV. POLYNUCLEAR SYSTEMS

Figure 5 outlines in schematic form several target classes of metallooligomers and metallopolymers to be constructed from small metallacarborane mononuclear and dinuclear precursors.

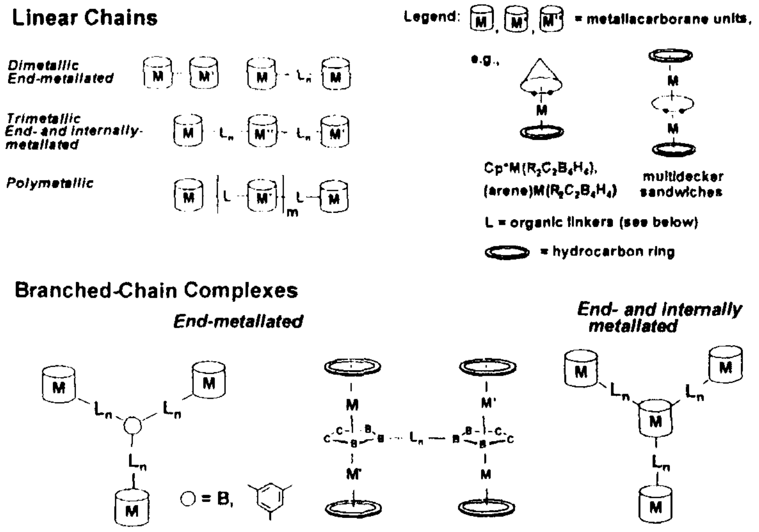


FIGURE 5. Current synthetic objectives in polynuclear metallacarborane chemistry.

Recent progress in this area has been achieved on several fronts. For example, multidecker sandwiches having up to six decks[1a,5] (currently the largest molecular polydeckers known) have been prepared and structurally characterized (Figure 6), and soluble, electron-delocalized oligomers based on fulvalene-connected tetradecker sandwich units (Figure 7) have been synthesized and isolated.[10] A useful approach that is currently under exploration combines metallacarborane and transition-metal organometallic synthetic methodologies, as in our efforts to construct alkynyl-linked polymetallacarborane systems (Figures 8 and 9).[7] More ambitious targets, not shown, include triangulated sheet polymers to be assembled from trigonally symmetric metallacarborane precursors.

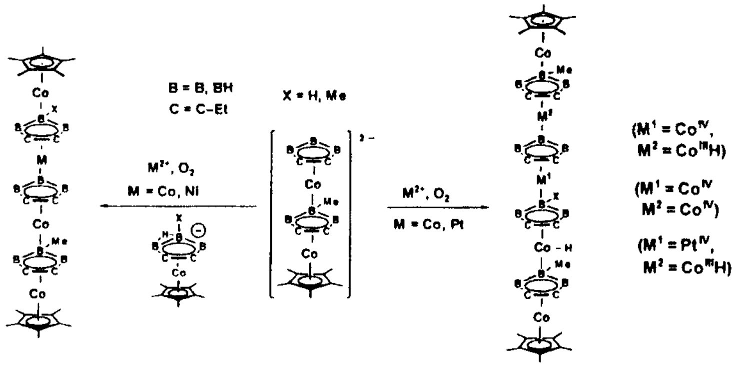


FIGURE 6. Synthesis of pentadecker and hexadecker metallacarborane sandwich complexes.[5]

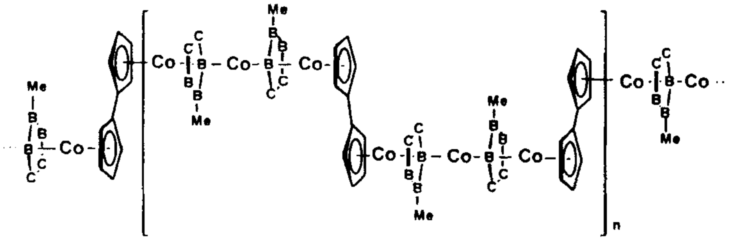


FIGURE 7. Hexane-soluble phenylene-linked tetradecker sandwich oligomers.[10]

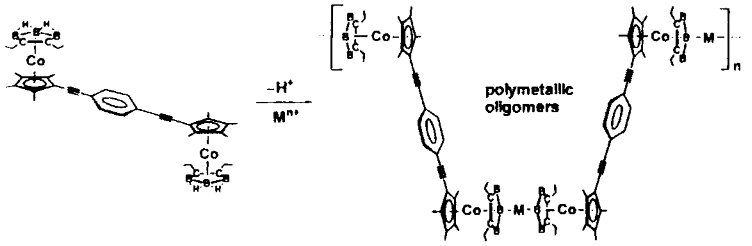


FIGURE 8. Route to alkynylphenylene-linked oligomers and polymers, studies in progress.

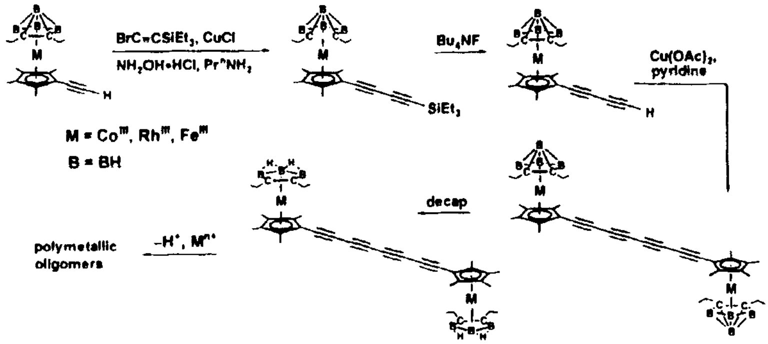


FIGURE 9. Route to polyalkynyl-linked oligomers, in progress.

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