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Metallacarboranes in the new millennium

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Contents

Abstract

The field of metallacarborane chemistry has grown in many different directions and now interfaces with several other disciplines including metal cluster and organometallic chemistry, transition-metal catalysis, materials science, environmental science, and biomedical applications. In this turn-of-the-century overview, some of the more significant recent developments and trends in this area are selectively examined and an attempt is made to project some useful directions in which this chemistry might develop over the next decade or two. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Metallacarboranes; Carborane ligands; Milennium

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1. Background and perspective

Metallacarboranes originated some 35 years ago in the laboratory of M.F. Hawthorne when polyhedral borane chemistry and transition metal organometallics — two areas that could hardly have seemed more dissimilar at that time — were effectively joined by the preparation and structural characterization of the first metal–carborane sandwich complexes [1]. Since then, researchers from a variety of scientific backgrounds have developed this field into a major subdiscipline of inorganic and organometallic chemistry [2], with significant application (actual and potential) in environmental chemistry, organic synthesis, medicine, and materials science [3]. Metallacarboranes have long since become standard fare in inorganic texts at the graduate and undergraduate level, and the area is reviewed frequently in journals and periodicals. Despite this attention, it is fair to ask whether metallacarborane chemistry has reached a plateau of sorts, with the main discoveries already behind us. Are the prospects of significant advances sufficient to justify further exploration as we enter the next century? As far as this reviewer is concerned the answer is Yes, for three reasons. First, the stable existence and properties of metallacarboranes — above all, their unparalleled versatility — continue to highlight important issues of structure, bonding, and reactivity that have relevance to other areas of chemistry. Second, as has already been mentioned and is further discussed below, metallacarboranes are finding unique and growing application in diverse areas of contemporary science and technology. And third, metallacarborane chemistry is still generating novel and unexpected discoveries with a regularity that is remarkable for a field as seemingly mature as this one. In short, despite its approaching middle age this area of science still offers a rich lode of new chemistry to be explored and developed.

In this somewhat free-ranging review I will make no attempt to be comprehensive (that would require many times more space than even the most generous editor would allow), nor will I focus on any one aspect of the field or look only at the most recent developments. Rather, I will try to convey a sense of the current state of affairs in this area of chemistry (the easier job) and to offer some thoughts on worthwhile synthetic targets for the new millennium — a much harder task, because of future discoveries of which we have no inkling at present.

Some basic information may be useful to readers who are not regular followers of the polyhedral borane literature. Carboranes (a contraction of the IUPAC term carbaborane) are molecular boron clusters that contain at least one carbon atom bound into an electron-delocalized ‘nonclassical’ cage skeleton, and metallacarboranes are carboranes having at least one metal atom present in, or associated with, the cage framework. A remarkable fact that dramatically underlines the breadth of this area, is that almost all of the metallic and metalloid elements in the Periodic Table (excluding the actinides) are represented in the family of isolated and characterized metallacarboranes. Moreover, the replacement of one or more boron atoms by other nonmetals such as O, S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn and Pb further expands the range of stable compositions, as does the fact that one can vary the number and locations of cage carbon, metal, and other heteroatom vertices in the cluster [2a].

Structurally, most metallacarborane clusters are either closed polyhedra having triangular faces (deltahedra) and labeled with the prefix *closo*, or are fragments of deltahedra in which one or more vertices are absent. Thus, *nido* and *arachno* clusters have respectfully one and two vacant vertices; for example, a complete 6-vertex octahedron is *closo*; removal of one of its vertices yields a 5-vertex *nido* square pyramid; and elimination of another vertex generates a 4-vertex *arachno* cluster that can have either a square planar or a butterfly shape depending on which vertex is removed. Alternatively, metallacarboranes can also be viewed as metal sandwich complexes in which a metal ion is facially coordinated to a carborane ligand via, for example, η^5- or η^6- binding analogous to metal–C_5R_5 interactions in metallocenes. In most cases the metal–carborane binding is strong, and separation of the ligand from the metal is rarely observed. The electron-delocalized bonding in these compounds, which is adequately represented only in terms of molecular orbital descriptions, has a powerful stabilizing influence. Thus, both high and low formal metal oxidation states are 'tamed' since the effects of oxidation or reduction at the metal center are mitigated via distribution over the cage skeleton. As a consequence, metallacarboranes more often than not are robust, air-stable crystalline compounds that can be handled in common solvents.

Known and characterized metallacarboranes vary in size from 4 to 14 vertices in a single polyhedral framework; much larger multicage systems can be assembled by fusion or linkage of two or more units [4]. The so-called 'icosahedral barrier', which has so far precluded the synthesis of individual boron-based molecular clusters having more than 12 vertices, does not apply to metallacarboranes, which feature a number of 13-vertex and a few 14-vertex polyhedra [2a,b]. However, the majority of known metallacarboranes contain C_2B_3, C_2B_4, or C_2B_9 ligands (Fig. 1), all of which normally function as formal 6-electron donors to metal atoms via η^5-face bonding (electron-rich metals may bond to the face in a slipped fashion wherein the hapticity is reduced to η^4, η^3 or η^2). The planar $R_2C_2B_3H_5^{2-}$ and $R_2C_2B_3H_3^{4-}$ rings readily

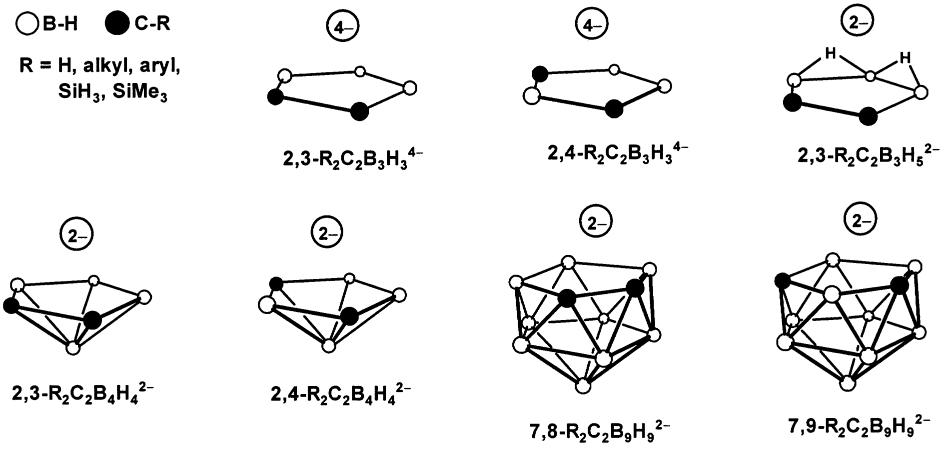


Fig. 1. Some common carborane ligands found in metallacarboranes, with formal charges.

bind to one and two metals respectively, generating in the former case 6-vertex *nido*-MC_2B_3 clusters, and in the latter case *closo*-$M_2C_2B_3$ multidecker sandwich systems [2,5]. Coordination of the isomeric 7,8- and 7,9-$R_2C_2B_9H_9^{2-}$ (dicarbollide) ligands to metal centers creates *closo*-MC_2B_9 icosahedral clusters. More detailed discussion of this topic can be found in numerous review chapters and books [2].

These (and most other) metallacarboranes are qualitatively similar to the metallocenes in terms of electronic structure, but two differences are immediately obvious: their multinegative carborane ligands vs. singly charged $C_5R_5^-$ ligands in metallocenes, and the heterocyclic nature of the C_2B_3 bonding faces in the carborane fragments. Also important is the greater covalent character in metal–carborane versus metal–hydrocarbon binding, owing to the lower electronegativity of boron relative to carbon that results in an intimate involvement of the metal center in the electron-delocalized cage system.

Fig. 1 depicts what might be called the ‘classic’ carborane ligands since their metal complexes, including C- and B-substituted derivatives, comprise the vast majority of the thousands of characterized metallacarboranes. However, many interesting and useful variations on these ligands are known, as indeed are some entirely different systems. For example, the number of cage carbon atoms can range from one to five; additional metals can be introduced to the cluster; the location of carbon atoms and metal atoms in the skeletal framework can be varied; other main-group heteroatoms can be placed in the framework; and a wide variety of organic and inorganic substituent groups can be placed on the cage at boron and/or carbon positions [2,5]. In addition, the metal center(s) may have other bound ligands in addition to the carborane; in some cases a metal atom may be simultaneously part of a metallacarborane cage and a metal cluster system, as will be shown.

This article generally excludes other classes of complexes that are closely related to the metallacarboranes, including externally metallated carboranes (in which the metal resides outside the cage), metallaboranes (which lack cage carbon atoms), and metal π-complexes of planar organoborane ligands [6] such as borabenzene, borole, and diborolyl, which constitute a fascinating field of study in their own right. Of course, the versatility of carborane chemistry is such that hybrid complexes abound, in which metallacarborane moieties are combined with other metallo classes in the same complex. The next section highlights a selection of recent developments that have advanced the frontiers of metallacarborane chemistry into new regions.

2. Pushing the envelope: some recent advances

2.1. New molecular architectures and ligands

Discoveries of previously unknown structural modes are of interest in two respects: they open up new possibilities in synthesis, and they broaden our notions of what may constitute a stable bonding arrangement. A case in point is the zinc–carborane dimer **1** (Fig. 2) [7], a crystalline solid that is novel in both its

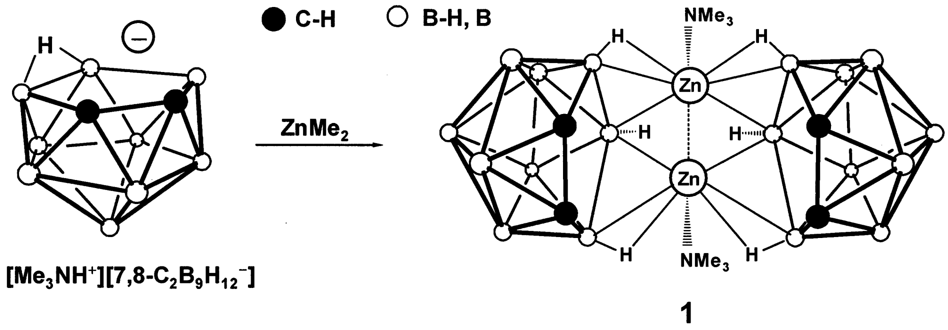


Fig. 2. Synthesis and structure of $[(nido\text{-}C_2B_9H_{11})ZnNMe_3]_2$ (**1**) (ref. [7]).

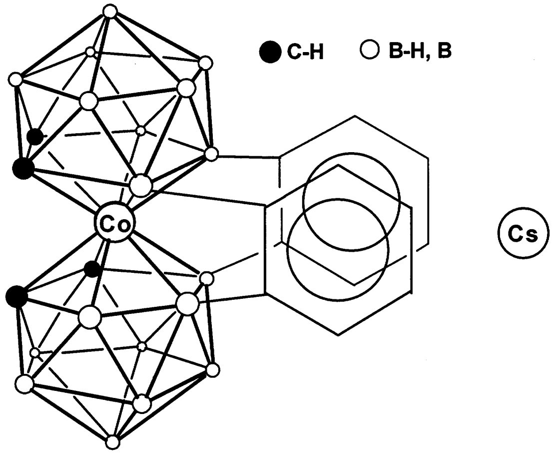
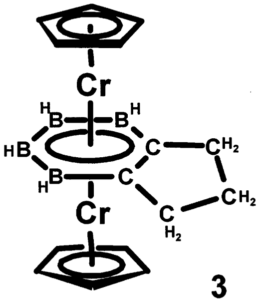


Fig. 3. Structure of [3-Co-4,8’-8,4’(*o*-$C_6H_4)_2(1,2\text{-}C_2B_9H_{11})_2]^-$ (**2**) (ref. [8]).

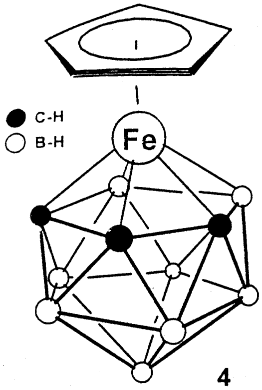
composition — as the first characterized zincacarborane — and in its structure. Its highly unusual planar, diamond-shaped Zn_2B_2 arrays contain octacoordinate zinc and heptacoordinate boron vertices, with the zinc atoms weakly bonded to each other (separation 2.800(1) Å) and to boron and hydrogen atoms in the cages via 3-center B–Zn–B interactions. Compound **1** may be the prototype of a new class of dimeric M_2-bridged dimetallacarborane complexes involving electron-rich metals. The relative rigidity of such structures might permit their use as scaffolds on which functional groups could be attached to the four cage carbons, enabling the design of reagents for organic synthesis having a high degree of steric selectivity.

A second example of architectural novelty that has recently come to light via X-ray crystallography [8] (although the compound itself was first prepared more than two decades ago [9]) is the bis(phenylene)-linked cobalt dicarbollyl sandwich [3-Co-4,8′-8,4′(*o*-$C_6H_4)_2(1,2\text{-}C_2B_9H_{11})_2]^-$ (**2**) shown in Fig. 3. While there are many examples of bis(C_2B_9) metal complexes in which the two carborane ligands are bridged by an exo-polyhedral atom or group (vide infra), this compound is the first deltahedral metallacarborane to be shown to have *two* such interligand bridges. Complex **2** is formed in 40% yield as a side product in the synthesis of the mono-8,8-phenylene-bridged species (a long-known compound [9]) in the reaction of $3\text{-Co-}(1,2\text{-}C_2B_9H_{11})_2^-$ Cs^+ with excess benzene. The formation of this complex was surprising because of the difficulties in introducing even one phenylene linker, and because its color and NMR spectra did not point to a doubly bridged species [8]. It has been suggested that its formation involves via a primary intermediate in which a Cl_2Al^+ moiety binds to the carborane cage via a B–H–Al interaction, whose disproportionation generates the observed mono- and diphenylene-bridged products [8].



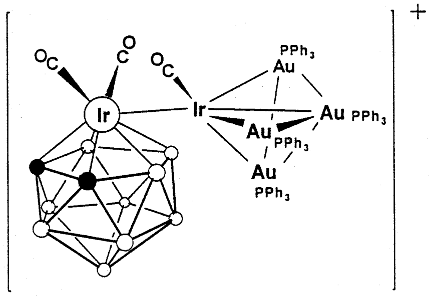
3

Another structurally novel metallacarborane is the 8-vertex dichromium triple-decker complex **3**, obtained serendipitously [10] in an attempted metallaborane synthesis wherein a $C_5H_5^-$ unit was incorporated into the cage framework, reminiscent of an earlier dicobalt 'fused-ring' triple-decker prepared in our group [11]. The novel feature of **3** is its hexagonal bipyramidal cluster structure, not previously seen in metallacarborane chemistry (although it is common in organoborane complexes containing planar C_4B_2 or C_5B rings [12]) and distinct from the normal 8-vertex polyhedra commonly found in polyhedral boranes. The cluster has only 24 valence electrons, in contrast to the 30 electrons typical of stable triple-decker sandwiches, and has been formulated as a pair of $CpCr^{III}$ moieties bridged by a 6π $R_2C_2B_4H_4^{4-}$ planar ring (isoelectronic with benzene) [10].



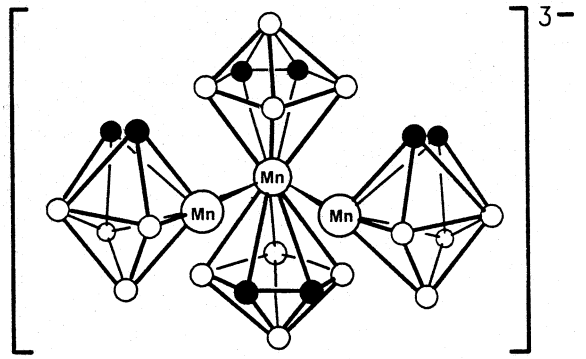
4

Tricarbon metallacarboranes (metallatricarbaboranes) represent another area of significant recent advances. These compounds contain ligands having the general formula $C_3B_nH_{n+3}^-$ that, because of their mononegative charge, are formally interchangeable with $C_5H_5^-$ (Cp); thus complexes such as $(C_3B_8H_{11})_2Fe^{II}$ and $CpFe^{II}(C_3B_8H_{11})$, for example, are isoelectronic neutral analogues of ferrocene. Although small tricarbon metallacarboranes were prepared in our group many years ago [13], the recent syntheses of 12-vertex icosahedral complexes [14] such as $CpFe(C_3B_8H_{11})$ (**4**), and of 10- and 11-vertex tricarbon systems [15] like $LM(MeC_3B_7H_9)$ [LM = CpFe, $(CO)_3Mn$, CpNi] and $(MeC_3B_7H_9)_2Fe$, are of considerable interest. The direct relationship of these compounds to metallocenes suggests possible application in areas such as catalysis and medicine; for example, some tricarbon metallacarboranes exhibit cytotoxicity toward certain strains of cancer cells [16] (this topic is discussed further in Section 2.4).



5 ● C-CH$_3$ ○ B-H

Among the more intriguing subclasses of metallacarboranes are those containing intercluster metal–metal bonds, which effectively bridge the two largest and most heavily developed areas of inorganic cluster chemistry, the polyhedral boranes and the metal clusters. Only rarely are such compounds obtained via designed synthesis; mostly they are generated in exploratory reactions, isolated via column chromatography, and characterized by spectroscopic techniques and X-ray diffraction. Stone and his colleagues have published extensively in this field [2a,b,17], reporting hundreds of structurally novel complexes in which 12- or 13-vertex metallacarborane cages are covalently bound to metal cluster moieties (which for purposes of this discussion we define as two or more metal atoms bonded together). A case in point is the iridium–gold cationic complex **5** in which an IrC_2B_9 icosahedron is connected to an $IrAu_4$ cluster by an Ir–Ir bond [18].



6 ● C-SiMe$_3$ ○ B-H

Examples of multimetal clustering can be found throughout metallacarborane chemistry, as in some of the d-block and f-block metal complexes of the $(SiMe_3)_2C_2B_4H_4^{2-}$ ligand explored by Hosmane and Maguire and their coworkers [19]. The trimanganese trianion **6** is an interesting mixed-valence system containing four dinegative carborane units and an Mn_3^{5+} open triangle, charge-balanced in the solid lattice by three Li^+ ions (not shown) [20]. In contrast, polylanthanide complexes of this ligand typically feature well-separated metal centers [19,21].

Metal–metal bonded arrays stabilized by carborane ligands are of current interest as candidate synthons for constructing multimetallic oligomers and polymers. Typical geometries are depicted in complexes **7a**, **7b**, **8** and **9** in Fig. 4, whose common feature is the presence of transition metal centers linked by a third metal (**7**) [22] or directly bonded to form an intercage metal–metal connection as in **8** and **9** [23,24].

The red–orange air-stable halogen-bridged dimers **9** were synthesized as shown in Fig. 5 and characterized via NMR spectroscopy. X-ray diffraction data on the Mo_2Br_2 species revealed an Mo–Mo distance of 2.961(3) Å, corresponding to a single bond. Decapitation of this complex afforded the red sandwich **10** [24], whose distinguishing characteristic is its open carborane faces at both ends of the molecule; following bridge-deprotonation, these faces may undergo linear stacking with metal or boron centers to create rigid rod polymers (vide infra).

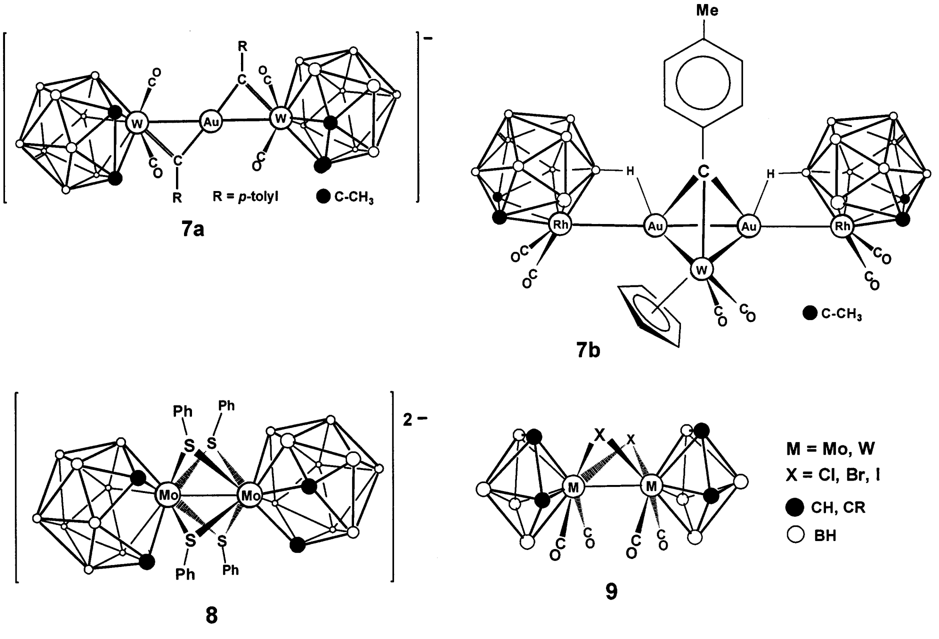


Fig. 4. Structures of $\{[W(CO)_2(\mu\text{-}CR)(Me_2C_2B_9H_9)]_2Au\}^-$ (**7a**) (ref. [22a]), $Cp(CO)_2W(\mu\text{-}CC_6H_4Me)[AuRh(CO)_2(Me_2C_2B_9H_9)]_2$ (**7b**) (ref. [22b]), $[(C_2B_9H_9)Mo(SPh)_2]_2^{2-}$ (**8**) (ref. [23]), and $[(Et_2C_2B_4H_4)M(CO)_2(\mu\text{-}X)_2$ (**9**) (ref. [24]).

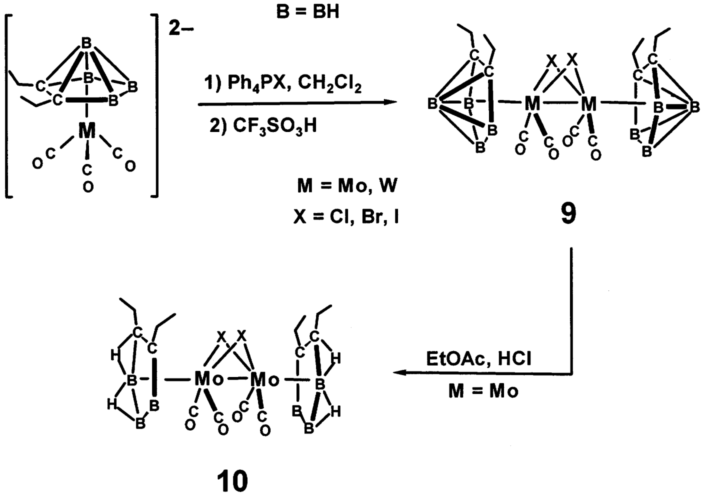


Fig. 5. Synthesis of the metal–metal bonded dimers **9** and conversion of the Mo–Mo species to the decapped complex **10** (ref. [24]).

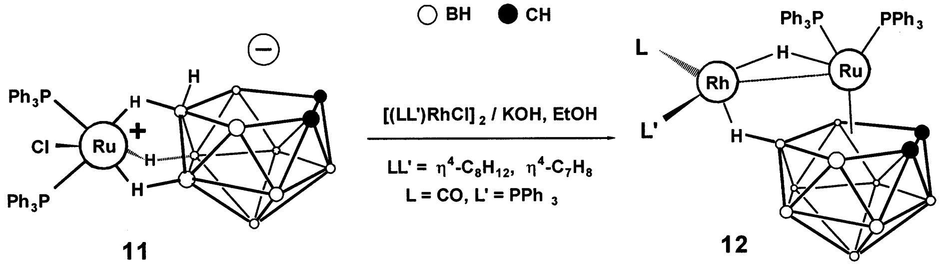
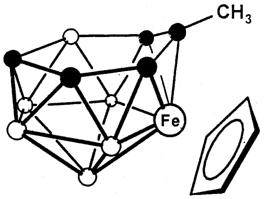


Fig. 6. Synthesis of mixed-metal Rh–Ru metallacarboranes from an exo-nido ruthenium–carborane anion (ref. [25]).

Another recent development involving dinuclear metallacarboranes is the synthesis of mixed-metal Rh–Ru complexes of type **12** from exo-nido-ruthenacarboranes **11** as shown in Fig. 6 [25]. This work represents a significant extension of earlier investigations by Hawthorne [26] and by Stone [17] on low-nuclearity metallacarborane systems containing 12-vertex RhC_2B_9 clusters, in that the ruthenium rather than rhodium is incorporated into the cage and an exo-polyhedral heterometallic interaction is created between the formal 18-electron Ru(II) and 16-electron Rh(I) centers. However, extended Hückel calculations on a model complex system similar to 12 indicate a small Ru–Rh bond order (ca. 0.025) and suggest that the Rh–Ru interaction is best described in terms of a pair of 2-center, 3-electron bonds (B–H–Rh and Ru–H–Rh) rather than a direct 2-electron metal–metal bond [25].



13

The borderline area between metal–hydrocarbon complexes and polyhedral metallaboron clusters is one of far-reaching theoretical significance, but experimental studies in this area have been hampered by the paucity of carbon-rich metallacarboranes. Until recently, no species having more than four carbon atoms [2,27] in a skeletal borane framework were known, but the synthesis and structural characterization [28] of the first pentacarbon metallacarborane, 2,7,8,9,10,12-CpFe($MeC_5B_6H_{10}$) (**13**), has effectively broken this barrier. The 13-vertex cage has 28 skeletal electrons (1 from the CpFe, 2 each from the six BH units, and 3 from each carbon) and adopts a nido geometry based on a 13-vertex closo docosahedron with one vertex removed, thus satisfying the requirements of Wade's Rules [2b] for clusters. Thus we see that the structural principles of polyhedral borane structures are adhered to even when the carbon content of the cage approaches 50%, a finding that provokes the question: at what point of increasing C/B ratio do these principles begin to fail? Eventually, high-level theoretical studies of metallacarborane systems may help to resolve this issue, but in the near term progress will most likely come about through further ground-breaking experimental efforts, and no doubt fortuitous discovery.

In addition to carbon-rich cages, new developments in the area of monocarbon metallacarboranes are also noteworthy, although for quite different reasons. The monocarbon electronic analogue of the dicarbollide anion ($C_2B_9H_{11}^{2-}$) is $CB_{10}H_{11}^{3-}$ (monocarbollide) whose trinegative charge allows it to form neutral sandwich compounds that are isoelectronic with cationic dicarbollide complexes, for example (arene)Fe^{III}($CB_{10}H_{11}$) versus [(arene)Fe^{III}($C_2B_9H_{11}$)]$^+$. This opens up new possibilities in the design of metallacarborane reagents for organic synthesis, especially in catalysis. Stone's group, for example, has prepared a series of novel rhodium monocarbollide charge-compensated complexes [29] (see below) in which an amino sub-

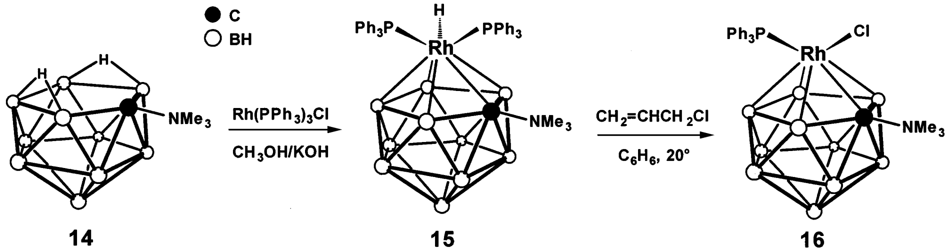
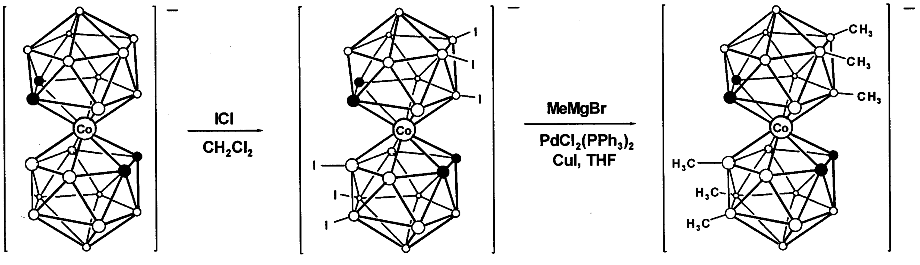


Fig. 7. Synthesis of an 18-electron rhodium monocarbollide complex **15** and conversion to a 16-electron complex **16** (ref. [30]).

stituent on the cage lowers the charge on the monocarbollide ligand from -3 to -2; examples include (arene)Rh($NHBu^t$-$CB_{10}H_{10}$) wherein the arene is C_6H_5Me, 1,3,5-$C_6H_3Me_3$, or [22]-1,4-paracyclophane [29a]. Another illustration of this approach is afforded by the work of Chizhevsky, et al. [30], who prepared the hydridorhodacarborane **15** (an 18-electron complex) and converted it to the 16-electron species **16** as shown in Fig. 7. Detailed NMR studies reveal that **15** exists in solution as a mixture of two conformers, both having C_s symmetry, in which the hydrido ligand occupies cis and trans locations, respectively, relative to the cage carbon atom. Using the same rhodacarborane system, Pisareva et al. have synthesized the first η^2-olefinic monocarbon metallacarborane [31], a species having a bis(propenyl)amino substituent whose N atom is bound to the carborane carbon while one of its C=C groups occupies an η^2 coordination position on the rhodium.

2.2. *New approaches to synthesis and derivitization*

Virtually all actual and projected applications of metallacarboranes require substituted derivatives in which organic or inorganic functional groups are introduced to the metal or the carborane framework; this in turn makes it essential to develop practical and efficient methods for derivatization [32]. One of the recent significant advances in this area is the hexa-B-methylation [33] of the bis(dicarbollyl)cobalt(III) anion, depicted in Fig. 8, that utilized a palladium-catalyzed cross-coupling B-alkylation reaction originally demonstrated by Zakharkin et al. in 1,2-$C_2B_{10}H_{12}$ [34]. The $Co(C_2B_9H_{11})_2^-$ parent ion **17** is an extremely stable species that resists degradation at high temperatures, attack by acids and bases, γ-ray irradiation, and degradation in vivo, attributes that make it a candidate for application in removal of radioactive isotopes and in radioimaging agents for medicinal use (further discussed below). In addition, this ion has the rather remarkable property that its salts are easily extractable from water into organic solvents, and moreover is only weakly coordinating to cations. However, the ion does slowly degrade in the presence of concentrated nitric acid, which limits its utility in radionuclide extraction. This is prevented by replacing the BH hydrogens at B8, B9, and B12 by methyl groups via iodination followed by reaction with a Grignard reagent, as shown in Fig. 8 [33].



17 **18** **19**

Fig. 8. Halogenation and methylation of the bis(dicarbollyl)cobalt(III) anion **17** (ref. [33]).

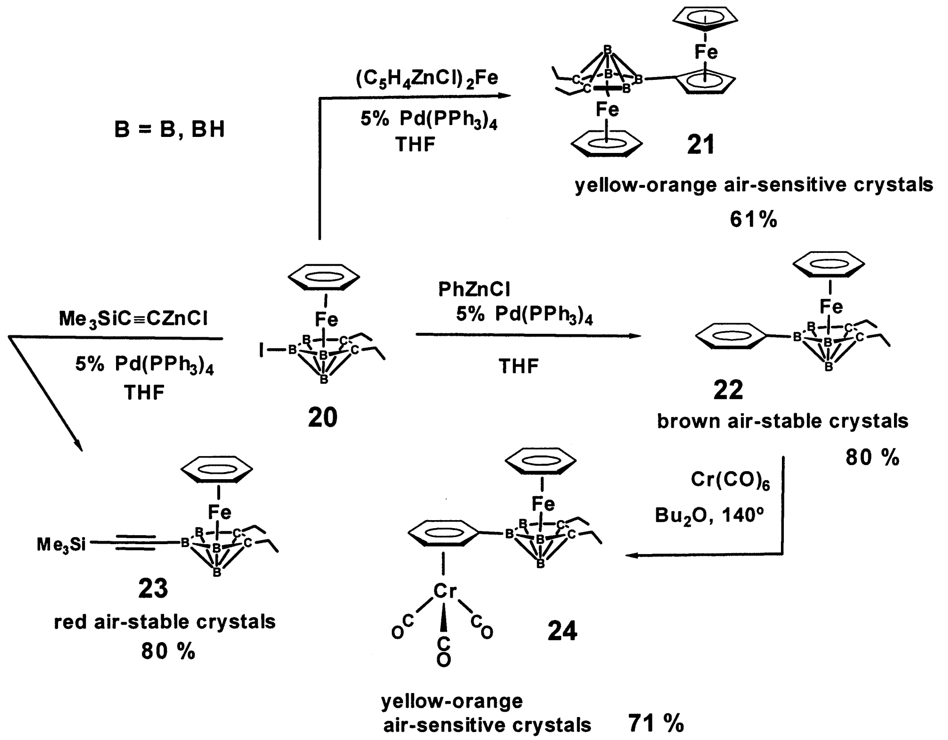
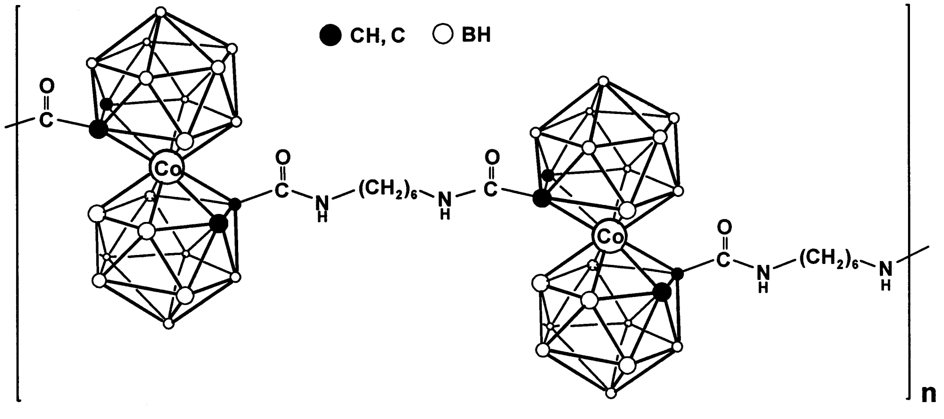


Fig. 9. Synthesis of B-organosubstituted ferracarboranes via Pd-catalyzed reactions of $(C_6H_6)Fe(Et_2C_2B_4H_3\text{-}5\text{-}I)$ (ref. [36]).

Palladium-catalyzed cross-coupling can also be used to effect aryl substitution at boron, as shown in the recent preparation of 3,1,2-$CpCo(C_2B_9H_{10}\text{-}9\text{-}Ph)$ [35]. Very recently, we have applied this method in the synthesis of B-organosubstituted small metallacarboranes (Fig. 9) [36]; as can be seen, this approach offers broad versatility.



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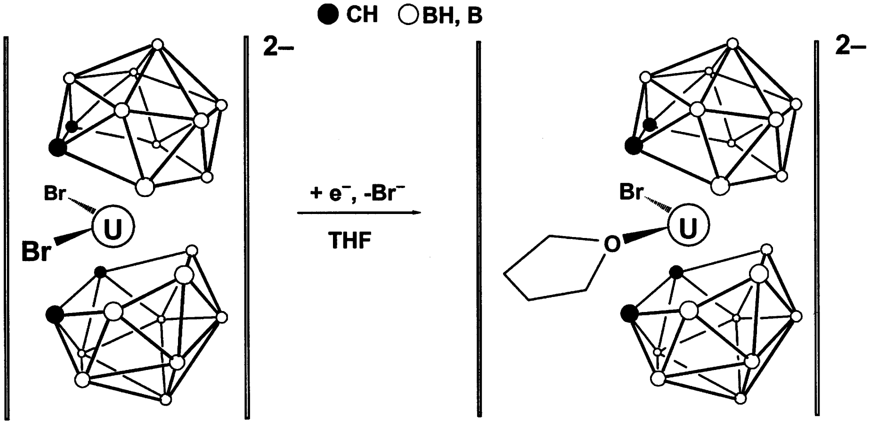
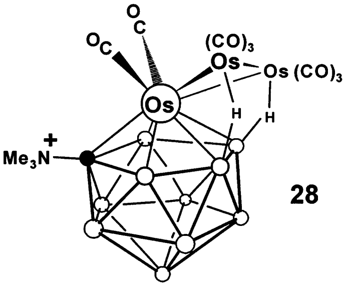


26 **27**

Fig. 10. Reductive interconversion of bis(dicarbollyl) uranium complexes (ref. [38b]).

The $Co(C_2B_9H_{11})_2^-$ anion has been employed in the synthesis of a novel amido-connected oligomer **25** via condensation polymerization of a C,C′-$(COCl)_2$ derivative of **17** with $H_2N(CH_2)_6NH_2$ [37]. Metallooligomers of this type are of interest as precursors to metal-containing polymers whose electronic, optical, and other properties are controlled by the metal centers.

Another recent illustration of the versatility of the dicarbollide ligand is given by the preparation of a family of uranium complexes [38] including **26** (Fig. 10), a U(IV) species which undergoes an irreversible electrochemical or chemical (Na amalgam) reduction to the U(III) anion **27** in the presence of THF [38b]. The electrochemical behavior of **26** differs from that of $Cp_2^*UCl_2$, whose reduction to the U(III) anion is completely reversible; in contrast, the reduction of **26** is evidently accompanied by a substantial molecular rearrangement [38b].



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The concept of charge-compensation, mentioned in the preceding section, is assuming increasing importance as a synthetic tool. The basic idea is that dicarbollide $(C_2B_9H_{11}^{2-})$ and other dinegative carborane ligands can be rendered mononegative like Cp^- by formal replacement of a terminal hydrogen atom on the cage with a positively charged substituent such as SMe_2^+; such charge-compensated ligands can subrogate for Cp^- in metallocene analogues [29–31,39]. This allows, for example, the preparation of neutral bis(dicarbollyl) complexes of Fe(II) that are isoelectronic with ferrocene (in contrast, the uncompensated $Fe^{II}(C_2B_9H_{11})_2^{2-}$ complex is a dianion). Stone and co-workers have applied this idea to monocarbollide complexes in the synthesis of the triosmium species **28** [39a], which contains the charge-compensated $Me_3N-CB_{10}H_{10}^{2-}$ ligand, isoelectronic with $C_2B_9H_{11}^{2-}$. In this molecule each of the exo-polyhedral osmium atoms acquires a filled 18-electron valence shell via formation of a B–H–Os 2-electron, 3-center bridge bond as shown, while the cage osmium reaches its 18-electron quota via a 5-electron interaction with the carborane ligand [40] supplemented by 2e donations from the two CO groups and one electron each from the remaining metal centers.

Another synthetic approach that was first employed in carborane chemistry [41] and has now been applied to metallacarboranes [42], is boron insertion or 'recapitation', in which monoboron reagents are used to convert *nido*-MC_2B_3 open-cage complexes into apically substituted *closo*-MC_2B_4 clusters (Fig. 11). This class of

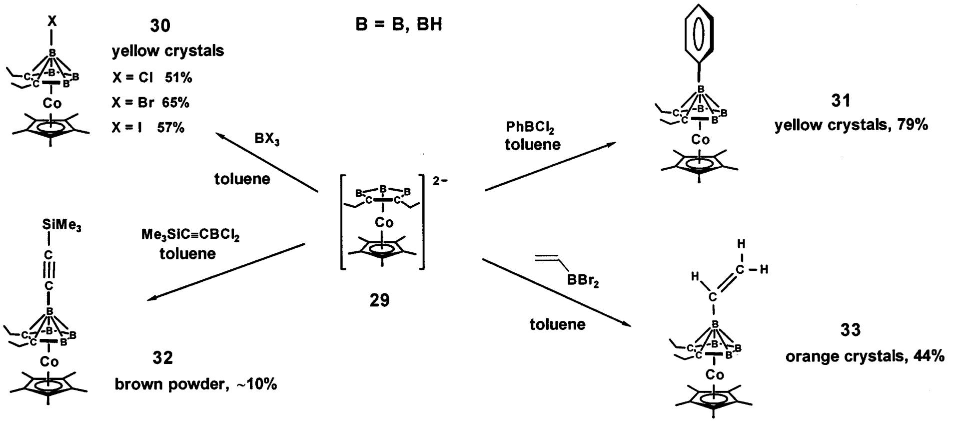


Fig. 11. Synthesis of apically substituted derivatives of Cp*Co(2,3-$Et_2C_2B_4H_6$) via 'recapitation' of *nido*-Cp*Co(2,3-$Et_2C_2B_3H_3$) $^{2-}$ (ref. [42]).

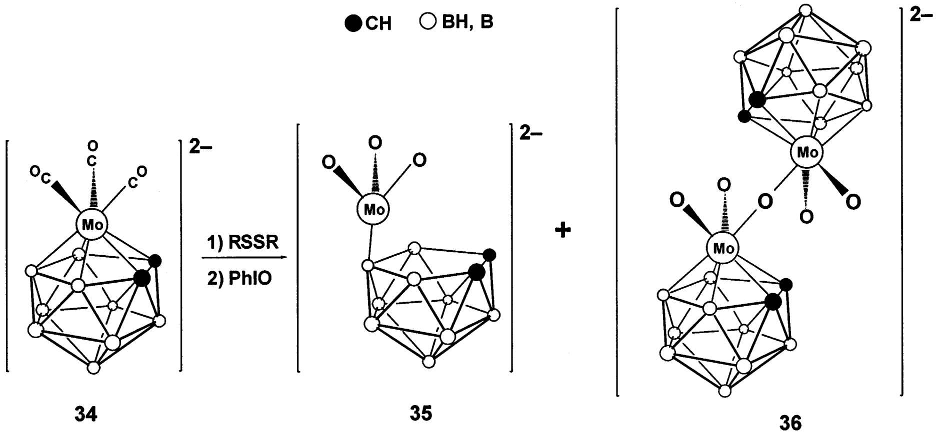
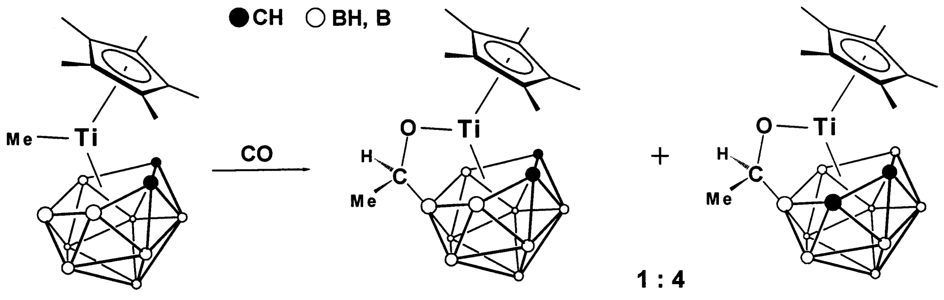


Fig. 12. Synthesis of oxomolybda(VI)carboranes (ref. [43]).



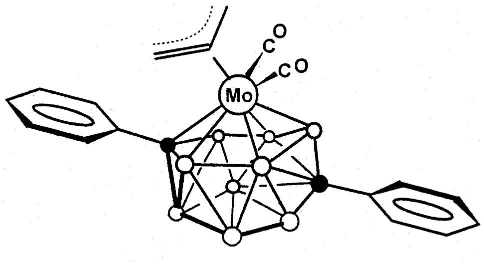
37 **38** **39**

Fig. 13. Formation of *ansa*-carborane-alkoxide complexes via insertion of CO (ref. [44]).

derivatives, previously inaccessible, may find use as precursors to linear metallopolymers (see below).

Many of the reported advances in metallacarborane chemistry also impact upon other areas of inorganic and organometallic chemistry and/or related fields such as organic synthesis, materials science, and biochemistry. An example is the preparation of the first oxomolybda(VI)carboranes by Do and coworkers [43], who found that the tricarbonyl anion **34** on treatment with diphenyl disulfide first formed $[(PhS)_2(CO)_2Mo(C_2B_9H_{11})]^{2-}$, which was reacted with an excess of iodosylbenzene to generate the trioxo anion $[O_3Mo(\eta^1\text{-}C_2B_9H_{11})]^{2-}$ (**35**) and the oxo-bridged product $\{[O_2Mo(\eta^5\text{-}C_2B_9H_{11})]_2O\}^{2-}$ (36) as shown in Fig. 12. These compounds serve to illustrate the ability of $C_2B_9H_{11}^{2-}$ and other carborane ligands to stabilize high (and low) oxidation states, an attribute that makes them potentially valuable in the synthesis of stable metal oxo complexes.

A different type of oxo-bridged complex — one that plays a significant role in the insertion chemistry of early transition metal metallacarboranes — is illustrated by the *ansa*-carborane-alkoxide species **38** and **39** which were generated from the Ti-methyl compound **37** as shown in Fig. 13 [44]. From ^{13}CO labeling experiments it is known that the exopolyhedral bridging carbon atom originates with the CO, implying that an acyl derivative (containing a Ti–C(=CO)Me group) is formed initially, this species then rearranging to **38** and **39** via net insertion of the acyl carbon into a B–H bond [44]. This process is closely related to the alkylidene insertions into dicarbollide B–H bonds studied earlier by Stone [17], and underlines the importance of B–H–M agostic interactions in organometallic metallacarborane chemistry [2c].



40

2.3. New modes of reactivity and insight into reaction mechanisms

Skeletal rearrangements of polyhedral boron clusters, including carboranes and metallacarboranes, have occupied the attention of theorists and experimentalists for many years. In the carborane field, the well-known thermal conversion of icosahedral 1,2-$C_2B_{10}H_{12}$ (*o*-carborane) to the 1,7 and 1,12 (m- and *p*-carborane) isomers is paralleled by similar rearrangements of metallacarboranes, although in the latter systems the process is complicated by the presence of metal as well as carbon heteroatoms in the cage framework [2a,b]. The mechanisms of these isomerizations are not well understood, and only in a few cases (e.g., the conversion of the triple-decker sandwich 1,7,2,3-$Cp_2Co_2C_2B_3H_5$ to the 1,7,2,4 isomer [45]) have intermediates actually been isolated. Recently Welch et al. succeeded in isolating and structurally characterizing the anionic cluster **40** as a *non-icosahedral* intermediate in the room-temperature rearrangement of icosahedral 3,1,2-$(C_3H_5)(CO)_2$-$Mo(PhC_2B_9H_{10})^-$ to its 3,1,9 isomer in which the cage carbon atoms are separated [46]. In this system the relief of steric crowding is believed to provide the main driving force for the isomerization. Intramolecular crowding is also evidently important in the rearrangement of icosahedral $L_2Ni(Ph_2C_2B_9H_9)$ isomers (L = phosphines), which involve so-called '1,2 to 1,2' isomerizations wherein the cage carbons remain adjacent to each other but one of them moves away from the metal in order to reduce the interaction between the C-phenyl groups and the phosphino ligands [47].

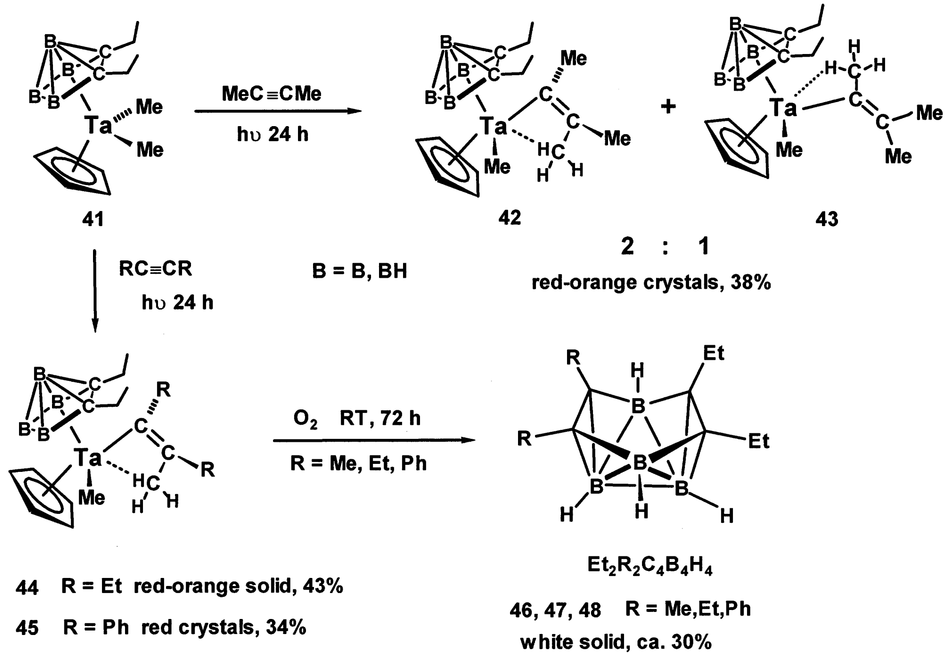


Fig. 14. Insertion of alkynes into the CpMeTa(carborane) complex **41** and formation of tetracarbon carboranes via oxidation of vinyl-Ta products **42**–**45** (ref. [49]).

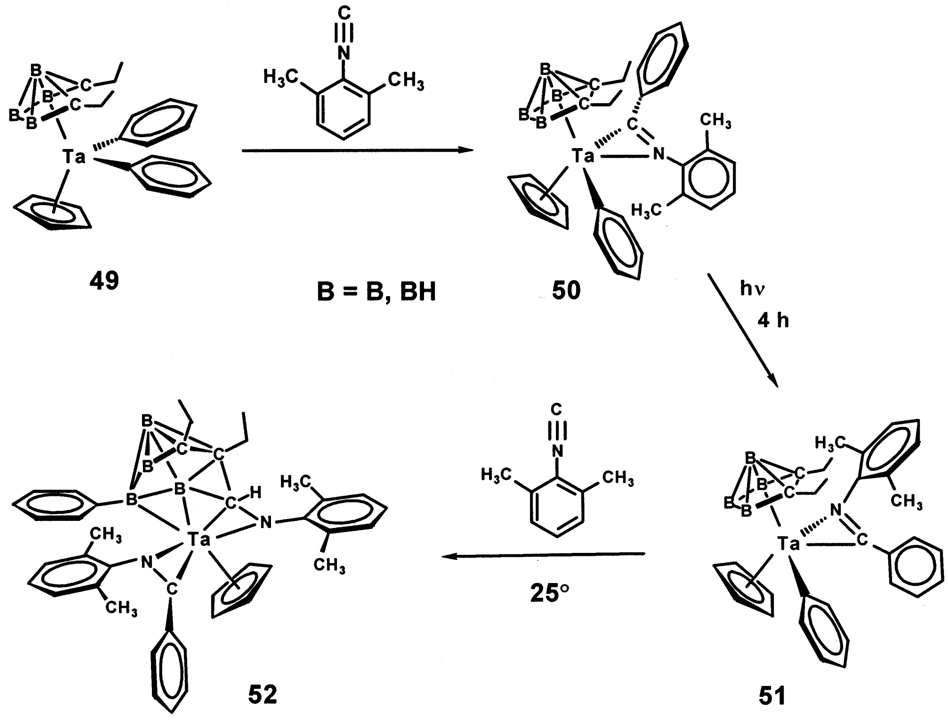


Fig. 15. Stepwise insertion of 2,6-dimethylphenylisocyanide into $CpPh_2Ta(Et_2C_2B_4H_4)$ (**49**) (ref. [52]).

Interactions of small metallacarboranes with organic substrates have been a focus of research in our group, and studies in this area have generated some unusual findings [2c]. Small metallacarboranes in general are of interest because of their very close electronic and steric relationship to Cp and Cp* metal sandwich complexes (see Section 1 of this article), especially those that promote organic reactions such as the polymerization of olefins and alkynes. In studies of alkyne insertions of tantalacarboranes such as $CpMe_2Ta(Et_2C_2B_4H_4)$ (**41**), for example, we found that dimethyl acetylene is unreactive under thermal conditions (in contrast to the behavior of isoelectronic metallocenes, which form methylidenes [48]) but does react under UV light to give, not methylidenes but the vinyltantalum products **42** and **43** (Fig. 14) [49]. Based on NMR evidence, these compounds are stabilized by γ-agostic interactions between the metal and the Ta-CH_3 protons; alkynes with bulkier R groups give only single isomers, e.g. **44** and **45**. Most remarkable, however, is the behavior of the vinyl derivatives **42–45** on standing in air at room temperature: the RCCR moiety is incorporated into the carborane ligand with expulsion of the CpTaMe unit and cleavage of the vinyl C–Me bond, affording the corresponding tetracarbon carborane products $Et_2R_2C_4B_4H_4$ (**46–48**). The nido cage structure shown for **46–48** is assigned from multinuclear NMR spectroscopy and by analogy with the recently published X-ray crystal structure [50] of $H_4C_4B_4Et_4$. Carboranes of the $R_2R'_2C_4B_4H_4$ type have been obtained by other routes [51], but the process in this instance involving C–C bond rupture seems without precedent.

Direct interaction of the C_2B_4 carborane ligand with organic substrates has also been found in some reactions with isonitriles. Nitriles and isonitriles in general undergo straightforward insertion into the Ta–Me bonds in **41**, giving η^2-iminoacyl products (although requiring UV excitation) [52], but a very different result is produced when $CpPh_2Ta(Et_2C_2B_4H_4)$ (**49**) and the bulky isonitrile 2,6-dimethylphenylisocyanide (DMPI) are combined (Fig. 15) [52]. The initial product **50** is thermally stable but isomerizes to **51** under UV irradiation. Isomer **51** is far more reactive than **50**, readily combining with a second equivalent of DMPI to generate the bizarre structure **52**, which was revealed by X-ray diffraction. As can be seen, the isonitrile carbon atom has been effectively incorporated into the TaC_2B_4 framework, creating a TaC_3B_4 cage (or a $TaNC_3B_4$ system if one views the nitrogen as part of the skeleton).

These and other studies clearly establish an important property [2c] of the $2,3\text{-}R_2C_2B_4H_4^{2-}$ ligands when bound to metals: their ability to function both as ‘spectators’ in which they influence reactivity at the metal center but are not themselves altered, and as direct participants in reactions, in which they undergo permanent change; in the latter respect their behavior is clearly different from that of Cp and Cp*. An example of the spectator mode of reactivity, also taken from our recent work, is provided by the dimer **53** (Fig. 16) [53] which is a Ta(V) analogue of Schwartz’s reagent, $Cp_2Zr(H)Cl$, a compound that readily undergoes insertion of alkenes and alkynes into its Zr–H bond to form alkyl- or alkynylzirco-

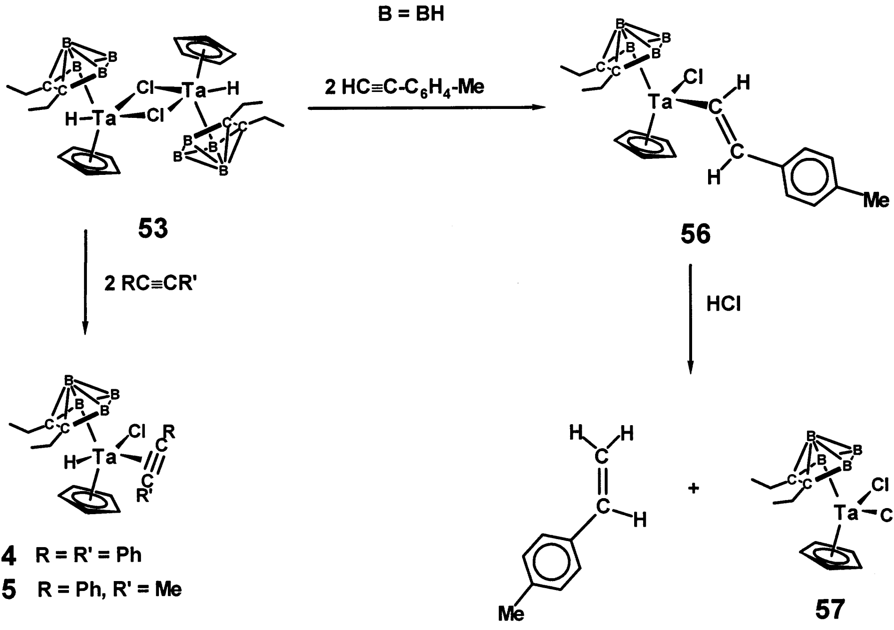


Fig. 16. Reactions of $[CpTa(H)Cl(Et_2C_2B_4H_4)]_2$ (**53**) with alkynes (ref. [53]).

nium species [54]. Unlike Schwartz's reagent, **53** dissolves readily in benzene and THF at room temperature and combines with phenylmethyl- or diphenylacetylene to generate products **54** and **55**, which are the first alkyne π-complexes of a formal d^0 metal to be reported. This finding, perhaps more than any other we have seen thus far, emphasizes the stabilizing power of the $2,3\text{-}R_2C_2B_4H_4^{2-}$ unit which far exceeds that of aromatic hydrocarbon ligands.

The interaction with *p*-toluyl acetylene takes a different pathway, affording only the *trans* complex **56** and showing that *cis*-addition to the Ta–H bond has occurred.

The versatility of the small carborane ligands has implications for several potential applications of this chemistry, as discussed in the following section.

2.4. Advances in applications

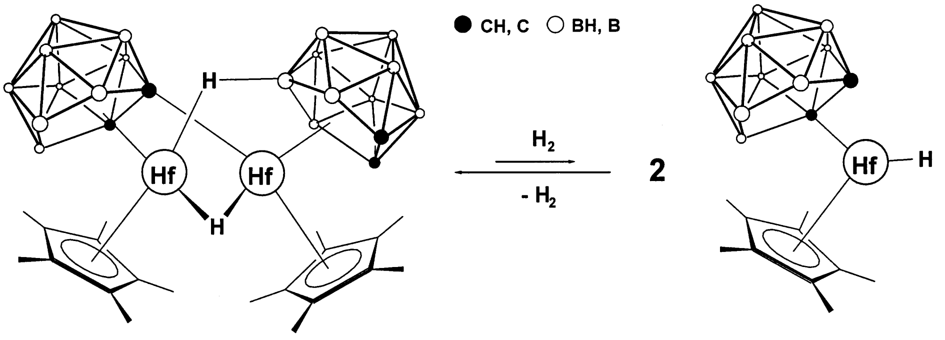
In parallel with the recent developments in fundamental metallacarborane chemistry just discussed, there has been increasing effort directed at the exploitation of the special properties of these compounds in a host of different areas. The scope of the actual and potential applications of metallacarboranes is remarkable, encompassing problems in biology and medicine, environmental science, industrial processes, materials and microelectronics, optics, and others. Essentially, the main attributes that metallacarboranes have to offer are high thermal and chemical stability, excellent solubility properties (neutral metallacarboranes tend to dissolve readily in organic solvents, ionic ones in aqueous media), tailorability (via changes in metals, carborane ligands, and substituents on the cage), electron-delocalized frameworks, and an ability to incorporate into the cage skeleton most of the elements in the periodic table, excluding only the most electropositive and electronegative ones. In principle, one can design a metallacarborane (or family of same) having the precise combination of properties required for a specific application; the reality is that despite more than thirty years of activity the field remains vastly underexplored, with relatively few research groups active around the globe, and the foundation of basic knowledge that is needed for serious practical development contains wide gaps. Consequently, many laboratories in working in this area are pursuing both fundamental and applied goals simultaneously, obscuring the traditional distinction between these activities.

Applications of boron clusters in general, including metallacarboranes, were discussed by Plesek in a 1992 article [3] and in general reviews [2a,b]; more recent information on specific areas can be found in a number of sources, including the papers presented at IMEBORON conferences (International Meetings on Boron Chemistry) which appear in bound volumes [55a,b] or in journals [55c]. Here I pick up on a few selected topics in which potentially useful advances have been reported within the last few years.

2.4.1. Homogeneous catalysis

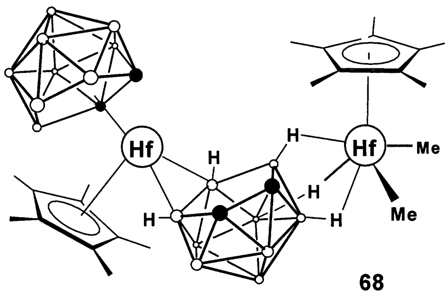
Hydridorhodium complexes of the type $3,1,2\text{-}H(Ph_3P)_2Rh^{III}(C_2B_9H_{11})$ (**58**) were shown by Hawthorne to be excellent precatalysts for the hydrogenation, hydrosilylation, and other reactions of unsaturated hydrocarbons, and extensive studies [56] by his group established that the catalytic activity is due to a 16-electron *exo*-*nido*-

$(Ph_3P)_2Rh^I$-$C_2B_9H_{12}$ tautomer in which the metal atom resides outside the cage (as in compound **11**, Fig. 6), that exists in equilibrium with the Rh(III) species. Relatively unexplored, however, have been the effects that substitution on the carborane cage have on the catalytic properties of this class of complexes. One might anticipate, for example, that the introduction of electron-withdrawing substituents to the carborane ligand would cause a reduction in electron density at the metal center and thereby affect its interaction with organic substrates relative to the unsubstituted compound **58**. Balagurova et al. [57] prepared a series of air-stable B-fluorinated rhodacarborane derivatives having the formulas $H(Ph_3P)_2Rh^{III}(C_2B_9H_{11-n}F_n)$, $n = 1$–3 (**59–61**) and $Cl(Ph_2MeP)_2Rh^{III}(C_2B_9H_{11-n}F_n)$, $n = 1$–3 (**62–64**). On comparison of their catalytic activity in benzene and THF toward the hydrosilylation of styrene and phenylacetylene with that exhibited by **58** and $(Ph_2MeP)_3RhCl$ (**65**), the principal differences observed were in selectivity. For example, of the three compounds formed from styrene — $PhCH_2CH_2SiMe_2Ph$ (I), $MePhC(H)SiMe_2Ph$ (ii), and the dehydrosilylation product *trans*-$PhHC{=}CHSiMe_2Ph$ (iii) — formation of the latter product is promoted to a greater extent by the fluoro derivatives than by **58**; overall, the fluorinated compounds gave lower selectivity than **58**. Presumably, it should be possible to tailor families of such catalysts so as to manipulate product ratios as desired, thereby taking advantage of the ease of functionalization of the carborane ligands.



66 **67**

Fig. 17. Formation of a catalytically active mononuclear Hf hydride from the dimer **66** via hydrogenation (ref. [58]).



68

Metallacarboranes of the early transition metals, especially those of Group 4, are of interest because of the isoelectronic relationship between neutral sandwich complexes of the type $Cp(R)M^{IV}(\eta^5\text{-}R'_2C_2B_nH_n)$ and the $Cp_2M^{IV}R^+$ cations that are active in the metallocene-catalyzed polymerization of olefins (the electroneutrality of the former arises, of course, from the dinegative carborane ligands; see the discussion in Section 1 and Fig. 1). Consequently, a number of groups are exploring the possibilities for developing novel metallacarborane-based catalyst systems. In recent work, Jordan and coworkers have explored the catalytic properties of a hydridohafnium-carborane complex (**66**) in the hydrogenation of internal alkynes to cis-alkenes, which evidently proceeds via a mononuclear intermediate **67** [58] as depicted in Fig. 17. The unsymmetrical dimeric structure of **66** in which the two metal centers are linked through Hf–H–Hf, B–H–Hf, and $Hf\text{-}\eta^1,\eta^5\text{-}C_2B_9H_{10}$ bridges, was determined crystallographically. While **66** reacts with internal alkynes in the presence of H_2 to yield *cis*-alkenes, NMR and other evidence suggests that the catalytically active species is in fact **67** (not isolated) [58]. In a different application of hafnium metallacarboranes in catalysis by the same group [59], the unsymmetrical bridged dinuclear complex **68** was shown to promote the regioselective dimerization of terminal alkynes, in which the formation of trimers or higher oligomers is blocked. This comes about because of an internal cyclization of a monohafnium reaction intermediate, formed from **68** in solution, that sterically prevents further interaction of alkyne molecules with the metal center.

In earlier work, chemists at Exxon Corporation had shown that zirconocene–carborane derivatives of the formula $Cp'_2Zr(Me)(C_2B_9H_{12})$ ($Cp' = C_5Me_5$, C_5Me_4Et) polymerize ethylene at 60°C and 300 psi [60]. Very recently, Do and coworkers have demonstrated that CpM(dicarbollyl) complexes of Group 4 metals in which an isopropyl group bridges the Cp and carborane ligands can promote the polymerization of olefins [61]. For example, rac-$(\eta^5{:}\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2M$ catalyzes the formation of syndiotactic poly(methyl methacrylate) in THF *in the absence of an alkylating agent*, while $(\eta^5\text{-}Cp^*)(\eta^5{:}\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)MCl$ and $(\eta^5\text{-}Cp^*)(\eta^5\text{-}CpCMe_2CB_{10}H_{10}C)MCl_2$ in the presence of methylaluminum oxane (MAO) are active in the catalytic polymerization of ethylene and propylene.

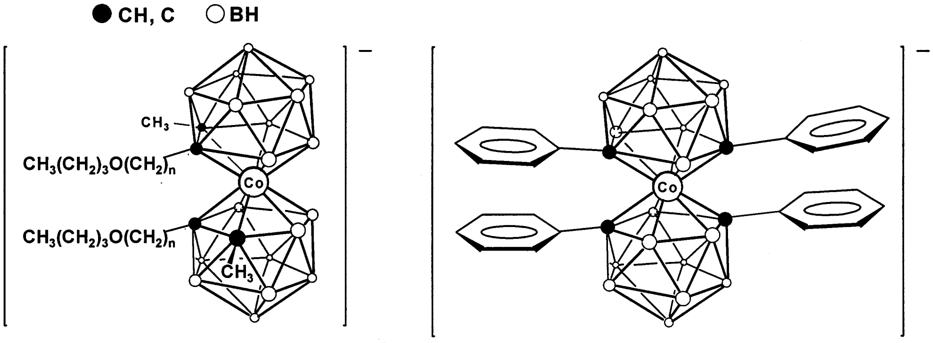
Catalytic activity in olefin and alkyne polymerization is also under exploration in *small* metallacarboranes, e.g. $L_2X_2Ti(Et_2C_2B_4H_4)$ ($X = Cl$, alkyl; $L_2 = 2PR_3$, $R_2P(CH_2)_nPR_2$, etc.; $R = Ph$ or alkyl) in combination with MAO [62]. Investigations in this area are continuing, but it is not yet clear whether there is serious commercial potential here. However, the facts that the MC_2B_4 carborane clusters tend to have higher thermal and oxidative stability than metallocenes, are soluble in a wide range of media, are easily tailored via introduction of functional groups on the carborane cage and/or the metal, and operate under very mild conditions (1 atm and room temperature) are good reasons for pursuing these studies.

Other intriguing reports of metallacarboranes in homogeneous catalysis continue to appear. For example, the alcoholysis of silicon hydrides to generate silyl ethers (a convenient method for protection of OH groups in organic synthesis) is promoted by rhodacarboranes of the type $(\eta^3\text{-cyclooctenyl})Co[(MeC{=}CH_2)C_2B_9H_{10})]$, a zwitterion in which the positive charge resides on the cyclooctenyl group [63]. Remarkably, even the Li^+ salt of the ubiquitous $Co(C_2B_9H_{10})_2^-$ anion is reported to function as a Lewis acid catalyst in the conjugate addition of silyl ketene acetals to hindered α,β-unsaturated CO compounds [64].

2.4.2. Metal ion extraction

A characteristic property of many polyhedral borane monoanions — somewhat surprising at first glance — is the high solubility of their salts in organic solvents, making them readily extractable from aqueous systems. This behavior is a consequence of the hydridic nature of the B–H hydrogen atoms arising from delocalization of the negative charge over the polyhedral framework [3], and is particularly strong in the bis(dicarbollyl)metalate sandwich anions of the type $3\text{-M}^{III}(1,2\text{-}C_2B_9H_{11})_2^-$, first prepared by Hawthorne in 1965 [1]. The sodium salt of $Co(C_2B_9H_{11})_2^-$ is comparable to NaCl as an electrolyte, yet when a 0.5 M aqueous solution of the compound is shaken with an equal volume of diethyl ether, the Na^+ $Co(C_2B_9H_{11})_2^-$ is transferred completely to the ether [3]! This property, together with its high thermal and chemical stability (including resistance to acids, bases, and radiation) attracted attention for possible use in the extraction of radionuclides from nuclear waste and as sensors for metal ions such as Cs^+ and Sr^{2+} in milk and body fluids. Following the initial successful application in this area by Czech chemists over 25 years ago [65], the $3\text{-Co}(1,2\text{-}C_2B_9H_{11})_2^-$ ions and related species have attracted intense interest, to the point that metal extraction now constitutes the most important practical utilization of metallacarboranes.

Over time, the solubility and other properties of the bis(dicarbollyl)cobaltate anion have been improved and refined via the introduction of substituents to the carborane ligands. An important discovery was that the hexachloro derivative $3\text{-Co}(1,2\text{-}C_2B_9H_5Cl_6)_2^-$ is much more resistant than the parent ion to 3 M nitric acid, which is a requirement for the large-scale selective recovery of ^{137}Cs and ^{90}Sr [3,65b,66]. In recent work, Teixidor and coworkers have explored the use of other metal-carborane anions including $3\text{-M}(1,2\text{-}C_2B_9H_{11})_2^-$ (M = Fe, Ni), the effects of adding oxygen-donor or aromatic substituents to the cage, and the extraction properties of $2\text{-Co}(1,7\text{-}C_2B_9H_{11})_2^-$ (carbons separated) salts [67]. Interestingly, the cobaltacarborane, ferracarborane, and nickelacarborane anions were found to exhibit very similar selectivity toward $^{137}Cs^+$, $^{90}Sr^{2+}$, and $^{152}Eu^{2+}$ in tests with PVC membranes; although the



69 n = 3 **70** n = 6 **71**

Fig. 18. C-substituted bis(dicarbollyl)cobaltate anions for radionuclide extraction (ref. [67a]).

overall performance of the iron species was best of the three, the cobalt anion is more easily prepared and shows the highest stability [67a]. Ether-substituted derivatives such as **69** and **70** (Fig. 18) gave enhanced performance over the parent complex, and the tetra-C-phenyl anion **71** proved to be the best agent yet found for extraction of Cs^+ under acidic conditions [67a]. Curiously, compounds containing ether chains having two oxygen atoms gave inferior results to those obtained with **69** and **70**.

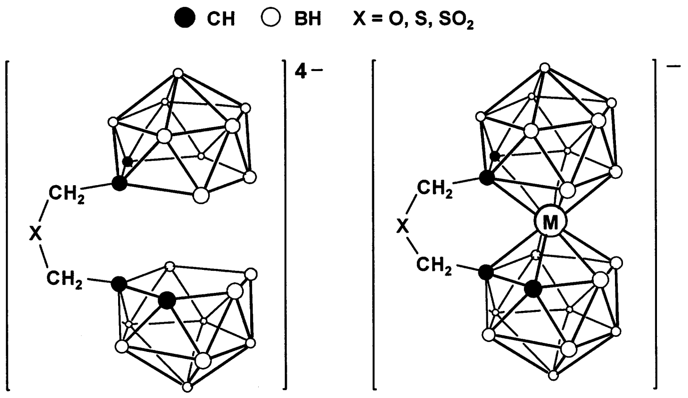
Other aspects of metal extraction employing the $3\text{-}Co(1,2\text{-}C_2B_9H_{11})_2^-$ system have been explored recently by Vanura et al., including their application to alkali and alkaline-earth metal cations using nitrobenzene solutions of the cobaltate anions in conjunction with calix[*n*]arenes, crown ethers, polyethylene glycols, and polyethers [68].

A current challenge in this area is to reduce or eliminate the use of nitrobenzene, an ecologically undesirable substance, in the extracting phase; while some progress has been reported, at this writing it appears that the best metal ion selectivities are obtained when it is present [67]. The clear advantages afforded by metallacarborane anions as sequestering agents for metals guarantees that this will remain an active research area, not only as a way of addressing the problem of radioactive waste disposal but also because in many cases the recovered metals have intrinsic value and can be recycled; examples are ^{137}Cs and ^{90}Sr, which are employed in such areas as thermoelectric generators and medical equipment sterilization [66].

2.4.3. Medicine and pharmacology

Of all the actual and potential applications of metallacarboranes (and polyhedral boron clusters in general), among the most intriguing are those involving medical diagnosis and treatment. Because of their high stability under a range of conditions and their distinctly 'inorganic' nature, carboranes and metallacarboranes are relatively resistant to metabolism in mammals and are therefore generally low-toxicity, benign substances; yet they can be readily functionalized by introduction of organic groups as needed. Currently, the most highly publicized medical application of boron cluster compounds is the anticancer treatment known as boron neutron capture therapy (BNCT), now in clinical trial in the USA and Europe [69]. The method exploits the high nuclear cross-section of the ^{10}B isotope, and utilizes the reaction between ^{10}B atoms (introduced into the target tumor) and a beam of slow neutrons to generate He^{2+} nuclei that carry sufficient kinetic energy to destroy the tumor tissue in the immediate vicinity (approximately 1 cell diameter). This approach, which shows considerable promise as a noninvasive treatment for inoperable brain cancers, requires stable, low-toxic compounds with high boron content, and interest has centered primarily on derivatives of icosahedral $C_2B_{10}H_{12}$ and $B_{12}H_{12}^{2-}$ rather than on metal derivatives. However, one metal that has attracted attention in this area is gadolinium, since ^{155}Gd and ^{157}Gd have even higher neutron-capture cross sections than ^{10}B, and the incorporation of the B and Gd isotopes in the same molecule may lead to greater efficiency in neutron capture therapy [70]. Nonetheless, metallacarboranes per se have not played a significant part in BNCT development.

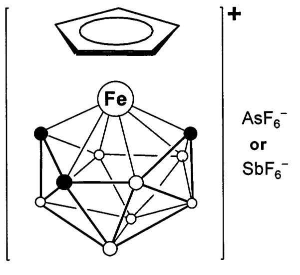
Two areas of medicinal chemistry in which metals are important, and are therefore potentially fertile ground for metallacarborane applications, are in radioimmunotherapy/radioimmunodiagnosis and in drug development. Here I will



72 **73**

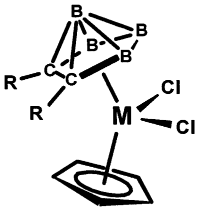
Fig. 19. A C,C-bridged bis(1,2-dicarbollide) anion **72** and complex **73** containing a trapped M^{3+} ion (ref. [72]).

briefly summarize some recent developments in both fields. Hawthorne several years ago prepared bridged bis(dicarbollide) anions and demonstrated their ability to complex irreversibly with metal ions via sandwich-binding to both C_2B_3 carborane faces, thereby functioning as 'Venus flytrap' (VFT) reagents [71]. The original complexes of this type utilized pyrazole rings or polymethylene chains as intramolecular linkers between the carborane ligands, and were difficult to synthesize because of the need for numerous protection and deprotection steps. In more recent work, the preparation of VFT complexes has been greatly simplified via the use of ether and thioether linkages as shown in Fig. 19 [72]. The medicinal application of this chemistry has been demonstrated via the incorporation of a radionuclide, ^{57}Co, in a VFT reagent that was bound to an anti-carcinogenic monoclonal antibody, T84.66. Subsequent biodistribution studies in tumor-bearing mice showed that the ^{57}Co-VFT-T84.66 was highly localized in the tumors, and that accumulation in the normal liver was low [71a]. These studies suggest that VFT complexes of ^{57}Co as well as other radionuclides including ^{90}Y, ^{67}Cu, ^{99m}Tc, ^{105}Rh, and ^{186}Re that are of potential or actual use in radioimmunodetection and/or radioimmunotherapy, may offer significant advantages over conventional complexing reagents such as diethylenetriaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA), that tend to form less stable radiopharmaceuticals and can be absorbed by normal tissues ([71a] and references therein).



74

The fact that certain ferrocenium salts and other metallocenes are known to have antitumor properties [73] raises the possibility that metallacarboranes may exhibit similar behavior, and if so, might offer advantages over the former group; for example, superior resistance to degradation in vivo and hence lower toxicity. Sneddon, Hall, and coworkers examined this possibility with salts of the 11-vertex ferratricarbaborane $[CpFe^{III}(MeC_3B_7H_9)]^+$ (**74**) and with neutral $CpFe^{II}$-$(MeC_3B_7H_9)$ (**75**), which contain the mononegative $[MeC_3B_7H_9]^-$ ligand and are therefore analogues of ferrocenium ion and ferrocene, respectively [16]. It was found that these compounds are indeed effective cytotoxic agents against several varieties of tumor cells including L-1210 lymphoid leukemia, $Tmolt_3$ leukemia, and HeLa-S^3 human uterine carcinoma, as well as lung broncogenic MB-9812; the mode of action involves interference with the synthesis of RNA and DNA in the tumor cells.



75

M = Ta, Nb
R = Me, Et, $SiMe_3$

Similar results have been observed in tests of small carborane complexes of tantalum and niobium prepared in our laboratory [74a]. Compounds of type **75** have been shown to be active against murine 1210 lymphoid leukemia, murine P388 lymphocytic growth, $Tmolt_3$ leukemia, and HeLa-S^3 human uterine carcinoma, Sk-2 melanoma, and Mcf-t breast effusion growth. It is noteworthy that the tantalum complexes exhibit greater potency than do the standard clinical drugs against certain glioma and breast cancer cell lines [74a]. In very recent work, small metallacarboranes containing iron, cobalt, molybdenum and other metals have been shown to be powerful cytotoxic agents [74b].

2.4.4. Stabilization of unusual organometallic systems

Coordination of carborane ligands to metal centers has made it possible to isolate a wide range of structurally novel complexes, as many of the examples cited in this review illustrate. The electron-donor capability of anionic carborane ligands such as $R_2C_2B_4H_4^{2-}$ and $R_2C_2B_9H_9^{2-}$ combined with the high degree of covalence in metal-carborane binding (see Section 1) can stabilize *organometallic* molecular architectures that are unstable, or not seen at all, in the absence of the carborane. Here I refer not to metallacarborane polyhedral clusters per se, but rather to *metal–hydrocarbon* moieties such as the Ta^V-alkyne complexes **54** and **55** (Fig. 16) that contain the unprecedented feature of a formal d^0 metal involved in stable π-coordination to a C≡C bond. Another example is afforded by the tantalum–benzyne complex **77** that was prepared from the Ta-diphenyl compound **49** as shown in Fig. 20, isolated as an air-stable solid, and characterized by X-ray diffraction and multinuclear NMR spectroscopy [75]. This remarkable compound is the most stable metal-η^2-benzyne complex known; it resists air oxidation indefinitely, can be recrystallized from methanol, and appears unreactive toward unsaturated organic substrates that typically undergo coupling reactions with metal-benzyne complexes, such as acetone, benzophenone, acetonitrile, bis(trimethylsilyl)–acetylene, and 3-hexyne [[75] and references cited therein]. This extraordinary behavior reflects the nonlability of the phosphine ligand, which is shown by the failure of **77** to exchange with PMe_3-d_9 in $CDCl_3$ [75]; in turn, this property reflects the participation of the formal Ta(V) center in an electron-delocalized metallacarborane framework.

Planar carborane ligands of the type $R_2C_2B_3H_3^{4-}$, which are isoelectronic as well as isosteric analogues of $C_5H_5^-$ (see Section 1) have the ability to form very strong η^5 sandwich bonds to metal ions on both sides of the ring plane, thereby allowing the construction of multidecker sandwich complexes in which metal centers alternate with planar C_2B_3 rings. Beginning with our isolation of two isomers of $CpCo(MeC_2B_3H_4)CoCp$ — the first air-stable triple-decker sandwiches — a quarter-century ago [76], we have developed this area to the point that stable complexes having up to six decks have been characterized [4,5,77] (Fig. 21, **79** and **80**); the hexadecker **80** (M = Co, M′ = CoH) is the largest molecular sandwich whose X-ray structure has been determined [77]. In parallel with this effort, Siebert and coworkers have prepared an extensive series of very similar multidecker sandwiches that incorporate planar organoboron rings such as diborolyl (C_3B_2) or thiadiborolyl (C_2B_2S) [6a,b,78].

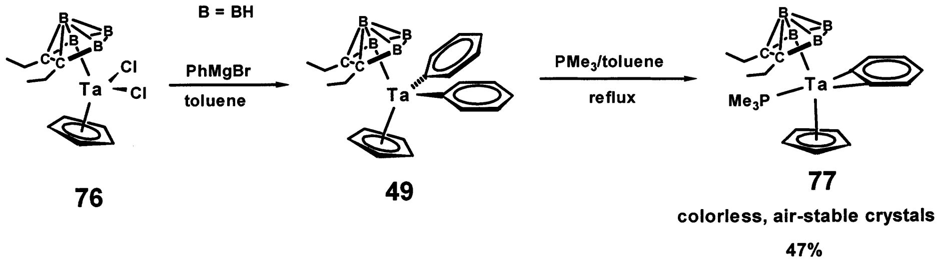
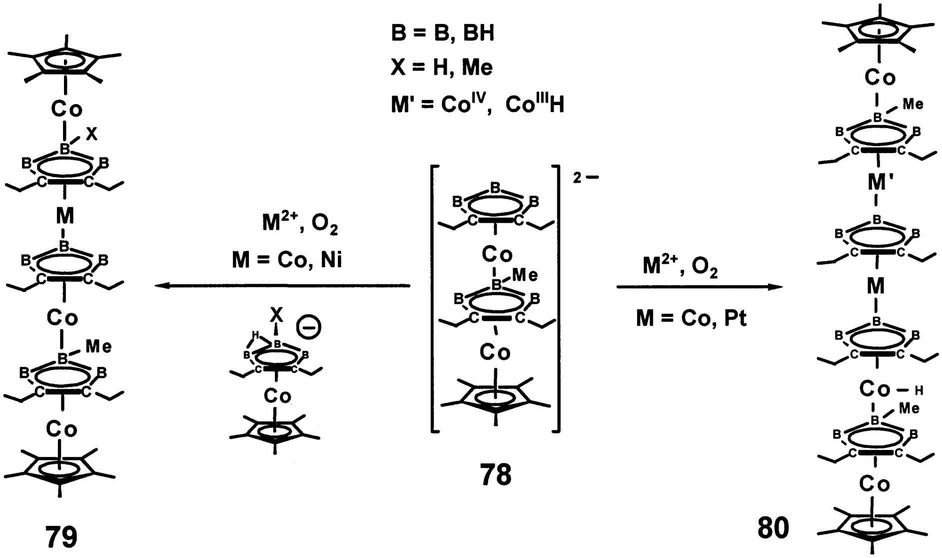


Fig. 20. Synthesis of $Cp(Me_3P)(\eta^2\text{-}C_6H_4)Ta(Et_2C_2B_4H_4)$ (**77**) (ref. [75]).



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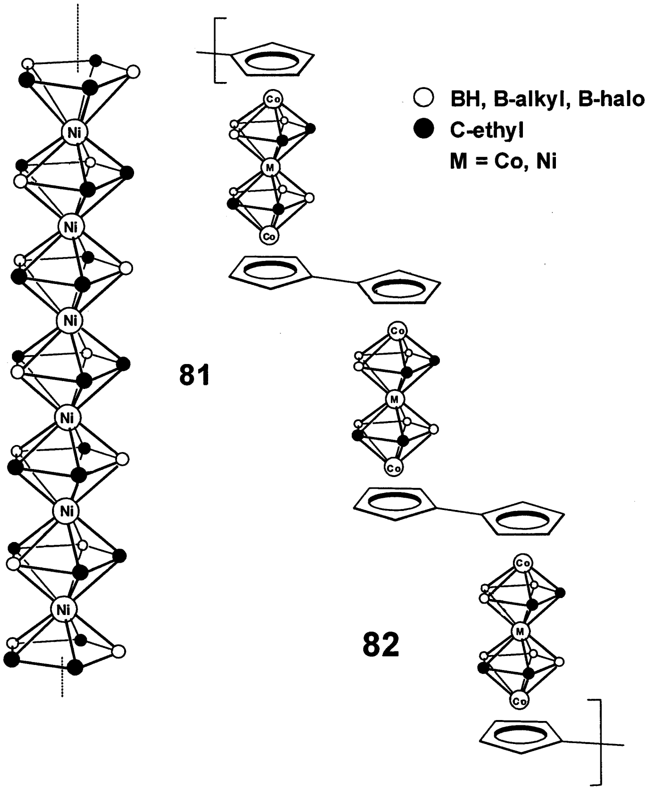
80

Fig. 21. Synthesis of pentadecker and hexadecker sandwich complexes [77].

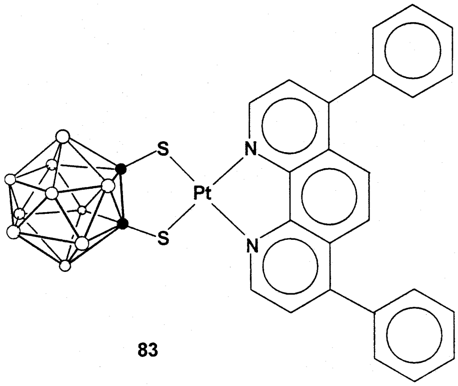


81

82

The stacking reactions that are employed in the preparation of these molecular complexes have also generated extended systems such as the diborolyl-linked polydecker **81**, an insoluble semiconducting solid [79], and the soluble fulvalene-linked 'staircase' oligomers **82** [80] in which extensive metal–metal communication (for M = Co) is indicated by electrochemical data [81]. Relevant to this work, detailed spectroelectro-chemical studies on several bimetallic and polymetallic mixed-valence small metallacarborane complexes [82] reveal that the degree of electron delocalization varies from very small (Class I) to fully delocalized (Class III); an example of the latter is the fulvalene-bridged dicobalt anion $[(Et_2C_2B_4H_4)Co^{2.5}(\eta^5\text{-}C_5H_4\text{–})]_2^-$ [82a].

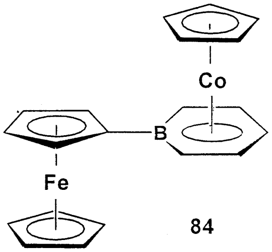
The synthesis of metallopolymers based on metallacarborane sandwich building blocks is at an early stage of development, and much fundamental work remains to be done on the synthetic and physicochemical aspects of this area. Nonetheless, the potential appears great for generating structurally novel molecule-based materials that exhibit useful electronic or optical properties and that take advantage of the inherent versatility, tailorability, solubility, and stability of metallacarboranes [2f]. On a more general note, the possibilities afforded by carborane ligands as stabilizing agents in organometallic systems seem considerable, although they have yet to be exploited as a general tool by synthetic chemists outside the metallacarborane field.



83

2.4.5. Nonlinear optical (NLO) materials

One of the most challenging current research areas, overlapping chemistry, physics, and engineering, is the search for new NLO-active materials, which are assuming increasing importance in a variety of technologies including data storage and retrieval, optical switching, and other applications [83a]. Given the special properties of polyhedral boron clusters, e.g., highly stable electron-delocalized structures and easy functionalization, these would appear prime candidates for exploration of their NLO properties, and systems containing metal chromophores seem especially attractive. Studies in this area thus far have included the 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ (*o*-, *m*-, and *p*-carborane) systems and their exo-cage-metallated derivatives [83], but just one investigation of metallacarboranes per se [84] has appeared. While only the latter work is directly relevant to this review, the finding of Abe and co-workers [83b] that $[B_{12}H_{11}\text{-}C_2B_{10}H_{11}]^{2-}$ linked-cluster dianions generate large hyperpolarizability [$\beta(0)$] values, comparable to those of 4-nitroaniline, is of interest. From these results one might anticipate that the effect can be substantially enhanced by introducing metal centers (especially different metals) into these cages, i.e. converting them into metallacarborane clusters. A moderately high β was found for the exo-metallated platinum-*o*-carborane derivative **83**, although larger values were observed for non-carborane Pt complexes in the same study [83a].

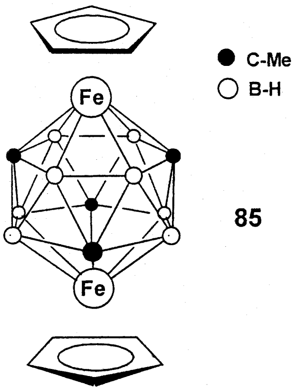


84

McKinney et al. [84] examined the second-order NLO behavior of several salts of $[M^{III}(C_2B_9H_{11})_2]^-$ bis(dicarbollyl)metal anions (M = Fe, Co, Ni) and found weak second-order harmonic generation only in the cobalt species. Although the few early studies of metal-carborane systems studied thus far have not turned up any particularly striking NLO activity, this is clearly an area ripe for exploration given the immense range of available metallacarborane structural types and compositions. In support of this view, it should be noted that unusually strong NLO activity has, in fact been found in closely related metal-organoboron compounds. The heterobimetallic linked-sandwich complex **84**, for example, shows a remarkably high β value of 90×10^{-30} esu, reflecting a charge-transfer transition between the ferrocenyl and borabenzene–cobalt groups [85]. The application of the basic design principle employed here, i.e. setting up an electronic 'push–pull' interaction between strong electron acceptor and donor units, seems particularly well suited to metallacarborane systems.

3. Some challenges for the future

The synthetic tools seem basically in hand for tailoring metallacarboranes to a wide variety of purposes, including those outlined in the previous sections as well as others that may not be apparent at this time. When this chemistry is combined with rapid advancements in organometallic synthesis that are generating an astonishing range of novel metal–hydrocarbon systems including conducting polymers, magnetically active salts, and other classes, one can only marvel at the possibilities that present themselves. There are nevertheless still some fundamental synthetic challenges in polyhedral borane chemistry that remain to be met; there are still a few summits to be conquered. One of these is the synthesis of ultralarge boron polyhedra, i.e. those exceeding 14 vertices. A stream of theoretical papers over the years has yielded predictions that $B_nH_m^q$ $(-2 \leq q \leq 0)$ deltahedral clusters (polyhedra having all triangular faces) in which n can be as large as 30 or greater, may exist as stable species if they can somehow be synthesized [86]. At present, the largest 'pure boron' polyhedron (i.e. having no heteroatoms in the cage framework) is the icosahedral $B_{12}H_{12}^{2-}$ dianion, and the largest carboranes (excluding metals) are also 12-vertex clusters [87]. In the case of metallacarboranes the current limit is 14 vertices; a fairly large number of 13-vertex MC_2B_{10} clusters are known [2a,b], as are two 14-vertex $Cp_2Co_2(C_2B_{10}H_{12})$ [90] and several 14-vertex $Cp_2Fe_2(Me_4C_4B_8H_8)$ isomers [91] although only the latter species have been structurally characterized by X-ray diffraction [91b,c]. These diiron-tetracarbon 14-vertex clusters are currently the largest structurally characterized boron-containing deltahedra. The most thermodynamically stable of these isomers is the bicapped hexagonal antiprismatic cluster **85**, generated by rearrangement of less symmetrical isomers at high temperature [91b].



85

Notwithstanding the calculations of their stability [86], the prospects for isolating 'trans-icosahedral' $B_nH_n^q$ clusters ($n > 12$) seem dubious, given the enormous stability of the icosahedral B_{12} unit, relative to which the larger clusters are thermodynamically unstable [86d]. However, more realistic possibilities may be presented by the metal-containing systems (as indeed structures such as **85** clearly imply). An example of one possible approach is schematically illustrated in Fig. 22, where the insertion of as many as four additional metal centers into the 12-vertex open-cage $Cp_2^*Fe_2Et_4C_4B_6H_6$ cluster **86** is suggested. The ferracarborane **86**, prepared in our laboratory and structurally characterized several years ago [92], is a fragment of a 16-vertex closo polyhedron of Td symmetry; perhaps significantly, this is the geometry calculated to be most stable for a $B_{16}H_{16}^q$ cluster where q may be either 0 or -2 [86c,93]. Thus, it is possible that stable 16-vertex $M_4Fe_2C_4B_6$ polyhedra represented by **87** could be isolated.

Clusters the size of **87** may be about the limit attainable for polyhedral 'hollow ball' geometries. Larger (perhaps much larger) metallacarboranes may be stabilized by adopting the structural principle of close-packing, as found in high-nuclearity

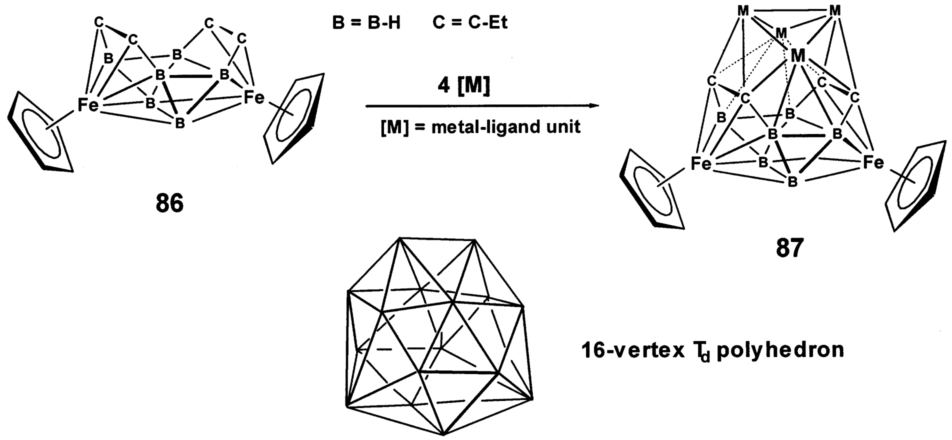
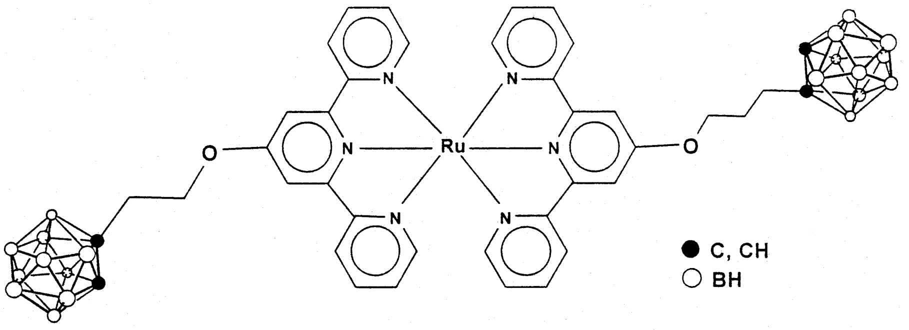


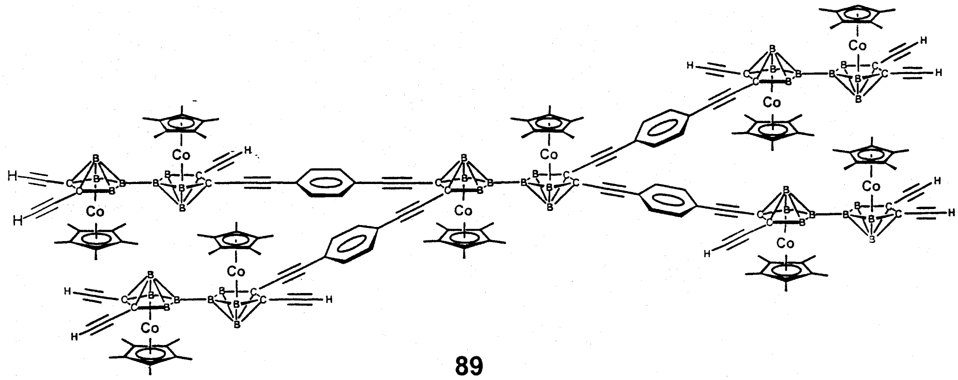
Fig. 22. Proposed synthesis of $M_4Fe_2C_4B_6$ clusters from the known metallacarborane **86**.

transition metal clusters that can reach truly remarkable sizes incorporating dozens of metal atoms, while remaining soluble molecular entities [94]. The scope of possibilities that may be opened by merging the metal-supercluster and metallacarborane structural motifs is mind-boggling; for example, metal-supercluster cores and metallacarborane polyhedra bound together in gigantic covalently bound soluble molecular entities containing hundreds of metal centers. One is reminded here of the extraordinary range of composition in solid-state metal borides, in which the metal–boron ratio varies more than 260-fold (from 1:66 to at least 4:1 in known compounds), which may well carry over into molecular species. Extensive work by Fehlner [95] and by Housecroft [96] on molecular boride-type metallaboranes that contain interstitial boron atoms and/or trans-polyhedral metal–metal bonds may presage the opening of vast new subareas of metallaborane and metallacarborane structural chemistry that exploit these principles.



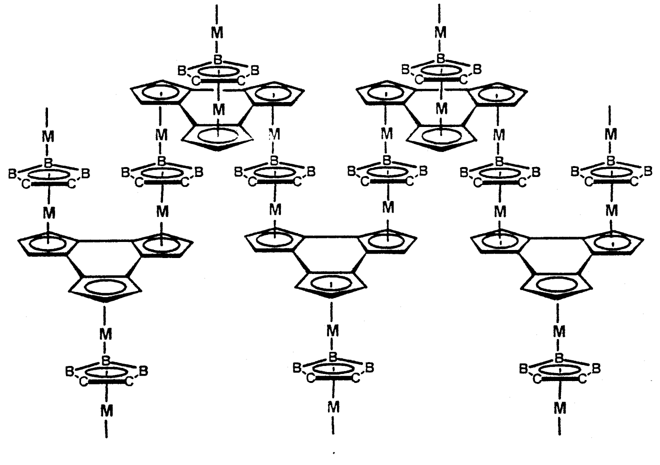
88

Another direction that appears to offer enormous potential for the exploitation of the unique properties and architectures of carboranes and metallacarboranes, is that of metallosupramolecular chemistry [97]. An example of the potential in this area is afforded by the recent synthesis of bis(terpyridine)ruthenium complexes in which the terpyridine units are functionalized with *o*-carborane ($1,2\text{-}C_2B_{10}H_{11}$) cages, e.g. **88**, that may find use in the targeting of biological sites [98]. The extension of this chemistry to metallacarboranes, which would introduce multiple metal centers into the periphery, seems well within the current synthetic state of the art.



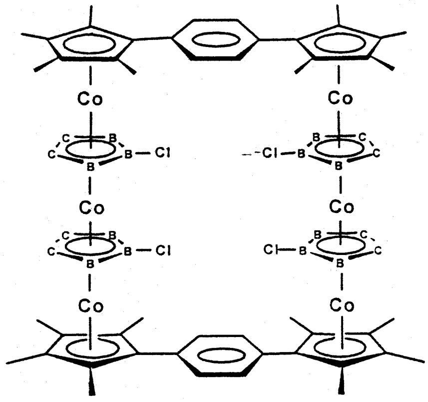
89

Metallodendrimers are also of considerable current interest as building blocks for new materials in which metal–metal interactions can be controlled through appropriate molecular design [99]. Thus the construction of arrays such as **89** might be feasible via the application of standard metal-catalyzed alkyne-linkage reactions to available metallacarborane systems.



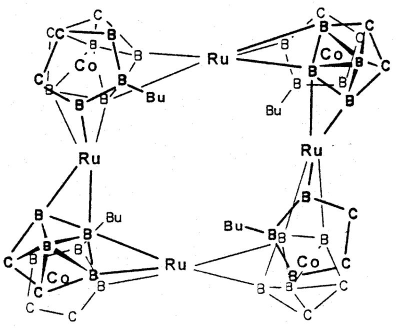
90

Three-dimensional organometallic networks incorporating multiple metal centers that interact electronically, stabilized by carborane rings or cages, represent another class of synthetic target worth pursuing. An example is the suggested array shown in **90**, in which trindenyl [$(C_5H_3)_3$] ligands [100] anchor triple-decker sandwich units containing $R_2C_2B_3H_3$ rings and metals [101]. Extended systems such as **90** might be tuned to exhibit desired electronic properties by changing the metal centers, metal oxidation states, and/or substituents on the carborane rings.



91

B = B, BH
C = C-Et



92

Still other architectural motifs ripe for investigation are suggested by theory and, more pointedly, by unexpected laboratory findings. In the latter category are the closed-loop complexes such as **91** and **92** which were serendipitously prepared in recent years and structurally characterized by X-ray diffraction [80,102]. Although these are low-yield products, their isolation as air- and thermally-stable soluble complexes demonstrates that such structures can indeed be assembled, and are viable. Hence extended structures such as ladder metallopolymers of type **94** might be attainable with appropriate synthetic strategies, perhaps along the lines suggested in Fig. 23.

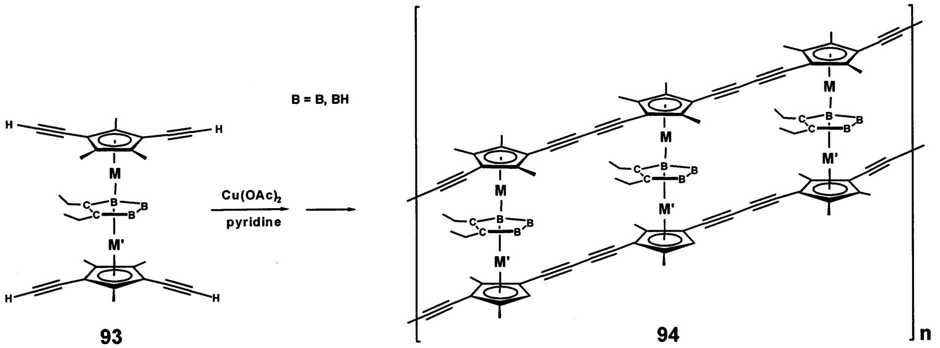
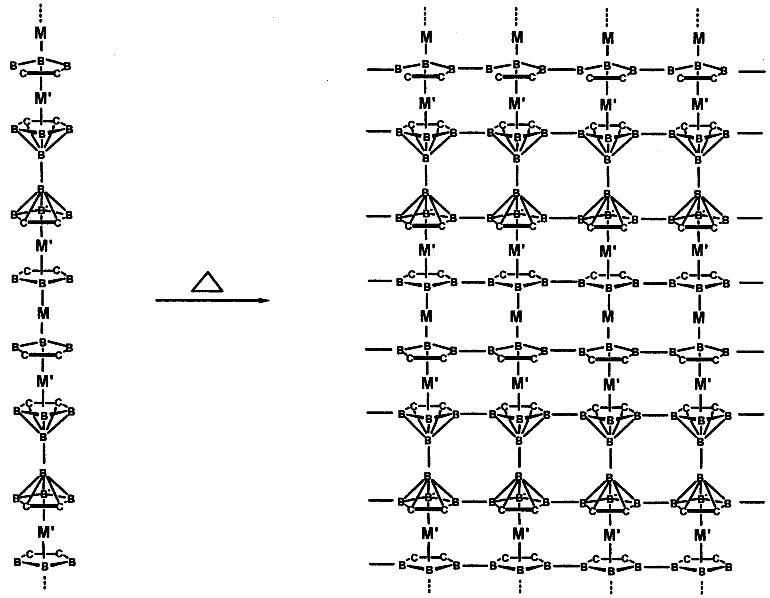


Fig. 23. A possible route to triple-decker metallacarborane ladder polymers.



95

96

Fig. 24. Postulated high temperature conversion of a linear sandwich polymer to a crosslinked sheet polymer.

One can also think of metallacarboranes as potentially attractive candidates for molecule-based 'designer' syntheses of solid-state materials [103], conducted under relatively mild conditions (e.g. temperatures below ca. 300°C) so that the integrity of the polyhedral cluster unit is preserved while linkage between the cages is effected. Here one of the main advantages of carborane chemistry — the robustness of the cage structure — may be exploited in an area where most metal–hydrocarbon systems are not suitable as building block units owing to their generally lower thermal stability. One possible approach, suggested in Fig. 24, might be to thermolyze linear polydeckers such as **95**, prepared via known linking and metal-stacking reactions [4,5], to generate crosslinked networks connected via intercage B–B links, e.g. **96**.

4. Concluding thoughts

My intention in this fin de siècle snapshot of metallacarborane chemistry has been to highlight some recent developments that seem to have implications for future directions in this field, to call attention to a few areas of actual and potential applications that exploit the unusual structural and chemical properties of these compounds, and to suggest some challenging synthetic problems that are of interest on both a fundamental and a practical level. The study of metallacarboranes is now in its fourth decade, and the scope and variety of this chemistry continue to grow. However, the truly intriguing story is the increasing entanglement of this field of research with other areas of organometallic and metal cluster chemistry, and it is fascinating to watch this process unfold. Carboranes and metallacarboranes are relatively expensive compounds and are likely to remain so for the foreseeable future, so the prospects for their practical use must center on special applications for which they are uniquely suited or demonstrably superior to other substances. This, however, is precisely the case with many materials that are crucial in modern technology (for example, the use of platinum in motor vehicle exhaust systems and in anticancer drugs). Metallacarboranes are more likely than not to find useful application in more than one area in the new millennium, no doubt in some ways that we have not even considered. Whether or not this proves true, the mind-expanding structures and chemistry of this class of compounds have already changed the landscape of organometallic chemistry in irrevocable ways.

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