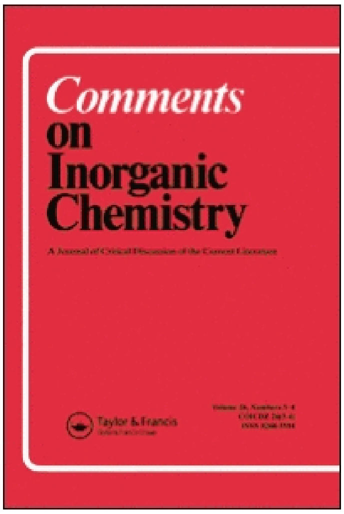

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FROM BORIC ACID TO ORGANOMETALLICS: LATEST DEVELOPMENTS IN METALLACARBORANE CHEMISTRY

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FROM BORIC ACID TO ORGANOMETALLICS: LATEST DEVELOPMENTS IN METALLACARBORANE CHEMISTRY

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An overview of the chemistry of polyhedral metallacarboranes, concentrating mainly on the $C_{(cage)}$-trimethylsilyl-substituted C_2B_4-carboranes will be discussed. While the main thrust of this account is on the results obtained in authors' laboratories, comparisons will be made to similar systems and to those involving both large and small cage carboranes in order to provide a full picture of the chemistry of these systems. In this way, we hope to demonstrate the unique chemistry of the small, C_2B_4-cage systems that has emerged over the past few years and provide an overview of the most recent results involving the chemistry of small-cage heterocarboranes.

INTRODUCTION

Carboranes are mixed hydride clusters of carbon and boron in which these elements occupy the vertices of "electron deficient" cages. These clusters can be expanded by incorporating other atoms into the cage structures to give heterocarboranes. When the heteroatom is a metal,

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the compounds are referred to as metallacarboranes. These compounds have been the subject of a number of reviews that attempt to cover the general literature of this rapidly expanding area.[1–5]

Although the chemistry of the full- and half-sandwich metallacarboranes of the C_2B_4-cage systems has been studied for the past 3–4 decades, the research so far has been limited mainly to US laboratories.[1–5] One factor in this geographic preference was the almost limitless supply of government surplus B_5H_9, which could be reacted with a suitable alkyne to form the carborane. Unfortunately, the last of that surplus of B_5H_9 was destroyed in 1999 and there is as yet no viable commercial source of this compound. Therefore, one of the more important contributions in recent years has been the synthesis of B_5H_9 by oxidative cage fusion of $[B_3H_8]^-$ (*vide infra*). Not only does this assure a continuing supply of this starting material, it also provides a source for other scientists around the globe who had previously no access to B_5H_9. In addition to continued access to pentaborane, earlier work had shown the way to the development of new and safer methods for the multigram-scale production of reasonably air-stable carborane derivatives and their subsequent conversion to the desired dilithium or sodium/lithium salt of the *nido*-C_2B_4-carborane dianion.[6] With a ready supply of the precursor it is now possible to pursue research into this fascinating area of chemistry. This review will focus specifically on the most promising recent research published on the complexes in which main group, transition and lanthanide metals are incorporated into C_2B_4-carborane cages, with earlier work being cited only to provide an overall picture of this field.

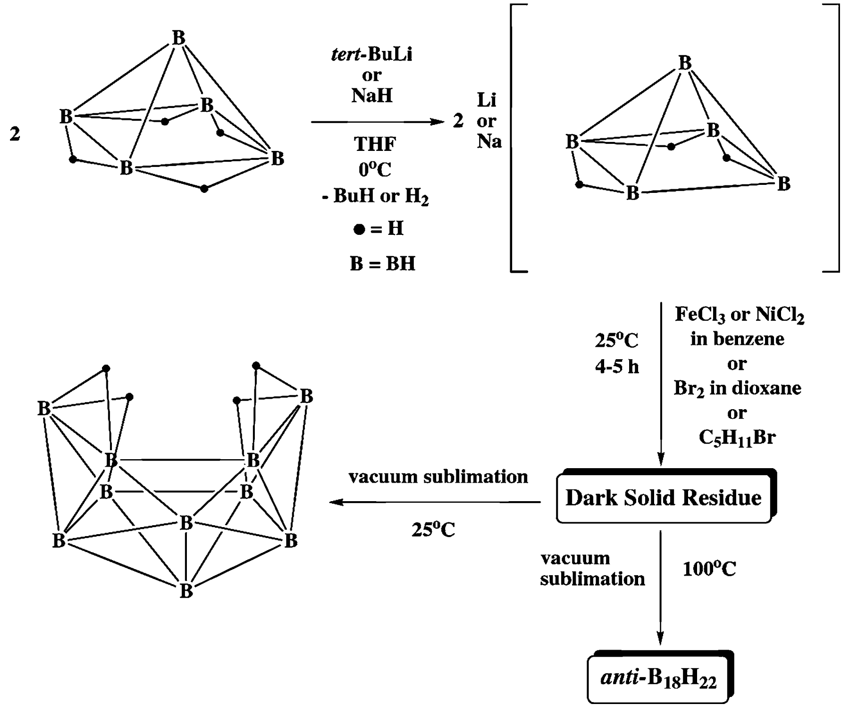
1. SYNTHESIS OF BORON-10 ENRICHED PENTABORANE(9) FROM BORIC ACID AND ITS CONVERSION TO *NIDO*-$^{10}B_{10}H_{14}$ AND *ANTI*-$^{10}B_{18}H_{22}$

Pentaborane(9) is an important synthon for a number of higher polyhedral borane cages, including decaborane, $B_{10}H_{14}$, $[B_{11}H_{14}]$, and anions such as $[B_9H_{14}]^-$, $[B_{12}H_{12}]^{2-}$, and others.[7–10] The corresponding ^{10}B-enriched species are precursors for a number of potentially useful boron neutron capture therapy (BNCT) drugs.[11] In the absence of a commercial source for any of these species, except the very expensive $^{10}B_{10}H_{14}$,[12] we developed a convenient synthesis for ^{10}B-enriched pentaborane(9), adapting literature methods [see equations (1) and (2)].[12–15] Specifically, $H_3{}^{10}BO_3$ was converted to the corresponding sodium borohydride, $Na^{10}BH_4$, in essentially quantitative yields, by using a slightly modified literature method, involving the formation of butyl borate, $(n\text{-}OBu)_3{}^{10}B$, and then reacting it with NaH in mineral oil at 250°C.[13,14] The subsequent oxidation reaction of $Na^{10}BH_4$with I_2 in diglyme, followed by the addition of dioxane, gave the dioxane-complexed sodium salt of octahydrotriborate (-1), $Na[^{10}B_3H_8]\cdot 3(C_4H_8O_2)$, in almost quantitative yields [see equation (1)].[15]

$$3\,Na^{10}BH_4 + I_2 \text{ (in diglyme/dioxane)} \rightarrow 2\,H_2 + 2\,NaI + Na[^{10}B_3H_8]\cdot 3(C_4H_8O_2) \qquad (1)$$

Treatment of the $Na[^{10}B_3H_8]\cdot 3(C_4H_8O_2)$ with $NiCl_2$ in anhydrous benzene or heavy mineral oil at 110°C [see equation (2)] gave the corresponding $^{10}B_5H_9$ as the first isolated ^{10}B-enriched pentaborane(9) in a laboratory environment.[16] Although there have been a number of other methods for the preparation of natural B_5H_9,[17,18] the reaction written in equation (2) is by far the most convenient and straightforward method described to date. Since the ^{10}B-enriched pentaborane is the only borane product of high volatility, this method is attractive not only to those who work with small-cage (C_2B_4) carboranes and metallacarboranes, but also to laboratories that did not previously have access to this material. Although the conversion of natural pentaborane(9) to decaborane(14) has been previously demonstrated by Brewer and Grimes using iron(II)- and iron(III) chloride-mediated cage fusion reactions,[19] we have slightly modified this procedure in the synthesis for ^{10}B-enriched decaborane (Scheme 1).[20] The synthetic methodology for the production of $^{10}B_{10}H_{14}$ is identical to that used for *anti*-$^{10}B_{18}H_{22}$ except for the oxidizing agent used and the room temperature sublimation of the former product as shown in Scheme 1.[19] This work constitutes the first systematic synthetic approach to natural and ^{10}B-enriched pentaborane(9) and

$$2\,Na[^{10}B_3H_8]\cdot 3\,(C_4H_8O_2) + NiCl_2 \xrightarrow[\substack{-2\,NaCl/-Ni^0 \\ -2\,C_4H_8O_2}]{\substack{\text{Benzene or} \\ \text{Heavy Mineral Oil} \\ 110^\circ C/12\,h}} {}^{10}B_5H_9 + 2\,H_2 + C_4H_8O_2\cdot{}^{10}BH_3 \qquad (2)$$



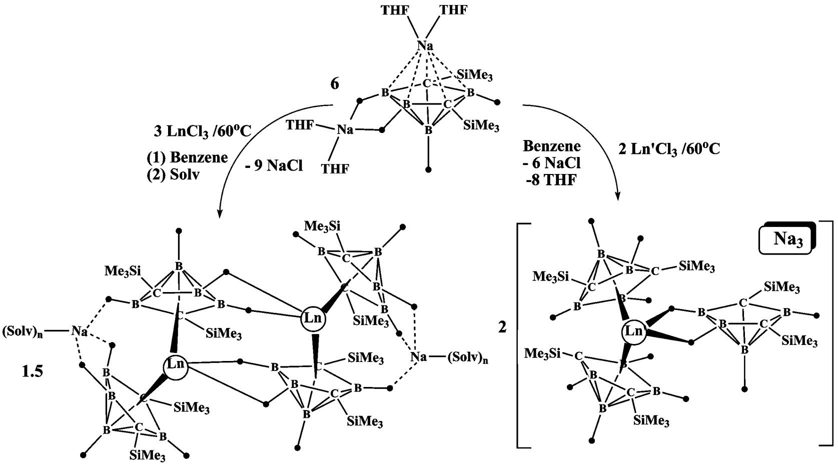
Scheme 1. Synthesis of *nido*-$^{10}B_{10}H_{14}$ and *anti*-$^{10}B_{18}H_{22}$ from $^{10}B_5H_9$.

decaborane(14) and to their cage–expanded neutral and anionic borane species.[16,20]

2. A NOVEL ROUTE TO METALLACARBORANE SYNTHESIS

The two-electron reductive cage opening of the *closo*-carboranes, in both the C_2B_{10} and C_2B_4 cage systems, have been well-documented in the literature.[21–25] In most cases, an alkali metal, along with the electron transfer reagent, naphthalene, was essential for the formation of the corresponding dianionic *nido*-cages. The cage carbons are always separated by a boron atom.[24,25]

The use of naphthalene in the traditional two-electron reductive cage opening reactions has several disadvantages. It introduces an additional reagent that must be removed from the reaction mixture before the *nido*-carborane products can be reacted further. Naphthalene also has a tendency to co-crystallize with any product or to substitute for a terminal



● = H

Ln = Nd, Gd, Tb, Dy, Ho, Er, Lu; Ln' = Dy, Er; Solv = THF and/or TMEDA; n = 1-3

Scheme 2. Conventional synthetic route for lanthanacarboranes.

B-H hydrogen, which often interferes with the reactivity of these dianionic ligands. The subsequent metalations of these ligands, in the conventional synthetic procedure, shown in Scheme 2 using lanthanide metals, produce metallacarboranes of different geometries depending on the ratios of

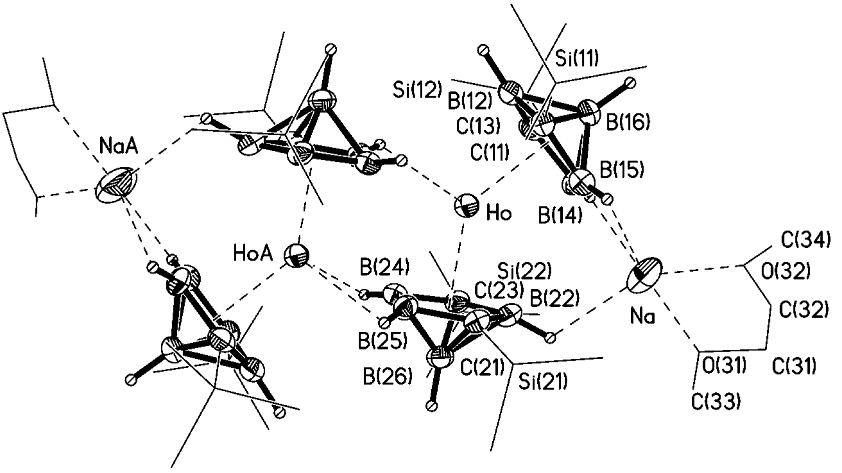


Figure 1. Crystal structure of a full-sandwiched dimeric holmacarborane complex.

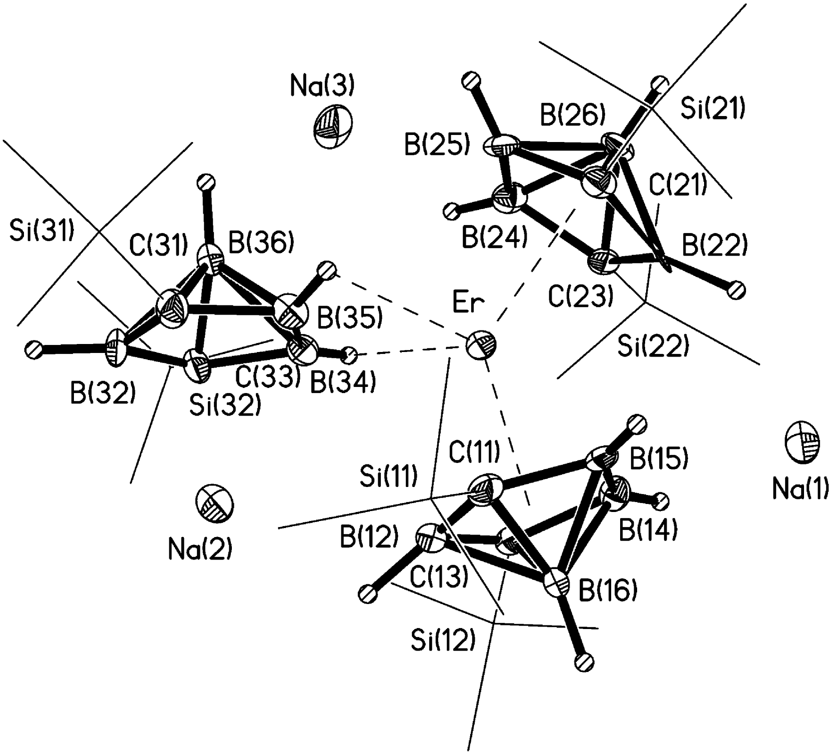
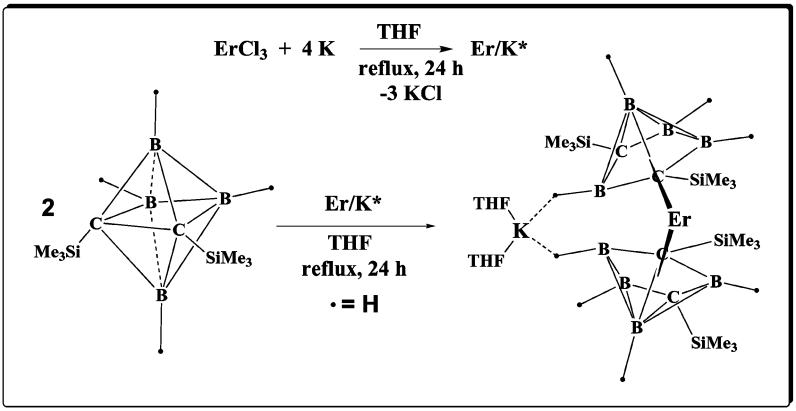


Figure 2. Crystal structure of an erbacarborane complex comprising three C_2B_4-carborane ligands.

reactants involved.[25–32] The structures of some representative compounds are depicted in Figures 1 and 2.[31,32]

The inability of the *closo*-carboranes to undergo reduction in the absence of naphthalene led us to question whether such carboranes could be reductively opened by the *in-situ* generation of reactive metal atoms whose cations are good coordinators of the carborane. To explore this possibility, anhydrous $ErCl_3$ was reacted with 4-equivalents of freshly cut potassium metal, under refluxing conditions in THF, to produce what we believe to be an active erbium metal alloy of the form of Er/K^* (see Scheme 3).[33]

The alloy was immediately treated with the *closo*-carborane, 1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$, which after refluxing overnight, produced a light-orange crystalline solid, identified as the "carbons apart" erbacarborane



Scheme 3. A synthetic route for one-pot two-electron reductive cage opening with concomitant metalation of the carborane ligand.

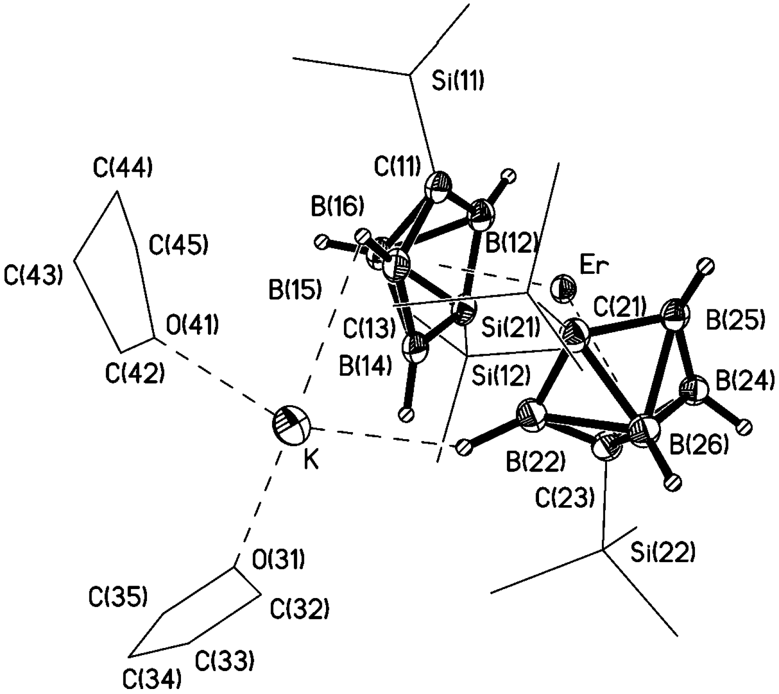


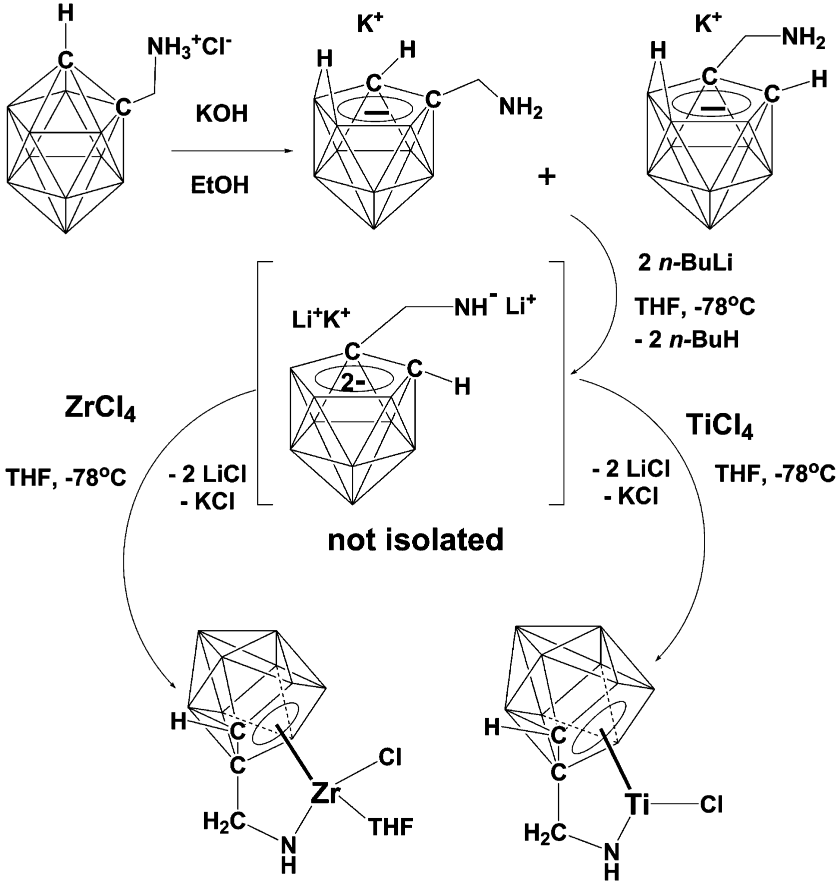
Figure 3. Crystal structure of a full-sandwiched erbacarborane complex.

sandwich, 2,2′,4,4′-$(SiMe_3)_4$-3,6′-[(μ-H)$_2$K(THF)$_2$]-1,1′-*commo*-Er(η^5-2,4-$C_2B_4H_4$)$_2$, in 82% yield (see Scheme 3 and Figure 3).[33] It is important to note that, under the same reaction conditions, neither the Er or K metal alone nor the one generated *in-situ* by reacting K with $ErCl_3$ in 3:1 ratio underwent reductive cage opening; in both cases the *closo*-carborane precursor was recovered unchanged. On the other hand, a reaction involving active lanthanide metal, prepared from the reaction between $LnCl_3$ (Ln = Dy, Er) and excess K metal, and *closo*-1-(R)-1,2-$C_2B_{10}H_{11}$ (R = organic substituent), produced, *via* a four-electron reductive cage-opening, the corresponding *arachno*-carborane ligand bonded to the lanthanide metal in an η^7-fashion.[34] Thus, the reactivity of the C_2B_4-cages toward activated lanthanide metal in the presence of potassium differs significantly from that observed in the larger C_2B_{10} carborane cage system. Although the Na/Hg alloy has been widely used in coupling reactions of many organometallic species,[35] there have been no reports of its use either in the reductive cage-opening of the carboranes or in the synthesis of mercuracarborane complexes. Therefore, the reaction shown in Scheme 3 is an unprecedented example of a new reductive cage opening process that should prove applicable to the *closo*-carboranes in both the icosahedral and sub-icosahedral cage systems.

3. CHEMISTRY OF HALF-SANDWICH, CONSTRAINED-GEOMETRY C_2B_9-METALLACARBORANES

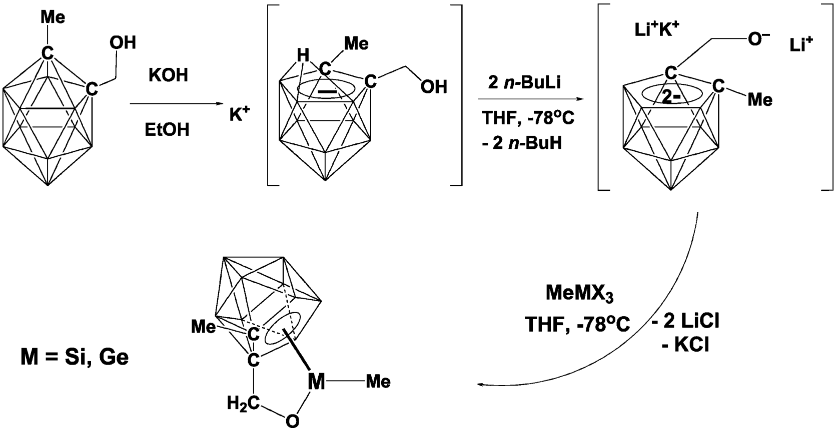
The potential applications of functionalized carborane clusters in catalytic organic reactions have resulted in the reports of the syntheses and reactivities of a number of new metallacarboranes.[36] Our preliminary research in this area has shown that the trianionic ligand [*nido*-7-(CH_2NH)-7,8-$C_2B_9H_{10}$]$^{3-}$, prepared from the reaction of [*nido*-7-(CH_2NH_2)-7,8-$C_2B_9H_{11}$]$^-$ with 2 equivalents of *n*-BuLi, reacts with MCl_4 (M = Ti, Zr) to give the corresponding half-sandwich metallacarboranes (see Scheme 4).[37]

There have been several reports in which an exopolyhedrally appended moiety forms either a coordinate covalent bond or another delocalized π-bond with the metal atom.[38] However, none demonstrated the additional stabilization of the metal by sigma bonding to the $C_{(cage)}$-appended moiety.[36] Therefore, our results are the first examples of half-sandwiched group 4 metallacarboranes in which the nitrogen atom of the exo- polyhedral $C_{(cage)}$-alkylamido unit is η^1(sigma)-bonded to the metal



Scheme 4. Synthesis of *ansa*-alkylamidometallacarboranes with unlabelled vertices as BH groups.

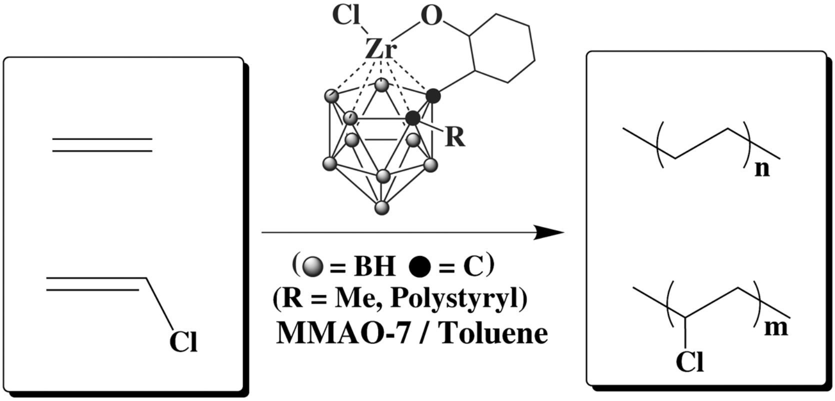
that is complexed with the open C_2B_3-bonding face of the carborane ligand (Scheme 4). These observations suggested the possibility of using other constrained-geometry ligands, such as the *ansa*-alkyloxocarborane, to prepare a series of $C_{(cage)}$-appended half-sandwich alkyloxometallacarboranes, as outlined in Scheme 5.[39] In these syntheses, the *in situ* generated trianionic ligand is reacted with anhydrous $MeMCl_3$ ($M = Si$, Ge) to form the corresponding half-sandwich group 14 metallacarboranes, *closo*-1-M(Me)-2-(1-$\eta^1(\sigma)$-OCH_2)-3-Me-η^5-2,3-$C_2B_9H_9$ [M = Si, Ge], in 48 and 56% yields, respectively, as shown in Scheme 5.[39]



Scheme 5. Synthesis of *ansa*-alkyloxometallacarboranes with unlabelled vertices as BH groups.

In a similar study, the reaction of the lithium salt of the carborane monoanion, [*closo*-1-Me-1,2-$C_2B_{10}H_{10}]^-$, with cyclohexene oxide afforded the ligand precursor, *closo*-1-Me-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_{10}H_{10}$, in 86% yield. The trianion, generated from this $C_{(cage)}$-appended carborane species, was allowed to react with $MCl_4 \cdot 2THF$ to produce *closo*-1-M(Cl)-2-Me-3-[2′-σ-O-cyclohexyl]-η^5-2,3-$C_2B_9H_9$ in 51 and 59% yields when M = Zr and Ti, respectively.[40]

An organic polymer substrate can be introduced onto the *closo*-1,2-$C_2B_{10}H_{10}$ by reaction of its lithium salt with Merrifield's peptide resin (1%) to produce, 1-polystyrenyl-1,2-$C_2B_{10}H_{11}$ that reacts *in situ* with *n*-BuLi and cyclohexene oxide in THF to give the polymer-supported ligand precursor, *closo*-1-polymeryl-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_{10}H_{10}$.[40] After decapitation and further deprotonaztion a trianionic intermediate was produced that reacted with $ZrCl_4 \cdot 2THF$ to form the corresponding immobilized zirconacarborane complex, *closo*-1-Zr(Cl)-2-polymeryl-3-(2′-σ-O-cyclohexyl)-η^5-2,3-$C_2B_9H_9$. A TGA analysis confirmed the presence of a metallated polymer.[40] Polymerizations of ethylene and vinyl chloride (see Scheme 6) in the presence of the immobilized group 4 metallacarborane complexes and MMAO-7 ([Al]/[Zr] = 2000) showed the metallacarboranes to be moderately active catalysts for olefin polymerization affording polymers with narrow molecular mass distributions (Mw/Mn = 1.2 ∼ 1.8).[40]

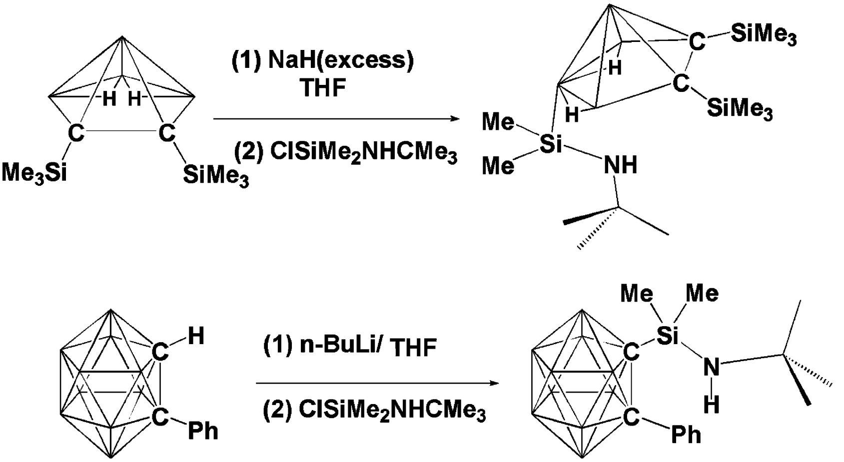


Scheme 6. Polymerization of olefins catalyzed by half-sandwich zirconacarboranes of constrained-geometry.

The catalytic activity of these metallacarboranes towards vinyl chloride is sufficiently high to warrant further investigations of these systems.

4. SYNTHESES AND REACTIVITIES OF $B_{(CAGE)}$-ALKYL- AND SILYLAMIDO-C_2B_4-CARBORANE LIGANDS

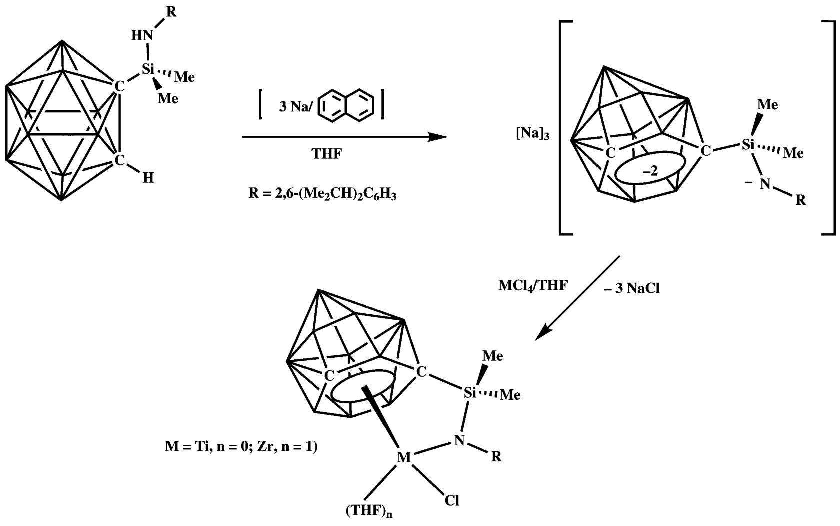
Carborane ligands' usefulness can be extended if substituents could be systematically introduced on the boron atoms of the 2,3- and 2,4-C_2B_4 carboranes. While isolated reports of such syntheses have been published,[41–43] there have been only two systematic studies of the B-alkylation of the *nido*-C_2B_4-cages, one on the C-alkyl substituted cages reported by Davis and Grimes,[44] the other involving the C-$SiMe_3$ substituted cages initiated in our laboratories.[45,46] The C-alkyl substituted *nido*-2,3-C_2B_4 cages underwent further alkylation at the 4-position, while alkylation of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ produced only *nido*-5-R-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$. The difference in the directing ability of $SiMe_3$ compared to C-alkyl groups is most likely due to the $SiMe_3$ moiety's steric bulk. The directive property of the $SiMe_3$ moiety was profitably exploited in the synthesis of *nido*-2,3-$(SiMe_3)_2$-5-[$Si(Me_2)NH(Me_3C)$]-2,3-$C_2B_4H_5$ from the reaction of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ and $ClSiMe_2NHCMe_3$ (see Scheme 7).[46] Unfortunately, this 5-substituted carborane proved of limited use as a ligand since it could not withstand deprotonation with a strong base. Metallation of the neutral compound by reaction with $M(NMe_2)_4$ (M = Zr and Ti) led to uncharacterizable



Scheme 7. Syntheses of the $B_{(cage)}$- and $C_{(cage)}$-substituted silylamidocarborane ligands; unlabelled vertices are BH groups.

products. However, $ClSiMe_2NHCMe_3$ was also found to react with the monolithium salt of [*closo*-1-Ph-1,2-$C_2B_{10}H_{10}]^-$ to produce *closo*-1-Ph-2-[Si(Me_2)NH(Me_3C)]-1,2-$C_2B_{10}H_{10}$ (see Scheme 7).[46]

This compound reacted with three equivalents of freshly-cut sodium metal in the presence of naphthalene to produce, in almost quantitative yield, the corresponding cage-opened sodium salt of the "carbons apart" carborane trianion, [*nido*-3-{Si(Me)$_2$N(2,6-(Me_2CH)$_2C_6H_3$)}-1,3-$C_2B_{10}H_{11}]^{3-}$, whose reaction with anhydrous MCl_4 (M = Ti and Zr) resulted in the formation of the corresponding half-sandwich neutral d^0-metallacarboranes, *closo*-1-M[(Cl)(THF)$_n$]-2-[1′-η^1·σ-N(2,6-(Me_2CH)$_2C_6H_3$)(Me)$_2$Si]-2,4-η^6-$C_2B_{10}H_{11}$ (M = Ti, n = 0; M = Zr, n = 1) (see Scheme 8).[46] The ligand precursor, *closo*-2-[Si(Me)$_2$NH(2,6-(Me_2CH)$_2C_6H_3$)]-1,2-$C_2B_{10}H_{11}$, was characterized by single crystal X-ray diffraction. The crystal structure (Figure 4) of this shows that it consists of a closed C_2B_{10} polyhedron with a distorted icosahedral cage geometry. The intracage bond distances are quite similar to those reported for *closo*-1-(methyl)-2-(phthalimidomethyl)-1,2-$C_2B_{10}H_{10}$.[47] The *exo*-polyhedral Si(Me)$_2$NH(2,6-(Me_2CH)$_2C_6H_3$) group in the molecule is attached to a cage carbon by a standard *2c2e* bond. The most interesting aspect of this structure is the large C(1)-N-Si angle of 125.5(2)°.[46] This is most likely due to the repulsion between the Si-Me groups and the large diisopropylphenyl moiety. Such an angle indicates that the lone pair on nitrogen atom would not be particularly available for bonding. However, as evidenced



Scheme 8. Cage-opening and concomitant metalation of the $C_{(cage)}$-substituted silylamido-carborane ligands; unlabelled vertices are BH groups.

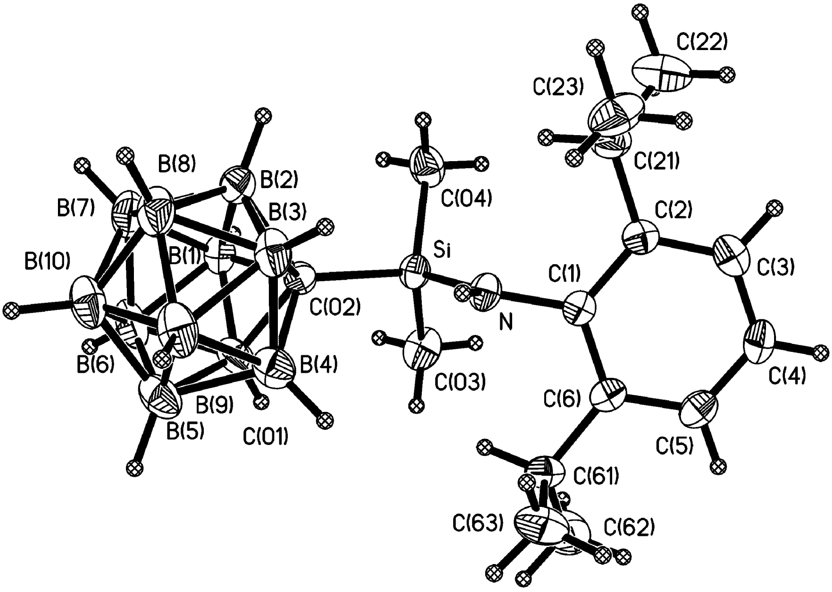


Figure 4. Crystal structure of the *ansa*-carborane ligand, *closo*-2-[Si(Me)$_2$NH(2,6-(Me$_2$CH)$_2$C$_6$H$_3$)]-1,2-C$_2$B$_{10}$H$_{11}$.

by its eventual conversion to the corresponding half-sandwich neutral d^0-metallacarborane, *closo*-1-M[(Cl)(THF)n]-2-[1′-$\eta^1 \cdot \sigma$-N(2,6-$(Me_2CH)_2C_6H_3$)$(Me)_2$Si]-2,4-η^6-$C_2B_{10}H_{11}$ (M = Ti, n = 0; M = Zr, n = 1), η^1-coordination of the N is possible after removal of its H to form the amido group.[46]

5. NOVEL SYNTHETIC APPROACH TO OXIDE-ION-ENCAPSULATED METALLACARBORANE CLUSTERS

Our interest in oxolanthanide compounds stems from our previous observation that, unlike the C_2B_9 and C_2B_{10} ligands, the C_2B_4-carboranes could form unusual oxo-lanthanacarboranes of the type {[η^5-1-Ln-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$]$_3$[(μ-1-Li-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$)$_3$(μ_3-OMe)][μ-Li(THF)]$_3$(μ_3-O)} (Ln = Nd, Sm, Gd, Tb, Dy and Ho).[48] The extension of this chemistry is limited by the use of THF as an oxygen source. It greatly complicates the development of any general synthetic scheme, it is difficult to control the stoichiometry of the synthesis, and it introduces a number of other degradation products such as MeO^- that can then influence the reaction. These complexities, inherent in the methodology, led us to question whether there could be alternative methods to synthesize oxolanthanacarborane routinely. We explored new synthetic approaches that led to an oxide ion-encapsulated tetralanthanide tetrahedron that is complexed with the “C-apart” C_2B_4-carborane ligands (see Figure 5).[49] These syntheses are interesting in that anhydrous $LnCl_3$ (Ln = La, Nd, Gd, Tb, Ho and Lu) must first be treated with stoichiometric quantities of freshly distilled H_2O under refluxing conditions in THF. The resulting mixtures are then reacted with *closo-exo*-5,6-$Na(THF)_2$-1-$Na(THF)_2$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ in an overall carborane to $LnCl_3$ to H_2O molar ratio of 5:4:1 to produce the oxolanthanacarboranes, {[η^5-1-Ln$(THF)_n$-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$_4$(μ-Cl)$_2$(μ_4-O)} $(THF)_y$ [Ln = La, n = 0, y = 1; Nd, n = 1, y = 0; Gd, n = 0, y = 1; Tb, n = 1, y = 0; Ho, n = 0, y = 1; Lu, n = 1, y = 0] in 73–86% yields.[49] A generalized synthesis is outlined in Scheme 9. The reactions are very sensitive to both stoichiometry and procedure: the $LnCl_3/H_2O$/THF mixture must be refluxed until a homogeneous solution is obtained and the reactions must be carried out initially at –78°C and then completed at reflux temperatures. If $LnCl_3$ and H_2O were added to a solution of the carborane ligand without prior refluxing, the water directly attacked and rapidly decomposed the carborane ligand.[49] The best yields were obtained from “exact” stoichiometric mixtures, assuming one carborane dianion acts as a proton scavenger;

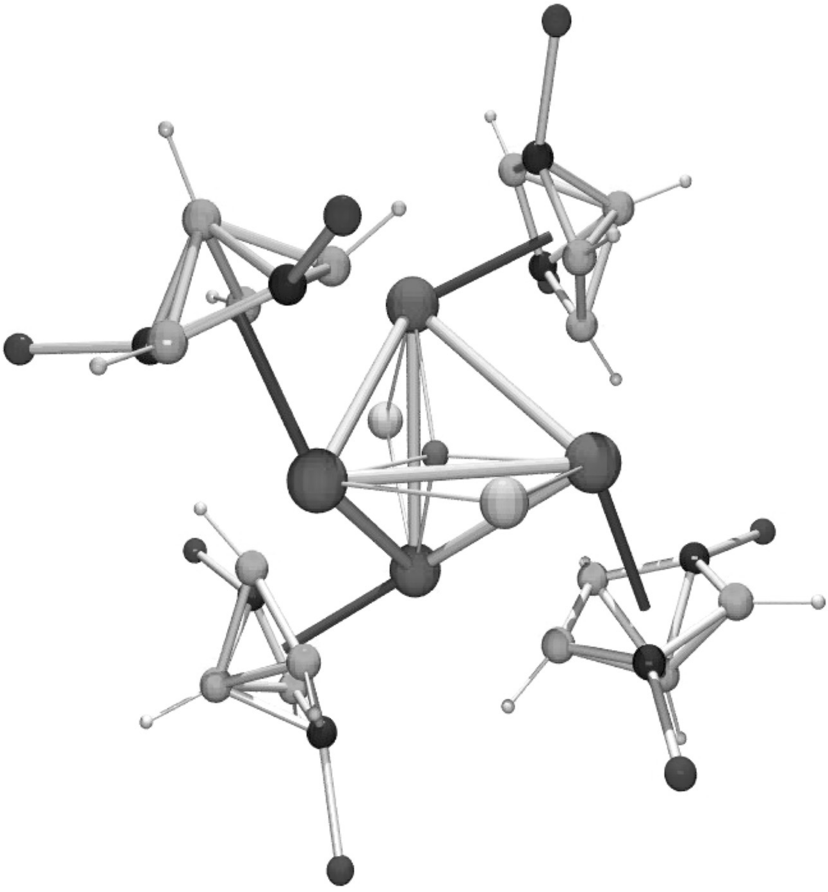
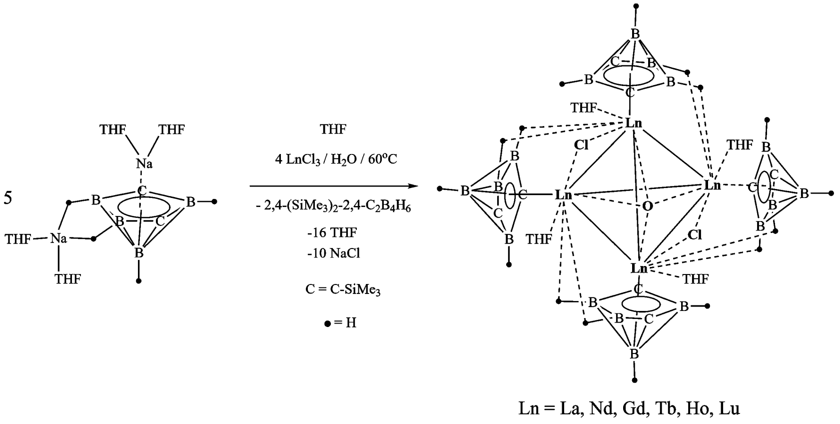


Figure 5. Crystal structure of an oxide ion encapsulating tetralanthanide tetrahedron, surrounded by "carbons apart" C_2B_4-carboranes.

there was NMR evidence for the formation of a neutral *nido*-carborane in the final reaction mixture. A 1:1 carborane:Ln molar ratio led to the same products, but in lower yields. In addition, reactions in which the Ln:H_2O ratios were less than 4:1 resulted in the formation of inseparable product mixtures, while higher ratios produced the tetralanthanide clusters and the unreacted carborane precursor.[49] The crystal structures of these tetrahedral tetra-lanthanacarboranes show that an oxide anion is at the center of the Ln_4 tetrahedron and two chlorine bridges are seen on two of the edges of the tetrahedron (Figure 5). Each lanthanide also has a *nido*-carborane

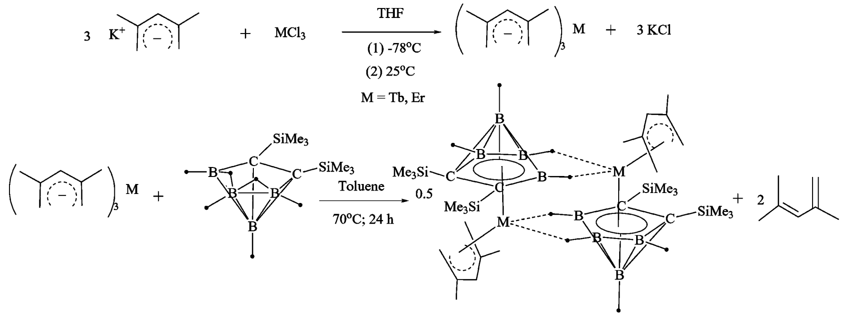


Scheme 9. Syntheses of an oxide ion encapsulating tetralanthanide tetrahedron, surrounded by "carbons apart" C_2B_4-carborane cages.

dianion η^5-bonded to it. The ionic nature of the bonding was demonstrated by DFT calculations on the model compound, $La_4OCl_2(2,4\text{-}C_2B_4H_6)_4(OH_2)_4$.[49b] The study demonstrates the results of a systematic synthetic approach based on the use water as one of the controlled reagents in constructing lanthanacarborane clusters.

6. SYNTHESES AND STRUCTURES OF OPEN-PENTADIENYLMETALLACARBORANE COMPLEXES

In addition to the well-studied cyclopentadienyl ligand, there is another π-electron donor, the open-pentadienyl ligand, R_7C_5, (R = H or an alkyl derivative). A number of so-called "open-metallocenes" where the pentadienyl group replaces one or more cyclopentadienyl ligands have been synthesized and characterized.[50] The pentadienyls have been shown to be similar to their cyclic analogues in some respects, but possess a unique chemistry that has led to a number of unusual compounds, such as the metallabenzenes and their π-complexes.[51] While both the metal-pentadienyl and the metallacarboranes have often been compared to the metallocenes, there is only one report of combining open metallocene and metallacarborane chemistry. This involved the syntheses and structural determinations of two open sandwich lanthanacarboranes, $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$(Ln = Tb, Er). The compounds were synthesized in a two–step process as outlined in Scheme 10.[52] The tris(pentadienyl)lanthanide complex was first synthesized by



Scheme 10. Synthesis of lanthanacarboranes of mixed open-pentadienyl and carborane ligands.

the 3:1 molar ratio reaction of $K[2,4\text{-}(Me)_2C_5H_5]$ and $LnCl_3$ (Ln = Tb, Er) that followed published procedures.[53,54] The $Ln(2,4\text{-}(Me)_2C_5H_5)_3$ compounds were then treated immediately with $2,3\text{-}(SiMe_3)_2$-*nido*-$2,3\text{-}C_2B_4H_6$ in a 1:1 molar ratio in toluene to give $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$(Ln = Tb, Er) dimers, in yields of 76 and 82%, respectively. The pentadienyl group can potentially act as an η^1-, η^3- or η^5-bonding ligand. The crystal structures show that each compound crystallizes as $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$ [Ln = Tb, Er (see Figure 6)], a dimer in which a planar pentadienyl and a carborane are η^5-bonded to the metal atom. In addition, each carborane is η^2-bonded to the neighboring metal in the dimer.[52] The synthesis outlined in Scheme 10 is based on the higher acidity of the bridged hydrogens in *nido*-$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_6$ compared to the methylene hydrogens on the neutral pentadiene, $2,4\text{-}(Me)_2C_5H_6$. The "diprotic" *nido*-$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_6$ removes two $[2,4\text{-}(Me)_2C_5H_5]^-$ ligands on the tris(pentadienyl)lanthanide by protonation, leading to the mixed-ligand products. Since the metal plays a somewhat passive role, it should be possible to expand the scope of these reactions to other metal-pentadienyl systems and *nido*-carboranes or their monoanions.

7. CARBORANYL-THIOL-APPENDED ANSA-LIGANDS: A NEW CLASS OF CONSTRAINED-GEOMETRY METALLOCENES

Recently, there have been reports of group 4 constrained-geometry complexes in which phenol has been used as both the linking group and to

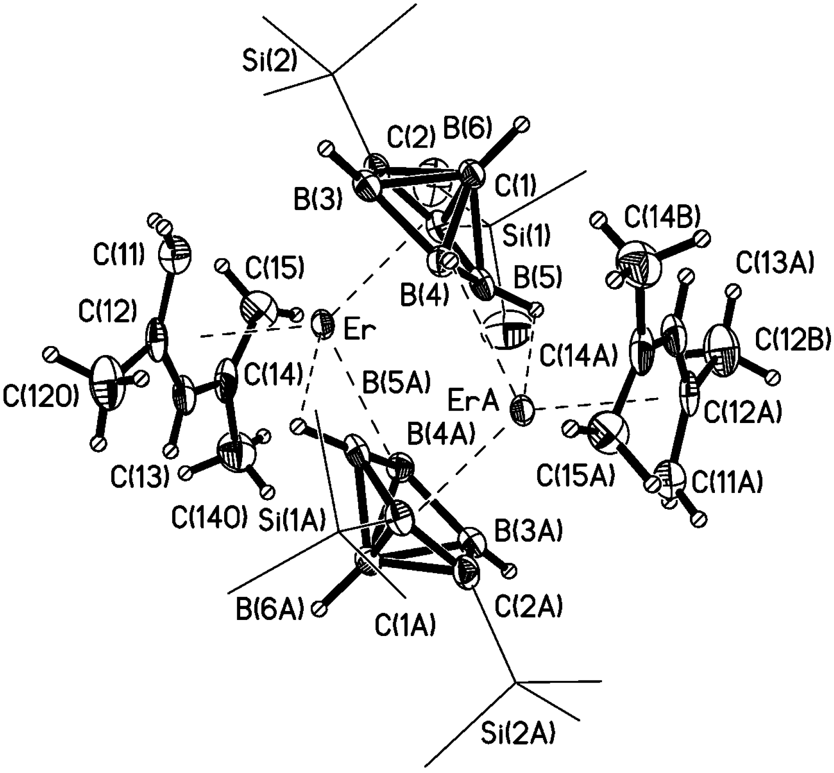
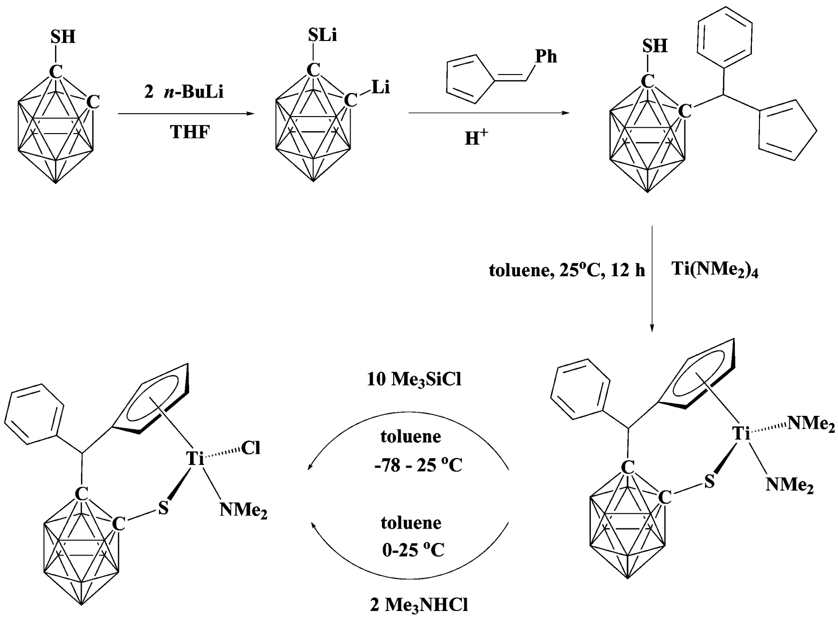


Figure 6. Crystal structure of the dimeric erbacarboranes derived from mixed open-pentadienyl and C_2B_4-carborane ligands.

provide the η^1-bonding site.[55] Since these complexes have been shown to be the basis of highly efficient catalytic systems, a further investigation of the early transition metal, constrained-geometry complexes having group 16 base sites seemed warranted. The high electron withdrawing ability of the carboranyl-chalcogenol moiety, if used as a linker to a Cp ligand, should alter the electronic properties of the ligand, and, hopefully, increase catalytic efficiency. As part of an exploratory study, 6-phenylfulvene was reacted with the dilithium salt of the 1-SH-*closo*-1,2-$C_2B_{10}H_{11}$[56] in a molar ratio of 1:1 in THF, and after hydrolysis, produced the carboranylthiol-appended cyclopentadiene ligand in 85% yield (see Scheme 11).[57] The further reaction of this species with $Ti(NMe_2)_4$ in toluene produced, *via* an amine elimination reaction, the



Scheme 11. Synthetic route for carboranyl-thiol-appended *ansa*-ligand and its conversion to titanocene derivatives; unlabelled vertices are BH groups.

constrained-geometry titanium complex, $[1\text{-}(\sigma\text{-S})\text{-}2\text{-}(\eta^5\text{-}C_5H_4CH(Ph))\text{-}1,2\text{-}C_2B_{10}H_{10})]Ti(NMe_2)_2$ that reacts further with Me_3SiCl or Me_3NHCl to form the corresponding monohalogenated species (Scheme 11).[57]

An X-ray diffraction study of $[1\text{-}(\sigma\text{-S})\text{-}2\text{-}(\eta^5\text{-}C_5H_4CH(Ph))\text{-}1,2\text{-}C_2B_{10}H_{10})]Ti(NMe_2)_2$ (see Figure 7) showed it to be a monomeric complex in which the Cp, S and the two NMe_2 groups surround the Ti in a nearly tetrahedral fashion. The good yields of the titanocene product show promise that similar reactions involving other heteroatoms of the group 16 should prove to be the efficient synthetic routes for a number of early transition metal constrained-geometry organometallics.

8. SANDWICH AND HALF-SANDWICH METALLACARBORANES OF IRON, COBALT AND NICKEL: NEW INSIGHTS INTO REACTION PATHWAYS OF CARBORANE LIGAND SYSTEMS

Most often, the open, metal bonding faces of both the *nido*-C_2B_9 and *nido*-C_2B_4 cages are pentagonal ones with the formula C_2B_3. There are

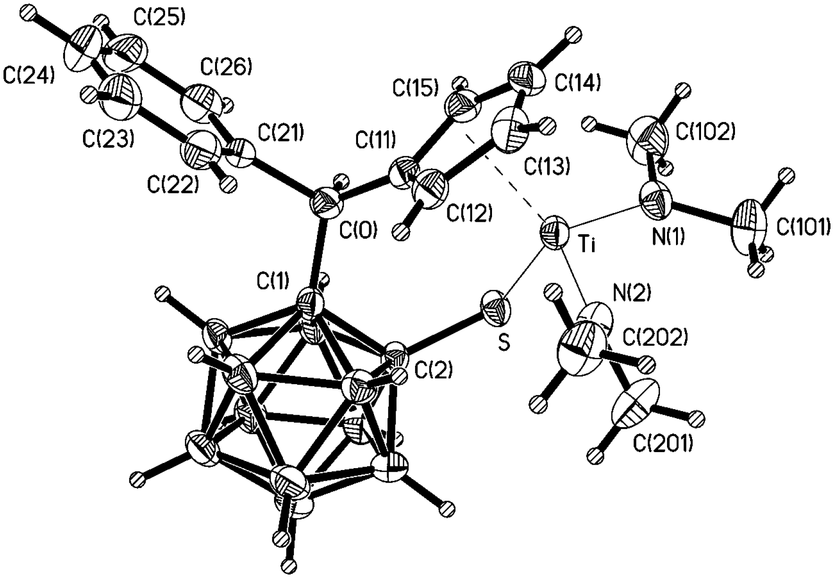
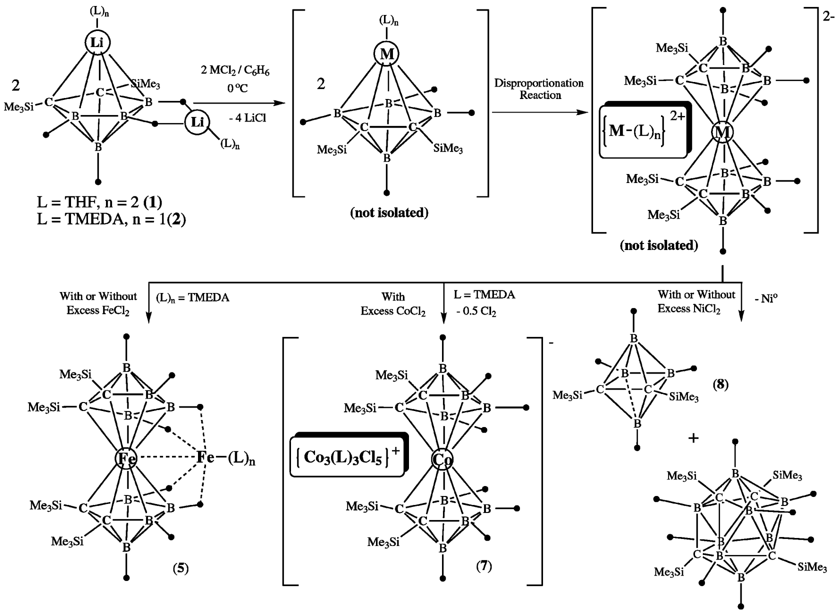


Figure 7. Crystal structure of a carboranyl-thiol-appended titanocene derivative.

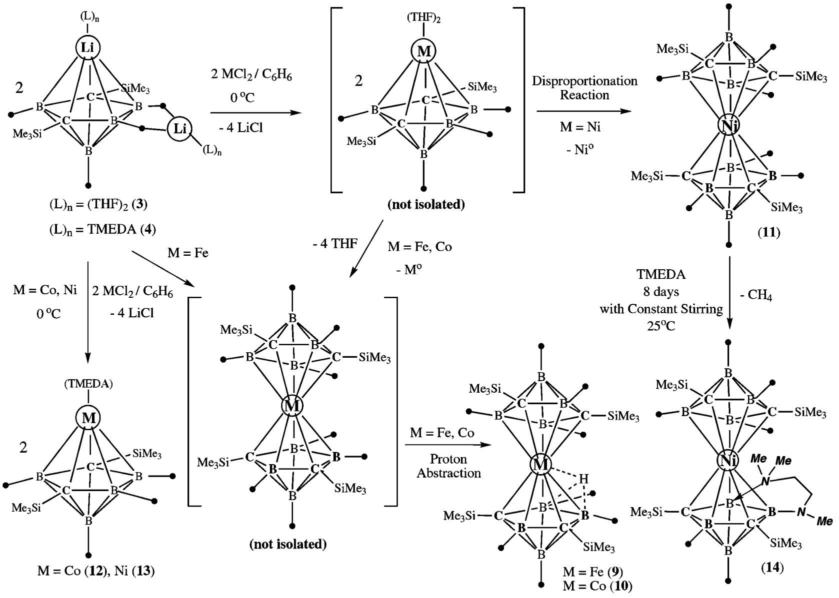
two isomeric forms, the "carbons adjacent" isomer where the two cage carbons occupy adjacent positions and the "carbons apart" isomer where they are separated by a boron atom.[58] In general both isomers seem to bind metals equally well, but the latter isomer is the thermodynamically more stable one. Many times this becomes important in determining the courses of the metalation reactions using late transition metals where oxidation number changes accompany metalation. Therefore, the sequence of reactions leading to the various products is quite important, but not always clear-cut. Hawthorne and co-workers reported that the reaction of Co(II) with $[C_2B_9H_{11}]^{2-}$ led to the isolation of the monoanionic Co(III) sandwich complex, $[(1,2\text{-}C_2B_9H_{11})_2Co]^-$, or in the presence of NaC_5H_5, the Co(III) mixed sandwich complex, $(C_5H_5)Co(1,2\text{-}C_2B_9H_{11})$, both with the concomitant formation of metallic cobalt.[59] This suggests a rapid oxidation, or disproportionation, of an initially formed Co(II) complex. The results in the C_2B_4-cage systems also point to a similar disproportionation sequence. For example, in a systematic study of the syntheses of the transition metal carborane complexes, MCl_2 (M = Fe, Co, Ni) salts were reacted with the "carbons adjacent" (Scheme 12) and "carbons apart" (Scheme 13) group 1 compounds,



Scheme 12. Synthetic Pathways to "Carbons Adjacent" Metallacarboranes of Fe, Co and Ni.

closo-*exo*-4,5-Li(THF)$_2$-1-Li(THF)$_2$-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (**1**), *closo*-*exo*-4,5-Li(TMEDA)-1-Li(TMEDA)-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (**2**), *closo*-*exo*-5,6-[(μ-H)$_2$Li(THF)$_2$]-1-Li(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$ (**3**) or *closo*-*exo*-5,6-[(μ-H)$_2$Li(TMEDA)]-1-Li(TMEDA)-2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$ (**4**) in 1:1 molar ratios.[60] The products with the "carbons adjacent" carboranes were *exo*-4,4′,5,5′-Fe(TMEDA)-*commo*-1,1′-Fe[2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$]$_2$ (**5**) (Figure 8), M$^+$[*commo*-1,1′-Co{2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$}$_2$]$^-$ [M = CoCl (**6**), M = Co$_3$(TMEDA)$_3$Cl$_5$ (**7**) (see Figure 9)], while, in the case of nickel, only the oxidative closure product, *closo*-1,2-(SiMe$_3$)$_2$-1,2-C$_2$B$_4$H$_4$ (**8**).[6e,64,65] The "carbons apart" carboranes gave *commo*-1,1′-M[2,4-(SiMe$_3$)$_2$-2,4-C$_2$B$_4$H$_4$]$_2$ (M = FeH (**9**) (Figure 10), CoH (**10**), Ni (**11**)), and 1-(TMEDA)-*closo*-2,4-(SiMe$_3$)$_2$-1,2,4-MC$_2$B$_4$H$_4$ (M = Co (**12**) (Figure 11), Ni (**13**)). The reactions are outlined in Schemes 12 and 13.[60]

Reference to these schemes show that, with the exception of **5**, all *commo*-metallacarboranes were the results of a redox process in addition to a ligation reaction; the co-product in all these reactions



Scheme 13. Synthetic Pathways to "Carbons Apart" Metallacarboranes of Fe, Co and Ni.

was the respective zero valent metal. The only two redox–free ligation reactions were found in the formations of the "carbons apart" *closo*-metallacarboranes, **12** and **13**.[61,62] In both complexes the metal ions are coordinated to bidentate TMEDA molecules, in addition to the more oxidation resistant "carbons apart" carborane ligand. On the other hand, the "carbons apart" carborane ligands favored a disproportion of Fe(II) in the formation of *commo*-1,1′-FeH[2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4]_2$ (**9**) and Fe(0), even in the presence of TMEDA, (Scheme 13, Figure 10).[60] The metal bound H in **9** could not be located in the X-ray structure shown in Figure 10, its presence was inferred for charge balance. Grimes and coworkers, described a similar diiron complex, [2,3-$(CH_3)_2$-2,3-$C_2B_4H_4]_2$Fe•Fe$(L)_2$ (L = TMEDA, THF), and found it to be an intermediate to the oxidative cage fusion product, $(CH_3)_4C_4B_8H_8$.[63] It is tempting to describe the wedged ferracarborane, **8**, as being similar, however, this compound was isolated in 90% yield and showed no tendency to react further in the absence of air.[60]

The results of the reaction of the late transition metal halides with the "carbons adjacent" and "carbons apart" *nido*-C_2B_4 carboranes can

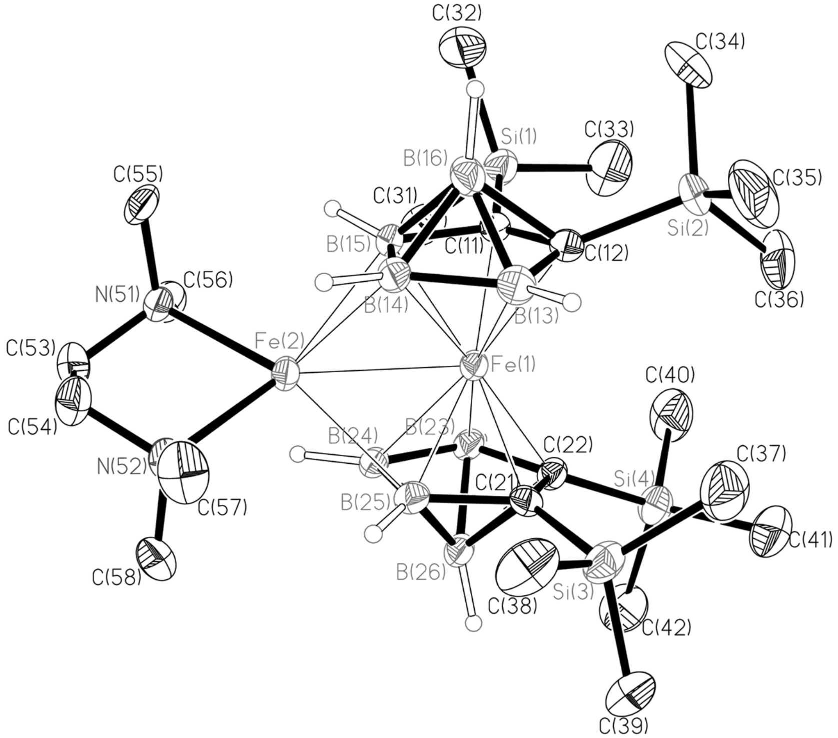


Figure 8. Crystal structure of a "wedge-bridged" diferracarborane sandwich complex (**5**).

be understood on the basis of an initial formation of a *closo*-MC_2B_4 complex, which could be sufficiently stable to be isolated or undergo further reactions yielding either the full sandwich *commo*-carborane and/or redox products. Since these reactions are run in nonpolar solvents (hexane, benzene), they are most likely between clusters and aggregates rather than isolated ions and metal proximity would be likely, facilitating metal-to-metal electron transfer. The exception seems to be that the "carbons adjacent" nickelacarborane, which decomposes directly to give Ni(0) and the oxidative closure product, *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ (**8**).[6e,64,65] It is of interest to note that the decomposition of Grimes' diiron complex, [2,3-$(CH_3)_2$-2,3-$C_2B_4H_4]_2$Fe•Fe$(L)_2$, led to the formation of the face-to-face fused C_4B_8 cages.[66–69]

The nickelacarboranes illustrate a factor that is prevalent in the metallacarborane chemistry of both transition metals and main group

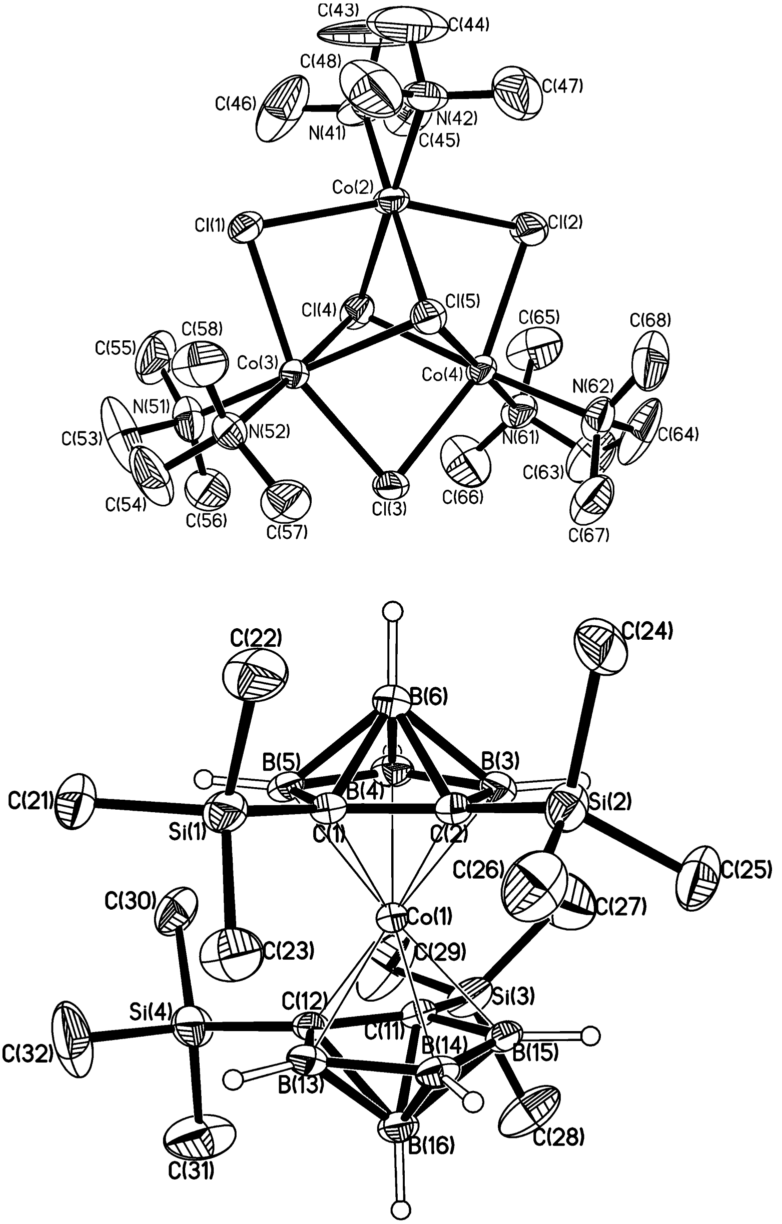


Figure 9. Crystal structure of an unusual cobaltacarborane complex comprising a paramagnetic $[Co_3(TMEDA)_3Cl_5]^+$ cation and a diamagnetic Co(III)-sandwiched dianionic complex (7).

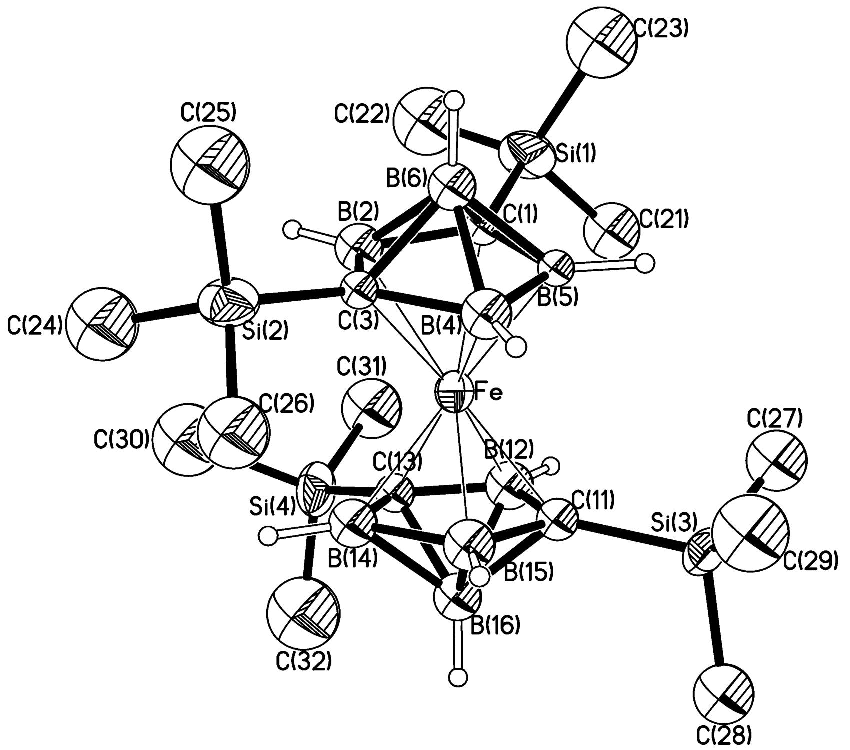


Figure 10. Crystal structure of a neutral, Fe(H)-sandwiched ferracarborane complex (**9**). The metal bound H was not found.

metals, that is the relationship between the metal's oxidation state and cluster structure. When different oxidation states are available to the metal, the higher states are found in the full-sandwich (*commo*-) compounds, while the half-sandwich (*closo*-) compounds support lower states. The metallacarboranes of Ni^{II}, Ni^{III} and Ni^{IV} have been reported in both the small, C_2B_4, and the larger, C_2B_9,[70,71] cage systems, with the Ni^{II} involved only in *closo*-metallacarboranes and the two higher oxidation states in sandwiched *commo*-complexes. The unusual charge-compensated, nickelacarborane, *commo*-1,1′-Ni^{III}-[(2,4-$(SiMe_3)_2$-5,6-B_2-{σ-N(Me)$(CH_2)_2$N-$(Me)_2$}-2,4-$C_2B_2H_2$) (2′,4′-$(SiMe_3)_2$-2′,4′-$C_2B_4H_4$)] (**14**) (see Figure 12), was the unexpected product of the reaction of **11** with carefully dried TMEDA (see Scheme 13). The high yield of **14** (89%) indicates that it was the main product of the reaction, rather than the result of an interesting side reaction. When the reaction was carried

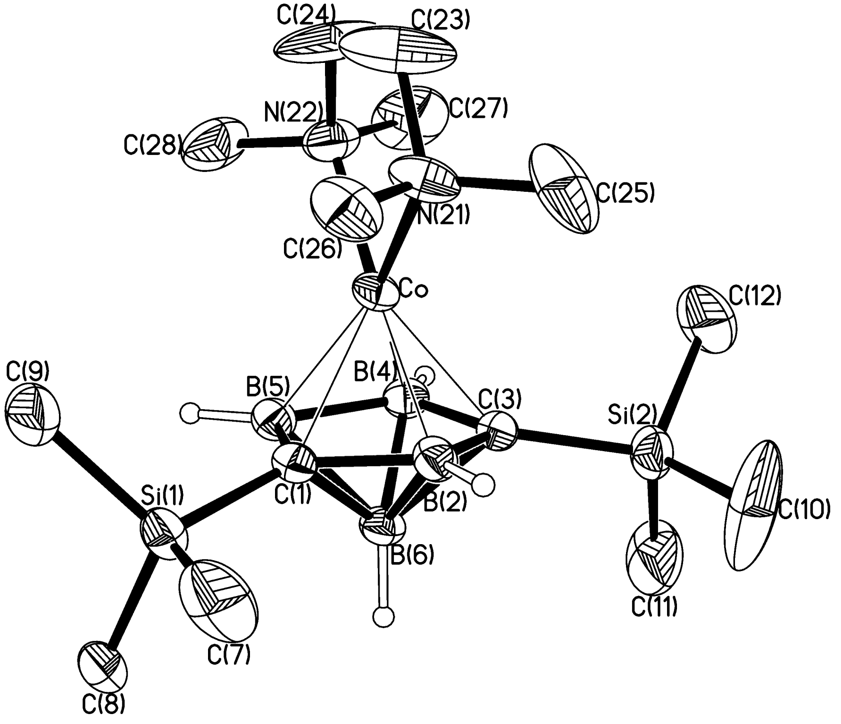


Figure 11. Crystal structure of a half-sandwich, TMEDA-stabilized, paramagnetic "carbons apart" cobaltacarborane complex (12).

out in the presence of moisture, 1-(TMEDA)-*closo*-2,4-$(SiMe_3)_2$-1,2,4-$NiC_2B_4H_4$ (**13**) was formed, in addition to *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ (**8**); this is the only example known to date of an oxidative cage closure reaction of the small cage "carbons apart" carboranes.[72] Hawthorne has recently proposed that the geometric changes accompanying the commo-Ni^{III}/Ni^{IV}-carborane interconversions be used as the basis for constructing molecular gates.[73]

CURRENT AND FUTURE DIRECTIONS

Our discussion highlights some of the research published during the past few years in the area of small-cage metallacarboranes. Although each individual report has its own particular focus, one main thrust has been directed toward systematizing the chemistry of the matallacarboranes in

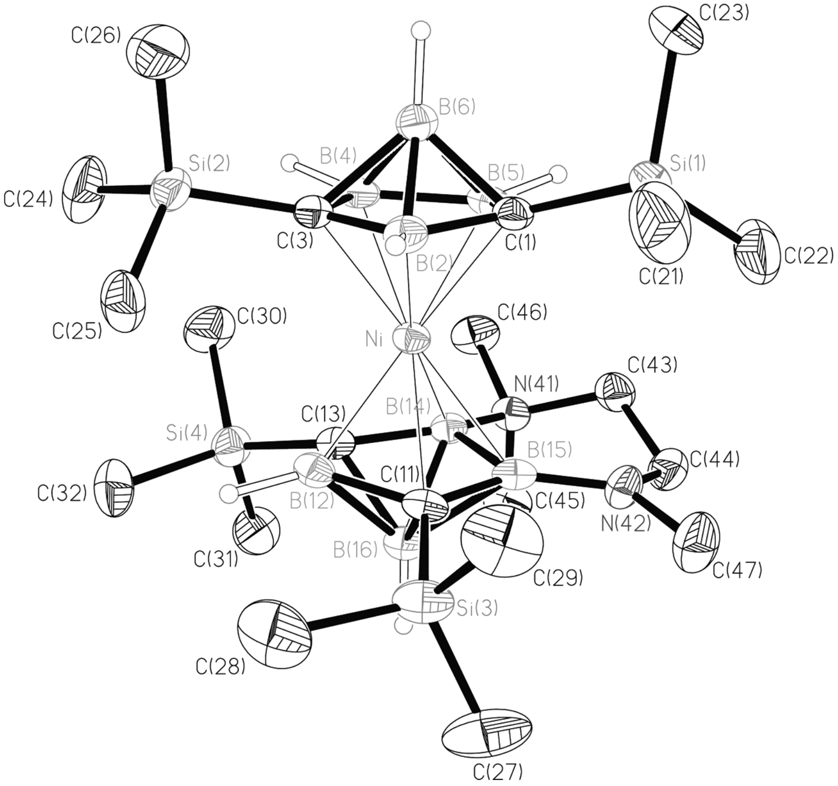


Figure 12. Crystal structure of a charge-compensated, Ni(III)-sandwiched nickelacarborane complex (**14**).

order to promote their use as possible electronic, ceramic, catalytic materials. Another thrust is to provide information on which to test and expand our knowledge of the fundamental interactions that are at work in determining the structures and properties of these fascinating clusters. The results of these studies are helping to establish a unique and useful area of organometallic chemistry that will continue to grow and bear fruit in twenty-first century.

ACKNOWLEDGMENTS

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REFERENCES

1. Grimes, R. N. Ed., 1982. *Metal Interactions with Boron Clusters*. Plenum, New York.
2. Various authors (1991). In *Electron-Deficient Boron and Carbon Clusters*, eds., Olah, G. A., K. Wade, and R. E. Williams, Wiley, New York; *Pure and Appl. Chem.*, *63*.
3. (a) Grimes, R. N. 1992. *Chem. Rev.*, **92**, 251. (b) Hosmane, N. S. and J. A. Maguire, 1990. *Adv. Organomet. Chem.*, **30**, 99. (c) Morris, J. H., H. J. Gysling, and D. Reed, 1985. *Chem. Rev.*, **85**, 51. (d) Hermanek, S. 1992. *Chem. Rev.*, **92**, 325. (e) Kennedy, J. D. 1987. In *Multinuclear NMR (NMR in Inorganic and Organometallic Chemistry)*, ed. J. Mason, Plenum, New York, Ch. 8, p. 221. (f) Wrackmeyer, B. 1988. *Annu. Rep. NMR Spectrosc.*, **20**, 61. (g) Bregadze, V. I. 1992. *Chem. Rev.*, **92**, 209. (h) Schubert, D. M., M. J. Manning, and M. F. Hawthorne, 1989. *Phosphorus, Sulphur and Silicon and Related Elements*, **41**, 253.
4. Grimes, R. N. 1982. In *Comprehensive Organometallic Chemistry*, eds. Wilkinson, G., F. G. A. Stone, and E. W. Abel, Pergamon, New York, Ch. 5.5, p. 459.
5. (a) Hosmane, N. S. and J. A. Maguire, 1993. *J. Cluster Sci.*, **4**, 297–349. (b) Saxena, A. K., J. A. Maguire, J. J. Banewicz, and N. S. Hosmane, 1993. *Main Group Chem. News* **1**(2), 14–24. (c) Saxena, A. K. and N. S. Hosmane, 1993. *Chem. Rev.*, **93**, 1081–1124. (d) Hosmane, N. S., Y. Wang, A. R. Oki, H. Zhang, D. Zhu, E. M. McDonald, and J. A. Maguire, 1994. *Phosphorus, Sulfur, and Silicon*, **93–94**, 253–256. (e) Hosmane, N. S. 1996. In *Main Group Elements and Their Compounds*, ed. Kumar Das, V. G., Narosa Publishing House/Springer-Verlag, New Delhi, India, pp. 299–327. (f) Saxena, A. K., J. A. Maguire, and N. S. Hosmane, 1997. *Chem. Rev.*, **97**, 2421–2462. (g) Hosmane, N. S. and J. A. Maguire, 1997. *Phosphorus, Sulfur, and Silicon*, **124/125**, 263–273. (h) Hosmane, N. S. and J. A. Maguire, 1998. In *Borane, Carborane, Carbocation Continuum*, ed. J. Casanova, Wiley, New York, Ch. 18, pp. 397–423. (i) Hosmane, N. S. 1999. *J. Organomet. Chem.*, **581**,

13–27. (j) Hosmane, N. S. 2000. *Curr. Sci.*, **78**, 475–486. (k) Hosmane, N. S. 2000. In *Contemporary Boron Chemistry*, Proceedings of the Tenth International Meeting on Boron Chemistry, held on 11–15 July, in Durham, England, eds., Davidson, M., A. K. Hughes, T. B. Marder, K. Wade, Royal Society of Chemistry, London, pp. 299–307. (l) Rana, G., J. A. Maguire, S. N. Hosmane, and N. S. Hosmane, 2000. *Main Group Met. Chem.*, **23**, 527–547. (m) Hosmane, N. S. and J. A. Maguire, 2000. *J. Organomet. Chem.*, **614/615**, 10–17.

6. (a) Hosmane, N. S. and R. N. Grimes, 1979. *Inorg. Chem.*, **18**, 3294. (b) Maynard, R. B., L. Borodinsky, and R. N. Grimes, 1983. *Inorg. Synth.*, **22**, 211. (c) Hosmane, N. S., N. N. Sirmokadam, and M. N. Mollenhauer, 1985. *J. Organomet. Chem.*, **279**, 359. (d) Hosmane, N. S. and R. D. Barreto, 1992. *Inorg. Synth.*, **29**, 89. (e) Hosmane, N. S., A. K. Saxena, R. D. Barreto, H. Zhang, J. A. Maguire, L. Jia, Y. Wang, A. R. Oki, K. V. Grover, S. J. Whitten, K. Dawson, M. A. Tolle, U. Siriwardane, T. Demissie, and J. S. Fagner, 1993. *Organometallics*, **12**, 3001.
7. Wallbridge, M. G. H. and C. G. Savory, 1973. *J. Chem. Soc., Dalton Trans.*, 179–184.
8. Hosmane, N. S., J. R. Wermer, H. Zhu, T. D. Getman, and S. G. Shore, 1987. *Inorg. Chem.*, **26**, 3638–3639.
9. (a) Middaugh, R. L. 1975. In *Boron Hydride Chemistry*, Ed. Muetterties, E. L., Academic Press, New York, Ch. 8, pp. 273–300. (b) Shore, S. G. 1983. In *Clusters, Rings and Polymers of the Main Group Elements*, ed. A. H. Cowley, ACS Symposium Series, Ch. 1. (c) Lawrence, S. H., J. R. Wermer, S. K. Boocock, M. A. Banks, P. C. Keller, and S. G. Shore, 1986. *Inorg. Chem.*, **25**, 367–372.
10. Toft, M. A., J. B. Leach, F. L. Himpsl, and S. G. Shore, 1982. *Inorg. Chem.*, **21**, 1952–1957.
11. (a) Soloway, A. H., W. Tjarks, B. A. Bauman, F. G. Rong, R. F. Barth, I. M. Codogni, and J. G. Wilson, 1998. *Chem. Rev. 98*, 1515–1562. (b) 1997. In *Advances in Neutron Capture Therapy, Chemistry and Biology*, Vol. II, eds., Larsson, B., J. Crawford, and R. Weinreich, Elsevier Science B. V., Amsterdam. (c) Hatanaka, H. 1991. *Borax Rev.*, **9**, 5. (d) Barth, R. F., A. H. Soloway, and R. G. Fairchild, 1990. *Cancer Res.*, **50**, 1061. (e) Hawthorne, M. F. 1993. *Angew. Chem. Int. Ed. Engl.*, **32**, 950–984. (f) Rawls, R. L. 1999. *Chem. Eng. News*, 26–29. (g) Salt, C., A. J. Lennox, M. Takagaki, J. A. Maguire, and N. S. Hosmane, 2004. *Russ. Chem. Bull.*, **53**, 1871–1888.
12. Natural and ^{10}B-enriched decaborane ($B_{10}H_{14}$), and *iso*-$B_{18}H_{22}$ are commercially available by KATCHEM LTD., Czech Republic, for the price per gram of \$15, \$250, \$151 and \$510, respectively.
13. Schlesinger, H. I., H. C. Brown, D. L. Mayfield, and J. R. Gilbreath, 1953. *J. Am. Chem. Soc.*, **75**, 213–215.

14. Schlesinger, H. I., H. C. Brown, and A. E. Finholt, 1953. *J. Am. Chem. Soc.*, **75**, 205–209.
15. Nainan, K. C. and G. E. Ryschkewitsch, 1970. *Inorg. Nucl. Chem. Lett.*, **6**, 765–766; Ryschkewitsch, G. E. and K. C. Nainan, 1974. *Inorg. Synth.*, **15**, 111–118.
16. Adams, L., S. N. Hosmane, J. E. Eklund, J. Wang, and N. S. Hosmane, 2002. *J. Am. Chem. Soc.*, **124**, 7292–7293.
17. McCarty, L. V. and P. A. Di Giorgio, 1951. *J. Am. Chem. Soc.*, **73**, 3138–3143.
18. (a) Ryschkewitsch, G. E. and V. R. Miller, 1975. *J. Am. Chem. Soc.*, **97**, 6258–6259. (b) Miller, V. R. and G. E. Ryschkewitsch, 1974. *Inorg. Synth.*, **15**, 118–122. (c) Hosmane, N. S. and R. N. Grimes, 1979. *Inorg. Chem.*, **18**, 3294–3297. (d) Davis, C. M., M. F. Klein, and K. T. Nicholson, 2002. *Phosphorus, Sulfur Silicon Relat. Elem.*, **177**, 659–664.
19. Brewer, C. T. and R. N. Grimes, 1985. *J. Am. Chem. Soc.*, **107**, 3552–3557.
20. Adams, L., S. Tomlinson, J. Wang, S. N. Hosmane, J. A. Maguire, and N. S. Hosmane, 2002. *Inorg. Chem. Commun.*, **5**, 765–767.
21. Zakharkin, L. I. and L. S. Podvisotskaya, 1967. *Zh. Obshch. Khim.*, **37**, 506; Zakharkin, L. I., V. N. Kalinin, and L. S. Podvisotskaya, 1967. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2310; Stanko, V. I., Goltyapin, Yu. V., and V. A. Brattsev, 1969. *Zh. Obshch. Khim.*, **39**, 1175.
22. (a) Hosmane, N. S., and J. A. Maguire, 2003. *Eur. J. Inorg. Chem.*, 3989–3999, and references therein. (b) Hosmane, N. S. 2003. *Pure Appl. Chem.*, **75**, 1219–1229, and references therein.
23. (a) Spencer, J. L., M. Green, and F. G. A. Stone, 1972. *J. Chem. Soc. Chem. Commun.*, 1178–1179. (b) Green, M., J. L. Spencer, F. G. A. Stone, and A. J. Welch, 1975. *J. Chem. Soc., Dalton Trans.*, 179–184. (c) Green, M., J. L. Spencer, and F. G. A. Stone, 1979. *J. Chem. Soc., Dalton Trans.*, 1679–1686. (d) Carroll, W. E., M. Green, F. G. A. Stone, and A. J. Welch, 1975. *J. Chem. Soc., Dalton Trans.*, 2263–2270. (e) Hawthorne, M. F., G. B. Dunks, and M. M. McKown, 1971 *J. Am. Chem. Soc. 93*, 2541–2543. (f) Getman, T. D., C. B. Knobler, and M. F. Hawthorne, 1990. *J. Am. Chem. Soc.*, **112**, 4593–4594. (g) Wilson. N. M. M., D. Ellis, A. S. F. Boyd, B. T. Giles, S. A. MacGregor, G. M. Rosair, and A. J. Welch, 2002. *Chem. Commun.*, 464–465. (h) Xie, Z., C. Yan, Q. Yang, and T. C. W. Mak, 1999. *Angew. Chem., Int. Ed. Engl.*, **38**, 1761–1763. (i) Chui, K., H.-W. Li, and Z. Xie, 2000. *Organometallics*, **19**, 5447–5453. (j) Zi, G., H.-W. Li, and Z. Xie, 2001. *Chem. Commun.*, 1110–1111. (k) Viñas, C., G. Barberà, and F. Teixidor, 2002. *J. Organomet. Chem.*, **642**, 16–19. (l) Chui, K., Q. Yang, T. C. W. Mak, and Z. Xie, 2000. *Organometallics*, **19**, 1391–1401.
24. Hosmane, N. S., L. Jia, H. Zhang, J. W. Bausch, G. K. S. Prakash, R. E. Williams, and T. P. Onak, 1991. *Inorg. Chem.*, **30**, 3793–3795.

25. Ezhova, M. B., H. Zhang, J. A. Maguire, and N. S. Hosmane, 1998. *J. Organomet. Chem.*, **550**, 409–422.
26. Hosmane, N. S., D. Zhu, J. E. McDonald, H. Zhang, J. A. Maguire, T. G. Gray, and S. C. Helfert, 1998. *Organometallics*, **17**, 1426–1437.
27. Hosmane, N. S., D. Zhu, H. Zhang, A. R. Oki, and J. A. Maguire, 1998. *Organometallics*, **17**, 3196–3203.
28. Zheng, C., J.-Q. Wang, J. A. Maguire, and N. S. Hosmane, 1999. *Main Group Met. Chem.*, **22**, 361–366.
29. Hosmane, N. S., S.-J. Li, C. Zheng, and J. A. Maguire, 2001. *Inorg. Chem. Commun.*, **4**, 104–107.
30. Hosmane, N. S., H. Zhang, J. A. Maguire, T. Demissie, A. R. Oki, A. K. Saxena, and W. N. Lipscomb, 2001. *Main Group Met. Chem.*, **24**, 589–596.
31. Wang, J., S.-J. Li, C. Zheng, J. A. Maguire, and N. S. Hosmane, 2002. *Organometallics*, **21**, 3314–3316.
32. Wang, J., S.-J. Li, C. Zheng, J. A. Maguire, and N. S. Hosmane, 2002. *Inorg. Chem. Commun.*, **5**, 602–605.
33. Wang, J., S.-J. Li, C. Zheng, J. A. Maguire, and N. S. Hosmane, 2002. *Organometallics*, **21**, 5149–5151.
34. Zi, G., H.-W. Li, and Z. Xie, 2001. *Organometallics*, **20**, 3836–3838. (b) Wang, Y., H. Wang, H.-W. Li, and Z. Xie, 2002. *Organometallics*, **21**, 3311–3313. (c) Zi, G., H.-W. Li, and Z. Xie, 2002. *Organometallics*, **21**, 3464–3470.
35. Wiberg, E., O. Stecher, H. J. Andraschek, L. Kreuzbichler, and E. Staude, 1963. *Angew. Chem. Int. Ed. Engl.*, **2**, 507; Eaborn, C., R. A. Jackson, and R. W. Walsingham, 1967. *J. Chem. Soc. C.*, 2188–2191; Wardell, J. L., 1982. *Comp. Organomet. Chem.*, **1**, 52–54; Billington, D. C. 1991. *Comp. Org. Syn.*, **3**, 413–434.
36. Fehlner, T. P. and N. S. Hosmane, Guest Eds. 2000 Special volume. *J. Organomet. Chem.*, **614–615**, 1–333. (b) Xie, Z. 2002. *Coord. Chem. Rev.*, **231**, 23–46.
37. Zhu, Y., K. Vyakaranam, J. A. Maguire, W. Quintana, F. Teixidor, C. Viñas, and N. S. Hosmane, 2001. *Inorg. Chem. Commun.*, **4**, 486–489.
38. (a) Park, J.-S., D.-H. Kim, J. Ko, S. H. Kim, S. Cho. C.-H. Lee, and S. O. Kang, 2001. *Organometallics*, **20**, 4632–4640. (b) Kim, D.-H., J. H. Won, S.-J. Kim, J. Ko, S. H. Kim, S. Cho, and S. O. Kang, 2001. *Organometallics*, **20**, 4298–4300. (c) Park, J.-S., D.-H. Kim, S.-J. Kim, J. Ko, S. H. Kim, S. Cho, C.-H. Lee, and S. O. Kang, 2001. *Organometallics*, **20**, 4483–4491. (d) Lee, J.-D., Y.-J. Lee, H.-J. Jeong, J. S. Lee, C.-H. Lee, J. Ko, and S. O. Kang, 2003. *Organometallics*, **22**, 445–449. (e) Lee, Y.-J., J.-D. Lee, J. Ko, S.-H. Kim, and S. O. Kang, 2003. *Chem. Commun.*, 1364–1365. (f) Shaw, K. F., B. D. Reid, and A. J. Welch, 1994. *J. Organomet. Chem.*, **482**, 207–220. (g) Cheung, M.-S., H.-S. Chan, and Z. Xie, 2004. *Organometallics*, **23**, 517–526.

39. Zhu, Y., J. A. Maguire, and N. S. Hosmane, 2002. *Inorg. Chem. Commun.*, **5**, 296–299.
40. Zhu, Y., Y. Zhong, K. Carpenter, J. A. Maguire, and N. S. Hosmane, 2005. *J. Organomet. Chem.*, **690**, 2802–2808.
41. Onak, T., D. Marynick, P. Mattschei, and G. B. Dunks, 1968. *Inorg. Chem.*, **7**, 1754–1757.
42. Hosmane, N. S. and R. N. Grimes, 1979. *Inorg. Chem.*, **18**, 2886–2891.
43. Wilczynski, R. and L. G. Sneddon, 1982. *Inorg. Chem.*, **21**, 506–514.
44. Davis, J. H. and R. N. Grimes, 1988. *Inorg. Chem.*, **27**, 4213–4219, and references therein.
45. Maguire, J. A., J.-Q. Wang, C. Zheng, C. Li, and N. S. Hosmane, 2002. *Inorg. Chim Acta*, **334C**, 91–104.
46. Wang, J., Y. Zhu, S.-J. Li, C. Zheng, J. A. Maguire, and N. S. Hosmane, 2003. *J. Organomet. Chem.*, **680**, 173–181.
47. Zhu, Y., J. A. Maguire, C. Zheng, S.-J. Li, and N. S. Hosmane, 2002. *Main Group Met. Chem.*, **25**, 173–174.
48. Hosmane, N. S., Y. Wang, A. R. Oki, H. Zhang, and J. A. Maguire, 1996. *Organometallics*, **15**, 626–638. (b) Zheng, C., N. S. Hosmane, H. Zhang, D. Zhu, and J. A. Maguire, 1999. *Internet. J. Chem.*, **2**, 10. (URL: http://www.ijc.com/articles/1999v2/10/).
49. Wang, J., S.-J. Li, C. Zheng, N. S. Hosmane, J. A. Maguire, H. W. Roesky, C. C. Cummins, and W. Kaim, 2003. *Organometallics*, **22**, 4390. (b) Wang, J., S.-J. Li, C. Zheng, A. Li, N. S. Hosmane, J. A. Maguire, H. W. Roesky, C. C. Cummins, and W. Kaim, 2004. *Organometallics*, **23**, 4621.
50. (a) Ernst, R. D. 1985. *Acc. Chem. Res.*, **18**, 56–62. (b) Ernst, R. D. 1988. *Chem. Rev.*, **88**, 1255–1291. (c) Clemente, M. E. N., P. J. Saavedra, M. C. Vasquez, M. A. Paz-Sandoval, A. M. Arif, and R. D. Ernst, 2002. *Organometallics*, **21**, 592–605. (d) Kulsomphob, V., A. M. Arif, and R. D. Ernst, 2002. *Organometallics*, **21**, 3182–3188. (e) Köhler, F. H., R. Molle, W. Strauss, B. Weber, R. W. Gedridge, R. Basta, W. Trakarnpruk, R. Tomaszewski, A. M. Arif, and R. D. Ernst, 2003. *Organometallics*, **22**, 1923–1930.
51. Bleeke, J. R. 2001. *Chem. Rev.*, **101**, 1205–1227.
52. Li, A., J. Wang, C. Zheng, J. A. Maguire, and N. S. Hosmane, 2004. *Organometallics*, **23**, 3091–3093.
53. Ernst, R. D. and T. H. Cymbaluk, 1982. *Organometallics*, **1**, 708–713.
54. Zhang, S., X. Zhuang, J. Zhang, W. Chen, and J. Liu, 1999. *J. Organomet. Chem.*, **584**, 135–139.
55. (a) Chen, Y.-X., P.-F. Fu, C. L. Stern, and T. J. Marks, 1997. *Organometallics*, **16**, 5958–5963. (b) Wang, J., Y. Mu, W. Pu, Y. Zhang, G. Yang, and J. Liu, 2001. *Chemical Research in Chinese Universities*, **17**, 115–116. (c) Pu, W., J. Wang, L. Ye, Y. Mu, G. Yang, and Y. Fan, 1999. *Acta Cryst.*, **C55**, 728–729.

56. (a) Zakharkin, L. I. and G. G. Zhigareva, 1967. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1358–1360. (b) Viñas, C., R. Benakki, F. Teixidor, and J. Casabó 1995. *Inorg. Chem.*, **34**, 3844–3845. (c) Kivekäs, R., R. Benakki, C. Viñas, and R. Sillanpää, 1999. *Acta Cryst., Cryst. Struct. Commun.*, **C55**, 1581–1583.
57. Wang, J., C. Zheng, J. A. Maguire, and N. S. Hosmane, 2003. *Organometallics*, **22**, 4839–4841.
58. (a) Hawthorne, M. F., D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebe, and P. A. Wegner, 1968. *J. Am. Chem. Soc.*, **90**, 862. (b) Hosmane, N. S., L. Jia, H. Zhang, J. W. Bausch, G. K. S. Prakash, R. E. Williams, and T. P. Onak, 1991. *Inorg. Chem.*, **30**, 3793.
59. Hawthorne, M. F., D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr. and P. A. Wegner, 1968. *J. Am. Chem. Soc.*, **90**, 879.
60. Tomlinson, S., C. Zheng, N. S. Hosmane, J. Yang, Y. Wang, H. Zhang, T. G. Gray, J. A. Maguire, F. Baumann, A. Klein, B. Sarkar, W. Kaim, T. Demissie, and W. N. Lipscomb, 2005. *Organometallics*, **24**, 2177–2187.
61. Zhang, H., Y. Wang, A. K. Sexena, A. R. Oki, J. A. Maguire, and N. S. Hosmane, 1993. *Organometallics*, **12**, 3933.
62. Hosmane, N. S., Y. Wang, H. Zhang, J. A. Maguire, E. Waldhör, and W. Kaim, 1993. *Organometallics*, **12**, 3785.
63. Grimes, R. N., R. B. Maynard, E. Sinn, G. A. Brewer, and G. J. Long, 1982. *J. Am. Chem. Soc.*, **104**, 5987.
64. Hosmane, N. S., H. Zhang, J. A. Maguire, Y. Wang, T. J. Colacot, and T. G. Gray, 1996. *Angew. Chem., Int. Ed. Engl.*, **35**, 1000–1002.
65. Hosmane, N. S., T. J. Colacot, H. Zhang, J. Yang, J. A. Maguire, Y. Wang, M. B. Ezhova, A. Franken, T. Demissie, K.-J. Lu, D. Zhu, J. L. C. Thomas, J. D. Collins, T. G. Gray, S. N. Hosmane, and W. N. Lipscomb, 1998. *Organometallics*, **17**, 5294–5309.
66. (a) Maxwell, W. M., V. R. Miller, and R. N. Grimes, 1976. *Inorg. Chem.*, **15**, 1343. (b) Maynard, R. B. and R. N. Grimes, 1982. *J. Am . Chem. Soc.*, **104**, 5983.
67. Boyter, H. A., Jr. and R. N. Grimes, 1988. *Inorg. Chem.*, **27**, 3075.
68. Grimes, R. N. 1983. *Adv. Inorg. Radio. Chem.*, **26**, 55.
69. Pipal, J. R. and R. N. Grimes, 1979. *Inorg. Chem.*, **18**, 263.
70. Hodson, B. E., T. D. McGrath, and F. G. A. Stone, 2004. *Inorg. Chem.*, **43**, 3090–3097.
71. Warren, L. F., Jr. and M. F. Hawthorne, 1970. *J. Am. Chem. Soc.*, **92**, 1157–1173.
72. Zhang, H., Y. Wang, A. K. Sexena, A. R. Oki, J. A. Maguire, and N. S. Hosmane, 1993. *Organometallics*, **12**, 3933.
73. Hawthorne, M. F., J. L. Zink, J. M. Skelton, M. J. Bayer, C. Liu, E. Livshits, R. Baer, and D. Neuhauser, 2004. *Science*, **303**, 1849.