Transition metal promoted reactions of polyhedral boranes and carboranes

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Abstract – The use of transition-metal catalysts has revolutionized the
synthetic strategies of organic chemistry; however, it has been only
recently that these reagents have been applied in the inorganic area. Our
work is described which has demonstrated that such reagents can be
used to catalyze or promote a variety of transformations involving
polyhedral boranes and carboranes, including: borane–acetylene addition,
acetylene–borane insertion, borane–olefin coupling, dehydrocoupling,
dehydrocondensation and cage-growth reactions. Selected examples which
illustrate the scope and possible mechanisms of these reactions are
discussed.

INTRODUCTION

One of the major problems in polyhedral boron cage chemistry has been the lack of general
synthetic routes for the construction of larger cage systems. This limitation has both
hampered the potential commercial applications of these types of compounds and seriously
retarded further exploratory research in the area. Our work is attempting to address this
problem by examining the use of transition metal reagents, similar to those widely employed
in organic and organometallic chemistry, to induce high yield, selective transformations in
polyhedral boranes and carboranes.

Transition-metal reagents are widely used in organic chemistry to catalyze or promote a
variety of transformations which may have parallels in polyhedral borane chemistry. Some
reaction types and examples of possible applications are summarized in the following table:

Metal Promoted Reactions	Organic	Polyhedral Boranes
1. Acetylene Addition	Synthesis of Olefins, Hydrosilylation	Synthesis of Alkenyl-boranes and –Carboranes
2. Olefin Substitution	Arene–Olefin Coupling, Synthesis of Substituted Olefins	Synthesis of Alkenyl-boranes and –Carboranes
3. Cyclo–Addition	Synthesis of Alicyclic Compounds	Synthesis of Two–, Four- or Higher Carbon Carborane Cages
4. Dehydrocoupling	Arene–Coupling	Synthesis of Multi–Cage Compounds
5. Dehydrogenations	Synthesis of Unsaturated Organics	Cage Closure Reactions; Generation of Reactive Fragements

It should be noted, however, that while there may indeed be close analogies between
metal-promoted organic and boron hydride reactions, there are also significant differences.
For example, a typical C–H bond energy is substantially greater than that for an analogous
B–H bond. This difference generally means that metal-catalyzed reactions involving boron
hydrides occur under much milder conditions than the analogous organic systems. Likewise,
polyhedral boranes are both more reactive (particularly toward basic ligands) and have sites
of different reactivity in the same molecule, leading to more complex (and as a result more
intriguing) reaction mechanisms and selectivities.

As a result of our work we have now developed six separate classes of transition metal
promoted polyhedral borane reactions which are described, with selected examples, in the
following sections.

ACETYLENE ADDITIONS

Our initial work in the use of transition metals to catalyze reactions in polyhedral boron chemistry focused on promoting the reactions of alkynes with small boranes (ref. 1-3) with the goal of developing new routes to small carboranes. As a result of this study, it was found that complexes, such as $Ir(CO)Cl[P(C_6H_5)_3]_2$ and $(RC_2R')Co_2(CO)_6$ catalyzed the reaction of pentaborane(9) with alkynes under mild conditions giving good yields of alkenyl-pentaboranes.

$$B_5H_9 + RC \equiv CR' \xrightarrow{\text{Catalyst}} \quad \text{(1)}$$
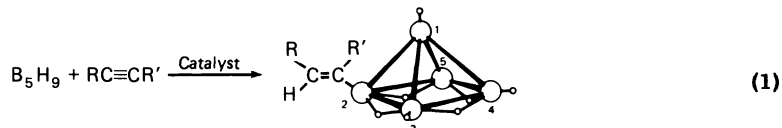
The results obtained for these complexes suggest that the reaction mechanism is similar to those previously proposed for the analogous hydrogenation reactions of these catalysts. Thus in the case of $Ir(CO)Cl[P(C_6H_5)_3]_2$, this would involve substitution of a triphenylphosphine ligand by an acetylene, followed by oxidative-addition at the metal of one of the basal B-H units of pentaborane(9). Subsequent insertions of the alkyne into the Ir-H and Ir-B bonds, followed by reductive elimination would give the alkenylborane products and regeneration of the catalytic species.
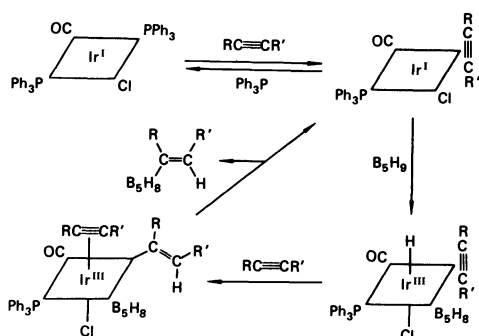

Fig. 1. Proposed catalytic sequence leading to the formation of alkenylboranes.

Only basally-substituted alkenyl-pentaborane products are produced in these reactions, suggesting that oxidative-addition reactions of pentaborane occur only at basal B-H units. This conclusion is further supported by the report (ref. 4) that pentaborane(9) will oxidatively add to $trans$-$Ir(CO)Cl(PMe_3)_2$ to yield the stable metalloborane complex 2-$[IrH(CO)Cl(PMe_3)]_2$-B_5H_8.

Since alkenylpentaboranes had been proposed to be possible intermediates in thermally induced carborane formation reactions, it was expected that these compounds could be readily converted into carboranes. We then demonstrated (ref. 1,2) that the thermolysis of these alkenylpentaboranes, under relatively mild conditions, resulted in high yield selective conversions to monocarbon carborane species based on the $nido$-2-CB_5H_9 cage system. For example, pyrolysis of 2-(cis-2-but-2-enyl)-pentaborane(9) was found to give the two alkyl-substituted isomers shown below in 85% yield.

$$\xrightarrow{355° C} \quad \text{(2)}$$
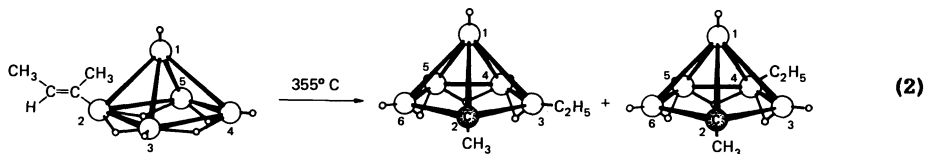
The major products observed in the thermolytic reactions are consistent with the reaction mechanism originally proposed (ref. 5,6) by Williams to account for the formation of 2-CB_5H_9 alkyl derivatives as minor products in the thermal reaction (215°C) of alkynes with pentaborane(9). A plausible reaction sequence based on this mechanism which allows the conversion of the alkenylpentaborane(9) compounds to the observed monocarbon carboranes is depicted in Fig. 2. The first step can be envisioned as an internal hydroboration of the alkenyl substituent by an adjacent B-H group (boron positions 1 or 3) with the boron adding to the α-carbon and the hydrogen to the β-carbon. Thus, the α-carbon is incorporated into the cage while the β-carbon becomes part of an alkyl group which migrates to adjacent boron positions 1 or 3. Alkyl migration from the apical boron can then occur to generate either the 3- or 4-substituted products.
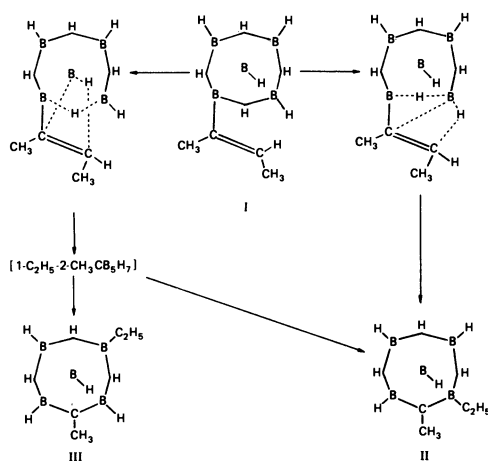
Fig. 2. Proposed mechanism for the formation of mono-carbon carboranes from alkenylpentaboranes.

The mechanism outlined above is also strongly supported by the results from the thermolytic reactions of the two isomeric propenylpentaboranes indicated below. Thus, if this mechanism is correct, then upon thermolysis these compounds should yield different carborane isomers. The isomer with an α-methyl group should form carboranes which are substituted with methyl groups at the carbon and either the 3 or 4 borons, while the β-isomer should give only boron-substituted ethyl derivatives. In both cases monocarbon carborane products are obtained in good yields with the major products consistent with these predictions.

$$(3)$$

$$(4)$$
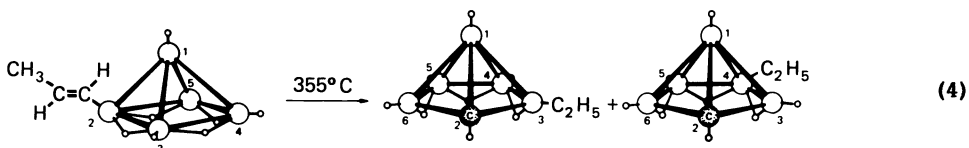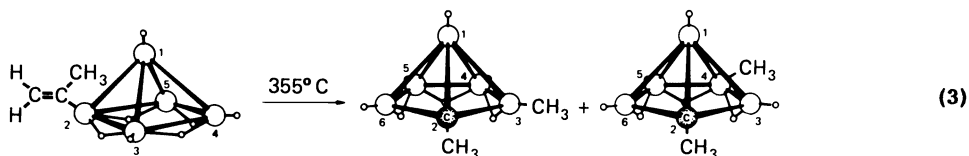
The initial work described above was very important since it demonstrated not only that transition metals could be used to catalyze reactions involving boron hydrides, but also that such reactions could lead to high yield, selective transformations. Furthermore, because of the mild conditions employed in these reactions, it is possible to isolate and study compounds which may be intermediates in thermally induced reactions and thus gain new insights into the mechanisms of such reactions.
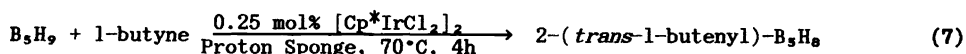
These acetylene-addition catalysts have now been applied to the synthesis of a variety of alkenyl-boron compounds including for example, alkenyl-carboranes (ref. 3) and alkenyl-borazines (ref. 7).

$$(5)$$

$2,4\text{-}C_2B_5H_7$

$$(6)$$

$B_3N_3H_6$
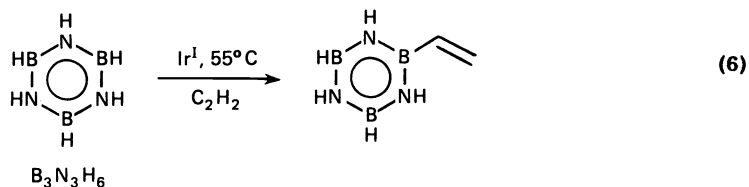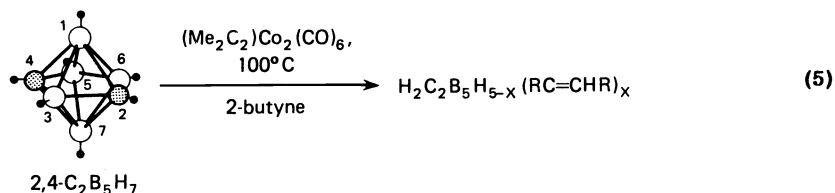
The metal-catalyzed acetylene addition reactions described above each employed complexes which contain dissociable basic ligands, such as carbon monoxide or phosphines, which can attack boranes and cause decomposition.   This problem led us to investigate new types of acetylene addition catalysts.
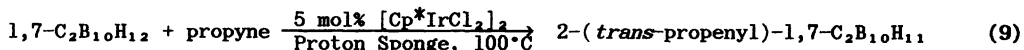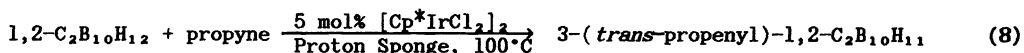
Maitlis (ref. 8) has developed a series of catalysts that do not contain basic ligands, based on pentamethylcyclopentadienyl-rhodium (Cp*Rh) and –iridium (Cp*Ir).   The catalysts are derived from [Cp*-MCl$_2$]$_2$ (M=Rh or Ir) and are air-stable solids which have good solubility in polar organic solvents.   It has been found that the Cp*-M bond is extremely inert and will allow the complex to undergo a variety of reactions without reduction to the metal occurring. Furthermore, these complexes have been shown to be highly reactive for a variety of organic transformations.   For example, both Cp*Rh and Cp*Ir catalysts show high activity as olefin hydrogenation catalysts at 20°C and 1 atm H$_2$ pressure (ref. 9).   Likewise, Bergman (ref. 10) and Graham (ref. 11) have each demonstrated that Cp*Ir complexes are extremely reactive and are capable of hydrocarbon C–H bond activation.

We have begun investigations of the use of Cp*Ir and Cp*Rh complexes to catalyze boron hydride reactions and our preliminary results (ref. 12) with Cp*Ir catalysts indicate that these complexes are <u>the most active catalysts that we have encountered to date</u>.   For example, the reaction of pentaborane(9) with 1-butyne was carried out in the presence of [Cp*IrCl$_2$]$_2$ as indicated:

$$B_5H_9 + \text{1-butyne} \xrightarrow[\text{Proton Sponge, 70°C, 4h}]{\text{0.25 mol\% [Cp*IrCl}_2]_2} \text{2-(}trans\text{-1-butenyl)-}B_5H_8 \qquad (7)$$

The product was obtained in good yields with over 130 catalyst turnovers in four hours. The reaction has not yet been optimized, but this turnover rate is already substantially higher than those observed with previous catalysts.

We had also previously found that while catalysts such as Ir(CO)Cl(PPh$_3$)$_2$ and R$_2$C$_2$Co$_2$(CO)$_6$ activated small boranes and carboranes, they were ineffective toward important larger cage systems such as ortho-carborane and decaborane(14).   We have now found in other recent work that Cp*Ir complexes are highly reactive toward these larger clusters.

$$1,2\text{-}C_2B_{10}H_{12} + \text{propyne} \xrightarrow[\text{Proton Sponge, 100°C}]{\text{5 mol\% [Cp*IrCl}_2]_2} \text{3-(}trans\text{-propenyl)-1,2-}C_2B_{10}H_{11} \qquad (8)$$

$$1,7\text{-}C_2B_{10}H_{12} + \text{propyne} \xrightarrow[\text{Proton Sponge, 100°C}]{\text{5 mol\% [Cp*IrCl}_2]_2} \text{2-(}trans\text{-propenyl)-1,7-}C_2B_{10}H_{11} \qquad (9)$$

The products are exclusively boron-substituted and the yields and turnover rate for the reaction appear excellent.
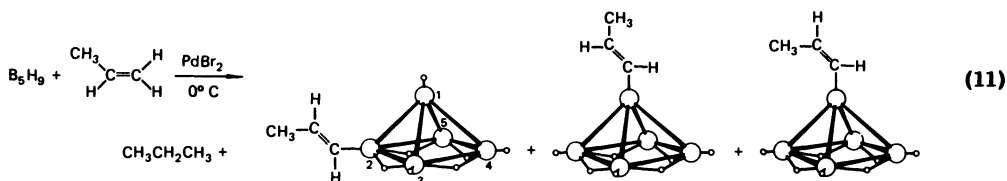
OLEFIN–BORANE COUPLING

The metal-catalyzed syntheses of alkenylpentaboranes described above each employ acetylenes as starting materials which could result in a number of serious practical and safety problems if these reactions were carried out on larger scales. In an effort to circumvent this problem, we investigated metal-promoted reactions of *olefins* with boron hydrides.   Of particular interest as potential catalysts were Pd(II) salts since such compounds have been widely employed in organic chemistry (ref. 13) to promote arene–olefin coupling reactions yielding vinyl-arene compounds.

$$C_6H_6 + H_2C=CH_2 + Pd(OAc)_2 \longrightarrow H_2C=CH\text{-}C_6H_5 + Pd + 2HOAc \qquad (10)$$
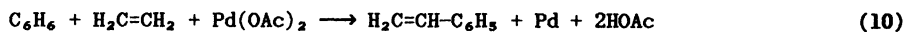
We have found (ref. 14) that pentaborane(9) undergoes an analogous borane–olefin coupling reaction with various olefins, including ethylene, propylene and 1-butene, in the presence of catalytic amounts of palladium(II) dibromide, to give excellent yields of alkenylpentaboranes under mild conditions.

For example, the reaction of pentaborane(9) with propylene in the presence of palladium bromide at 0°C was found to give an 87% yield of propenylpentaboranes, as indicated below:

Of particular importance is the fact that the reaction is observed to be **catalytic** with respect to the palladium bromide (7.6 equivalents of propenylpentaboranes/equiv. of $PdBr_2$) and, in contrast to arene–olefin coupling reactions, does not require an additional oxidant. Most significantly, alkenylboranes can be prepared from olefins, rather than more difficult to handle acetylenes, and that these reactions can be carried under mild, low temperature/pressure conditions.

We have also extended (ref. 15) our studies to other boron hydride systems and have shown that palladium dibromide catalysts can be used to prepare, for example, boron-substituted alkenylcarboranes in high yields.

$$Et_2C_2B_4H_6 + CH_3CH=CH_2 \xrightarrow[12\ h]{PdBr_2}$$

(12)
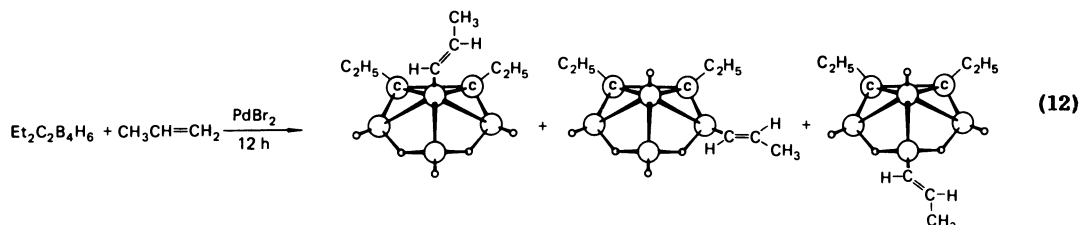
ACETYLENE-INSERTION REACTIONS

As described in the preceding sections, we have demonstrated that various metal reagents can catalyze the reaction of a borane with either an acetylene or olefin to yield alkenyl–boranes. While these alkenyl–boranes were shown to be precursors to mono–carbon carboranes, it is also significant that no two–carbon insertions were observed. This suggests that such insertions do not occur via these types of alkenyl–boranes. This conclusion prompted us to investigate other types of potential catalysts for acetylene/borane reactions which might lead to carborane formation.

We have now found (ref. 16) that Ni(II) salts promote two–carbon acetylene insertions into certain polyhedral borane anions. For example, the reaction of the carborane *nido*-2,3-$Et_2C_2B_4H_6$ with 2-butyne, in the presence of sodium hydride and nickel(II) chloride has been found to produce the four–carbon carborane *nido*-4,5,7,8-$Me_2Et_2C_4B_4H_4$, in ~30–35% yield.

$$+ NaH + MeC \equiv CMe + NiCl_2 \xrightarrow{THF}$$

(13)

2,3-$Et_2C_2B_4H_6$ 4,5,7,8-$Me_2Et_2C_4B_4H_4$
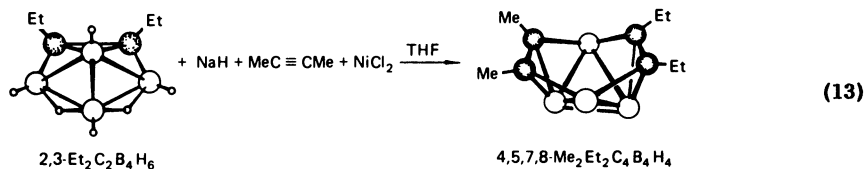
While the mechanism of reaction has not yet been proven, our experimental observations suggest that the reaction may involve the formation of a nickelacarborane complex, such as shown below, which, upon warming, could intramolecularly eliminate NaCl and react with 2-butyne to generate an alkyne/metallacarborane intermediate.


(14)

$Na^{\oplus}[\eta^5$-$Et_2C_2B_4H_4$-Ni-Cl$]^{\ominus}$ Me_2C_2-Ni-$Et_2C_2B_4H_4$
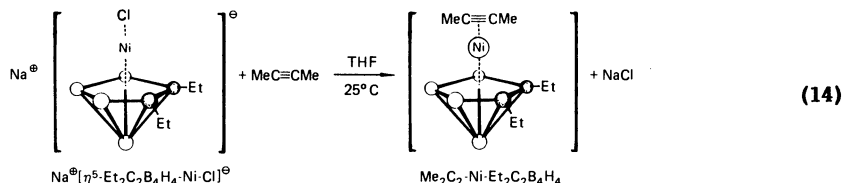
Upon standing, this alkyne/nickelacarborane complex may then undergo reductive cycloaddition to form the four–carbon carborane and nickel metal:

(15)

4,5,7,8-$Me_2Et_2C_4B_4H_4$
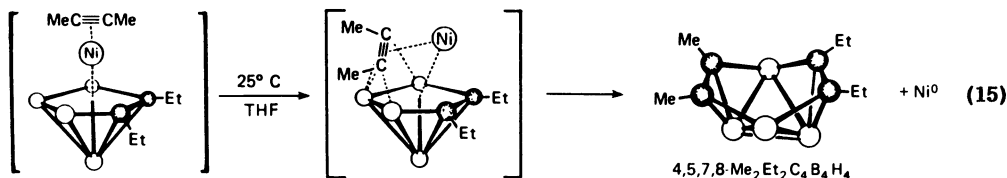
This synthetic route has several significant advantages over those previously reported (ref. 17-19). The reaction involves a convenient "one-pot" procedure and employs the readily accessible carborane (ref. 20) 2,3-$Et_2C_2B_4H_6$ as a starting material. Furthermore, the product is easily isolated in high purity by simple vacuum-line fractionation.

The nickel chloride reaction demonstrated that metal ions can promote alkyne insertion reactions into polyhedral borane cages; however, the reaction is limited in that it is not catalytic.   Furthermore, extension to other carborane and borane anions has been less successful. These problems have led us to explore new ideas for catalytic routes for alkyne insertions.

The overall reaction for the alkyne insertion into, for example, the neutral $Et_2C_2B_4H_6$ cage system would be:

$$Et_2C_2B_4H_6 + RC\equiv CR \longrightarrow Et_2R_2C_4B_4H_4 + H_2 \qquad (16)$$
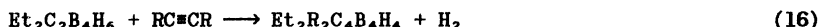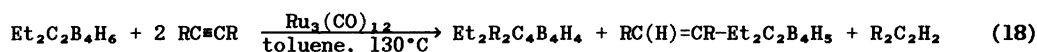
Thus, the desired reaction is formally a dehydro-alkyne-insertion.   Related dehydro-addition reactions in organometallic chemistry are well known.   For example, various metal carbonyls, including $Fe(CO)_5$ and $Ru_3(CO)_{12}$, have been found (ref. 21-23) to catalyze the dehydrosilylation of olefins:

$$HSiEt_3 + H_2C=CRH \xrightarrow{\text{catalyst}} Et_3SiC(H)=CRH + Et_3SiCH_2CH_2R + CH_3CH_2R \qquad (17)$$
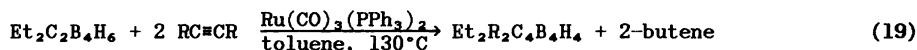
Both thermal and photocatalysts are known and it has been found that the ratio of the vinyl to saturated products are highly dependent on the particular olefin, catalyst and reaction conditions.

We have recently begun to investigate the use of these known dehydrosilylation catalysts to promote dehydro-alkyne insertion reactions with the goal of obtaining general routes to two, four or higher carbon content carboranes. Initial studies (ref. 24) with $Ru_3(CO)_{12}$ have demonstrated the catalytic high yield reaction of alkynes with the 2,3-$Et_2C_2B_4H_6$ cage system, according to the reaction:

$$Et_2C_2B_4H_6 + 2\ RC\equiv CR \xrightarrow[\text{toluene, 130°C}]{Ru_3(CO)_{12}} Et_2R_2C_4B_4H_4 + RC(H)=CR-Et_2C_2B_4H_5 + R_2C_2H_2 \qquad (18)$$

Other recent studies in our laboratory have shown that both the cluster, $Ru_3(CO)_9(PPh_3)_3$, and the monometallic complex $Ru(CO)_3(PPh_3)_2$ also catalyze the reactions of $Et_2C_2B_4H_6$ with internal alkynes, but in each case give >98% selectivity for alkyne insertions.

$$Et_2C_2B_4H_6 + 2\ RC\equiv CR \xrightarrow[\text{toluene, 130°C}]{Ru(CO)_3(PPh_3)_2} Et_2R_2C_4B_4H_4 + 2-\text{butene} \qquad (19)$$

These observations strongly support the proposed similarity of dehydrosilylation reactions and dehydro-alkyne insertion reactions.   While the exact mechanism of these reactions has not yet been established, a reasonable reaction sequence based on those proposed for dehydrosilylation reactions is outlined below:
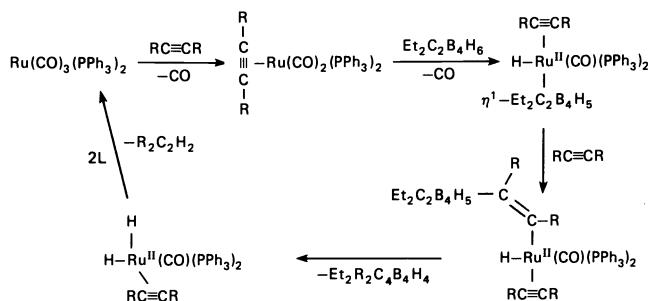

Fig. 3. Proposed reaction sequence for catalytic dehydroalkyne-insertion reactions.

Thus, key steps in the above mechanism are oxidative-addition of the carborane to the metal site, insertion of a bound acetylene into a metal-boron bond, transfer of two carborane hydrogens to an additional acetylene, and reductive-elimination of products.   We have proposed a similar mechanistic sequence for the palladium bromide catalyzed borane-olefin coupling reaction discussed earlier.

These initial studies clearly indicate that dehydrosilylation catalysts have excellent potential for use as alkyne insertion catalysts into polyhedral borane clusters and suggest that metal reagents may be able to promote two-carbon insertions into a variety of polyhedral boron cage systems leading to new routes to two, four, and perhaps, higher carbon carborane clusters.

DEHYDROCOUPLING

During the course of exploring other potential borane–olefin coupling catalysts, the reaction of pentaborane(9) with olefins and platinum dibromide was investigated. Surprisingly, the platinum salt did not promote borane–olefin coupling, but instead, **catalyzed** the dehydrocoupling reaction of pentaborane(9) to yield a coupled–cage product (ref. 25, 26).

$$2 \quad B_5H_9 \quad \xrightarrow[25°C]{PtBr_2} \quad 1,2'\text{-}[B_5H_8]_2 \quad + H_2 \qquad (20)$$
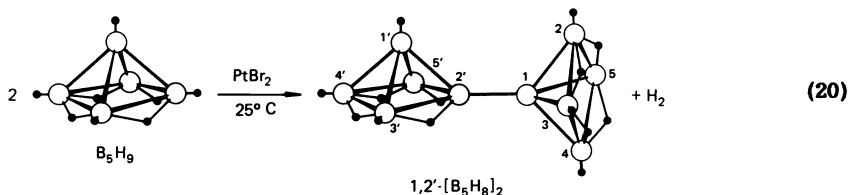
The reaction involves simply stirring liquid pentaborane(9) over $PtBr_2$ powder in vacuo with periodic removal of evolved hydrogen and product. Nearly quantitative yields of $1:2'\text{-}[B_5H_8]_2$ are obtained, and, although the reaction is slow (<1 catalyst-turnover/day), we have had reactions continuing for greater than one month with little decrease in rate. It is also significant that the reaction is highly selective in producing only one coupled-cage isomer.
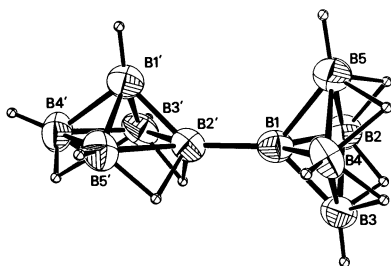

Fig. 4. ORTEP drawing of the molecular structure of $1:2'\text{-}[B_5H_8]_2$.

As can be seen in the above figure (ref. 27), the product, $1:2'\text{-}[B_5H_8]_2$, is composed of two pentaborane cage units which are joined by means of a single two-center, boron–boron bond. Although all three coupled-cage isomers, $1:1'\text{-}[B_5H_8]_2$, $2:2'\text{-}[B_5H_8]_2$, and $1:2'\text{-}[B_5H_8]_2$, are known, it is significant that the platinum bromide promoted reaction of pentaborane gives exclusively $1:2'\text{-}[B_5H_8]_2$. This selectivity suggests that both electrophilic attack by the metal and oxidative-addition at the metal may be involved in the reaction. A single mechanistic sequence which can account for the observed products is outlined below.
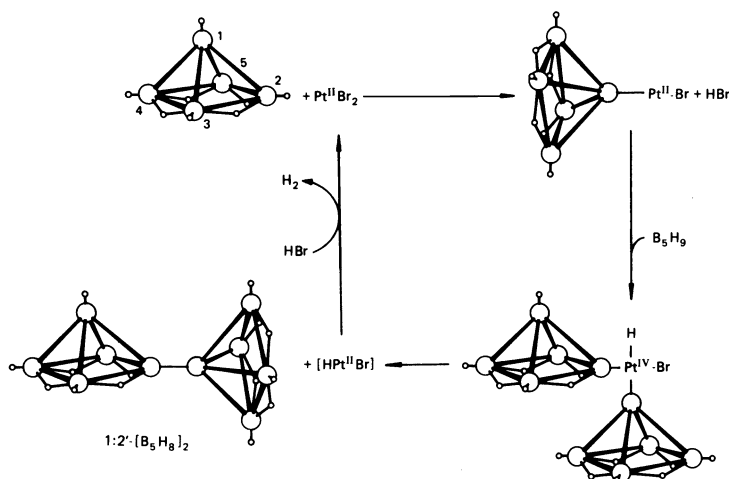

Fig. 5. Proposed catalytic sequence leading to the formation of $1:2'\text{-}[B_5H_8]_2$.

The expected first step in the reaction of pentaborane(9) with platinum(II) bromide would be the electrophilic attack by the metal at the borane. This would lead to the formation of a 1-pentaboranylplatinum(II) intermediate which could then react with a second pentaborane(9) molecule, by means of an oxidative-addition reaction of the metal at a basal B–H group, to give the corresponding platinum(IV) intermediate. Reductive elimination would then yield the

observed product, 1:2′-[B₅H₈]₂, and a [HPtBr] species which could react further with HBr to give PtBr₂ and hydrogen. The selective formation of only the 1:2′-[B₅H₈]₂ isomer, instead of the 1:1′-[B₅H₈]₂ and 2:2′-[B₅H₈]₂ isomers, is consistent with this mechanism, and indicates that the PtBr₂ has a dual function in these reactions. However, the initial electrophilic substitution at the apex appears to be the key step in the pentaborane(9) reaction, since it was found that when the apex position was blocked with a methyl substituent, no reaction with PtBr₂ occurred.

Boron-boron coupled-cage compounds, such as 1:2′-[B₅H₈]₂, have until recent times been somewhat of a rarity. In fact, although the first boron-boron coupled polyhedral cage compound, 1:1′-[B₅H₈]₂, was synthesized and structurally characterized more then 20 years ago, (ref. 28) as late as 1977 fewer than ten of these compounds had been reported. Generally, these complexes have been synthesized using either light, heat, or electrical discharge to induce boron-hydrogen bond cleavage in the parent borane or carborane with the resulting fragments or radicals further reacting to give the corresponding coupled-cage compound. These types of reactions have usually been found to give low yields of products and/or are non-selective, resulting in the production of several different boron-boron linked isomers. Selective syntheses for certain coupled-cage species have been developed but are still quite limited; therefore, we further investigated the PtBr₂ catalyzed reaction with the aim of developing a general route to these complexes. It was subsequently found that platinum(II) bromide could be used to catalyze the formation of a wide range of boron-boron coupled polyhedral cage systems.
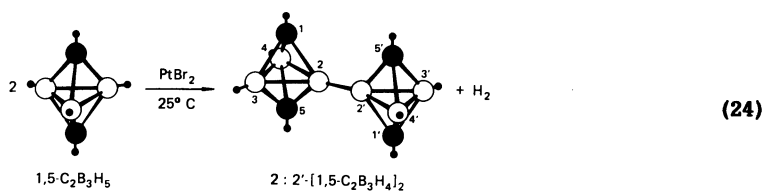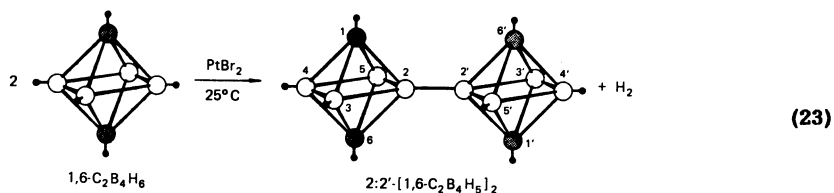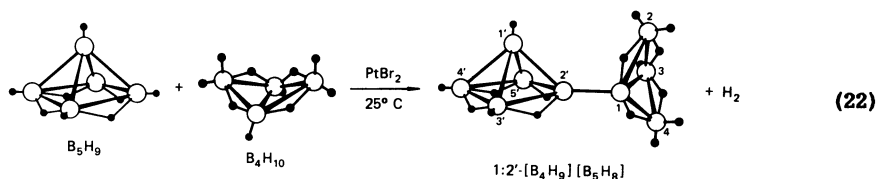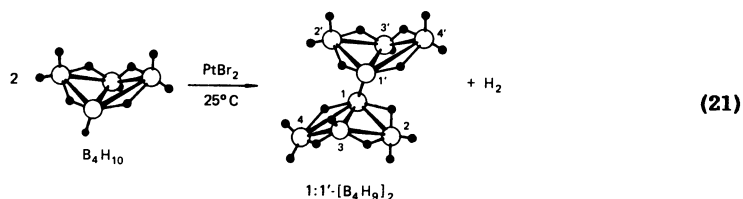
The facile formation of multicage systems is potentially of great significance in polyhedral borane chemistry since the procedures used for their syntheses provide new pathways to higher boron content materials which avoid the problems inherent in traditional thermally induced cage-growth reactions. Furthermore, if these multicage compounds could be converted to fused-cage boranes or carboranes, then this would represent an alternative to decaborane(14) based synthetic procedures for the formation of large-cage materials.

We have now found (ref. 27) that under suitable conditions 1:2′-[B₅H₈]₂ will, in fact, undergo coupled-cage to single-cage fusions resulting in the production of a number of important larger cage systems (Fig. 6).

These results indicate that a synthetic sequence involving the catalytic dehydrocondensation of a small borane or carborane followed by a multicage to single cage fusion reaction may be a viable new route to larger-cage systems. We are now investigating further extensions of this synthetic methodology.
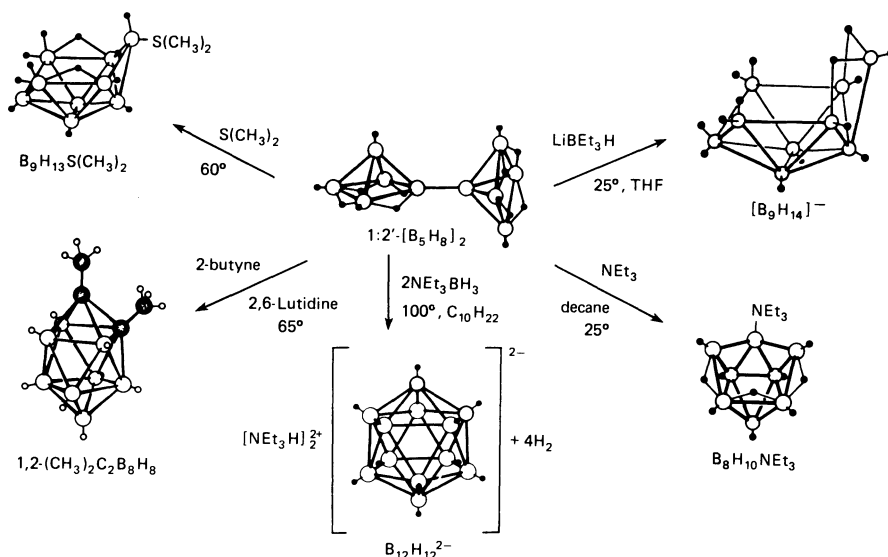
**Fig. 6.** 1:2′-[B$_5$H$_8$]$_2$ cage condensation reactions.

DEHYDROCONDENSATION AND CAGE-GROWTH REACTIONS

The work described above has shown that platinum(II) bromide promotes dehydrocoupling reactions of a variety of polyhedral boranes and carboranes. These results suggested that it might also be possible to react a polyhedral borane with a very reactive small borane or borane fragment to produce an unstable coupled complex which could then condense generating a larger, single-cage molecule. Indeed, we have now observed (ref. 29) that platinum(II) bromide catalyzes the reactions of diborane with a number of polyhedral boranes and carboranes to yield either cage-growth or dehydrocondensation products.
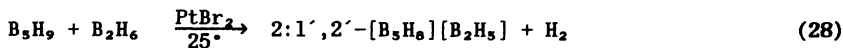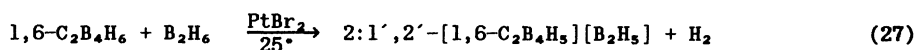
Thus, the platinum(II) bromide promoted reaction of diborane with 1,5-C$_2$B$_3$H$_5$, which was carried out at room temperature, was found to give the new carborane 5,6-C$_2$B$_6$H$_{12}$ in nearly quantitative yields.

(25)
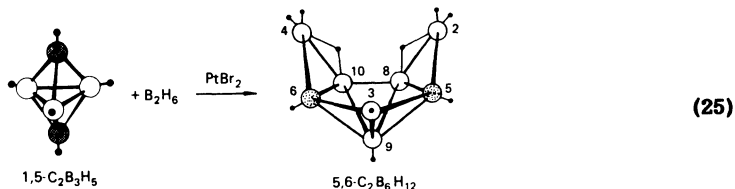
In light of the studies of the platinum(II) bromide catalyzed dehydrocoupling reactions, the platinum(II) bromide catalyzed reaction of diborane with 1,5-C$_2$B$_3$H$_5$ again probably involves an initial dehydrocoupling reaction to yield an [1,5-C$_2$B$_3$H$_4$][B$_2$H$_5$] intermediate. This complex, which is not observed in the reaction, could then add a BH$_3$ group to yield, after cage rearrangement, the single-cage 5,6-C$_2$B$_6$H$_{12}$ product.

(26)
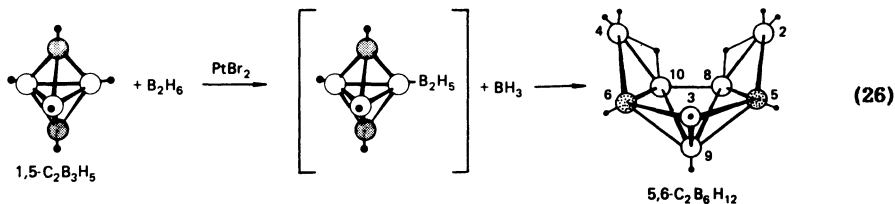
Support for the formation of a coupled [1,5-C$_2$B$_3$H$_4$][B$_2$H$_5$] intermediate in the above reaction sequence was obtained from the results of the platinum(II) bromide catalyzed reactions of 1,6-C$_2$B$_4$H$_6$ and B$_5$H$_9$ with diborane. In each case the mass spectral data indicated that a dehydrocondensation reaction had occurred to generate diborane-coupled species, [1,6-C$_2$B$_4$H$_5$][B$_2$H$_5$] and [B$_5$H$_8$][B$_2$H$_5$], respectively, instead of expanded single-cage systems.

$$1,6-C_2B_4H_6 + B_2H_6 \xrightarrow[25°]{PtBr_2} 2:1′,2′-[1,6-C_2B_4H_5][B_2H_5] + H_2 \qquad (27)$$

$$B_5H_9 + B_2H_6 \xrightarrow[25°]{PtBr_2} 2:1′,2′-[B_5H_8][B_2H_5] + H_2 \qquad (28)$$

Based on the results observed for the platinum(II) bromide catalyzed dehydrocoupling reactions it was expected that the $[1,6\text{-}C_2B_4H_5][B_2H_5]$ and $[B_5H_8][B_2H_5]$ compounds would consist of boron-boron linked diborane-polyhedral borane systems, however, the spectroscopic data (including 2-D $^{11}B\text{-}^{11}B$ NMR) indicate the compounds have instead the $2:1',2'\text{-}[1,6\text{-}C_2B_4H_5][B_2H_5]$ and $2:1',2'\text{-}[B_5H_8][B_2H_5]$ structures shown below:
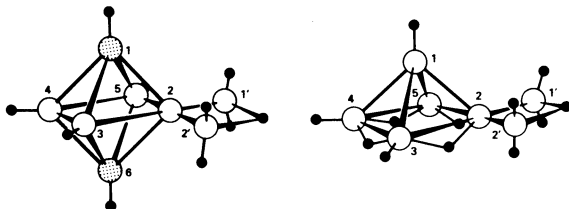

Fig. 7. Proposed structures for $2:1',2'\text{-}[1,6\text{-}C_2B_4H_5][B_2H_5]$ and $2:1',2'\text{-}[B_5H_8][B_2H_5]$.

The isolation of the above compounds suggest that the use of transition metal catalysts not only have the potential for the development of more efficient cage-growth reactions, but may also allow, because of the mild reaction conditions employed, the isolation of many previously unobserved condensation products which may be intermediates in polyhedral expansions. Indeed, one of the most important points raised by these results is that intermolecular dehydrocoupling and dehydrocondensation reactions may play a more signficant role in thermally-induced cage growth reactions than previously assumed.

CONCLUDING REMARKS

The use of transition metal reagents to catalyze reactions involving polyhedral boranes and carboranes is an area in its initial stages of investigation. However, it is clear from both our work and that emanating from other laboratories that this synthetic approach has great potential for the development of high yield, selective reaction schemes.

Future work will continue to examine the scope of the few reactions which are presently known, along with exploratory investigations of new types of catalytic processes. In addition, the systematic development of borane catalysis will now also require, as was the case in organic catalysis, more detailed mechanistic studies so that the basic reaction steps and catalyst properties can be better understood and refined.

Acknowledgements

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