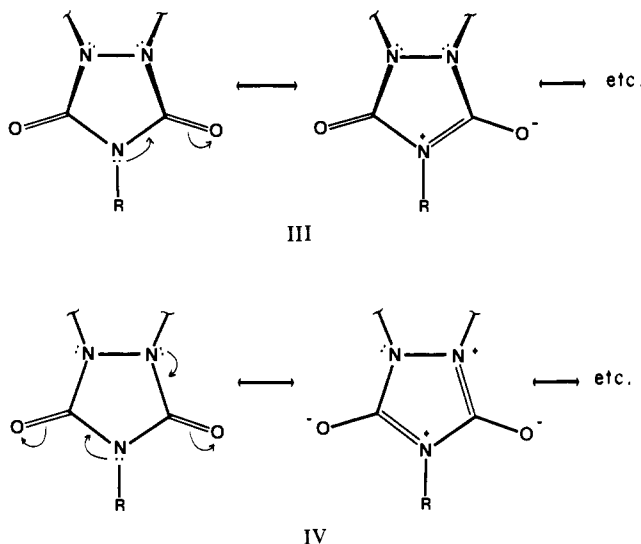happens, albeit to a lesser extent, when R = Ph. It is believed that the change would have been more significant if the phenyl ring were coplanar with the five-membered ring.

Factor analysis shows that three centers are mainly affected during the simultaneous inversion process. The first (N1 and N2) is related to the flattening effect, resulting from a change of hybridization; the second (N3) involves the redistribution of the electron densities; and the third (O1) is concerned with the unaffected parameters (C3–O1, N3–C3–O1).

At the transition state N3 competes with N1 and N2 for conjugation with the carbonyl groups. It is therefore expected that the potential barrier for inversion will be lower in those systems that are lacking potentially competing groups. The calculated energy barrier[25] is found to be ca. 9 kcal mol^{-1}. This explains the relatively large number of systems with nearly tetrahedral geometry at the N–N bond, compared to the few examples of nearly planar ones.

A schematic stereodrawing of the inversion path is shown in Figure 15, assuming a symmetrical molecule. The resonance structures in the tetrahedral and planar forms are given in III and IV.

III

IV

The inference that replacing N3 by another substituent would lower the inversion barrier was considered and checked. It was found[26] that amine VI has α_{av} = 113.2° while in the dimethylmethane derivative (V) α_{av} = 119.6°.

V   VI
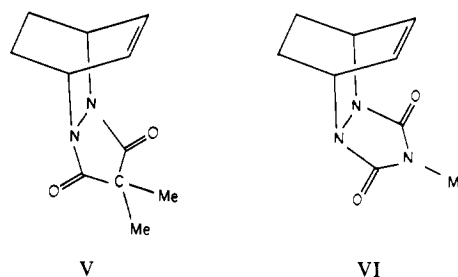
Conclusions

The method of deriving the reaction path from geometrical data, obtained by crystal structure determination, is again shown to be rewarding. The advantages of the method go beyond the detection of variations in geometry occurring during the reaction. It also enables deduction of the molecular (or fragmental) structure at transition states, where experimental data are not available, and thus affords better data for theoretical calculations of energy barriers.

It was shown that the variations in the internal parameters during the inversion process are dependent upon the substitution at the N3 of the triazolidine ring. We therefore believe that electron-acceptor groups at this position will lower the barrier to inversion and hence the ionization potential of the N atoms accordingly.

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Transition-Metal-Promoted Reactions of Boron Hydrides. 6.[1] Platinum(II) Bromide Catalyzed Borane and Carborane Dehydrodimerization Reactions: A New Synthetic Route to Boron–Boron Linked Multicage Boranes and Carboranes

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Abstract: Platinum dibromide has been found to be a general dehydrodimerization catalyst for boron hydrides and carboranes leading to the formation of boron–boron linked polyhedral cage compounds. The reactions of a variety of small cage systems were explored, and all coupling reactions were found to proceed at moderate temperatures, were highly selective, and gave excellent yields of linked-cage products. These techniques have been used to prepare a number of new coupled cage boron hydrides and carboranes, including 1:1′-[B$_4$H$_9$]$_2$, 1:2′-[B$_4$H$_9$][B$_5$H$_8$], 1:2′-[B$_4$H$_9$][1′-CH$_3$B$_5$H$_7$], 1:2′-[2-CH$_3$B$_5$H$_7$][3′-CH$_3$B$_5$H$_7$], and 2:2′-[1,6-C$_2$B$_4$H$_5$]$_2$, as well as to provide improved synthetic routes to the previously known compounds, 1:2′-[B$_5$H$_8$]$_2$ and 2:2′-[1,5-C$_2$B$_3$H$_4$]$_2$.

Although the first boron–boron coupled polyhedral cage compound was synthesized and structurally characterized[2,3] more than

20 years ago, the development of this area of boron chemistry has been limited. In fact, as late as 1977 fewer than ten of these

multicage compounds had been reported.[2-11] In recent years, however, there has been new interest in the development of techniques for forming exopolyhedral cage linkages since such synthetic routes could potentially offer attractive pathways to higher boron content materials which would not involve polyhedral cage expansion reactions. As a result, a great number of new neutral boron–boron linked boranes and carboranes are now becoming available,[12-28] allowing initial investigations of the physical and chemical properties of these unique cage systems.[29]

The most common methods which have been used to obtain boron–boron linked boranes and carboranes have employed heat,[5,7,11,12,14,19,20,22,23] electrical discharge,[2,3] light,[10,13-15,20,21] or other radiation[17] to induce boron–hydrogen bond cleavage in the parent borane or carborane to yield a fragment or radical which could then further react to give the corresponding coupled cage compound. In general, these types of reactions have been found to give low yields of products and/or are nonselective resulting in the production of several different boron–boron linked isomers. The chemical generation of reactive fragments has also been used to produce compounds such as $2:2'-[B_4H_9]_2$[4,8] and $4:4'-[1,2-C_2B_{10}H_{11}]_2$[9] in low to moderate yields.

Only a few planned selective syntheses of coupled cage systems have been developed. For example, the compounds $1:2'-[B_5H_8]_2$ and $2:2'-[B_5H_8]_2$ can be obtained in moderate yields with use of Friedel–Crafts and metathesis reactions,[16,27] respectively, and the coupled carborane, $5:5'-[2,3-(CH_3)_2C_2B_4H_5]_2$, has been obtained in good yields via the thermal decomposition of the mercury-bridged compound $Hg[2,3-(CH_3)_2C_2B_4H_5]_2$.[18]

We previously reported our preliminary results concerning the first metal-catalyzed dehydrodimerization reaction of a boron hydride, in which platinum(II) bromide was found to catalyze the conversion of pentaborane(9) to the coupled cage compound, $1:2'-[B_5H_8]_2$, in essentially quantitative yields under mild conditions.[24] These results suggested that dehydrodimerization catalysts might provide new high-yield pathways for the production of boron–boron linked polyhedral cage systems. With this goal in mind we have now examined the reactions of a variety of small boranes and carboranes with platinum(II) bromide and these results are described herein.

Experimental Section

Materials. $PtBr_2$ was used as received from Aldrich Chemicals. Pentaborane(9) was obtained from laboratory stock. Tetraborane(10),[30] 1- and 2-methylpentaborane,[31] and hexaborane(10)[32] were prepared with use of standard literature methods. The small *closo* carboranes, $1,5-C_2B_3H_5$ and $1,6-C_2B_4H_6$, were purchased from Chemical Systems, Inc., and were purified by vacuum line fractionation. All manipulations involving boron hydrides or carboranes were carried out in vacuo.

Gas–liquid chromatography (GLC) was conducted on a Varian Aerograph Model 920 gas chromatograph equipped with a 10 ft × 0.25 in. 30% Apiezon L on Chromosorb W (100/120 mesh) column. The chromatographic solvent was spectroquality grade pentane purchased from MCB and was dried over P_2O_5.

Physical Measurements. Boron-11 NMR spectra at 115.5 MHz were obtained on a Bruker WH-360 Fourier transform spectrometer located in the Mid-Atlantic Regional NMR Facility at the University of Pennsylvania. Proton NMR spectra at 250 MHz were obtained on a Bruker WH-250 Fourier transform spectrometer. Proton NMR spectra at 200 MHz and boron-11 NMR spectra at 64.2 MHz were obtained on an IBM WH-200 Fourier transform spectrometer. Unit and high-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer interfaced to a Kratos DS50-S data system. Infrared spectra were recorded on a Perkin-Elmer 337 grating infrared spectrometer.

Boron and hydrolytic hydrogen analyses were obtained by first decomposing the samples to $B(OCH_3)_3$ with methanol and then measuring the evolved hydrogen on a calibrated Toepler system. The boron content was measured by further decomposition of the $B(OCH_3)_3$ with water and titration with use of the standard identical pH mannitol method.[33]

$1:2'-[B_5H_8]_2$. In a typical reaction, 1.057 g of $PtBr_2$ powder (2.98 mmol) were stirred with 19.0 mmol of pentaborane(9) at room temperature in vacuo. After 24 h the reaction mixture was separated by fractionation through a –55, –196 °C trap series to give 0.073 g (0.58 mmol) of $1:2'-[B_5H_8]_2$, 0.72 mmol of H_2, and 17.5 mmol of unreacted B_5H_9. The $PtBr_2$ catalyst appeared to be unchanged, with no indication of the formation of platinum metal. The remaining B_5H_9 was then recondensed over the $PtBr_2$ and the reaction continued with daily removal of product and hydrogen. After 7 days it was found that a total of 3.86 mmol of $1:2'-[B_5H_8]_2$ and 4.09 mmol of H_2 had been produced and 8.4 mmol of B_5H_9 had reacted. This corresponds to a 92% yield of $1:2'-[B_5H_8]_2$, based on consumed B_5H_9, and ~0.2 catalyst turnovers/day. Analysis by GLC and NMR confirmed the identity and purity of $1:2'-[B_5H_8]_2$ ($R_v = 0.51$, $R_v = 1.0$ for $B_{10}H_{14}$). There was no evidence for the formation of either of the symmetrical isomers, $2:2'-[B_5H_8]_2$ ($R_v = 0.57$), or $1:1'-[B_5H_8]_2$ ($R_v = 0.35$), in the reaction. Some reactions were continued for up to 1 month with periodic hydrogen and product removal, although the rate of reaction was found to gradually decrease.

Moderate heating (50 °C) of the reaction increased the rate slightly, but at higher temperatures (>70 °C) the yield of product decreased and the formation of $1-BrB_5H_8$ was observed. Sonication, however, was observed to increase the rate of reaction. For example, the reaction of 1.052 g of $PtBr_2$ and 19.0 mmol of B_5H_9, which was sonicated for 24 h

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at room temperature in an E/MC Corp. Model 450 ultrasonic cleaner, was found to produce 0.162 g (1.28 mmol) of 1:2'-[B$_5$H$_8$]$_2$, corresponding to a turnover frequency of 0.43 catalyst turnovers/day.

1:2'-[2-CH$_3$B$_5$H$_7$][3'-CH$_3$B$_5$H$_7$]. A reaction vessel was charged with 0.114 g of PtBr$_2$ (0.32 mmol) and 1.07 mmol of 2-CH$_3$B$_5$H$_8$ and the mixture stirred in vacuo at room temperature for 72 h. The hydrogen evolved during the reaction was then measured (0.25 mmol) and the volatile components were fractionated through a −50, −196 °C trap series. 1:2'-[2-CH$_3$B$_5$H$_7$][3'-CH$_3$B$_5$H$_7$] (0.017 g) was stopped by the first cold trap and analysis using GLC confirmed this to be the only isomer formed in the reaction. The −196 °C fraction was recondensed over the original catalyst and stirred at room temperature for an additional 72 h, with periodic removal of hydrogen. The reaction was fractionated as before, yielding a total of 0.032 g (0.21 mmol) of 1:2'-[2-CH$_3$B$_5$H$_7$][3'-CH$_3$B$_5$H$_7$] and 0.36 mmol of H$_2$. Exactly 0.54 mmol of 2-CH$_3$B$_5$H$_8$ had been consumed. This corresponds to a 77.2% yield based on reacted 2-CH$_3$B$_5$H$_8$ with 0.11 catalyst turnovers/day. The mass spectrum of the compound has a characteristic parent envelope with a sharp cutoff at *m/e* 154, corresponding to the proposed C$_2$B$_{10}$H$_{20}$ formula.

Reaction with 1-CH$_3$B$_5$H$_8$. A 0.530-g sample of PtBr$_2$ (1.49 mmol) was allowed to react with 0.38 g of 1-CH$_3$B$_5$H$_8$ at room temperature for 72 h. Only a trace amount of H$_2$ was observed, and fractionation yielded no coupled products. The 1-CH$_3$B$_5$H$_8$ was quantitatively recovered.

1:1'-[B$_4$H$_9$]$_2$. A 0.173-g sample of PtBr$_2$ (0.49 mmol) was allowed to react with tetraborane(10) (10 mmol) at room temperature for 2.5 h. During this time the catalyst appeared to be partially soluble and to undergo no change. The reaction was found to have evolved 0.45 mmol of H$_2$, and fractionation of the volatiles through a −78, −196 °C trap series gave 0.013 g of a material in the −78 °C trap which was then further purified on a low-temperature distillation column[34] (exit temperature ranging from −55 to −60 °C) to give 1:1'-[B$_4$H$_9$]$_2$. The −196 °C fraction was recondensed over the original catalyst and stirred at room temperature for an additional 10 h with H$_2$ and product removal, as described above, every 2.5 h. This yielded a total of 0.056 g (0.54 mmol) of 1:1'-[B$_4$H$_9$]$_2$ and 1.60 mmol of H$_2$, and it was found that 1.04 mmol of B$_4$H$_{10}$ had been consumed. Yields, based on consumed B$_4$H$_{10}$, were quantitative (calcd 104%) with 2.11 catalyst turnovers/day. Two different determinations of the boron-to-hydrogen ratio in the compound both gave a value of 0.485; calcd for B$_8$H$_{18}$ 0.444.

1:2'-[B$_4$H$_9$][B$_5$H$_8$]. A 40-mL reaction flask containing 0.187 g of PtBr$_2$ (0.53 mmol) was charged with 6.0 mmol of B$_4$H$_{10}$ and 2.0 mmol of B$_5$H$_9$. The mixture was warmed to room temperature and stirred for 5 h. The catalyst appeared to be soluble and to undergo no change during this time. The reaction evolved 0.63 mmol of H$_2$, and the volatiles were fractionated through a −65, −196 °C trap series. The −65 °C fraction was further purified (0.0273 g) on a low-temperature distillation column[34] (exit temperature of −45 °C) to yield 1:2'-[B$_4$H$_9$][B$_5$H$_8$]. The −196 °C fraction was recondensed over the original catalyst and stirred at room temperature for an additional 15 h, with H$_2$ and product removal every 5 h as above. The reaction was found to yield 0.086 g (0.75 mmol) of 1:2'-[B$_4$H$_9$][B$_5$H$_8$] and 1.76 mmol of H$_2$ while 1.23 mmol of B$_4$H$_{10}$ and 0.78 mmol of B$_5$H$_9$ were consumed. This corresponds to 96.5% and 61.2% yields, based on consumed B$_5$H$_9$ and B$_4$H$_{10}$, respectively, with 1.7 catalyst turnovers/day. Methanolysis of the compound followed by hydrolysis and titration of the boric acid as the D-mannitol complex gave a boron-to-hydrogen ratio of 0.523; calcd for B$_9$H$_{17}$ 0.529.

1:2'-[B$_4$H$_9$][1'-CH$_3$B$_5$H$_7$]. A 40-mL reaction flask containing 0.192 g of PtBr$_2$ (0.54 mmol), 4.0 mmol of 1-CH$_3$B$_5$H$_8$, and 6.0 mmol of B$_4$H$_{10}$ was stirred in vacuo at room temperature for 4 h. The catalyst appeared to be soluble and to undergo no change during the course of the reaction. The evolved H$_2$ (0.66 mmol) was measured, and the volatiles were fractionated through a −50, −196 °C trap series. The −50 °C fraction was further purified (0.0136 g) on a low-temperature distillation column (exit temperatures of −40 to −42 °C) yielding 1:2'-[B$_4$H$_9$][1'-CH$_3$B$_5$H$_7$]. The −196 °C fraction was recondensed over the original catalyst and stirred at room temperature for an additional 12 h with H$_2$ and product removal every 4 h as described above. The reaction yielded a total of 0.096 g (0.76 mmol) of 1:2'-[B$_4$H$_9$][1'-CH$_3$B$_5$H$_7$] and 2.03 mmol of H$_2$ and was found to have consumed 1.03 mmol of B$_4$H$_{10}$ and 0.86 mmol of 1-CH$_3$B$_5$H$_8$. Yields, based on consumed B$_4$H$_{10}$ and 1-CH$_3$B$_5$H$_8$, were 73.9% and 88.5%, respectively, with 2.11 catalyst turnovers/day. Methanolysis of the compound followed by hydrolysis and titration of the boric acid as the D-mannitol complex gave a boron-to-hydrolytic hydrogen ratio of 0.563; calcd for H$_3$CB$_9$H$_{16}$ 0.563.

Reaction with B$_6$H$_{10}$. A reaction flask containing 0.284 g of PtBr$_2$ (0.80 mmol) was evacuated and charged with 3.0 mmol of B$_6$H$_{10}$. The flask was warmed to room temperature and stirred overnight. After this time, there was only a trace of noncondensable gas. The volatile com-

ponents were removed and fractionated, but no new products were obtained. Extraction of the reaction residue, filtration, and evaporation yielded yellow crystals which were found to be (after comparison of properties to literature data[35]) *trans*-Pt(B$_6$H$_{10}$)$_2$Br$_2$.

2:2'-[1,5-C$_2$B$_3$H$_4$]$_2$. A 0.201-g sample of PtBr$_2$ (0.57 mmol) was weighed in a 15-mL reaction flask (fitted with a break seal) and evacuated. A 6.5-mmol sample of 1,5-C$_2$B$_3$H$_5$ was condensed into the flask which was then sealed. The mixture was stirred at room temperature for 18 h, the evolved H$_2$ removed, and the volatiles fractionated through a −95, −196 °C trap series. Exactly 0.032 g (0.26 mmol) of 2:2'-[1,5-C$_2$B$_3$H$_4$]$_2$ stopped in the −95 °C trap while 6.0 mmol of 1,5-C$_2$B$_3$H$_5$ was retained by the −196 °C trap (0.50 mmol of 1,5-C$_2$B$_3$H$_5$ consumed). This corresponds to a quantitative yield (calcd 104%) based on consumed 1,5-C$_2$B$_3$H$_5$ with 0.61 catalyst turnovers/day.

2:2'-[1,6-C$_2$B$_4$H$_5$]$_2$. A 0.193-g sample of PtBr$_2$ (0.55 mmol) was allowed to react in a 10-mL reaction flask with a 4.9-mmol sample of 1,6-C$_2$B$_4$H$_6$ at room temperature for 48 h. The evolved H$_2$ was removed, and the mixture was fractionated through a −95, −196 °C trap series. Exactly 0.008-g (0.055 mmol) of 2:2'-[1,6-C$_2$B$_4$H$_5$]$_2$ was retained by the −95 °C trap. The −196 °C fraction was recondensed over the original catalyst and stirred at room temperature for an additional 48 h. Fractionation, as before, yielded a total of 0.024 g (0.17 mmol) of 2:2'-[1,6-C$_2$B$_4$H$_5$]$_2$, and it was found that 0.3 mmol of 1,6-C$_2$B$_4$H$_6$ had been consumed. This corresponds to a quantitative yield based on consumed 1,5-C$_2$B$_3$H$_5$ with 0.14 catalyst turnovers/day. Exact mass for ^{12}C$_4$^{1}H$_{10}$^{11}B$_8$: calcd 146.1533, found 146.1528. IR (∼3 cm of pressure): 3110 (w), 2649 (s), 1275 (w), 1160 (s), 855 cm^{-1} (m).

Results

Platinum(II) dibromide has been found to be a general dehydrodimerization catalyst for the formation of boron–boron linked polyhedral boranes and carboranes. The reactions of a variety of small cage systems were explored, and all reactions were found to proceed at moderate temperatures, be highly selective, and give excellent yields of coupled cage products. All reactions were conducted in the absence of solvent, generally for periods ranging from 2.5 h to 3 days, although some reactions could be continued for longer times (up to 30 days) with only a slight decrease in the rate of product formation. In addition, it was found that in every case a single coupled-cage product could be isolated in reasonable purity after only initial vacuum line fractionation.

The reaction with pentaborane(9) was found to produce the coupled-compound 1:2'-[B$_5$H$_8$]$_2$ in high yield (92%) according to the equation:

$$\text{(1)}$$
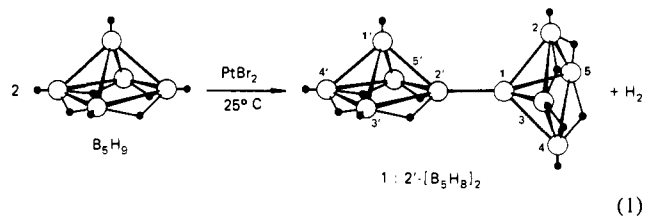
This compound was originally characterized by Gaines, who discovered the compound in the lower volatile residues of pentaborane(9) storage tanks.[6] Although other reaction mechanisms are possible, the results reported herein suggest that a metal-catalyzed dehydrodimerization reaction could have been the source of the 1:2'-[B$_5$H$_8$]$_2$ found in the metal storage cylinders. The first synthesis of 1:2'-[B$_5$H$_8$]$_2$ was reported in 1979, when Gaines described[16] its formation in 20% yield by the reaction of NaB$_5$H$_8$ with 1-BrB$_5$H$_8$. We have also reported that the compound can be obtained, along with 2:2'-[B$_5$H$_8$]$_2$ and 1:1'-[B$_5$H$_8$]$_2$, from the mercury-sensitized photolysis of pentaborane(9).[15]

The metal-catalyzed dehydrodimerization reaction involves simply stirring liquid pentaborane(9) over PtBr$_2$ powder, with periodic removal of evolved hydrogen and 1:2'-[B$_5$H$_8$]$_2$. The product can be obtained in pure form by simple vacuum line fractionation through a −55 °C trap. It is also significant that the reaction is highly selective in producing only the 1:2'-[B$_5$H$_8$]$_2$

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Table I. ^{11}B NMR Data (115.5 MHz)

compound	δ^a (J(Hz) assignment)	relative areas
1:2'-[2-CH$_3$B$_5$H$_7$][3'-CH$_3$B$_5$H$_7$]^b	2.0 (s, B$_{2,3'}$), −4.0 (s, B$_{2'}$, J_{B-B} = 112), −12.9 (d, 162, B$_{3,5,4'}$), −17.8 (d, 162, B$_{4,5'}$), −49.1 (d, 177, B$_{1'}$), −55.0 (s, B$_1$, J_{B-B} ~ 115)	2:1:3:2:1:1
1:1'-[B$_4$H$_9$]$_2$^{b}	−5.7 (t, 131, B$_{2,2',4,4'}$), −38.1 (s, B$_{1,1'}$), −39.5 (d, 174, B$_{3,3'}$)	2:1:1
1:2'-[B$_4$H$_9$][B$_5$H$_8$]^b	−5.9 (t, 126, B$_{2,4}$), −5.9 (s, B$_{2'}$),^{d} −11.6 (d, 159, B$_{3',5'}$), −13.1 (d, 157, B$_{4'}$, J_{B-B} = 21), −39.2 (d, 170, B$_3$), −41.5 (s, B$_1$, J_{B-B} = 103), −50.9 (d, 168, B$_{1'}$)	2:1:2:1:1:1:1
1:2'-[B$_4$H$_9$][1'-CH$_3$B$_5$H$_7$]^b	−7.1 (t, 124, B$_{2,4}$), −7.1 (s, B$_{2'}$),^{d} −12.3 (d, 157, B$_{3',5'}$), −13.7 (d, 171, B$_{4'}$, J_{B-B} = 25), −40.3 (d, 153, B$_3$), −41.8 (s, B$_1$),^{d} −43.3 (s, B$_{1'}$)	2:1:2:1:1:1:1
2:2'-[1,6-C$_2$B$_4$H$_5$]$_2$^{c}	−13.8 (d, 202, B$_{4,4'}$), −15.3 (s, B$_{2,2'}$), −15.6 (d, 196, B$_{3,3',5,5'}$)	1:1:2

^{a} Chemical shifts are relative to external BF$_3$·O(C$_2$H$_5$)$_2$, with a negative sign indicating an upfield shift: s = singlet, d = doublet, t = triplet. ^{b} Spectra obtained in dried 1,2-dibromotetrafluoroethane with 10% C$_6$D$_6$ lock solvent; room temperature. ^{c} Spectra obtained in dried pentane in a 5-mm tube placed co-axially inside a 10-mm tube containing C$_6$D$_6$ in the annular space between the two tubes. ^{d} Resonance obscured by another resonance.

Table II. ^{1}H NMR Data

compound	δ^a (assignment)	relative areas
1:2'-[2-CH$_3$B$_5$H$_7$][3'-CH$_3$B$_5$H$_7$]^b	2.47 (q, B-H$_A$, J = 152), 2.19 (q, B-H$_B$, J = 157), 1.02 (q, B-H$_C$, J = 169), 0.32 (s, CH$_3$), 0.16 (s, CH$_3$), −2.12 (s, Hμ), −2.65 (s, Hμ)	2:3:1:3:3:4:4
1:1'-[B$_4$H$_9$]$_2$^{c}	2.44 (q, B-H$_{2,2',4,4'(e\,or\,a)}$, J = 128), 2.16 (q, B-H$_{2,2',4,4'(a\,or\,e)}$, J = 136), 1.16 (q, B-H$_{3,3'}$, J = 168), −1.48 (s, Hμ)	4:4:2:8
1:2'-[B$_4$H$_9$][B$_5$H$_8$]^d	2.22 (q, B-H$_A$, J = 165), 1.79 (q, B-H$_B$, J = 165), 0.30 (q, B-H$_C$, J = 175), −1.60 (s, Hμ), −2.51 (s, Hμ')	4:4:1:4:4
1:2'-[B$_4$H$_9$][1'-CH$_3$B$_5$H$_7$]^d	2.19 (q, B-H$_A$, J = 161), 1.88 (q, B-H$_B$, J = 156), −0.11 (s, CH$_3$), −1.54 (s, Hμ), −2.09 (s, Hμ')	4:4:3:4:4
2:2'-[1,6-C$_2$B$_4$H$_5$]$_2$^{b}	2.74 (s, C-H), 2.14 (q, B-H, J = 185)	2:3

^{a} Key: s = singlet, q = quartet; all J values are given in Hz; shifts in ppm based on 7.15 ppm for C$_6$D$_6$ (relative to Me$_4$Si at 0.00 ppm). ^{b} Spectra run in C$_6$D$_6$ at 250 MHz; room temperature. ^{c} Spectra run in dried CS$_2$ with 10% C$_6$D$_6$ lock solvent at 200 MHz; 20 °C. ^{d} Spectra run in dried 1,2-dibromotetrafluorethane with 10% C$_6$D$_6$ lock solvent at 200 MHz; −20 °C.

isomer. This was confirmed by GLC analysis, which indicated that neither of the symmetrical isomers, 1:1'-[B$_5$H$_8$]$_2$ or 2:2'-[B$_5$H$_8$]$_2$, were produced. Although the reaction is slow (~0.2 catalyst turnovers/day), the high yields and facile product isolation make this route a significant improvement over existing methods. Attempts to increase the reaction rate by increasing the temperature generally resulted in lower yields of 1:2'-[B$_5$H$_8$]$_2$, presumably due to product decomposition, as well as the formation of small amounts of 1-BrB$_5$H$_8$ (>70 °C). However, sonication of the reaction was found to enhance the rate significantly (~0.4 catalyst turnovers/day) with the yields of 1:2'-[B$_5$H$_8$]$_2$ being slightly lowered (72%).

The metal-catalyzed dehydrodimerization reactions of the methyl-substituted pentaboranes, 1-CH$_3$B$_5$H$_8$ and 2-CH$_3$B$_5$H$_8$, were also investigated. It was found that 1-CH$_3$B$_5$H$_8$ appeared to undergo no reaction in the presence of PtBr$_2$ but that 2-CH$_3$B$_5$H$_8$ reacted with the evolution of hydrogen to produce a 1:2'-coupled cage product in good yield (77%).

1 : 2'-[2-CH$_3$B$_5$H$_7$] [3'-CH$_3$B$_5$H$_7$]

(2)
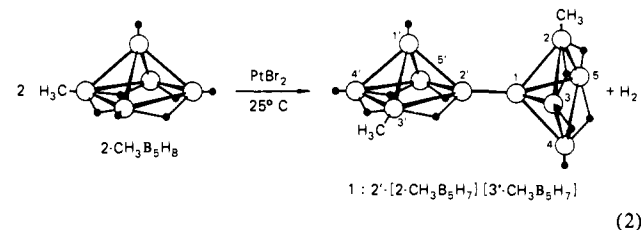
There are two possible 1:2'-coupled isomers for such a compound derived from 2-CH$_3$B$_5$H$_8$, 1:2'-[2-CH$_3$B$_5$H$_7$][3'-CH$_3$B$_5$H$_7$], and 1:2'-[2-CH$_3$B$_5$H$_7$][4'-CH$_3$B$_5$H$_7$], which if formed in statistical amounts should be present in a 2:1 ratio. GLC analysis indicates, however, that only one compound is produced in the reaction and the NMR data are consistent with the 1:2'-[2-CH$_3$B$_5$H$_7$][3'-CH$_3$B$_5$H$_7$] formulation shown above. The ^{11}B NMR spectrum at 115.5 MHz (Table I) shows two resonances upfield corresponding to the 1'- and 1-boron positions. The 1-boron resonance is broadened owing to coupling with the 2'-boron, with this latter resonance appearing downfield at 4.0 ppm and showing a clear quartet structure (J = 112 Hz) characteristic of boron–boron coupling. These results are consistent with our previous observations^{36,37} of large boron–boron coupling constants found for

chemically inequivalent boron atoms involved in two-center, two-electron boron–boron bonds linking other polyhedral cage systems. The chemical shift of the basal boron resonance, which occurs slightly upfield at −17.8 ppm, is highly characteristic^{38} of a basal boron atom situated trans to a methyl-substituted boron and is assigned to overlapping resonances arising from the 4- and 5'-boron atoms, thus leading to the 1:2'-[2-CH$_3$B$_5$H$_7$][3'-CH$_3$B$_5$H$_7$] structural assignment. The remaining basal resonances from the 4'-, 3-, and 5-borons, which are cis to the methyl-substituted borons, are overlapped and occur at a normal pentaborane(9) basal boron shift, −12.9 ppm.^{39} The resonances arising from the methyl-substituted boron 2 and 3' are also overlapped and occur at low field, as in 2-CH$_3$B$_5$H$_8$.^{38,40} The proton NMR spectrum (Table II) cannot be completely assigned, but the observation of two different methyl resonances, as well as a single apical B–H quartet, is consistent with the proposed structure.

The reaction with tetraborane(10) was found to proceed at room temperature to give the very reactive coupled-cage product 1:1'-[B$_4$H$_9$]$_2$.

1 : 1'-[B$_4$H$_9$]$_2$

(3)
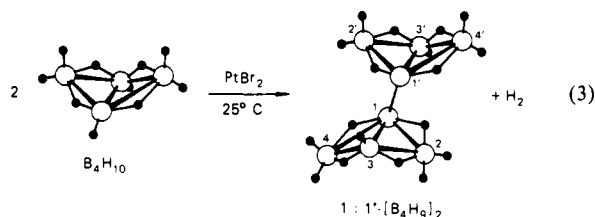
The compound can again be obtained essentially pure by vacuum line fractionation but decomposes rapidly upon transfer, or in the liquid state above −30 °C; therefore, analytical samples

(36) Astheimer, R. J.; Plotkin, J. S.; Sneddon, L. G. *J. Chem. Soc., Chem. Commun.* **1979**, 1108–1109.

(37) Anderson, J. A.; Astheimer, R. J.; Odom, J. D.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 2275–2283.

(38) Tucker, P. M.; Onak, T.; Leach, J. B. *Inorg. Chem.* **1970**, *9*, 1430–1441.

(39) Lipscomb, W. N.; Gareth, E. R. "NMR Studies of Boron Hydrides and Related Compounds"; Benjamin: New York, 1969; pp 92–99.

(40) Onak, T.; Dunks, G. B.; Searcy, I. W.; Spielman, J. *Inorg. Chem.* **1967**, *6*, 1465–1471.
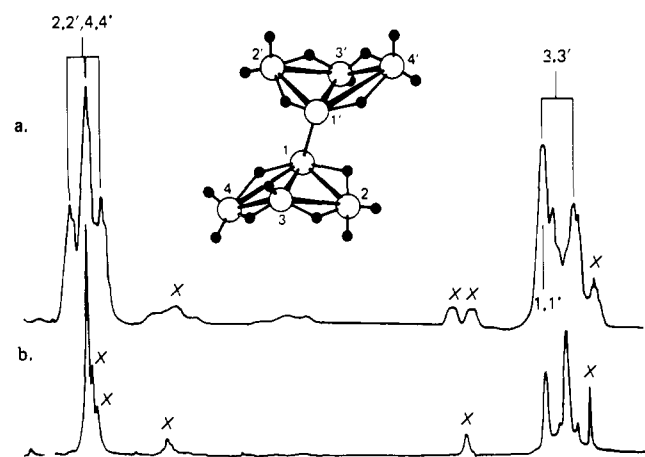
Transition-Metal-Promoted Reactions of Boron Hydrides

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Figure 1. The 115.5-MHz ^{11}B NMR spectrum of 1:1'-[B_4H_9]$_2$. Spectrum b is proton spin decoupled. X indicates impurity resulting from decomposition.
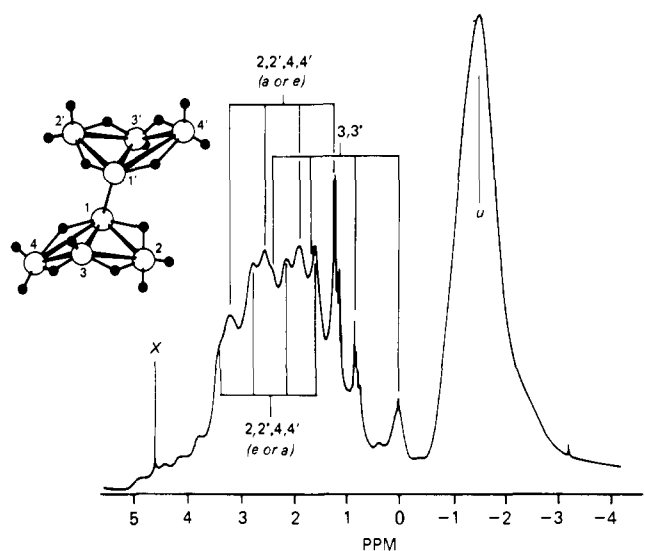

Figure 2. The 200-MHz ^{1}H NMR spectrum of 1:1'-[B_4H_9]$_2$.

Figure 3. The 115.5-MHz ^{11}B NMR spectrum of 1:2'-[B_4H_9][B_5H_8]. Spectrum b is proton spin decoupled.

were obtained by using low-temperature column separations.[34] Another isomer of this compound, 2:2'-[B_4H_9]$_2$, is known and has been assigned a coupled-cage structure based on the X-ray, NMR, and mass spectral data.[4,8,41,42] That the new compound is, in fact, the 1:1'-isomer is supported by both the boron-11 and proton NMR data. The NMR spectrum at 115.5 MHz, shown in Figure 1, shows three resonances, a triplet, singlet, and doublet, in a 4:2:2 ratio. The triplet at low field arises from the four equivalent 2-, 4-, 2'-, and 4'-borons, each coupled to two protons, while the singlet at −38.1 ppm is assigned to the linked 1- and 1'-borons and the doublet to the 3- and 3'-boron atoms. It should be noted that since the 1- and 1'-borons are chemically equivalent, no boron-boron coupling is observed between these borons and the singlet resonance appears sharp. The proton NMR spectrum shown in Figure 2 is very similar to that of 2:2'-[B_4H_9]$_2$ except that the quartet at 1.16 ppm, which had been assigned[42] to the protons on the 1-, 3-, 1'-, and 3'-borons in 2:2'-[B_4H_9]$_2$, has only an intensity of two, leading again to the conclusion that the compound is linked through the 1- and 1'-borons.

The new boron hydride, 1:2'-[B_4H_9][B_5H_8], and its methyl derivative, 1:2'-[B_4H_9][1'-$CH_3B_5H_8$], were prepared in high yields

by the room-temperature cross-coupling reaction of tetraborane(10) with pentaborane(9) or 1-methylpentaborane(9).

$$1\ 2'\text{-}[B_4H_9][B_5H_8] \quad (4)$$

$$1\ 2'\text{-}[B_4H_9][1'\text{-}CH_3B_5H_8] \quad (5)$$
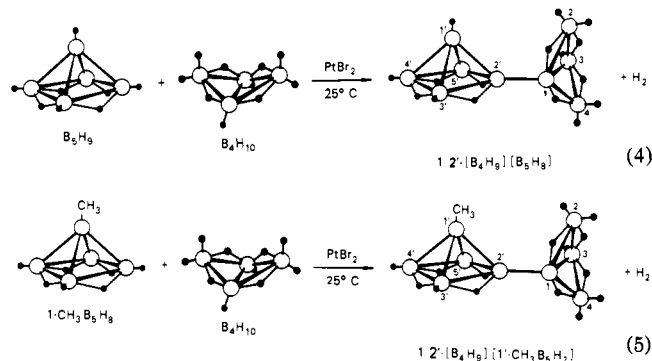
In both reactions an excess of tetraborane(10) was employed in order to supress the formation of coupled-pentaborane(9) product. The compounds can again be obtained essentially pure by vacuum line fractionation, but were found to decompose rapidly in the liquid state above −20 °C; therefore, analytical samples of 1:2'-[B_4H_9][B_5H_8] were obtained by using cold column distillation.

The NMR data obtained for these compounds strongly support their coupled pentaborane–tetraborane formulations. The ^{11}B NMR spectrum (Figure 3) of 1:2'-[B_4H_9][B_5H_8] shows at high field three resonances each of intensity one. The doublet at −50.9 ppm is indicative of an apical boron position in pentaborane(9),[39] while the doublet at −39.2 ppm and the broad singlet at −41.5 ppm have chemical shifts similar to those of the 1,3-borons in tetraborane(10) (−41.8 ppm).[43] The singlet is seen to exhibit the quartet structure ($J = 103$ Hz) characteristic of borons involved in two-center, boron–boron, exopolyhedral linkages[36,37] and is thus assigned to the 1-boron in the −B_4H_9 cage. At lower field in the spectrum there are two overlapping doublets of 2:1 ratio, characteristic of the 3, 5, and 4 basal borons of a 2-substituted pentaborane(9).[38,40] The 4'-boron resonance shows a quartet structure ($J = 21$ Hz) in the proton-decoupled spectrum due to coupling with the apical boron.[44] Finally, at lowest field there is a triplet resonance at a position (−5.9 ppm) consistent with the 2,4-borons in tetraborane(10) (−5.16 ppm).[43] Integration of this peak reveals,

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(43) Leach, J. B.; Onak, T.; Spielman, J.; Rietz, R.; Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1970**, *9*, 2170–2175.

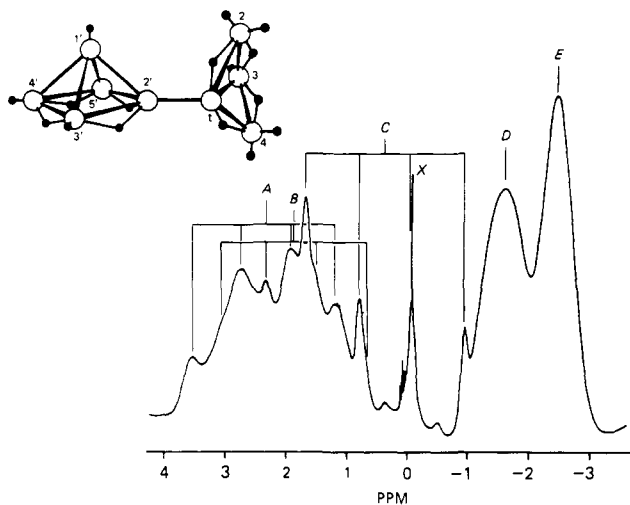(44) Odom, J. D.; Ellis, P. D.; Walsh, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 3529–3530.

Figure 4. The 200-MHz ^{1}H NMR spectrum of 1:2′-[B_4H_9][B_5H_8].

however, that it has an intensity of 3. Thus this triplet must overlap the 2′-boron resonance, which is, of course, broadened by the coupling to the 1-boron. The ^{11}B NMR spectrum of the methyl derivative, 1:2′-[B_4H_9][1′-$CH_3B_5H_7$], is similar to that of 1:2′-[B_4H_9][B_5H_8] except that the highest field peak is a sharp singlet, reflecting the methyl substitution at the apical pentaborane boron, and is shifted downfield slightly obscurring the boron–boron coupled 1-boron resonance. Although the proton spectra of these compounds are complex and cannot be completely assigned, they are consistent with the proposed structures. In the spectrum of 1:2′-[B_4H_9][B_5H_8] (Figure 4) two different bridge hydrogen resonances (D and E) each of intensity four are observed at −1.60 and −2.51 ppm. These chemical shifts are characteristic of the bridge hydrogen resonances in tetraborane(10),[43] −1.34 ppm, and pentaborane(9),[39] −2.20 ppm, respectively. Also apparent is a quartet centered at 0.30 ppm (C) which may be assigned to the apical B–H proton in the pentaborane cage. The remaining B–H quartets are overlapped and cannot be conclusively assigned. The proton spectrum of 1:2′-[B_4H_9][1′-$CH_3B_5H_7$] is also similar, showing two different bridge hydrogen resonances at −1.54 and −2.09 ppm; however, the apical B–H quartet is absent and has been replaced by a singlet of intensity three arising from the methyl protons.

The reaction of hexaborane(10) with $PtBr_2$ was not found to give a coupled cage product, but instead it resulted in the formation of the metalloborane complex, [4,5;4′,5′-μ-*trans*-$PtBr_2$(B_6H_{10})$_2$]. The corresponding chloro compound, [4,5;4′,5′-μ-*trans*-$PtCl_2$-(B_6H_{10})$_2$], has previously been prepared[35] by the reaction of K[$PtCl_3$(C_2H_4)] with B_6H_{10}.

In addition to the boron hydrides discussed above, the coupling reactions of two small carboranes, 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$, were examined. In both cases the reactions were found to be catalytic and give excellent yields of coupled cage products:
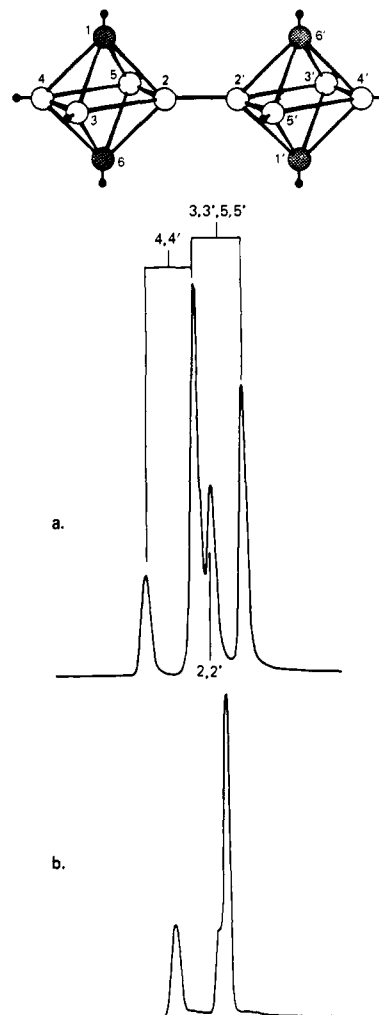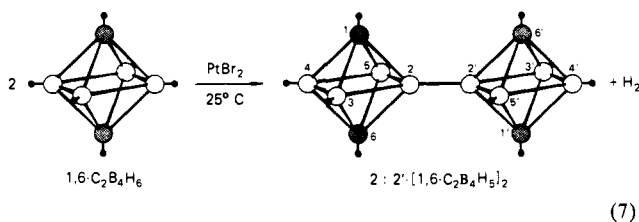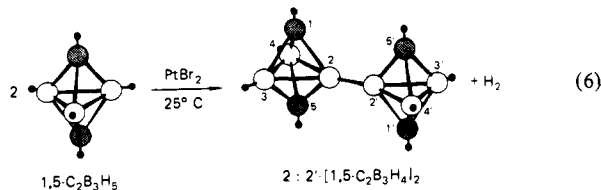

(6)

(7)

Figure 5. The 115.5-MHz ^{11}B NMR spectrum of 2:2′-[1,6-$C_2B_4H_5$]$_2$. Spectrum b is proton spin decoupled.

The compound 2:2′-[1,5-$C_2B_3H_4$]$_2$ has previously been found[7,11,19,23] as a product of the thermolytic reactions of 1,5-$C_2B_3H_5$ with use of hot/cold reaction techniques. The best yield of this compound which has been reported[19] is only 41%; therefore, the platinum(II) bromide catalyzed route, which gives quantitative yields at room temperature, is clearly a much more attractive synthetic procedure.

The new coupled-cage carborane, 2:2′-[1,6-$C_2B_4H_5$]$_2$, can also be prepared in quantitative yields via the platinum(II) bromide dehydrodimerization reaction.[45] The compound is easily isolated as a thermally stable liquid by fractionation into a −95 °C trap. Both the boron-11 and proton NMR data support the proposed boron–boron coupled structure. The boron-11 NMR spectrum (Figure 5) shows a sharp singlet arising from the linked borons, as well as two doublets in a ratio of 2:1 which can be assigned to the remaining basal borons. The proton NMR spectrum shows a sharp singlet of intensity four at 2.74 ppm due to the CH protons and a single quartet of intensity six due to the overlapping BH protons.

Discussion

Dehydrodimerization catalysts have previously been widely employed in organic chemistry to promote transformations, such as arene-coupling reactions (the Scholl and related reactions);[46]

(45) Evidence has previously been obtained that a coupled-cage carborane of the formula [$C_2B_4H_5$]$_2$ is produced in low yields from pyrolysis reactions, see: (a) Williams, R. E.; Gerhart, F. J.; Hickey, G. I., Ditter, J. F. *U.S. F.S.T.I., AD Rep.* **1969**, *No. 693314*. (b) Ditter, J. F.; Gotcher, A. J. *ONR, AD Rep.* **1973**, *No. 770625*.

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however, there has apparently been little attempt to use similar catalysts to activate the dehydrodimerization reactions of inorganic compounds. The work presented above has demonstrated that platinum(II) bromide is, in fact, a general dehydrodimerization catalyst for small polyhedral boranes and carboranes and has resulted in the production of a number of new boron–boron coupled cage boranes and carboranes, including 1:1′-[B_4H_9]$_2$, 1:2′-[B_4H_9][B_5H_8], 1:2′-[B_4H_9][1′-$CH_3B_5H_7$], 1:2′-[2-$CH_3B_5H_7$]-[3′-$CH_3B_5H_7$], and 2:2′-[1,6-$C_2B_4H_5$]$_2$, as well as provided improved synthetic routes to the previously known compounds, 1:2′-[B_5H_8]$_2$ and 2:2′-[1,5-$C_2B_3H_4$]$_2$.

Although the platinum(II) bromide catalyzed borane and carborane reactions are slow (<2 catalyst turnovers/day), this synthetic route is a significant improvement over previous higher energy routes (e.g., thermolysis, photolysis, and discharge reactions). Most importantly, the platinum(II) bromide catalyzed reactions were found to give excellent yields and to be highly selective in producing only a single coupled-cage compound. In addition, the mild temperatures employed allow the use of these catalysts to produce a number of very reactive coupled-cage systems which would be inaccessible under more severe conditions.

The mechanism of the platinum(II) bromide catalyzed polyhedral borane-coupling reaction has not been elucidated, but it may be related to that which has been proposed[47] for the oxidative–dimerization reaction of arenes promoted by palladium(II) salts:

$$2ArH + PdCl_2 + 2NaOAc \rightarrow$$
$$Ar\!-\!Ar + Pd + 2HOAc + 2NaCl \quad (8)$$
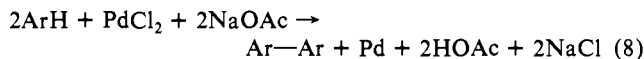
The first step in the arene-coupling reaction is thought to involve the electrophilic attack of the palladium reagent on the arene to generate an arylpalladium(II) intermediate:

$$ArH + PdX_2 \rightarrow ArPdX + HX \quad (9)$$
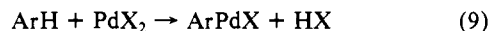
Subsequent conversion of this intermediate to the coupled arene has been proposed to occur by either homolytic or heterolytic mechanisms.[47]

Polyhedral boron hydrides and carboranes have also been shown to be susceptible to electrophilic substitution reactions using conditions, such as Friedel–Crafts type catalysts, typical of those employed for arene-substitution reactions. For example, the chlorination of pentaborane(9) using $AlCl_3$ catalyst occurs to give 1-ClB_5H_8 with high selectivity,[48] in agreement with the predicted[49] high electron density at the apex 1-position of the cage. Given this similarity in substitution–reactivity between boranes and arenes, it is reasonable that the borane and carborane coupling reactions may, like the Pd^{II}-catalyzed arene-coupling reaction, involve an initial electrophilic attack by the metal reagent. In the case of pentaborane(9), for example, this would then lead to the selective formation of a 1-pentaboranylplatinum(II) intermediate.

(46) For example, see the following, plus references therein: (a) Balaban, A. T.; Nenitzescu, C. D. "Friedel-Crafts and Related Reactions"; Olah, G. A., Ed.; Interscience: New York, 1964; Vol. 2, Part 2, 979–1047. (b) McKillop, A.; Turrel, A. G.; Young, D. W.; Taylor, E. C. *J. Am. Chem. Soc.* **1980**, *102*, 6504–6512. (c) Musgrave, O. C. *Chem. Rev.* **1969**, *69*, 499–531. (d) Yatsimirsky, A. K.; Deiko, S. A.; Ryabov, A. D. *Tetrahedron* **1983**, *39*, 2381–2392.

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(48) (a) Gaines, D. F. *J. Am. Chem. Soc.* **1966**, *92*, 3837. (b) Gaines, D. F.; Martens, J. A. *Inorg. Chem.* **1968**, *7*, 704–706.

(49) Switkes, E.; Epstein, I. R.; Tossell, J. A.; Stevens, R. M.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1970**, *92*, 3837–3846.

$$+ Pt^{II}Br_2 \longrightarrow \cdots Pt^{II}\!\cdot\!Br + HBr \quad (10)$$
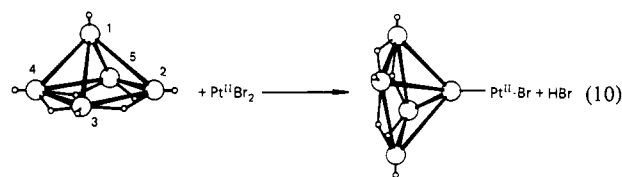
This intermediate could then react with an additional pentaborane(9) molecule, by means of an oxidative-addition reaction of the metal with a B–H group, to give the corresponding platinum(IV) intermediate.


$$(11)$$
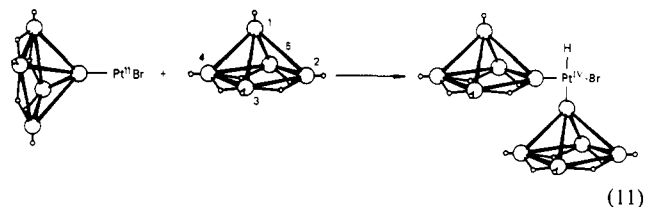
As indicated above, oxidative-addition would be expected to occur at a basal position in pentaborane(9). This conclusion is supported by results[50] obtained from the reactions of pentaborane(9) with other d^8 metal complexes, such as *trans*-Ir(CO)Cl[PMe$_3$]$_2$, and has previously been proposed[51] as the key step in the *cis*-Ir(CO)Cl[PPh$_3$]$_2$ catalyzed reaction of alkynes with pentaborane(9), which was shown to give exclusively 2-alkenylpentaborane(9) products.

Reductive-elimination of the platinum(IV) intermediate would then yield the observed product, 1:2′-[B_5H_8]$_2$, and the formation of an [HPtBr] species which could react with HBr, completing the catalytic cycle, to give $PtBr_2$ and hydrogen.

$$1\!:\!2'\text{-}[B_5H_8]_2 \quad (12)$$

$$[HPt^{II}Br] + HBr \longrightarrow Pt^{II}Br_2 + H_2 \quad (13)$$
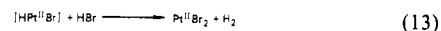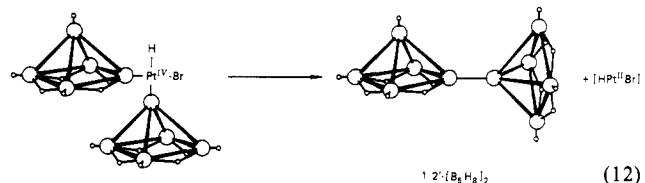
The selective formation of the 1:2′-[B_5H_8]$_2$ isomer is consistent with the mechanism outlined above and indicates that the $PtBr_2$ has a dual function in these reactions. The initial electrophilic substitution at the apex, however, appears to be the key step in the pentaborane(9) reaction, since it was found that when the apex position was blocked with a methyl substituent no reaction with $PtBr_2$ occurred.

$$+ Pt^{II}Br_2 \longrightarrow no\ reaction \quad (14)$$
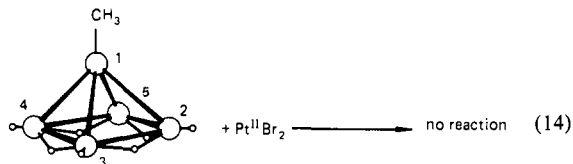
While 1-methylpentaborane(9) undergoes no reaction by itself with PtBr$_2$, it reacts in the presence of tetraborane(10) to form the new coupled-cage compound, 1:2′-[B_4H_9][1′-$CH_3B_5H_7$]. This observation suggests that initial electrophilic attack of PtBr$_2$ on tetraborane(10), to generate a tetraboranylplatinum intermediate, is the key step in this reaction.

$$B_4H_{10} + PtBr_2 \rightarrow 1\text{-}B_4H_9\!-\!Pt\!-\!Br + HBr \quad (15)$$
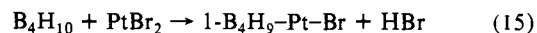
Molecular orbital calculations[49] predict that the 1,3-boron atoms in tetraborane(10) have a higher electron density than the 2,4-boron atoms; therefore, an electrophilic attack by PtBr$_2$ would be expected to occur at one of these positions, as indicated above.

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If this step is followed by an oxidative-addition of 1-methylpentaborane at a basal position, the selective formation of the 1:2'-[B$_4$H$_9$][1'-CH$_3$B$_5$H$_7$] isomer would then result following reductive-elimination. A similar reaction sequence could lead to formation of 1:1'-[B$_4$H$_9$]$_2$; however, the oxidative-addition of the second tetraborane(10) molecule must also occur at a 1-boron position to account for the formation of the symmetrical isomer.

In contrast to the results with 1-methylpentaborane, 2-methylpentaborane was found to react readily in the presence of PtBr$_2$ to give a coupled-cage product, 1:2'-[2-CH$_3$B$_5$H$_7$][3'-CH$_3$B$_5$H$_7$]. The fact that no 1:2'-[2-CH$_3$B$_5$H$_7$][4'-CH$_3$B$_5$H$_7$] isomer is observed in the reaction indicates that the oxidative-addition of 2-methylpentaborane(9) must occur at a B–H position adjacent (cis) to the basal methyl substituent. A similar cis preference has been observed in the formation of dimethyl-substituted pentaboranes and has been proposed to result from steric repulsions between the methyl group and adjacent bridge hydrogens.[52]

It is significant that the reaction of hexaborane(10) with PtBr$_2$ does not result in the formation of a coupled-cage product but instead gives the metalloborane complex, [4,5;4',5'-μ-*trans*-PtCl$_2$(B$_6$H$_{10}$)$_2$]$_2$,[35] in which each hexaborane(10) is bound in an η^2-fashion across a basal boron–boron bond. Thus, hexaborane(10), because of its unique basal single bond, is able to coordinate in an olefin-like bonding fashion that is not possible for other boron hydrides and carboranes. As a result, processes such as oxidative-addition of a cage B–H bond to platinum are less likely and no coupling occurs.

Platinum(II) bromide was also found to be effective for catalyzing the reactions of the small carboranes, 1,5-C$_2$B$_3$H$_5$ and 1,6-C$_2$B$_4$H$_6$, to give the corresponding boron–boron linked coupled carboranes, 2:2'-[1,5-C$_2$B$_3$H$_4$]$_2$ and 2:2'-[1,6-C$_2$B$_4$H$_5$]$_2$. There was no evidence for the formation of any carbon–carbon or boron–carbon linked isomers in the reactions, which agrees both with the proposed electrophilic nature of the catalyst and with the relative bond strengths of B–H (~91 kcal) and C–H (~98 kcal) bonds.[53] The observation of only boron–boron linked products is also consistent with our earlier studies of the transition-metal-catalyzed reactions of small carboranes with acetylenes, which was found to yield only boron-substituted alkenylcarborane products.[54]

In conclusion, we feel that the results described herein represent a major step toward the development of rational, high-yield procedures for the formation of multicage polyhedral boranes and carboranes. Furthermore, this work again illustrates the potential for the use of transition-metal catalysts, which until now have been primarily employed in organic chemistry, to promote analogous reactions of inorganic compounds. Work is now continuing in this laboratory aimed toward both the discovery of new types of dehydrodimerization catalysts, which may exhibit higher reactivity and different selectivity, and the development of new classes of metal-catalyzed borane and carborane reactions.

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4-Phenyl-1,2,4-triazoline-3,5-dione: A Prosthesis for the μ-η¹-S$_2$ Ligand in Organovanadium Sulfide Chemistry

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Abstract: 4-Phenyl-1,2,4-triazoline-3,5-dione (PTD) reacts with (CH$_3$C$_5$H$_4$)$_2$V$_2$(μ-S)$_2$(μ-η¹-S$_2$) (1) to yield primarily (CH$_3$C$_5$H$_4$)$_2$V$_2$(μ-S)(μ-η²-S$_2$)(μ-η¹-PTD) (2) along with other minor products. The structure of 2 was inferred from the structure of its Pt(PPh$_3$)$_2$ adduct (CH$_3$C$_5$H$_4$)$_2$V$_2$S$_3$(PTD)Pt(PPh$_3$)$_2$ (5), which was determined by single-crystal X-ray diffraction techniques. The crystals of 5 belong to space group P2$_1$/c with a = 22.181 (7) Å, b = 13.176 (4) Å, c = 19.303 (5) Å, β = 111.10 (2)°, Z = 4. Conventional full-matrix least-squares refinement with non-carbon atoms anisotropic, carbon atoms independently isotropic, and hydrogen atoms identically isotropic gave R = 0.059 and R$_w$ = 0.065 for 6934 reflections having 2θ < 55° and I > 3σ(I). The structure consists of an isosceles triangle of metal atoms capped by two μ$_3$-S ligands, with the V–V edge spanned by a μ-S and a μ-η¹-PTD ligand. An evaluation of the V–S and V–Pt distances indicates that formation of the Pt(PPh$_3$)$_2$ adduct effects only minor perturbations on the electronic structure of 2. Compound 2 is efficiently desulfurized by tri-*n*-butylphosphine to yield (CH$_3$C$_5$H$_4$)$_2$V$_2$(μ-S)$_2$(μ-η¹-PTD) (3). Compound 3 reacts further with PTD to yield (CH$_3$C$_5$H$_4$)$_2$V$_2$S$_2$(PTD)$_2$ (4). Both 3 and 4 are minor products of the reaction of 1 with PTD. The high symmetry of 3 and 4 is supported by spectroscopic measurements. Compound 4 forms a stable Pt(PPh$_3$)$_2$ adduct, (CH$_3$C$_5$H$_4$)$_2$V$_2$S$_2$(PTD)$_2$Pt(PPh$_3$)$_2$ (6), whose properties indicate a structure consisting of a [(CH$_3$C$_5$H$_4$)V]$_2$ moiety bridged by two μ-η¹-PTD ligands and a μ-η²-S$_2$Pt(PPh$_3$)$_2$ ligand. The structure of 4 thus arises from oxidative coupling of the two μ-S ligands in 3. Comparison of 2 and 3 with (CH$_3$C$_5$H$_4$)$_2$V$_2$(μ-η¹-S$_2$)(μ-η²-S$_2$) and (CH$_3$C$_5$H$_4$)$_2$V$_2$(μ-S)$_2$(μ-η¹-S$_2$) illustrates that the μ-η¹-PTD ligand functions as prosthesis for the μ-η¹-S$_2$ ligand in these cyclopentadienylvanadium dimers.

Recent work has shown that organometallic sulfide complexes can exhibit considerable sulfur-centered reactivity. Compounds of the type (RC$_5$H$_4$)$_2$TiS$_5$ (R = H, CH$_3$),[2] (RC$_5$H$_4$)$_2$V$_2$S$_4$ (R = H, CH$_3$, (CH$_3$)$_2$CH),[3] (C$_5$H$_5$)$_2$Cr$_2$S(S-*t*-Bu)$_2$,[4] (CH$_3$R$_4$C$_5$)$_2$Mo$_2$S$_4$

(R = CH$_3$, H)[5], and Fe$_2$(S$_2$)(CO)$_6$[6] have been employed for organic synthesis, for the assembly of unusual mixed-metal

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