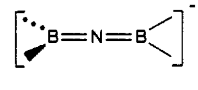
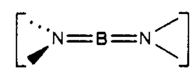
compound $Li(Et_2O)_2NPhBMes_2$[11] (**5**), which is monomeric and has a three-coordinate planar environment at the nitrogen. The higher degree of association seen in **2** compared to **5** is presumably due to reduced steric crowding or, perhaps, a preference of the Li^+ ion for solvation by N donors over O donors. This also results in longer BN distances compared with the precursor **1**, whereas a decrease was noted in the case of **5**. The increase seen in **2** is presumably due to the higher (4) coordination number at the nitrogen.

The reaction between **2** and a further 1 equiv of Mes_2BF gives the diborylamine $HN(BMes_2)_2$ as recently described in the literature.[22] Although both di- and triborylamines have been known for some time, it was only recently that the structures of some diborylamines were reported. The main feature of interest in the structure of **3** is the wide BNB angle of 139.3 (2)°. This is much wider than the corresponding angle in secondary amines. It is perhaps comparable with the SiNSi angle (~136°) in $K(1,4\text{-dioxane})_2N(SiMe_3)_2$.[28] The BN distance in **3**, 1.435 (2) Å, is considerably longer than that in **1** since the two borons compete for the nitrogen lone pair.

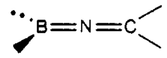
The wide BNB angle in **3** suggested that the removal of the proton would effect an increase in this parameter and perhaps afford a linear BNB system. This hypothesis proved to be correct. compound **3** reacts smoothly with n-BuLi in Et_2O to give **4** in quantitative yield. The X-ray crystal structure reveals that the BNB moiety is essentially linear with rather short[29] BN distances and CBC planes, which are almost perpendicular (88°) to each other. The



moiety is thus electronically and structurally very similar to allenes, the borinium cations[18]



and the neutral hybrid system



in $Mes_2B{=}N{=}CPh_2$.[30] The similarity is underlined by the almost identical BN distances in **4** and in $[B(NCH_2Ph(t\text{-Bu}))_2]^+$ [18,31] (1.331 (5) and 1.334 (5) Å) or $[Me_2NBTMP]^+$ (1.30 (4) Å and 1.42 (4)°; av 1.36 (4) Å).

In summary, the use of the $BMes_2$ group allows ready stabilization of monomeric primary borylamines, which can be lithiated to the synthetically useful **2**. Two $BMes_2$ groups on nitrogen produce the secondary diborylamine **3**, which can be readily and quantitatively converted to the interesting "inorganic allene" species **4**.

Note Added in Proof. After this paper had been submitted, the synthesis and spectroscopic characterization of the diborylamide species $[(t\text{-Bu})_2BNB(t\text{-Bu})_2]^-$ was published (see ref 32).

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Notes on structural solutions, thermal ellipsoid plot of **3**, summary of data collection and refinement, and tables of atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates (26 pages). Ordering information is given on any current masthead page.

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Transition-Metal-Promoted Reactions of Boron Hydrides. 9.[1] Cp*Ir-Catalyzed Reactions of Polyhedral Boranes and Acetylenes

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Abstract: The complex $[Cp^*IrCl_2]_2$, in the presence of Proton Sponge, has been found to catalyze reactions of pentaborane(9) with terminal and internal acetylenes, resulting in the formation, in good yields, of the corresponding alkenylpentaboranes. Reaction rates in excess of 30 catalyst turnovers/h were found and represent the fastest turnover rates reported for this type of transformation. The $[Cp^*IrCl_2]_2$/Proton Sponge catalyst system was also found to catalyze the reactions of alkynes with several polyhedral boranes that were previously found to be unreactive for borane/alkyne addition. Thus, hexaborane(10), $1,2\text{-}C_2B_{10}H_{12}$, and $1,7\text{-}C_2B_{10}H_{12}$ reacted with propyne and catalyst to form, respectively, 2-(1-propenyl)hexaborane(10), 3-(*trans*-1-propenyl)-*o*-carborane, and 2-(*trans*-1-propenyl)-*m*-carborane.

We have previously reported[2-5] the discovery of transition-metal-catalyzed synthetic routes to a variety of alkenylboranes and carboranes (eq 1 and 2).

$$B_5H_9 + RC{\equiv}CH \xrightarrow{IrCl(CO)(PPh_3)_2} 2\text{-}(RHC{=}CH)B_5H_8 \quad (1)$$

$$B_5H_9 + RHC{=}CH_2 \xrightarrow{PdBr_2} 1\text{- and }2\text{-}(RHC{=}CH)B_5H_8 + RC_2H_5 \quad (2)$$

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[1] Part 8: Mirabelli, M. G. L.; Sneddon, L. G. *Organometallics* **1986**, *5*, 1510–1511.

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The facile formation of alkenyl-substituted polyhedral boranes is potentially quite important since subsequent investigations have shown, for example, that alkenylpentaboranes are high-yield precursors to monocarbon carboranes (eq 3).[2,3]

$$2\text{-(RHC}{=}\text{CH)B}_5\text{H}_8 \xrightarrow{\Delta} nido\text{-3-R}'\text{CB}_5\text{H}_8 + nido\text{-4-R}'\text{CB}_5\text{H}_8 \quad (3)$$

Previous catalysts for polyhedral borane–acetylene addition reactions were limited, however, by slow turnover rates, relatively rapid catalyst deactivation, and side reactions resulting from the attack of basic ligands (such as PR_3 and CO) at the borane cages. These problems have led us to investigate new types of acetylene addition catalysts.

Maitlis[6] has developed a series of catalysts that do not contain basic ligands, based on (pentamethylcyclopentadienyl)rhodium (Cp*Rh) and –iridium (Cp*Ir) complexes. The catalysts are derived from $[Cp^*MCl_2]_2$ (M = Rh or Ir) and are air-stable solids that 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 of 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 (1-atm H_2 pressure).[7] Likewise, Bergman[8] and Graham[9] have each demonstrated that Cp*Ir complexes are extremely reactive and are capable of hydrocarbon C–H bond activation.

The work described here shows that $[Cp^*IrCl_2]_2$, in the presence of Proton Sponge, is a highly effective catalyst system for promoting the reactions of pentaborane(9) with terminal and internal acetylenes, resulting in the synthesis of basally substituted alkenylpentaboranes. Furthermore, we have discovered that this catalyst can promote the reactions of alkynes with a number of polyhedral boranes that were previously found to be inactive for this type of transformation. These include reactions of acetylenes with hexaborane(10), 1,2-$C_2B_{10}H_{12}$, and 1,7-$C_2B_{10}H_{12}$, with the results of these studies reported herein.

Experimental Section

Materials. Proton Sponge (1,8-bis(dimethylamino)naphthalene) was used as received from Aldrich Chemical Co. Propyne and 2-butyne were obtained from Farchan Laboratories and were purified by vacuum-line fractionation. The 1-butyne was obtained from Columbia Organic Chemicals and was used as received. The 1,2-ethylene dichloride was purchased from MCB and distilled from P_2O_5. Methylene chloride was obtained from EM Science and was used without further purification. The *closo*-carboranes 1,2- and 1,7-$C_2B_{10}H_{12}$ were purchased from the Dexsil Chemical Corp. Hexaborane(10)[10] and $[Cp^*IrCl_2]_2$[11] were prepared by standard literature methods.

Gas–liquid chromatography was conducted on a Varian Aerograph Series 1400 gas chromatograph equipped with a 6 ft × 0.25 in. 10% SE-30 on a Chromosorb W (100/120-mesh) column.

Physical Measurements. ^{11}B NMR spectra at 160.5 MHz were obtained on a Bruker AM-500 Fourier transform spectrometer. ^1H NMR spectra at 200 MHz and ^{11}B NMR spectra at 64.2 MHz were obtained on an IBM AF-200 Fourier transform spectrometer. Chemical shifts for ^{11}B NMR spectra are relative to external $BF_3{\cdot}O(C_2H_5)_2$, with a negative sign indicating an upfield shift. Chemical shifts for ^1H NMR spectra are in ppm based on 7.15 ppm for C_6D_6 (relative to Me_4Si at 0.00 ppm). Unit and high-resolution mass spectra were obtained on a VG-7070H high-resolution mass spectrometer interfaced to a VG 11-250J data system. Infrared spectra were recorded on a Perkin-Elmer 1310 infrared spectrophotometer.

Reactions of Pentaborane(9). B_5H_9 and Propyne. In a typical reaction, 20 mg (0.025 mmol) of $[Cp^*IrCl_2]_2$ and 20 mg (0.10 mmol) of Proton Sponge were charged into a 88-mL Fisher-Porter pressure vessel, and the vessel was evacuated. Pentaborane(9) (716 mg, 11.4 mmol) and 25 mmol of propyne were condensed into the flask at −196 °C, and the mixture was warmed to 70 °C. Within minutes the orange solution turned golden yellow and became completely homogeneous. After 2 h at 70 °C, the flask was attached to a vacuum line, frozen to −196 °C, and degassed to remove any noncondensible gas. The volatile material was then fractionated through a −63, −95, and −196 °C trap series where 155 mg (1.50 mmol) of pure 2-(*trans*-1-propenyl)pentaborane(9) was stopped at −63 °C, and 586 mg of unreacted B_5H_9 was stopped in the −95 °C trap. This corresponds to 71% yield based on consumed B_5H_9 and 60 catalyst turnovers in the 2-h period. The unreacted starting materials were placed back over the catalyst for an additional 4 h at 70 °C, but no products could be isolated. The ^{11}B and ^1H NMR data match previously reported[3] literature values for 2-(*trans*-1-propenyl)pentaborane(9) and confirm its purity.

B_5H_9 and 1-Butyne. A similar reaction was performed with 20 mg (0.025 mmol) of $[Cp^*IrCl_2]_2$, 20 mg (0.10 mmol) of Proton Sponge, 10 mmol of B_5H_9, and 25 mmol of 1-butyne. After 4 h of reaction at 70 °C, 386 mg (3.30 mmol) of pure 2-(*trans*-1-butenyl)pentaborane(9) was collected in a −63 °C trap, corresponding to 132 catalyst turnovers in the 4-h period. The ^{11}B and ^1H NMR spectra of the product are consistent with those previously reported.[5]

B_5H_9 and 2-Butyne. In a 88-mL reaction flask were placed 20 mg (0.025 mmol) of $[Cp^*IrCl_2]_2$, 20 mg (0.10 mmol) of Proton Sponge, 10 mmol of B_5H_9, and 20 mmol of 2-butyne. After 4 h of reaction at 70 °C, 350 mg (3.0 mmol) of pure (97% by GLC) 2-(*cis*-2-butenyl)pentaborane(9) was stopped in a −55 °C trap. This corresponds to 120 catalyst turnovers in a 4-h period. The ^{11}B and ^1H NMR data match previously reported literature values.[2,3]

Reactions of Hexaborane(10). B_6H_{10} and Propyne. An evacuated reaction flask containing 40 mg (0.05 mmol) of $[Cp^*IrCl_2]_2$ and 40 mg (0.20 mmol) of Proton Sponge was charged with 1.12 g (15.0 mmol) of B_6H_{10} and 30 mmol of propyne. The reaction mixture was warmed and allowed to stir at room temperature for 22 h. The volatile components were removed and fractionated through a −30, −95, and −196 °C trap series, giving 94 mg (0.82 mmol) of an isomeric mixture (cis/trans) of 2-(1-propenyl)hexaborane(10) and 12.5 mmol of unreacted B_6H_{10}. This corresponds to 32.8% yield based on consumed B_6H_{10} with 16 catalyst turnovers. The 2-(1-propenyl)hexaborane(10) was separated from trace amounts of lower volatile impurities on a 10% SE-30 GLC column; R_v = 4.8 (R_v = 1.0 for B_6H_{10}). ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 28.7 (s, 1), 14.3 (d, 2, J = 154 Hz), 6.6 (d, 2, J = 148 Hz), −49.6 (d, 1, J = 154 Hz). ^1H NMR (200 MHz, δ, C_6D_6), 60:40 cis/trans isomeric mixture: isomer A, 6.77 (m, 1, J = 6.0 Hz), 6.58 (d, 1, J = 16.0 Hz), 1.79 (dd, 3, J = 6.0 and 1.4 Hz), −1.16 (br m); isomer B, 6.15 (m, 1, J = 6.0 Hz), 5.98 (d, 1, J = 18.0 Hz), 1.66 (d, 3, J = 6.0 Hz), −1.16 (br m). Exact mass for $^{12}C_3{}^1H_{14}{}^{11}B_6$: calcd, 116.1654; found, 116.1654.

B_6H_{10} and 1-Butyne. A reaction flask containing 40 mg (0.05 mmol) of $[Cp^*IrCl_2]_2$ and 40 mg (0.20 mmol) of Proton Sponge was evacuated and charged with 561 mg (7.5 mmol) of B_6H_{10} and 20 mmol of 1-butyne. After 17 h of stirring at room temperature, the volatiles were fractionated through a −30, −95, and −196 °C trap series. The −30 °C fraction (95 mg, 0.74 mmol) was purified from trace impurities on a 10% SE-30 GLC column to yield (95% pure by GLC) 2-(*trans*-1-butenyl)hexaborane(10), R_v = 10.4 (R_v = 1.0 for B_5H_9). ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 29.0 (s, 1), 14.6 (d, 2, J = 152 Hz), 6.7 (d, 2, J = 152 Hz), −49.6 (d, 1, J = 150 Hz). ^1H NMR (200 MHz, δ, C_6D_6), 6.25 (td, 1, J = 17.4 and 5.4 Hz), 5.98 (d, 1, 17.1 Hz), 2.00 (q, 2, J = 5.2 Hz), 0.96 (t, 3, J = 5.2 Hz). This corresponds to 15 catalyst turnovers.

Reactions with 1,2- and 1,7-$C_2B_{10}H_{12}$. 1,2-$C_2B_{10}H_{12}$ and Propyne. A 88-mL Fisher-Porter pressure vessel was charged with 40 mg (0.05 mmol) $[Cp^*IrCl_2]_2$, 40 mg (0.20 mmol) of Proton Sponge, 160 mg (1.11 mmol) of *o*-carborane, 5 mmol of propyne, and 3 mL of 1,2-ethylene dichloride. The flask was placed in an oil bath at 100 °C, and the mixture was stirred for 48 h. The volatiles were then removed, leaving an oily, yellow solid in the flask. This material was dissolved in methylene chloride, filtered through a short plug (~4 cm) of silica gel, and eluted with 10 mL of methylene chloride. GLC analysis with a 10% SE-30 on Chromosorb W column showed 40% conversion of *o*-carborane into 3-(*trans*-1-propenyl)-*o*-carborane, R_v = 2.42 (R_v = 1 for 1,2-$C_2B_{10}H_{12}$). This corresponds to ~4 catalyst turnovers/day. A pure sample of 3-(*trans*-1-propenyl)-*o*-carborane was obtained by preparative GLC. ^{11}B NMR (160.5 MHz, ppm, C_6D_6): −1.9 (d, 2, J = 146 Hz),

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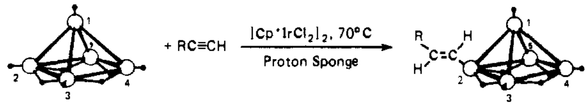
−6.1 (s, 1), −8.1 (d, 1, J = 151 Hz), −11.9 (d, 1, $J \sim$ 150 Hz), −12.3 (d, 2, $J \sim$ 152 Hz), −13.1 (d, 2, $J \sim$ 139 Hz), −13.6 (d, 1, $J \sim$ 152 Hz). ^{1}H NMR (200 MHz, δ, C_6D_6): 5.86 (m, 1, J = 6.0 Hz), 5.17 (d, 1, J = 17.5 Hz), 2.14 (s, 2), 1.55 (dd, 3, $J_{CH_3-H_B}$ = 6.3, $J_{CH_3-H_A}$ = 1.5 Hz). Exact mass for $^{12}C_5{}^1H_{16}{}^{11}B_{10}$: calcd, 186.2183; found, 186.2200. IR (NaCl plates): 3065 (m), 3010 (w), 2950 (w), 2910 (w), 2570 (vs), 1640 (s), 1440 (s), 1370 (w), 1310 (m), 1275 (m), 1210 (s), 1180 (s), 1135 (m), 1085 (s), 1025 (s), 1005 (m), 975 (s), 930 (w), 915 (w), 720 (m) cm^{-1}.

1,7-$C_2B_{10}H_{12}$ and Propyne. In a similar reaction, 40 mg (0.05 mmol) of $[Cp^*IrCl_2]_2$, 40 mg (0.20 mmol) of Proton Sponge, 150 mg (1.0 mmol) of 1,7-$C_2B_{10}H_{12}$, 5 mmol of propyne, and 3 mL of 1,2-ethylene dichloride were placed in a reaction flask, and the mixture was warmed to 100 °C. After 48 h of stirring, GLC analysis on 10% SE-30 showed a 14% conversion of *m*-carborane into 2-(*trans*-1-propenyl)-*m*-carborane, R_v = 3.1, (R_v = 1.0 for 1,7-$C_2B_{10}H_{12}$). This corresponds to ~1.5 catalyst turnovers/day. Pure samples were obtained by preparative GLC. ^{11}B NMR (160.5 MHz, ppm, C_6D_6): −5.6 (d, 2, J = 156 Hz), −8.6 (s, 1), −10.2 (d, 1, J = 173 Hz), −11.8 (d, 2, $J \sim$ 144 Hz), −12.8 (d, 3, $J \sim$ 160 Hz), −15.0 (d, 1, J = 161 Hz). ^{1}H NMR (200 MHz, δ, C_6D_6): 5.83 (m, 1, J = 6.4 Hz), 5.37 (d, 1, J = 18.0 Hz), 2.17 (s, 2), 1.59 (dd, 3, J = 6.1 and 1.5 Hz).

Results

$[Cp^*IrCl_2]_2$ has been found to be a highly effective catalyst precursor for the formation of a variety of alkenylboranes and carboranes. The reactions proceed at moderate temperatures, are highly selective, and provide good yields of boron-substituted products.

The reaction of $[Cp^*IrCl_2]_2$ with pentaborane(9) and substituted acetylenes was found to produce alkenyl-B_5H_8 in approximately 70% yield according to eq 4.

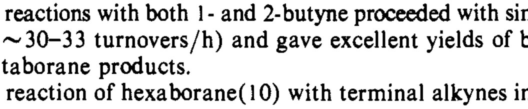


(4)

A typical reaction involved stirring pentaborane(9) and propyne in the presence of 0.22 mol % $[Cp^*IrCl_2]_2$ and Proton Sponge at 70 °C without solvent. An induction period (~2 min) was observed where the solution went from orange to a completely homogeneous golden yellow color, which then remained unchanged throughout the 2-h reaction period. The product was obtained in pure form by simple vacuum line fractionation through a −63 °C trap. It is also significant that the reaction is highly regio- and stereoselective, producing only the trans isomer of 2-propenylpentaborane(9). Furthermore, the reaction is fast, with typical catalyst turnover rates exceeding 30/h.

It was also found that Cp*Ir catalyzed reactions of pentaborane(9) with other terminal and internal acetylenes. For example, reactions with both 1- and 2-butyne proceeded with similar rates (~30–33 turnovers/h) and gave excellent yields of butenylpentaborane products.

The reaction of hexaborane(10) with terminal alkynes in the presence of catalytic amounts of $[Cp^*IrCl_2]_2$ was found to proceed at room temperature to form basally substituted 2-(alkenyl)B_6H_9 (eq 5).



(5)

The compound 2-propenylhexaborane(10), which was produced from the reaction of B_6H_{10} with propyne, could be obtained (95% pure by NMR) as a thermally sensitive, colorless oil in ~35% yield by vacuum fractionation through a −30 °C trap.

The room-temperature ^{11}B NMR spectrum for 2-propenylhexaborane(10) consists of a low-field singlet and three doublets in a ratio of 1:2:2:1. The assignment of these resonances to the B(2), B(4,5), B(3,6), and B(1) borons, respectively, (as shown in Figure 1) is consistent with the assignments previously made by Shore for the spectrum of 2-$CH_3B_6H_9$.[12]

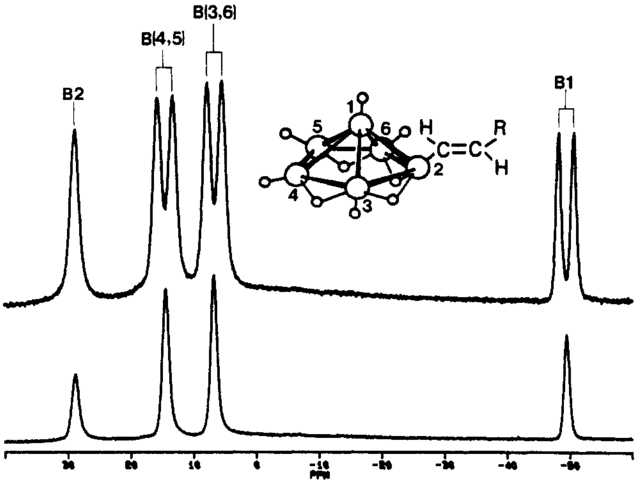


Figure 1. 64.2-MHz ^{11}B NMR spectrum of 2-(1-propenyl)hexaborane-(10).

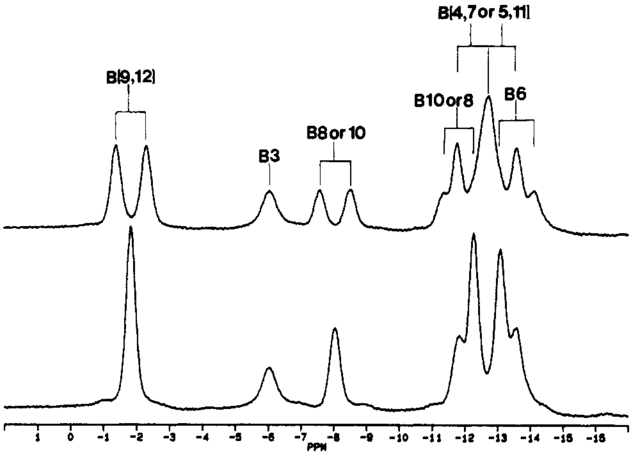
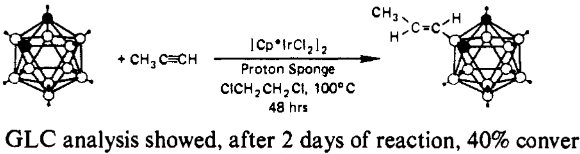


Figure 2. 160.5-MHz ^{11}B NMR spectrum of 3-(*trans*-1-propenyl)-*o*-carborane.

The ^{1}H NMR spectrum indicates that the product is an isomeric mixture of 2-propenylhexaborane(10) in a 60:40 cis to trans ratio, with two sets of vinylic hydrogens at 6.77 and 6.58 ppm and 6.15 and 5.98 ppm. All attempts to separate these isomers failed due to the sensitivity of these compounds to polar GLC column supports. However, the reaction of hexaborane(10) with 1-butyne was stereoselective and produced only the trans isomer of 2-butenylhexaborane(10), as evidenced by the proton NMR spectrum, which shows only one set of olefinic hydrogens at 6.25 and 5.98 ppm. Attempts to prepare alkenyl-B_6H_9 from internal acetylenes resulted in the formation of polymeric material.

We have found that a number of transition-metal catalysts, such as $(R_2C_2)Co_2(CO)_6$ and $IrCl(CO)(PPh_3)_2$, which were active for small-cage boranes and carboranes, do not promote reactions of large-cage systems; however, we have now found that $[Cp^*IrCl_2]_2$ is quite reactive toward these types of systems. For example, the compound 3-(*trans*-1-propenyl)-*o*-carborane was prepared from 1,2-$C_2B_{10}H_{12}$ and propyne at 100 °C in 1,2-dichloroethane with catalytic amounts (5 mol %) of $[Cp^*IrCl_2]_2$ (eq 6).



(6)

GLC analysis showed, after 2 days of reaction, 40% conversion to the 3-propenyl derivative.[13]

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[12] Brice, V. T.; Johnson, H. D., II; Shore, S. G. *J. Am. Chem. Soc.* **1973**, *95*, 6629–6635.

[13] Reactions in ketone solvents show higher conversion rates but give more complex products. Mirabelli, M. G. L.; Sneddon, L. G., unpublished results.

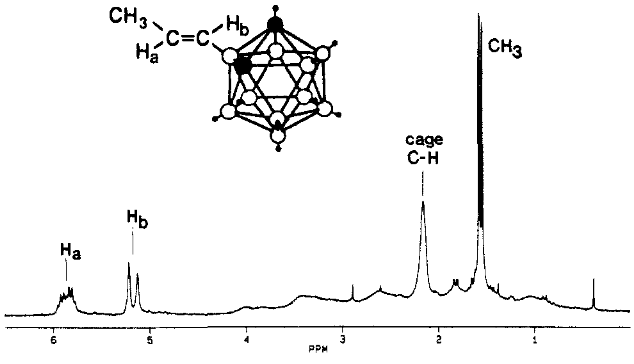
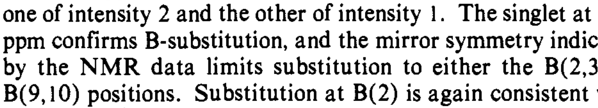


Figure 3. 200-MHz ^1H NMR spectrum of 3-(*trans*-1-propenyl)-*o*-carborane.

The 160.5-MHz line-narrowed ^{11}B NMR spectrum (Figure 2) of the isolated product shows seven resonances with relative intensities of 2:2:2:1:1:1:1, with the singlet of intensity 1 at −6.1 ppm confirming B-substitution. The plane of symmetry indicated by the NMR data can only be consistent with substitution of the carborane at B(3,6) or B(8,10). Substitution at B(3) is consistent with the earlier work by Hawthorne[14] and Hoel, who showed that 1,2-$C_2B_{10}H_{12}$ will oxidatively add at B(3) to $[Ir(C_8H_{14})_2Cl]_2$ in the presence of triphenylphosphine to yield 3-$[(PPh_3)_2IrHCl]$-1,2-$C_2B_{10}H_{11}$.

The ^1H NMR spectrum (Figure 3) confirms the presence of a propenyl group showing a doublet of doublets of intensity 3 at 1.55 ppm and two vinyl resonances at 5.86 and 5.17 ppm, with coupling constants consistent with trans stereochemistry. Infrared spectral data show a sharp absorbance at 1640 cm^{-1} attributed to the C=C double-bond stretch.

The propenyl derivative of 1,7-$C_2B_{10}H_{12}$ can also be prepared from $[Cp^*IrCl_2]_2$, Proton Sponge, and propyne (eq 7).



(7)

Although reaction was slow (14% conversion after 48 h), the catalyst again showed high regio- and stereoselectivity by forming only the trans isomer of 2-(1-propenyl)-*m*-carborane.[13]

The 160.5-MHz line-narrowed ^{11}B NMR spectrum shows six resonances of relative intensity 2:2:3:1:1:1, with the peak of intensity 3 appearing to result from the overlap of two resonances, one of intensity 2 and the other of intensity 1. The singlet at −8.6 ppm confirms B-substitution, and the mirror symmetry indicated by the NMR data limits substitution to either the B(2,3) or B(9,10) positions. Substitution at B(2) is again consistent with the studies[14] of Hawthorne and Hoel, which showed B(2) to be the preferred site of oxidative addition of *m*-carborane to low-valent iridium complexes.

Discussion

The work presented here has demonstrated that the $[Cp^*IrCl_2]_2$/Proton Sponge system is a general catalyst for the acetylene addition reactions of various polyhedral boron cage compounds and has resulted in the production of a number of new alkenylboranes and carboranes, including 2-(1-propenyl)hexaborane(10), 3-(*trans*-1-propenyl)-*o*-carborane, and 2-(1-propenyl)-*m*-carborane, as well as provided an improved synthetic route to the previously known alkenyl derivatives of pentaborane(9).

Maitlis has proposed[7] that $[Cp^*IrCl_2]_2$ undergoes bridge splitting in the presence of solvent and that mononuclear iridium fragments are actually the catalytic species (eq 8).

$$[Cp^*IrCl_2]_2 \rightleftarrows 2Cp^*IrCl_2(S) \qquad S = \text{solvent} \qquad (8)$$

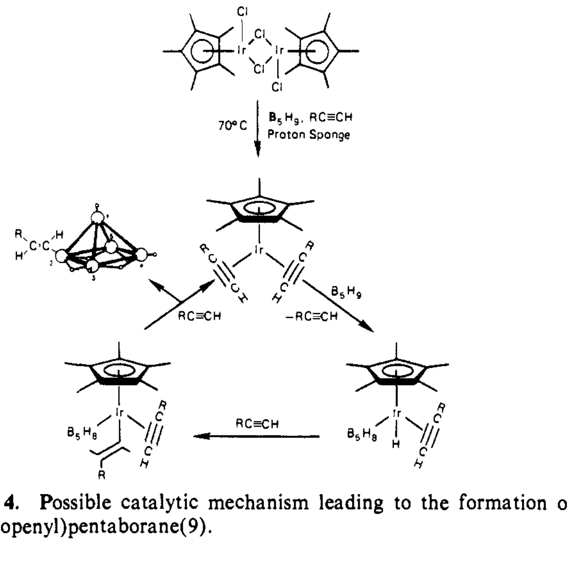


Figure 4. Possible catalytic mechanism leading to the formation of 2-(1-propenyl)pentaborane(9).

It was also shown that the catalytic activities of these complexes are affected by the presence of a noncoordinating base such as triethylamine. On the basis of these observations, Maitlis suggested that heterolytic activation of hydrogen may be a predominant reaction in the catalytic cycle (eq 9 and 10).

$$Cp^*IrCl_2(S) + H_2 \rightleftarrows Cp^*IrHCl(S) + HCl \qquad (9)$$

$$Cp^*IrHCl(S) + H_2 \rightleftarrows Cp^*IrH_2(S) + HCl \qquad (10)$$

The purpose of the base could be to facilitate the binding of HCl, although the possibility that the base stabilizes active catalytic intermediates was not excluded.

In the presence of B_5H_9, alkyne, and Proton Sponge, the orange dimer reacts during the first 2–3 min to form a golden yellow, homogeneous solution. There was no color change in the absence of base, and it was necessary to add 4 equiv of base/equiv of $[Cp^*IrCl_2]_2$ to effect high turnover rates. Strong bases, such as triethylamine, are incompatible with polyhedral boranes, such as B_5H_9 and B_6H_{10}, due to base–adduct formation[15] and decomposition reactions. However, the nonnucleophilic base 1,8-bis(dimethylamino)naphthalene (Proton Sponge) was found to be unreactive toward these borane cages and was used as the catalyst promoter in these reactions.

Although the mechanisms of the reactions reported herein have not been determined, the above observations suggest that the reaction with pentaborane(9) may involve steps analogous to those given in eq 8–10 to yield a metalloborane complex, which could then undergo reductive elimination to produce a coordinatively unsaturated Cp*Ir fragment (Figure 4). This fragment could then bind alkyne and oxidatively add a B_5H_9. Only 2-substituted alkenylpentaboranes are produced in these reactions, indicating that the oxidative-addition step must occur at one of the basal B–H units. Thus, the Cp*Ir fragment must act as a nucleophile, attacking the cage borons of highest positive charge density, which in the case of pentaborane(9) is predicted to be the basal borons.[16] This conclusion is further supported by the reactions of pentaborane(9) with other d^8 metal complexes such as *trans*-$[Ir(CO)Cl(PMe_3)_2]$, which gives exclusively 2-$[IrH(CO)(Cl)[P(CH_3)_3]]B_5H_8$[17] and with our earlier studies of the reactions of B_5H_9, alkynes, and $IrCl(CO)(PPh_3)_2$, which showed only basal cage substitution.[2,3]

The oxidative addition may then be followed by insertion of the acetylene into a metal hydride bond forming a metallovinyl complex, which, following reductive elimination, would form alkenylpentaborane and regenerate the catalytic cycle.

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The high activity of the Cp*Ir catalysts is also evidenced by their ability to promote the reactions of alkynes with several cage compounds for which previous catalysts had failed. Thus, the $[Cp^*IrCl_2]_2$/Proton Sponge catalyst system was found to be effective at promoting the addition reactions of 1,2-$C_2B_{10}H_{12}$, 1,7-$C_2B_{10}H_{12}$, and B_6H_{10} with terminal alkynes to form the corresponding *B*-alkenylcarboranes and -borane.

The C-substituted alkenyl derivatives of both 1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$ have been previously reported,[18] and such compounds have been used to obtain carborane polymers.[19,20] The B-substituted compounds, 3-vinyl-*o*-carborane and 2-vinyl-*m*-carborane, have been prepared from the reaction of the appropriate isomer of $C_2B_9H_{11}^{2-}$ with vinyldichloroborane.[21,22] Pyrolysis of 3-vinyl-*o*-carborane was then used to prepare a variety of B-substituted derivatives of *m*-carborane.[23] Recently, high-yield, metal-promoted synthetic routes to the 9-alkenyl derivatives of both *o*- and *m*-carborane, via the reaction of the 9-iodo-substituted compounds with vinylmagnesium halides in the presence of catalytic amounts of $(Ph_3P)_4Pd$, have been reported.[24] The syntheses described herein result in the selective formation of 3-propenyl-*o*-carborane and 2-propenyl-*m*-carborane in high yields directly from the carboranes and propyne, and the method should be applicable to the synthesis of any alkenyl derivative substituted at these positions.

Alkenylhexaborane compounds were previously unknown and our earlier attempts to oxidatively add hexaborane(10) to transition-metal species such as $PtBr_2$[25] or $IrCl(CO)(PPh_3)_2$[26] resulted only in the formation of an η^2-complex or decomposition of the hexaborane(10). Although yields of Cp*Ir-catalyzed reactions of hexaborane(10) are low (35%), the facile product isolation under mild conditions will make the exploration of the chemistry of this compound possible. For example, alkenylhexaboranes may, like alkenylpentaboranes, prove to be precursors to monocarbon carboranes, and we are presently exploring the possibility of their thermolytic conversion to such species.

Reactions involving 1,2-$C_2B_{10}H_{12}$, 1,7-$C_2B_{10}H_{12}$, and B_6H_{10} were all highly selective and would seem to follow the same general mechanism as the one outlined for pentaborane(9). It should also be noted that in each case substitution was observed at the most positively charged boron atom. Thus, for 1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$, PRDDO[27] calculations have indicated that the cage boron atoms of lowest electron density correspond to B(3) in 1,2-$C_2B_{10}H_{12}$ and B(2) in 1,7-$C_2B_{10}H_{12}$, in agreement with the observed substitution preferences. These results are also consistent with the work of Hoel and Hawthorne,[14] who showed that 1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$ oxidatively add at B(3) and B(2), respectively, to $[Ir(C_8H_{14})_2Cl]_2$ in the presence of 2 equiv of triphenylphosphine.

For hexaborane(10), the B(2) basal boron is again predicted[28] to be of lower electron density relative to both the apical boron and the other basal borons, and again substitution is observed exclusively at this position.

In conclusion, we feel that the $[Cp^*IrCl_2]_2$/Proton Sponge catalyst system not only is a substantial improvement for the synthesis of alkenylpentaboranes but also represents a major step toward the development of general syntheses for a variety of alkenylboranes and -carboranes. In addition, this work further demonstrates the importance of transition-metal reagents as synthetic tools in main-group chemistry. We are continuing to explore these and other types of catalysts for promoting reactions of inorganic compounds.

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Registry No. B_5H_9, 19624-22-7; $[Cp^*IrCl_2]_2$, 12354-84-6; 2-(*trans*-1-prp)B_5H_8, 78837-93-1; 2-(*trans*-1-but)B_5H_8, 87281-27-4; 2-(*cis*-2-but)B_5H_8, 73910-58-4; B_6H_{10}, 23777-80-2; 2(*cis*-1-prp)B_6H_9, 111583-13-2; 2-(*trans*-1-prp)B_6H_9, 111583-14-3; 1,2-$C_2B_{10}H_{12}$, 16872-09-6; 1,7-$C_2B_{10}H_{12}$, 16986-24-6; 3-(*trans*-1-prp)-1,2-$C_2B_{10}H_{11}$, 111583-15-4; 3-(*trans*-1-prp)-1,7-$C_2B_{10}H_{11}$, 111615-32-8; propyne, 74-99-7; 1-butyne, 107-00-6; 2-butyne, 503-17-3; 1,8-bis(dimethylamino)naphthalene, 20734-58-1.

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