$W_2(DMP)_6$ (60% yield).[11] We believe that this synthesis may be improved even further so that even larger quantities of $W_2(DMP)_6$ can be prepared in two easy steps from WCl_6.

Acknowledgment. This work has been supported by the National Science Foundation (Grant CHE84-02892) and the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC02-78ER04949-A003.

Registry No. $W_2(DMP)_6$, 102307-39-1; $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9; DMPH, 576-26-1; $CH_3C{\equiv}CCH_3$, 503-17-3; $W(C_3Me_3)(DMP)_3$, 102367-79-3; $W(C_3Et_3)(DMP)_3$, 102307-40-4; $CH_3CH_3\text{-}C{\equiv}\text{-}CH_2CH_3$, 928-49-4; *cis,mer*-$W(CMe)(DMP)_3(py)_2$, 102286-60-2; $W(C_3Me_3)Cl_3$, 102342-00-7; $W(C_3Et_3)Cl_3$, 102307-41-5; *mer*-$W(DMP)_3Cl_3$, 102307-42-6; WCl_6, 13283-01-7.

---

(11) Na powder (2.25 g) was added to a suspension of 20 g of $W(DMP)_3Cl_3$ in 200 mL of diethyl ether that had been cooled to −55 °C. Mercury (10 g) was added, and the mixture was stirred and allowed to warm to 25 °C. After 4 h at 25 °C the crude product was filtered off and recrystallized from THF; yield 10 g (60%).

Transition-Metal-Promoted Reactions of Boron Hydrides. 8.[1] Nickel-Promoted Alkyne Insertion Reactions: A New Synthesis of the Four-Carbon Carborane *nido*-4,5,7,8-$R_4C_4B_4H_4$

Mario G. L. Mirabelli and Larry G. Sneddon*

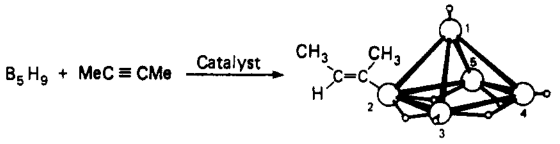
Department of Chemistry and
Laboratory for Research on the Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

Received April 1, 1986

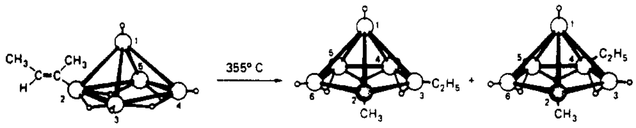
Summary: A new type of metal-promoted alkyne/polyhedral borane insertion reaction is reported. The reaction of the carborane *nido*-2,3-$Et_2C_2B_4H_6$ with 2-butyne in the presence of sodium hydride and nickel(II) chloride has been found to result in a two-carbon insertion into the cage system to produce the tetracarbon carborane *nido*-4,5,7,8-$Me_2Et_2C_4B_4H_4$.

We have previously demonstrated that transition-metal reagents can be used to catalyze a variety of reactions of polyhedral boron cage compounds, including acetylene-addition,[2-4] olefin-substitution,[5] dehydrodimerization,[6,7] dehydrocondensation,[1] and cage-growth reactions.[1] We report here the development of a new type of metal-promoted borane/alkyne reaction which leads to direct two-carbon insertion of the acetylenic unit into the polyhedral boron cage system.

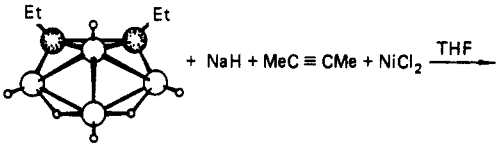
We have already reported[2-4] that various transition-metal reagents, such as $(R_2C_2)Co_2(CO)_6$ and $IrCl(CO)(PPh_3)_2$ catalyze the addition reactions of polyhedral boranes with acetylenes to give boron-substituted alkenylboranes and carboranes.



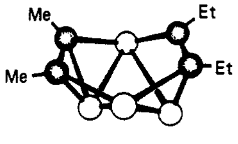
We have also demonstrated that these alkenylpentaboranes are precursors to monocarbon carboranes.



In contrast to the metal-catalyzed acetylene-addition reactions described above, we have now found that Ni(II) salts promote two-carbon acetylene insertions into 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-$Me_2Et_2C_4B_4H_4$,[8] as shown.



2,3-$Et_2C_2B_4H_6$



4,5,7,8-$Me_2Et_2C_4B_4H_4$

In a typical reaction, 0.174 g (1.34 mmol) of 2,3-$Et_2C_2B_4H_6$, 0.048 g (2.0 mmol) of sodium hydride, 0.174 g (1.34 mmol) of anhydrous nickel(II) chloride, and 13.4 mmol of 2-butyne were reacted in 5 mL of THF in vacuo. The reaction mixture was initially warmed to −20 °C whereupon 1 equiv of hydrogen gas was generated, indicating the formation of the carborane anion.[9]

$$2,3\text{-}Et_2C_2B_4H_6 + NaH \xrightarrow{-20\ °C} Na^+[2,3\text{-}Et_2C_2B_4H_5^-]$$

The solution also gradually turned dark green, suggesting the formation of a nickelacarborane complex. The reaction was then allowed to react at 0 °C for 1 h, during which time the solution darkened and an additional 0.30 mmol of H_2 was evolved. The solution was stirred for another 18 h at room temperature, resulting in metal reduction and the formation of a black, viscous solution. Vacuum-line fractionation of the contents of the reaction flask gave 76 mg (0.413 mmol, 31% yield) of pure *nido*-4,5,7,8-$Me_2Et_2C_4B_4H_4$ retained in a −23 °C trap.[10]

---

(1) For part 7, see: Corcoran, E. W., Jr.; Sneddon, L. G. *J. Am. Chem. Soc.* **1985**, *107*, 7446–7450.

(2) Wilczynski, R.; Sneddon, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 2857–2858.

(3) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1981**, *20*, 3955–3962.

(4) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 506–514.

(5) Davan, T.; Corcoran, E. W., Jr.; Sneddon, L. G. *Organometallics* **1983**, *2*, 1693–1694.

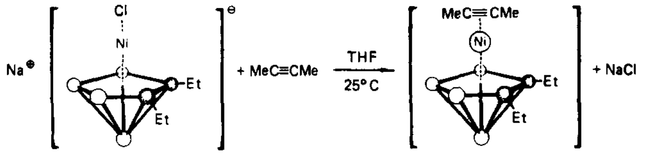
(6) Corcoran, E. W., Jr.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 7793–7800.

(7) Corcoran, E. W., Jr.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 182.

(8) The 4,5,7,8-$Me_2Et_2C_4B_4H_4$ carborane has been numbered according to conventional procedures to allow comparisons to previously isolated compounds; however, using the new nomenclature rules recently proposed for polyhedral boranes this compound would be 2,3-Me_2-4,5-Et_2-tetracarba-1-debor[C_{2v}-($1v^62v^42v^52v^5$)-Δ^{14}-*closo*]nonaborane(8). See: Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1983**, *22*, 2228–2235, 2236–2245.

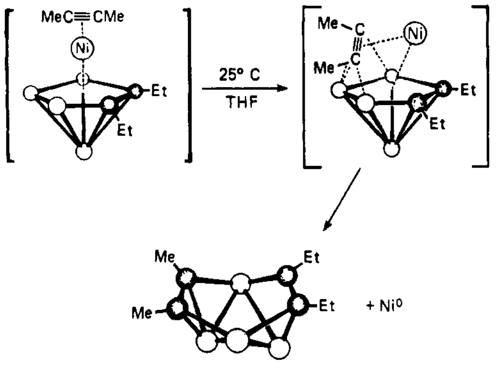
(9) Dunks, G. B.; Onak, T. *Inorg. Chem.* **1966**, *5*, 439–442.

While the mechanism of reaction has not yet been proven, the above observations suggest that the reaction may involve the formation of a nickelacarborane complex, such as shown below, which upon warming can intramolecularly eliminate NaCl and react with 2-butyne to generate an alkyne/metallacarborane intermediate.



$\mathrm{Na^{\oplus}[\eta^5\text{-}Et_2C_2B_4H_4\cdot Ni\cdot Cl]^{\ominus}}$ $\mathrm{Me_2C_2\cdot Ni\cdot Et_2C_2B_4H_4}$

Upon standing this alkyne/nickelacarborane complex could then undergo reductive cycloaddition to form the four-carbon carborane and nickel metal:



$\mathrm{4,5,7,8\text{-}Me_2Et_2C_4B_4H_4}$

Fehlner[11,12] first synthesized the carborane 4,5,7,8-$\mathrm{Me_4C_4B_4H_4}$ in 60% yield from the photolytic reaction of $\mathrm{B_4H_8Fe(CO)_3}$ and 2-butyne; however, this synthesis is limited by the difficult, low-yield (10–20%), synthesis of the ferraborane $\mathrm{B_4H_8Fe(CO)_3}$. The peralkylated derivative has also been prepared[13] by El-Essawi and Siebert in 30% yield by treating 2,3,5-thiadiborolene with 2 equiv of potassium metal.

The carborane synthesis described here has several significant advantages over those previously reported. The reaction involves a convenient "one-pot" procedure and employs the readily accessible[14] 2,3-$\mathrm{Et_2C_2B_4H_6}$ as a starting material. Furthermore, the product is easily isolated in high purity by simple vacuum-line fractionation.

The above results are important, not only because they provide a reasonable synthetic route to the *nido*-$\mathrm{R_4C_4B_4H_4}$ carborane system but also because they 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. We are continuing to study both the scope of these reactions and the chemistry of the unique hybrid "organic–inorganic" cluster *nido*-$\mathrm{R_4C_4B_4H_4}$.

Acknowledgment. We thank the National Science Foundation and the Army Research Office for the support of this work.

Registry No. *nido*-2,3-$\mathrm{Et_2C_2B_4H_6}$, 80583-48-8; MeC≡CMe, 503-17-3; $\mathrm{NiCl_2}$, 7718-54-9; *nido*-4,5,7,8-$\mathrm{Me_2Et_2C_4B_4H_4}$, 102493-34-5.

---

(10) ^{11}B NMR (115.5 MHz, ppm, $\mathrm{CH_2Cl_2}$, $\mathrm{C_6D_6}$): −11.1 (d, 2), −12.5 (d, 1), −12.9 (d, 1). ^{1}H NMR (200 MHz, δ, $\mathrm{C_6D_6}$): 1.02 (t, 6), 1.88 (s, 6), 2.30 (m, 4). Mass spectrum: cutoff at *m/e* 184, corresponding to $\mathrm{C_{10}H_{20}B_4}$.

(11) Fehlner, T. P. *J. Am. Chem. Soc.* **1977**, *99*, 8355–8356.

(12) Fehlner, T. P. *J. Am. Chem. Soc.* **1980**, *102*, 3424–3430.

(13) Siebert, W.; El-Essawi, M. E. M. *Chem. Ber.* **1979**, *112*, 1480–1481.

(14) Maynard, R. B.; Borodinsky, L.; Grimes, R. N. *Inorg. Synth.* **1983**, *22*, 211–214.

Insertion of 3,3-Dimethylcyclopropenes into the Pd–C Bond of Cyclopalladated Dimethylbenzylamine,[1] Leading to C–C Bond Cleavage or Cyclopropyl Ring Retention. X-ray Crystal and Molecular Structure of $\mathrm{[Pd\{C(CO_2Me)CMe_2CHC_6H_4CH_2NMe_2\}pyCl]}$

Fida Maassarani,[2a] Michel Pfeffer,*[2a] Guy Le Borgne,[2b] and Daniel Grandjean[2b]

Laboratoire de Chimie de Coordination, UA 416 du CNRS
Université Louis Pasteur
F-67070 Strasbourg Cédex, France
and Laboratoire de Cristallochimie, LA 254 du CNRS
Université de Rennes I, F-35042 Rennes Cédex, France

Received October 30, 1985

Summary: When 3,3-dimethylcyclopropenes $\mathrm{CR^1{=}CR^2CMe_2}$ (where R^1, R^2 = H, $\mathrm{CO_2Me}$) are allowed to react with the complex $\mathrm{[\{Pd(C_6H_4CH_2NMe_2)(\mu\text{-}Cl)\}_2]}$ (**1**), insertion into the Pd–C bond of the cyclopalladated dimethylbenzylamine (dmba) takes place to give two types of compound. Opening of the strained ring of the olefin affords monomeric $\mathrm{[Pd\{(\eta^3\text{-}CMe_2\cdots CR^2\cdots CR^1)C_6H_4\text{-}CH_2NMe_2\}Cl]}$ (**2**), whereas simple insertion without C–C bond cleavage leads to dimeric $\mathrm{[\{Pd(CR^1CMe_2CR^2\text{-}C_6H_4CH_2NMe_2)(\mu\text{-}Cl)\}_2]}$ (**3**), in which the cyclopropyl ring is bonded to both the dmba moiety and the Pd atom. With 3,3-dimethylcyclopropene itself (R^1 = R^2 = H) only compound **2a** is obtained, whereas 1,2-dicarbomethoxy-3,3-dimethylcyclopropene (R^1 = R^2 = $\mathrm{CO_2Me}$) affords only compound **3a**. However, the cyclopropene where R^1 = H and R^2 = $\mathrm{CO_2Me}$ gives a mixture of both **2b** and **3b** in a 1:1 ratio. Compounds **3** react with pyridine in a bridge-splitting reaction to give the monomers **4a** and **4b**, the latter being fully characterized by an X-ray diffraction study. Crystals of $\mathrm{[Pd\{C(CO_2Me)\text{-}CMe_2CHC_6H_4CH_2NMe_2\}pyCl]}$ (**4b**) belong to the space group $P2_12_12_1$ with a = 12.408 (5) Å, b = 16.315 (4) Å, c = 10.423 (5) Å, v = 2109.9 Å^3, and Z = 4. The structure has been refined to R = 0.028 and R_w = 0.038. The pyridine is located trans to the nitrogen atom of the dmba. The cyclopropyl unit is σ-bonded to Pd via the carbon atom which bears the $\mathrm{CO_2Me}$ group whereas its CH group is bonded to the previously metalated carbon atom of the dmba. The geometry of the new seven-membered organometallic ring compares favorably with that of related compounds obtained by insertion of alkynes into the Pd–C bond of cyclopalladated dmba.

It has been shown that cyclopropenes display versatile behavior toward transition-metal complexes. Indeed, it

---

(1) Reactivity of cyclopalladated compounds. Part 12. Part 11: Arlen, C.; Pfeffer, M.; Bars, O.; Le Borgne, G. *J. Chem. Soc., Dalton Trans.* 1986, 359.

(2) (a) Laboratoire de Chimie de Coordination. (b) Laboratoire de Cristallochimie.

0276-7333/86/2305-1511$01.50/0