J. Am. Chem. Soc. 1989, 111, 592-597

Transition-Metal-Promoted Reactions of Boron Hydrides. 11.[1] Catalytic and Stoichiometric Alkyne Insertion Reactions. Synthesis and Structural Characterization of a (Metallovinyl)carborane Containing a Boron–Boron Bridging Carbon Atom: *nido*-4,5-μ-[CpFe(CO)(PPh_3)(η^1:μ-*trans*-MeC=CMe)]-2,3-$Et_2C_2B_4H_5$

Mario G. L. Mirabelli, Patrick J. Carroll, and Larry G. Sneddon*

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

Received June 27, 1988

Abstract: The use of transition-metal complexes to promote or catalyze the two-carbon insertion of an acetylene into the small carborane *nido*-2,3-$Et_2C_2B_4H_6$ is reported. It was found that the reaction of $Na^+[2,3\text{-}Et_2C_2B_4H_5]^-$ with [CpFe(CO)(PPh_3)(η^2-$(CH_3)_2C_2$)]$^+BF_4^-$ in THF results in the formation of the first (metallovinyl)carborane complex, *nido*-4,5-μ-[CpFe(CO)(PPh_3)(η^1:μ-*trans*-MeC=CMe)]-2,3-$Et_2C_2B_4H_5$ (I). The structure of I was confirmed by means of a single-crystal X-ray study, which showed that the carborane is bound to the olefin via a B–C–B three-center, two-electron bond with the cage situated trans with respect to the iron atom. I is thus the first structurally characterized example of a polyhedral boron cage compound containing a boron–boron bridging carbon atom. Crystal data for I; space group $Pca2_1$; $Z = 4$; $a = 16.697$ (3), $b = 10.887$ (3), $c = 18.015$ (4) Å; $V = 3274.8$ Å^3. The structure was refined by full-matrix least-squares to a final R of 0.047 and R_w of 0.052 for the 1767 unique reflections that had $F_o^2 > 3\sigma(F_o^2)$. Subsequent thermolysis of I at 110 °C produced the two-carbon insertion product *nido*-4,5-Me_2-7,8-$Et_2C_4B_4H_4$ (II) in 80% yield presumably via a β-hydride-abstraction alkene-elimination mechanism. Catalytic dehydro alkyne insertion reactions resulting in the formation of *nido*-4,5-Me_2-7,8-$Et_2C_4B_4H_4$ were observed when either trinuclear or mononuclear ruthenium complexes, including $Ru_3(CO)_{12}$, $Ru_3(CO)_9(PPh_3)_3$, and $Ru(CO)_3(PPh_3)_2$, were used to catalyze the reactions of 2-butyne with *nido*-2,3-$Et_2C_2B_4H_6$. The hydroboration product 5-[(H)MeC=CMe)]-2,3-$Et_2C_2B_4H_5$ was also observed in reactions promoted by $Ru_3(CO)_{12}$; however, the phosphine-substituted complexes exhibited >98% selectivity toward the insertion product.

As part of our interest[2] in the development of new high-yield synthetic routes to higher boranes and carboranes, we have investigated the reactions of alkynes with boranes in the presence of a variety of potential transition-metal catalysts. We have previously reported that complexes such as $IrCl(CO)(PPh_3)_2$,[3,4] $(R_2C_2)Co_2(CO)_6$,[5] and $(Cp^*IrCl_2)_2$[6] catalyze BH additions of polyhedral boranes to acetylenes to give *B*-alkenyl products (eq 1 and 2),

$$2,4\text{-}C_2B_5H_7 + RC{\equiv}CH \xrightarrow{Co_2(CO)_8} H_2C_2B_5H_{5-x}(RHC{=}CH)_x \tag{1}$$

$$B_5H_9 + RC{\equiv}CH \xrightarrow[\text{Proton Sponge}]{[Cp^*IrCl_2]_2,\ 70\ °C} 2\text{-}(RHC{=}CH)B_5H_8 \tag{2}$$

We have also shown[3,4] that compounds such as alkenylpentaboranes can be converted to monocarbon carboranes in high yields (eq 3),

$$2\text{-}(RHC{=}CH)B_5H_8 \xrightarrow{\Delta} nido\text{-}3\text{-}R'CB_5H_8 + nido\text{-}4\text{-}R'CB_5H_8 \tag{3}$$

The fact that reactions such as eq 3 do not yield two-carbon-insertion products suggests that polyhedral alkenylboranes are not precursors to two-carbon carboranes and that the reaction sequence leading to the formation of dicarbon carboranes does not involve, as an initial step, the hydroboration of the acetylene. This conclusion has prompted our investigations of alternative types of metal-promoted reactions involving alkynes and polyhedral boranes or carboranes with the goal of developing high-yield selective routes for two-carbon insertions.

The work presented in this paper describes two new methods, one stoichiometric and the other catalytic, whereby transition-metal complexes can be employed to promote two-carbon insertions into the small *nido*-carborane 2,3-$Et_2C_2B_4H_6$ to form the tetracarbon carborane *nido*-4,5-Me_2-7,8-$Et_2C_4B_4H_4$.

Experimental Section

Materials. Methylene chloride and toluene were purchased from EM Science and distilled from P_2O_5 and sodium metal, respectively. The 2-butyne was obtained from Farchan Laboratories and purified by vacuum-line fractionation through a −78 °C trap. The carborane, *nido*-2,3-$Et_2C_2B_4H_6$,[7] and the complexes $Ru_3(CO)_9(PPh_3)_3$,[8] $Ru(CO)_3(PPh_3)_2$,[9] and [CpFe(CO)(PPh_3)(η^2-$(CH_3)_2C_2$)]$^+BF_4^-$ [10] were prepared by standard literature methods. The $Ru_3(CO)_{12}$ was used as received from Aldrich Chemicals.

Gas–liquid chromatography, which was used to confirm the purity of the products and monitor product formation, was conducted on a Varian Aerograph Series 1400 gas chromatograph equipped with a 6 ft × 0.25 in. 10% SE-30 on Chromosorb-W (100/120-mesh) column.

Physical Measurements. ^1H NMR spectra at 200 MHz and ^{11}B NMR 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). Fast atom bombardment mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1310 infrared spectrophotometer.

Reactions with [CpFe(CO)(PPh_3)(η^2-$(CH_3)_2C_2$)]$^+BF_4^-$. A two-neck 100-mL round bottomed flask, charged with 68 mg (1.7 mmol, 60% dispersion in mineral oil) of NaH and fitted with a side-arm tube containing 855 mg (1.58 mmol) of [CpFe(CO)(PPh_3)(η^2-$(CH_3)_2C_2$)]$^+BF_4^-$,

---

(1) Part 10: Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1987**, *109*, 5867–5868.

(2) Sneddon, L. G. *Pure Appl. Chem.* **1987**, *59*, 837–846.

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

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

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

(6) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 449–453.

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

(8) Piacenti, F.; Bianchi, M.; Benedetti, E.; Braca, G. *Inorg. Chem.* **1968**, *9*, 1815–1817.

(9) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 50–51.

(10) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73–84.

was attached to a vacuum line and evacuated. Tetrahydrofuran (5 mL) and 203 mg (1.55 mmol) of 2,3-$Et_2C_2B_4H_6$ were condensed into the flask at −196 °C. The solution was allowed to warm to room temperature whereupon vigorous bubbling occurred, indicating evolution of H_2 gas and formation of the $Na^+[Et_2C_2B_4H_5]^-$ anion. The flask was degassed at −196 °C and then allowed to stir at room temperature for an additional 1 h. The solution was then cooled to −78 °C, and the contents of the side-arm tube were added. The reaction was maintained at −78 °C for 0.5 h and then allowed to warm slowly to room temperature. Next, the solvent was evaporated to yield a bright red, oily solid. This material was redissolved in CH_2Cl_2 and filtered through a short mat of neutral alumina. Recrystallization of the resulting oil from a 50/50 benzene/octane solution at −10 °C afforded a dark red solid identified as *nido*-4,5-μ-[CpFe(CO)(PPh_3)(η^1:μ-*trans*-MeC═CMe)]-2,3-$Et_2C_2B_4H_5$ (I; 464 mg, 50.3% yield). ^{11}B NMR (64.2 MHz, ppm, C_6D_6): −1.1 (d, 1, J = ~150 Hz, basal boron), −6.6 (d, 1, J = ~150 Hz, basal boron), −11.3 (d, 1, J = ~150 Hz, basal boron), −42.6 (d, 1, J = ~130 Hz, B1). ^1H NMR (200 MHz, ppm, C_6D_6): 7.15 (m, 15, PPh_3), 4.06 (s, 5, η-C_5H_5), 2.68 (s, 3, vinyl CH_3), 2.61 (m, 4, J = 8.0 Hz, cage CH_2), 1.88 (s, 3, vinyl CH_3), 1.43 (t, 6, J = 6.0 Hz, cage CH_3). IR (NaCl plates): 3050 (m), 2950 (s), 2920 (m), 2860 (m), 2550 (s), 2480 (m), 1925 (vs), 1475 (m), 1450 (m), 1430 (s), 1390 (m), 1305 (w), 1260 (w), 1180 (m), 1160 (w), 1115 (s), 1090 (s), 1050 (m), 1020 (m), 1010 (m), 970 (w), 960 (w), 900 (s), 870 (m), 840 (m), 820 (m), 790 (w), 740 (s), 720 (s), 690 (vs). Exact mass (FAB). Calcd for $^{12}C_{34}{}^1H_{41}{}^{11}B_4{}^{56}Fe^{31}P^{16}O$ 596.2616. Found: 596.2690.

Thermolysis of I. A 30-mL reaction flask was charged with 292 mg (0.49 mmol) of I and evacuated. Toluene (5 mL) was condensed into the flask, and the solution was heated in an oil bath at 110 °C for 18 h. The flask was next attached to a vacuum line and degassed at −196 °C to remove any noncondensables. The volatile material was fractionated through a −23 °C trap where pure (96% by GLC) *nido*-4,5-Me_2-7,8-$Et_2C_4B_4H_4$ (II) was retained (72 mg, 80.1% yield). The ^{11}B and ^1H NMR data match previously reported literature values.[11]

An ^1H NMR of the soluble nonvolatile yellow residue remaining in the reaction flask showed a metal–hydride resonance (−11.8 ppm, J_{PH} = ~70 Hz) characteristic[12] of CpFe(CO)(PPh_3)(H).

Reactions with Ru⁰ Reagents. $Ru_3(CO)_{12}$. In a typical procedure, a 88-mL Fischer–Porter pressure vessel was charged with 128 mg (0.2 mmol) of $Ru_3(CO)_{12}$, 263 mg (2.0 mmol) of 2,3-$Et_2C_2B_4H_6$, 20 mmol of 2-butyne, and 5 mL of toluene. The flask was placed in an oil bath at 140 °C and stirred until all of the metal carbonyl dissolved (~10 min). The flask was then attached to a vacuum line, frozen at −196 °C, and degassed to remove evolved CO. The flask was placed back in the oil bath and heated at 140 °C for 24 h. The solution appeared homogeneous throughout the entire reaction period and appeared to undergo no change during this time. Vacuum fractionation of the volatile materials through a −23 °C trap stopped 40 mg of a low-volatile, oily material. The ^{11}B NMR spectrum showed this material to consist of ~70% *nido*-4,5-Me_2-7,8-$Et_2C_4B_4H_4$ (~0.15 mmol) and ~30% 5-[(H)MeC═CMe]-2,3-$Et_2C_2B_4H_5$ (~0.06 mmol). Fractionation through a −95 °C trap stopped (~0.1 mmol) of 2-butene which was confirmed by ^1H NMR. When the unreacted starting material was placed back over the catalyst at 140 °C for an additional 24 h of reaction, 14 mg of an oily material was stopped in the −23 °C trap. A ^{11}B NMR spectrum showed this material to be ~50% 4,5-Me_2-7,8-$Et_2C_4B_4H_4$ (~0.04 mmol) and ~50% 5-[(H)MeC═CMe]-2,3-$Et_2C_2B_4H_5$ (~0.04 mmol). Further reaction of the starting material with the original catalyst resulted only in the formation of trace amounts of 5-[(H)MeC═CMe]-2,3-$Et_2C_2B_4H_5$. The absolute yield of the reaction could not be determined because unreacted 2,3-$Et_2C_2B_4H_6$ could not be quantitatively separated from the toluene solvent. Analysis by GLC of reactions allowed to proceed for periods of 1–5 days without product separation showed no decrease in rate (~1 catalyst turnover/day) and the constant production of ~70/30 mixtures of II and III.

$Ru_3(CO)_9(PPh_3)_3$. In a similar procedure, $Ru_3(CO)_9(PPh_3)_3$, which was separately prepared from 128 mg (0.20 mmol) of $Ru_3(CO)_{12}$ and 157 mg (0.60 mmol) of PPh_3, was placed in a Fischer–Porter pressure flask with 271 mg (2.1 mmol) of 2,3-$Et_2C_2B_4H_6$, 20 mmol of 2-butyne, and 5 mL of toluene. After 24 h at 140 °C, vacuum fractionation through a −23, −95, −196 °C trap series produced 36 mg (0.20 mmol) of pure (98% by GLC) 4,5-Me_2-7,8-$Et_2C_4B_4H_4$ stopping in the −23 °C trap and 1 equiv of butene (~0.2 mmol) trapped at −196 °C. This corresponds to a stoichiometric amount of product in the 24-h reaction period. Reactions for longer periods of time (3–5 days) without product separation were found to continue at a constant rate of ~1 catalyst turnover/day.

Table I. Data Collection and Structure Refinement Information

space gp	$Pca2_1$
a, Å	16.697 (3)
b, Å	10.887 (3)
c, Å	18.015 (4)
V, Å^3	3274.8
Z	4
ρ(calcd), g cm^{-3}	1.208
cryst dimens, mm	0.35 × 0.25 × 0.12
mol formula	$C_{34}H_{41}B_4FePO$
mol wt	595.77
λ(Mo Kα), Å	0.71073
scanning range	$4° \le 2\theta \le 55°$
scan mode	ω–2θ
$\pm h,\pm k,\pm l$, collcd	+21,+14,+23
no. of measd I's	4214
no. of $F_o^2 > 3\sigma(F_o^2)$	1767
no. of variables	369
abs coeff (μ), cm^{-1}	5.31
transmssn coeff, %	90.9
max, min, %	95.5, 84.5
R	0.047
R_w	0.052

$Ru(CO)_3(PPh_3)_2$. A 88-mL reaction flask was charged with 177 mg (0.25 mmol) of $Ru(CO)_3(PPh_3)_2$, 656 mg (5.0 mmol) of 2,3-$Et_2C_2B_4H_6$, 50 mmol of 2-butyne, and 10 mL of toluene. The flask was placed in an oil bath at 140 °C until all of the metal complex had dissolved (~10 min) to form a homogeneous brownish red solution. The flask was degassed at −196 °C to remove evolved CO and then placed back in the oil bath and stirred for 5 days with daily removal of noncondensable gas. Vacuum fractionation through a −23 °C trap stopped 183 mg (1.0 mmol) of pure (98% by GLC) 4,5-Me_2-7,8-$Et_2C_4B_4H_4$. Fractionation of the remaining volatiles stopped an equivalent amount (~1.0 mmol) of 2-butene, slightly contaminated with 2-butyne (by ^1H NMR). This corresponds to 4 catalyst turnovers in 5 days.

Reaction of 2,3-$Et_2C_2B_4H_6$ with PPh_3 and 2-Butyne. A control reaction was performed with 131 mg (1.0 mmol) of 2,3-$Et_2C_2B_4H_6$, 157 mg (0.60 mmol) of PPh_3, 10 mmol of 2-butyne, and 5 mL of toluene. After this solution was stirred at 140 °C for 3 days, analysis by ^{11}B NMR showed only the presence of starting carborane and no evidence for the formation of II.

Crystallographic Data for *nido*-4,5-μ-[CpFe(CO)(PPh_3)(η^1:μ-*trans*-MeC═CMe)]-2,3-$Et_2C_2B_4H_5$ (I). A single crystal of I was grown by recrystallization from 1/1 benzene/octane at −10 °C. A suitably sized crystal was mounted and transferred to the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Mo Kα radiation from a highly oriented graphite-crystal monochromator (Table I). The intensities of 3 standard reflections measured at intervals of 100 reflections showed no systematic change during data collection. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program BEGIN.

Solution and Refinement of the Structure. All calculations were performed on a VAX 11/750 computer using the Enraf-Nonius structure package.[13] The full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $4F_o^2/(\sigma(F_o^2))^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The neutral-atom scattering factors and complex anomalous dispersion corrections were taken from ref 14 and 15. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. A three-dimensional Patterson synthesis gave the coordinates of the iron atom. Subsequent Fourier maps led to the location of the remaining heavy atoms. Anisotropic refinements followed by difference Fourier syntheses resulted in the location of all cage and ring hydrogens and at least one hydrogen on each of the methylene and methyl carbons. Hydrogens not found were added in calculated positions with the program HYDRO. No hydrogen positions

---

(11) Mirabelli, M. G. L.; Sneddon, L. G. *Organometallics* **1986**, *5*, 1510–1511.

(12) Davies, S. G.; Hibberd, J.; Simpson, S. J.; Thomas, S. E.; Watts, O. *J. Chem. Soc., Dalton Trans.* **1984**, 701–709.

(13) B. A. Frenz and Associates, Inc., College Station, TX 77840, and Enraf-Nonius, Delft, Holland.

(14) (a) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

(15) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B_{eq},[a] Å^2
Fe	0.81770 (6)	0.9538 (1)	0.5000	3.70 (2)
P	0.8008 (1)	0.9745 (2)	0.3797 (1)	3.38 (4)
B1	0.9270 (8)	0.450 (1)	0.5457 (8)	6.3 (3)
C2	1.0189 (6)	0.4791 (9)	0.5841 (6)	5.5 (3)
C2a	1.0857 (8)	0.391 (1)	0.6069 (8)	9.8 (4)
C2b	1.1317 (9)	0.441 (2)	0.666 (1)	16.4 (6)
C3	1.0107 (6)	0.5165 (8)	0.5092 (6)	5.6 (2)
C3a	1.0632 (8)	0.474 (1)	0.4471 (9)	10.6 (4)
C3b	1.126 (1)	0.548 (2)	0.430 (1)	18.3 (6)
B4	0.9319 (6)	0.586 (1)	0.4877 (7)	5.3 (3)
C5	0.9044 (5)	0.7132 (7)	0.5329 (5)	3.7 (2)
C5a	0.9724 (6)	0.779 (1)	0.5693 (6)	6.3 (3)
B5	0.8747 (7)	0.575 (1)	0.5748 (7)	5.3 (3)
B6	0.9489 (7)	0.497 (1)	0,6344 (8)	6.0 (3)
C4	0.8404 (4)	0.7727 (7)	0.5001 (6)	4.0 (2)
C4a	0.7763 (5)	0.6988 (8)	0.4641 (5)	5.1 (2)
C1	0.9155 (5)	1.0079 (8)	0.4941 (6)	4.9 (2)
O	0.9779 (3)	1.0540 (6)	0.4901 (4)	6.2 (2)
C11	0.7870 (7)	1.1039 (9)	0.5716 (6)	6.2 (3)
C12	0.7213 (6)	1.0768 (9)	0.5268 (5)	5.9 (3)
C13	0.6983 (5)	0.953 (1)	0.5426 (5)	5.8 (3)
C14	0.7488 (6)	0.9061 (9)	0.5953 (5)	5.1 (2)
C15	0.8032 (7)	1.001 (1)	0.6147 (6)	7.9 (3)
C21	0.7847 (5)	1.1316 (8)	0.3493 (5)	4.2 (2)
C22	0.8304 (6)	1.2276 (9)	0.3801 (6)	6.1 (3)
C23	0.8250 (7)	1.3432 (9)	0.3535 (8)	8.0 (3)
C24	0.7724 (7)	1.370 (1)	0.2991 (7)	7.7 (3)
C25	0.7252 (6)	1.2848 (9)	0.2674 (6)	6.2 (3)
C26	0.7324 (6)	1.1628 (9)	0.2935 (6)	5.6 (2)
C31	0.7167 (4)	0.8941 (7)	0.3384 (5)	3.2 (2)
C32	0.6375 (5)	0.9241 (8)	0.3572 (5)	4.1 (2)
C33	0.5737 (5)	0.8626 (9)	0.3308 (6)	4.7 (2)
C34	0.5852 (5)	0.7615 (9)	0.2828 (6)	5.7 (3)
C35	0.6633 (6)	0.7286 (9)	0.2633 (5)	5.2 (2)
C36	0.7272 (5)	0.7965 (8)	0.2897 (5)	4.3 (2)
C41	0.8846 (5)	0.9292 (7)	0.3199 (5)	3.6 (2)
C42	0.8921 (5)	0.9773 (9)	0.2485 (5)	5.0 (2)
C43	0.9529 (5)	0.9342 (9)	0.2025 (6)	5.3 (2)
C44	1.0082 (5)	0.857 (1)	0.2261 (6)	5.7 (3)
C45	1.0025 (6)	0.807 (1)	0.2971 (6)	6.2 (3)
C46	0.9401 (5)	0.8447 (8)	0.3437 (6)	4.4 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

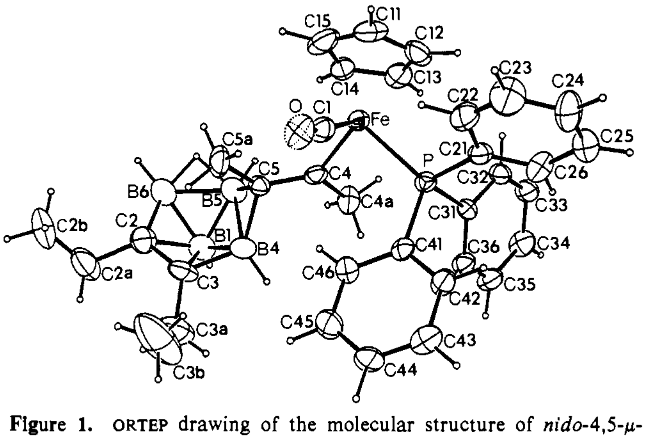
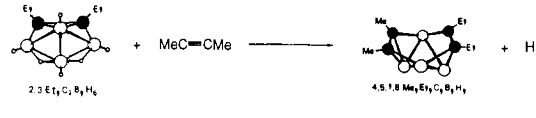


Figure 1. ORTEP drawing of the molecular structure of *nido*-4,5-μ-[CpFe(CO)(PPh$_3$)(η^1:μ-*trans*-MeC=CMe)]-2,3-Et$_2$C$_2$B$_4$H$_6$ (I).

were refined. The largest peaks in the final difference Fourier were 0.29 and −0.24 e/Å^3.

Results and Discussion

The overall reaction for an alkyne insertion into the neutral *nido*-2,3-Et$_2$C$_2$B$_4$H$_6$ carborane cage system would be

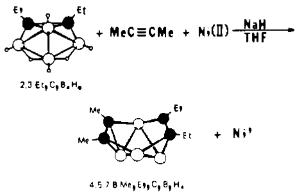


(4)

Table III. Selected Bond Distances and Angles

	Bond Distances (Å)		
Fe–P	2.198 (2)	B4–C3	1.57 (1)
Fe–C4	2.008 (8)	B4–B1	1.82 (2)
Fe–C1	1.739 (8)	B5–B6	1.85 (2)
Fe–C11	2.14 (1)	B5–B1	1.71 (2)
Fe–C12	2.148 (9)	B6–C2	1.49 (2)
Fe–C13	2.136 (9)	B6–B1	1.72 (2)
Fe–C14	2.132 (9)	C2–C2a	1.53 (2)
Fe–C15	2.14 (1)	C2–C3	1.42 (2)
C1–O	1.16 (1)	C2–B1	1.71 (2)
C4–C4a	1.49 (1)	C3–C3a	1.49 (2)
C4–C5	1.38 (1)	C3–B1	1.71 (2)
C5–C5a	1.50 (1)	B4–B5	1.84 (2)
C5–B5	1.75 (1)		
C5–B4	1.67 (1)		
	Bond Angles (deg)		
P–Fe–C4	97.2 (3)	C5–C4–C4a	119.3 (7)
P–Fe–C1	91.5 (4)	C5–B4–B5	59.7 (6)
C4–Fe–C1	98.9 (3)	C5–B5–B4	55.3 (6)
Fe–C1–O	174.1 (7)	B5–C5–B4	65.0 (6)
Fe–P–C21	114.4 (3)	B5–B4–C3	101.2 (8)
Fe–P–C31	117.0 (3)	B4–C3–C2	117.1 (9)
Fe–P–C41	117.0 (3)	C3–C2–B6	117.7 (9)
Fe–C4–C4a	113.3 (6)	C2–B6–B5	103.5 (9)
Fe–C4–C5	127.3 (6)	B6–B5–B4	100.2 (8)
C4–C5–C5a	123.3 (8)		

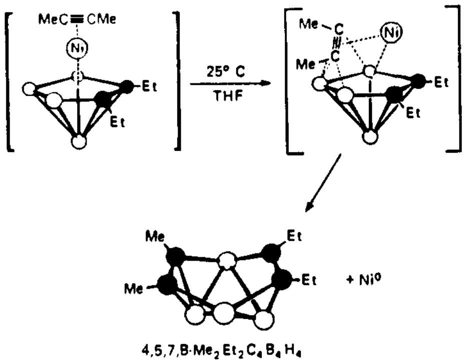
Thus, the transformation is formally a dehydro alkyne insertion, There are various pathways by which such a reaction could take place and as a result, it is possible to envision several different ways that a transition-metal reagent could promote this insertion,[16] For example, we demonstrated in an earlier paper[11] that anhydrous NiCl$_2$ could promote the two-carbon insertion of 2-butyne into *nido*-2,3-Et$_2$C$_2$B$_4$H$_6$, according eq 5.



II

(5)

It was proposed that the reaction proceeded through several steps resulting in the formation of an intermediate alkyne–nickelacarborane complex, such as shown in eq 6, which upon warming to room temperature decomposed to give nickel metal and the four-carbon carborane.



(6)

The reaction could be described as a type of cycloaddition reaction in which the alkyne adds to the open face of the [2,3-Et$_2$C$_2$B$_4$H$_4$] fragment. Therefore, the proposed key step in this reaction is the formation of a complex in which both the alkyne and carborane are bound to the metal.

---

[16] In this regard, Fehlner reported the first synthesis of (CH$_3$)$_4$C$_4$B$_4$H$_4$ from photolysis of 2-butyne with the ferraborane B$_4$H$_8$Fe(CO)$_3$, see; (a) Fehlner, T. P. *J. Am. Chem. Soc.* **1977**, *99*, 8355–8356. (b) Fehlner, T. P. *J. Am. Chem. Soc.* **1980**, *102*, 3424–3430.

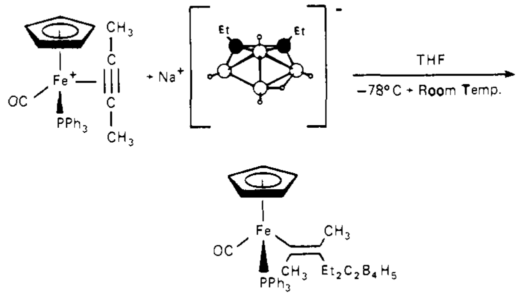
While such a pathway may be reasonable for reaction 5, it is not the only way in which a metal could promote this type of transformation. For example, it could be that it is not necessary for both the alkyne and carborane to be bound to the metal center prior to insertion. Instead, it is possible that the alkyne binds first to the metal and that this bonding interaction activates the alkyne toward attack by the carborane (or carborane anion) with the metal then facilitating the removal of remaining bridging hydrogens. This type of activation has many parallels in organometallic chemistry.

For example, Reger[10,17-25] and co-workers have studied the addition of nucleophiles to cationic complexes such as $[CpFe(CO)(PPh_3)(\eta^2\text{-}(CH_3)_2C_2)]^+BF_4^-$ and shown that the η^2-alkyne ligands in these complexes are activated for attack by a variety of anionic nucleophiles,[19] yielding the corresponding metallovinyl complexes (eq 7 and 8).

$$[CpFe(CO)(PPh_3)(\eta^2\text{-}(CH_3)_2C_2)]^+BF_4^- + NaCH(CO_2R)_2 \rightarrow CpFe(CO)(PPh_3)[\eta^1\text{-}CH_3C{=}CCH_3(CH(CO_2R)_2)] + NaBF_4 \quad (7)$$

$$[CpFe(CO)(PPh_3)(\eta^2\text{-}(CH_3)_2C_2)]^+BF_4^- + KCN \rightarrow CpFe(CO)(PPh_3)[\eta^1\text{-}CH_3C{=}CCH_3(CN)] + KBF_4 \quad (8)$$

The corresponding (metallovinyl)carborane complex I was prepared by adding the η^2-alkyne complex $[CpFe(CO)(PPh_3)(\eta^2\text{-}(CH_3)_2C_2)]^+BF_4^-$ to a cold solution (−78 °C) of the carborane anion $Na^+[Et_2C_2B_4H_5]^-$ in THF.



(9)

I

After workup and recrystallization, I was isolated as a mildly air-sensitive, red solid in ~50% yield. The room-temperature 64.2-MHz ^{11}B NMR spectrum of I is indicative of a static, bridge-substituted carborane cage showing four broad doublets of equal intensity. Likewise, the IR spectrum exhibits a split B–H stretching band (2550 and 2480 cm^{-1}), as is generally observed in heteroatom-bridged 2,3-$R_2C_2B_4H_6$ derivatives.[26] The 200-MHz ^1H NMR shows the appropriate resonances for the η^5-C_5H_5, PPh_3, olefinic methyl groups, and cage protons.

The structure of I was confirmed by a single-crystal X-ray study, as shown in the ORTEP diagram in Figure 1. The complex is composed of a $CpFe(CO)(PPh_3)(\eta^1\text{-}MeC{=}CMe)$– metallovinyl group, which is trans substituted at the β-carbon of the olefin by the 2,3-$Et_2C_2B_4H_5$– carborane cage. The environment around the iron supports octahedral coordination, with the C4–Fe–P, C1–Fe–C4, and C1–Fe–P bond angles varying between 90 and 99°. The C4–C5 bond length of 1.38 (1) Å indicates the presence of a double bond but is longer than the olefinic distances observed in other metallovinyl complexes, such as $CpFe(CO)(PPh_3)(\eta^1\text{-}(CO_2Et)C{=}CMe_2)$,[20] 1.352 (4) Å, and $CpFe(CO)[P(OPh)_3][\eta^1\text{-}(Z)\text{-}(Me)C{=}C(Ph)Me]$,[22] 1.34 (1) Å. However, the planarity of the Fe–C4–C4a–C5–C5a unit and the bond angles observed around C4 (Fe–C4–C4a, 113.3°; Fe–C4–C5, 127.3°; C4a–C4–C5, 119.3°) and C5 (C5a–C5–C4, 123.3°; C5a–C5–B_m, 120.0°; C4–C5–B_m, 116.7°; B_m = midpoint of B4–B5 distance) strongly support formal sp^2 hybridization. The remaining distances and angles in the $CpFe(CO)(PPh_3)$ fragment are normal and in the ranges observed for the two metallovinyl compounds cited above.

The most unusual feature of the structure of I regards the mode of attachment of the carborane to the olefin. The olefin plane is perpendicular [90.9 (3)°] to the plane of the carborane open face (C2, C3, B4, B5, B6), and, in agreement with the spectral data, C5 is found to occupy a bridging site between B4 and B5 on the cage. Although there are numerous cage compounds containing boron–boron bonds bridged by a wide variety of heteroatoms, I is, in fact, the first such compound containing a bridging carbon atom to be structurally characterized. The bonding interaction between the carborane cage and C5 would appear to involve a three-center, two-electron bond to which C5 contributes one sp^2 orbital. This is also, to our knowledge, the first time that this type of bonding has been found in a bridging unit on a polyhedral borane.

The distances and angles observed in the carborane cage are consistent with those observed in other bridge-substituted 2,3-$R_2C_2B_4H_5$– derivatives, such as [*nido*-(4,5-μ)-{*trans*-$(Et_3P)_2Pt(H)$}-(5,6-μ)-H-2,3-$C_2B_4H_6$][27] and 6:4′,5′-[1-(η-C_5H_5)Co-2,3-$Me_2C_2B_4H_3$][2′,3′-$Me_2C_2B_4H_5$].[28] In I, C5 is asymmetrically bound, being closer to B4, 1.67 (1) Å, than to B5, 1.75 (1) Å. The B4–B5 distance 1.84 (2) Å is identical with that found for the hydrogen-bridged borons B5–B6, 1.85 (2) Å. The C5–B4–B5 plane has a dihedral angle of 63.4° with respect to the carborane face, which is similar to the 66.8° angle observed between the B4–B6′–B5 borons and the carborane face in 6:4′,5′-[1-(η-C_5H_5)Co-2,3-$Me_2C_2B_4H_3$][2′,3′-$Me_2C_2B_4H_5$].

Reger has shown that functionalized olefins such as $CpFe(CO)(PPh_3)[\eta^1\text{-}MeC{=}CMe(H)]$ can be freed from the iron center by reaction of the complexes with Br_2 at low temperature, forming the halogen-substituted olefin and metal bromide.[19] On the other hand, the analogous metalloalkyl compounds $CpFe(CO)(PPh_3)$(alkyl), where the alkyl groups are ethyl, *n*-butyl, *sec*-butyl, or isobutyl, have been found to undergo a clean thermally induced β-hydride elimination to form the free olefin and metal hydride.[25] This latter type of dehydro elimination reaction is, in fact, similar to one of the steps needed to transform I into II and prompted our investigations of the thermolytic reactions of I.

Thermolysis of I in refluxing toluene for 18 h was found to produce 4,5-Me_2-7,8-$Et_2C_4B_4H_4$ (II) in 80% yield (eq 10). The compound was easily isolated in pure form by vacuum-line fractionation through a −23 °C trap.

Also formed was a light yellow solid, which had a ^1H NMR spectrum, and color consistent with the formation of $CpFe(CO)(PPh_3)(H)$, supporting a reaction process involving hydride

---

(17) Reger, D. L. *Acc. Chem. Res.* **1988**, *21*, 229–235.

(18) (a) Reger, D. L.; Klaeren, S. A.; Babin, J. E.; Adams, R. D. *Organometallics* **1988**, *7*, 181–189. (b) Reger, D. L.; Klaeren, S. A.; Lebioda, L. *Organometallics* **1988**, *7*, 189–193.

(19) Reger, D. L.; McElligott, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5923–5924.

(20) Reger, D. L.; McElligott, P. J.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1982**, *1*, 443–448.

(21) Reger, D. L.; Belmore, K. A.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 5710–5711.

(22) Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1983**, *2*, 101–105.

(23) Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. S. *Organometallics* **1984**, *3*, 134–140.

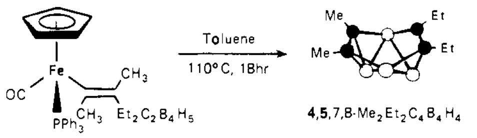
(24) Reger, D. L.; Swift, C. A. *Organometallics* **1984**, *3*, 876–879.

(25) Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789–2794.

(26) (a) Thompson, M. L.; Grimes, R. N. *Inorg. Chem.* **1972**, *11*, 1925–1930. (b) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1972**, 918–923. (c) Tabereaux, A.; Grimes, R. N. *Inorg. Chem.* **1973**, *12*, 792–798. (d) Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *J. Am. Chem. Soc*, **1973**, *95*, 6623–6629. (e) Magee, C. P.; Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *J. Organomet. Chem.* **1975**, *86*, 159–167. (f) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 2886–2891. (g) Beck, J. S.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 3467–3472.

(27) (a) Barker, G. K.; Green, M.; Onak, T. P.; Stone, F. G. A.; Ungermann, C. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1978**, 169–171. (b) Barker, G. K.; Green, M.; Stone, F. G. A.; Welch, A. J.; Onak, T. P.; Siwapanyoyos, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1687–1692.

(28) Borelli, A. J., Jr.; Plotkin, J. S.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 1328–1331.



(10)

1 II

elimination to the iron, However, since the carborane cage is situated trans with respect to the iron atom, the iron to bridging-hydrogen distance is quite long (4,91 Å), Thus, direct abstraction of this hydrogen by the iron atom is unlikely, Alternatively, an initial abstraction could involve the hydrogens on the geminal methyl group, Such β-hydride reactions are, of course, well-known in organometallic chemistry.

Of particular relevance is the work of Schwartz and co-workers[29] who have prepared various isomers of (η^1-2-butenyl)Ir(CO)L_2 and studied their β-hydride eliminations. Thermolysis of the complex (η^1-*trans*-2-butenyl)Ir(CO)$(PPh_3)_2$ resulted in elimination of a β-allylic hydrogen and formation of a η^3-crotyl species, presumably via a (η^2-allene)Ir(CO)$(PPh_3)_2$ intermediate.

If hydride abstraction were to occur at the geminal methyl group in I, a free allenyl–carborane intermediate and a metal hydride could be formed as shown in Figure 2, Since we have previously established that cage-bound α-olefins readily undergo intramolecular hydroboration (eq 3), it would be expected that an intermediate allenyl–carborane should undergo a similar hydroboration reaction to produce II. It should also be noted that this reaction sequence is consistent with the results obtained from reactions with the ruthenium catalysts discussed below.

The reactions employing nickel (eq 5) or iron reagents (eq 9 and 10) each resulted in alkyne insertions to produce the tetracarbon carborane II; however, neither reaction is catalytic since it is necessary in both cases to remove the two bridge hydrogens of the starting 2,3-$Et_2C_2B_4H_6$ carborane with stoichiometric reagents (excess NaH or NaH–Fe complex). A catalytic alkyne dehydro insertion reaction therefore requires a different pathway for dehydrogenation,

Dehydro addition catalysts have been previously employed in silicon chemistry to promote transformations, such as the dehydro silylation of olefins.[30–33] For example, both Wrighton and Sonada have shown that various metal carbonyls, including $Fe(CO)_5$,[30] $Fe_3(CO)_{12}$,[31] and $Ru_3(CO)_{12}$,[31,32] can catalyze the reactions of trialkylsilanes with olefins to form alkenylsilanes,

$$\text{1-pentene} + Me_3SiH \xrightarrow[h\nu,\ 25\ ^\circ C]{Fe(CO)_5} C_5H_{11}SiMe_3 + C_5H_9SiMe_3 + C_5H_{12} \quad (11)$$

$$C_6H_5CH{=}CH_2 + R_3SiH \xrightarrow[80\ ^\circ C]{Ru_3(CO)_{12}} C_6H_5CH{=}CH(SiMe_3) + C_6H_5C_2H_5 \quad (12)$$

These reactions can be performed either thermally or photochemically, and the ratio of alkenylsilane to alkylsilane products is critically dependent on reaction conditions. It is also important to note that the yield of saturated hydrocarbon (pentane or ethylbenzene in eq 11 and 12) is approximately equivalent to the total yield of alkenylsilanes, Thus, the hydrogenation of an additional 1 equiv of olefin may well promote the formation of alkenylsilane products by providing a favorable pathway for removal of the eliminated hydrogens.

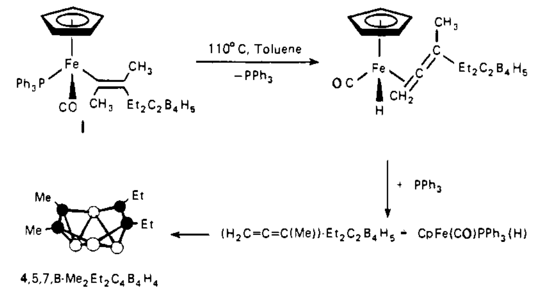


Figure 2. Possible mechanism leading to the formation of *nido*-4,5-Me_2-7,8-$Et_2C_4B_4H_4$ (II) from I.

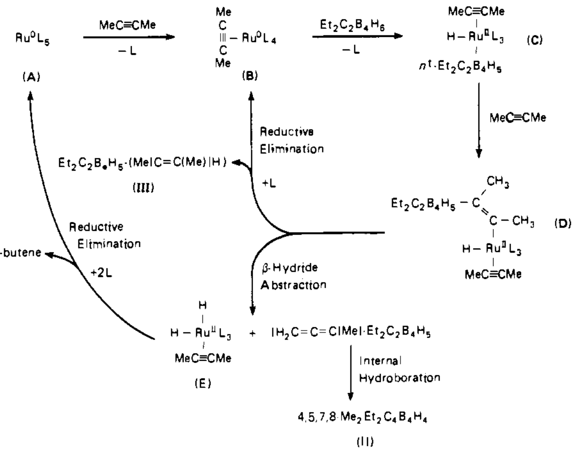


Figure 3, Possible reaction sequence leading to the formation of II and III from 2,3-$Et_2C_2B_4H_6$ and 2-butyne catalyzed by ruthenium complexes.[35]

The similarity between the two transformations, dehydro silylation and dehydro alkyne insertion, prompted our investigations of the use of known dehydro silylation catalysts for promoting two-carbon insertions into polyhedral boron cage compounds,

The reaction of 2-butyne with neutral 2,3-$Et_2C_2B_4H_6$, in the presence of catalytic amounts of $Ru_3(CO)_{12}$, was found to produce II, as well as the known hydroboration product, III (eq 13),

$$\text{2,3-}Et_2C_2B_4H_6 + \text{excess 2-butyne} \xrightarrow{Ru_3(CO)_{12}} \underset{\text{II}}{\text{4,5-}Me_2\text{-7,8-}Et_2C_4B_4H_4} + \underset{\text{III}}{\text{5-[(H)MeC}{=}\text{CMe]-2,3-}Et_2C_2B_4H_5} + \text{2-butene} \quad (13)$$

A typical reaction involved stirring 2,3-$Et_2C_2B_4H_6$ with a 10-fold excess of 2-butyne in the presence of 10 mol % $Ru_3(CO)_{12}$ in 5 mL of toluene at 140 °C, The metal carbonyl began to dissolve immediately, and the solution was completely homogeneous in 3–5 min. After 24 h of reaction, a colorless, oily material was separated from the reaction mixture by vacuum-line fractionation through a −23 °C trap. The ^{11}B NMR spectrum of this product indicated that it was a 70/30 mixture of II and III, When the starting material was placed back over the original catalyst for 18 h, a product mixture was formed, which ^{11}B NMR showed to be a 50/50 mixture of II and III, All subsequent reactions with the original catalyst resulted only in the formation of the alkenylcarborane,

The reactions catalyzed by $Ru_3(CO)_{12}$ were observed to be very sluggish (~1 catalyst turnover/day), but reactions that were monitored by GLC for up to 5 days showed no decrease in rate. The formation of both insertion (II) and addition (III) products and of approximately equal amounts of 2-butene and II in the

---

(29) Schwartz, J.; Hart, D. W.; McGiffert, B. *J. Am. Chem. Soc.* **1974**, *96*, 5613–5614.

(30) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345–358.

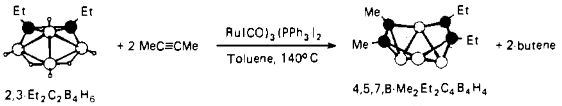
(31) Austin, R. G.; Paonessa, R. S.; Giordano, P. J.; Wrighton, M. S. *Adv. Chem. Ser.* **1978**, *168*, 189–214.

(32) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonada, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 928.

(33) (a) Reichel, C. L.; Wrighton, M. S. *Inorg. Chem.* **1980**, *19*, 3858–3860. (b) Millan, A.; Fernandez, M. J.; Bentz, P.; Maitlis, P. M. *J. Mol. Catal.* **1984**, *26*, 89–104. (c) Oro, L. A.; Fernandez, M. J.; Esteruelas, M. A.; Jimenez, M. S. *J. Mol. Catal.* **1986**, *37*, 151–156. (d) Ojima, I.; Fuchikami, T.; Yatabe, M. *J. Organomet. Chem.* **1984**, *260*, 335–346. (e) Cornish, A. J.; Lappert, M. F. *J. Organomet. Chem.* **1984**, *271*, 153–168. (f) Marciniec, B.; Gulinski, J. *J. Organomet. Chem.* **1983**, *253*, 349–362. (g) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389–3392. (h) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101–5105.

reaction are entirely consistent with the results of the dehydro silylation reactions discussed earlier.

Both the phosphine-substituted cluster $Ru_3(CO)_9(PPh_3)_3$ and the mononuclear complex $Ru(CO)_3(PPh_3)_2$ were also found to catalyze the reaction of 2,3-$Et_2C_2B_4H_6$ with 2-butyne; however, in contrast to the reaction with $Ru_3(CO)_{12}$, high selectivity for the insertion product II was observed. In both cases the formation of II was again accompanied by the production of approximately equivalent amounts of 2-butene.



II

(14)

While the mechanism of reaction involving the ruthenium complexes has not yet been established, a reasonable sequence based on those proposed[34] for dehydro silylation reactions can be formulated, as outlined in Figure 3.[35] Thus, important initial steps probably involve (1) binding of the 2-butyne, (2) oxidative addition of the carborane, and (3) insertion of 2-butyne into a Ru–boron bond to form a (η^1-vinylcarborane)ruthenium species (D). If D then undergoes a β-hydride-elimination reaction involving the geminal methyl group, such as was proposed above for I, then formation of II would result. If, on the other hand, reductive elimination occurs, then the alkenylcarborane III would be formed. Thus, the degree of product selectivity should be dependent on the relative rates of β-hydride- and reductive-elimination reactions. Furthermore, the elimination reactions should be influenced by, for example, the electronic and steric properties of the other ligands present at the metal. Thus, the higher selectivity for the insertion product (II) observed with $Ru_3(CO)_9(PPh_3)_3$ and $Ru(CO)_3(PPh_3)_2$ rather than $Ru_3(CO)_{12}$ could result from the fact that phosphine ligands may destabilize Ru^0 intermediates, relative to carbon monoxide, and reduce the driving force for the reductive-elimination step.[36]

The above comments concerning the mechanism of the reactions with ruthenium complexes are, of course, entirely speculative, and the determination of the exact reaction sequence will require detailed studies; however, the similarity of dehydro silylation and dehydro alkyne insertion reactions seems clear. Furthermore, in both the iron and ruthenium systems important steps leading to insertion appear to involve β-hydride alkene elimination and intramolecular hydroboration steps. This conclusion suggests, for example, that other dehydrogenation or olefin isomerization catalysts should now be examined for dehydro alkyne insertion activity and that the development of general metal-catalyzed carbon insertion reactions based on these types of catalysts may be possible.

Acknowledgment. We thank the National Science Foundation for the support of this research. We also thank Dr. Don Berry for many useful discussions concerning this research.

Supplementary Material Available: Tables of anisotropic temperature factors, hydrogen atom coordinates, bond distances, bond angles, and least-squares planes (10 pages); listings of observed and calculated structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

---

(34) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289–291.

(35) This reaction sequence assumes that mononuclear ruthenium fragments are the catalytically active species. For $Ru_3(CO)_{12}$ and $Ru_3(CO)_9(PPh_3)_3$, this may not be true and either di- or trimetallic units may be involved in the reaction; however, steps similar to those presented in Figure 3 are still possible.

(36) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332–338 and references therein.

Stepwise Dehydrogenation of a Ru(III) Hexaamine Cage Complex to a Hexaimine Ru(II) Complex via Ru(IV) Intermediates

Paul Bernhard* and Alan M. Sargeson*

Contribution from the Research School of Chemistry, The Australian National University, G.P.O. Box 4, Canberra 2601, Australia.
Received March 28, 1988

Abstract: The sexidentate ligand sarcophagine (sar: 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) when coordinated to ruthenium(III) (**1**) rapidly undergoes oxidative dehydrogenation to introduce an imine group into the cap portion of the ligand. Successive two-electron oxidations lead to a stable Ru(II) hexaimine complex, with all the imine groups in the cage caps. Each of the imine groups stabilizes the Ru(II) state by ~0.15 V leading to a stability of the Ru(II) hexaimine complex which is comparable to that of $Ru(2,2'\text{-bipyridine})_3^{2+}$. $Ru(sar)^{3+}$ disproportionates in aqueous solution to $Ru^{II}sar^{2+}$ and a singly deprotonated Ru(IV) intermediate (λ_{max} (ϵ_{max}); 445 nm (7800 M^{-1} cm^{-1})) which is converted into the Ru(II) imine product by both a base- and an acid-catalyzed pathway. Intermediate di- and triimine complexes were also observed en route to the hexaimine species. The kinetic and thermodynamic data for the disproportionation process imply that the secondary nitrogen in $Ru(sar)^{3+}$ is quite acidic (pK_a: 5–6) and that the Ru(IV) state is stabilized by ≥ 2 V. Acid catalysis of the dehydrogenation process from $[Ru^{IV}sar\text{-}H]^{3+}$ as well as a reversible hydration of $Ru(imsar)^{2+}$ below pH 2.5 are interpreted in terms of protonation at the metal center.

The reactivity of amine ligands coordinated to ruthenium, in particular their oxidation to imines and nitriles, has been the focus of a number of studies[1,2] sparked by the general interest in metal ion catalysis of such oxidation processes and the photochemical properties of Ru(II) complexes with unsaturated N ligands. Due to the stability of encapsulated metal complexes[3] in general, it was thought that the Ru(II)/(III) complexes of such ligands and

---

(1) (a) Lane, B. C.; Lester, J. E.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1971**, 1618. (b) Mahoney, D. F.; Beattie, J. K. *Inorg. Chem.* **1973**, *12*, 2561. (c) Diamond, S. E.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 2661. (d) Brown, G. M.; Weaver, T. R.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 190. (e) Adcock, P. A.; Keene, F. R.; Smythe, R. S.; Snow, M. R. *Inorg. Chem.* **1984**, *23*, 2336.

(2) (a) Ridd, M. J.; Keene, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 5733. (b) Keene, F. R.; Ridd, M. J.; Snow, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 7075 and references therein.

(3) Sargeson, A. M. *Pure Appl. Chem.* **1984**, *56*, 1603 and references therein.

0002-7863/89/1511-0597$01.50/0