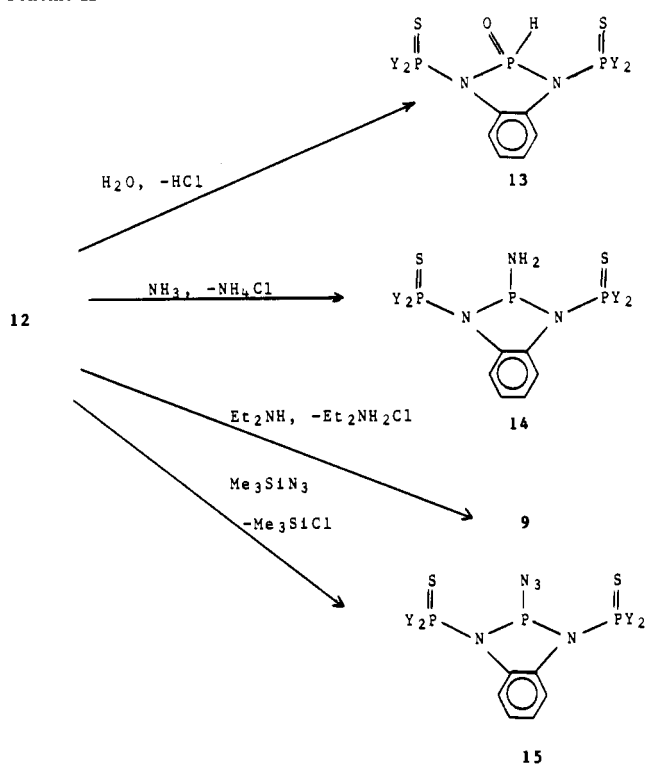


Scheme II



attempted amination of **12** with *i*-Pr<sub>2</sub>NH or excess **14**, however, gave no products; **12** appears unreactive to these bulky amines. These results suggest the cleft around the P-Cl bond unit is small enough to be selective toward amines, with the Et<sub>2</sub>N unit being the approximate upper limit in size.

Trimethylsilyl azide (Me<sub>3</sub>SiN<sub>3</sub>) reacts with **12** to form the phosphine azide **15**, even though the Me<sub>3</sub>SiN<sub>3</sub> molecule is large. **15** is indefinitely stable as a solid or in solution. An intense IR absorption at 2190 cm<sup>-1</sup>, characteristic of a P-N<sub>3</sub> group is seen,<sup>41,42</sup>

(41) Paciorek, K. L.; Kratzer, R. *Inorg. Chem.* 1964, 3, 594.

along with a <sup>31</sup>P NMR spectrum that is consistent with the assigned structure. Thermolysis and UV photolysis of **15** both give similar results, producing product mixtures that exhibit complex <sup>31</sup>P NMR spectra consisting of several peaks centered around δ 64.5. **15** appears to be more thermally stable than most previously reported P(III) phosphine azides,<sup>42</sup> but apparently less stable than the recently reported (*i*-Pr<sub>2</sub>N)<sub>2</sub>PN<sub>3</sub>.<sup>43,44</sup> Although the product spectra have not been assigned, no resonance(s) corresponding to either di- or tricyclophosphazenes appear.<sup>41,42</sup> This is interesting, since other phosphine azides, including (*i*-Pr<sub>2</sub>N)<sub>2</sub>PN<sub>3</sub>, decompose thermally to dimeric or trimeric cyclophosphazenes.<sup>42-44</sup>

The physical size of the cleft in the triphosphazene **6** and the triphosphazene disulfides **9** and **12** is defined to some degree by the derivatization reactions studied. Whereas small nucleophilic molecules such as H<sub>2</sub>O, NH<sub>3</sub>, and Et<sub>2</sub>NH react easily with the P-Cl bond, larger groups do not due to steric constraints. The inability of either *i*-Pr<sub>2</sub>NH or **14** to react with the P-Cl bond of **12** sets an upper limit on the accessibility of reagents to P(2). In a similar way, the failure of **15** to form cyclophosphazene oligomer products from the thermolysis/photolysis reactions can be ascribed to the overwhelming steric hindrance that must be overcome for such reactions to occur. It seems likely that Me<sub>3</sub>SiN<sub>3</sub> can react with **12**, because reaction occurs via a front-side four-center elimination process,<sup>44</sup> in which steric effects are less important, and consequently is mechanistically different from reactions of **12** with H<sub>2</sub>O or amines.

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**Supplementary Material Available:** Listings of the crystal structure determination and crystal structure data, hydrogen positional and thermal parameters, anisotropic thermal parameters, bond distances, bond angles, and least-squares planes, deviations, and dihedral angles (10 pages); a listing of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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## Reactions of Nitriles with Polyhedral Borane Anions. Reductive-Cyclocondensation and Carbon-Insertion Reactions: Syntheses of *hypho*-5-CH<sub>3</sub>-5,11,7,14-CNS<sub>2</sub>B<sub>7</sub>H<sub>9</sub> and *nido*-6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub>

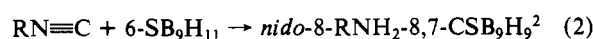
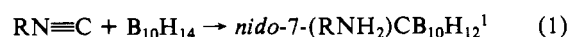
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The reactions of the polyhedral borane anions *arachno*-S<sub>2</sub>B<sub>7</sub>H<sub>8</sub><sup>-</sup> and *arachno*-C<sub>2</sub>B<sub>7</sub>H<sub>12</sub><sup>-</sup> with acetonitrile have been explored and found to result in reduction of the nitrile and either the incorporation of a CN unit into the cage framework or a one-carbon insertion accompanied by deamination. Thus, the reaction of the *arachno*-S<sub>2</sub>B<sub>7</sub>H<sub>8</sub><sup>-</sup> anion with acetonitrile under reflux conditions was found to yield the *hypho*-CH<sub>3</sub>CNS<sub>2</sub>B<sub>7</sub>H<sub>8</sub><sup>-</sup> anion I, which upon protonation gave the corresponding neutral, air-stable cluster *hypho*-5-CH<sub>3</sub>-5,11,7,14-CNS<sub>2</sub>B<sub>7</sub>H<sub>9</sub> (II) in excellent yield. In contrast, the isoelectronic carborane anion *arachno*-C<sub>2</sub>B<sub>7</sub>H<sub>12</sub><sup>-</sup> reacted with acetonitrile under reflux conditions to give a one-carbon insertion forming the tricarbonyl carborane anion *nido*-CH<sub>3</sub>C<sub>3</sub>B<sub>7</sub>H<sub>9</sub><sup>-</sup> (III). Acidification of III then gave *nido*-6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub> (IV) in good yield. A single-crystal X-ray study of II confirmed that the compound has four different main-group cage substituents (boron, sulfur, carbon, and nitrogen) and demonstrated that it adopts a unique *hypho*-cage geometry that can be derived from a bicapped hexagonal square antiprism by removing three vertices. The structure thus has two puckered six-membered and one planar five-membered open face. Crystal data for II: space group C2/c, Z = 8, a = 19.889 (9) Å, b = 8.999 (2) Å, c = 11.718 (2) Å, β = 105.00 (3)°. The structure was refined by full-matrix least squares to final R = 0.052 and R<sub>w</sub> = 0.063 for the 998 unique reflections having F<sub>o</sub><sup>2</sup> > 3σ(F<sub>o</sub><sup>2</sup>).

### Introduction

The reactions of isocyanides with a number of neutral boron hydrides have previously been explored and shown in several cases to result in one-carbon-insertion products:<sup>1-3</sup>



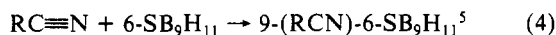
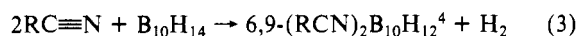
The reactions of nitriles with boron hydrides have also been

Table I.  $^{11}\text{B}$  NMR Data

compd	$\delta$ , ppm ( $J$ , Hz; assgnt)	cross peaks
<i>hypho</i> - $\text{CH}_3\text{CNS}_2\text{B}_7\text{H}_8^-$ (I)	5.0 (120; B3), -3.5 (125; B12), -7.0 (150; B1,9), -16.4 (135; B2,8), -31.6 (110; B4) <sup>a</sup>	B3-B1,9 (s), B3-B2,8 (m), B3-B4 (m), B1,9-B4 (s) <sup>a</sup>
<i>hypho</i> -5- $\text{CH}_3$ -5,11,7,14- $\text{CNS}_2\text{B}_7\text{H}_9$ (II)	21.0 (160; B1,9), -3.9 (145; B3), -6.5 (140; B12), -17.3 (155; $J_{\text{BH}}$ = 45 Hz; B2,8), -27.0 (120; B4) <sup>b</sup>	B1,9-B3 (s), B1,9-B4 (s), B3-B2,8 (s), B3-B4 (m) <sup>a</sup>
<i>nido</i> - $\text{CH}_3\text{C}_3\text{B}_7\text{H}_9^-$ (III)	8.6 (125; B8), 6.2 (130; B7), -3.0 (135; B1), -8.1 (130; B3), -10.3 (135; B10), -21.4 (160; B2), -30.0 (145; B4) <sup>b</sup>	B8-B7 (s), B8-B3 (s), B8-B4 (w), B7-B3 (s), B7-B2 (m), B1-B3 (s), B1-B10 (m), B1-B2 (s), B1-B4 (s), B3-B2 (s), B3-B4 (s), B10-B4 (m) <sup>b</sup>
<i>nido</i> -6- $\text{CH}_3$ -6,7,9- $\text{C}_3\text{B}_7\text{H}_{10}$ (IV)	22.8 (170; B8), 2.5 (150; B7), -0.2 (160; B10), -3.2 (155; B1), -8.6 (190; B2), -10.1 (155; B3), -34.7 (165; B4) <sup>b</sup>	B8-B7 (s), B8-B3 (s), B8-B4 (m), B7-B2 (w), B7-B3 (s), B10-B1 (w), B10-B4 (w), B1-B2 (s), B1-B3 (s), B1-B4 (s), B2-B3 (s), B3-B4 (s) <sup>b</sup>

<sup>a</sup>64.2 MHz. <sup>b</sup>160.5 MHz. <sup>c</sup>s, strong; m, medium; w, weak.

investigated but, in contrast to the reactions with isocyanides, have yielded only nitrogen-boron-bonded acid-base adducts:



In each of the reactions outlined above the boron hydride is functioning as an electrophile and initially attacks the negative center in either the isocyanide (carbon) or nitrile (nitrogen). We have recently discovered that the reactions of certain polyhedral borane anions with nitriles follow a different course, involving an initial nucleophilic attack at the carbon of the nitrile group. Subsequent reaction can then result in either carbon or CN-group cage insertions. While these results are unprecedented in polyhedral borane chemistry, they appear to parallel reactions previously observed between certain transition-metal cluster anions and nitriles. As an illustration, we report here our studies of the reactions of acetonitrile with two isoelectronic anions, *arachno*- $\text{S}_2\text{B}_7\text{H}_8^-$  and *arachno*- $\text{C}_2\text{B}_7\text{H}_{12}^-$ , which have resulted in the formation of the unique *hypho* cluster *hypho*-5- $\text{CH}_3$ -5,11,7,14- $\text{CNS}_2\text{B}_7\text{H}_9$  and the new tricarbon carborane *nido*-6- $\text{CH}_3$ -5,6,9- $\text{C}_3\text{B}_7\text{H}_{10}$ , respectively.

### Experimental Section

All manipulations were carried out by using standard high-vacuum or inert-atmosphere techniques as described by Shriver.<sup>6</sup>

**Materials.** The compounds *arachno*-6,8- $\text{S}_2\text{B}_7\text{H}_9^7$  and *arachno*-6,8- $\text{C}_2\text{B}_7\text{H}_{13}^8$  were prepared as reported previously. Acetonitrile was predried with  $\text{CaH}_2$  and then freshly vacuum-distilled from  $\text{P}_2\text{O}_5$ . Methylene chloride was dried over calcium chloride. Anhydrous gaseous HCl (Matheson) was fractionated quickly through a  $-116^\circ\text{C}$  trap prior to use. Oil-dispersed sodium hydride was obtained from Aldrich and was washed with hexane under a nitrogen atmosphere prior to use. All other reagents were commercially obtained, as indicated, and used as received.

**Physical Measurements.** Boron-11 NMR spectra at 160.5 MHz were obtained on a Bruker AM-500 spectrometer equipped with the appropriate decoupling accessories. Proton NMR spectra at 200 MHz and boron-11 NMR spectra at 64.2 MHz were obtained on a Bruker AF-200 Fourier transform spectrometer. Selective proton-decoupled carbon-13 NMR spectra (50.3 MHz) were obtained on the Bruker AF-200 spectrometer. Low-power decoupling was employed with irradiation frequencies determined from the low-temperature proton spectrum. All boron-11 chemical shifts are referenced to  $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$  (0.0 ppm) with a negative sign indicating an upfield shift. All proton and carbon chemical shifts were measured relative to internal residual benzene from

the lock solvent (99.5%  $\text{C}_6\text{D}_6$ ) and then referenced to  $\text{Me}_4\text{Si}$  (0.00 ppm).

Two-dimensional COSY  $^{11}\text{B}$ - $^{11}\text{B}$  NMR experiments<sup>9</sup> (Table I) were performed with *s*-type selection parameters at 160.5 MHz for III and IV and at 64.2 MHz for I and II. For I and II the sweep width in the  $F_2$  direction was 20 000 Hz and in the  $F_1$  direction 10 000 Hz and a total of 128 increments (increment size 0.05 ms) was collected, with each slice having 512W  $F_2$  data points. For III and IV the sweep widths in the  $F_2$  direction were 10 000 and 12 000 Hz and in the  $F_1$  direction 5000 and 6000 Hz, respectively, and a total of 256 increments (increment size 0.084 ms) were collected, each slice having 1K data points. The data were zero-filled twice for I and II and once for III and IV in the  $F_1$  directions and subjected to 2D Fourier transformation with sine-bell apodization in both domains. A total of 96 scans for I, II, and III and 160 for IV were taken for each increment with a recycling time of 100 ms. Broad-band  $^{11}\text{B}$ -decoupled phase-sensitive proton COSY spectra of IV were acquired by the TPPI<sup>10</sup> method at 200.13 MHz. Heteronuclear correlated  $^1\text{H}$ - $^{11}\text{B}$  NMR spectra of IV were collected at 160.4 MHz for  $^{11}\text{B}$  and 500.13 MHz for  $^1\text{H}$ . The  $t_1$  and  $t_2$  delays were calculated by following the method of Burum.<sup>11</sup>

High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer. All melting points are uncorrected. Elemental analyses were obtained from Schwarzkopf Laboratories, Woodside, NY.

**Reaction of *arachno*- $\text{S}_2\text{B}_7\text{H}_8^-$  with Acetonitrile.** A 100-mL round-bottom flask fitted with a vacuum stopcock was charged with 1.04 g (6.99 mmol) of *arachno*-6,8- $\text{S}_2\text{B}_7\text{H}_9$  and 0.36 g (15.0 mmol) of NaH. Tetrahydrofuran (20 mL) was distilled into the reaction flask in vacuo, and the flask was allowed to warm to room temperature, whereupon hydrogen gas was evolved. After gas evolution ceased ( $\sim 1.5$  h), the resulting yellow solution was filtered and concentrated under vacuum. This yellow concentrate was transferred to a flask fitted with a reflux condenser, and 20 mL of predried acetonitrile was introduced. The solution was then heated at reflux overnight.  $^{11}\text{B}$  NMR spectra taken at this point indicated that the starting material had been completely consumed and that the *hypho*- $\text{CH}_3\text{CNS}_2\text{B}_7\text{H}_8^-$  anion I was the sole product. Acetonitrile was then vacuum-evaporated and the resulting yellow solid suspended in 30 mL of methylene chloride. To this suspension was added dropwise 10 mL of aqueous 5 N HCl at  $-5^\circ\text{C}$ . The solution was stirred for 30 min and the methylene chloride layer then separated. The aqueous phase was further washed with two 20-mL portions of methylene chloride. The combined methylene chloride solutions were dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. Further vacuum drying gave 1.14 g (6.0 mmol, 86%) of *hypho*-5- $\text{CH}_3$ -5,11,7,14- $\text{CNS}_2\text{B}_7\text{H}_9$  (II) as a yellow solid. Further sublimation in vacuo at  $60^\circ\text{C}$  gave 0.92 g (4.8 mmol, 69%) of the white crystalline material II:  $R_f = 0.42$  in hexane; mp  $128\text{--}128.5^\circ\text{C}$ . Mass measurement: calcd for  $^{12}\text{C}_2^{14}\text{N}_1^{32}\text{S}_2^{11}\text{H}_{12}^{11}\text{B}_7$ , 191.1062; found, 191.1032. Anal. Calcd for  $\text{C}_2\text{NS}_2\text{B}_7\text{H}_{12}$ : C, 12.65; H, 6.37; N, 7.37; B, 39.84; S, 33.76. Found: C, 13.15; H, 6.18; N, 10.21; B, 37.76; S, 31.89.  $^1\text{H}$  NMR (200 MHz, ppm,  $\text{C}_6\text{D}_6$ , boron-11 spin decoupled): 5.9 (NH,  $J_{\text{NH}} = 57$  Hz), 4.2 (BH), 3.2 (BH), 2.9 (BH), 2.6 (BH), 2.4 (BH), 1.80 ( $\text{CH}_3$ ), 0.9 (BHB). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3320 (s), 2970 (w), 2550 (s), 2540 (s, sh), 2530 (s, sh), 2500 (s), 2450 (s), 1540 (s), 1445 (m), 1395 (m), 1360 (m), 1260 (w), 1185 (s), 1080 (s),

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1010 (s), 970 (m), 950 (m), 905 (w), 860 (w), 835 (w), 800 (w), 740 (m), 730 (m), 725 (s), 705 (m), 665 (w), 625 (w), 600 (w), 550 (w), 510 (w), 465 (w), 425 (w), 365 (w), 300 (w), 230 (w). The following data were collected for the PPN salt of I.  $^1\text{H}$  NMR (200 MHz, ppm,  $\text{CD}_2\text{Cl}_2$ , PPN resonances not listed): 2.78 ( $\text{CH}_3$ ). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3280 (m), 3050 (w), 2970 (w), 2860 (w), 2500 (s, sh), 2470 (s), 2440 (s), 1580 (w), 1520 (w), 1505 (w), 1480 (w), 1485 (s), 1395 (w), 1310 (m, sh), 1295 (m, sh), 1280 (s), 1265 (s), 1190 (w), 1180 (w, br), 1160 (w), 1110 (s), 1080 (w), 1070 (w), 1020 (m), 995 (m), 970 (w), 860 (w), 800 (m), 760 (w), 755 (w), 740 (m), 720 (s), 690 (s), 620 (w), 550 (s), 525 (s), 495 (s), 435 (w), 395 (w).

**Reaction of I with DCl.** The sodium salt of I was prepared by the reaction of 0.04 g (1.7 mmol) of NaH with 0.30 g of *hypho*-5- $\text{Me}_5$ ,11,7,14- $\text{CNS}_2\text{B}_7\text{H}_9$  in THF- $d_6$  in vacuo at  $\sim -20^\circ\text{C}$ . After evolution of  $\text{H}_2$  had ceased, the solvent was removed in vacuo and the remaining solids were suspended in 30 mL of methylene chloride. To this suspension was added 5 mL of 6.6 N DCl (in  $\text{D}_2\text{O}$ ) at  $-5^\circ\text{C}$ . The solution was stirred for 30 min and the methylene chloride layer then separated. The methylene chloride was vacuum-evaporated and the residue sublimed at  $60^\circ\text{C}$  to yield 0.24 g (1.3 mmol) of *hypho*-5- $\text{CH}_3$ -5,11,7,14- $\text{CNS}_2\text{B}_7\text{H}_9$ . IR (KBr,  $\text{cm}^{-1}$ ): 3310 (s), 2960 (w), 2560 (s), 2530 (s), 2500 (s), 2450 (s), 1540 (s), 1485 (w), 1445 (m), 1430 (w), 1395 (m), 1365 (m), 1275 (m), 1260 (w), 1185 (s), 1100 (w, sh), 1080 (s), 1045 (w), 1010 (s), 990 (w), 970 (w), 955 (m), 925 (m), 865 (w), 835 (w), 800 (m), 740 (m), 720 (s), 695 (m), 665 (w), 635 (w), 625 (w), 605 (w), 550 (w), 510 (w), 490 (w), 420 (w), 360 (w), 300 (w). Exact mass measurement for  $^{12}\text{C}_4^{14}\text{N}^{32}\text{S}_2^{11}\text{B}_7^{2}\text{D}$ : calcd, 192.1125; found, 192.1062.

**Reaction of *arachno*- $\text{C}_2\text{B}_7\text{H}_{12}^-$  with Acetonitrile.** A 100-mL round-bottom flask fitted with a vacuum stopcock was charged with 1.14 g (10.1 mmol) of *arachno*-6,8- $\text{C}_2\text{B}_7\text{H}_{13}$  and slightly less than 1 equiv,  $\sim 0.24$  g (10 mmol), of NaH. Tetrahydrofuran (20 mL) was distilled into the reaction flask in vacuo. When the mixture was warmed to room temperature, vigorous hydrogen evolution was observed. After 1 h the solution was filtered and transferred to a three-neck flask fitted with a reflux condenser and the THF vacuum-evaporated. Predried acetonitrile (20 mL) was introduced to the flask, which was then heated at reflux for 2 weeks.  $^{11}\text{B}$  NMR spectra taken at this point confirmed the exclusive formation of the *nido*- $\text{CH}_3\text{C}_2\text{B}_7\text{H}_9^-$  anion III. (Subsequent NMR studies showed that the reaction is, in fact, 90% complete in as little as 1 week.) The solvent was removed in vacuo and the residue dissolved in 20 mL of methylene chloride. This suspension was maintained at  $-110^\circ\text{C}$  while 40 mmol of gaseous HCl was added. After 20 min a detachable U-trap was interposed between the flask containing the reaction mixture and the pump, and overnight fractionation through this trap, which was maintained at  $-45^\circ\text{C}$ , allowed gaseous HCl and methylene chloride to pass while retaining 0.48 g (3.5 mmol, 35%) of *nido*-6- $\text{CH}_3$ -5,6,9- $\text{C}_2\text{B}_7\text{H}_{10}$  (IV), mp  $\sim -10$  to  $-15^\circ\text{C}$ . Mass measurement for  $^{12}\text{C}_4^{14}\text{H}_{13}^{11}\text{B}_7$ : calcd, 138.167; found, 138.163.  $^1\text{H}$  NMR (200 MHz, ppm,  $\text{C}_6\text{D}_6$ , boron-11 spin decoupled, assignments made from  $^1\text{H}$ - $^1\text{H}$  and  $^1\text{H}$ - $^{11}\text{B}$  COSY spectra): 4.2 (B8 H), 3.3 (C5 H, B7 H, B1 H), 3.0 (B10 H), 2.7 (B3 H), 2.2 (B2 H), 1.78 ( $\text{C}_9\text{H}_{\text{endo}}$ ), 1.58 ( $\text{CH}_3$ ), 1.3 (B4 H),  $-1.56$  ( $\text{C}_9\text{H}_{\text{endo}}$ ,  $J_{\text{HH}} = 13$  Hz).  $^{13}\text{C}$  NMR (50.3 MHz, ppm,  $\text{C}_6\text{D}_6$ ,  $-83^\circ\text{C}$ , proton coupled): 159.5 (s, C6), 61.7 (d, C5,  $J_{\text{CH}} = 172$  Hz), 31.8 (d of d, C9,  $J_{\text{CH}_{\text{endo}}} = 160$  Hz,  $J_{\text{CH}_{\text{exo}}} = 116$  Hz), 23.7 ( $\text{CH}_3$ ,  $J_{\text{CH}} = 131$  Hz). IR (gas phase, 10-cm cell, KBr windows,  $\text{cm}^{-1}$ ): 2980 (w), 2930 (w), 2600 (s), 2580 (s, sh), 1380 (m, br), 1260 (w), 1230 (w), 1215 (w), 1170 (w), 1080 (w, sh), 1035 (s), 870 (w), 820 (w). Anal. Calcd for III,  $\text{NP}_2\text{C}_4\text{B}_7\text{H}_{12}$ : C, 71.23; H, 6.29; N, 2.08. Found: C, 69.46; H, 6.19; N, 1.97.  $^1\text{H}$  NMR (200 MHz, ppm,  $\text{CD}_2\text{Cl}_2$ , PPN resonances not listed): 4.63 (CH), 2.87 (CH), 1.89 ( $\text{CH}_3$ ). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3050 (w), 2990 (w), 2900 (w), 2850 (w), 2540 (s, sh), 2490 (s), 1585 (m), 1480 (m), 1435 (s), 1315 (s), 1305 (s), 1290 (s), 1265 (s), 1180 (m), 1160 (w), 1140 (w), 1115 (s), 1100 (m, sh), 1025 (m), 995 (m), 920 (w), 805 (w), 790 (w), 755 (m), 745 (s), 720 (s), 690 (s), 660 (w), 615 (w), 545 (s), 535 (s), 500 (s), 445 (w), 385 (w), 315 (w). IV slowly decomposes in vacuo at room temperature, but its sodium salt was found to be very stable and may be kept as a stock solution for further synthesis purposes.

**Crystallographic Data for *hypho*-5- $\text{CH}_3$ -5,11,7,14- $\text{CNS}_2\text{B}_7\text{H}_9$  (II).** Single crystals of II were grown by slow sublimation inside a sealed tube. A suitably sized crystal was placed inside a capillary tube, which was then sealed with glue. This tube 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 Cu  $K\alpha$  radiation from a highly oriented graphite-crystal monochromator. The intensities of three standard reflections measured at intervals of 100 reflections showed no systematic change during data

**Table II.** Data Collection and Structure Refinement Information for *hypho*-5- $\text{CH}_3$ -5,11,7,14- $\text{CNS}_2\text{B}_7\text{H}_9$  (II)

space group	$C2/c$	scanning range, deg	$6 \leq 2\theta \leq 140$
$a$ , Å	19.889 (9)	scan mode	$\omega-2\theta$
$b$ , Å	8.999 (2)	$\pm h, \pm k, \pm l$ collected	$\pm 24, \pm 10, 14$
$c$ , Å	11.718 (2)	no. of measd intens	4022 (total), 1918 (unique)
$\beta$ , deg	105.00 (3)	no. of intens with $F_o^2 > 3\sigma(F_o^2)$	998
$V$ , Å <sup>3</sup>	2026.0	$\rho$ (calcd), g cm <sup>-3</sup>	1.245
$Z$	8	mol formula	$\text{C}_2\text{NH}_{12}\text{S}_2\text{B}_7$
		mol wt	189.93
		radiation ( $\lambda$ , Å)	Cu $K\alpha$ , (1.54184)
			$R$ 0.052
			$R_w$ 0.063

**Table III.** Atomic Positional Parameters and Their Estimated Standard Deviations for II

atom	$x$	$y$	$z$	$B$ , Å <sup>2</sup>
S7	-0.48536 (4)	0.2278 (1)	-0.0255 (1)	6.85 (3)
S14	-0.33629 (5)	0.2564 (1)	-0.0189 (1)	6.70 (3)
N11	-0.3747 (1)	0.0861 (4)	-0.0783 (3)	5.84 (8)
B1	-0.4401 (2)	0.1537 (6)	0.1244 (5)	6.4 (1)
B2	-0.4563 (2)	0.3609 (6)	0.1038 (5)	6.9 (1)
B3	-0.3774 (2)	0.2839 (6)	0.1929 (5)	6.5 (1)
B4	-0.3490 (2)	0.1129 (5)	0.1429 (4)	5.4 (1)
B8	-0.3710 (2)	0.4446 (6)	0.1106 (5)	6.8 (1)
B9	-0.3074 (2)	0.2855 (6)	0.1304 (5)	6.0 (1)
B12	-0.4076 (2)	0.2358 (6)	-0.0991 (5)	6.2 (1)
C5	-0.3486 (1)	0.0312 (4)	0.0261 (3)	5.18 (9)
C5A	-0.3166 (2)	-0.1192 (5)	0.0346 (4)	6.7 (1)
HN11	-0.367 (1)	0.039 (5)	-0.130 (3)	6.0
HB1	-0.472 (1)	0.087 (4)	0.177 (3)	6.0
HB2	-0.492 (2)	0.409 (4)	0.143 (3)	6.0
HB3	-0.365 (2)	0.302 (4)	0.282 (4)	6.0
HB4	-0.325 (2)	0.048 (4)	0.218 (3)	6.0
HB8	-0.352 (1)	0.554 (5)	0.146 (3)	6.0
HB9	-0.254 (2)	0.305 (5)	0.186 (3)	6.0
HB12	-0.431 (2)	0.270 (4)	-0.189 (4)	6.0
HB28	-0.434 (1)	0.470 (5)	0.059 (3)	6.0

**Table IV.** Interatomic Distances (Å) for II

S7-B1	1.876 (5)	B3-B4	1.788 (7)
S7-B2	1.900 (6)	B3-B8	1.760 (8)
S7-B12	1.958 (5)	B3-B9	1.731 (7)
S14-B8	1.924 (6)	B4-B9	1.783 (7)
S14-B9	1.882 (5)	B8-B9	1.885 (7)
S14-B12	1.951 (5)	N11-HN11	0.78 (4)
N11-B12	1.490 (6)	B1-HB1	1.15 (4)
N11-C5	1.298 (5)	B2-HB2	1.03 (4)
B4-C5	1.555 (6)	B3-HB3	1.02 (4)
C5-C5A	1.488 (5)	B4-HB4	1.06 (4)
B1-B2	1.897 (8)	B8-HB8	1.10 (4)
B1-B3	1.747 (7)	B9-HB9	1.10 (3)
B1-B4	1.805 (6)	B12-HB12	1.08 (4)
B2-B3	1.785 (6)	B2-HB28	1.25 (4)
B2-B8	1.839 (7)	B8-HB28	1.26 (3)

collection. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program BEGIN.

**Structure and Refinement of the Structure.** All calculations were performed on a VAX 11/750 computer using the Enraf-Nonius structure package.<sup>12</sup> 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 those stored in the SDP package. Agreement factors are defined as  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$ . Direct methods were used to locate the sulfur atoms. Subsequent Fourier maps led to the location of the remaining non-hydrogen atoms. Anisotropic refinements followed by difference Fourier syntheses resulted in the location of all hydrogens except those on the methyl. The methyl hydrogens were calculated by using the program HYDRO and included (but not refined) in structure factor calculations. The largest residual peak in the final difference Fourier was 0.16 e/Å.

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

Table V. Interatomic Bond Angles (deg) for II

B1-S7-B2	60.3 (2)	B4-B3-B8	117.0 (4)
B1-S7-B12	100.5 (2)	B4-B3-B9	60.9 (3)
B2-S7-B12	102.5 (2)	B8-B3-B9	65.3 (3)
B8-S14-B9	59.4 (2)	B1-B4-B3	58.2 (3)
B8-S14-B12	102.8 (2)	B1-B4-B9	106.6 (3)
B9-S14-B12	100.1 (2)	B1-B4-C5	102.9 (3)
B12-N11-C5	123.4 (4)	B3-B4-B9	58.0 (3)
B12-N11-HN11	122 (3)	B3-B4-C5	140.2 (4)
C5-N11-HN11	114 (3)	B9-B4-C5	103.4 (4)
S7-B1-B2	60.5 (2)	S14-B8-B2	110.5 (3)
S7-B1-B3	107.7 (3)	S14-B8-B3	105.1 (3)
S7-B1-B4	114.1 (4)	S14-B8-B9	59.2 (2)
B2-B1-B3	58.5 (3)	B2-B8-B3	59.4 (3)
B2-B1-B4	110.4 (3)	B2-B8-B9	106.0 (3)
B3-B1-B4	60.4 (3)	B3-B8-B9	56.6 (3)
S7-B2-B1	59.2 (2)	S14-B9-B3	108.1 (3)
S7-B2-B3	105.1 (3)	S14-B9-B4	114.7 (3)
S7-B2-B8	112.3 (4)	S14-B9-B8	61.4 (2)
B1-B2-B3	56.6 (3)	B3-B9-B4	61.2 (3)
B1-B2-B8	105.8 (3)	B3-B9-B8	58.1 (3)
B3-B2-B8	58.1 (3)	B4-B9-B8	111.1 (3)
B1-B3-B2	64.9 (3)	S7-B12-S14	111.8 (3)
B1-B3-B4	61.4 (3)	S7-B12-N11	104.9 (3)
B1-B3-B8	116.3 (4)	S14-B12-N11	105.9 (2)
B1-B3-B9	111.6 (4)	N11-C5-B4	123.9 (3)
B2-B3-B4	116.5 (3)	N11-C5-C5A	118.0 (4)
B2-B3-B8	62.5 (3)	B4-C5-C5A	118.1 (3)
B2-B3-B9	115.6 (4)		

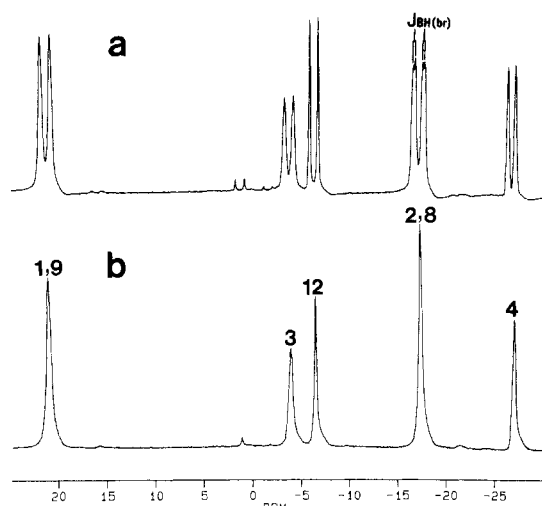
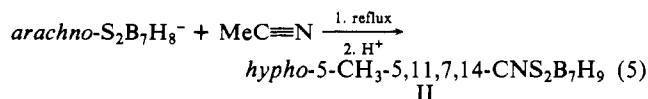


Figure 1.  $^{11}\text{B}$  NMR spectra (160.5 MHz) of II. Spectrum b is proton spin decoupled.

## Results

The reaction of the *arachno*- $\text{S}_2\text{B}_7\text{H}_8^-$  anion with refluxing acetonitrile, followed by protonation of the resulting anion I with aqueous HCl, resulted in the formation of compound II, which was isolated as an air-stable, yellow crystalline product in excellent yield:



Elemental analysis and exact mass measurements support the proposed composition of II, but the absence of any singlet resonances in its  $^{11}\text{B}$  NMR spectrum indicates that it is not a simple nitrile-borane adduct, such as is generally observed in the reactions of nitriles with *neutral* boron hydrides. The spectrum (Figure 1) exhibits five doublet resonances in a 2:1:1:2:1 ratio, indicating a molecular mirror plane. In addition, the resonance at  $-17.3$  ppm shows fine coupling ( $J = 45$  Hz), indicating coupling to a boron-boron-bridging proton.

The  $^1\text{H}$  NMR spectrum of II contains resonances consistent with the presence of one bridging hydrogen and a methyl group.

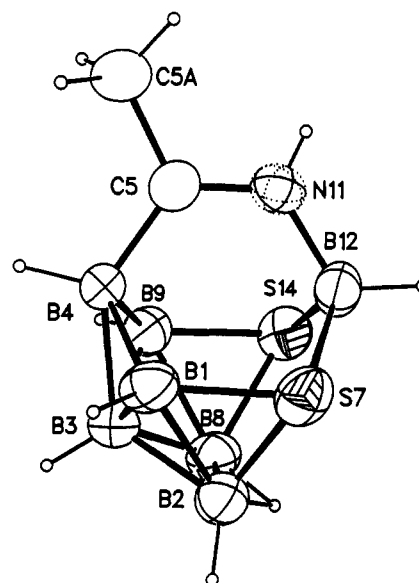


Figure 2. ORTEP drawing of the molecular structure of *hypho*-5- $\text{CH}_3$ -5,11,7,14-CNS $_2$ B $_7$ H $_9$  (II). Non-hydrogen atoms are shown as 50% thermal ellipsoids.

The boron-decoupled proton NMR spectrum shows resonances attributed to terminal BH protons, as well as an additional triplet centered at 5.9 ppm with a coupling constant (57 Hz) typical of nitrogen-hydrogen coupling.<sup>13</sup> The infrared spectrum shows absorptions consistent with N-H stretching ( $3320\text{ cm}^{-1}$ ) and C=N stretching ( $1540\text{ cm}^{-1}$ ), further suggesting that reduction of the nitrile has occurred.

A single-crystal X-ray structural study of II revealed that the compound adopts the unique *hypho* structure shown in Figure 2 and contains four different (boron, sulfur, carbon, and nitrogen) main-group cage substituents. As can be seen in the figure, hydroboration of the nitrile has occurred to produce an imine that bridges two borons (B4 and B12). The structure thus formed contains three open faces. There are two puckered hexagonal faces on either side of the CN group (C5, B4, B9, S14, B12, N11 and C5, B4, B1, S7, B12, N11) and one planar pentagonal face containing the two sulfur atoms and three borons (B12, S14, B8, B2, S7). In agreement with the assignments made on the basis of the NMR data discussed below, a single bridge hydrogen is found between B2 and B8 on the five-membered open face. The isolated boron B12 is four-coordinate, sitting between the nitrogen and two sulfur atoms, and has approximate tetrahedral geometry (S7-B12-HB12 =  $104(2)^\circ$ ; S7-B12-N11 =  $104.9(3)^\circ$ ; S14-B12-N11 =  $105.9(2)^\circ$ ).

There are at least two different ways in which this structure may be viewed. First, if the CN group is considered to be part of the cluster, then the cluster would have 30 skeletal electrons and be an  $11$ -vertex  $n + 4$  *hypho* cage system. Such a cluster should then have a structure based on a *closo* 14-vertex polyhedron<sup>14</sup> missing three vertices. Indeed, a structure consistent with that observed for II can be derived from a *bicapped*-hexagonal-antiprism structure, as shown in Figure 3. Thus, removal of three five-coordinate vertices, accompanied by additional bond breaking between positions 1 and 5 and positions 11 and 14 to allow the CN group to adopt a symmetrical position, generates the observed structure.

- (13) Alei, M., Jr.; Florin, A. E.; Litchman, W. M.; O'Brien, J. F. *J. Phys. Chem.* **1971**, *75*, 932-938.
- (14) (a) Evans, W. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 38-39. (b) Brown, L. D.; Lipscomb, W. N. *Inorg. Chem.* **1977**, *16*, 2989-2996. (c) Maxwell, W. M.; Bryan, R. F.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 4008-4015. (d) Maxwell, W. N.; Weiss, R.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 4016-4029. (e) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 6-10. (f) Bicerano, J.; Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1978**, *17*, 2041-2042. (g) Bicerano, J.; Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1978**, *17*, 3443-3453.

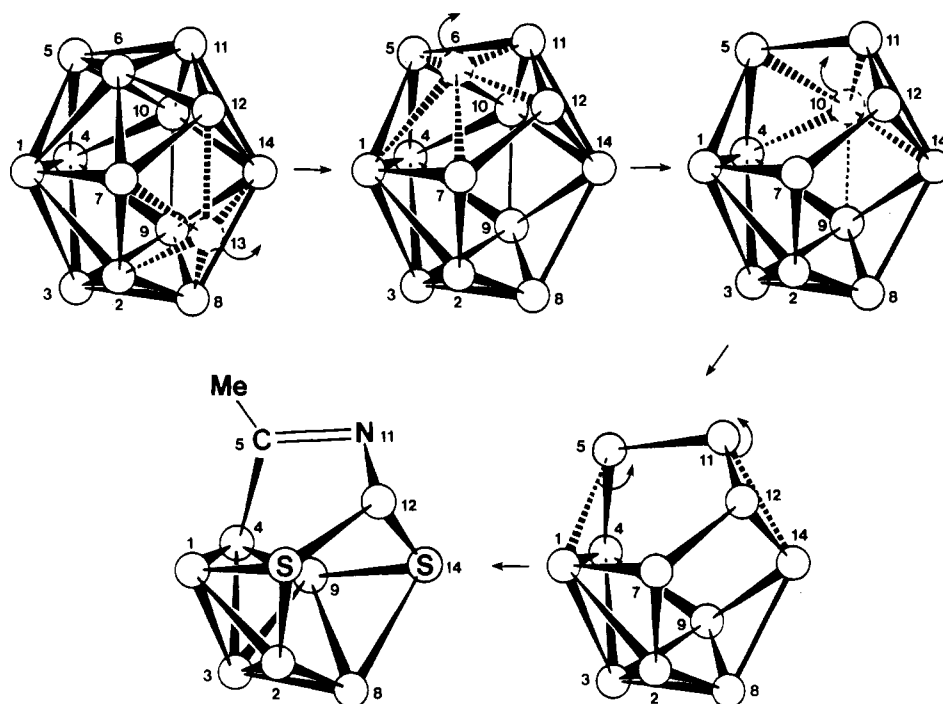
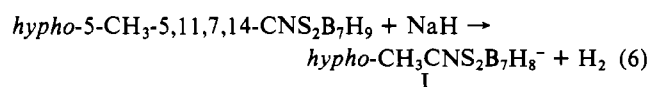


Figure 3. Derivation of an 11-vertex hypho structure from a bicapped hexagonal antiprism by stepwise removal of three vertices.

Alternatively, II can be viewed as a hybrid molecule that contains a "nonclassical" thiaaborane cluster framework substituted by a "classical" bridging exopolyhedral imine group. Supporting this interpretation are the facts that the C5–N11 bond distance (1.298 (5) Å) is within the normal CN double-bond range<sup>15</sup> and the bond angles about C5 indicate formal  $sp^2$  hybridization (C5A–C5–B4 = 118.1 (3)°; C5A–C5–N11 = 118.0 (4)°; B4–C5–N11 = 123.9 (3)°). Thus, the imine group would be bound to the thiaaborane cage via one boron–carbon  $\sigma$  bond between B4 and C5 (1.555 (6) Å) and a nitrogen–boron dative bond between N11 and B12 (1.490 (6) Å) and as a result would be a three-electron donor to the  $S_2B_7H_8$  cage framework. The thiaaborane cage would contain 26 skeletal electrons and therefore be a nine-vertex hypho cluster. Such a cluster should have a structure based on an icosahedron missing three vertices, which is consistent with the geometry observed for the  $S_2B_7$  framework.

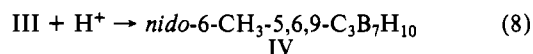
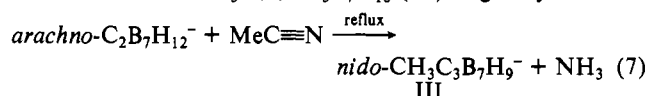
The structure of the bridging imine in II can also be compared with those of other clusters containing coordinated imino ligands. For example, in the complexes  $(\mu-H)Fe_3(CO)_9(\mu_3-\eta^2-HNCMe)^{16}$  and  $(\mu-H)Os_3(CO)_9(\mu_3-\eta^2-HNCCF_3)^{17}$  the ligands are bound to three metal atoms and the CN bond distances are 1.344 (2) and 1.40 (2) Å, while in clusters such as  $(\mu-H)Os_3(CO)_9(P(O)Me)_3(\mu-\eta^2-HCNPh)^{18}$  and  $(\mu-H)Os_3(CO)_{10}(\mu-\eta^2-PhCNMe)^{19}$  the CN group bridges only two metal centers and the distances are shorter, 1.32 (1) and 1.28 (1) Å, respectively. Clearly, the CN bond distance in II is closer to those observed in the last two compounds, again suggesting the presence of significant double-bond character.

The *hypho*- $CH_3CNS_2B_7H_8^-$  anion I, which is initially generated in the reaction with acetonitrile, may also be produced by the reaction of II with sodium hydride:



In principle, II contains two acidic hydrogens, the BHB bridging hydrogen and the NH hydrogen; however, both NMR and chemical evidence establishes that the bridging hydrogen is lost upon deprotonation. Thus, upon deprotonation the resonance at 0.9 ppm (BHB) disappears while the one at 5.9 ppm is unaffected. Likewise, addition of DCl to I generates only the bridge-deuterated derivative, as evidenced by both  $^1H$  NMR spectroscopy and the disappearance of the bridge proton fine coupling on the B2,8 boron resonance (–17.3 ppm) in the  $^{11}B$  NMR spectrum of II.

In contrast to the reaction with *arachno*- $S_2B_7H_8^-$ , the reaction of acetonitrile with *arachno*- $C_2B_7H_{12}^-$  did not result in the incorporation of a CN unit but instead gave the three-carbon carborane anion *nido*- $CH_3C_3B_7H_9^-$  (III) as the sole product. The reaction was very slow, requiring up to 2 weeks at reflux to reach completion. Subsequent acidification of III gave the neutral carborane *nido*-6- $CH_3$ -5,6,9- $C_3B_7H_{10}$  (IV) in good yield:



The spectroscopic data discussed below support the formation of IV as a 10-vertex tricarbon carborane formed by a one-carbon insertion reaction of acetonitrile. The data further indicate that IV is a cage isomer of the *nido*-5,6,10- $Me_3C_3B_7H_8$  carborane recently reported by the Czech group.<sup>20</sup>

Thus, on the basis of its  $2n + 4$  skeletal electron count, IV is proposed to have a nido cage geometry based on an octadecahedron missing one vertex. A number of different arrangements of the carbons within this framework are possible, but a single-crystal X-ray determination<sup>21</sup> of an iron derivative, *closo*-1-( $\eta-C_5H_5$ )- $Fe$ -2,3,4- $Me_3C_3B_7H_9$ , obtained from the reaction of III with  $(\eta-C_5H_5)Fe(CO)_2I$ , established the carbon atom positions proposed for IV in Figure 4. The two carbons of the starting  $C_2B_7$  carborane are nonadjacent in the cage 5- and 9-positions, and the C–Me group, derived from acetonitrile, occupies the 6-position.

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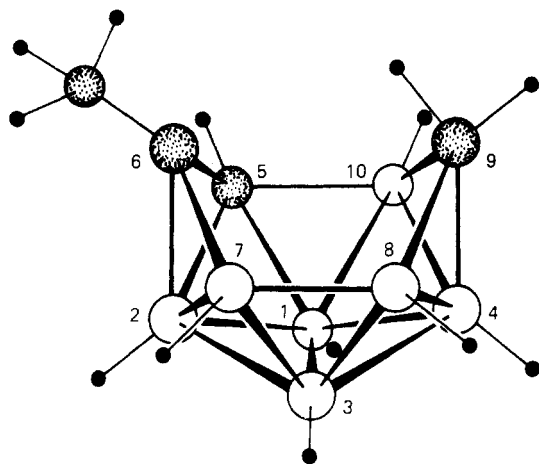


Figure 4. Proposed structure for *nido*-6-CH<sub>3</sub>-5,6,9-C<sub>3</sub>B<sub>7</sub>H<sub>10</sub> (IV).

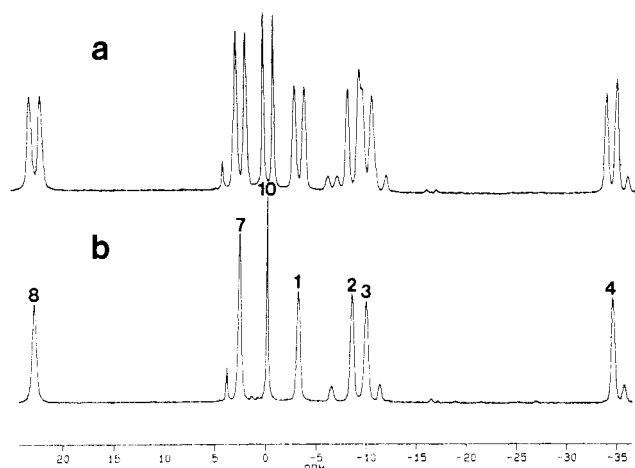


Figure 5. <sup>11</sup>B NMR spectra (160.5 MHz) of IV. Spectrum b is proton spin decoupled.

The <sup>11</sup>B NMR spectrum (Figure 5) of IV is also consistent with the proposed cage skeleton, showing seven different doublets of intensity 1, with the peak at  $-0.2$  ppm having a narrow line width characteristic of a boron (B10) located between two heteroatoms (C5 and C9).<sup>7,22</sup> Furthermore, the <sup>11</sup>B-<sup>11</sup>B COSY 2D NMR spectra show all the expected cross peaks between adjacent borons.

The <sup>1</sup>H and <sup>13</sup>C NMR data are likewise in agreement with the proposed cage structure and confirm the presence of a CH<sub>2</sub> group at the cage 9-position. The <sup>1</sup>H NMR spectrum contains one methyl and three cage CH resonances. The peak at  $-1.56$  ppm is assigned to the 6-CH<sub>endo</sub> proton on the basis of the similarity of its chemical shift to the high-field shifts normally observed for the endo-proton resonances in other carboranes containing CH<sub>2</sub> groups.<sup>7,23</sup> The resonance appears as a triplet owing to coupling (as determined by <sup>1</sup>H-<sup>1</sup>H COSY and <sup>1</sup>H-<sup>11</sup>B heteronuclear correlated NMR experiments) to both the 6-CH<sub>exo</sub> proton and

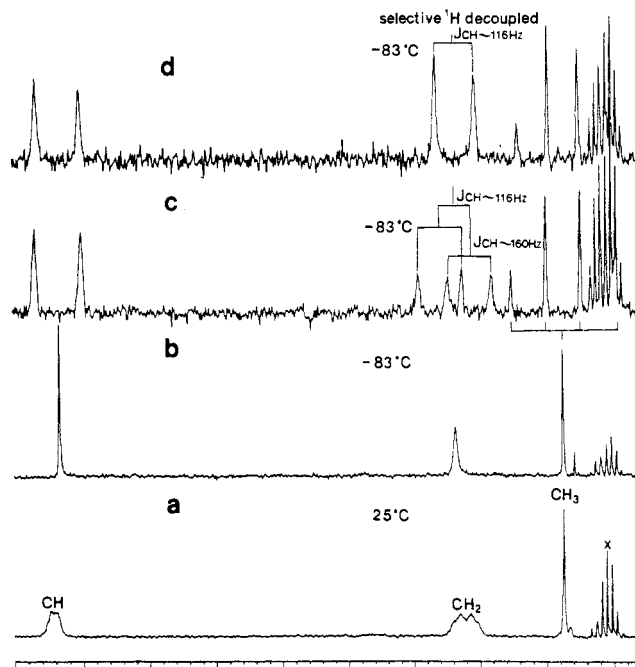


Figure 6. <sup>13</sup>C NMR spectra (50.3 MHz) of IV (resonance arising from C6 at 159.5 ppm not shown): (a) proton-decoupled spectrum at room temperature; (b) proton-decoupled spectrum at  $-83$  °C; (c) proton-coupled spectrum at  $-83$  °C; (d) selective proton-decoupled spectrum with irradiation at the CH<sub>endo</sub> resonance ( $-1.56$  ppm).

the terminal hydrogen on B4. The room-temperature proton-spin-decoupled <sup>13</sup>C NMR spectrum (Figure 6a) shows four broad carbon resonances, corresponding to one methyl carbon and the three cage carbons; however, at low temperatures ( $-83$  °C) the boron-carbon-13 interactions are decoupled<sup>24</sup> and the resonances sharpen dramatically (Figure 6b). The proton-coupled (Figure 6c) and selective proton-decoupled (Figure 6d) spectra recorded at  $-83$  °C confirm the presence of the 5-position CH group (doublet,  $J_{CH} = 172$  Hz) and the 9-position CH<sub>2</sub> group (doublet of doublets,  $J_{CH_{endo}} = 160$  Hz,  $J_{CH_{exo}} = 116$  Hz).

The CH<sub>2</sub> vertex observed in IV is unusual, since in other iso-electronic cages having additional hydrogens, such as B<sub>10</sub>H<sub>14</sub>,<sup>25</sup> *nido*-6-SB<sub>3</sub>H<sub>11</sub>,<sup>5,26</sup> *nido*-5,6-C<sub>2</sub>B<sub>8</sub>H<sub>12</sub>,<sup>27</sup> *nido*-5,7-C<sub>2</sub>B<sub>8</sub>H<sub>12</sub>,<sup>28</sup> and *nido*-5,6,10-Me<sub>3</sub>C<sub>3</sub>B<sub>7</sub>H<sub>8</sub>,<sup>20</sup> the hydrogens bridge to the 6- or 9-position. In IV these positions are occupied by carbons; therefore, the extra hydrogen must either bridge the B7-B8 edge or form a CH<sub>2</sub> group. A B7-B8 bridging hydrogen is unlikely since these are normally only observed in *arachno*-B<sub>10</sub>H<sub>14</sub><sup>2-</sup> analogues, such as *arachno*-6,9-(MeCN)<sub>2</sub>B<sub>10</sub>H<sub>12</sub>,<sup>4,29</sup> *arachno*-9-NEt<sub>3</sub>-6-SB<sub>3</sub>H<sub>11</sub>,<sup>5,30</sup> and *arachno*-6-Me<sub>3</sub>Si-6,9-C<sub>2</sub>B<sub>8</sub>H<sub>13</sub>.<sup>31</sup> Furthermore, since the starting *arachno*-C<sub>2</sub>B<sub>7</sub>H<sub>12</sub><sup>-</sup> anion has one CH<sub>2</sub> group, the retention of this structural unit in IV is reasonable.

## Discussion

The reactions of neutral boron hydrides with nitriles have usually involved initial electrophilic addition at nitrogen and re-

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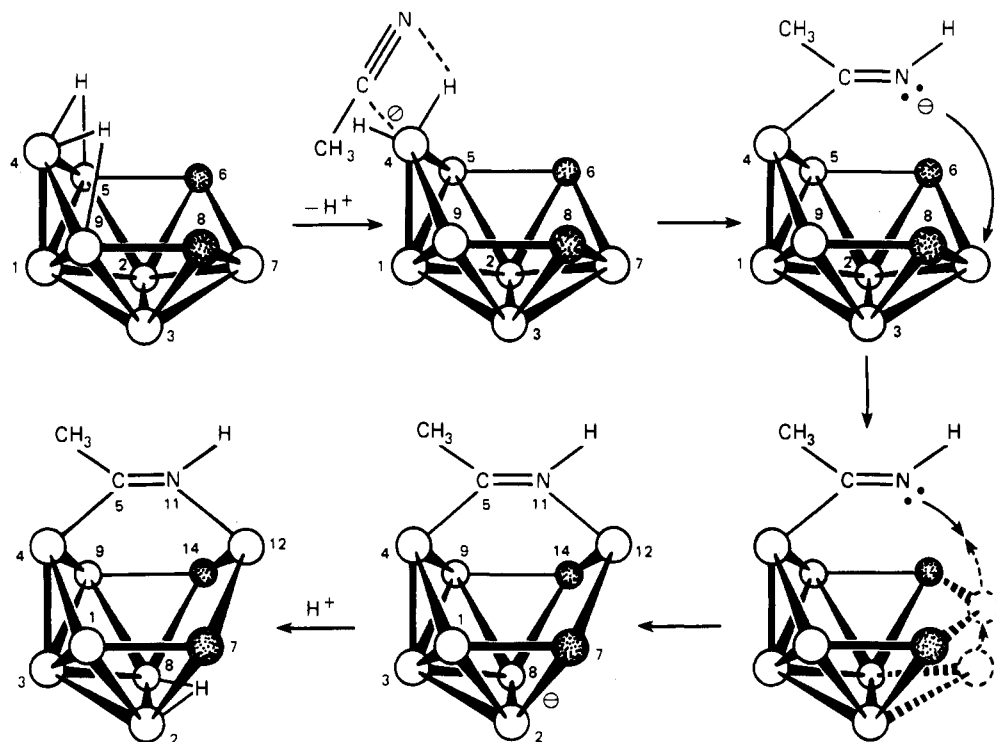
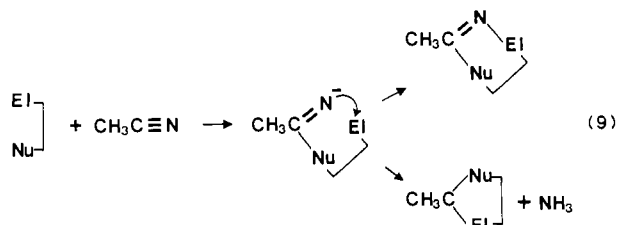


Figure 7. Possible reaction sequence leading to the formation of I and II.

sulted in the production of simple base adducts. However, the  $C\equiv N$  bond in a nitrile is strongly polarized and nucleophilic addition at the electropositive carbon can also occur. For example, acylguanidines react with phenylacetonitrile to produce 1,3,5-triazine derivatives,<sup>32</sup> presumably by a reaction sequence involving initial attack at the nitrile carbon. Likewise, it has been shown that mercaptoamines will react at the nitrile carbon to yield, upon elimination of ammonia, cyclic thiazolines.<sup>33</sup>

We felt that certain polyhedral borane anions might also be capable of undergoing similar types of cyclizations, leading to the formation of new types of clusters derived from nitriles. For example, as outlined in eq 9, if a reactant borane anion is strongly



nucleophilic, then initial addition to a nitrile could form an intermediate, which might then undergo either intramolecular condensation to yield CN incorporation or further elimination of ammonia and one-carbon insertion.

Indeed, it was found that when acetonitrile was reacted with the *arachno*- $S_2B_7H_8^-$  anion, the CN-insertion product *hypho*-5- $CH_3$ -5,11,7,14-CNS $_2B_7H_9$  was produced. A reasonable reaction sequence (Figure 7) could involve an initial nucleophilic attack of the anion at the acetonitrile carbon followed by hydroboration of the nitrile bond. This would then generate a strongly nucleophilic imine intermediate. The most positively charged boron in the original  $S_2B_7$  framework would be expected to be the 7-boron atom, because of its location between the two electronegative sulfur atoms. Therefore, cluster condensation driven by the formation of a nitrogen-boron dative bond between N11 and B7 could result in the rearrangement of the cage in the manner shown in Figure 7 to yield the observed final structure containing

the unique tetrahedral boron B12.

This type of reaction between a polyhedral borane anion and acetonitrile has not been observed previously; however, similar reactions have been reported in metal cluster chemistry. For example, Kaesz<sup>16,34</sup> has studied the stepwise reduction of nitriles at a metal cluster and observed, for example, that  $HF_3(CO)_{11}^-$ , as well as certain other iron carbonyl anions, react with acetonitrile to give the  $Fe_3(CO)_9(\mu-\eta^3-MeCNH)^-$  and  $Fe_3(CO)_9(\mu-\eta^3-MeHCN)^-$  anions, which can then be protonated to yield neutral compounds (Scheme I).

Other clusters containing imino ligands have been generated by, for example, the reaction of metal cluster hydrides with activated nitriles<sup>17,35</sup> or isocyanides.<sup>18</sup> It is also of interest to note that 3 can be thermally converted to 4 and that when 4 is treated with  $H_2$  under pressure further reduction of the  $C=N$  unit occurs to give the nitrene cluster  $(\mu_3-EtN)Fe_3(CO)_9$ . I and II are the polyhedral borane analogues of 1 and 3, but no rearrangement of the nitrile such as observed in the formation of 2, 4, or the nitrene cluster was found. Further reduction of the  $C=N$  unit leading to carbon, rather than nitrogen, cage insertion was observed in the reaction with the *arachno*- $C_2B_7H_{12}^-$  anion, giving *nido*-6- $CH_3$ -5,6,9- $C_3B_7H_{10}$  (IV) as the final product.

A reaction sequence leading to the formation of IV, which is consistent with that proposed for II, is shown in Figure 8. Previous studies have shown that in *arachno*- $C_2B_7H_{12}^-$  the negative charge is localized on a carbon site.<sup>23a,b</sup> Nucleophilic attack of the anion at the nitrile carbon should then generate a product (as is observed for IV) having one of the original cage carbons and the acetonitrile carbon in adjacent positions. Hydroboration of the nitrile would again create an imine intermediate; however, in the carborane there are two additional hydrogens present and complete reduction to

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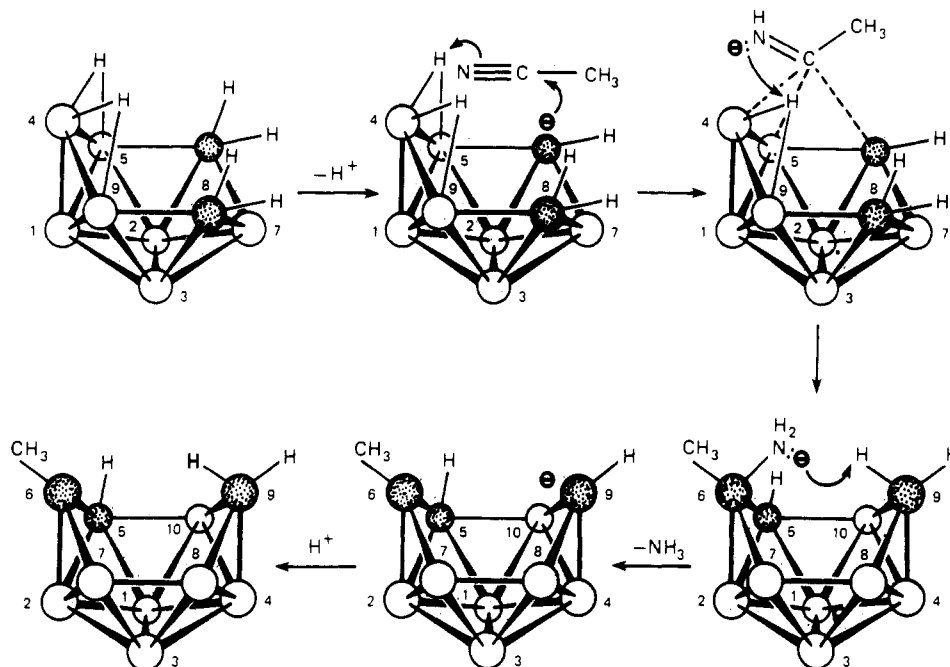
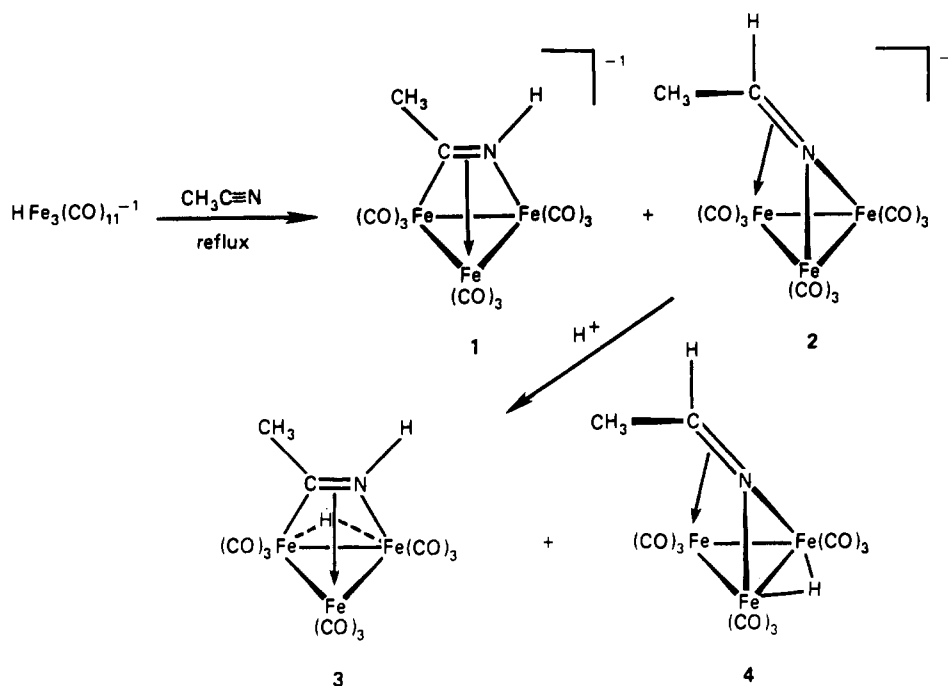


Figure 8. Possible reaction sequence leading to the formation of III and IV.

#### Scheme I



ammonia is possible. This reductive cleavage then allows the incorporation of the nitrile carbon into the cage. This type of sequence is similar to that shown in Scheme I and to that proposed to account for the formation of C-NH<sub>2</sub> cage substituents in the reactions of isocyanides with boranes.<sup>1-3</sup> Likewise, a related type of reductive cleavage of acetonitrile, by hydrogen in the presence of sulfido-bridged molybdenum complexes, that is also accompanied by a one-carbon cluster-insertion reaction to form the molybdenum cluster [(CpMo)<sub>2</sub>(S<sub>2</sub>CH<sub>2</sub>)(S<sub>2</sub>CCH<sub>3</sub>)]<sup>+</sup> has recently been reported by DuBois.<sup>36</sup>

The results presented above indicate that both the thia borane and carborane anions are activated for nucleophilic attack at the acetonitrile carbon. The differences in reactivity observed appear to be directly related to the number of hydrogen atoms available

for reduction. Thus, in the S<sub>2</sub>B<sub>7</sub>H<sub>8</sub><sup>-</sup> anion there is only one extra hydrogen and the formation of an imine group occurs, while in the C<sub>2</sub>B<sub>7</sub>H<sub>12</sub><sup>-</sup> anion three hydrogens are available for reaction, allowing complete reduction resulting in deamination and one-carbon insertion. This conclusion suggests that the reactions of other polyhedral boranes should now be examined and that, depending on the number of bridging hydrogens present, a range of new clusters resulting from either carbon or carbon-nitrogen cage insertions are possible.

Both compounds II and IV can be prepared in large scales and are expected to have a rich chemistry. II is the first member of a new class of larger cage hypophosphorus clusters. Most polyhedral boranes have been found to fall in the closo, nido, and arachno electronic classes with relatively few examples having the *n* + 4 hypophosphorus skeletal electron count. Examples include B<sub>6</sub>H<sub>10</sub>(PMe<sub>3</sub>)<sub>2</sub>,<sup>37</sup>

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$B_5H_{12}^{-38}$ ,  $B_5H_9 \cdot L_2$  ( $L = NR_3$  or  $PR_3$ ),<sup>39,40</sup>  $B_5H_9 \cdot L$  ( $L = dppe$ ,  $dppe$ ,  $tmeda$ , etc.),<sup>41,42</sup>  $B_3H_5 \cdot 3PMe_3$ ,<sup>40b,43</sup>  $Me_3NCB_3H_{11}$ ,<sup>44</sup>  $B_4H_8 \cdot PR_3$ ,<sup>45</sup>  $B_4H_8 \cdot tmeda$ ,<sup>46</sup> and  $B_7H_{12}Fe(CO)_4$ .<sup>47</sup> The isolation of II suggests that a variety of larger cage hypophosphite cluster systems are possible based on the  $S_2B_7$  cage system, and indeed, recent work in our laboratory has already resulted in the synthesis of a number of eight- and nine-vertex hypophosphite clusters.<sup>48</sup>

The fact that II contains three open faces suggests that it may also serve as a versatile starting material for the construction of new hybrid clusters in which various heteroatoms can be inserted into these faces. Of particular interest is the 5-fold face B2, B8, S14, B12, S7, which contains the boron-boron-bridging hydrogen. If the bridging proton is removed, then a pentagonal face is

generated with a formal -1 charge. This would be a direct analogue of a  $C_5H_5^-$  ligand; however, because the B-S distances in the ring ( $\sim 1.90$ - $1.96$  Å) are longer than the C-C distances in a cyclopentadienyl ring (average C-C  $\approx 1.4$  Å), the thiaaborane ring is larger. Thus, the distances across the face, S7-S14 = 3.24 Å and B2-B12 = 3.01 Å, are considerably longer than the  $\sim 2.3$  Å observed between nonadjacent carbons in a cyclopentadienyl ring. This difference in size may result in unique bonding abilities.

IV is one of the few members of the tricarbon carborane series, the only others being *nido*- $C_3B_3H_7$ ,<sup>49</sup> *closo*- $C_3B_3H_7$ ,<sup>50</sup> and the recently reported *nido*-5,6,10- $Me_3C_3B_3H_8$ ,<sup>20</sup> and is the only such compound to have a  $CH_2$  cage vertex. Given the few compounds in this series and the absence of efficient synthetic routes, the chemistry of this carborane class has not yet been extensively developed. IV is now the most available tricarbon carborane and may serve as both a useful precursor to other such carboranes and as a starting material for the construction of new heteroatom cluster systems.

**Acknowledgment.** We thank the National Science Foundation for the support of this research. We also thank Dr. Robert Williams for his comments concerning the structure of II.

**Supplementary Material Available:** Tables of anisotropic temperature factors, hydrogen atom coordinates, bond angles, and least-squares planes (4 pages); a listing of observed and calculated structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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## Complexes of Rhenium Carbonyl Containing Ferrocenyl-Derived Ligands: Tunable Electron Density at Rhenium by Control of the Redox State of the Ferrocenyl Ligand

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The new complexes  $(Fe(C_5H_4PPh_2)_2)Re(CO)_3Cl$ , *cis*- $(FcPPh_2)Re(CO)_4Cl$ , *fac*- $(FcPPh_2)_2Re(CO)_3Cl$ , *fac*- $(FcPy)_2Re(CO)_3Cl$ , and  $FcRe(CO)_5$  ( $Fc = ferrocenyl$ ;  $Py = 4$ -pyridyl) have been synthesized and characterized for the purpose of investigating the tunability of the electron density on Re by changes in the redox state of the ferrocene center(s). The structures of  $(Fe(C_5H_4PPh_2)_2)Re(CO)_3Cl$  and *fac*- $(FcPPh_2)_2Re(CO)_3Cl$  were solved by X-ray crystallography. Structural parameters: for  $(Fe(C_5H_4PPh_2)_2)Re(CO)_3Cl$ ,  $a = 11.650$  (2) Å,  $b = 19.534$  (5) Å,  $c = 14.318$  (2) Å,  $\beta = 93.76$  (1)°,  $V = 3251$  (2) Å<sup>3</sup>,  $Z = 4$ , space group  $P2_1/c$ ,  $R_1 = 0.032$ ,  $R_2 = 0.033$ ; for *fac*- $(FcPPh_2)_2Re(CO)_3Cl$ ,  $a = 11.859$  (2) Å,  $b = 20.105$  (4) Å,  $c = 17.060$  (3) Å,  $\beta = 92.26$  (1)°,  $V = 4064$  (2) Å<sup>3</sup>,  $Z = 4$ , space group  $P2_1/c$ ,  $R_1 = 0.049$ ,  $R_2 = 0.049$ . All of the complexes exhibit ferrocene-based, reversible oxidations. The oxidized complexes were prepared in situ, either by electrochemical cell or by chemical oxidation, and characterized by spectroscopic methods (IR and UV/vis) and by reduction back to the neutral complexes. The carbonyl stretching frequencies in all of the complexes shift to higher energy upon oxidation. The magnitudes of the shifts range from 12-33  $cm^{-1}$  for  $FcRe(CO)_5$  to 4-7  $cm^{-1}$  for  $(FcPy)_2Re(CO)_3Cl$  and are closely related to the number of bonds separating the ferrocene moiety and the Re atom.

We wish to report the synthesis, characterization, and properties of the Re carbonyl complexes shown in Scheme I, all of which have ligands derived from ferrocene. We are interested in organometallic complexes having pendant redox-active ligands, because changing the oxidation state of a pendant ligand should change the spectroscopic properties and reactivity of the metal in such complexes without changing the immediate coordination

sphere. Numerous series of complexes have been studied where systematic changes in the ligand, e.g.  $C_5H_5$  vs  $C_5Me_5$ , have profound effects on the spectroscopic properties and reactivity of the metal center.<sup>1-3</sup> In such situations, changes in chemical properties often stem from a combination of electronic and steric effects. Tuning of electron density in the central metal of a

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