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METAL-PENTABORANE(9) DERIVATIVES: 2-[$Co(CO)_4$]B_5H_8 AND 2-[(η^5-C_5H_5)$Fe(CO)_2$]B_5H_8

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Summary

Reaction of 2-XB_5H_8 (X = Cl, Br) with $NaCo(CO)_4$ produces the transiently stable 2-[$Co(CO)_4$]B_5H_8. The similar 2-[(η^5-C_5H_5)$Fe(CO)_2$]B_5H_8, which exhibits much greater thermal stability, is prepared by reaction of LiB_5H_8 with (η^5-C_5H_5)$Fe(CO)_2I$. Reactions of $Co_2(CO)_8$ with B_5H_9 under a variety of conditions produce 2-[$Co(CO)_4$]B_5H_8 along with an inseparable impurity that appears to be 1-[$Co(CO)_4$]B_5H_8.

Introduction

Though several σ bonded monodentate borane complexes of transition metals have been described, they are by no means common. Our interest in the chemistry of pentaborane(9), B_5H_9, as a ligand, led to the preparation of 2-[$M(CO)_5$]B_5H_8 (M = Mn, Re) via nucleophilic displacement of chloride in 1- or 2-ClB_5H_8 with $NaM(CO)_5$ in ethereal solvents [1]. More recently Churchill, Davison et al. [2] and Wreford et al. [3] found that σ bonded 2-B_5H_8 complexes can also be obtained by oxidative addition of 1- or 2-XB_5H_8 (X = Cl, Br) or B_5H_9 to *trans*-$IrCl(CO)(PMe_3)_2$, producing 2-[$IrBr_2(CO)(PMe_3)_2$]B_5H_8, 2-[$IrCl_2(CO)(PMe_3)_2$]B_5H_8, 2-[$IrClH(CO)(PMe_3)_2$]B_5H_8, and 1-Cl-2-[$IrClH(CO)(PMe_3)_2$]B_5H_7. We report here two methods for the preparation of σ bonded B_5H_8 complexes of transition metals. One method involves electrophilic displacement of halide from (η^5-C_5H_5)$Fe(CO)_2I$ by the $B_5H_8^-$ anion to produce moderate yields of 2-[(η^5-C_5H_5)$Fe(CO)_2$]B_5H_8. The other method involves the reaction of $Co_2(CO)_8$ with B_5H_9 to produce low yields of 1- and 2-[$Co(CO)_4$]-B_5H_8. The 2-[$Co(CO)_4$]B_5H_8 may also be prepared via nucleophilic displacement of halide in 2-XB_5H_8 (X = Cl, Br) by reaction with $NaCo(CO)_4$.

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Experimental

All air-sensitive compounds were handled using inert-atmosphere or high vacuum techniques [4]. Pentane, benzene, and diethyl ether were dried over $LiAlH_4$, and CH_2Cl_2 was dried over 3 Å molecular sieves. All solvents were vacuum distilled before use. Deuterated solvents were treated in the same manner as their protonic counterparts.

The B_5H_9 was laboratory stock. LiB_5H_8 was prepared from n-butyllithium and pentaborane(9) [5]. 1-Cl- [6], 2-Cl- [6], 1-Br- [7], and 2-Br-B_5H_8 [8], and $Co_2(CO)_8$ [9] were prepared using published methods. Other reagents were obtained commercially and were used as received.

The ultraviolet irradiation sources used were a General Electric Mercury Projector Spot (No. H100PSP444). All gas- and solution-phase infrared spectra were obtained in cells with NaCl windows. Low resolution (±10 cm^{-1}) infrared spectra were obtained on a Perkin—Elmer Model 700 infrared spectrophotometer.

Mass spectra were obtained using an AEI MS 902 spectrometer.

The NMR spectra were obtained on a Bruker WH-270 spectrometer, operating at 270.071 MHz (^1H) and 86.653 MHz (^{11}B).

Syntheses of $[Co(CO)_4]B_5H_8$

A. Photolysis of $Co_2(CO)_8$ *in liquid* B_5H_9. A typical photolysis reaction flask was constructed from 8 cm of 12 mm o.d. quartz tubing sealed at one end and attached via a graded seal to a 4 mm Kontes o-ring stopcock. The flask was loaded with 0.77 g (2.3 mmol) of $Co_2(CO)_8$, evacuated, and cooled in liquid nitrogen. Then 6.8 ml (67 mmol) of B_5H_9 was condensed onto the solid. The flask was warmed to ambient, stirred magnetically, and irradiated for 23 h with a General Electric ultraviolet lamp, during which 0.196 mmol of noncondensible gas was formed. The flask was warmed to ambient and the volatile contents distilled in high vacuum into traps cooled to —63 and —196°C in series. The —196°C trap contained B_5H_9 and $HCo(CO)_4$. The —63°C trap contents were distilled quickly into another trap at —196°C several times to separate the yellow-brown liquid from the excess $Co_2(CO)_8$. The liquid was then condensed several times into —63°C traps. The liquid, thermally unstable and obtained in low yield, consisted primarily of 2-$[Co(CO)_4]B_5H_8$ as shown by NMR and mass spectroscopy, but also contained small amounts of 1-substituted B_5H_9 derivative, most probably 1-$[Co(CO)_4]B_5H_8$.

B. Reaction of $NaCo(CO)_4$ *and* 2-ClB_5H_8. A 100 ml round-bottomed flask, equipped with two 4 mm Kontes o-ring stopcocks (one for connection to the vacuum line and the other for removal of unreacted sodium amalgam) and a magnetic stir bar, was loaded with 0.17 g (0.50 mmol) $Co_2(CO)_8$ and 2.8 ml of 1% sodium amalgam (1.6 mmol Na). The flask was evacuated, cooled with liquid nitrogen, and 10 ml diethyl ether was condensed into the flask, which was then charged with one atmosphere of carbon monoxide, and stirred for 22 h at room temperature. The amalgam was decanted and the carbon monoxide and diethyl ether were removed. The flask was then cooled in liquid nitrogen, and 0.082 g (0.84 mmol) of 2-ClB_5H_8 and 20 ml pentane were condensed onto the salt. The flask was charged with one atmosphere of carbon monoxide and allowed to warm to room temperature. The solution was stirred for five days and then cooled in liquid nitrogen. The carbon monoxide was removed at —196° C, and, as the reaction flask slowly warmed up to room temperature, the volatile contents distilled into traps cooled to —63 and —196° C in series. The contents of the —196° C trap was confirmed as 2-ClB_5H_8 and pentane by infrared spectroscopy. The —63° C trap contained 2-$[Co(CO)_4]B_5H_8$ along with some 2-ClB_5H_8 as confirmed by infrared spectroscopy. This mixture was distilled into traps cooled to —50° C several times. The 2-ClB_5H_8 and pentane were returned to the reaction flask to continue reacting as before for three days. This process was repeated for a total of four times and gave low yields of isomerically pure 2-$[Co(CO)_4]B_5H_8$.

C. Pyrolysis of $Co_2(CO)_8$ in liquid B_5H_9. A 12 mm o.d. U-shaped tube of approximately 7 ml volume, equipped with a break-tip and 14/35 standard taper joint on one end and a constriction and 14/35 standard taper joint on the other end, was loaded with 0.98 g (2.9 mmol) $Co_2(CO)_8$, evacuated and cooled with liquid nitrogen. Approximately 4 ml (39 mmol) B_5H_9 was condensed in, and the tube was sealed and allowed to warm up to room temperature. After the $Co_2(CO)_8$ was dissolved, the tube was heated to 75°C for three days. (Temperatures between 60 and 90°C were effective). The tube was then cooled in liquid nitrogen, opened, and 1.4 mmoles of noncondensible gases were measured. The volatile contents of the reaction tube were distilled into traps cooled to —78 and —196°C in series. The contents of the —78°C trap were then purified in the same manner as described in synthesis A. Yields were moderate but superior to the other methods.

Synthesis of 2-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_5H_8$

8.03 mmol (2.44 g) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ were loaded into an addition tube, which was then connected through a ground glass joint to a 100 ml flask equipped with a Teflon o-ring stopcock. Then 8.0 mmol of LiB_5H_8 in diethyl ether solution were prepared in the flask, and the $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ was added to the solution at —40°C. The solution was stirred for 3.5 h while the temperature rose slowly to 0°C. Volatile products were removed on the vacuum line and the residue was dissolved in a minimum of dichloromethane and placed on a florisil chromatography column. A yellow band was eluted with hexane, the solvent was stripped and the residue distilled in high vacuum at room temperature to yield a yellow oil identified as 2-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_5H_8$ by its infrared, ^{11}B and ^1H NMR, and mass spectra. The yield was 0.210 g (0.875 mmol, 10.9%).

Physical properties. 2-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_5H_8$ is a low volatility, yellow-brown oil soluble in hexane, benzene, methylene chloride and diethyl ether. It is not stable in air, but in a stopped container it is only partially decomposed after 10 days at room temperature.

2-$[Co(CO)_4]B_5H_8$ is a thermally unstable yellow-brown liquid, leaving a brown residue upon distillation from one vacuum line U-trap to another. Solutions in benzene-d_6 also decompose, leaving a brown flocculent material. In the gas phase it appears sufficiently stable for infrared studies. Trace amounts left in the chamber connecting the IR cell to the vacuum line often flash upon contact with air. Its volatility is appreciably greater than its relative, 2-$[Mn(CO)_5]B_5H_8$. It is soluble in pentane, benzene-d_6, diethyl ether, and pentaborane(9).

Infrared spectrum. The uncompensated infrared spectrum of 2-[(η^5-C_5H_5)Fe(CO)$_2$]B_5H_8 in hexane solution contains the following absorptions: 2600(s) (B—H stretch), 2010(vs) and 1955(vs) (carbonyl stretches), 1800(vw) (B—H—B), 1365(w), 970(m), 890(s), 840(s), 825(m), and 760(m) cm^{-1}.

The saturated vapor gas-phase spectrum of 2-[Co(CO)$_4$]B_5H_8 contains one frequency in the B—H stretch region at 2650(m) cm^{-1} and four C—O stretching frequencies at 2150(m), 2080(ms), 2060(s), and 2030(s) cm^{-1}. No other frequencies are discernable. All frequencies are ±10 cm^{-1}.

Mass spectra. The 70 eV mass spectrum of 2-[(η^5-C_5H_5)Fe(CO)$_2$]B_5H_8 exhibits a pattern similar to that of other metalloboranes [10]. Envelopes at *m/e* values corresponding to the P, $P - \mathrm{CO}$ and $P - 2\ \mathrm{CO}$ peaks are evident. A peak match for the parent peak was used for molecular weight determinations. Calculated for $^{12}C_5{}^1H_5{}^{56}Fe(^{12}C^{16}O)_2{}^{11}B_5{}^1H_8$, 240.0729; found, 240.0731. The 70 eV mass spectrum of 2-[Co(CO)$_4$]B_5H_8 exhibits envelopes at the P, $P - \mathrm{CO}$, $P - 2\ \mathrm{CO}$, $P - 3\ \mathrm{CO}$ and $P - 4\ \mathrm{CO}$ peaks. A peak match for the parent peak was used for molecular weight determination: calculated for $(^{12}C^{16}O)_4{}^{59}Co^{11}B_5{}^1H_8$, 234.0219; found, 234.0216.

NMR spectra. The 86.653 MHz ^{11}B NMR spectral data for 2-[(η^5-C_5H_5) Fe(CO)$_2$]B_5H_8 and 2-[Co(CO)$_4$]B_5H_8 are tabulated in Table 1 along with comparative data of other 2-*exo*-metallo-substituted pentaboranes. The suspected 1-[Co(CO)$_4$]B_5H_8 gives two resonances: a larger resonance at -12.57 ppm (doublet) and a smaller resonance at -47.73 ppm (singlet). Upon ^{1}H decoupling the -12.57 resonance exhibited a residual quartet coupling of 24 hz. Such coupling results from ^{11}B apical—^{11}B basal coupling which is observed in B_5H_9 and in apically (1—) substituted derivatives.

The 270.971 MHz ^{1}H NMR spectrum of 2-[(η^5-C_5H_5)Fe(CO)$_2$]B_5H_8 in C_6D_6 shows slight overlapping of the basal terminal proton quartets at δ 2.68 ppm ($J = 152$ Hz) with the apical terminal proton quartet at δ 1.04 ppm ($J = 169$ Hz). The two different types of bridge hydrogens give broad resonances at δ -1.28 and -2.19 ppm. In addition, there is a singlet at δ 4.17 ppm attributed to the cyclopentadienyl ring.

The 270.071 MHz ^{1}H NMR spectrum of 1- and 2-[Co(CO)$_4$]B_5H_8 in C_6D_6

TABLE 1

^{11}B NMR RESONANCES [a] OF 2-*exo*-METALLO-SUBSTITUTED PENTABORANES 2-M-B_5H_8 AND 2-M-1-Cl-B_5H_7

M	B(2)	B(3,5)	B(4)	B(1)
(η^5-C_5H_5)Fe(CO)$_2$ [b,c,e]	+7.57	−11.02(159)	−14.78(164)	−48.56(169)
Co(CO)$_4$ [b,c]	−4.51	−11.04(133)	−14.48(171)	−48.97(181)
Mn(CO)$_5$ [c,d]	−0.78	−10.59(133)	~−11.50 (approx. 130)	−48.86(170)
Re(CO)$_5$ [d]	−11.5	−10.6(155)	−10.6(155)	−49.0(171)
IrBr$_2$(CO)(PMe$_3$)$_2$ [f,g,h]	−11.3	−14.4	−17.3	−50.2
IrCl$_2$(CO)(PMe$_3$)$_2$ [g]	−15.4(b)	−15.4(b)	−15.4(b)	−50.0(160)
1-Cl, 2-IrClH(CO)(PMe$_3$)$_2$ [g,h]	−17.7(b)	−17.7(b)	−17.7(b)	−27.9

[a] Chemical shifts are positive downfield from $BF_3 \cdot O(C_2H_5)_2 = 0.00$ ppm, with coupling constants in Hz where known in parentheses, d = doublet, b = broad and unresolved. [b] This work. [c] Measured at 86.653 MHz. [d] Ref. 1. [e] Ref. 20. [f] Ref. 22. [g] Ref. 3. [h] Only ^{11}B-{^{1}H} NMR spectral data reported.

shows overlapping quartets due to hydrogens terminally bonded to boron with peaks at δ +3.36, +2.85, +2.15, +1.64, +0.87, and +0.30 ppm relative to TMS at δ 0.00 ppm. Broad resonances of unequal area attributed to hydrogens bridging two borons appear at δ −1.79 and −2.36 ppm.

Results and discussion

[Co(CO)$_4$]B$_5$H$_8$. Both photolysis and pyrolysis of $Co_2(CO)_8$ in B_5H_9 produce the mixture of 1- and 2-$[Co(CO)_4]B_5H_8$. Reactions of $NaCo(CO)_4$ with 2-ClB_5H_8 or 2-BrB_5H_8 in pentane produce only the 2-$[Co(CO)_4]B_5H_8$ isomer; however, yields produced by this route are quite low. Unfortunately, in diethyl ether the latter reaction produces an inseparable mixture of 2-$[Co(CO)_4]B_5H_8$ with a suspected ether cleavage product, 2-$C_2H_5OB_5H_8$ [10]. The idealized reactions are:

$$Co_2(CO)_8 + 2\ B_5H_9 \xrightarrow[B_5H_9]{h\nu \text{ or } \Delta} 2\ \ 1\text{- and } 2\text{-}[Co(CO)_4]B_5H_8 + H_2 \qquad (1)$$

$$NaCo(CO)_4 + 2\text{-}XB_5H_8 \xrightarrow[C_5H_{12}]{} 2\text{-}[Co(CO)_4]B_5H_8 + NaX \qquad (X = Cl, Br) \qquad (2)$$

The photolysis and pyrolysis reactions possibly involve initial production of $Co(CO)_4$ radicals [11] which could attack B_5H_9 in either the apical or basal positions to give both isomers of the σ-bonded product. Other examples that may involve radical species reacting with pentaborane(9) include the uncatalyzed reaction with chlorine to give a 15% yield of 2-ClB_5H_8 with only a trace of 1-ClB_5H_8 [12], the uncatalyzed reaction with bromine to give 4% 2-BrB_5H_8 and 82% 1-BrB_5H_8 [8], the photolysis reaction with bromine to give 25% 2-BrB_5H_8 and 20% 1-BrB_5H_8 [8], and the photolysis of pentaborane(9) in the presence of mercury vapor to produce 2,2′-$(B_5H_8)_2$ [13]. The reaction involving $NaCo(CO)_4$ and 2-XB_5H_8 most likely proceeds by a nucleophilic displacement of halide by the cobalt carbonyl anion

The infrared spectrum contains one frequency in the B—H (terminal) stretch region, while the C—O (terminal) region has four distinct bands, which suggests that the borane likely occupies an equatorial substituent position in the trigonal bipyramid coordination about the cobalt [14]. Other compounds of general formula $RCo(CO)_4$ have been crystallographically shown [15] or spectroscopically assigned [16] trigonal bipyramidal coordination with the R in an axial position. The reason given for axial substitution is that equatorial substitution would be energetically less favorable owing to the fact that two (strongly π-bonding) *trans*-CO groups are both competing for the same electrons in the cobalt d_{xz} and d_{yz} orbitals with which they have equally good overlap [16]. Since 2-$[Co(CO)_4]B_5H_8$ appears to have equatorially substituted trigonal bipyramidal coordination about the cobalt, two *trans*-CO groups appear to be energetically more favorable than a CO-group *trans* to the pentaboran(9)yl ligand. A possible explanation for the equatorial substitution lies in the filled metal d orbitals of the metal interacting with π acceptor cage orbitals of the pentaboran(9)yl ligand. An X ray crystal structure of $Ir(B_5H_8)Br_2(CO)(PMe_3)_2$ showed that the bromine *trans* to 2-pentaboran(9)yl ligand was 2.64 Å from the iridium, which was much longer than the iridium—bromine distance of 2.52 Å for the bromine *trans* to the CO group and normal Ir^{III}—Br distances of 2.50—2.53 Å. The conclusion was that σ-bonded boron exerts a stronger *trans*-lengthening effect than either carbonyl ligands or σ-bonded carbon [2]. Several crystal structures [17] and variable temperature NMR studies [18] of trigonal bipyramidal transition metal complexes suggest that strong π-acceptor ligands prefer equatorial sites in trigonal bipyramidal coordination.

2-[(η⁵-C₅H₅)Fe(CO)]B₅H₈. The reaction of LiB_5H_8 with $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ illustrates nucleophilic displacement of a halide from a metal by a borane anion to form a σ metal—borane bond. A related reaction is that between $B_{10}H_{13}^-$ salts and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\text{cyclohexene})]PF_6$ which produces $6\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_{10}H_{13}$ [19].

The $2\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_5H_8$ was identified as a 2-substituted B_5H_9 derivative on the basis of its ^{11}B and ^1H NMR spectra (Table 1 and Figs. 1 and 2). Its proposed structure, shown in Fig. 3, is consistent with the structure deduced by Greenwood et al. [20].

Other pentaboranes that are terminally substituted by a transition metal are listed in Table 1 along with their ^{11}B chemical shifts. The chemical shift of the B(2) resonance of $2\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_5H_8$ is at quite low field. Only the shift for the B(2) atom in $2\text{-}FB_5H_8$ (+8.2 ppm) is at lower field among 2-substituted pentaborane derivatives. By comparison, the ^{11}B NMR spectra of other pentaborane metal complexes indicate a much smaller effect from Mn, Co, Re and Ir on the boron atom to which it is bonded. The change in the B(2) shift in these species compared to B(2—5) in B_5H_9 is as follows: $2\text{-}[IrCl_2(CO)(PMe_3)_2]B_5H_8$, —1.7, $2\text{-}[Re(CO)_5]B_5H_8$, +2.2; $2\text{-}[IrBr_2(CO)(PMe_3)_2]B_5H_8$, +2.4; $2\text{-}[Co(CO)_4]B_5H_8$, +9.2; $2\text{-}[Mn(CO)_5]B_5H_8$, +12.9; and $2\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_5H_8$, +21.3. The Co and Mn complexes show significant change, but not nearly as large as occurs for $2\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_5H_8$. The resonance arising from the boron atom *trans* to the position of substitution, B(4), in $2\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_5H_8$ is shifted upfield by approximately 2 ppm. Empirical correlations of the ^{11}B NMR spectra of several 2-substituted B_5H_9 derivatives indicate that a

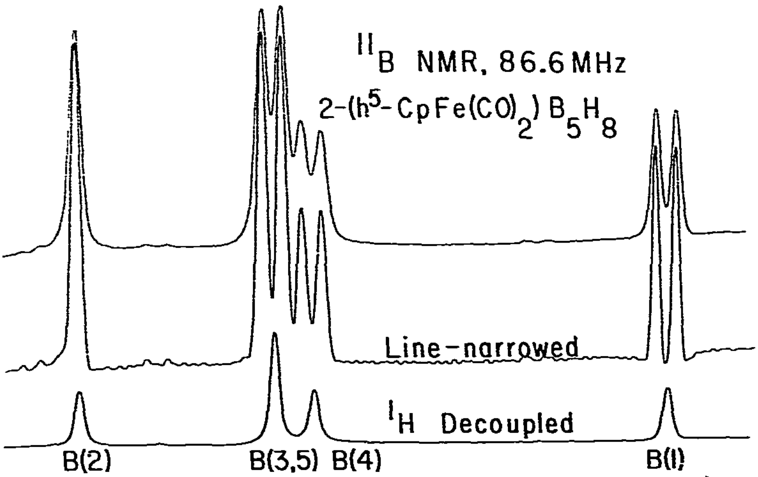

Fig. 1. The 86.6 MHz ^{11}B NMR spectra of $2\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_5H_8$ in C_6D_6 solution.

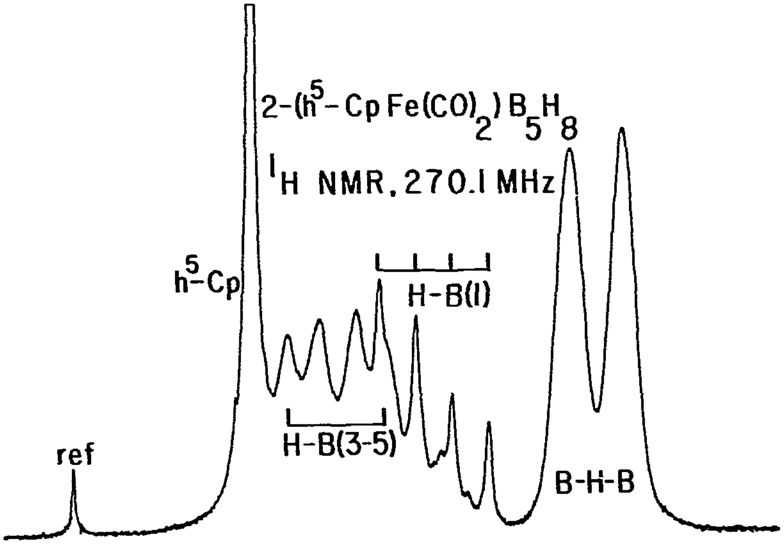

Fig. 2. The 270.1 MHz ^1H NMR spectrum of 2-[(η^5-C_5H_5)Fe(CO)$_2$]B_5H_8 in C_6D_6 solution.

substituent on B(2) that causes the *trans* B(4) resonance to shift upfield from the B(2—5) resonance in B_5H_9 is an indicator of greater thermodynamic stability for that isomer compared to the corresponding 1-substituted isomer. Examples exhibiting this upfield *trans* effect are 2-ClB_5H_8 [7], 2-BrB_5H_8 [21], 2-$CH_3B_5H_8$ [21], and 2-$C_2H_5B_5H_8$ [21]. Those species in which the B(2) substituent causes a downfield *trans* effect, such as 2-IB_5H_8, 2-$H_3SiB_5H_8$ [22], and 2-$(CH_3)_3SiB_5H_8$ [22], are more stable as their 1-isomers. The upfield *trans* effect exhibited by 2-[(η^5-C_5H_5)Fe(CO)$_2$]B_5H_8 thus suggests that this isomer is the more thermodynamically stable. Since 2-[Co(CO)$_4$]B_5H_8 has an upfield shifted B(4) resonance, the 2-isomer should be more stable, and it is a little surprising to see resonances attributable to a 1-isomer. On the other hand, the manganese and rhenium derivatives have downfield shifted B(4) resonances but their corresponding 1-isomers are unknown.

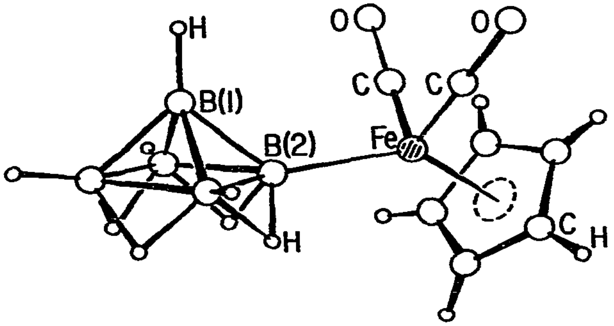

Fig. 3. The proposed structure of 2-[(η^5-C_5H_5)Fe(CO)$_2$]B_5H_8.

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