# Examples of Three-Center Transition Metal to Boron Bonding. The Hexaborane(10) Complexes

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**Abstract:** Hexaborane(10) is shown to form the complexes $\mu$-Fe(CO)$_4\cdot$B$_6$H$_{10}$, *trans*-Pt(B$_6$H$_{10}$)$_2$Cl$_2$, Rh(B$_6$H$_{10}$)$_2$-(acac), [Rh(B$_6$H$_{10}$)$_x$Cl]$_2$, and [Ir(B$_6$H$_{10}$)$_2$Cl]$_2$. The compounds have been characterized by elemental analysis and ir, $^1$H nmr, and $^{11}$B nmr spectral studies. The ligand is thought to be bound *via* a three-center, two-electron bond with the transition metal in the 4,5 bridging position.

Hexaborane(10) has been shown to possess an anomalously short boron–boron bond along a basal edge of its pentagonal pyramidal structure.[1] The basicity of this site has been postulated to be responsible for exchange of bridge protons with D$_2$O[2] and DCl.[3] Indeed, the presumed intermediate B$_6$H$_{11}$$^+$ has been isolated[4] and had previously been predicted to be stable.[5] B$_{15}$H$_{23}$ has been prepared from the reaction of B$_6$H$_{10}$ with *i*-B$_9$H$_{15}$ and has been suggested to consist of a B$_9$H$_{13}$ unit bound to the B$_6$H$_{10}$ substrate *via* a three-center bond.[6]

In this paper we describe a variety of transition metal complexes of B$_6$H$_{10}$, in which the metal is regarded as having inserted into the unique basal boron–boron bond to form a three-center, two-electron bond. Some of these results have been communicated previously.[7]

## Results and Discussion

$\mu$-**Fe(CO)$_4\cdot$B$_6$H$_{10}$.** Inasmuch as Fe$_2$(CO)$_9$ reacts under mild conditions with a variety of Lewis bases, it appeared an ideal candidate for the preparation of B$_6$H$_{10}$ complexes. Subsequently, we found reaction 1

$$\text{Fe}_2(\text{CO})_9 + \text{B}_6\text{H}_{10} \longrightarrow \text{Fe(CO)}_5 + \mu\text{-Fe(CO)}_4\cdot(\text{B}_6\text{H}_{10}) \quad (1)$$

proceeds in high yield under ambient conditions. The product is a volatile, yellow, crystalline solid. The same product may be obtained from photolysis of Fe(CO)$_5$ and B$_6$H$_{10}$[8] or from shaking B$_4$H$_{10}$ with excess Fe$_2$(CO)$_9$.[9]

The presence of coordinated B$_6$H$_{10}$ is suggested by liberation of the same during thermal decomposition of the complex. The formulation is further supported by the mass spectral evidence: a molecular ion is observed (*m/e* 243 for $^{10}$B$^{11}$B$_5$$^{56}$Fe$^{12}$C$_4$$^{16}$O$_4$) with an isotope pattern agreeing very closely with that calculated for a B$_6$C$_4$Fe-containing fragment; isotope clusters 28, 56, 84, and 112 mass units below the parent ion are consistent with the presence of an Fe(CO)$_4$ unit; free B$_6$H$_{10}$ is the dominant feature of the spectrum. Further, the four carbonyl bands with near degeneracy of

the lower energy B$_1$ and B$_2$ modes are typical of an Fe(CO)$_4$ unit under local $C_{2v}$ symmetry.[10]

The $^{11}$B nmr spectrum in Figure 1 shows a low field multiplet (5B) and a high field doublet (1B, $J_{BH}$ = 159 Hz), which collapse on proton decoupling to resonances at $-11.4$ (B$_2$), $-4.9$ (B$_3$, B$_6$), $-0.2$ (B$_4$, B$_5$), and 54.4 (B$_1$) (the assignments to B$_3$, B$_6$ and B$_4$, B$_5$ are ambiguous and may be reversed). Thus, the $^{11}$B nmr data support the $C_S$ symmetry required by the 4,5-bridged structure, which is not observed for uncomplexed B$_6$H$_{10}$.[11] The $^1$H nmr spectrum in Figure 2 shows a broad, partially resolved multiplet extending from $-9.4$ to 4.8. On basal $^{11}$B decoupling the multiplet collapses to relatively sharp resonances at $-4.1$ (B$_2$, B$_3$, B$_6$–H$_T$), $-3.1$ (B$_4$, B$_5$–H$_T$), $-0.1$ (B$_{2,3}$–H$_\mu$, B$_{2,6}$–H$_\mu$), and 1.2 (B$_{3,4}$–H$_\mu$, B$_{5,6}$–H$_\mu$) (the assignments to the two sets of bridge hydrogens are ambiguous and may be reversed) superimposed on a weak quartet (B$_1$–H$_T$) whose high field member is clearly visible at 3.2. Hence, the $^1$H nmr data also conform to the postulated $C_S$ symmetry. Such behavior is observed in uncomplexed B$_6$H$_{10}$ only on cooling to $-147°$.[12]

In the valence bond formalism two reasonable resonance structures may be written



1



2

B = BH

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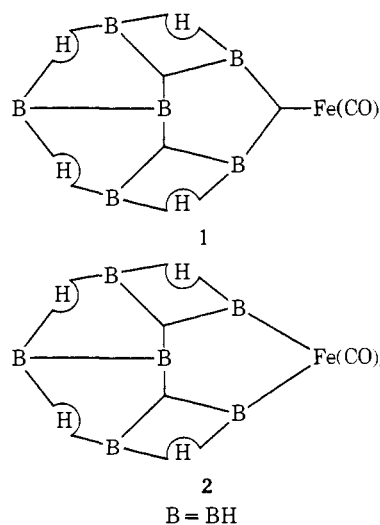
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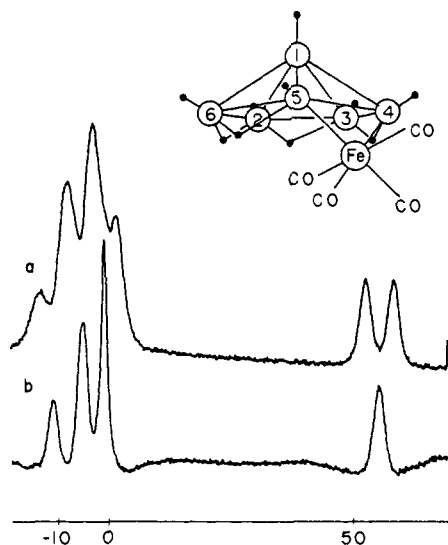(12) V. T. Brice, H. D. Johnson, II, and S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 1128 (1972).

Figure 1. (a) The $^{11}$B nmr spectrum of $\mu$-Fe(CO)$_4$·B$_6$H$_{10}$ in hexane at 26°. (b) The $^{11}$B-{$^1$H} (in conformance with contemporary usage, X-{Y} represents the Y decoupled spectrum of X) nmr spectrum of $\mu$-Fe(CO)$_4$·B$_6$H$_{10}$.



Figure 2. (a) The $^1$H nmr spectrum of $\mu$-Fe(CO)$_4$·B$_6$H$_{10}$ in CS$_2$ at 34°. (b) The $^1$H-{apical $^{11}$B} nmr spectrum of $\mu$-Fe(CO)$_4$·B$_6$H$_{10}$. (c) The $^1$H-{basal $^{11}$B} nmr spectrum of $\mu$-Fe(CO)$_4$·B$_6$H$_{10}$. The signal at −1.0 is an impurity.

In 1, the transition metal analog of B$_6$H$_{11}^+$, B$_6$H$_{10}$ is formally regarded as a two-electron donor bound via a three-center, two-electron bond containing Fe(0) in the bridging position. In 2 the 16-electron, d$^8$ Fe(CO)$_4$ unit is formally regarded as having oxidatively added (as in cis-Fe(CO)$_4$I$_2$) to the boron–boron bond to generate an Fe(II) center. The ir spectrum supports 1, in that the carbonyl bands are uniformly 50–60 cm$^{-1}$ lower than those for the corresponding modes in cis-Fe(CO)$_4$I$_2$,[13] and are more typical of Fe(CO)$_4$L (L = R$_3$P or olefin) complexes.[14]

Further, the Mössbauer parameters ($\delta$ −0.4, $\Delta E_Q$ = 1.71 mm/sec relative to iron metal) are typical of those found for Fe(CO)$_4$L complexes,[15] and differ markedly from those in Fe(CO)$_4$I$_2$.[16] Thus, the physical evidence supports the formulation of Fe(0) bound to B$_4$, B$_5$ via a three-center, two-electron bond.

Such a bonding arrangement is being recognized as an increasingly common feature in metalloboranes and metallocarboranes. Sneddon and Grimes[17] have postulated a similar structure in $\mu$-[($\pi$-C$_5$H$_5$)Fe(CO)$_2$]-C$_2$B$_4$H$_7$. The B$_{10}$H$_{12}^{2-}$ transition metal complexes may be regarded as having three-center, two-electron, boron–transition metal–boron bonds.[18] The salt Cu$_2$[B$_{10}$H$_{10}$] appears to contain such a feature in the solid state,[19] as may B$_5$H$_8^-$ and B$_6$H$_9^-$ derivatives of (Ph$_3$P)$_2$Cu$^I$.[20]

**The Ni(CO)$_4$–B$_6$H$_{10}$ System.** Observations of the reaction of Ni(CO)$_4$ with B$_6$H$_{10}$ support the formation of a weakly bonded Ni(CO)$_3$ complex. One equivalent of CO is rapidly evolved by mixtures of excess B$_6$H$_{10}$ and

Ni(CO)$_4$, to give a yellow liquid phase. However, only starting materials, Ni metal, and CO are obtained when a vacuum is applied. Therefore, the equilibrium presented in eq 2 seems likely. Unfortunately, the weak

$$Ni(CO)_4 + B_6H_{10} \rightleftharpoons Ni(CO)_3(B_6H_{10}) + CO$$

$$\downarrow \text{yellow}$$

$$^1/_2Ni(CO)_4 + {}^1/_2Ni^0 + CO \longleftarrow [Ni(CO_3)] + B_6H_{10} + CO \quad (2)$$

interaction does not permit isolation of the yellow species. Other complexes such as Ni(CO)$_2$(B$_6$H$_{10}$)$_2$, etc., may also be present.

**Complexes of Pt, Rh, and Ir.** To the extent that both the trans halide and ethylene in Zeise's salt are labile, the former being displaced by a variety of Lewis bases[21] and the latter by other olefins,[22] it seemed likely B$_6$H$_{10}$ would displace at least one ligand about the platinum center. Accordingly, we found reaction 3 takes place in

$$K[PtCl_3(C_2H_4)] + 2B_6H_{10} \longrightarrow$$

$$trans\text{-}Pt(B_6H_{10})_2Cl_2 + KCl + C_2H_4 \quad (3)$$

good yield when B$_6$H$_{10}$ is taken in excess. A transient violet color, visible at low temperatures in the early stages of the reaction, may be a five-coordinate intermediate. However, we were unable to isolate this species. Similarly, ethylene in Rh(C$_2$H$_4$)$_2$(acac)[23] and [Rh(C$_2$-H$_4$)$_2$Cl]$_2$[23b,24] and cyclooctene in [Ir(C$_8$H$_{14}$)$_2$Cl]$_2$[25] are labile and may be displaced by olefins and phosphines. Subsequently, we found reactions 4, 5, and 6 occur.

$$Rh(C_2H_4)_2(acac) + 2B_6H_{10} \longrightarrow Rh(B_6H_{10})_2(acac) + 2C_2H_4 \quad (4)$$

$$[Rh(C_2H_4)_2Cl]_2 + 4B_6H_{10} \longrightarrow [Rh(B_6H_{10})_2Cl]_2 + 4C_2H_4 \quad (5)$$

$$[Ir(C_8H_{14})_2Cl]_2 + 4B_6H_{10} \longrightarrow [Ir(B_6H_{10})_2Cl]_2 + 4C_8H_{14} \quad (6)$$

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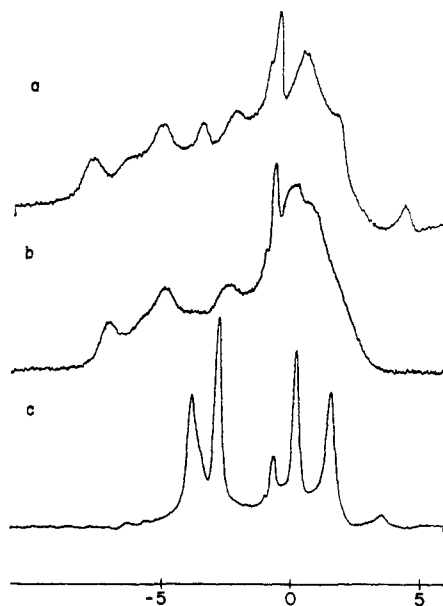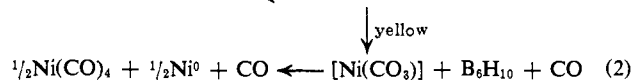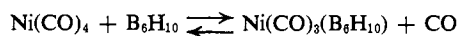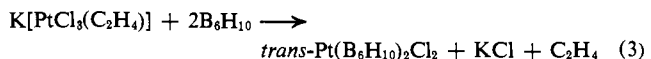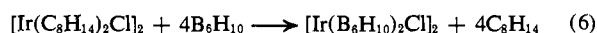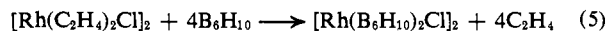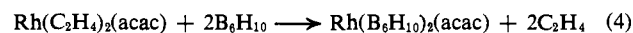(21) (a) J. V. Quagliano and L. Schubert, Chem. Rev., 50, 201 (1952); (b) I. Leden and J. Chatt, J. Chem. Soc., 2936 (1955).

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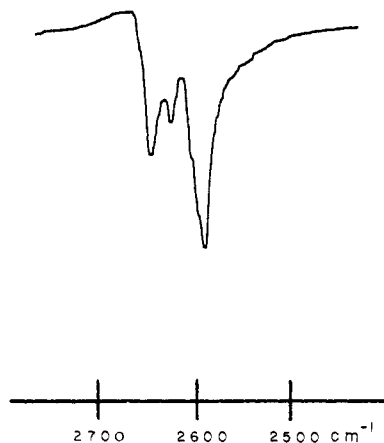
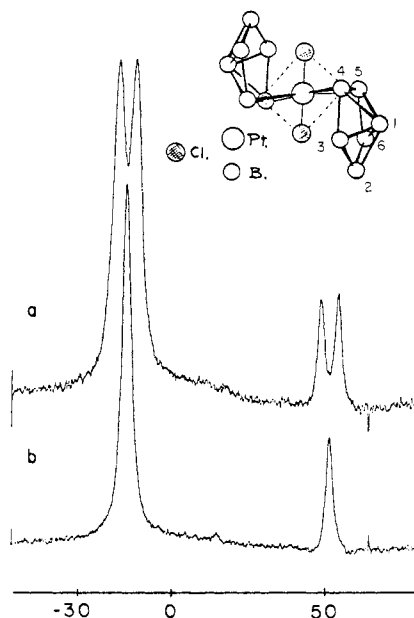Figure 3. The ir spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂ (Kel-F mull).



Figure 4. (a) The ¹¹B nmr spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂ in toluene at 26°. (b) The ¹¹B-{¹H} nmr spectrum of *trans*-Pt(B₆H₁₀)₂-Cl₂.

All complexes are similar in color to their ethylene analogs.[23b,24,25a,26] Thermal stability of the solid compounds ranges from very good in the case of *trans*-Pt(B₆H₁₀)₂Cl₂, which may be kept at room temperature for indefinite periods, to poor for Rh(B₆H₁₀)₂(acac) which is best stored at −78°. Attempts to obtain mass spectra resulted in extensive decomposition with B₆H₁₀ as the only volatile species observed. This observation in itself characterizes the compounds as B₆H₁₀ complexes. Further, satisfactory analyses have been obtained, and an X-ray structure determination of *trans*-Pt(B₆H₁₀)₂Cl₂ has been published.[7b]

In contrast to the ir spectrum of uncomplexed B₆H₁₀, which has a single band in the B–H stretching region (although B₆H₁₀ has been shown to possess $C_s$ symmetry in the crystal),[27] coordinated B₆H₁₀ character-istically exhibits the pattern shown in Figure 3. Since six bands are expected under $C_s$ symmetry, some near degeneracies occur. Nevertheless, the ir spectra imply the true symmetry of the borane fragment, which is not exhibited by the free ligand.

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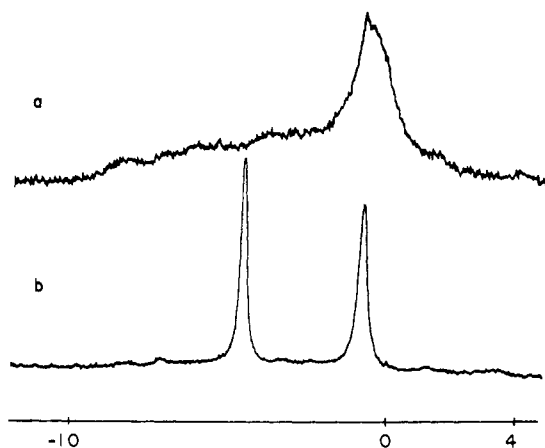


Figure 5. (a) The ¹H nmr spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂ in CS₂ at 34°. (b) The ¹H-{basal ¹¹B} nmr spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂.

The ¹¹B nmr spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂ in Figure 4 shows two doublets at −14.7 (5B, $J_{BH}$ = 166 Hz) and 50.4 (1B, $J_{BH}$ = 166 Hz), which collapse to singlets on proton decoupling. At temperatures to −90° both resonances broaden without noticeable asymmetry. Similarly, the ¹¹B-{¹H} nmr spectrum of Rh(B₆H₁₀)₂(acac) in toluene at −60° is two very broad resonances at −4.3 (5B) and 49.7 (1B). Except for small differences in chemical shifts these spectra are identical with that of uncomplexed B₆H₁₀.[11]

The presence of small concentrations of free B₆H₁₀ in solutions of these complexes seems likely, in that the compounds, although involatile, smell strongly of B₆H₁₀ and show (except for *trans*-Pt(B₆H₁₀)₂Cl₂) dim-inution of the B–H stretching bands after storage at room temperature. Additionally, chemical evidence for the substitutional lability of B₆H₁₀ can be cited; the reaction of *trans*-Pt(B₆H₁₀)₂Cl₂ with 1 equiv of tetrabutylammonium chloride gives a yellow-orange solid, which the ir spectrum suggests is [(C₄H₉)₄N]-[Pt(B₆H₁₀)Cl₃], but ([C₄H₉)₄N]₂[PtCl₄] is obtained on recrystallization. As both are 16-electron, d⁸, square-planar complexes, rapid exchange involving the vacant coordination site is likely. Such behavior has been postulated for the similar Rh(C₂H₄)₂(acac)[23b] and K[Pt(C₂H₄)Cl₃].[28] It must be noted, the same mech-anism responsible for the nmr equivalence of the basal borons in B₅H₈⁻, B₆H₉⁻, and B₆H₁₀[29] might be opera-tive in these metal complexes.

The ¹H nmr spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂ in Figure 5 displays a broad resonance at −0.9 super-imposed on a very broad unresolved signal extending from −9.6 to 4.0. At −85° the unresolved resonance sharpens to a broad single line at −4.7 (140 Hz at half maximum). The ¹H-{basal ¹¹B} spectrum shows two sharp signals (ca. 12 Hz at half maximum) at −4.7 and −0.9, superimposed on a weak quartet (B₁-H_T) cen-tered at 0.0. Thus, the ¹H spectra are consistent with the ¹¹B results, since the terminal hydrogens bound to the basal borons are equivalent, as are the bridge hydrogens. Cooling affects only the boron coupling of the basal terminal hydrogens. Similar loss of cou-pling has been noted in B₆H₁₀ and other cases.[29,30]

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## Experimental Section

All solvents were distilled from sodium benzophenone ketyl except $CH_2Cl_2$ and $CS_2$, which were distilled from $P_4O_{10}$. $K[Pt(C_2H_4)Cl_3]$,[28] $[Ir(C_8H_{14})_2Cl]_2$,[25a] $[Rh(C_2H_4)_2Cl]_2$,[24] $Rh(C_2H_4)_2(acac)$,[23b] and $B_6H_{10}$[31] were prepared by literature methods. Other reagents were commercial grades. Manipulations throughout were performed using either standard high-vacuum technique,[32] Schlenk tube techniques,[33] or in a nitrogen-filled Vacuum/Atmosphere drybox. Melting points were determined in nitrogen-filled capillaries. Infrared spectra were obtained on a Perkin-Elmer 337 or 621 spectrometer. Mass spectra were run on a Hitachi Perkin-Elmer RMU-6 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. All $B_6H_{10}$ complexes survive brief exposure to the atmosphere.

**Nmr Spectra.** All proton spectra were obtained at 60 MHz on a Perkin-Elmer Model R-20B spectrometer interfaced[34] with a Digilab FTS/NMR-3 Fourier transform data system. Typical parameters employed were 4096-point transform, 5-KHz band width, 90° nutation angle, 2.0 sec between repetitive pulses, 100–2000 pulses, and $^{11}B$ decoupling at ca. 19.25 MHz with a band width of ca. 300 Hz. All chemical shifts are in parts per million relative to external TMS, and positive values represent higher shieldings. All boron spectra were obtained at 28.877 MHz[35] on a Bruker HFX-90 spectrometer interfaced with the Digilab system described above. The field/frequency lock was provided by a capillary containing $C_6F_6$ for room temperature spectra or $(CF_2Br)_2$ for low temperature spectra. Typical parameters employed were 4096-point transform, 5-KHz band width, 60° nutation angle, 1.6 sec between repetitive pulses, 400–5000 pulses, and $^1H$ broadband decoupling. All chemical shifts are given in parts per million relative to external $BF_3 \cdot (C_2H_5)_2O$, and positive values represent higher shieldings. The chemical shifts are believed to be accurate to ±0.1 and the coupling constants were reproducible to ±5 Hz.

**$\mu$-Fe(CO)$_4$B$_6$H$_{10}$.** $B_6H_{10}$ (348 mg, 4.55 mmol) and pentane (2 ml) were condensed onto $Fe_2(CO)_9$ (700 mg, 1.92 mmol) at −196° in a 20-mm tube equipped with a sublimation probe. The slurry was warmed to 25° and stirred until the $Fe_2(CO)_9$ was consumed (12 hr). The vessel was cooled to −22° and pentane, excess $B_6H_{10}$, and $Fe(CO)_5$ (as determined by ir spectroscopy) were distilled out. The product was sublimed from the dark residue at 30° onto the probe (−78°), to yield 360 mg (1.48 mmol, 77%) of yellow crystals (mp 37–38°). The compound should be stored at low temperatures. The ir spectrum has prominent bands in the B–H stretching region (2578 (s), 2555 (sh), and 2495 (m) cm⁻¹ Kel-F mull) and in the carbonyl stretching region (2078 (vs), 2018 (vs), 1986 (vs), and 1981 (sh) cm⁻¹ in methylcyclohexane).

**trans-Pt(B$_6$H$_{10}$)$_2$Cl$_2$.** $B_6H_{10}$ (105 mg, 1.40 mmol) was condensed onto $K[Pt(C_2H_4)Cl_3]$ (508 mg, 1.38 mmol) in a 20-mm tube at −196°, and the vessel allowed to warm to 25°. When the vigorous reaction had subsided, additional $B_6H_{10}$ (248 mg, 3.31 mmol) and $CH_2Cl_2$ (2 ml) were condensed onto the yellow mass, and the slurry was stirred overnight. The volatile components were removed at 25° and the residue extracted with toluene (five 10-ml portions). The extracts were filtered, combined, and evaporated at 0° to 10 ml. Addition of hexane (25 ml), rapid filtration and cooling to −20° gave yellow needles, which were collected, washed with hexane, and dried in vacuo to yield 310 mg (0.74 mmol, 54%). The compound begins to darken at ca. 120°, and is, seemingly, stable at 25°, but solutions slowly darken unless cooled.

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(34) Details of this interface have been submitted for publication by D. D. Traficante and J. A. Simms to *Rev. Sci. Instrum.*, in press.

(35) Details of the multinuclei modification utilized for obtaining these spectra were presented at the 13th Experimental Nmr Conference at Asilomar (March 1972) and will be published elsewhere.

*Anal.* Calcd for $B_{12}Cl_2H_{20}Pt$: B, 31.19; Cl, 17.05; H, 4.85; Pt, 46.91. Found: B, 30.66; Cl, 16.55; H, 5.89; Pt, 46.65.

The ir spectrum has prominent bands in the B–H stretching region (2622 (m), 2600 (w), and 2566 (s) Kel-F mull). The mass spectrum is that of $B_6H_{10}$.[27]

**Rh(B$_6$H$_{10}$)$_2$(acac).** $B_6H_{10}$ (163 mg, 2.15 mmol) was condensed onto $Rh(C_2H_4)_2(acac)$ (100 mg, 0.388 mmol) in a 10-mm tube at −196°. The vessel was warmed briefly to 0°, then cooled to −196° and toluene (1 ml) condensed onto the orange mass. Stirring at 0° for 5 min, followed by rapid removal of toluene, excess $B_6H_{10}$, and $C_2H_4$ (as determined by ir spectroscopy) by vacuum distillation gave a dark yellow residue. This residue was taken up in hexane (20 ml, 0°) and quickly filtered through a Celite pad into a receiver cooled to −78°. When crystallization was complete, the solvent was removed with a syringe, and the yellow crystals were washed with pentane (two 2-ml portions, −78°). The product was dried *in vacuo* at −78° to yield 20 mg of $Rh(B_6H_{10})_2(acac)$ (0.06 mmol, 15%). The compound blackens without melting on heating. Solutions rapidly precipitate Rh metal at room temperature. The solid is best stored at −78°.

*Anal.* Calcd for $C_5H_{27}B_{12}O_2Rh$: C, 17.07; H, 7.73; B, 36.87; Rh, 29.24. Found: C, 18.77; H, 7.96; B, 31.00; Rh, 26.13.

The ir spectrum has prominent bands in the B–H stretching region (2540 (s) and 2520 (sh) Kel-F mull), as well as bands indicative of coordinated acac (1575 (s), 1555 (s), 1520 (s) Kel-F mull). The mass spectrum is that of $B_6H_{10}$.[27]

**[Rh(B$_6$H$_{10}$)$_2$Cl]$_2$.** $[Rh(C_2H_4)_2Cl]_2$ (251 mg, 0.65 mmol) was charged to a vacuum line filtration apparatus. Pentane (5 ml) and $B_6H_{10}$ (380 mg, 5.1 mmol) were distilled into the apparatus at −196°. The dark red slurry was briefly warmed to 0°, then stirred at −78° for 5 hr. $C_2H_4$ (identified by ir spectroscopy) could be isolated from the vapor over the solution. The orange-red solid was collected at −78°, washed with pentane (three 2-ml portions), and dried at −78° *in vacuo*, to yield 242 mg (0.42 mmol, 64%). The compound darkens rapidly above 90° without melting. Solutions rapidly precipitate Rh metal unless cooled.

*Anal.* Calcd for $B_{12}Cl_2H_{20}Rh$: B, 45.01; Cl, 12.30; H, 6.99; Rh, 35.70. Found: B, 42.90; Cl, 11.05; H, 7.16; Rh, 32.33.

The ir spectrum has prominent bands in the B–H stretching region (2600 (sh), 2586 (s), 2565 (w), 2545 (w), 2509 (m), and 2490 (sh) Kel-F mull).

**[Ir(B$_6$H$_{10}$)$_2$Cl]$_2$.** In an identical manner the iridium complex was prepared from $[Ir(C_8H_{14})_2Cl]_2$ (322 mg, 0.36 mmol) and $B_6H_{10}$ (510 mg, 6.8 mmol) in hexane (6 ml). The yield of orange powder was 104 mg (0.14 mmol, 38%). The compound darkens above 90° without melting.

*Anal.* Calcd for $B_{12}Cl_2H_{20}Ir$: B, 34.36; Cl, 9.39; H, 5.34; Ir, 50.91. Found: B, 30.27; Cl, 7.97; H, 5.84; Ir, 50.85.

The ir spectrum has an unresolved, asymmetric band in the B–H stretching region (2590 cm⁻¹ Nujol mull).

**Reaction of Ni(CO)$_4$ and B$_6$H$_{10}$.** $Ni(CO)_4$ (171 mg, 1.0 mmol) and $B_6H_{10}$ (149 mg, 1.96 mmol) were condensed into a 10-mm tube at −196°. Warming to 25° immediately produced a clear yellow solution. The solution was stirred for 15 min, cooled to −196°, and 0.7 mmol of noncondensable gas was collected with a Toepler pump. Repetition of this cycle resulted in deepening of color and collection of another 0.4 mmol of noncondensable gas. Attempts at isolation of the yellow species were unsuccessful, as exposure to the pumps at any temperature high enough to ensure a reasonable rate of removal of excess $B_6H_{10}$ gave only a black involatile residue, $B_6H_{10}$, $Ni(CO)_4$, and noncondensable gas.