

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 $\mu\text{-Fe}(\text{CO})_4 \cdot \text{B}_6\text{H}_{10}$, $\text{trans-Pt}(\text{B}_6\text{H}_{10})_2\text{Cl}_2$, $\text{Rh}(\text{B}_6\text{H}_{10})_2(\text{acac})$, $[\text{Rh}(\text{B}_6\text{H}_{10})_2\text{Cl}]_2$, and $[\text{Ir}(\text{B}_6\text{H}_{10})_2\text{Cl}]_2$. The compounds have been characterized by elemental analysis and ir, ^1H 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_2O^2 and DCI^3 . Indeed, the presumed intermediate $\text{B}_6\text{H}_{11}^+$ has been isolated⁴ and had previously been predicted to be stable.⁵ $\text{B}_{15}\text{H}_{23}$ has been prepared from the reaction of B_6H_{10} with $i\text{-B}_9\text{H}_{15}$ and has been suggested to consist of a B_9H_{13} unit bound to the B_6H_{10} substrate *via* a three-center bond.⁶

In this paper we describe a variety of transition metal complexes of B_6H_{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

$\mu\text{-Fe}(\text{CO})_4 \cdot \text{B}_6\text{H}_{10}$. Inasmuch as $\text{Fe}_2(\text{CO})_9$ reacts under mild conditions with a variety of Lewis bases, it appeared an ideal candidate for the preparation of B_6H_{10} complexes. Subsequently, we found reaction 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 $\text{Fe}(\text{CO})_5$ and B_6H_{10} ⁸ or from shaking B_4H_{10} with excess $\text{Fe}_2(\text{CO})_9$.⁹

The presence of coordinated B_6H_{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 $^{10}\text{B}^{11}\text{B}_5^{56}\text{Fe}^{12}\text{C}_4^{16}\text{O}_4$) with an isotope pattern agreeing very closely with that calculated for a $\text{B}_6\text{C}_4\text{Fe}$ -containing fragment; isotope clusters 28, 56, 84, and 112 mass units below the parent ion are consistent with the presence of an $\text{Fe}(\text{CO})_4$ unit; free B_6H_{10} is the dominant feature of the spectrum. Further, the four carbonyl bands with near degeneracy of

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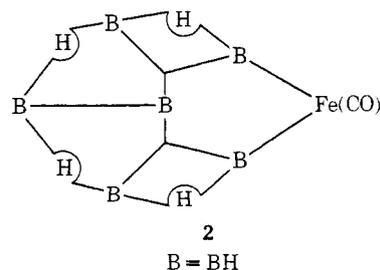
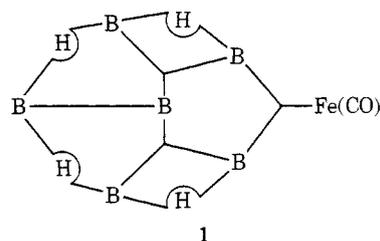
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the lower energy B_1 and B_2 modes are typical of an $\text{Fe}(\text{CO})_4$ unit under local C_{2v} symmetry.¹⁰

The ^{11}B nmr spectrum in Figure 1 shows a low field multiplet (5B) and a high field doublet (1B, $J_{\text{BH}} = 159$ 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_6H_{10} .¹¹ The ^1H 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 ($\text{B}_2, \text{B}_3, \text{B}_6\text{-H}_T$), -3.1 ($\text{B}_4, \text{B}_5\text{-H}_T$), -0.1 ($\text{B}_{2,3}\text{-H}_\mu, \text{B}_{2,6}\text{-H}_\mu$), and 1.2 ($\text{B}_{3,4}\text{-H}_\mu, \text{B}_{5,6}\text{-H}_\mu$) (the assignments to the two sets of bridge hydrogens are ambiguous and may be reversed) superimposed on a weak quartet ($\text{B}_1\text{-H}_T$) whose high field member is clearly visible at 3.2 . Hence, the ^1H nmr data also conform to the postulated C_s symmetry. Such behavior is observed in uncomplexed B_6H_{10} only on cooling to -147° .¹²

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



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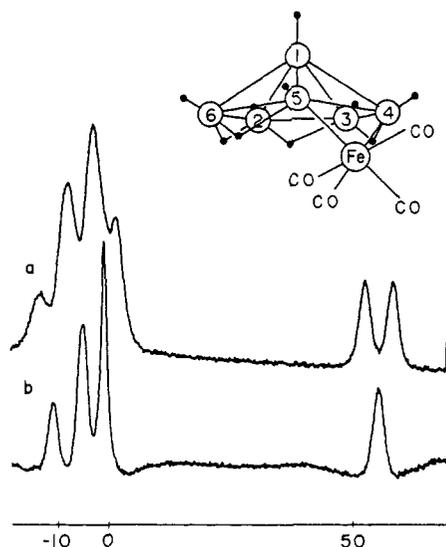


Figure 1. (a) The ^{11}B nmr spectrum of $\mu\text{-Fe}(\text{CO})_4 \cdot \text{B}_6\text{H}_{10}$ in hexane at 26° . (b) The $^{11}\text{B}\{-^1\text{H}\}$ (in conformance with contemporary usage, X- $\{Y\}$ represents the Y decoupled spectrum of X) nmr spectrum of $\mu\text{-Fe}(\text{CO})_4 \cdot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

In **1**, the transition metal analog of $\text{B}_6\text{H}_{11}^+$, B_6H_{10} is formally regarded as a two-electron donor bound *via* a three-center, two-electron bond containing $\text{Fe}(0)$ in the bridging position. In **2** the 16-electron, d^8 $\text{Fe}(\text{CO})_4$ unit is formally regarded as having oxidatively added (as in *cis*- $\text{Fe}(\text{CO})_4\text{I}_2$) to the boron-boron bond to generate an $\text{Fe}(\text{II})$ center. The ir spectrum supports **1**, in that the carbonyl bands are uniformly $50\text{--}60\text{ cm}^{-1}$ lower than those for the corresponding modes in *cis*- $\text{Fe}(\text{CO})_4\text{I}_2$,¹³ and are more typical of $\text{Fe}(\text{CO})_4\text{L}$ ($\text{L} = \text{R}_3\text{P}$ or olefin) complexes.¹⁴

Further, the Mössbauer parameters ($\delta -0.4$, $\Delta E_Q = 1.71\text{ mm/sec}$ relative to iron metal) are typical of those found for $\text{Fe}(\text{CO})_4\text{L}$ complexes,¹⁵ and differ markedly from those in $\text{Fe}(\text{CO})_4\text{I}_2$.¹⁶ Thus, the physical evidence supports the formulation of $\text{Fe}(0)$ 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 Grimes¹⁷ have postulated a similar structure in $\mu\text{-}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{-C}_2\text{B}_4\text{H}_7$. The $\text{B}_{10}\text{H}_{12}^{2-}$ transition metal complexes may be regarded as having three-center, two-electron, boron-transition metal-boron bonds.¹⁸ The salt $\text{Cu}_2[\text{B}_{10}\text{H}_{10}]$ appears to contain such a feature in the solid state,¹⁹ as may B_5H_8^- and B_6H_9^- derivatives of $(\text{Ph}_3\text{P})_2\text{Cu}^+$.²⁰

The $\text{Ni}(\text{CO})_4\text{-B}_6\text{H}_{10}$ System. Observations of the reaction of $\text{Ni}(\text{CO})_4$ with B_6H_{10} support the formation of a weakly bonded $\text{Ni}(\text{CO})_3$ complex. One equivalent of CO is rapidly evolved by mixtures of excess B_6H_{10} and

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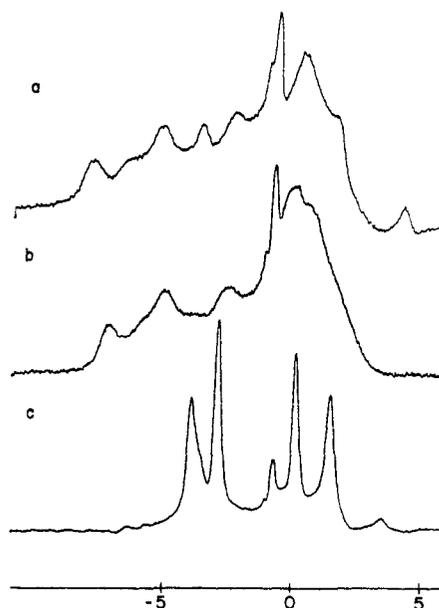
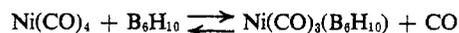


Figure 2. (a) The ^1H nmr spectrum of $\mu\text{-Fe}(\text{CO})_4 \cdot \text{B}_6\text{H}_{10}$ in CS_2 at 34° . (b) The $^1\text{H}\{-\text{apical } ^{11}\text{B}\}$ nmr spectrum of $\mu\text{-Fe}(\text{CO})_4 \cdot \text{B}_6\text{H}_{10}$. (c) The $^1\text{H}\{-\text{basal } ^{11}\text{B}\}$ nmr spectrum of $\mu\text{-Fe}(\text{CO})_4 \cdot \text{B}_6\text{H}_{10}$. The signal at -1.0 is an impurity.

$\text{Ni}(\text{CO})_4$, 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



↓yellow

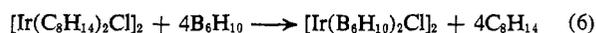
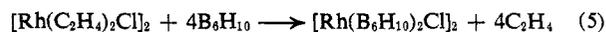
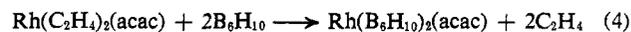


interaction does not permit isolation of the yellow species. Other complexes such as $\text{Ni}(\text{CO})_2(\text{B}_6\text{H}_{10})_2$, etc., may also be present.

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 bases²¹ and the latter by other olefins,²² it seemed likely B_6H_{10} would displace at least one ligand about the platinum center. Accordingly, we found reaction 3 takes place in



good yield when B_6H_{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 $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})$ ²³ and $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ ^{23b,24} and cyclooctene in $[\text{Ir}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2$ ²⁵ are labile and may be displaced by olefins and phosphines. Subsequently, we found reactions 4, 5, and 6 occur.



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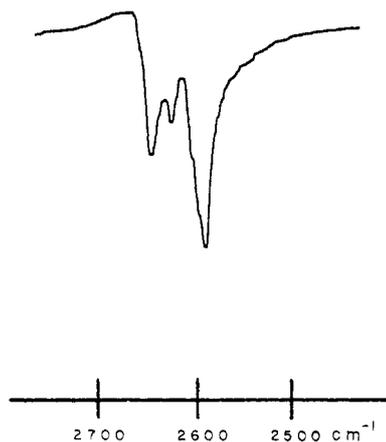


Figure 3. The ir spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂ (Kcl-F mull).

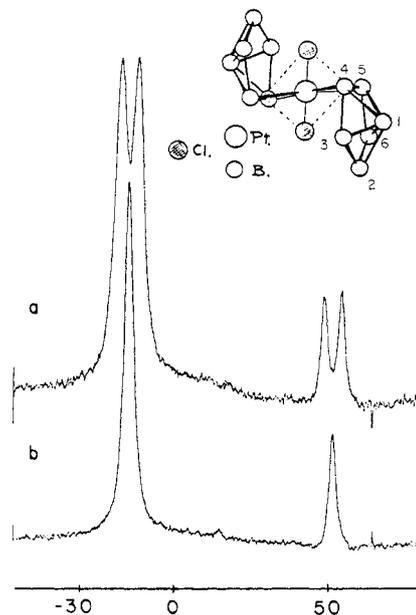


Figure 4. (a) The ¹¹B nmr spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂ in toluene at 26°. (b) The ¹¹B-¹H nmr spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂.

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 characteristically 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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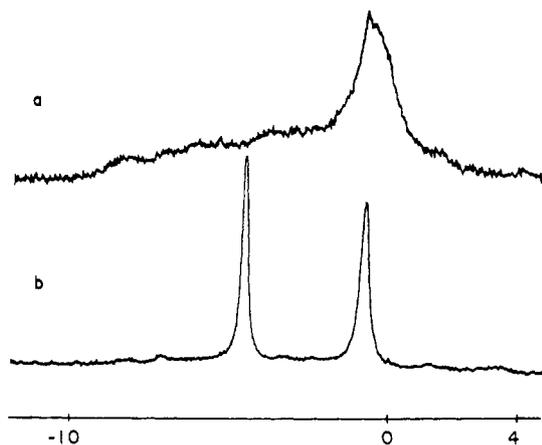


Figure 5. (a) The ¹H nmr spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂ in CS₂ at 34°. (b) The ¹H-¹¹B nmr spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂.

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) diminution 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]⁺[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 mechanism responsible for the nmr equivalence of the basal borons in B₅H₈⁻, B₆H₉⁻, and B₆H₁₀²⁹ might be operative in these metal complexes.

The ¹H nmr spectrum of *trans*-Pt(B₆H₁₀)₂Cl₂ in Figure 5 displays a broad resonance at -0.9 superimposed 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-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) centered 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 coupling 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} . $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)_2\text{Cl}_2]$,²⁸ $[\text{Ir}(\text{C}_5\text{H}_4)_2\text{Cl}]_2$,^{25a} $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$,²⁴ $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})$,^{23b} and B_6H_{10} ²¹ 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 interfaced³⁴ 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 ¹¹B 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 MHz³⁵ 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 $(\text{CF}_2\text{Br})_2$ 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 $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, 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.

$\mu\text{-Fe}(\text{CO})_5\text{B}_6\text{H}_{10}$. B_6H_{10} (348 mg, 4.55 mmol) and pentane (2 ml) were condensed onto $\text{Fe}_2(\text{CO})_9$ (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 $\text{Fe}_2(\text{CO})_9$ was consumed (12 hr). The vessel was cooled to -22° and pentane, excess B_6H_{10} , and $\text{Fe}(\text{CO})_5$ (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 $37\text{--}38^\circ$). 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- $\text{Pt}(\text{B}_6\text{H}_{10})_2\text{Cl}_2$. B_6H_{10} (105 mg, 1.40 mmol) was condensed onto $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)_2\text{Cl}_2]$ (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 $\text{B}_{12}\text{Cl}_2\text{H}_{20}\text{Pt}$: 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

$\text{Rh}(\text{B}_6\text{H}_{10})_2(\text{acac})$. B_6H_{10} (163 mg, 2.15 mmol) was condensed onto $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})$ (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 $\text{Rh}(\text{B}_6\text{H}_{10})_2(\text{acac})$ (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 $\text{C}_6\text{H}_{27}\text{B}_6\text{O}_2\text{Rh}$: 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

$[\text{Rh}(\text{B}_6\text{H}_{10})_2\text{Cl}]_2$. $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (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 $\text{B}_{12}\text{Cl}_2\text{H}_{20}\text{Rh}$: 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).

$[\text{Ir}(\text{B}_6\text{H}_{10})_2\text{Cl}]_2$. In an identical manner the iridium complex was prepared from $[\text{Ir}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (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 $\text{B}_{12}\text{Cl}_2\text{H}_{20}\text{Ir}$: 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 $\text{Ni}(\text{CO})_4$ and B_6H_{10} . $\text{Ni}(\text{CO})_4$ (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} , $\text{Ni}(\text{CO})_4$, and noncondensable gas.

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