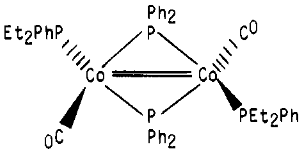
composition $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2\cdot 2MeCN$.

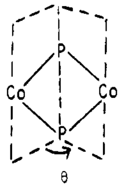
The molecular structure of **1** has been determined by X-ray crystallography and is shown in Figure 1. The spectroscopic data are consistent with this structure. In particular, its $^{31}P\{^1H\}$ NMR spectrum shows an upfield resonance at δ −102.9 s due to the μ-PPh_2 ligands and a PPh_2H resonance at δ 43.7 d. The latter shows a 360-Hz ^{31}P–^1H coupling in the ^1H-coupled ^{31}P NMR spectrum. The upfield position of the μ-PPh_2 resonance is consistent with the absence of a metal–metal bond in **1**.[2,12]

Upon being heated, complex **1** loses CO and forms $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_2H)_2$ (**2**) in quantitative yield. This reaction is more conveniently carried out in refluxing cyclohexane since **2** is insoluble in this solvent and precipitates as it forms. Spectroscopic data imply that **2** is isostructural with $Co_2(\mu\text{-}PPh_2)_2(CO)_2(PEt_2Ph)_2$ (**6**)[13] and $Co_2(\mu\text{-}P\text{-}t\text{-}Bu_2)_2(L)_2(PMe_3)_2$ (L = CO, N_2),[14] whose structures have recently been established by X-ray diffraction studies. The latter showed short (2.343 (2) Å for **6**) Co–Co separations, consistent with the presence of metal–metal double bonds as required by the 18-electron rule, and a distorted tetrahedral geometry at each metal. The IR spectra of **2** and **6** are similar, with each showing a single ν(CO) stretch (**2**, 1917.5 vs cm^{-1}; **6**, 1905 vs cm^{-1}). The $^{31}P\{^1H\}$ NMR spectra are also similar, showing downfield resonances due to the μ-PPh_2 ligands (**2**, δ 182.7 s; **6**, δ 175.8 s). In **2**, the PPh_2H ligand appears as a doublet in the proton-coupled spectrum at δ 33.8 with J(P–H) = 332 Hz.



6

Crystal and Molecular Structure of $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2\cdot 2CH_3CN$ (1). An ORTEP drawing showing the atom-numbering scheme is given in Figure 1. The Co atoms are bridged by the two μ-PPh_2 ligands, and each Co is further coordinated by two CO's and a PPh_2H ligand. Figure 2 shows a different view of the molecule down the Co–Co axis, which illustrates the slightly bent character of the $Co_2(\mu\text{-}P)_2$ core and the near-eclipsed arrangment of the terminal ligands. The dihedral angle (θ) between the P2–Co1–P3 and P2–Co2–P3 planes is 153.3°.



The two PPh_2H ligands lie on opposite sides of the molecule, an arrangement that minimizes steric interaction between these bulky ligands. The PPh_2H hydrogen atoms were located and refined; their positions are indicated in Figures 1 and 2.

The overall geometry of complex **1** is very similar to that of the bent form of $Co_2(\mu\text{-}PPh_2)_2(CO)_6$ (**7**), from which it formally derives by substitution of two CO's by the PPh_2H ligands. In the bent form of complex **7**, the corresponding P1–Co1–P2/P1–Co2–P2 dihedral angle is 155.0° and the terminal ligands are also nearly eclipsed. Both complex **1** and the bent form of **7** can be viewed as comprised of two edge-shared CoL_5 square pyramids, as clearly illustrated in Figure 1.

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Registry No. **1**, 98541-18-5; **2**, 98541-19-6; **5**, 98541-22-1; $CoCl_2(PPh_2H)_2$, 98541-20-9; $CoCl_2(CO)(PPh_2H)_2$, 98541-21-0.

Supplementary Material Available: Tables of thermal parameters and structure factors (18 pages). Ordering information is given on any current masthead page.

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Improved Synthesis of $2,2,2\text{-}(CO)_3\text{-}2\text{-}MnB_5H_{10}$ via Heterogeneous Catalysis. Synthesis and Characterization of the New Rhenahexaborane $2,2,2\text{-}(CO)_3\text{-}2\text{-}ReB_5H_{10}$

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An improved synthesis of the *nido*-manganahexaborane $2,2,2\text{-}(CO)_3\text{-}2\text{-}MnB_5H_{10}$ has been developed that utilizes H_2 pressures of ca. 100 atm and certain heterogeneous catalysts. Yields up to 41% have been obtained by using 5% Ru/C as catalyst. The new rhenahexaborane $2,2,2\text{-}(CO)_3\text{-}2\text{-}ReB_5H_{10}$ has been obtained in a similar manner and has been characterized spectroscopically. Possible mechanisms of formation of these metallaboranes in the catalyzed and uncatalyzed reactions are discussed.

Introduction

Metallaborane chemistry has rapidly become one of the most interesting and diverse areas of boron hydride research.[1] Our studies in this area have centered primarily on manganese–borane clusters (manganaboranes) and have yielded a variety of structural types.[2-7] Structural analogues of several of these clusters containing different metals are known, while others are thus far unique.

Many examples of metallahexaborane (MB_5) clusters are known, several of which exhibit the pentagonal-pyramidal

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[1] See, for example: Grimes, R. N., Ed. "Metal Interactions with Boron Clusters"; Plenum Press: New York, 1982.

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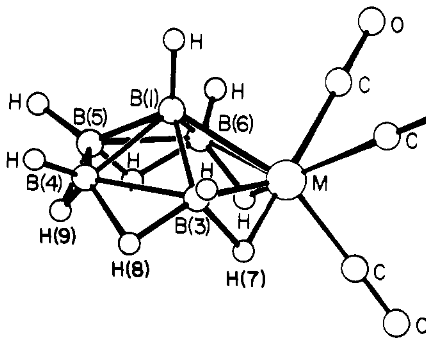

Figure 1. Proposed structure of 2,2,2-$(CO)_3$-2-MB_5H_{10} (M = Mn, Re). Terminal hydrogens are numbered the same as the boron to which they are attached.

Table I. Preparation of 2,2,2-$(CO)_3$-2-MnB_5H_{10} Using Selected Heterogeneous Catalysts[a]

catalyst	temp, °C	time, days	% yield[b]
5% Rh/C	140	5.75	1.0
5% Pd/C	140	5.75	9.2
5% Pt/C	122	5.75	3.5
	140	5.75	13.4
5% Ru/C	100	5.75	12.5
	120	5.75	31.8
	120	14.00	40.9
	133	12.00	35.0
	140	5.75	37.7

[a] Each reaction was performed by using approximately 5 mmol of $Mn_2(CO)_{10}$, 25 mmol of B_5H_9, and 0.5 mmol of catalyst. In all cases the reaction cylinders were pressurized to 60 atm with the lower half of the cylinders immersed in liquid nitrogen. Actual pressures at the reaction temperatures were estimated to be over 100 atm. [b] Yields are based on initial $Mn_2(CO)_{10}$.

B_6H_{10}-type structure.[4,8-14] We recently reported the synthesis and characterization of the manganahexaborane 2,2,2-$(CO)_3$-2-MnB_5H_{10} (**1**), whose proposed structure is shown in Figure 1.[4] Synthetic routes to **1** via the reaction of B_5H_9 with $HMn(CO)_5$ (or with $Mn_2(CO)_{10}$ and H_2) were studied. Under optimum conditions, the highest yield of **1** was 2.2% based on initial $Mn_2(CO)_{10}$ or 9.4% based on $Mn_2(CO)_{10}$ consumed. Compound **1** is unusual in its high thermal stability and in its resistance to oxidation, hydrolysis, and alcoholysis. Also reported for **1** were its bromination to give 1-Br-2,2,2-$(CO)_3$-2-MnB_5H_9 and its deprotonation to give the $[2,2,2\text{-}(CO)_3\text{-}2\text{-}MnB_5H_9]^-$ anion. We have reexamined the reaction of B_5H_9 with $Mn_2(CO)_{10}$ and H_2, and we report here a rare example of hydrogenation of a boron hydride cluster fragment facilitated by heterogeneous catalysis. This synthetic procedure has also been extended to give a new rhenahexaborane, 2,2,2-$(CO)_3$-2-ReB_5H_{10}.

Results and Discussion

Although the formation of **1** apparently involves the incorporation of hydrogen from H_2 into the product (eq 1), the reported synthesis used only a stoichiometric amount of H_2 at ca. 1 atm.[4]

$$Mn_2(CO)_{10} + 2B_5H_9 + H_2 \xrightarrow[138\ h]{140\ °C} 2(CO)_3MnB_5H_{10} + 4CO \quad (1)$$

Table II. ^{11}B NMR Data (86.7 MHz) in Benzene-d_6 Solvent

compd	B(3,6)[a]	B(4,5)	B(1)
2,2,2-$(CO)_3$-2-MnB_5H_{10} (**1**)	31.8 (140)	11.3 (156)	-53.7 (142)
2,2,2-$(CO)_3$-2-ReB_5H_{10} (**2**)	28.3 (133)	10.0 (156)	-54.1 (147)

[a] Values are chemical shifts in ppm with positive values downfield from $BF_3 \cdot O(C_2H_5)_2 = 0$. Values in parentheses are coupling constants in Hz. For B(3,6) the terminal J_{BH} coupling constants were obtained from selectively μ-H_{BRe}-decoupled spectra.

We have found that the yield of **1** improves dramatically when the synthesis is carried out under 100 atm of H_2 in the presence of certain heterogeneous catalysts (Table I), in the form of 5% transition metal on a carbon support. In parallel experiments, the yield of **1** varied considerably, depending on which metal catalyst was used. The Rh/C catalyst gave almost no product (<1%) while improved yields were obtained by using Pd/C (9.2%), Pt/C (13.4%), and Ru/C (37.7%). The highest yield of **1**, 40.9%, was obtained with Ru/C at 120 °C for 14 days. The necessity for both catalyst and high H_2 pressure was demonstrated by two experiments in which only the H_2 pressure differed. With Ru/C at 120 °C for 6 days, yields of **1** at 7 atm of H_2 were 1.4% but at 100 atm of H_2 were 31.8%.

The new rhenahexaborane, 2,2,2-$(CO)_3$-2-ReB_5H_{10} (**2**), the rhenium analogue of **1**, has been prepared in low yield by substitution of $Re_2(CO)_{10}$ for $Mn_2(CO)_{10}$ in the reaction with B_5H_9 and H_2 (ca. 100 atm) in the presence of Ru/C catalyst.

The ^{11}B NMR spectrum of **2** (Table II) consists of three doublets in a ratio of 2:2:1 that collapse to sharp singlets upon broad-band ^1H decoupling, indicating one terminal hydrogen on each boron. As with **1**, the resonances arising from the basal boron atoms are broadened somewhat in the ^1H-coupled spectrum by secondary coupling to neighboring bridge hydrogens. ^1H decoupling at the frequency corresponding to the B-H-Re bridge hydrogen resonance improves the resolution of the B(3,6) resonance, as expected. The ^1H NMR spectrum of **2** (Table III) consists of three groups of resonances. The lowest field group contains two partially overlapping quartets from the terminal hydrogens on B(3,6) and B(4,5). The center group of three resonances consists of a sharp quartet arising from the terminal hydrogen on B(1) partially overlapping the two broad peaks arising from the B-H-B bridge hydrogens. The resonance at highest field arises from the B-H-Re bridge hydrogens. Although it appears as a doublet, this resonance shape is derived from coupling to the neighboring ^{11}B atom.[15] Virtually all features of the NMR spectra of **2** are analogous to those of **1**. The ^{11}B and ^1H NMR parameters for **1** are included in Tables II and III, respectively, for purposes of comparison. The high-resolution mass spectrum of **2** confirms the molecular formula.

Compound **2** may be added to the short list of known rhenium boranes, which includes $[(CO)_5Re(BH_3)_n]^-$ (n = 1, 2),[16] $(CO)_4ReB_3H_8$,[2a,c] 2-$[(CO)_5Re]B_5H_8$,[3] $[6,6,6\text{-}(CO)_3\text{-}6\text{-}ReB_9H_{13}]^-$,[5b] and $[(CO)_3ReSB_{10}H_{10}]^-$.[6]

The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with B_5H_9 under 100 atm of H_2 in the presence of 5% Ru/C was also briefly examined. The expected product, 2-$(\eta^5\text{-}C_5H_5)$-2-FeB_5H_{10},[8a] was observed in low but unoptimized yield.

Mechanism of Formation

The catalytic role of the transition-metal surface is central to the mechanism of formation of $(CO)_3MnB_5H_{10}$ and $(CO)_3ReB_5H_{10}$ reported herein.

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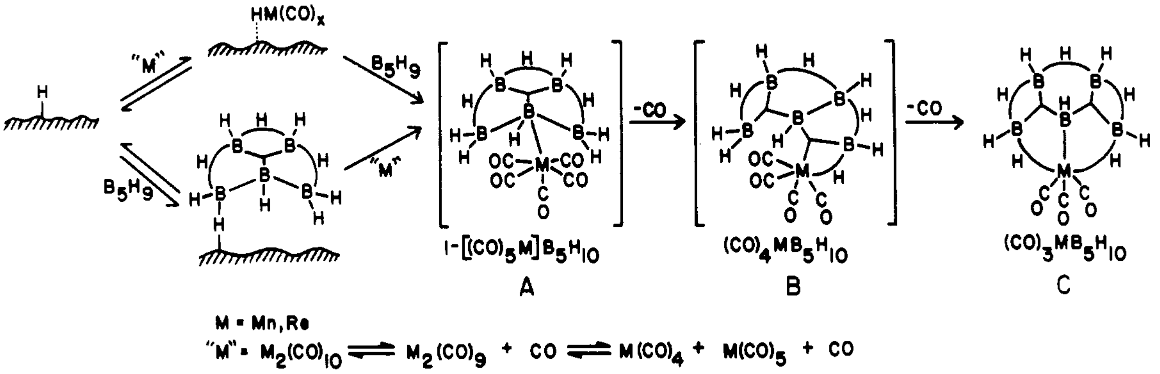
Table III. ^1H NMR Data (270.13 MHz) in Benzene-d_6 Solvent

compd	H(3,6)[a]	H(4,5)	H(1)	μ-H(8,10)	μ-H(9)	μ-H(7,11)
2,2,2-$(CO)_3$-2-MnB_5H_{10} (**1**)	5.11 (148)	3.92 (159)	-1.11 (144)	-1.24	-1.24	-12.25 (84)
2,2,2-$(CO)_3$-2-ReB_5H_{10} (**2**)	5.60 (126, 178)	4.44 (145, 204)	-1.11 (146)	-2.27 (61)	-0.54	-8.33 (79)

[a] Values are chemical shifts in ppm, measured relative to internal C_6D_5H = 7.15. Values in parentheses are coupling constants in Hz. As these values were obtained directly from the spectra, in some cases they are only "apparent" coupling constants. For the overlapping quartets due to B(3,6) and B(4,5), the two values given correspond to the observed outer and inner spacings for each quartet, respectively (see ref 14). The value for the coupling constant of the H(1) quartet is the separation between the two well-resolved peaks.

Scheme I



Recent work by Muetterties and co-workers[17] has shown that thermolysis of $M_2(CO)_{10}$ (M = Mn, Re) results in initial loss of CO and that, in the absence of a replacement ligand, this is followed by M–M bond scission (eq 2). Each of the four metal

$$M_2(CO)_{10} \underset{+CO}{\overset{\Delta, -CO}{\rightleftharpoons}} [M_2(CO)_9] \overset{\Delta}{\rightleftharpoons} [M(CO)_5] + [M(CO)_4] \quad (2)$$

carbonyl species in eq 2 is expected to be present under our reaction conditions and may react with surface hydrides to give free or surface-bound $HM(CO)_4$ or $HM(CO)_5$. $HM(CO)_4$ and $HM(CO)_5$ might then react with B_5H_9. This process, along with hypothetical structures for possible intermediates, is illustrated in Scheme I. Intermediate A represents a $(CO)_5M$-substituted pentaborane(11) and is shown as the 1-isomer. Loss of carbon monoxide from A could give B (an *arachno*-metallahexaborane) or the observed product C. Although there is no precedent for structure B, cage closure of B to C should be facile upon loss of carbon monoxide.

An alternative mechanism, also shown in Scheme I, begins with the reaction of a surface hydride with B_5H_9 to form surface-bound $B_5H_{10}^-$. While hydride addition to B_5H_9 does not occur per se and the $B_5H_{10}^-$ anion is unstable above -80 °C,[18] a surface-stabilized B_5H_{10} moiety as a reactive intermediate is not unreasonable. Reaction of this species with $M_2(CO)_{10}$ or fragments thereof could lead to the observed product.

A previous discussion of the mechanism of formation of **1** suggested 2-$[(CO)_5Mn]B_5H_8$ (**3**) as a possible intermediate (eq 3 and 4).[4] We have performed the thermolysis of **3** under H_2

$$HMn(CO)_5 + B_5H_9 \rightleftharpoons 2\text{-}[(CO)_5Mn]B_5H_8 + H_2 \quad (3)$$

$$2\text{-}[(CO)_5Mn]B_5H_8 + H_2 \rightarrow (CO)_3MnB_5H_{10} + 2CO \quad (4)$$

with and without a heterogeneous catalyst and have observed mostly decomposition. Analysis of the reaction mixture by ^{11}B NMR invariably showed a mixture of **1**, **3**, and B_5H_9. An intractable brown solid was also formed. The fact that no **3** has ever been observed in the reaction of $Mn_2(CO)_{10}$ with B_5H_9 and H_2 leads us to suggest that **3** is an unlikely intermediate in the direct synthesis of **1**. More likely is the direct formation of a $(CO)_xMnB_5H_{10}$ species, where x = 4 or 5, which then loses CO and rearranges to the observed $(CO)_3MnB_5H_{10}$.

Experimental Section

Manipulations of volatile compounds were performed in a standard high-vacuum line. The ^{11}B and ^1H NMR spectra were obtained at 86.7 and 270.13 MHz, respectively, on a Bruker WP270SY spectrometer. Mass spectra were obtained by using a KRATOS MS80 spectrometer.

Pentaborane(9) was from laboratory stock. B_2H_6,[19] B_4H_{10},[20] 2-$[(CO)_5Mn]B_5H_8$,[3] and $(CO)_5MnBr$[21] were prepared by standard methods. Reagent grade hydrogen (Chemetron, purity listed as 99.994%) was used as received. Hydrogen chloride (Matheson, technical grade) was purified by repeated high-vacuum distillation through a -126 °C U-trap and condensation in a -196 °C U-trap. Pentane, dimethyl ether, and benzene-d_6 were dried over $LiAlH_4$ and vacuum transferred directly into the vacuum line as needed. $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were sublimed immediately before use. The 5% palladium on powdered carbon and platinum on powdered carbon (Matheson Coleman and Bell), rhodium on powdered carbon (Engelhard), and ruthenium on powdered carbon (Alfa) were degassed before use (see below).

General Procedure for Pressurized Reactions. Conditions and yields for each reaction of $Mn_2(CO)_{10}$ with B_5H_9 are given in Tables I and II. The quantities of materials used were approximately 0.5 mmol of 5% metal/carbon catalyst, 5 mmol of $Mn_2(CO)_{10}$, and 25 mmol of B_5H_9. When a heterogeneous catalyst was used, it was loaded into a 30- or 75-mL single-ended stainless-steel cylinder of seamless one-piece construction (rated at 1800 psig—for example part no. 6HS75 supplied by Hoke, Inc.), equipped with a stainless-steel needle valve, and the system was carefully evacuated. (If evacuation is too rapid, the ensuing outgassing distributes the catalyst throughout the vacuum system.) Evacuation was continued for at least 12 h to ensure complete degassing of the catalyst. Dry nitrogen gas was then admitted to the cylinder, the valve was removed, and the metal carbonyl and other solid materials were added quickly. When the valve was reattached, the system was again evacuated, the lower half of the cylinder was cooled with liquid nitrogen, and B_5H_9 was added by condensation. With the lower half of the cylinder still immersed in liquid nitrogen, the valve was closed, disconnected from the vacuum line, and connected to an H_2 tank through a coil of copper tubing and a two-stage high-pressure regulator. After the tubing was flushed with H_2 from the tank at a preset pressure (see Table I), the cylinder valve was opened for about 2 min. During this time, some hydrogen was absorbed by the catalyst. When the pressure remained constant, the valve was closed, the tubing was vented, and the cylinder was allowed to warm to ambient temperature. After heating for the specified period in an oven, the reaction was cooled to ambient temperature and the lower half of the cylinder was immersed in liquid nitrogen for 30 min. Noncondensable gases were then vented slowly through a

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mineral oil bubbler. The cylinder was attached to the vacuum line, evacuated, and then warmed to ambient temperature. Volatile materials were condensed in a −196 °C U-trap while the cylinder was continuously evacuated for at least 24 h. The volatile materials were subsequently separated by high-vacuum fractional condensation. 2,2,2-$(CO)_3$-2-MnB_5H_{10} (**1**) was separated from B_5H_9 and hydrocarbon byproducts by fractional condensation in a −35 °C U-trap. When fractionation was terminated as soon as all of the **1** had distilled into the −35 °C U-trap, most of the unreacted $Mn_2(CO)_{10}$ stayed behind. Multiple fractionations were often required to remove all of the $Mn_2(CO)_{10}$.

Thermolysis of 2-[$(CO)_5$Mn]B_5H_8 (3) and H_2. Two millimoles of **3** was condensed into a 75-mL stainless-steel cylinder equipped with a stainless-steel needle valve. The cylinder was then pressurized with H_2 to 75 atm at ambient temperature and then heated in an oven at 100 °C for 38.5 h. The H_2 pressure at 100 °C was estimated to be ca. 94 atm. Fractionation of the products on a high-vacuum line yielded a mixture of **1** and **3** in a ratio of ca. 1:8 (by ^{11}B NMR). Examination of the nonvolatile solid left in the cylinder indicated decomposition to intractable materials.

Thermolysis of 3 and H_2 with Pt/C. A 75-mL stainless-steel cylinder was loaded with 1.56 g of 5% Pt/C (0.4 mmol of Pt), a needle valve was attached, and the system was evacuated for 18 h. Dry N_2 was admitted, and under N_2, a solution of 1.00 g of **3** (3.9 mmol) in 3 mL of pentane was added by syringe. The cylinder was pressurized with H_2 at ambient temperature to 61 atm. It was then heated at 100 °C for 9.8 days. The H_2 pressure at 100 °C would be ca. 76 atm. After the pressure was released at −196 °C, the volatiles were fractionated on a high-vacuum line, yielding 0.098 g of manganese-containing material in addition to a small amount of $Mn_2(CO)_{10}$. Analysis by ^{11}B NMR showed this to be an approximately equimolar mixture of **1** and **3**. This accounted for less than 15% of the starting manganese.

Reaction of K[B_5H_{12}] with $(CO)_5$MnBr. A procedure developed by Shore et al.[17] was used to prepare 2.0 mmol of K[B_5H_{12}] from K[B_4H_9] and B_2H_6 in 2.7 mL of dimethyl ether. At −78 °C the solvent and excess B_2H_6 were removed by vacuum distillation. After condensation of 3.0 mL of diethyl ether at −196 °C, 0.598 g of $(CO)_5$MnBr (2.2 mmol) was added under N_2 flow. The system was evacuated, stirred at −78 °C for 1 h and then warmed to ambient temperature over several hours. The ^{11}B NMR spectrum of the diethyl ether solution showed B_5H_9 and smaller amounts of other compounds, which were not identified. No evidence for **1** or **3** was obtained.

Preparation of 2,2,2-$(CO)_3$-2-ReB_5H_{10} (2). Compound **2** was prepared from $Re_2(CO)_{10}$, B_5H_9, and H_2 by using the general procedure for pressurized reactions described above. In each case, 5% Ru/C was used as catalyst. The volatile contents of the cylinder were distilled into the vacuum line during 48 h, and a partial separation was effected by distillation into U-traps cooled to −35 and −196 °C in series. The −196 °C trap contained unreacted B_5H_9, while the −35 °C trap contained a mixture of $B_{10}H_{14}$, 2-[$(CO)_5$Re]B_5H_8, and **2**. Compound **2** was subsequently isolated by condensation in a −10 °C trap.

From a reaction using 5.03 mmol of $Re_2(CO)_{10}$, 25 mmol of B_5H_9, 0.51 mmol of 5% Ru/C, and ca. 100 atm of H_2 at 140–145 °C for 5.8 days was obtained 0.244 g of **2** (0.73 mmol, 7.3% yield based on Re). Another reaction, using 4.22 mmol of $Re_2(CO)_{10}$, 25 mmol of B_5H_9, 0.51 mmol of 5% Ru/C, and ca. 100 atm of H_2 at 120–125 °C for 14 days, gave 0.350 g of **2** (1.05 mmol, 12.4% yield based on Re).

The ^{11}B and ^1H NMR spectra of **2** are tabulated in Tables II and III. The high-resolution mass spectrum of **2** confirmed the molecular formula: calcd for $(^{12}C^{16}O)_3{}^{187}Re^{11}B_4{}^{10}B^1H_{10}$, *m/e* 335.0661; found, *m/e* 335.0664.

Reaction of [$(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with B_5H_9 and H_2 over Ru/C. The general procedure for pressurized reactions (described above) was followed by using 0.51 mmol of 5% Ru/C, 5.04 mmol of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, and 25 mmol of B_5H_9. With its lower half immersed in liquid nitrogen, the cylinder was pressurized with H_2 to 60 atm. After warming to ambient temperature, it was heated at 142 °C for 6 days. The pressure was released at −196 °C, and the volatile contents of the cylinder were removed by vacuum distillation as it was warmed to ambient temperature. A small amount of yellow-brown solid was isolated by condensation in a −35 °C U-trap. This material was identified by ^{11}B NMR as impure 2-$(\eta^5\text{-}C_5H_5)$-2-FeB_5H_{10}.[8a] More of this compound was obtained by extraction of the solid residue remaining in the cylinder with CH_2Cl_2. The total amount of 2-$(\eta^5\text{-}C_5H_5)$-2-FeB_5H_{10} obtained was small and was not measured.

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Registry No. **1**, 71230-48-3; **2**, 98586-75-5; **3**, 98586-76-6; $Mn_2(CO)_{10}$, 10170-69-1; B_5H_9, 19624-22-7; K[B_5H_{12}], 11056-98-7; $(CO)_5$MnBr, 14516-54-2; $Re_2(CO)_{10}$, 14285-68-8; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9; 2-$(\eta^5\text{-}C_5H_5)$-2-Fe$B_5H_{10}$, 71661-61-5.

Supplementary Material Available: Figures 2 and 3, showing the ^{11}B and ^2H NMR spectra of 2,2,2-$(CO)_3$-2-ReB_5H_{10} (2 pages). Ordering information is given on any current masthead page.

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Electrocatalysis of Oxygen Reduction. 5. Oxygen to Hydrogen Peroxide Conversion by Cobalt(II) Tetrakis(*N*-methyl-4-pyridyl)porphyrin

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Cobalt(III) tetrakis(*N*-methyl-4-pyridyl)porphyrin (abbreviated Co^{III}TMPyP), although water soluble, adsorbs irreversibly on the surface of a highly polished glassy-carbon electrode. This porphyrin readily undergoes a one-electron reduction, either in solution or adsorbed, to produce the cobaltous form, which catalyzes the reduction of oxygen quantitatively to hydrogen peroxide. The pK_{a_1} of Co^{III}TMPyP is found to shift from a value of 6.0 for the solution to 2.0 for the adsorbed case. Thus, the electrode potential at which oxygen catalysis occurs is dependent on the pH and on the concentration ratio of the solution cobalt porphyrin to oxygen. However, at a pH of ca. 4 the redox potential of the solution CoTMPyP becomes more positive in value than that of the reversible O_2/H_2O_2 potential so that the electrogenerated cobaltous porphyrin no longer catalyzes the reduction of oxygen. The potential of catalysis then shifts negatively to the adsorbed CoTMPyP, which, upon reduction, converts the O_2 to H_2O_2. The addition of thiocyanate ion to the solution can accelerate the rate of electron transfer from the electrode to the cobalt porphyrin. This addition, in low concentrations, can favorably affect the potential at which oxygen is catalytically reacted by decreasing the overpotential for the Co^{III}TMPyP reduction.

Introduction

Of numerous studies[1-31] on the electrocatalysis of dioxygen with monomeric metal macrocyclic complexes, our laboratory has concentrated on water-soluble iron[19-25] and cobalt[26-28] porphyrins (abbreviated FeP and CoP or PCo^{II,III}) and the elucidation of their catalytic mechanism for dioxygen reduction at glassy-carbon

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