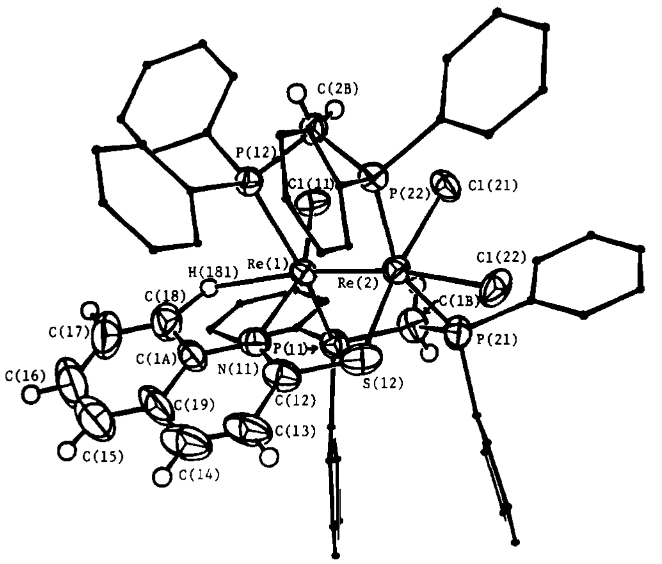

Figure 2. ORTEP view of the structure of the $[Re_2Cl_3(dppm)_2(2\text{-mq})]^+$ cation. For clarity, the atomic numbering scheme is given for all atoms except the phenyl carbon atoms of the dppm ligands and the nitrogen atom of the 2-mq ligand. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings, which are circles of arbitrary radius.

2. A trans disposition of bridging dppm ligands is present, and the deprotonated 2-mercaptoquinoline ligand assumes a bridging mode. The Re–Re distance of 2.2540 (5) Å is consistent with a Re–Re bond order of 3.5.[1,5] The structure is slightly twisted away from an eclipsed rotational geometry, although this is hardly surprising in view of the disparate set of ligands. The torsional angles P(11)–Re(1)–Re(2)–P(21), P(12)–Re(1)–Re(2)–P(22), N(11)–Re(1)–Re(2)–Cl(21), and Cl(11)–Re(1)–Re(2)–S(12), which reflect the magnitude of this distortion, are 6.3 (1), 1.5 (1), 4.5 (2), and 5.1 (1)°, respectively. There are three terminal Re–Cl bonds, one of which is collinear with the Re–Re bond and is, as expected, the longest of the three (2.553 (2) Å versus 2.330 (2) and 2.393 (2) Å). Actually, the Re(1)–Re(2)–Cl(22) unit does deviate somewhat from linearity, with the angle being 166.97 (6)°. While the Re–N and Re–S distances and other parameters associated with the μ-(2-mq) ligand are normal, one feature of special note is that the hydrogen atom (H(181)) on C(18) of the quinoline ring forms a very close contact with Re(1), the Re(1)–H(181) distance being 2.3 (1) Å. While this doubtless reflects, at least in part, the constraints imposed by the rigid planar aromatic ring forcing a close approach of H(181), the associated weakening of the C–H bond (C(18)–H(181) = 1.3 (1) indicates that this may represent an agostic Re···H interaction. In view of the variety and stability of lower valent dirhenium polyhydrides,[16] this is perhaps not unreasonable.

Concluding Remarks. The key features of the chemistry that involves the reactions of $Re_2X_4(dppm)_2$ (X = Cl, Br) with the 2-mqH ligand are summarized by eqs 1–5 in Scheme I. Of particular note is the observation that the oxidation represented by (2) can be accomplished either chemically or electrochemically; this process is of interest, since it is followed by a chemical transformation (3) involving dehydrohalogenation. These complexes represent the first examples of the coordination of a thiolato ligand to a multiply bonded dirhenium unit.

Acknowledgment. Support from the National Science Foundation, through Grant No. CHE88-07444 to R.A.W. and Grant No. CHE86-15556 for the purchase of the microVAX computer and diffractometer, is gratefully acknowledged. We also acknowledge the National Institutes of Health (Grant No. RR-01077) and the National Science Foundation (Grant No. 87-14258) for funds to purchase the NMR spectrometer.

Supplementary Material Available: Tables giving full details of crystal data and data collection parameters (Table S1), positional parameters and their errors for the non-hydrogen atoms (Table S2) and for the hydrogen atoms (Table S3), thermal parameters (Table S4), bond distances (Tables S5), and bond angles (Table S6) and a figure (Figure S1) showing the X-band ESR spectra of $[Re_2Cl_4(dppm)_2(2\text{-mqH})]^+$ and $[Re_2X_3(dppm)_2(2\text{-mq})]PF_6$ (X = Cl, Br) (21 pages); tables of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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Formation and Reactions of Bis(trimethylphosphine)–Methyldiborane(4)

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Received February 21, 1990

Treatment of $1\text{-}CH_3B_5H_8$ or $2\text{-}CH_3B_5H_8$ with $P(CH_3)_3$ resulted in the cleavage of the pentaborane framework to give $CH_3B_2H_3\cdot 2P(CH_3)_3$ and $B_3H_5\cdot 3P(CH_3)_3$. The methylated diborane(4) adduct $CH_3B_2H_3\cdot 2P(CH_3)_3$ was characterized by mass and NMR spectroscopy, and its reaction chemistry was studied. Hydrogen chloride reacted with $CH_3B_2H_3\cdot 2P(CH_3)_3$ to give $BH_3\cdot P(CH_3)_3$ and $CH_3BHCl\cdot P(CH_3)_3$. The reaction of $CH_3B_2H_3\cdot 2P(CH_3)_3$ with B_4H_{10} in CH_2Cl_2 at −40 °C gave $1\text{-}CH_3B_3H_5\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$. The $1\text{-}CH_3B_3H_5\cdot 2P(CH_3)_3{}^+$ cation isomerized to the $3\text{-}CH_3B_3H_5\cdot 2P(CH_3)_3{}^+$ cation above −35 °C. Likewise, $CH_3B_2H_3\cdot 2P(CH_3)_3$ reacted with B_2H_6 to form $1\text{-}CH_3B_3H_5\cdot 2P(CH_3)_3{}^+B_2H_7{}^-$, which isomerized to $3\text{-}CH_3B_3H_5\cdot 2P(CH_3)_3{}^+B_2H_7{}^-$. Both of these $B_2H_7{}^-$ salts decomposed at room temperature to give $B_3H_7\cdot P(CH_3)_3$, $CH_3B_3H_6\cdot P(CH_3)_3$, $BH_3\cdot P(CH_3)_3$, and $CH_3BH_2\cdot P(CH_3)_3$.

Introduction

An earlier report from this laboratory showed that the treatment of pentaborane(9) with excess trimethylphosphine resulted in the cleavage of the pentaboron framework to give bis(trimethylphosphine)–diborane(4) $[B_2H_4\cdot 2P(CH_3)_3]$ and tris(trimethylphosphine)–triborane(5) $[B_3H_5\cdot 3P(CH_3)_3]$in a 1:1 molar ratio.[1] Subsequently, the reaction chemistry of these cleavage products was investigated, and the results were reported elsewhere.[2–6]

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The unexpectedly clean cleavage of B_5H_9 brought about questions regarding the behavior of substituted pentaboranes (XB_5H_8) toward $P(CH_3)_3$: Would XB_5H_8 be cleaved in the manner similar to that observed for B_5H_9? If so, would the substituent X be on the B_2H_4 or B_3H_5 fragment, and what would be the reactivity of the substituted B_2H_4 or B_3H_5 adduct? In this paper, the results of the study performed on methylpentaborane(9) are reported.

Results and Discussion

Reaction of $CH_3B_5H_8$ with $P(CH_3)_3$. Methylpentaborane(9), $1\text{-}CH_3B_5H_8$ or $2\text{-}CH_3B_5H_8$, reacted with excess trimethylphosphine according to eq 1. The product, $CH_3B_2H_3\cdot 2P(CH_3)_3$, could be

$$CH_3B_5H_8 + 5P(CH_3)_3 \rightarrow CH_3B_2H_3\cdot 2P(CH_3)_3 + B_3H_5\cdot 3P(CH_3)_3 \quad (1)$$

separated in a good yield from the triborane(5) adduct by sublimation. Its purity, however, was only about 90%, $B_2H_4\cdot 2P(CH_3)_3$ being the major contaminant. The residue from the sublimation was a mixture of borane compounds containing $B_6H_{10}\cdot 2P(CH_3)_3$ as the major component. The triborane(5) adduct $B_3H_5\cdot 3P(CH_3)_3$ is known to dimerize at room temperature under vacuum to give $B_6H_{10}\cdot 2P(CH_3)_3$.[1]

The 10% contamination of $B_2H_4\cdot 2P(CH_3)_3$ in the sublimed sample of $CH_3B_2H_3\cdot 2P(CH_3)_3$ is thought to be the secondary byproduct that was formed during the dimerization process of $B_3H_5\cdot 3P(CH_3)_3$ rather than the primary cleavage byproduct of the pentaborane. The earlier observation showed that, when $B_2H_4\cdot 2P(CH_3)_3$ was sublimed from the 1:1 mixture of $B_2H_4\cdot 2P(CH_3)_3$ and $B_3H_5\cdot 3P(CH_3)_3$, $B_2H_4\cdot 2P(CH_3)_3$ was obtained in a 110% yield,[1] indicating that the extra $B_2H_4\cdot 2P(CH_3)_3$ was produced as byproduct. Thus, the reaction of $CH_3B_5H_8$ with $P(CH_3)_3$ seemed to proceed exclusively according to eq 1.

In the reaction of B_5H_9 with $P(CH_3)_3$, the formation of $B_5H_9\cdot 2P(CH_3)_3$ is the first step, and then this adduct undergoes the cleavage reaction with $P(CH_3)_3$.[1] With trimethylamine, $CH_3B_5H_8$ is known to form the 1:1 adduct, $CH_3B_5H_8\cdot N(CH_3)_3$.[7] However, attempts to identify intermediates in the reaction of $CH_3B_5H_8$ with $P(CH_3)_3$ were unsuccessful. The reactivity of the initial reaction intermediate, e.g., $CH_3B_5H_8\cdot P(CH_3)_3$ or $CH_3B_5H_8\cdot 2P(CH)_3$, toward $P(CH_3)_3$ appeared to be comparable to, or even higher than, that of $CH_3B_5H_8$. The details of the observation are described in the Experimental Section.

Mass and NMR Spectra of $CH_3B_2H_3\cdot 2P(CH_3)_3$. Elimination of $B_2H_4\cdot 2P(CH_3)_3$ from the sublimed sample of $CH_3B_2H_3\cdot 2P(CH_3)_3$ could not be achieved by the fractional condensation that was employed, due to the similar volatility of the two solids. The mass spectrum of the sublimed sample of $CH_3B_2H_3\cdot 2P(CH_3)_3$ showed the highest mass cutoff at *m/z* 192, the center of the cluster of peaks being at *m/z* 190; calculated mass for $CH_3{}^{11}B_2H_3\cdot 2P(CH_3)_3 = 192$. The second cluster of peaks was centered at *m/z* 176 with the mass cut-off at *m/z* 178, representing $B_2H_4\cdot 2P(CH_3)_3$ and $CH_3B_2H_3\cdot 2P(CH_3)_3 - CH_3$. The $^{11}B\{^1H\}$ NMR spectra (96.2 MHz) of the mixture in CH_2Cl_2 showed the two signals of $CH_3B_2H_3\cdot 2(CH_3)_3$ and the signal of $B_2H_4\cdot 2P(CH_3)_3$ clearly separated from each other (see Figure 1). Methyl substitution for the hydrogen atom on a boron atom is known to shift the ^{11}B signal to the low field.[8a] Therefore, the signals at −30.2 and −34.6 ppm are assigned to the B_1 (or *B*-CH_3) and B_2 boron atoms, respectively. The multiplet appearance of each of the two boron signals suggests that the spectrum is of an AB pattern containing the B–P and B–B couplings; the appearance of the B–P doublet is obscured by its further splitting into the $^{11}B–^{11}B$ quartet and $^{11}B–^{10}B$ septet. In the $^{31}P\{^1H\}$ NMR spectrum (121.4 MHz) that is shown in Figure 2, the signals of the two phosphorus atoms appeared as two doublets ($P_1–P_2$) of quartets (P–B) with an AB pattern. The center of the pattern was at 1.9 ppm, the $J_{P_1P_2}$ value was 120.8 Hz, and the two doublets were 337.5 Hz apart (+3.3 and +0.6 ppm). The high-field doublet is assigned to the P_1 (or *P*-B-CH_3) atom ($J_{P_1B_1} \approx 48$ Hz) and the low-field doublet to the P_2 atom ($J_{P_2B_2} = 51$ Hz), since the ^{31}P signal for $CH_3BH_2\cdot P(CH_3)_3$ appears at a higher field than that for $BH_3P\cdot P(CH_3)_3$. The overlap of the $B_2H_4\cdot 2P(CH_3)_3$ signal with the +3.3 ppm signal also supports the above assignment.

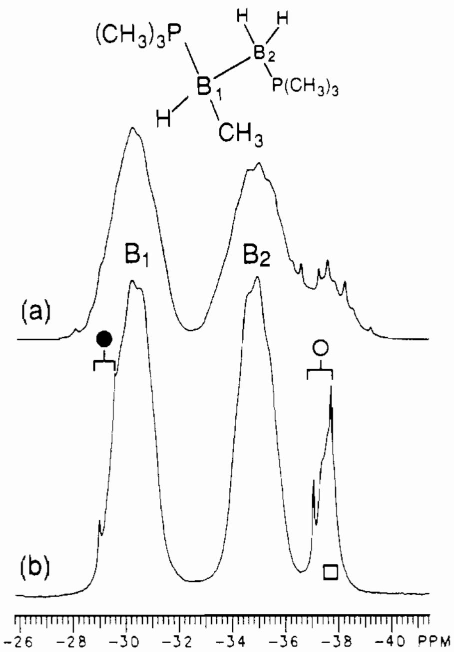

Figure 1. ^{11}B NMR spectrum (96.2 MHz) of $CH_3B_2H_3\cdot 2P(CH_3)_3$ in CH_2Cl_2 at +20 °C: (a) normal spectrum, (b) proton-spin decoupled spectrum. Impurities: (○) $BH_3\cdot P(CH_3)_3$; (●) $CH_3BH_2\cdot P(CH_3)_3$; (□) $B_2H_4\cdot 2P(CH_3)_3$.

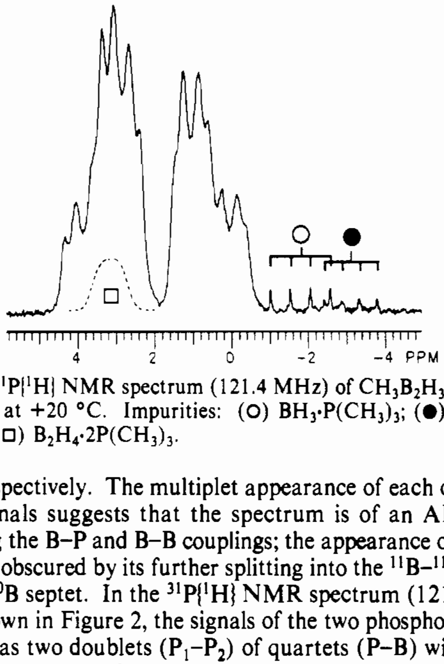

Figure 2. $^{31}P\{^1H\}$ NMR spectrum (121.4 MHz) of $CH_3B_2H_3\cdot 2P(CH_3)_3$ in CH_2Cl_2 at +20 °C. Impurities: (○) $BH_3\cdot P(CH_3)_3$; (●) $CH_3BH_2\cdot P(CH_3)_3$; (□) $B_2H_4\cdot 2P(CH_3)_3$.

Reactions of $CH_3B_2H_3\cdot 2P(CH_3)_3$. (a) With HCl. Like $B_2H_4\cdot 2P(CH_3)_3$,[1] $CH_3B_2H_3\cdot 2P(CH_3)_3$ reacted readily with anhydrous chloride according to eq 2. A small amount of $BH_2Cl\cdot P(CH_3)_3$

$$CH_3B_2H_3\cdot 2P(CH_3)_3 + HCl \rightarrow CH_3BHCl\cdot P(CH_3)_3 + BH_3\cdot P(CH_3)_3 \quad (2)$$

(ca. 7%) was produced, but *no $CH_3BH_2\cdot P(CH_3)_3$ was found* in the product. The presence of $B_2H_4\cdot 2P(CH_3)_3$ impurity in the original sample of $CH_3B_2H_3\cdot 2P(CH_3)_3$ accounts for the formation of $BH_2Cl\cdot P(CH_3)_3$ in the HCl reaction. Thus, the cleavage of

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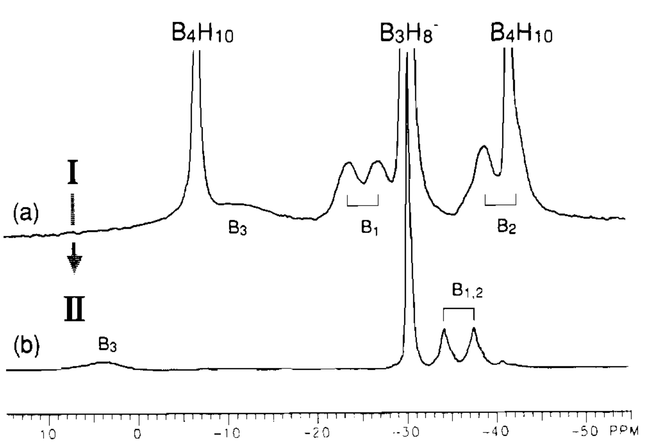

Figure 3. $^{11}B\{^1H\}$ NMR spectra (32.1 MHz), showing the formation of I and II. (a) I ($1\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+$) with excess B_4H_{10}. (b) II ($3\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+$).

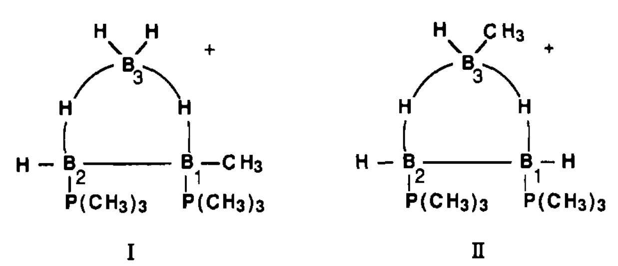

Figure 4. Structures proposed for I, the $1\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+$ cation, and II, the $3\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+$ cation.

the B_1–B_2 bond by HCl occurred exclusively in the manner indicated by eq 2. This exclusive pattern of cleavage may be due to the greater stability of the $CH_3BH{\cdot}P(CH_3)_3^+$ cation over the $BH_2{\cdot}P(CH_3)_3^+$ cation, just as the stability of carbenium ions increases with the degree of alkylation on the central carbon atom.

(b) With Tetraborane (10). When $CH_3B_2H_3{\cdot}2P(CH_3)_3$ was treated with B_4H_{10} in CH_2Cl_2, a slow reaction occurred at -50 °C to form the $B_3H_8^-$ salt of a cationic species, I. When the temperature was raised above -40 °C, or when the excess B_4H_{10} and solvent were removed by pumping at -35 °C, I changed to another cationic species, II, which was reasonably stable at room temperature. The ^{11}B NMR spectra in Figure 3 shows this formation and transformation of the $B_3H_8^-$ salts.

The reaction of $B_2H_4{\cdot}2P(CH_3)_3$ with B_4H_{10} is known to give the $B_3H_8^-$ salt of the $B_3H_6{\cdot}2P(CH_3)_3^+$ cation:[2]

$$B_2H_4{\cdot}2P(CH_3)_3 + B_4H_{10} \rightarrow B_3H_6{\cdot}2P(CH_3)_3^+B_3H_8^- \quad (3)$$

Accordingly, $CH_3B_2H_3{\cdot}2P(CH_3)_3$ reacted with B_4H_{10} to first give the $B_3H_8^-$ salt of a methyl derivative of the triboron complex cation, [$1\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+$] (I), which changed at higher temperatures to an isomer of the cation, [$3\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+$] (II). The proposed structures of the two new cations, I and II, are shown in Figure 4. The isomerization of I to II is attributed to the favorable dative bond strength for P→B–H over that for $P{\rightarrow}B\text{–}CH_3$.

The two ^{11}B NMR signals of I at -25.3 [d (-40 °C), J_{BP} = 103 Hz] and -40.7 [t (-40 °C), $J_{BH} \approx 100$ Hz, J_{BP} = 115 Hz] ppm are assigned to the B_1 and B_2 atoms, respectively, of the $1\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+$ cation. The signal of II at -35.5 ppm [t (-40 °C), $J_{BH} \approx 100$ Hz, J_{BP} = 108 Hz] is assigned to the $B_{1,2}$ atoms of the $3\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+$ cation. The broad signals at -11.0 and +4.0 ppm are due to the B_3 atoms of I and II, respectively. The signals of the $B_3H_6{\cdot}2P(CH_3)_3^+$ cation appear at -39.0 ($B_{1,2}$) and -10.5 (B_3) ppm.[2]

(c) With Diborane (6). The reaction of $CH_3B_2H_3{\cdot}2P(CH_3)_3$ with B_2H_6 in CH_2Cl_2 proceeded in the manner similar to that which was observed for the B_4H_{10} reaction. As a reaction mixture containing $CH_3B_2H_3{\cdot}2P(CH_3)_3$ and B_2H_6 in a 1:1 molar ratio in CH_2Cl_2 was allowed to warm from -80 to -40 °C, $CH_3B_2H_3{\cdot}2P(CH_3)_3$ was rapidly consumed. At -40 °C, $1\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+B_2H_7^-$ was the major product. A small amount of $3\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+B_2H_7^-$ was present. As the temperature was raised to -20 °C, the amount of the 3-isomer increased, and the decomposition of the salts began to occur. The decomposition was faster at -10 °C, but both isomers were still present. The $B_2H_7^-$ salts disappeared completely within 1 h at room temperature.

The initial formation of the two methyltriboron complex cation salts are expressed by the equations

$$CH_3B_2H_3{\cdot}2P(CH_3)_3 + \tfrac{1}{2}B_2H_6 \rightarrow 1\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+B_2H_7^- \quad (4)$$

$$1\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+B_2H_7^- \rightarrow 3\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+B_2H_7^- \quad (5)$$

The subsequent decomposition of these $B_2H_7^-$ salts compares with the decomposition of $B_3H_6{\cdot}2P(CH_3)_3^+B_2H_7^-$, which is expressed by eq 6.[2] Accordingly, the $CH_3B_3H_5{\cdot}2P(CH_3)_3^+B_2H_7^-$ salts are

$$B_3H_6{\cdot}2P(CH_3)_3^+B_2H_7^- \rightarrow B_3H_7{\cdot}P(CH_3)_3 + BH_3{\cdot}P(CH_3)_3 + \tfrac{1}{2}B_2H_6 \quad (6)$$

thought to decompose in the manner represented by eqs 7 and 8. Thus, the overall equation is given by eq 9, where the value of x was about 0.7.

$$1\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+B_2H_7^- \rightarrow B_3H_7{\cdot}P(CH_3)_3 + CH_3BH_2{\cdot}P(CH_3)_3 + \tfrac{1}{2}B_2H_6 \quad (7)$$

$$3\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+B_2H_7^- \rightarrow CH_3B_3H_6{\cdot}P(CH_3)_3 + BH_3{\cdot}P(CH_3)_3 + \tfrac{1}{2}B_2H_6 \quad (8)$$

$$CH_3B_2H_3{\cdot}2P(CH_3)_3 + B_2H_6 \rightarrow xB_3H_7{\cdot}P(CH_3)_3 + xCH_3BH_2{\cdot}P(CH_3)_3 + (1-x)CH_3B_3H_6{\cdot}P(CH_3)_3 + (1-x)BH_3{\cdot}P(CH_3)_3 \quad (9)$$

When B_2H_6 was used in excess of the amount that was required by eq 9, the excess B_2H_6 reacted with the $3\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+$ cation at -20 °C:

$$B_2H_6 + 3\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+ \rightarrow CH_3B_2H_5 + B_3H_6{\cdot}2P(CH_3)_3^+ \quad (10)$$

$$CH_3B_2H_5 + 3\text{-}CH_3B_3H_5{\cdot}2P(CH_3)_3^+ \rightarrow (CH_3)_2B_2H_4 + B_3H_6{\cdot}2P(CH_3)_3^+ \quad (11)$$

Thus, in the final products, the ratio $CH_3B_3H_6{\cdot}P(CH_3)_3/B_3H_7{\cdot}P(CH_3)_3$ was small, and B_2H_6, $CH_3B_2H_5$, and *cis*- and *trans*-$(CH_3)_2B_2H_4$ were present.

Note on $CH_3B_3H_6{\cdot}P(CH_3)_3$. The $P(CH_3)_3$ adducts of triborane(7) and methyltriborane(7) were separated out, as a mixture of solids, by fractional condensation from the decomposition products of $CH_3B_3H_5{\cdot}2P(CH_3)_3^+B_2H_7^-$. Complete separation of $CH_3B_3H_6{\cdot}P(CH_3)_3$ from $B_3H_7{\cdot}P(CH_3)_3$ was not accomplished. The volatilities of the two compounds were very close. The mass spectrum of this triborane adduct mixture showed the first cluster centered at m/z 127 [mass (absolute height): m/z 125.1 (7), 126.1 (19), 127.1 (132), 128.0 (168), 129.0 (25)]; calculated mass for $CH_3{}^{11}B_3H_6{\cdot}P(CH_3)_3$ = 130. Apparently, successive loss of hydrogen atoms occurred in the mass spectrometer. Similar successive losses of hydrogen atoms have been reported for other borane compounds.[9] The second cluster of peaks that represented $B_3H_7{\cdot}P(CH_3)_3$ was seen centered at m/z 114 [mass (absolute height): m/z 111 (8), 112.1 (41), 113.1 (224), 114.1 (504), 115.1 (90), 116.1 (59)].

The $^{11}B\{^1H\}$ NMR spectrum of the mixture (Figure 5) showed three separate signals in a 1:1:1 intensity ratio for $CH_3B_3H_6{\cdot}P(CH_3)_3$, suggesting that the compound has the structures that

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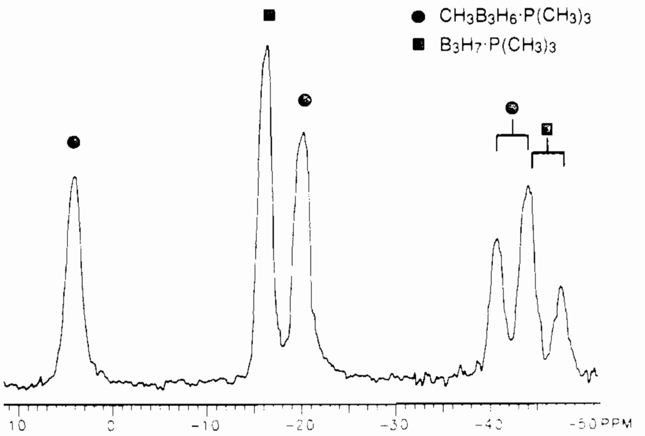

Figure 5. $^{11}B\{^1H\}$ NMR spectrum (32.1 MHz) of a $CH_3B_3H_6{\cdot}P(CH_3)_3$–$B_3H_7{\cdot}P(CH_3)_3$ mixture in CH_2Cl_2 at +15 °C.

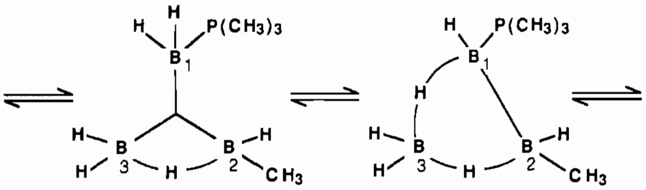

Figure 6. Structures proposed for $CH_3B_3H_6{\cdot}P(CH_3)_3$, showing its tautomerization.

are illustrated in Figure 6. The signals at +4.4, −20.0, and −42.0 (J_{BP} = 106 Hz) ppm are assigned to the B_2, B_3, and B_1 atoms, respectively. These signals in the normal ^{11}B spectrum are broader than those of the proton-spin-decoupled spectrum, and did not show the B–H multiplets that would be expected from either of the two static structures in Figure 6. Thus, the compound appeared to be fluxional at room temperature with respect to the migration of the borane hydrogen atoms.

Experimental Section

Chemicals and Equipment. Standard vacuum-line techniques were used throughout for the handling of the volatile and air-sensitive compounds. 1-Methylpentaborane(9) was prepared by the literature method,[10] and $2\text{-}CH_3B_5H_8$ by the reported procedure.[11] Trimethylphosphine, B_2H_6, and B_4H_{10} were our laboratory stock. The NMR spectra were recorded on a Varian XL-100 or XL-300 NMR spectrometer. The shift standards were $BF_3{\cdot}O(C_2H_5)_2$ for ^{11}B, and 85% orthophosphoric acid for ^{31}P. The ^{11}B chemical shift values of B_2H_6,[8b] B_4H_{10},[8c] $B_3H_7{\cdot}P(CH_3)_3$,[12] $BH_3{\cdot}P(CH_3)_3$,[8d] $BH_2Cl{\cdot}P(CH_3)_3$,[1] $B_2H_4{\cdot}2P(CH_3)_3$,[1] $B_3H_6{\cdot}2P(CH_3)_3{}^+$,[2] $CH_3B_2H_5$,[8e] and *cis*- and *trans*-$(CH_3)_2B_2H_4$[8e] were found in the references cited for the respective compounds. These values were used for the identification of the species that were encountered.

Reaction of $1\text{-}CH_3B_5H_8$ with $P(CH_3)_3$. (a) Treatments of $1\text{-}CH_3B_5H_8$ with Varied Amounts of $P(CH_3)_3$. A measured amount of $1\text{-}CH_3B_5H_8$ was dissolved in about 1.5 mL of CH_2Cl_2 in a 10-mm-o.d. Pyrex tube equipped with a Teflon valve, and then a measured amount of $P(CH_3)_3$ was condensed into the tube. The mixture was agitated at −80 °C for mixing, and then the tube was placed in the probe of the XL-100 NMR spectrometer to monitor the reaction progress by recording the ^{11}B NMR spectra at different temperatures, which were increased in a stepwise manner. Five reaction mixtures were examined. These contained the two reactants in varied molar ratios [$1\text{-}CH_3B_5H_8$:$P(CH_3)_3$]: namely, 0.543 mmol:0.541 mmol ("1:1"), 0.543 mmol:1.116 mmol ("1:2"), 0.503 mmol:1.567 mmol ("1:3"), 0.503 mmol:2.017 mmol ("1:4"), and 0.502 mmol:15.74 mmol ("1:excess", no solvent CH_2Cl_2 used).

Generally, when the solvent CH_2Cl_2 was used, the reaction did not occur until the temperature was raised to −10 to 0 °C, and slow changes continued to occur at room temperature. The solution remained clear at all times, and no hydrogen gas was produced. On the other hand, when the excess $P(CH_3)_3$ served as the solvent, the reaction occurred at around −40 °C and was completed as the mixture was warmed to room temperature. A large amount of a white precipitate that was observed at −40 °C disappeared as the temperature increased to −20 to 0 °C.

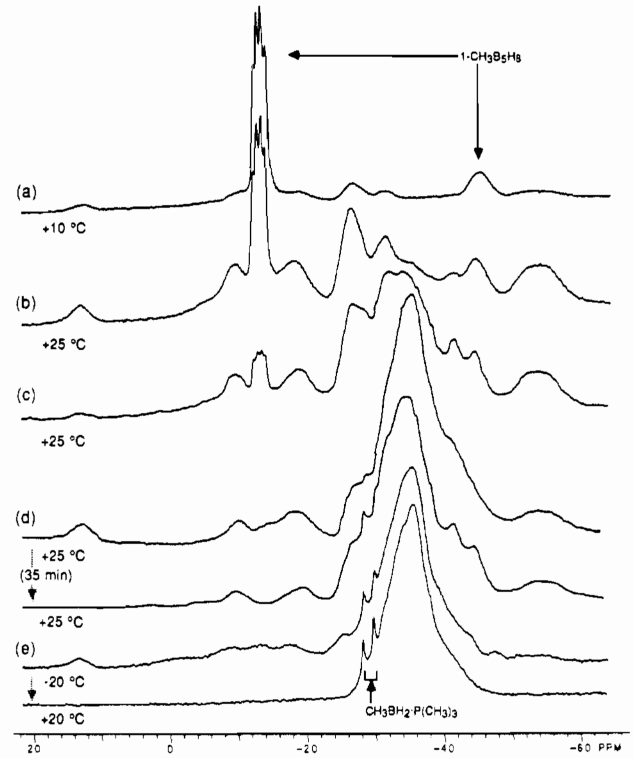

Figure 7. $^{11}B\{^1H\}$ NMR spectra (32.1 MHz) of $CH_3B_5H_8$–$P(CH_3)_3$ reaction mixtures: (a) "1:1"; (b) "1:2"; (c) "1:3"; (d) "1:4"; (e) "1:excess".

In Figure 7, the ^{11}B NMR spectra of these reaction mixtures are shown. When the "1:1" and "1:2" mixtures were allowed to warm to room temperature, some $1\text{-}CH_3B_5H_8$ remained unchanged, and at least two intermediate species were produced in the solution. Very small amounts of the final cleavage products[13] were detectable in the "1:2" solution. When the mixing ratio was "1:3", $1\text{-}CH_3B_5H_8$ was totally consumed eventually at room temperature, and fair amounts of the final products were produced; the $1\text{-}CH_3B_5H_8$ signal in Figure 7c disappeared within 1 h after the recording of the spectrum. When the "1:4" mixture was allowed to warm to room temperature, $1\text{-}CH_3B_5H_8$ was consumed rapidly to give the final cleavage products, and the intermediates that were observed in other mixtures were present in small amounts in the solution. When $P(CH_3)_3$ was used as the solvent (the "1:excess" case), the final cleavage products[13] formed rapidly through the formation of the intermediates (observed at −40 to 0 °C). The formation of the final cleavage products is always accompanied by the formation of a very small amount of $CH_3BH_2{\cdot}P(CH_3)_3$ [−29.0 ppm, t of d, J_{BH} = 91 Hz, J_{BP} = 56 Hz] as indicated in Figure 7. However, no $BH_3{\cdot}P(CH_3)_3$ was found in the products.

(b) Reaction of $2\text{-}CH_3B_5H_8$ with Excess $P(CH_3)_3$. A 0.274-mmol sample of $2\text{-}CH_3B_5H_8$ was mixed with a 1.615-mmol sample of $P(CH_3)_3$ in a 10-mm-o.d. Pyrex tube. The ^{11}B NMR spectrum of the reaction mixture at room temperature was identical with that shown in Figure 1e, except for the presence of the weak signal of $BH_3P(CH_3)_3$ in addition to the weak signal of $CH_3BH_2{\cdot}P(CH_3)_3$.

(c) Preparation of $CH_3B_2H_3{\cdot}2P(CH_3)_3$ Samples. A 5.35-mmol sample of $1\text{-}CH_3B_5H_8$ was placed in a 50-mL round-bottom flask containing a spin bar. Then, a 3.098-g (40.77-mmol) sample of $P(CH_3)_3$ was condensed into the flask at −197 °C. The mixture was stirred at −80 °C for 10 min, and then the flask was allowed to warm, in a stepwise manner, to −35 °C (15 min), 0 °C (15 min), and finally to room temperature (25 min). The solution was clear until about 10 min after the flask was warmed to room temperature, and then it suddenly became turbid. The solvent $P(CH_3)_3$ was briefly pumped out from the flask. The flask was then attached to point A of the sublimation apparatus that is shown in Figure 8 and evacuated. The volatiles ($CH_3B_2H_3{\cdot}2P(CH_3)_3$ and $P(CH_3)_3$) were condensed in part B which was cooled with liquid nitrogen.

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(13) In the 32.1-MHz ^{11}B NMR spectra, the B_1 and B_2 signals of $CH_3B_2H_3{\cdot}2P(CH_3)_3$ appear as an overlapped broad peak that is centered at ∼−33 ppm. The spectrum of the final cleavage products (Figure 7e) is the superposition of the $CH_3B_2H_3{\cdot}2P(CH_3)_3$ signal over the low-field side of the $B_3H_5{\cdot}3P(CH_3)_3$ signal.[1]

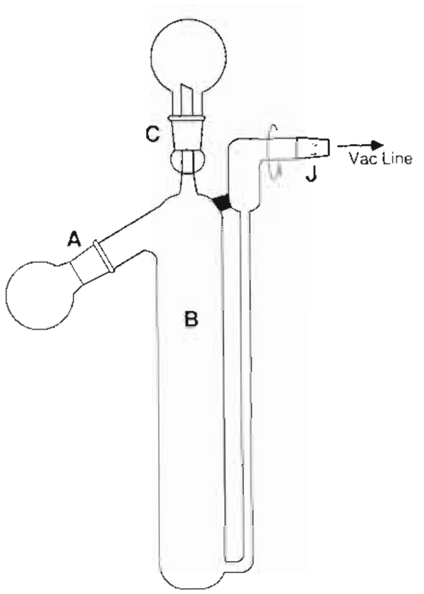

Figure 8. Apparatus for the sublimation of $CH_3B_2H_3 \cdot 2P(CH_3)_3$.

This sublimation process was continued for a period of 60 h or until no volatiles came out of the flask. Nitrogen gas was then admitted into the apparatus, and the flask was replaced with a cap. The apparatus was reevacuated, inverted around the joint J, and the sublimate in part B was washed into flask C with $P(CH_3)_3$ as solvent. After the removal of $P(CH_3)_3$ from flask C by pumping at 0 °C, the solid sample was weighed and found to be 1.033 g (or 5.39 mmol, 100.7% yield assuming a pure sample of $CH_3B_2H_3 \cdot 2P(CH_3)_3$. In another preparation, where 3.45 mmol of $1\text{-}CH_3B_5H_8$ and 30.57 mmol of $P(CH_3)_3$ were employed, the sublimed product weighed 0.680 g (or 3.55 mmol, 102.8% yield).

Reaction of $CH_3B_2H_3 \cdot 2P(CH_3)_3$ with HCl. A 0.485-mmol sample of $CH_3B_2H_3 \cdot 2P(CH_3)_3$ was dissolved in about 1.5 mL of CH_2Cl_2 in a 10-mm-o.d. Pyrex tube that was equipped with a stopcock. The solution was frozen at −197 °C, and a 0.498-mmol sample of anhydrous HCl was condensed into the tube. The tube was placed in a −80 °C bath, shaken to mix the reactants, and then allowed to warm slowly to room temperature. The solution remained clear, and only a trace of noncondensable gas was found in the tube. The ^{11}B spectrum of the reaction solution consisted of the signals of $BH_3 \cdot P(CH_3)_3$ and $CH_3BHCl \cdot P(CH_3)_3$ (−10.0 ppm, d of d, $J_{BP} = 80$ Hz, $J_{BH} = 110$ Hz) in an approximately 1:1 intensity ratio and the weak signal (ca. 7% of the total boron signal) of $BH_2Cl \cdot P(CH_3)_3$. No other signals were present in the spectrum.

Reaction of $CH_3B_2H_3 \cdot 2P(CH_3)_3$ with B_4H_{10}. A solution containing 0.490 mmol of $CH_3B_2H_3 \cdot 2P(CH_3)_3$ in 1.5 mL of CH_2Cl_2 was prepared in a 10-mm-o.d. Pyrex tube, and a 0.594-mmol sample of B_4H_{10} was condensed into the tube. The tube was shaken in a −80 °C bath to mix the reactants and then placed in the probe of the XL-100 NMR spectrometer. The reaction began to occur slowly at −50 °C and was completed in a period of 30 min at −40 °C (see Figure 3a). The tube was then placed in a −35 °C bath, and the volatile components were pumped out. The NMR spectrum of the distillate showed only the signals of B_4H_{10}. A fresh 1.5-mL portion of CH_2Cl_2 was condensed into the reaction tube to record the NMR spectrum of the residue (see Figure 3b).

Reaction of $CH_3B_2H_3 \cdot 2P(CH_3)_3$ with B_2H_6. A solution containing 0.549 mmol of $CH_3B_2H_3 \cdot 2P(CH_3)_3$ in 1.5 mL of CH_2Cl_2 was prepared in a 10-mm-o.d. Pyrex tube, and a 0.548-mmol sample of B_2H_6 was condensed into the tube. The contents of the tube were mixed at −80 °C, and the tube was placed in the probe of the XL-100 NMR spectrometer. In another run, a 0.557-mmol sample of $CH_3B_2H_3 \cdot 2P(CH_3)_3$ and 1.12 mmol of B_2H_6 were treated in the similar manner. The observed reaction progresses were described in the Results and Discussion section.

Acknowledgment. This work was supported by the U.S. Army Research Office through Grants DAAG 29-79-C-0129 and 29-85-K-0034.

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Comparative Studies on Charge Distribution for the Ruthenium and Osmium Quinone Complexes $[M(bpy)_2(quinone)]^n$ (M = Ru, Os; n = 0, +1, +2)

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Received January 24, 1990

The apparent shift in charge distribution that occurs for quinone complexes of metals of the iron triad has been investigated for members of the $M(bpy)_2(Q)^n$ (M = Ru, Os) redox series for values of n ranging from 0 to +2 and for complexes prepared with catechol (Cat), 3,5-di-*tert*-butylcatechol (DBCat), and tetrachlorocatechol (Cl_4Cat). The members of the series with n = +1 may have one of two localized charge distributions, M(II)–SQ or M(III)–Cat, related by internal transfer of charge between the metal and the quinone ligand. Earlier characterization on $Ru(bpy)_2(DBSQ)^+$ indicated that the semiquinone form was most appropriate on the basis of the spectroscopy and structure of the complex cation. The osmium analogue, $[Os(bpy)_2(DBCat)](ClO_4)$, has been the subject of a crystallographic structure determination. Crystals of the complex form in the monoclinic space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions $a = 15.265$ (3) Å, $b = 24.153$ (6) Å, $c = 10.944$ (2) Å and $\beta = 102.89$ (2)°. Carbon–oxygen bond lengths of the structure indicate that the quinone ligand is catecholate and that the charge distribution for the complex is Os(III)–DBCat. Spectroscopic characterization on the complex confirms the trivalent nature of the metal. It exhibits a rhombic EPR spectrum and low-energy transitions in the near-infrared region that are characteristic of Os(III). A comparative study on the electrochemical properties of the six complexes prepared with the two metals and three quinone ligands fails to show shifts in redox potentials that would be expected for species with metal- and ligand-localized electronic structures. This result, with earlier characterization on the Ru members of the series, points to significant metal–quinone charge delocalization for certain members of the series.

Introduction

The coordination chemistries of congeneric metals of the second and third transition series are generally regarded to be quite similar. Electron distribution in complexes containing semiquinone and catecholate ligands has been found to be sensitive to the orbital energy of metal valence electronic levels. Clear differences in charge distribution have been noted for first-row metals relative to larger members of a group.[2] Specific examples exist for the Cr, Mo, and W triad, where chromium complexes are of the form $Cr^{III}(SQ)_3$,[3] while related complexes of the larger metals contain hexavalent metals bonded by catecholate ligands, $M^{VI}(Cat)_3$ (M

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