contact between the complex cation and one *d*-tartrate anion.

The $[Co(sen)]^{3+}$ cation seems to bear a fairly hydrophobic character compared with $[Co(en)_3]^{3+}$ owing to the presence of the trimethyleneethane group. Thus, the packing modes of Λ-$[Co(sen)]Cl(d\text{-}C_4H_4O_6)\cdot 6H_2O$ and Λ-$[Co(en)_3]Cl(d\text{-}C_4H_4O_6)\cdot 5H_2O$ would be presumed to be considerably different. Actually, the less soluble diastereomer formed with *d*-tartrate contains the Δ isomer in the former system, while it contains the Λ isomer in the latter. Despite these differences, the common existence of the face-to-face contact mode in both systems as well as in other systems suggests strongly the following. If the complex cation has three axial NH hydrogens as in $[M(en)_3]^{3+}$, $[M(sen)]^{3+}$, $[M(pn)_3]^{3+}$, or $[M(chxn)_3]^{3+}$ and the anion has three oxygen atoms that can associate favorably with these NH hydrogens, a similar face-to-face close contact may be expected in solution as well as in the solid state.

That the mode of close contact in solution should be similar to that found in the solid state is supported by several experimental results.[1] These include the following.

(i) Δ-$[Co(en)_3]^{3+}$, Δ-$[Co(sen)]^{3+}$, Δ-*fac*- and Δ-*mer*-$[Co(l\text{-}pn)_3]^{3+}$, and Δ-$[Co(l\text{-}chxn)_3]^{3+}$, which have axial NH hydrogens suitable for triple hydrogen bonding along the C_3 (or pseudo-C_3) axis, discriminate more or less between the *d*- and *l*-tartrate ions in solution, as evidenced by chromatographic optical resolution and different ion association constants. In contrast, the $[Co(sep)]^{3+}$ ion, which lacks such NH hydrogens, does not discriminate at all. For example, $[Co(sen)]^{3+}$ was found to be resolved by ion-exchange chromatography with SP-Sephadex C-25 (cation exchanger); the complex was loaded on a column (1 × 30 cm) and eluted by a 0.1 M aqueous solution of sodium *d*-tartrate or sodium (*d*-tartrato)antimonate(III). For both eluents, the Λ enantiomer was eluted first, as for $[Co(en)_3]^{3+}$, $[Co(pn)_3]^{3+}$, and $[Co(chxn)_3]^{3+}$. Likewise, the association constants (at 25 °C and $\mu = 0.1$ with sodium perchlorate) for the *d*- and *l*-tartrates were $K_d = 50 \pm 1\ M^{-1}$ and $K_l = 72 \pm 1\ M^{-1}$ for Δ-$[Co(sen)]^{3+}$ and $K_d = K_l = 39 \pm 1\ M^{-1}$ for Δ-$[Co(sep)]^{3+}$.

(ii) The effect of *d*- and *l*-tartrate ions upon the CD spectra of Δ-$[Co(sen)]^{3+}$, Δ-$[Co(en)_3]^{3+}$, Δ-*fac*- and Δ-*mer*-$[Co(l\text{-}pn)_3]^{3+}$, and Δ-$[Co(l\text{-}chxn)_3]^{3+}$ is such that they enhance the A_2 rotational strength, while the direction of CD change of Δ-$[Co(sep)]^{3+}$ is just the opposite. This observation is consistent with the idea that the tartrates approach the former group of cations along the C_3 axis, forming hydrogen bonds with three axial NH hydrogens. For Δ-$[Co(sep)]^{3+}$, which has only equatorial NH hydrogens directing approximately parallel to the C_2 axis, the tartrate ion will be forced to approach along the C_2 axis. This C_2 access will enhance the E_a rotational strength in the same way as the C_3 access enhances the A_2 rotational strength.

(iii) From the association constant and the difference CD spectrum due to tartrates, the CD spectrum of the ion pair Λ-$[Co(sen)]^{3+}\cdots d\text{-tartrate}^{2-}$ can be obtained. The CD spectrum of this ion pair tends to be similar in shape to that of Λ-$[Co(sep)]^{3+}$ itself, which has one more covalent cap than $[Co(sen)]^{3+}$ does. If we note that the CD of $[Co(sep)]^{3+}$ is dominated by the A_2 rotational strength, this observation will be seen to be in line with the idea that the addition of atoms or groups, whether covalent or hydrogen bonded, to the D_3 polar region of the $[Co(N)_6]^{3+}$ complexes enhances generally the A_2 rotational strength.[22]

All the above facts point to the relevance of the face-to-face contact mode in the crystal to the mode of stereoselective association in solution.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, final atomic coordinates for hydrogen atoms with isotropic thermal parameters (Table II), and final anisotropic thermal parameters for non-hydrogen atoms (Table III) and a stereoview of the unit cell (Figure 2) (9 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of Potassium Nonahydro(trimethylphosphine)tetraborate(1−)

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Received August 18, 1982

Potassium nonahydrotetraborate(1−) reacted with trimethylphosphine in tetrahydrofuran and gave the salt of a new complex anion $B_4H_9P(CH_3)_3^-$. The compound was stable below 0 °C but decomposed slowly at room temperature. A nonrigid, trigonal-pyramid structure having the phosphine attached at the apical boron was suggested for the anion on the basis of the NMR data (^{11}B, −26.4 (intensity 3), −35.8 ppm (1); ^1H, δ 1.23 (H_C, 1), 0.03 (H_B, 1); ^{31}P, 2.1 ppm). Diborane treatment of the adduct anion resulted in the formation of $B_4H_8\cdot P(CH_3)_3$. The reaction with HCl in tetrahydrofuran produced hydrogen gas and gave a mixture containing $B_4H_8\cdot P(CH_3)_3$, $(CH_3)_3P\cdot BH_3$, and $THF\cdot B_3H_7$ in a 1:2.4:1.8 molar ratio.

Introduction

Lewis base adducts of tetraborane(8), $B_4H_8\cdot L$, react with Lewis bases to give hypho class tetraborane adducts:

$$B_4H_8\cdot L + L' \rightarrow B_4H_8\cdot L\cdot L'$$

Thus, ammonia and methylamines add to $B_4H_8\cdot N(CH_3)_3$ in 1:1 molar ratios,[1,2] and $P(CH_3)_3$ adds to $B_4H_8\cdot P(CH_3)_3$ likewise.[3] Other examples are the additions of CH_3CN,[4] $(CH_3)_2O$,[4] and $N(CH_3)_3$[5] to $B_4H_8\cdot CO$. In these reactions the monobase adducts of tetraborane(8) are acting as Lewis acids toward the various bases.

The nonahydrotetraborate(1−) anion, $B_4H_9^-$, can formally be regarded as the hydride (H^-) adduct of B_4H_8. This for-

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[3] Kodama, G.; Kameda, M. *Inorg. Chem.* **1979**, *18*, 3302.

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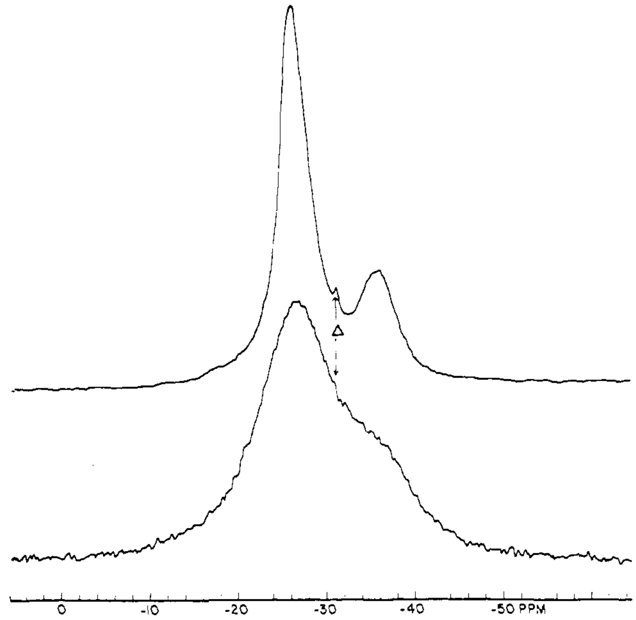


Figure 1. $^{11}B\{^1H\}$ NMR spectra of $KB_4H_9P(CH_3)_3$ in tetrahydrofuran at +10 (top) and −40 °C (bottom). The signal indicated by Δ is due to $B_3H_8^-$.

malism suggests that the $B_4H_9^-$ anion may also function as an acid and may combine with certain Lewis bases to give hypho class anionic adducts. Experimental tests of the idea revealed that trimethylphosphine reacted with the $B_4H_9^-$ ion in a 1:1 molar ratio. This paper describes the formation and characterization of the new, hypho class anion $B_4H_9P(CH_3)_3^-$.

Results and Discussion

A. Formation and Properties of $KB_4H_9P(CH_3)_3$. Treatment of a tetrahydrofuran solution of potassium nonahydrotetraborate(1−) (KB_4H_9) with trimethylphosphine resulted in the formation of a 1:1 adduct, potassium nonahydro(trimethylphosphine)tetraborate(1−):

$$KB_4H_9 + P(CH_3)_3 \xrightarrow[\text{THF}]{-30\ ^\circ\text{C}} KB_4H_9P(CH_3)_3 \qquad (1)$$

The adduct anion was stable in the presence of excess $P(CH_3)_3$, and no further addition of the phosphine occurred. The compound was insoluble in diethyl ether. It was stable below 0 °C but decomposed slowly at room temperature. One of the decomposition products was $(CH_3)_3P\cdot BH_3$. The tetrahydrofuran solution of the compound was stable at 10 °C long enough for quick recording of its NMR spectra. The adduct anion remained unchanged when pumped under high vacuum at −35 °C. The compound reacted with diborane(6) in tetrahydrofuran, and $B_4H_8\cdot P(CH_3)_3$ was produced:

$$KB_4H_9P(CH_3)_3 + {}^1/_2B_2H_6 \xrightarrow[\text{THF}]{-60^\circ\text{C}} KBH_4 + B_4H_8\cdot P(CH_3)_3 \qquad (2)$$

When the compound, $KB_4H_9P(CH_3)_3$, was treated with anhydrous hydrogen chloride in a *1:1* molar ratio at −80 °C in tetrahydrofuran, hydrogen gas evolved rapidly. The amount of hydrogen gas was no more than 0.31 mol/mol of $B_4H_9P(CH_3)_3^-$. The original complex anion was consumed completely and was converted into $B_4H_8\cdot P(CH_3)_3$, $THF\cdot B_3H_7$, and $(CH_3)_3P\cdot BH_3$. None of these three borane adducts are the product of the secondary reaction of the other two adducts with HCl: tetrahydrofuran–triborane(7) would interact with HCl only to the extent of hydrogen exchange at the temperature of the experiment,[6] and $B_4H_8\cdot P(CH_3)_3$ would give $(CH_3)_3P\cdot B_3H_7$ and $BH_2Cl\cdot THF$[1,3] if reacted with HCl. The relative amounts of the three adducts indicated that the products could be grouped into two sets. Thus

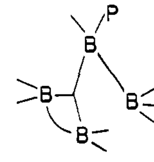


Figure 2. Proposed structure for $B_4H_8\cdot 2P(CH_3)_3$.[3]

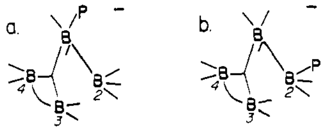
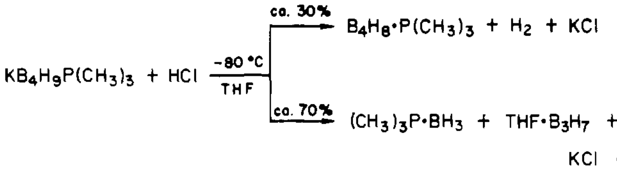
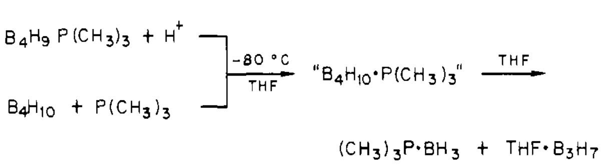


Figure 3. Structures for $B_4H_9P(CH_3)_3^-$ derived from the structure of $B_4H_8\cdot 2P(CH_3)_3$.



$$KB_4H_9P(CH_3)_3 + HCl \xrightarrow[\text{THF}]{-80\ ^\circ\text{C}} \begin{cases} \xrightarrow{\text{ca. 30\%}} B_4H_8\cdot P(CH_3)_3 + H_2 + KCl & (3) \\ \xrightarrow{\text{ca. 70\%}} (CH_3)_3P\cdot BH_3 + THF\cdot B_3H_7 + KCl & (4) \end{cases}$$

The cause of the two different routes has not been made clear. An intermediate with the formula "$B_4H_{10}\cdot P(CH_3)_3$" is thought to be formed first by the addition of H^+ to the complex anion. A subsequent reaction of the intermediate with tetrahydrofuran would give the final products in eq 4. An interemediate with the same formula, $B_4H_{10}\cdot P(CH_3)_3$, has been suggested for the reaction of B_4H_{10} with $P(CH_3)_3$.[7] Indeed, when B_4H_{10} was treated with $P(CH_3)_3$ in a 1:1 molar ratio in tetrahydrofuran at −80 °C, $(CH_3)_3P\cdot BH_3$ and $THF\cdot B_3H_7$ were produced in a 1:1 molar ratio.[8] Thus, the mechanistic models for the two reactions are consistent with each other:



$$\left.\begin{array}{l} B_4H_9P(CH_3)_3 + H^+ \\ B_4H_{10} + P(CH_3)_3 \end{array}\right] \xrightarrow[\text{THF}]{-80\ ^\circ\text{C}} \text{"}B_4H_{10}\cdot P(CH_3)_3\text{"} \xrightarrow{\text{THF}} (CH_3)_3P\cdot BH_3 + THF\cdot B_3H_7 \qquad (5)$$

The final products in these reactions are not those expected on the basis of the currently accepted acid–base strength of the species involved.[10] However, a slow ligand-exchange reaction occurs at room temperature between $(CH_3)_3P\cdot BH_3$ and $THF\cdot B_3H_7$ in a tetrahydrofuran solution.[8] The "anomalous" formation of the two adducts at −80 °C, therefore, appears to be a kinetically controlled process of the cleavage of "$B_4H_{10}\cdot P(CH_3)_3$".

B. NMR Spectra of $KB_4H_9P(CH_3)_3$. The ^{11}B NMR spectrum of $KB_4H_9P(CH_3)_3$ at +10 °C consisted of two resonance signals at −26.4 and −35.8 ppm ($BF_3\cdot O(C_2H_5)_2$ standard) in a 3:1 intensity ratio. See Figure 1. At the temperatures below −60 °C these signals appeared as a broad hump in the range from +20 to −55 ppm. The ^1H NMR

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(8) See Experimental Section. The initial reaction that occurs at the low temperature is the deprotonation of B_4H_{10}: $(CH_3)_3P + B_4H_{10} \rightleftharpoons (CH_3)_3PH^+B_4H_9^-$. Then, two types of cleavage reactions follow. One is that given in eq 5 and the other gives $H_2B(THF)_2{}^+B_3H_8^-$, which was reported by Schaeffer et al.[9] The results of a detailed study on the reactions of B_4H_{10} with some bases in ethereal solutions will be described in a separate report.

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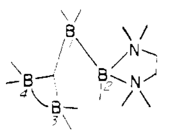

Figure 4. Structure proposed for $B_4H_8\cdot[(CH_3)_2NCH_2-]_2$.[11]

spectrum (^{11}B spin decoupled) of the compound in tetrahydrofuran-d_8 consisted of two signals at δ 1.23 (doublet, J_{HCP} = 10.8 Hz) and 0.03 (doublet, $J_{HBP} \simeq 4.5$ Hz) in an intensity ratio 1:1. The two-signal feature remained unchanged down to −80 °C, although the H_B signal broadened considerably. The ^{31}P NMR signal appeared at +2.1 ppm (OPA standard) as a singlet. The width of the ^{31}P signal narrowed as the temperature was lowered.

C. Structure of the $B_4H_9P(CH_3)_3^-$ Ion. Shown in Figure 2 is the low-temperature, static structure proposed for $B_4H_8\cdot 2P(CH_3)_3$.[3] At room temperature the two B–$P(CH_3)_3$ groups appear equivalent in the ^{11}B NMR spectrum due, presumably, to the rapid exchange of their surroundings. Replacement of one of the two phosphine ligands in the structure with a hydride ion results in the structure a or b shown in Figure 3. The NMR data for the $B_4H_9P(CH_3)_3^-$ anion suggest that, down to −60 to ∼−80 °C, three of the four boron atoms are equivalent and the nine hydrogen atoms of the borane group are all equivalent. Both structures in Figure 3 satisfy the condition of equivalency of the atoms if the three atoms, which are not bonded to the phosphine, rapidly exchange their surroundings. A structure similar to structure b in Figure 3 was proposed for another hypho compound $B_4H_8\cdot[(CH_3)_2NCH_2-]_2$.[11] See Figure 4. The ^{11}B NMR spectrum of the diamine compound at room temperature is that expected for the static structure shown in the figure. It is necessary to heat the sample above +50 °C in order to bring about the equivalency of the three boron atoms.[11] This behavior of the compound contrasts sharply with that observed for the $B_4H_9P(CH_3)_3^-$ ion and may suggest that structure a in Figure 3 represents the static structure of the anion more appropriately than structure b.

D. Notes on the Reactions of Other Lewis Bases. Several Lewis bases were tested for their possible 1:1 adduct formation with KB_4H_9. The tests were performed under the conditions similar to those used for the preparation of $KB_4H_9P(CH_3)_3$. Triphenylphosphine, phosphine, trimethylamine, or pyridine did not give a compound that could be considered as a 1:1 adduct. Up to −10 °C, only the resonance signals of the $B_4H_9^-$ ion appeared in the spectrum of the reaction mixture. At higher temperatures precipitates began to form and the spectrum of such a reaction mixture contained signals of various identified and unidentified compounds. Treatment of a KB_4H_9 solution in tetrahydrofuran with dimethyl sulfide at −80 °C produced a weak, broad ^{11}B signal at −32.4 ppm, while the $B_4H_9^-$ signals were strong. Ammonia reacted slowly with KB_4H_9 in tetrahydrofuran or in diethyl ether at −80 °C, and a white precipitate formed. The solid was soluble in liquid ammonia and was characterized by its ^{11}B NMR signals that appeared at −8.6, −22.8, and −29.1 ppm in an intensity ratio 1:2.5:3.5. It was unstable above −40 °C with respect to the decomposition which gave $B_3H_8^-$, H_2, and others. Further characterization and the implication of the formation of the ammoniate of $B_4H_9^-$ will be reported elsewhere.

Experimental Section

General Data. Conventional vacuum line techniques were used for the handling of volatile compounds. Air- and moisture-sensitive solids were handled in glovebags filled with dry nitrogen gas. Laboratory stock, pure tetraborane(10)[12] and trimethylphosphine[13] were used. Diborane(6), (Callery Chemical Co.) and hydrogen chloride (Matheson Gas Products) from cylinders were purified by fractional condensation on the vacuum line. A suspension of potassium hydride in mineral oil (Alfa Products) was filtered, and the solid was washed with ether. Diethyl ether and tetrahydrofuran had been stored over $LiAlH_4$ and were distilled directly into the reaction vessels on the vacuum line. Tetrahydrofuran-d_8 (Merck Sharp and Dohme, Canada, Ltd.) was dried by refluxing over $LiAlH_4$.

The ^{11}B, ^1H, and ^{31}P NMR spectra were recorded on a Varian XL-100-15 spectrometer operating in the FT mode at 32.1, 100.1, and 40.5 MHz, respectively. Chemical shifts were expressed with respect to $BF_3\cdot O(C_2H_5)_2$, tetramethylsilane and 80% orthophosphoric acid, high-field shifts being taken as negative.

Preparation of $KB_4H_9P(CH_3)_3$. Potassium nonahydrotetraborate(1−) was prepared by the reaction reported in the literature.[14] Potassium hydride (26.8 mg) was allowed to react with B_4H_{10} (0.828 mmol) in diethyl ether (1.3 mL) at −80 °C overnight. A 0.527-mmol quantity of hydrogen gas evolved in the reaction. The solvent ether and the excess, unchanged B_4H_{10} were pumped out at −80 °C, and then a fresh portion of diethyl ether (2.7 mL) was condensed in the tube. The resulting solution, which contained small amounts of KB_3H_8 and KBH_4, was filtered at −80 °C through a glass frit into a 10 mm o.d. tube, which was equipped with a stopcock at the upper end. The tube was then sealed off from the reaction–filtration unit, and the solvent ether was removed by pumping at −80 °C. A 2-mL quantity of tetrahydrofuran was condensed in the tube to dissolve the solid KB_4H_9, and an excess amount of $P(CH_3)_3$ (1.035 mmol) was added to the solution. The reaction mixture was maintained at −35 °C for 4 h. A white solid of $KB_4H_9P(CH_3)_3$ could be obtained by pumping out the unchanged, excess trimethylphosphine and the solvent tetrahydrofuran from the mixture at −45 °C. A sample of $KB_4H_9P(CH_3)_3$ that was prepared in a manner similar to that described above was dissolved in tetrahydrofuran-d_8 for the NMR measurements. When KB_4H_9 was treated with $P(CH_3)_3$ in diethyl ether as the solvent, the product $KB_4H_9P(CH_3)_3$ formed at −40 °C as the temperature was raised from −80 °C and precipitated rapidly.

Reaction Stoichiometry. The reaction of KH and excess B_4H_{10} in diethyl ether was performed in a 10 mm o.d. Pyrex tube equipped with a stopcock at the upper end. The amount of hydrogen gas evolved in the reaction was taken as the amount of KB_4H_9 producted in the reaction, a minor side reaction being $2KH + B_4H_{10} \rightarrow KB_3H_8 + KBH_4$.[15] The solvent ether and unchanged B_4H_{10} were pumped out at −80 °C, and then tetrahydrofuran was condensed in the tube to prepare a solution of KB_4H_9. The ^{11}B NMR spectrum of the KB_4H_9 solution contained no impurity signals except a weak signal of the $B_3H_8^-$ ion. A measured quantity of $P(CH_3)_3$ was condensed in the tube and mixed in the solution at −80 °C. The tube was then placed in the cold probe (−30 °C) of the NMR spectrometer to record the ^{11}B NMR spectra of the solution. It usually took 30–40 min at the probe temperature before any change in the spectra became undetectable. Then, the intensity of the $B_4H_9^-$ signal relative to the intensity of the $B_3H_8^-$ signal (impurity in the sample) was measured. The process was repeated with successive additions of $P(CH_3)_3$ until the signal of the $B_4H_9^-$ disappeared. The plot of the relative intensity values against R, where R = mmol of $P(CH_3)_3$ added/mmol of $B_4H_9^-$ originally present, gave a line that intersected the R axis at 1.0.

Reaction of $KB_4H_9P(CH_3)_3$ with B_2H_6. A 0.515-mmol sample of $KB_4H_9P(CH_3)_3$ was prepared in a 10 mm o.d. Pyrex tube and was dissolved in 1.3 mL of tetrahydrofuran. Diborane(6) (0.232 mmol) was condensed in the tube, and the mixture was warmed to −80 °C. The tube was then placed in the cold probe (−80 °C) of the NMR instrument to monitor the reaction. A reaction was occurring at −80 °C as evidenced by the appearance of a broad doublet signal of $B_4H_8\cdot P(CH_3)_3$ at −51 ppm. As the temperature was raised stepwise to −20 °C in increments of 20 °C, the intensity of the $B_4H_9P(CH_3)_3^-$ signals diminished, and the signals of $B_4H_8\cdot P(CH_3)_3$ (−1.6, −6.6, and −51.1 ppm)[3] grew intense. At 0 °C the reaction was complete. In the final spectrum weak signals of $B_4H_9P(CH_3)_3^-$ and $B_3H_8^-$ (impurity in the original $B_4H_9^-$ sample) were seen and a faint signal of $(CH_3)_3P\cdot BH_3$ could be detected besides the strong signals of $B_4H_8\cdot P(CH_3)_3$.

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Reaction of $KB_4H_9P(CH_3)_3$ with HCl. A 0.40-mmol sample of $KB_4H_9P(CH_3)_3$ was dissolved in 3.7 mL of tetrahydrofuran in a 14 mm o.d. Pyrex tube containing a magnetic spinbar. The solution was frozen with liquid nitrogen, 0.39 mmol of HCl was condensed above the frozen solution, the tube was immersed in a −80 °C bath, and the spinbar was activated. Hydrogen gas evolved rapidly as the solution melted. By the time the solution melted completely, the gas evolution had stopped. The amount of the hydrogen gas was 0.122 mmol. No further evolution of hydrogen gas could be seen even when the solution was kept at −45 °C for 3 h. The ^{11}B NMR spectrum of the resulting solution at −80 °C (and also at room temperature) contained the signals of $B_4H_8{\cdot}P(CH_3)_3$, $(CH_3)_3P{\cdot}BH_3$, and $THF{\cdot}B_3H_7$ in an intensity ratio 1:2.4:1.8. A molar ratio 1:2.2:2.2 for the three products is expected if reactions 3 and 4 occurred simultaneously and if reaction 3 was responsible for all the hydrogen gas evolved. No other signals could be detected in the spectrum.

Reaction of B_4H_{10} with $P(CH_3)_3$ in Tetrahydrofuran. A 0.448-mmol sample of $P(CH_3)_3$ was dissolved in 2 mL of tetrahydrofuran in a 10 mm o.d. Pyrex tube equipped with a stopcock. The solution was frozen, and 0.461 mmol of B_4H_{10} was condensed in the tube. The tube was immersed in a −90 °C bath, shaken to mix the reactants, and then placed in the cold (−90 °C) probe of the NMR instrument for spectrum recording. At −90 °C the signals of B_4H_{10} and $B_4H_9^-$ were strong and the weak signals of $B_3H_8^-$ and $(CH_3)_3P{\cdot}BH_3$ were seen also. As the probe temperature was raised to −70 °C, the intensity of the $B_4H_9^-$ signal diminished rapidly and the B_4H_{10} signal intensity gradually decreased. At the same time, the signals of $(CH_3)_3P{\cdot}BH_3$, $THF{\cdot}B_3H_7$, and $B_3H_8^-$ became intense. In 30 min the signals of B_4H_{10} and $B_4H_9^-$ disappeared, and the signals of $(CH_3)_3P{\cdot}BH_3$, $THF{\cdot}B_3H_7$, and $B_3H_8^-$ were in an intensity ratio 1:1:0.3.

A tetrahydrofuran solution containing $(CH_3)_3P{\cdot}BH_3$ and $THF{\cdot}B_3H_7$ in a 1:1 molar ratio was prepared and kept at room temperature. The ^{11}B NMR spectrum remained unchanged for several days. One month later, the signals of $(CH_3)_3P{\cdot}B_3H_7$ could be seen clearly, but the signals of the original two adducts were quite strong. Two months later, the intensity of $(CH_3)_3P{\cdot}B_3H_7$ was about the same as that of $THF{\cdot}B_3H_7$.

Acknowledgment. The authors acknowledge support of this work by the U.S. Army Research Office through Grant DAAG 29-81-0101.

Registry No. $KB_4H_9P(CH_3)_3$, 85185-84-8; KB_4H_9, 57406-39-0; B_2H_6, 19287-45-7; $B_4H_8{\cdot}P(CH_3)_3$, 71749-92-3; B_4H_{10}, 18283-93-7; HCl, 7647-01-0; $P(CH_3)_3$, 594-09-2.

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Preparation, Characterization, and Reactivity of Osmium(VI) Complexes of the Type *trans*-$OsO_2X_2(PR_3)_2$ (X = Cl or Br)

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Received September 20, 1982

At room temperature the reactions between osmium tetraoxide, concentrated hydrohalic acids (HCl or HBr), and tertiary phosphines in ethanol produce the diamagnetic, light-sensitive Os(VI) compounds $OsO_2X_2(PR_3)_2$ (PR_3 = PPh_3, $PMePh_2$, $PEtPh_2$, and PEt_2Ph) as intermediates on the way to *trans*-$OsX_4(PR_3)_2$ and *mer*-$OsX_3(PR_3)_3$. The compound previously formulated as $OsOBr_3(PPh_3)_2$ has been shown to be a mixture of $OsO_2Br_2(PPh_3)_2$ and *trans*-$OsBr_4(PPh_3)_2$. The reactions of $OsO_2X_2(PPh_3)_2$ (X = Cl and Br) with HL (HL = 2-hydroxypyridine, 2-hydroxy-6-methylpyridine, and picolinic acid) in refluxing ethanol give mononuclear $OsX_2(L)(PPh_3)_2$. When $OsO_2X_2(PPh_3)_2$ (X = Cl and Br) is reacted with a mixture of 1,3-diphenyltriazine and *n*-butyllithium in tetrahydrofuran, the related Os(III) species $OsX_2(PhN_3Ph)(PPh_3)_2$ are produced. In contrast to this, $OsO_2Cl_2(PEt_2Ph)_2$ reacts with 2-hydroxy-6-methylpyridine in ethanol to yield $OsCl_3(CO)(PEt_2Ph)_2$. The monocarbonyl derivatives of Os(II) OsX(mhp)(CO)$(PPh_3)_2$ are prepared by reacting *trans*-$OsX_4(PPh_3)_2$ with 2-hydroxy-6-methylpyridine (Hmhp). X-ray photoelectron spectroscopy (XPS) and ESR spectroscopy have been used to characterize many of these complexes. A comparison has been made between the redox chemistry of these Os(VI), Os(IV), and Os(III) complexes by using the cyclic voltammetry technique.

Introduction

In 1978 we published[1] the results of a study aimed at clarifying the nature of the unusual Os(V) complex $OsOCl_3(PPh_3)_2$.[2] This molecule was noteworthy, among other reasons, in that its preparation from the reaction of osmium tetroxide with triphenylphosphine and hydrochloric acid[2] did not produce a complex of the type $OsCl_4(PR_3)_2$ or $OsCl_3(PR_3)_3$ as other tertiary phosphines do.[3] In a thorough characterization of the material purported to be $OsOCl_3(PPh_3)_2$, we discovered that it was a mixture of $OsO_2Cl_2(PPh_3)_2$ and *trans*-$OsCl_4(PPh_3)_2$.[1]

In the belief that the Os(VI) complex $OsO_2Cl_2(PPh_3)_2$ was the prototype of a range of osmyl complexes of this type, we have explored further the reactions of osmium tetraoxide with tertiary phosphines and proven that this is indeed the case. The preparation and characterization of these compounds are described herein. Additionally, we have investigated the reactions of these complexes (particularly the triphenylphosphine derivatives) with those bridging ligands, e.g. 2-hydroxypyridine, 2-hydroxy-6-methylpyridine, and 1,3-diphenyltriazine, that are often very effective in inducing coupling of metal centers to give complexes containing metal–metal bonds.[4] These latter reactions are part of a detailed study we are conducting into the use of $OsO_2X_2(PR_3)_2$ (X = Cl or Br) as synthetic starting materials.[5]

Experimental Section

Starting Materials. Osmium tetraoxide, tertiary phosphines, 2-hydroxypyridine, 2-hydroxy-6-methylpyridine, picolinic acid, 1,3-

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