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Preparation and Characterization of $B_2H_4\cdot 2P(CH_3)_3$

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Diborane(4)–bis(Lewis base) adducts, $B_2H_4\cdot 2L$, are generally formed from the direct reaction of B_4H_{10} with a Lewis base or from the reaction of a triborane(7)–Lewis base adduct, $B_3H_7\cdot L$ (eq 1–3). Additionally, the adduct $B_2H_4\cdot 2CO$ has

$$B_4H_{10} + 2L \rightarrow B_3H_7\cdot L + L\cdot BH_3 \qquad (1)$$

$$B_3H_7\cdot L + 2L \rightarrow B_2H_4\cdot 2L + L\cdot BH_3 \qquad (2)$$

$$L = P(C_6H_5)_3,^1\ PF_3,^{2,3}\ PF_2Cl,^4 \text{ or } PF_2Br^4$$

$$B_3H_7\cdot L'' + 3L' \rightarrow B_2H_4\cdot L_2' + L'\cdot BH_3 + L'' \qquad (3)$$

$$L' = PF_3,^4\ PF_2Cl,^4\ PF_2Br,^4 \text{ or } PF_2H^5$$

$$L'' = O(CH_3)_2,\ N(CH_3)_3$$

been isolated from the thermal decomposition of $B_3H_7\cdot CO$,[6] while a cyclic adduct $\underline{BH_2\cdot PF_2N(CH_3)PF_2\cdot BH_2}$ has been prepared by the reaction of $B_2H_4\cdot 2PF_3$ with $H_3CN(PF_2)_2$.[7] Since B_4H_{10} and triborane(7) adducts are not commercially available, reactions using these substances require considerable preliminary effort in the preparation of starting materials. However, a report by Lory and Ritter[8] which indicates that $B_2H_4\cdot 2(CH_3)_2NPF_2$ is a product of the reaction of $(CH_3)_2NPF_2$ with B_5H_9 suggests that a potential route to some $B_2H_4\cdot L_2$ systems is offered by B_5H_9, a boron hydride which is commercially available.

We describe here the preparation and characterization of $B_2H_4\cdot 2P(CH_3)_3$. NMR spectral data (^{11}B, ^1H, ^{31}P, ^{13}C) are presented and discussed.

Results and Discussion

Bis(trimethylphosphine)–diborane(4) was obtained in 70% yield (based upon one $B_2H_4\cdot 2P(CH_3)_3$ per B_5H_9) from the following reaction:

$$B_5H_9 + 3P(CH_3)_3 \xrightarrow[24\text{ h at }25\ ^\circ\text{C}]{\text{toluene}} B_2H_4\cdot 2P(CH_3)_3 + (CH_3)_3P\cdot BH_3 + \text{viscous oil} \qquad (4)$$

In view of the availability of B_5H_9, this represents by far the easiest method available for the synthesis of a $B_2H_4\cdot 2L$ compound.

Bis(trimethylphosphine)–diborane(4) is a white, crystalline solid which sublimes slowly under vacuum at room temperature. It melts under nitrogen in a sealed capillary at 100 °C with no apparent decomposition but slowly decomposes upon standing at room temperature under vacuum or under a dry nitrogen atmosphere. It is sensitive to moisture. Its molecular structure was determined from an X-ray study. The structure is like that of a 1,2-disubstituted ethane with a center of symmetry.[9] This is consistent with the structures reported for $B_2H_4\cdot 2P(C_6H_5)_3$,[10] $B_2H_4\cdot 2CO$,[6] and $B_2H_4\cdot 2PF_3$.[11]

The reaction of B_5H_9 with $P(CH_3)_3$ in a 2:1 molar ratio gives $B_5H_9\cdot 2P(CH_3)_3$,[12] a shallow four-sided pyramid with basal and apical attachment of $P(CH_3)_3$ groups.[13] Treatment of this diadduct with a third mole of Lewis base, not necessarily $P(CH_3)_3$, results in the formation of $B_2H_4\cdot 2P(CH_3)_3$ (eq 5).

$$B_5H_9\cdot 2P(CH_3)_3 + L \xrightarrow{\text{toluene}} B_2H_4\cdot 2P(CH_3)_3 + L\cdot BH_3 + \text{viscous oil} \qquad (5)$$

$$L = P(CH_3)_3,\ N(CH_3)_3$$

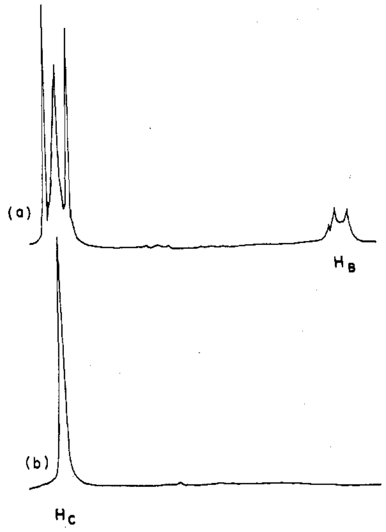

Figure 1. Proton NMR spectra of $B_2H_4\cdot 2P(CH_3)_3$ in CH_2Cl_2 at ambient temperature: (a) boron-11 spin decoupled; (b) phosphorus-31 spin decoupled.

Addition of $P(CH_3)_3$ to $B_5H_9\cdot 2P(CH_3)_3$ under conditions comparable to those employed for reaction 4 gives a comparable yield of $B_2H_4\cdot 2P(CH_3)_3$. Addition of $N(CH_3)_3$ to $B_5H_9\cdot 2P(CH_3)_3$ under similar conditions gives about half the yield of $B_2H_4\cdot 2P(CH_3)_3$ (ca. 35%) obtained from the reaction with $P(CH_3)_3$.

The reaction of $B_5H_9\cdot 2N(CH_3)_3$ with $N(CH_3)_3$ was studied in an unsuccessful attempt to prepare $B_2H_4\cdot 2N(CH_3)_3$. A viscous oil and $(CH_3)_3N\cdot BH_3$ were produced. The failure of this reaction to yield $B_2H_4\cdot 2N(CH_3)_3$ might be due to its inherent instability or due to a molecular structure of $B_5H_9\cdot 2N(CH_3)_3$ which is not suited to the formation of this compound. Unlike $B_5H_9\cdot 2P(CH_3)_3$, the molecular structure of $B_5H_9\cdot 2N(CH_3)_3$ contains both ligands at basal boron sites either cis or trans to each other.[12,13] A trans arrangement might be especially unfavorable to the formation or $B_2H_4\cdot 2N(CH_3)_3$.

NMR Spectra. The boron-11 NMR spectrum of $B_2H_4\cdot 2P(CH_3)_3$ consists of a single broad resonance upfield of $BF_3\cdot O(C_2H_5)_2$ (δ −37.4). [Note: An upfield chemical shift is given a minus sign while a downfield chemical shift is given a plus sign. This convention for boron-11 chemical shifts was agreed upon at the Third International Meeting on Boron Chemistry, Ettal, Germany, July 1976.] Spin-coupling with ^1H and ^{31}P is not resolved in the boron-11 NMR spectrum; however, simultaneous irradiation at the ^1H resonance frequency results in a markedly sharpened spectrum.

A first-order proton NMR spectrum of the methyl hydrogens of $B_2H_4\cdot 2P(CH_3)_3$ is expected to be a doublet arising from spin-coupling with only the ^{31}P atom which is directly bound to the methyl groups. The actual spectrum, however, consists of a triplet of area 2:3:2 centered at τ 8.81 with adjacent peaks at 4.8-Hz separation (Figure 1a). Irradiation at the phosphorus-31 decoupling frequency causes collapse of the triplet to a sharp singlet (Figure 1b). Similar triplet spectra have been observed for di(tertiary phosphines) such as $(CH_3)_2PCH_2CH_2P(CH_3)_2$[14] and for a number of transition-metal complexes containing two alkylphosphine groups.[15–18] These triplet patterns are believed to be due to virtual coupling in which the hydrogens of the methyl groups "see" the combined spin states of both ^{31}P nuclei.[15,19] The multiplet produced in such a situation is the average of the coupling constants for methyl hydrogen coupling with near and far phosphorus atoms. Resonances of hydrogens which are bound to boron in $B_2H_4\cdot 2P(CH_3)_3$ are not visible in the undecoupled ^1H NMR spectrum. However, when the sample

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is irradiated at the boron-11 resonance frequency, a broad doublet appears at τ 9.99 (J_{PH_B} = 4.9 Hz) (Figure 1a). It arises from spin-coupling of each ^{31}P atom with the ^1H atoms of its associated BH_2 group.

The proton spin-decoupled carbon-13 NMR spectrum is a triplet (δ 66.2 with respect to Me_4Si). It is qualitatively similar to the proton NMR spectrum of the methyl hydrogens and is believed to arise from virtual coupling between ^{13}C and ^{31}P nuclei. The separation of adjacent peaks is 18.4 Hz.

A broad featureless resonance is observed in the phosphorus-31 NMR spectrum of $B_2H_4\cdot 2P(CH_3)_3$ (δ 3.2 with respect to 85% H_3PO_4). Irradiation at the proton resonance frequency results in partial resolution of the resonance into a doublet with maxima separated by 24 Hz. This doublet is believed to result from spin-coupling of the magnetically nonequivalent (but symmetry equivalent) phosphorus-31 nuclei.

Experimental Section

All reactions were carried out under an inert atmosphere or in a standard Pyrex high-vacuum system. All solvents were dried over $LiAlH_4$ and distilled before use. Pentaborane(9) (Callery Chemical Co.) was fractionated through a −45 °C trap and collected at −78 °C. Trimethylphosphine was obtained in pure form by heating its silver iodide complex, which was prepared as described in the literature.[20-22] Trimethylamine (Matheson) was dried over $LiAlH_4$, and ammonia (Matheson) was dried over sodium before use. The adducts $B_5H_9\cdot 2P(CH_3)_3$ and $B_5H_9\cdot 2N(CH_3)_3$ were prepared from B_5H_9, $P(CH_3)_3$, and $N(CH_3)_3$ as described in the literature.[12] All other chemicals were reagent grade and were used without further purification.

Proton nuclear magnetic resonance (^1H NMR) spectra were taken at 100 MHz on a Varian HA-100 spectrometer. Chemical shifts are expressed in τ units with τ_{Me_4Si} = 10.00. Spin-decoupling was accomplished with a General Radio Company 1164-A coherent decade frequency synthesizer, a Hewlett-Packard 230B tuned rf power amplifier, and an Electronic Navigation Industries 3100L rf power amplifier. Boron-11 NMR spectra were recorded at 32.1 MHz on a Varian HA-100 spectrometer. The phosphorus-31 NMR spectrum was recorded at 36.4 MHz on a Bruker HX-90 spectrometer, while the carbon-13 NMR spectrum was recorded at 20.1 MHz on a Bruker WP-80 spectrometer operated in the FT mode.

Infrared spectra were obtained in CCl_4 solution on a Perkin-Elmer 457 spectrophotometer using a KBr cell. All samples were prepared in an inert atmosphere.

X-ray powder data were collected using a Debye-Scherer 114.6-mm diameter powder camera with a nickel filter and Cu Kα radiation at a wavelength of 1.54 Å. Powdered samples were scaled in 0.3-mm X-ray capillaries, under inert-atmosphere conditions.

Preparation of $B_2H_4\cdot 2P(CH_3)_3$. In a typical reaction, 10 mmol of B_5H_9 and 30 mmol of $P(CH_3)_3$ were dissolved in 10 mL of toluene on the vacuum line and stirred for 24 h at room temperature. The solvent was removed under vacuum at 0 °C. The residue was warmed to room temperature and fractionally sublimed through a water-cooled condenser and a −78 °C trap. The $B_2H_4\cdot 2P(CH_3)_3$ collected in the condenser, whereas the more volatile $(CH_3)_3P\cdot BH_3$ passed into the −78 °C trap. A yellow, syrupy residue of variable composition was left behind in the reaction vessel. The ^{11}B NMR spectrum of the residue consists of a very broad resonance centered at 48.9 ppm upfield of $BF_3\cdot O(C_2H_5)_2$. The ^1H NMR spectrum is a complex multiplet centered near τ 9. Hydridic hydrogen and boron were found to be in the ratio 9.2 H to 2.0 B.

A typical yield of $B_2H_4\cdot 2P(CH_3)_3$ from reaction conditions described above was about 7 mmol (70% yield based upon 1 B_5H_9 yielding 1 $B_2H_4\cdot 2P(CH_3)_3$). Yields were markedly diminished at temperatures above room temperature.

Hydrolysis of $B_2H_4\cdot 2P(CH_3)_3$ in 6 M hydrochloric acid over a period of several days yielded 3.92 mol of hydrogen/mol of compound. The resulting hydrolyzate was found to reduce silver ion to metallic silver, which indicated that a boron–boron bond was present in the molecule. Hydrolysis with aqueous KOH on a fresh sample of adduct produced 5.1 mol of hydrogen gas/mol of compound. As basic hydrolysis is known to be quite effective in cleaving boron–boron bonds, the extra mole of hydrogen given off resulted from the rupture of this boron–boron bond.[23] Base hydrolysis in D_2O gave hydrogen gas with an HD–D_2 ratio of 4:1.

Anal. Calcd for $C_6H_{22}B_2P_2$: B, 12.1; hydridic H, 2.3; mol wt 117.6. Found: B, 11.9; hydridic H, 2.2; mol wt (cryoscopic, benzene solution) 181.

Infrared spectrum of $B_2H_4\cdot 2P(CH_3)_3$ (CCl_4 solution) (cm^{-1} (relative intensity)): 2990 (vs), 2910 (vs), 2410 (sh), 2370 (sh), 2310 (vs), 2200 (w), 1430 (vs), 1415 (vs), 1288 (vs), 1308 (vs), 1215 (vs), 1135 (w), 1108 (w), 1062 (m), 1030 (m), 980 (sh), 950 (vs), 921 (s), 900 (m), 850 (m), 850 (m), 700 (m), 663 (m), 640 (w), 618 (w), 546 (m).

X-ray powder diffraction pattern of $B_2H_4\cdot 2P(CH_3)_3$ (*d*, Å (relative intensity)): 3.63 (s), 2.72 (vs), 2.57 (s), 2.41 (vs), 2.34 (m), 2.23 (m), 2.09 (s), 1.96 (m), 1.79 (w), 1.74 (vw), 1.64 (m), 1.58 (m), 1.52 (m), 1.42 (m), 1.38 (m), 1.31 (m), 1.17 (m).

Reaction of $B_5H_9\cdot 2P(CH_3)_3$ with Lewis Bases. In a typical reaction, 5 mmol of Lewis base ($P(CH_3)_3$ or $N(CH_3)_3$) was condensed into a vessel which contained 5 mmol of $B_5H_9\cdot 2P(CH_3)_3$ in 10 mL of toluene. The solution was stirred for 24 h at room temperature. The products consisted of borane adducts $L\cdot BH_3$ (L = $P(CH_3)_3$ or $N(CH_3)_3$), $B_2H_4\cdot 2P(CH_3)_3$, and $(CH_3)_3P\cdot BH_3$ and a viscous, yellow, nonvolatile liquid. These materials were separated as described in the preceding section. The yield of $B_2H_4\cdot 2P(CH_3)_3$ when the added base was $P(CH_3)_3$ was comparable (70%) to that obtained from the direct reaction of B_5H_9 with $P(CH_3)_3$ in a 1:3 molar ratio. The yield of $B_2H_4\cdot 2P(CH_3)_3$ when $N(CH_3)_3$ was the added base was about half the yield (ca. 35%) when $P(CH_3)_3$ was the added base.

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Registry No. $B_2H_4\cdot 2P(CH_3)_3$, 67113-98-8; B_5H_9, 19624-22-7; $P(CH_3)_3$, 594-09-2; $B_5H_9\cdot 2P(CH_3)_3$, 39661-74-0; ^{13}C, 14762-74-4.

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Complex Halides of the Transition Metals. 26.[1] Reactions of the Octachlorodirhenate(III) Anion with Sodium Borohydride in the Presence of Tertiary Phosphines. Facile Routes to the Dimers $Re_2Cl_4(PR_3)_4$ and $Re_2H_8(PR_3)_4$

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Sodium borohydride has found extensive application as a synthetic reagent in transition-metal chemistry. In its reactions with transition-metal complexes $NaBH_4$ most often effects