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A Method for Trimethylphosphine–Pentaborane(9) Preparation Utilizing Facile Formation of Trimethylamine–Trimethylphosphine–Pentaborane(9)

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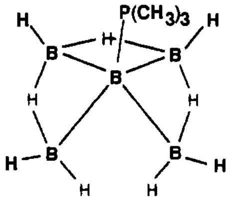
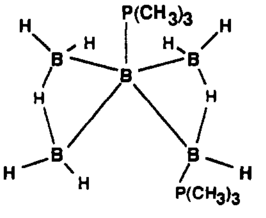
Pentaborane(9) reacts with trimethylphosphine to form $B_5H_9\cdot 2P(CH_3)_3$.[1] In the process of this bis(phosphine) adduct formation, no evidence has been found for the formation of a 1:1 adduct, $B_5H_9\cdot P(CH_3)_3$, even when $P(CH_3)_3$ was mixed with *excess* B_5H_9. On the other hand, in the processes of $B_4H_8\cdot 2P(CH_3)_3$[2] and $B_6H_{10}\cdot 2P(CH_3)_3$[3] formation, the respective mono(phosphine) adducts, $B_4H_8\cdot P(CH_3)_3$[2] and $B_6H_{10}\cdot P(CH_3)_3$[4], were produced as precursors. The mono(trimethylphosphine) adduct of B_5H_9 was first reported by Long in 1973 as a decomposition product of unstable $B_6H_{12}\cdot P(CH_3)_3$.[5]

$$B_6H_{12} + P(CH_3)_3 \rightarrow B_6H_{12}\cdot P(CH_3)_3 \rightarrow B_5H_9\cdot P(CH_3)_3 + {}^1/_2B_2H_6 \quad (1)$$

The molecular structures of the two $P(CH_3)_3$ adducts of B_5H_9 are illustrated as follows:[5–7]

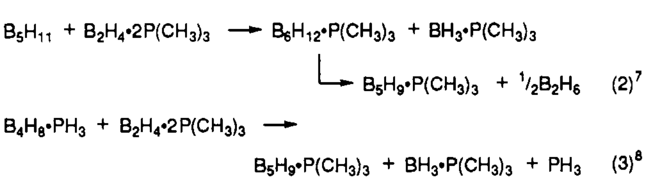


$B_5H_9\cdot P(CH_3)_3$



$B_5H_9\cdot 2P(CH_3)_3$

Subsequently, two other reactions were reported from our laboratory for the formation of $B_5H_9\cdot P(CH_3)_3$. These were based on the borane cluster expansion by $B_2H_4\cdot 2P(CH_3)_3$[7,8] as indicated in the following equations (eqs 2 and 3). However, none of these



$$B_5H_{11} + B_2H_4\cdot 2P(CH_3)_3 \longrightarrow B_6H_{12}\cdot P(CH_3)_3 + BH_3\cdot P(CH_3)_3$$

$$\hookrightarrow B_5H_9\cdot P(CH_3)_3 + {}^1/_2B_2H_6 \quad (2)^7$$

$$B_4H_8\cdot PH_3 + B_2H_4\cdot 2P(CH_3)_3 \longrightarrow B_5H_9\cdot P(CH_3)_3 + BH_3\cdot P(CH_3)_3 + PH_3 \quad (3)^8$$

three reactions (eqs 1–3) can be used conveniently for the preparation of $B_5H_9\cdot P(CH_3)_3$; the yields are low, and the starting compounds are not readily accessible. A better preparative method is desired for the reactivity studies of the compound. Therefore, we took a closer look at the behavior of bis(base) adducts of B_5H_9, and formulated a method feasible for the preparation of $B_5H_9\cdot P(CH_3)_3$.

Results

A. Reaction of $B_5H_9\cdot 2N(CH_3)_3$ with $P(CH_3)_3$. When $B_5H_9\cdot 2N(CH_3)_3$ was treated with $P(CH_3)_3$ in a 1:1 molar ratio in toluene or dichloromethane at room temperature, a mixture consisting of $B_5H_9\cdot 2P(CH_3)_3$, $B_5H_9\cdot 2N(CH_3)_3$, and a smaller quantity of $B_5H_9\cdot P(CH_3)_3\cdot N(CH_3)_3$ was produced first. Then, the amount of $B_5H_9\cdot P(CH_3)_3\cdot N(CH_3)_3$ in the mixture slowly increased at the expense of the other two adducts. Within 2 h, $B_5H_9\cdot P(CH_3)_3\cdot N(CH_3)_3$ became the major component of the mixture. A small amount of $BH_3\cdot N(CH_3)_3$ was produced also. The following equations (eqs 4–6) are appropriate for the above observation.

$${}^1/_2B_5H_9\cdot 2N(CH_3)_3 + P(CH_3)_3 \rightarrow {}^1/_2B_5H_9\cdot 2P(CH_3)_3 + N(CH_3)_3 \quad (4)$$

$${}^1/_2B_5H_9\cdot 2N(CH_3)_3 + {}^1/_2B_5H_9\cdot 2P(CH_3)_3 \rightarrow B_5H_9\cdot P(CH_3)_3\cdot N(CH_3)_3 \quad (5)$$

$$B_5H_9\cdot P(CH_3)_3\cdot N(CH_3)_3 + N(CH_3)_3 \rightarrow BH_3\cdot N(CH_3)_3 + \text{unidentified borane compounds} \quad (6)$$

B. Formation of $B_5H_9\cdot P(CH_3)_3$ from $B_5H_9\cdot 2P(CH_3)_3$. When equimolar quantities of B_5H_9 and $P(CH_3)_3$ (0.41 mmol each) were mixed in toluene, a 1:1 mixture of $B_5H_9\cdot 2P(CH_3)_3$ and B_5H_9 was produced. A mixture prepared in this manner remains unchanged for several hours. However, when a small quantity (0.07 mmol) of $N(CH_3)_3$ was added to the mixture, $B_5H_9\cdot P(CH_3)_3$ was slowly produced in the solution; within 1 h after the addition of the amine, the ^{11}B NMR signals of $B_5H_9\cdot P(CH_3)_3$ were clearly seen along with the signals of B_5H_9 and $B_5H_9\cdot 2P(CH_3)_3$. A weak signal of $BH_3\cdot N(CH_3)_3$ was also discernible. The amount of $B_5H_9\cdot P(CH_3)_3$ slowly increased, and after 5 days, the molar ratio $B_5H_9\cdot P(CH_3)_3/B_5H_9/B_5H_9\cdot 2P(CH_3)_3$ was about 1.0/1.0/0.8. The ratio did not change significantly thereafter. However, signals of unidentified borane compounds became noticeably strong.

C. Preparation of $B_5H_9\cdot P(CH_3)_3\cdot N(CH_3)_3$. The observation and interpretation described in section A suggested that $B_5H_9\cdot P(CH_3)_3\cdot N(CH_3)_3$ would be produced if B_5H_9, $P(CH_3)_3$ and $N(CH_3)_3$ were mixed in a 1:1:1 molar ratio. Indeed, when 1.39 (±0.01) mmol each of the three reagents were mixed in 3 mL of toluene, the conversion into $B_5H_9\cdot P(CH_3)_3\cdot N(CH_3)_3$ was complete within 17 h at room temperature. Removal of the solvent by pumping gave a white solid of $B_5H_9\cdot P(CH_3)_3\cdot N(CH_3)_3$. The product could be used, without purification, for the synthesis of $B_5H_9\cdot P(CH_3)_3$ which is described in section D.

NMR Spectra of $B_5H_9\cdot P(CH_3)_3\cdot N(CH_3)_3$. The $^{11}B\{^1H\}$ NMR spectra of $B_5H_9\cdot P(CH_3)_3\cdot N(CH_3)_3$ in toluene at –30 and +20 °C are shown in Figure 1. The shift values at +20 °C are –8.4 (B_2), –19.0 (B_4), –25.5 ($B_{3,5}$), and –56.7 (B_1) ppm relative to the $BF_3\cdot O(C_2H_5)_2$ signal. The ^1H spin-coupled spectrum showed no fine structure on any of the signals. The data are in fair agreement with those reported by Long,[9] except that the current data show the details owing to the use of a higher field instrument. The coalesced signal of the $B_{3,5}$ atoms at –25.5 ppm is split into two signals (–21.2 and –29.2 ppm) at –30 °C. The nonrigidity of the molecule appears to be suppressed in dichloromethane. Thus, in this solvent the B_3 and B_5 signals are not coalesced at +20 °C, and appear at –22.3 and –28.9 ppm, other signals being at –7.2 (B_2), –19.5 (B_4) and –56.2 (B_1) ppm. In Table I the above shift values are compared with those of related borane adducts. Noted

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(9) Reference 5, p 72. The compound was prepared by the reaction of $B_5H_9\cdot P(CH_3)_3$ with $N(CH_3)_3$.

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Table I. Comparison of ^{11}B NMR Shift Values (in ppm[a]) for $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$ and Related $P(CH_3)_3$ Adducts

$B_5H_9{\cdot}P(CH_3)_3$[b]	−4.2 ($B_{2,3,4,5}$)				−52.6 (B_1)
$B_5H_9{\cdot}2P(CH_3)_3$[c]		−19.8 (B_4)	−25.4 ($B_{3,5}$)	−32.4 (B_2)	−56.1 (B_1)
$B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$	−7.2 (B_2)	−19.0 (B_4)	−25.6[d] ($B_{3,5}$)		−56.7 (B_1)
$BH_3{\cdot}P(CH_3)_3$[e]				−37.0	
$BH_3{\cdot}N(CH_3)_3$[f]	−8.1				

[a] $(C_2H_5)_2O{\cdot}BF_3$ as standard. [b] Reference 7. [c] Reference 12. [d] The average of the B_3 and B_5 signals is taken. [e] Eaton, G. R.; Lipscomb, W. N. *NMR Studies of Boron Hydrides and Related Compounds*; W. A. Benjamin: New York, 1969; p 460. [f] *Ibid.*, p 459.

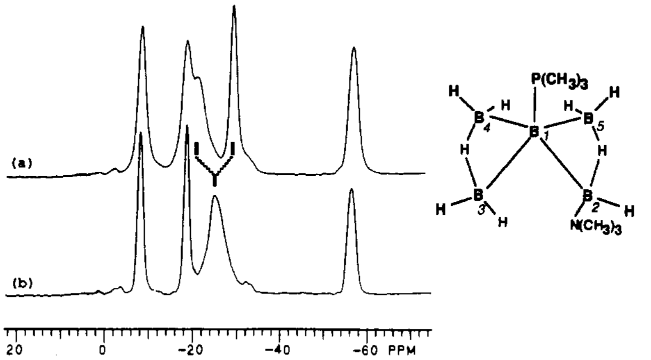

Figure 1. $^{11}B\{^1H\}$ NMR spectra of $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$ in toluene at (a) −30 °C and (b) +20 °C. The sample was a mixture of B_5H_9, $P(CH_3)_3$, and $N(CH_3)_3$ in a 1:1:1 molar ratio, and was allowed to stand at room temperature for 24 h before the spectra were recorded. The small hump at −32.4 ppm is the B_2 signal of $B_5H_9{\cdot}2P(CH_3)_3$. Shown on the right is the proposed structure of $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$, which is drawn after the structure of $B_5H_9{\cdot}2P(CH_3)_3$.[6]

in the table, in going from $B_5H_9{\cdot}2P(CH_3)_3$ to $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$, are that the shifts of the B_1, $B_{3,5}$ and B_4 atoms change little and that the shift and its change of the B_2 atom are reminiscent of those for the BH_3 adducts.

D. Preparation of $B_5H_9{\cdot}P(CH_3)_3$. Treatment of $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$ with B_2H_6 in toluene resulted in the quantitative formation of $B_5H_9{\cdot}P(CH_3)_3$.

$$B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3 + {}^1/_2B_2H_6 \rightarrow B_5H_9{\cdot}P(CH_3)_3 + BH_3{\cdot}N(CH_3)_3 \quad (7)$$

The trimethylamine–borane(3) in the product mixture could be removed by sublimation at 0 °C, and the resulting residue was sublimed at room temperature to obtain a pure sample of $B_5H_9{\cdot}P(CH_3)_3$ in a 80% overall yield based on the amount of B_5H_9 initially employed. An overall synthesis of $B_5H_9{\cdot}P(CH_3)_3$ in a larger scale is described in the Experimental Section.

E. Reactions of $B_5H_9{\cdot}P(CH_3)_3$. (a) Protolysis. When treated with methanol in dichloromethane at 0 °C, $B_5H_9{\cdot}P(CH_3)_3$ gave $B_4H_8{\cdot}P(CH_3)_3$ according to

$$B_5H_9{\cdot}P(CH_3)_3 + CH_3OH \rightarrow B_4H_8{\cdot}P(CH_3)_3 + \text{“}CH_3OBH_2\text{”} \quad (8)$$

The co-product "CH_3OBH_2" underwent further reactions, giving off H_2 gas, to finally produce $B(OCH_3)_3$. The reaction with water proceeded similarly to give $B_4H_8{\cdot}P(CH_3)_3$.

The reaction of $B_5H_9{\cdot}P(CH_3)_3$ with HCl in tetrahydrofuran proceeded at −80 °C to give $B_4H_8{\cdot}P(CH_3)_3$ and $BH_2Cl{\cdot}THF$. However, in dichloromethane, the reaction gave a complex mixture of borane compounds including B_2H_6, chlorodiboranes, $B_4H_8{\cdot}P(CH_3)_3$, $B_3H_7{\cdot}P(CH_3)_3$ and others. The observed pattern of these HCl reactions paralleled that of $B_4H_8{\cdot}P(CH_3)_3$.[10]

(b) Hydride Elimination with BCl_3. Boron trichloride readily reacted with $B_5H_9{\cdot}P(CH_3)_3$ at −80 °C to give the $B_5H_8{\cdot}P(CH_3)_3^+$ salt of the $HBCl_3^-$ anion, which could subsequently be converted into the BCl_4^- salt by treatment with HCl. This reactivity of $B_5H_9{\cdot}P(CH_3)_3$ toward BCl_3 provided an improved route for the preparation of the $B_5H_8{\cdot}P(CH_3)_3^+$ cation.[11]

Discussion

Formation of $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$. The key finding in this study was the ligand exchange between $B_5H_9{\cdot}2P(CH_3)_3$ and $B_5H_9{\cdot}2N(CH_3)_3$ that led to the virtually quantitative conversion into $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$. The reaction of $B_5H_9{\cdot}2N(CH_3)_3$ with *excess* $P(CH_3)_3$ was known to produce $B_5H_9{\cdot}2P(CH_3)_3$.[1b,12] Trimethylphosphine being a stronger base than $N(CH_3)_3$, the displacement of $N(CH_3)_3$ by the phosphine is naturally expected. However, even when $P(CH_3)_3$ was used in a deficient amount, e.g., a 1:1 molar ratio, the initial major products were $B_5H_9{\cdot}2P(CH_3)_3$ and $B_5H_9{\cdot}2N(CH_3)_3$. This pattern is reminiscent of that of the reaction of B_5H_9 with $P(CH_3)_3$ in a 1:1 molar ratio, where a 1:1 mixture of $B_5H_9{\cdot}2P(CH_3)_3$ and B_5H_9 is produced. The strong nucleophilicity of $P(CH_3)_3$ is thought to be responsible for the initial, preferential formation of $B_5H_9{\cdot}2P(CH_3)_3$ in these reactions. The $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$ formation that follows is the equilibration which is triggered by $N(CH_3)_3$. The amine that is needed for the process is provided by the dissociation of $B_5H_9{\cdot}2N(CH_3)_3$,[13] $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$, and, to a lesser extent, $B_5H_9{\cdot}N(CH_3)_3$.

Preparation of $B_5H_9{\cdot}P(CH_3)_3$. Generally, the second base in a bis(base) adduct of borane is bonded less strongly than the first. Thus, the following two reactions have been observed for the bis(base) adducts of B_4H_8:

$$B_4H_8{\cdot}2N(CH_3)_3 \rightarrow B_4H_8{\cdot}N(CH_3)_3 + N(CH_3)_3 \text{ (above 0 °C)} \quad (9)^{14}$$

$$B_4H_8{\cdot}2P(CH_3)_3 + {}^1/_2B_2H_6 \rightarrow B_4H_8{\cdot}P(CH_3)_3 + BH_3{\cdot}P(CH_3)_3 \quad (10)^{10}$$

However, B_5H_9 is a stronger borane acid than B_4H_8.[15] Therefore, the second bases in the corresponding B_5H_9 adducts are held more strongly than those in the B_4H_8 adducts. Thus, $B_5H_9{\cdot}2N(CH_3)_3$ can be isolated at room temperature[1] and, contrary to eq 10, treatment of $B_5H_9{\cdot}2P(CH_3)_3$ with B_2H_6 results in the formation of a complex mixture of borane compounds including $B_5H_9{\cdot}P(CH_3)_3$, $B_4H_8{\cdot}P(CH_3)_3$, $B_3H_7{\cdot}P(CH_3)_3$, $BH_3{\cdot}P(CH_3)_3$, B_5H_9, $B_3H_6{\cdot}2P(CH_3)_3^+$ and $B_3H_8^-$.[16] Apparently, the strong B–P bond in $B_5H_9{\cdot}2P(CH_3)_3$ prohibits the facile displacement of the second $P(CH_3)_3$ by B_2H_6, and other complex reaction patterns set in. However, $N(CH_3)_3$ being a weaker base can be removed readily from $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$ by the B_2H_6 treatment. Although treatment of $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$ with BF_3 does the same, the isolation of $B_5H_9{\cdot}P(CH_3)_3$ is made difficult by the low volatility of $BF_3{\cdot}N(CH_3)_3$, and by the side reactions that involve F–H exchange.

Experimental Section

General Experimental Procedure. Conventional high-vacuum line techniques were used for the handling of volatile compounds. Solids of $B_5H_9{\cdot}P(CH_3)_3{\cdot}N(CH_3)_3$ and $B_5H_9{\cdot}P(CH_3)_3$ were handled in polyethylene

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bags filled with dry nitrogen gas. Pentaborane(9), $P(CH_3)_3$, and $N(CH_3)_3$ were laboratory stock which were described elsewhere.[17] Samples of bis(trimethylamine)–pentaborane(9) were prepared,[1b] as needed, in the reaction tubes which are described below. Reagent grade toluene was refluxed over calcium hydride and had been stored over the hydride in a flask which was equipped with a Teflon valve.

For the investigation of behaviors of the B_5H_9 adducts, normally a 0.1–0.3 mmol quantity of the borane compound was dissolved in 1–3 mL of the solvent in a 9- or 14-mm-o.d. Pyrex tube, unless mentioned otherwise. The tube was then sealed with a torch if not equipped with a Teflon valve. The reaction tube was inserted into the probe of an NMR spectrometer (Varian XL-300 or FT-80A) to monitor the progress of the reaction.

A Larger Scale Preparation of $B_5H_9 \cdot P(CH_3)_3$. A 0.9655-g (15.30-mmol) sample of B_5H_9 was taken in a 50-mL long-necked, round-bottom flask on the vacuum line and was dissolved in 15 mL of toluene. Then, a 0.9163-g (15.50-mmol) sample of $N(CH_3)_3$ and a 1.1675-g (15.35-mmol) sample of $P(CH_3)_3$ were condensed, in the given order, into the flask at −197 °C. As the mixture was allowed to slowly warm with continuous stirring to room temperature, a white precipitate formed. Five hours later, the mixture was a clear solution with a slight tinge of yellow.

After following the above reaction mixture to stand for 24 h at room temperature, the flask was cooled to −197 °C to condense another 15-mL portion of toluene and a 7.93-mmol sample of B_2H_6 into the flask. Then, the flask was allowed to warm slowly to 0 °C while the pressure was carefully monitored on a manometer. The initial pressure rise due to B_2H_6 vaporization was followed by a slow pressure drop which lasted for 20 min. Successive cooling and warming of the flask between −197 °C and room temperature were repeated several times to ensure the complete reaction. During this reaction time, no noncondensable gas was produced. Then, the solvent and other volatile components were pumped out briefly from the flask at room temperature, and the flask containing a solid residue was attached to a sublimation apparatus.[18] The flask was exposed to the ambient temperature of 28 °C, and the condensation chamber of the sublimation unit was immersed in an ice bath. The co-product, $BH_3 \cdot N(CH_3)_3$, and a small amount of remaining solvent were pumped through the apparatus while $B_5H_9 \cdot P(CH_3)_3$ was condensed on the wall of the condensation chamber. The sublimation was continued for 40 h. A small amount of yellow residue remained in the reaction flask. The product that was collected in the sublimation unit was washed into a weighing flask with toluene in the manner which was described elsewhere.[18] Yield of sublimed $B_5H_9 \cdot P(CH_3)_3$: 1.738 g (12.49 mmol) or 82%. The compound is sensitive to moisture as described in part E of the Results and should be handled in a dry atmosphere.

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[17] See, for example: Ishii, M.; Kodama, G. *Inorg. Chem.* **1990**, *29*, 2181 and refs 10 and 14.

[18] Kameda, M.; Driscoll, J. A.; Kodama, G. *Inorg. Chem.* **1990**, *29*, 3791.