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The Reactions of Monosilylphosphine with Boron Trichloride, Diborane, and Monobromodiborane

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Monosilylphosphine reacts with boron acceptors to form the adducts $\mathrm{SiH_3PH_2BCl_3}$, $\mathrm{SiH_3PH_2BH_3}$, $\mathrm{SiH_3PH_2B_2H_5Br}$, and $\mathrm{SiH_3PH_2BH_2Br}$. These are analogous to the adducts formed by unsubstituted phosphine. The differences in their thermal stabilities are discussed.

Evidence is presented that monosilylphosphine reacts with boron trichloride, diborane, and monobromodiborane to form adducts similar to those formed by unsubstituted phosphine.

Phosphine forms adducts with boron trichloride,[1] diborane,[2] and monobromodiborane,[3] which are solids at −78°. $\mathrm{PH_3BCl_3}$ is the most stable being virtually undissociated at −23°. At that temperature the 1:2 diborane–phosphine adduct is appreciably dissociated. However, under pressure (*e.g.*, in a sealed nmr tube) the solid melts at 32° without much dissociation so that the structure $\mathrm{PH_3BH_3}$ can be confirmed by the proton and $^{11}\mathrm{B}$ nmr spectra of the liquid.[4] The 1:1 monobromodiborane–phosphine adduct is the least stable being irreversibly decomposed at −45° to diborane and the 1:1 monobromoborane–phosphine adduct. This adduct is a reasonably stable liquid at 0° so that the structure $\mathrm{PH_3BH_2Br}$ can be confirmed by the proton nmr spectrum.[3] At room temperature it slowly decomposes with the evolution of hydrogen.

Monosilylphosphine reacts with boron trichloride at −78° to give a white solid 1:1 adduct which shows no signs of dissociation as the temperature is raised to −23°. Above −23° it decomposes to a glass-like polymer and monochlorosilane in the amount quantitatively required for the reactions

$$\mathrm{SiH_3PH_2 + BCl_3 \xrightarrow{-78^\circ} SiH_3PH_2BCl_3}$$

$$\mathrm{SiH_3PH_2BCl_3 \xrightarrow{-23^\circ} SiH_3Cl} + (1/n)(\mathrm{BCl_2PH_2})_n$$

The nucleophilic attack on silicon, which is also found with the boron trifluoride adduct,[5] provides a decomposition route that is not available to $\mathrm{PH_3BCl_3}$. Thus the decrease in stability cannot be related to a change in donor ability resulting from the silyl substitution. In fact, when equimolar amounts of monosilylphosphine, phosphine, and boron trichloride are condensed together at −78°, only about 10% of the boron trichloride reacts with phosphine. The rest forms $\mathrm{SiH_3PH_2BCl_3}$ which yields the expected amount of monochlorosilane when warmed to room temperature. Removal of excess reactants at −78° has no effect on the stoichiometry of these reactions. This preferential formation of $\mathrm{SiH_3PH_2BCl_3}$ may arise because both monosilylphosphine and boron trichloride are liquids under these conditions at −78°, whereas phosphine is still in the gaseous state.

There is no reaction when monosilylphosphine and diborane are held together under the same experimental conditions that lead to the formation of the boron trichloride adducts. If the reaction is carried out under pressure, a liquid adduct is obtained at room temperature and the structure $\mathrm{SiH_3PH_2BH_3}$ can be confirmed by its proton nmr spectrum.[6] The values of the J_{PH} and J_{BH} coupling constants for $\mathrm{SiH_3PH_2BH_3}$ and $\mathrm{PH_3BH_3}$ are similar indicating that there is no appreciable change in the degree of hybridization of the phosphorus and boron atoms. The liquid adduct slowly decomposes over a period of 12 hr at room temperature to give monosilane in the amount required for the reactions

$$\mathrm{SiH_3PH_2} + {}^1/_2\mathrm{B_2H_6} \xrightarrow[\text{under pressure}]{-78^\circ} \mathrm{SiH_3PH_2BH_3}$$

$$\mathrm{SiH_3PH_2BH_3} \xrightarrow[\text{under pressure}]{-25^\circ} \mathrm{SiH_4} + (1/n)(\mathrm{BH_2PH_2})_n$$

This proton transfer to silicon is similar to that found for the decomposition of $\mathrm{SiH_3CN \cdot BH_3}$.[7] The dissociation pressure of the adduct is such[8] that monosilylphosphine and diborane are immediately liberated if the tube is broken open before decomposition to monosilane is completed.

The over-all reaction for the 1:1 addition of monosilylphosphine and monobromodiborane is shown by the equation

$$\mathrm{SiH_3PH_2 + B_2H_5Br \longrightarrow SiH_3Br} + {}^1/_2\mathrm{B_2H_6} + (1/n)(\mathrm{BH_2PH_2})_n$$

The initial stage of the reaction is the formation of a white solid 1:1 adduct at −78°. This shows no signs of dissociation up to −45° because the pressure remains negligible although "free" monosilylphosphine and monobromodiborane have significant vapor pressures at these temperatures. The subsequent decomposition of the adduct indicates that the boron atom at-

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tached to bromine is the one involved in the formation of the coordinate bond. Thus as the temperature is raised above −45°, decomposition occurs with the evolution of diborane and a white solid remains. The amount of diborane evolved is that quantitatively required for the reaction

$$SiH_3PH_2B_2H_5Br \xrightarrow{-45°} SiH_3PH_2BH_2Br + {}^1/_2B_2H_6$$

The corresponding reaction between phosphine and monobromodiborane definitely gives PH_3BH_2Br and diborane at about the same temperature, but whereas PH_3BH_2Br is stable to 0°, $SiH_3PH_2BH_2Br$ is completely decomposed at −23°. This decomposition is similar to that of $SiH_3PH_2BCl_3$ in that the halogen is transferred to silicon. Thus monobromosilane is evolved in the amount quantitatively required for the reaction

$$SiH_3PH_2BH_2Br \xrightarrow{-23°} SiH_3Br + (1/n)(BH_2PH_2)_n$$

Some monobromosilane is evolved below −23° indicating that the adduct is slightly less stable than the corresponding boron trichloride one.

In the reaction of a twofold excess of phosphine with monobromodiborane it was found[8] that diborane is not evolved at −45° but that PH_3BH_3 is formed instead. Similarly, with a twofold excess of monosilylphosphine with monobromodiborane, diborane is not detected at −45° and so $SiH_3PH_3BH_3$ is probably formed. The volatile products obtained when the solid decomposes are consistent with this assumption. Monobromosilane is evolved as is to be expected for the decomposition of $SiH_3PH_2BH_2Br$, and monosilane, diborane, and monosilylphosphine are evolved as is to be expected for the decomposition and dissociation of $SiH_3PH_2BH_3$.

Therefore, we find consistent evidence that monosilylphosphine forms adducts with these boron Lewis acids under very similar conditions to those needed for the formation of the phosphine adducts. The difference in their thermal stability results from alternative decomposition routes rather than from changes in donor strength. Thus it seems that monosilyl substitution has little effect on the donor properties of phosphine.

Experimental Section

Apparatus.—The experiments were carried out in a conventional Pyrex-glass vacuum system.[9] Greaseless stopcocks (G. Springham and Co. Ltd., Harlow, Essex, England, Viton A diaphragm) were used in preference to mercury cutoffs where reactants were susceptible to grease. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer using a gas cell (5-cm path length) fitted with KBr windows. Proton nmr spectra were recorded on a Varian A-60 spectrometer.

Materials.—Monosilylphosphine was prepared by the decomposition of a mixture of monosilane and phosphine in an ozonizer-type silent electric discharge.[10] It was separated from other compounds formed in the discharge by trap-to-trap distillation on the vacuum line.[11] The monosilylphosphine (mol wt: found, 64.5; 64.11) was trapped at −126° and a further check on its purity was provided by ensuring that its proton nmr spectrum[12] gave no indication of other hydrides as impurities. Diborane was prepared by the action of sulfuric acid on potassium borohydride[13] and purified by vacuum-line distillation (mol wt: found, 27.9; calcd, 27.69). Careful distillations were carried out to purify commercial samples of boron trichloride (mol wt: found, 118.1; calcd 117.2) and boron tribromide (vapor pressure at 0°, 19.0 mm; lit.[14] value, 19.0 mm). The reaction of diborane with boron tribromide provided the source for monobromodiborane[15] (vapor pressure at −45°, 42 mm; lit.[16] value, 41 mm).

Reaction of Monosilylphosphine and Boron Trichloride.—In a typical experiment, monosilylphosphine (0.96 mmole) and boron trichloride (0.96 mmole) were condensed together at −196° into a reaction vessel (approximately 25-ml capacity). The reactants were allowed to warm up to −78° and held at that temperature for 1 hr. During this time a white solid was formed and the pressure remained negligible. The solid was unchanged—as was the pressure—when the contents were warmed to −23° in stages. Between −23 and 0° the white adduct changed to a glass-like solid and the pressure increased sharply with the evolution of monochlorosilane (0.95 mmole, identified by its infrared spectrum;[17] mol wt: found, 65.7; calcd, 66.57). There was no further evolution of volatile products even when the solid was heated to 100°, but it changed to a wax-like material which showed broad bands at 2450 and at 960 cm^{-1} in its infrared spectrum (Nujol mull).

Reaction of Monosilylphosphine and Boron Trichloride in the Presence of Phosphine.—In a typical experiment, monosilylphosphine (0.66 mmole), phosphine (0.66 mmole), and boron trichloride (0.66 mmole) were condensed together at −196° into the 25-ml reaction vessel, warmed to −78°, and held at that temperature for 1 hr. A white solid was formed. The volatile material was distilled off and fractionated. The fraction passing through a trap at −126° was phosphine (0.6 mmole, identified by its infrared spectrum;[18] mol wt: found, 33.5; calcd, 33.9). The fraction held in the −126° trap was monosilylphosphine (0.06 mmole). The solid was then warmed to room temperature. It decomposed to give a glass-like nonvolatile solid, a volatile white solid, which was retained by a trap at −96°, and a fraction which passed through the −96° trap. The volatile solid was PH_3BCl_3 (0.06 mmole, identified by its infrared spectrum) and the other fraction was monochlorosilane (0.59 mmole).

The experiment was repeated using identical conditions and the same amounts of reactants. The white solid was again formed at −78° but the excess volatiles were not removed. The solid decomposed as it was warmed to room temperature to give again a glass-like nonvolatile solid and PH_3BCl_3 (0.06 mmole). The volatiles passing through the −96° trap were further fractionated to give monosilylphosphine (0.05 mmole) and an approximately 50–50 mixture of monochlorosilane and phosphine (a total of 1.2 mmoles). The relative amounts were determined by the method already described in detail elsewhere,[19] which in essence involved the conversion of SiH_3Cl to $(SiH_3)_2O$ and PH_3 to PH_4Cl.

Reaction of Monosilylphosphine and Diborane.—Monosilylphosphine (1.0 mmole) and diborane (0.5 mmole) were condensed together into the 25-ml reaction vessel. The mixture was allowed to stand for 3 hr at various temperatures ranging from −112 to 25°, but the pressures recorded were those to be expected for a nonreacting mixture of hydrides and there was no

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sign of solid formation. In all cases the starting materials were recovered quantitatively.

More positive results were obtained when the experiments were repeated in small-volume reaction vessels. Typically, monosilylphosphine (0.33 mmole) and diborane (0.16 mmole) were condensed at −196° into a micro nmr tube which was then sealed. When the contents were warmed, a liquid formed which was reasonably stable up to room temperature. Over a period of about 12 hr at room temperature bubbles of gas were formed as the liquid decomposed to a white solid. The tube was then recooled to −196° and opened onto the vacuum line. The volatile products contained no noncondensable gas and were all sufficiently volatile to pass through a trap at −126°. The infrared spectrum of the material was essentially that of monosilane.[20] At high pressure extra peaks at 1602 and 2617 cm^{-1} could be detected and identified as being due to a small amount of diborane,[21] which is the likely impurity of that volatility. Thus the major product of the reaction was monosilane (approximately 0.3 mmole).

Reaction of Monosilylphosphine and Monobromodiborane. 1:1 Addition.—In a typical reaction, monosilylphosphine (0.82 mmole) and monobromodiborane (0.82 mmole) were condensed together at −196° into the 25-ml reaction vessel, warmed to −78°, and held at that temperature for 1 hr. A white solid was formed and the pressure remained negligible even when the temperature was raised to −63°. At −45° volatile products were formed which were separated into two components. The fraction passing through a trap at −126° was diborane (0.40 mmole; mol wt: found, 27.5; calcd, 27.6; identified by its infrared spectrum[21]) and the fraction trapped at −126° was monobromosilane (0.26 mmole; mol wt: found, 110.6; calcd, 111.02; identified by its infrared spectrum[22]). There was much frothing and bubbling when the temperature was raised to −23°. The white solid changed to a viscous transparent liquid and more monobromosilane (0.53 mmole) was evolved. The liquid showed no signs of further decomposition even when it was warmed up to 100°.

Reaction of Monosilylphosphine and Monobromodiborane. 2:1 Addition.—A white solid was formed when monosilylphosphine (0.75 mmole) and monobromodiborane (0.38 mmole) were condensed together under the same conditions as those described for the 1:1 additions and held for 1 hr at −78°. There was no evidence for the formation of diborane when the temperature was raised to −45° although there was a slight increase in the pressure because a small amount of monobromosilane (0.06 mmole) was liberated. On warming to −23°, the solid decomposed with much frothing and bubbling to evolve a mixture of diborane, monosilane, monosilylphosphine, and monobromosilane. The decomposition was not complete until the temperature had been raised to 25°, but, from other experiments where the volatiles were taken off as the temperature was raised in steps, it was apparent that all of the monobromosilane was evolved at −23°. The volatile fraction passing through a −126° trap was the mixture of diborane and monosilane (a total of 0.31 mmole), and the fraction trapped at −126° but passing through a −96° trap was the mixture of monosilylphosphine and monobromosilane (a total of 0.51 mmole).

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Reactions of Silane, Germane, and Stannane with Metal- and Amide-Ammonia Solutions

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Germane reacts with liquid ammonia solutions of potassium or potassium amide at −77° to form potassium germyl, germanium imide ($Ge(NH)_2 \cdot xNH_3$), and hydrogen gas. The fraction of the germane converted to germanium imide increases with increasing potassium concentration but remains constant with increasing potassium amide concentration. Amide ion is an intermediate in the reaction of germane with metal–ammonia solutions. In the case of silane, the main reaction is ammonolysis, whereas, in the case of stannane, no ammonolysis occurs. A general mechanism is proposed to explain the results.

Introduction

It has been reported by Kraus and his co-workers[1,2] that sodium germyl ($NaGeH_3$) and potassium germyl ($KGeH_3$) can be prepared quantitatively by passing germane through liquid ammonia solutions of the appropriate metals

$$e^- + GeH_4 \longrightarrow GeH_3^- + {}^1/_2H_2 \qquad (1)$$

However, when Emeléus and Mackay[3] conductometrically titrated sodium–ammonia solutions with germane, hydrogen gas in excess of that required by eq 1 was evolved. Early attempts in this laboratory to prepare pure potassium germyl also failed, as evidenced by excess hydrogen gas evolution.[4] Because of these conflicting results, we have reinvestigated the reaction of germane with metal–ammonia solutions. Less extensive studies of silane and stannane have also been carried out. From the results of these studies, we propose a mechanism for the reactions.

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