1169. *The Preparation and Some Reactions of Potassium Phosphinidodiborane and Potassium Dimethylphosphinidobis(trimethylboron)*

By N. R. Thompson

Potassium phosphinide and potassium dimethylphosphinide react readily in ether with diborane and trimethylboron, respectively, to form potassium phosphinidodiborane $K^+[H_3B\cdot PH_2\cdot BH_3]^-$ and potassium dimethylphosphinidobis(trimethylboron) $K^+[Me_3B\cdot PMe_2\cdot BMe_3]^-$. When heated, potassium phosphinidodiborane loses hydrogen leaving a solid residue which on hydrolysis evolves hydrogen and phosphine. Potassium dimethylphosphinidobis(trimethylboron) evolves methane when heated, and hydrolysis of the residual solid produces hydrogen, methane, and trimethylboron. Both compounds are hydrolysed readily in acid media but under alkaline conditions hydrolysis is very slow. Neither compound reacted with phosphine or dimethylphosphine, but with ammonia slow replacement of the PH_2^- group in potassium phosphinidodiborane by an NH_2^- group took place. With potassium dimethylphosphinidobis(trimethylboron) replacement of the PMe_2^- group by NH_2^- was much more rapid. A replacement reaction took place between potassium dimethylphosphinidobis(trimethylboron) and diborane but not between potassium phosphinidodiborane and trimethylboron. With oxygen, potassium dimethylphosphinidobis(trimethylboron) reacts at room temperature to give methoxy-boron compounds and potassium dimethylphosphonate. No reaction occurs between potassium phosphinidodiborane and oxygen at room temperature. Potassium phosphinidodiborane reacts with gaseous hydrogen chloride at room temperature producing hydrogen, potassium tetrachloroborate, and phosphinoborine polymer hydrochlorination products. Potassium dimethylphosphinidobis(trimethylboron) reacts with hydrogen chloride to give potassium chloride, trimethylboron, dimethylboron chloride, and methane.

It has been reported [1] that in liquid ammonia potassium reacts with boron trifluoride with the formation of hydrogen and fluoride ions:

$$H_3NBF_3 + e^- \longrightarrow H_2NBF_2 + F^- + \tfrac{1}{2}H_2$$

while with trimethylboron only hydrogen is evolved.[2]

$$H_3NBMe_3 + e^- \longrightarrow H_2NBMe_3^- + \tfrac{1}{2}H_2$$

Potassium aminotrimethylborate $K^+[H_2NBMe_3]^-$ was found to react with diborane in the presence of ether to give potassium aminodiborane[3] $K^+[H_3B\cdot NH_2\cdot BH_3]^-$ but there was some doubt as to its identity, it being conceivable that the " compound " could be a mixture of potassium borohydride and aminoborine $(NH_2\cdot BH_2)_x$.

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[1] W. J. McDowell and C. W. Keenan, *J. Amer. Chem. Soc.*, 1956, **78**, 2065.

[2] C. A. Kraus and J. E. Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 2751.

[3] N. R. Thompson, preceding Paper.

This Paper presents the results obtained in a study of the analogous compounds containing phosphorus instead of nitrogen and also with methyl groups replacing the hydrogen atoms.

It was found impossible to prepare compounds of the type $K^+[X_2PBY_3]^-$ (where X and Y = H or Me) by the method used to prepare the analogous nitrogen derivatives, a reduction reaction in liquid ammonia solution, as in every attempt the product was the amino-compound—presumably due to the greater donor strength of ammonia compared with phosphine, or even dimethylphosphine, causing replacement of the phosphine donor molecule in the phosphine–boron acceptor complex by ammonia before reduction occurred. It has been reported that potassium in liquid ammonia will reduce phosphine and dimethylphosphine to give potassium phosphinide KPH_2 and potassium dimethylphosphinide $KPMe_2$, respectively, which can be recovered as white solids on removal of the solvent.[3] These compounds were used in attempts to prepare the desired compounds.

Dry potassium phosphinide was unaffected by exposure to gaseous diborane over the temperature range from −78° to room temperature; dry potassium dimethylphosphinide similarly did not react with trimethylboron. However, in the presence of diethyl ether both systems reacted to form not the monoacceptor compounds $K^+[X_2P{\cdot}BX_3]^-$, but the diacceptor compounds $K^+[X_3B{\cdot}PX_2{\cdot}BX_3]^-$ where X = H or Me. Potassium phosphinidodiborane was insoluble in ether while potassium dimethylphosphinidobis(trimethylboron) was very soluble.

That the compound of empirical formula $K^+[H_3B{\cdot}PH_2{\cdot}BH_3]^-$ was a single substance and not a mixture of potassium borohydride and phosphinoborine $(H_2P{\cdot}BH_2)_x$, was shown by comparison of the *X*-ray powder diffraction patterns of potassium borohydride and "$K^+[H_3B{\cdot}PH_2{\cdot}BH_3]^-$." The patterns obtained were completely dissimilar, none of the lines being coincident.

Some properties of potassium phosphinidodiborane and potassium dimethylphosphinidobis(trimethylboron) are described below.

Thermal Decomposition.—Both compounds are very stable towards heat. Potassium phosphinidodiborane did not react at temperatures much below 200° but then nearly one mol. of hydrogen was rapidly produced. Further heating to 300° succeeded in removing only another $\frac{1}{2}$ mol. of hydrogen. This extra hydrogen was evolved slowly over the whole of the range 200—300°. It is suggested that fission across a B–P bond is responsible for the first mol. of hydrogen recovered, while the hydrogen evolved on more vigorous pyrolysis is from hydrogen attached to boron only, probably with polymerisation of the ion. This mechanism is substantiated by the behaviour of the pyrolysed residue on acid hydrolysis.

Hydrolysis was extremely violent, even at room temperature, but to ensure complete reaction the mixture was heated to 90° for several hours. Hydrogen and phosphine were recovered. Summing the amount of hydrogen evolved on pyrolysis and half that obtained on hydrolysis (the other half being derived from water), only seven of the original eight equivalents of hydrogen in the compound had been recovered. This must of necessity mean that a P–H bond is left in the material after pyrolysis or it would have been hydrolysed.

Potassium dimethylphosphinidobis(trimethylboron) was equally stable towards heat, the white solid melting at 180° with gentle effervescence. At 215° evolution of gas ceased after 12 hr. and the residue was a brown solid. Somewhat more than one mol. of methane was recovered together with approximately $\frac{1}{2}$ mol. of trimethylboron and a trace of the phosphinoborine $P_3B_3Me_{12}$. The brown, involatile residue was hydrolysed vigorously by dilute hydrochloric acid producing hydrogen, methane, and trimethylboron as the volatile products.

No ethane—the expected reaction product—was evolved, and the methane must all have been derived from methyl groups attached to one of the boron atoms only, otherwise the total amount of trimethylboron produced on pyrolysis and hydrolysis can not be accounted for, unless rearrangement during hydrolysis is assumed. Thus the initial pyrolysis is probably

$$K^+[Me_3B{\cdot}PMe_2{\cdot}BMe_3]^- \longrightarrow K^+[Me_3B{\cdot}PMeCH_2{\cdot}BMe_2]^- + CH_4$$

A similar mechanism is postulated for the thermal decomposition of the dimethylaminotrimethylborate ion.[4] This new ion appears to have weaker B–P bonds than the parent dimethylphosphinidobis(trimethylboron) ion since trimethylboron is a second decomposition product, its formation being more significant at the higher temperatures studied.

On prolonged pyrolysis more than three mol. of methane were evolved and some must be formed from methyl groups attached to the second boron atom

$$K^+[Me_3B{\cdot}P(CH)(CH_2){\cdot}B]^- \longrightarrow K^+[Me_2B{\cdot}P(CH)_2{\cdot}B]^- + CH_4$$

This is reflected in the low yield of trimethylboron recovered in the subsequent hydrolysis reaction, it being reasonable to suppose that the ion $Me_3B{\cdot}P(CH)(CH_2){\cdot}B^-$ but not the ion $Me_2B{\cdot}P(CH)_2{\cdot}B^-$ would liberate trimethylboron at some stage during its hydrolysis. The hydrogen produced on hydrolysis probably signifies B–B bond formation during pyrolysis, these then hydrolysing according to

$$>B{-}B< + 2H_2O \longrightarrow 2B{-}OH + H_2$$

Hydrolysis.—Both potassium phosphinidodiborane and potassium dimethylphosphinidobis(trimethylboron) were hydrolysed violently in acid, the hydrolysis of the former being complete within a few minutes at room temperature and being quantitative according to

$$K^+[H_3B{\cdot}PH_2{\cdot}BH_3]^- + HCl{-}H_2O \longrightarrow KCl + PH_3 + 2B(OH)_3 + 6H_2$$

thus confirming the formula.

Initial hydrolysis of potassium dimethylphosphinidobis(trimethylboron) was very vigorous at room temperature but insoluble white particles were left which only dissolved during 6 hr. at 60—70°. The hydrolysis reaction was

$$K^+[Me_3B{\cdot}PMe_2{\cdot}BMe_3]^- + HCl{-}H_2O \longrightarrow KCl + Me_2PH + 2BMe_3$$

followed by the secondary reaction

$$BMe_3 + HCl{-}H_2O \longrightarrow Me_2B{\cdot}OH + CH_4,$$

partially occurring.

In alkaline conditions, hydrolysis of both these compounds was extremely slow, no reaction at all taking place at room temperature with potassium phosphinidodiborane; even after 72 hours at 100° hydrolysis was incomplete. The reaction is represented by the equation

$$K^+[H_3B{\cdot}PH_2{\cdot}BH_3]^- + NaOH{-}H_2O \longrightarrow KOH + PH_3 + 2B(OH)_3 + 6H_2$$

but the phosphine yield was low, due to thermal decomposition giving more hydrogen than that expected from the above reaction alone.

Potassium dimethylphosphinidobis(trimethylboron) reacted partially at room temperature in alkaline solution forming trimethylboron and dimethylphosphine, but prolonged heating (7 days at 100°) was necessary to complete the reaction,

$$K^+[Me_3B{\cdot}PMe_2{\cdot}BMe_3]^- + NaOH{-}H_2O \longrightarrow KOH + Me_2PH + 2BMe_3$$

Under these violent conditions hydrolysis also occurred according to

$$Me_3B + H_2O \longrightarrow Me_2B{\cdot}OH + CH_4$$
$$Me_2PH + H_2O \longrightarrow MePH_2{:}O + CH_4$$

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[4] E. J. Woodward, Ph.D. Thesis, Liverpool, 1962.

The methylphosphine oxide then partially rearranging to phosphine and dimethylphosphorous acid.[5]

$$\mathrm{2MePH_2{:}O \longrightarrow PH_3 + Me_2P{:}O{\cdot}OH}$$

This was then further hydrolysed to the corresponding phosphorous acid.[6]

Reactions with Donor Molecules.—Phosphine, dimethylphosphine, and ammonia were used as donors. Neither potassium phosphinidodiborane nor potassium dimethylphosphinidobis(trimethylboron) was very reactive, the B–P–B " backbone " of the anions being very stable, and no breakdown occurred in the presence of phosphine or dimethylphosphine. Even with ammonia only a very slow replacement of the PH_2^- group in the phosphinidodiborane ion occurred (12% in 18 hours at room temperature). This replacement was much more rapid with the dimethylphosphinidobis(trimethylboron) ion. In neither case was any B–N adduct formed. The reactions occurring were

$$\mathrm{K^+[X_3B{\cdot}PX_2{\cdot}BX_3]^- + NH_3 \longrightarrow K^+[X_3B{\cdot}NH_2{\cdot}BX_3]^- + PX_2H}$$

where X = H or Me.

Reactions with Acceptor Molecules.—Trimethylboron and diborane were chosen as acceptor molecules. No reaction occurred between trimethylboron and potassium phosphinidodiborane at room temperature either as the solid or in diethyl ether, whereas almost complete replacement occurred between dry potassium dimethylphosphinidobis(trimethylboron) and diborane at room temperature during 72 hr., the *B*-methyl groups appearing as methyldiboranes on removal of volatile material present at the end of the reaction.

$$\mathrm{K^+[Me_3B{\cdot}PMe_2{\cdot}BMe_3]^- + B_2H_6 \longrightarrow K^+[H_3B{\cdot}PMe_2{\cdot}BH_3]^- + B_2H_{6-\mathit{x}}Me_{\mathit{x}}}$$

This reaction is in complete contrast with the behaviour of the corresponding dimethylamino-compound where even repeated treatment with diborane failed to replace all the *B*-methyl groups.[4]

Reaction with Gaseous Oxygen.—No reaction was observed between potassium phosphinidodiborane and gaseous oxygen at room temperature but oxygen reacted readily with potassium dimethylphosphinidobis(trimethylboron), and the dimethylphosphinidobis(trimethylboron) anion was oxidised to methoxy-boron compounds and dimethylphosphinic acid anions. The reactions occurring can be represented by the equations

$$\mathrm{0{\cdot}90\ K^+[Me_3B{\cdot}PMe_2{\cdot}BMe_3]^- + 1{\cdot}70\ O_2 \longrightarrow 0{\cdot}92\ MeO{\cdot}BMe_2 + 0{\cdot}31\ (MeO)_2{\cdot}BMe + S}$$

$$\mathrm{S + HCl{-}H_2O \longrightarrow 0{\cdot}28\ BMe_3 + KO_2PMe_2}$$

The nature of S is unknown.

Reaction with Gaseous Hydrogen Chloride.—Both potassium phosphinidodiborane and potassium dimethylphosphinidobis(trimethylboron) reacted with gaseous hydrogen chloride at room temperature but in different ways, which can be explained by the much more basic nature of the dimethylphosphinide ion compared with the phosphinide ion.

Reaction of potassium phosphinidodiborane was rapid at room temperature until four mol. of hydrogen had been produced. Thereafter, a slow reaction set in with the evolution of more hydrogen, together with some phosphine and boron trichloride on prolonged treatment (90 days). From this behaviour and that observed on subsequent hydrolysis, the solid reaction products could only be potassium tetrachloroborate and hydrochlorination products of phosphinoborine.

It is known that $\mathrm{PH_4^+[H_3B{\cdot}PH_2{\cdot}BH_3]^-}$ reacts with hydrogen chloride to give $\mathrm{PH_4^+[Cl_2HB{\cdot}PH_2{\cdot}BHCl_2]^-}$.[7] Since the same negative ion is being considered it is reasonable to assume that the initial reaction may be similar, followed by rearrangement to give potassium tetrachloroborate and polymer $\mathrm{(H_2P{\cdot}BH_2)_{\mathit{x}}}$, the latter then reacting very slowly with hydrogen chloride. This would explain the rapid evolution of the first four mol. of

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[5] N. L. Paddock, R.I.C. Lecture Series, 1962, No. 2, 40.

[6] Van Wazer, " Phosphorus and its Compounds," vol. 1, Interscience, 1958, p. 363.

[7] E. L. Gamble and P. Gilmont, *J. Amer. Chem. Soc.*, 1940, **62**, 717.

hydrogen followed by the slow evolution of more hydrogen. The reaction can be represented by

$$K^+[H_3B\cdot PH_2\cdot BH_3]^- + 4HCl \longrightarrow 4H_2 + K^+[Cl_2HB\cdot PH_2\cdot BHCl_2]^-$$

$$K^+[Cl_2HB\cdot PH_2\cdot BHCl_2]^- \longrightarrow KBCl_4 + \frac{1}{x}(H_2P\cdot BH_2)_x$$

$$\frac{1}{x}(H_2P\cdot BH_2)_x + HCl \longrightarrow \text{Further hydrochlorination products}$$

Potassium dimethylphosphinidobis(trimethylboron) reacts with hydrogen chloride in a much more straightforward manner. After 9 weeks' reaction at room temperature, methane, dimethylboron chloride, and trimethylboron were present, together with excess of hydrogen chloride. The methane and dimethylboron chloride would be formed by the reaction

$$Me_3B + HCl \longrightarrow Me_2BCl + CH_4$$

involving trimethylboron liberated in the primary reaction

$$K^+[Me_3B\cdot PMe_2\cdot BMe_3]^- + HCl \longrightarrow KCl + 2Me_3B + Me_2PH_2Cl$$

and the excess of hydrogen chloride. Evidence for this reaction scheme is the equivalence of the methane and dimethylboron chloride recovered and also the observation that the sum of the trimethyl boron and dimethylboron chloride (or methane) recovered is approximately twice the amount of potassium dimethylphosphinidobis(trimethylboron) used.

The solid residue contained dimethylphosphonium chloride and potassium chloride.

EXPERIMENTAL

All manipulations of volatile material were carried out in a high vacuum system by standard techniques. Diborane was prepared by heating a mixture of potassium borohydride and anhydrous stannous chloride to 200°, and purified by fractionation.[8] Other starting materials were prepared by conventional methods.

Preparation of Potassium Phosphinidodiborane and Potassium Dimethylphosphinidobis-(trimethylboron).—These compounds were prepared by reducing [3] the corresponding phosphine to the phosphinide ion, followed by removal of the ammonia, and addition of dry ether and the acceptor molecule at $-78°$. The excess of diborane was determined by hydrolysis with dilute hydrochloric acid and measurement of the hydrogen evolved. Excess of trimethylboron was determined by condensing it into aqueous propionic acid and then warming the mixture to 40°. One mole of methane is evolved by each mole of trimethylboron.[9]

Potassium phosphinide (0·92 mmole) reacts in ether with excess of diborane (1·08 mmoles) to give a white, ether-insoluble solid. Excess (0·18 mmole) of diborane was recovered, *i.e.*, 0·90 mmole of diborane has reacted. Similarly potassium dimethylphosphinide (0·80 mmole) reacts in ether with excess of trimethylboron (2·11 mmoles) to give ether-soluble material which is recovered as a white solid on removal of the ether. Excess (0·52 mmole) of trimethylboron were recovered, *i.e.*, 1·59 mmoles of trimethylboron have reacted.

The compounds thus have empirical formulæ KPB_2H_8 and KPB_2Me_8. The absence of ether in the compounds is shown by the fact that in none of the subsequent reactions with these compounds was any appreciable amount of ether recovered, even though some of these reactions involved the complete breakdown of these compounds. From valency and chemical considerations it becomes clear that the structural formulæ of these compounds must be $K^+[H_3B\cdot PH_2\cdot BH_3]^-$ and $K^+[Me_3B\cdot PMe_2\cdot BMe_3]^-$.

Hydrolysis.—Potassium phosphinidodiborane (0·98 mmole) on hydrolysis with dilute hydrochloric acid gave hydrogen (5·63 mmoles) and phosphine (0·94 mmole) as the volatile products. The residual solution contained boric acid (2·00 mmoles) and potassium ions (0·96 milliatom).

Potassium dimethylphosphinidobis(trimethylboron) (1·15 mmoles) hydrolysed with increased difficulty (70° for 6 hr.) in hydrochloric acid to give methane (0·67 mmole) and trimethylboron (1·51 mmoles) together with undetermined amounts of dimethylphosphine as the volatile products. The solution contained potassium ions (1·13 milliatoms).

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[8] W. Jeffers, *Chem. and Ind.*, 1961, 431.

[9] J. Crighton, A. K. Holliday, A. G. Massey, and N. R. Thompson, *Chem. and Ind.*, 1960, 347.

In alkaline solution both compounds were much more difficult to hydrolyse and potassium phosphinidodiborane (0·60 mmole) after 72 hr. at 100° in sodium hydroxide solution gave hydrogen (3·34 mmoles), and phosphine (0·49 mmole) as volatile products. The solution contained potassium ions (0·59 milliatom) and an indeterminable amount of boric acid, the determination being hindered because of the silicates present in the solution.

Potassium dimethylphosphinidobis(trimethylboron) (1·00 mmole) after 7 days at 100° in strong sodium hydroxide solution gave hydrogen (0·20 mmole), methane (3·00 mmoles), and a trace of phosphine as volatile products. The residual solution contained potassium ions (0·98 milliatom), all the boron in the original compound, probably as dimethylboric acid, and all the phosphorus, probably mainly as methylphosphine oxide.

Pyrolysis.—Potassium phosphinidodiborane (0·90 mmole) was heated at 200° for 24 hr., hydrogen (1·02 mmoles) was produced. Further heating to 300° for 48 hr. produced more hydrogen (0·53 mmole) and left a solid residue which on acid hydrolysis produced hydrogen (3·21 mmoles), and phosphine (0·24 mmole).

Potassium dimethylphosphinidobis(trimethylboron) (0·99 mmole) when heated to 215° for 12 hr. evolved methane (1·30 mmoles), and trimethylboron (0·48 mmole) as the more volatile products and left a trace of a white, volatile, crystalline solid, thought to be $[Me_2P{\cdot}BMe_2]_3$, together with a brown, residual tar which hydrolysed with dilute hydrochloric acid to give hydrogen (0·15 mmole), methane (0·28 mmole), and trimethylboron (0·66 mmole). More methane could be recovered from the original solid on more prolonged heating.

Reactions with Donor Molecules.—Potassium phosphinidodiborane was unreactive towards phosphine and dimethylphosphine at room temperature but with ammonia a replacement reaction slowly occurred and after 18 hr. 0·09 mmole of phosphine were liberated from 0·74 mmole of potassium phosphinidodiborane.

Potassium dimethylphosphinidobis(trimethylboron) (1·31 mmoles) similarly did not react with phosphine or dimethylphosphine but in the presence of ammonia, after 66 hr. at room temperature 1·28 mmoles of dimethylphosphine were recovered.

Reactions with Acceptor Molecules.—Potassium phosphinidodiborane and trimethylboron did not react at room temperature but potassium dimethylphosphinidobis(trimethylboron) (1·07 mmoles) and diborane (1·62 mmoles) did react and after 72 hr. methylated diboranes containing 6·30 m-equivs. of B–Me were recovered, *i.e.*, almost complete replacement of the methyl groups attached to the boron atoms in potassium dimethylphosphinidobis(trimethylboron), by hydrogen atoms occurred.

Reaction with Oxygen.—Potassium phosphinidodiborane was stable with oxygen at room temperature. However potassium dimethylphosphinidobis(trimethylboron) was found to react and 0·90 mmole of the compound consumed 1·70 mmoles of oxygen in 72 hr. Methoxydimethylboron (0·92 mmole), and dimethoxymethylboron (0·31 mmole) were the only volatile reaction products. Removal of these left a white, involatile solid which on hydrolysis with dilute hydrochloric acid produced trimethylboron (0·28 mmole) and potassium dimethylphosphonate.

Reactions with Hydrogen Chloride.—In a typical experiment potassium phosphinidodiborane (0·95 mmole) reacted with gaseous hydrogen chloride (5·43 mmoles) and after 90 days at room temperature hydrogen (4·65 mmoles), phosphine (0·28 mmole), boron trichloride (0·20 mmole), and a solid residue were recovered. This residue on hydrolysis with distilled water for 10 hr. at 80° produced hydrogen (0·57 mmole), phosphine (0·45 mmole), hydrochloric acid (3·02 mmoles), boric acid (1·39 mmoles), and potassium chloride (0·94 mmole).

Gaseous hydrogen chloride (2·48 mmoles) also reacted with potassium dimethylphosphinidobis(trimethylboron) (0·85 mmole) and after 9 weeks at room temperature trimethylboron (0·93 mmole), dimethylboron chloride (0·48 mmole), methane (0·49 mmole), potassium chloride (0·84 mmole), and an unknown quantity of dimethylphosphonium chloride were recovered. On removal of all the volatile material from the vessel only potassium chloride was left.

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