Phenylberyllium Hydride–Trimethylamine: Some Observations on Alkylberyllium Hydrides

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Phenylberyllium hydride–trimethylamine, prepared from diphenylberyllium, beryllium chloride, sodium triethylborohydride, and trimethylamine, is a dimer $[(Me_3N)PhBeH]_2$ in benzene. The analogous trimethylphosphine complex dissociates in benzene solution.

The trimethylamine complex of methylberyllium hydride may be prepared from dimethylberyllium and triethylstannane in the presence of ether; alkyl–alkyl exchange does not take place. The reaction between ether-free diethylberyllium and triethylstannane results in the precipitation of hydride-rich material, in which tin compounds are held, containing Be–H : Be–Et in ratio up to *ca.* 7 : 1. Hydrogen is also formed in this reaction.

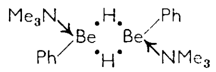
Reaction between ethylberyllium hydride–trimethylamine and diethylmercury gives Et_2BeNMe_3, mercury, and ethane.

Alkylberyllium hydrides can be prepared in diethyl ether by reaction between alkylberyllium bromides and lithium hydride, but the corresponding reaction between lithium hydride and phenylberyllium bromide is very slow and does not readily go to completion.[1] However, addition of *NNN'N'*-tetramethylethylenediamine to the product of this reaction gives a white precipitate, $[(PhBeH)_2Me_2NC_2H_4NMe_2]_x$, analogous to the insoluble tetramethylethylenediamine complex of methylberyllium hydride.[2] Since the trimethylamine complex of ethylberyllium hydride can be prepared by an alkyl–hydrogen exchange reaction between diethylberyllium and triethylstannane in the presence of ether, followed by addition of trimethylamine,[2] we attempted the preparation of a phenylberyllium hydride complex by a similar method. The reaction between diphenylberyllium and triphenylstannane in a mixture of ether and benzene gives a precipitate, and a solution in which the ratio of hydridic hydrogen to beryllium is close to unity. We were, however, unable to isolate any pure product from this reaction, though addition of tetramethylethylenediamine gave a pale yellow precipitate containing hydridic hydrogen : beryllium : diamine approximately in the ratio 2 : 2 : 1, and whose infrared spectrum was identical to that of $[(PhBeH)_2Me_2NC_2H_4NMe_2]_x$ prepared by another method.[1] The product from the triphenylstannane reaction was contaminated with phenyltin compounds, and tin hydride–diphenylberyllium exchange does not appear to be a promising route to phenylberyllium hydrides.

Since the reaction sequence shown gave the ethylberyllium hydride–trimethylamine complex in high yield,[3] we have successfully applied the same method to the preparation of phenylberyllium hydride complexes, though it was necessary to use a large excess of trimethylamine (or trimethylphosphine) to obtain a product free from boron. The trimethylamine complex is a dimer (I) in benzene, like the analogous alkylberyllium hydride complexes,[2] and has infrared absorptions (Nujol mull) at 1342 and 1316 cm.$^{-1}$ in the region characteristic [4] of compounds containing the BeH_2Be bridge.

$$Et_2Be + BeCl_2 + 2NaEt_3BH \xrightarrow{Et_2O} (EtBeHOEt_2)_2 + 2Et_3B + 2NaCl$$

$$(EtBeHOEt_2)_2 + 2Me_3N \longrightarrow (EtBeHNMe_3)_2 + 2Et_2O$$



(I)

The analogous trimethylphosphine complex differs in being appreciably dissociated in benzene, and we have not yet been able to examine the products of this dissociation. No tertiary phosphine beryllium hydride complex has been described previously.

For the earlier preparation [2] of an alkylberyllium

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[1] N. A. Bell and G. E. Coates, *J. Chem. Soc.* (*A*), 1966, 1069.

[2] N. A. Bell and G. E. Coates, *J. Chem. Soc.*, 1965, 692.

[3] N. A. Bell and G. E. Coates, unpublished observation.

[4] N. A. Bell, G. E. Coates, and J. W. Emsley, *J. Chem. Soc.* (*A*), 1966, 49.

hydride complex by tin hydride–alkylberyllium exchange, the combination of triethylstannane and diethylberyllium was chosen to avoid possible complications due to alkyltin–alkylberyllium exchange. Though we regard this route as less satisfactory than that involving lithium hydride,[1] it was desirable to know whether alkyl–alkyl exchange complicates the reaction. Since the successful preparation of $[(Me_3N)MeBeH]_2$ from triethylstannane and dimethylberyllium is described below, it is apparent that alkyl–alkyl exchange does not interfere under the reaction conditions used. Attempts to prepare a methylberyllium hydride–trimethylphosphine complex by addition of the phosphine in excess to a diethyl ether solution of methylberyllium hydride yielded a crystalline product which lost the phosphine rapidly during normal handling procedures. It had a dissociation pressure of about 2 cm. at room temperature, which is not surprising since the trimethylphosphine complex of phenylberyllium hydride, though sufficiently stable to be isolated analytically pure, dissociates in solution, and metal aryls commonly have stronger acceptor properties than metal alkyls.

Since, in contrast to alkylberyllium–tin hydride exchange, alkylaluminium–tin hydride exchange is inhibited by ethers[5] it might be anticipated that the beryllium reaction would be considerably faster in the absence than in the presence of ether. We find it is faster, but that it gives insoluble alkylberyllium hydrides of indefinite composition inseparably contaminated with tin compounds, and that the process is probably complicated by the reaction $2Et_3SnH \longrightarrow Et_6Sn_2 + H_2$, which is apparently catalysed by the ethylberyllium compounds in the absence, though not in the presence, of ether. The catalysis of the reaction $2Me_3SnH \longrightarrow Me_6Sn_2 + H_2$ by diborane has been reported,[6] and similar catalysis by other electron-deficient alkyls or hydrides is not surprising. The white amorphous ethylberyllium hydrides that resulted from these reactions had hydridic hydrogen to ethylberyllium ratios in the range 2·3 : 1 to 6·8 : 1, and the ratio [(Be–H) + (Be–Et)]/Be was always close to 2 : 1.

The trimethylamine complex of aluminium hydride reacts with organomercury compounds as follows:[7]

$$Me_3N{\cdot}AlH_3 + \tfrac{3}{2}R_2Hg \longrightarrow \tfrac{3}{2}Hg + \tfrac{3}{2}H_2 + Me_3N{\cdot}AlR_3$$

The formation of hydrogen and of metallic mercury was believed to arise from the decomposition of the unstable mercury(II) hydride or from disproportionation of RHgH giving R_2Hg, mercury, and hydrogen.

We agree that these reactions are likely to proceed by an electrophilic attack by the aluminium atom on the alkyl or aryl group bound to mercury, but do not believe there is any evidence for mercury hydride intermediates.

The reaction between ethylberyllium hydride–trimethylamine goes smoothly and practically quantitatively at 60°, but no molecular hydrogen is produced, the only gaseous product being ethane.

$$[(Me_3N)EtBeH]_2 + 2\,Et_2Hg \longrightarrow 2\,Hg + 2\,C_2H_6 + 2\,Me_3N{\cdot}BeEt_2$$

EXPERIMENTAL

Reaction of Diphenylberyllium and Triphenylstannane.—A solution of diphenylberyllium (1·84 g., 0·0113 mole) and triphenylstannane (2·09 g., 0·0112 mole) in diethyl ether (35 c.c.) was boiled for 1 hr.; no precipitate appeared during this time. After benzene (10 c.c.) had been added, the mixture was heated at 70° for 1 hr., when ether was removed by distillation, a white precipitate was slowly deposited, and a slight yellow colour developed. The temperature was then raised to 75° for a further hour. During the final 30 min. no further precipitate formed and the colour deepened to bright yellow. The mixture was then filtered and the precipitate washed with ether (10 c.c.), which was added to the filtrate. Analysis of a sample of the filtrate showed that the ratio of hydridic hydrogen to beryllium was 1·02 : 1. Addition of tetramethylethylenediamine (2·0 c.c.) in ether (10 c.c.) to the rest of the filtrate resulted in the immediate precipitation of a pale yellow solid, which was separated, washed twice with ether, and dried under reduced pressure (Found: Be, 4·67; diamine, 27·9; hydrolysable hydrogen, 0·435%; ratio H : Be : diamine, 0·84 : 1 : 0·46. Calc. for $C_9H_{14}BeN$: Be, 6·04; diamine, 39·0; hydrolysable hydrogen, 0·67%). The material remaining after hydrolysis was extracted with benzene, and this yielded a solid, m. p. 220°, whose infrared spectrum corresponded to that of tetraphenylstannane containing some hexaphenyldistannane.

Phenylberyllium Hydride–Trimethylamine.—A solution of sodium triethylborohydride[8] (0·0641 mole) in diethyl ether (95·6 c.c.) was added to a mixture of diphenylberyllium (0·0321 mole) and beryllium chloride (0·0322 mole) in ether (113 c.c.), with the immediate formation of a white precipitate and perceptible warming. The mixture was set aside for 1 hr., when some of the precipitate settled. Analysis of a small sample of clear supernatant liquid showed the ratio hydridic hydrogen : beryllium : chloride was 0·98 : 1 : 0·03. The addition of sufficient sodium triethylborohydride to react with the chloride present resulted in immediate coagulation of the precipitate, and the ratio hydridic hydrogen : beryllium : sodium was then determined as 1·01 : 1 : 0·002.

Ether was evaporated from 60 c.c. of this solution and the residue kept under low pressure for 1 hr. to evaporate some of the triethylborane. After benzene (20 c.c.) and trimethylamine (8 g.) had been added, the mixture was kept overnight, when a crystalline solid separated, which was recrystallised from benzene as colourless *needles* [Found: Be, 6·14; hydrolysable hydrogen, 0·69; trimethylamine, 40·3%; *M* (cryoscopically; 0·41, 0·42 wt. % in benzene), 285, 290. $C_{18}H_{30}Be_2N_2$ requires Be, 6·16; hydrolysable hydrogen, 0·685; trimethylamine, 40·4%; *M*, 292]. The complex did not melt when heated in a sealed tube under nitrogen, but charred in the range 180—230°.

Phenylberyllium Hydride–Trimethylphosphine.—A similar procedure, with the substitution of trimethylphosphine (10 g.) for trimethylamine resulted in the separation of

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[5] W. P. Neumann and H. Niermann, *Angew. Chem.*, 1963, **75**, 788.

[6] A. B. Burg and J. R. Spielman, *J. Amer. Chem. Soc.*, 1961, **83**, 2667.

[7] J. K. Ruff, *J. Amer. Chem. Soc.*, 1961, **83**, 1798.

[8] J. B. Honeycutt and J. M. Riddle, *J. Amer. Chem. Soc.*, 1961, **83**, 369.

crystalline product only after much of the solvent had been evaporated. The composition of this product was approximately $PhBeH(Me_3P)_{0\cdot8}$. The infrared spectrum contained a broad absorption at *ca.* 1750 cm.$^{-1}$, characteristic of the beryllium hydride polymer,[2,9] as well as two absorptions in the 1300—1350 cm.$^{-1}$ region.

Since the complex evidently loses phosphine fairly readily, the product was dissolved in toluene (10 c.c.), trimethylphosphine (3·4 g.) was added, and the mixture cooled to $-78°$. The resulting crystalline *complex* was washed with hexane containing trimethylphosphine, and dried at $-15°$ under reduced pressure [Found: Be, 5·46; hydrolysable hydrogen, 0·61; trimethylphosphine, 46·7%; *M* (cryoscopically; 0·41 wt. % in benzene), 271. $C_{18}H_{30}Be_2P_2$ requires Be, 5·49; hydrolysable hydrogen, 0·62; trimethylphosphine, 46·9%; *M*, 326]. When heated in a sealed tube under nitrogen, the complex charred in the range 190—220°. The infrared spectrum (Nujol mull) contained absorptions at 1356 and 1312 cm.$^{-1}$ in the region characteristic of the BeH_2Be bridge.

Methylberyllium Hydride–Trimethylamine from Dimethylberyllium and Triethylstannane.—A mixture of triethylstannane (0·0268 mole) and dimethylberyllium (0·0267 mole) in diethyl ether (18 c.c.) was heated at 65—70° for 4 hr. During this time most but not all of the ether distilled from the mixture, which was then left to cool to room temperature and kept under reduced pressure overnight, leaving a viscous oil. The oil was dissolved in ether (100 c.c.) and hydrolysis of a sample of solution showed the ratio of methyl to hydridic hydrogen was 1·01 : 1; no ethane could be detected.

Trimethylamine (1·05 g.) was added to part (30 c.c.) of the ethereal solution of methylberyllium hydride and volatile matter was then removed under reduced pressure. Sublimation at 40—45° (*ca.* 0·001 mm.) yielded the *trimethylamine complex*, m. p. 70—72° (lit.,[2] m. p. 73°) (Found: Be, 10·7; hydrolysable-methyl, 17·6; -hydride, 1·20. Calc. for $C_4H_{13}BeN$: Be, 10·7; hydrolysable-methyl, 17·8; -hydride, 1·20%). The infrared spectrum was identical to that of the dimer $[(Me_3N)MeBeH]_2$ described earlier.

A crystalline complex was formed when an ether solution (30 c.c.) of methylberyllium hydride, prepared as described above, to which trimethylphosphine (1·35 g.) had been added, was cooled to $-50°$. This material lost trimethylphosphine very easily, and analysis of one preparation showed the ratio methyl : hydridic hydrogen : phosphine was 1 : 1 : 0·64.

Reactions between Ether-free Diethylberyllium and Triethylstannane.—The stannane (0·0175 mole) was condensed on a frozen solution of diethylberyllium (0·0086 mole) in hexane (10 c.c.). When the mixture had warmed to *ca.* 0° a cloudiness developed in the initially clear solution. This was followed, at room temperature, by gas evolution and by precipitation of white solid. The mixture was heated at 60—70° for 2 hr. Gas evolution ceased after 30 min. and there was no further apparent precipitation after 1 hr. Solid matter was separated [Found: Be, 23·1; hydrolysable-ethyl, 49·5; -hydride, 3·62%. Ratio of (Et + H): Be, 2·02 : 1]. The analysis corresponds to 76 wt. % of $Et_{0\cdot61}BeH_{1\cdot41}$, and the remaining 24% probably consisted of ethyltin compounds. Tin was detected qualitatively in the hydrolysis residue.

In a separate experiment, triethylstannane (0·0052 mole) and diethylberyllium (0·00265 mole) in hexane (3 c.c.) were heated at 65° overnight in a vessel containing no nitrogen. The mixture was then cooled ($-196°$) and volatile material (18·5 c.c. at s.t.p.) collected and ignited with an excess of oxygen. No carbon dioxide was produced, only water, so the gas evolved in the reaction was hydrogen.

With the object of examining the effect of a longer reaction time, a mixture of triethylstannane (0·130 mole), diethylberyllium (0·0661 mole), and hexane (8 c.c.) was sealed in a previously evacuated vessel incorporating a sintered filter disc and was kept 8 weeks at 75°. The apparatus was then attached to a vacuum-line by a break-seal, and the gas volatile at $-196°$ was collected and shown by combustion to be hydrogen (46·5 c.c. at s.t.p., 0·00207 mole). Solid material was collected on the sintered disc and washed five times with hexane [Found: Be, 19·4; hydrolysable-ethyl, 18·4; -hydrogen, 3·77%. Ratio (Et + H) : Be, 2·00 : 1]. The analysis corresponds to a material, 41 wt. % of which is of composition $Et_{0\cdot29}BeH_{1\cdot71}$. The infrared spectrum (Nujol mull) consisted largely of a broad absorption centred on 1742 cm.$^{-1}$, and a mull in perfluorokerosene showed weaker absorptions in the 2900—3100 cm.$^{-1}$ region. If the main impurity is tetraethylstannane, then the ethylberyllium hydride component would be over 90 mole-% of the whole.

The filtrate was separated by fractional condensation into three components, hexane, tetraethylstannane, and hexaethyldistannane (both identified by infrared spectra).

Another very similar experiment (also 8 weeks at 75°) gave a product, 22% of which was $Et_{0\cdot26}BeH_{1\cdot74}$, and tetraethylstannane and hexaethyldistannane were identified in the filtrate. However, in this instance, some triethylstannane was detected (absorption at 1801 cm.$^{-1}$) in the former fraction, and a weak and rather broad absorption at 1796 cm.$^{-1}$ indicated the presence of some tin–hydride species in the hexaethyldistannane fraction.

Thermal Decomposition of Triethylstannane.—After some of the stannane (4·60 g.) had been heated at 75° for 36 hr. hydrogen (107·4 c.c. at s.t.p.) was collected, equivalent to the decomposition of just under one half of the triethylstannane, and both the latter and hexaethyldistannane were identified in the residue.

No metallic tin was deposited in any of the experiments using triethylstannane.

Reaction between Ethylberyllium Hydride–Trimethylamine and Diethylmercury.—Diethylmercury (0·968 mmole) was condensed on the beryllium hydride complex (0·968 mmole). No signs of reaction were seen when the evacuated and sealed reaction vessel warmed to room temperature. At 60° gas was evolved, the mixture became entirely liquid, and then gas evolution ceased. The reaction vessel was attached to a vacuum-line by means of a break-seal, and matter volatile at room temperature separated into ethane (21·7 c.c. at s.t.p., 0·969 mmole, identified by infrared spectrum) and diethylberyllium–trimethylamine (identical infrared spectrum to that of authentic sample [2]), leaving a residue of mercury. No gas volatile at $-196°$ was present.

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[9] L. Banford and G. E. Coates, *J. Chem. Soc.*, 1964, 5591; *J. Chem. Soc.* (*A*), 1966, 274.