

### 1071. *Some Beryllium Borohydride Complexes.*

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Beryllium borohydride forms an isobutylamine complex,  $[\text{Be}(\text{Bu}^i\text{NH}_2)_4]\text{-(BH}_4)_2$ , which can be sublimed at low pressure and is nearly insoluble in diethyl ether. Reactions with some ethers are discussed. Triphenylphosphine forms a 1:1 adduct which is monomeric in benzene solution and decomposes when heated with formation of triphenylphosphine-borane. Reaction with 2 mol. of triphenylphosphine gives only the 1:1 adduct at room temperature, but between 100 and 180° triphenylphosphine-borane is formed in high yield together with beryllium hydride which is contaminated with some strongly held triphenylphosphine-borane. The main feature of the infrared spectrum of the best specimen of beryllium hydride prepared by this method consists of a broad absorption centred on 1758  $\text{cm.}^{-1}$ .

THE co-ordination chemistry of beryllium borohydride has been relatively little explored. The 1:1 trimethylamine adduct reacts reversibly with more amine giving trimethylamine-borane and a compound<sup>1</sup>  $(\text{BeBH}_5\text{NMe}_3)_2$ . Many years later<sup>2</sup> it was stated that the borohydride is soluble in anisole and diethyl and diphenyl ether, but insoluble in tetrahydrofuran, 1,2-dimethoxyethane, and some other ethers.

Though we have not studied ether complexes closely we find that beryllium borohydride reacts exothermically with the three ethers we investigated, diethyl ether, tetrahydrofuran, and 1,2-dimethoxyethane. Diethyl ether can be evaporated from a solution of beryllium borohydride in this solvent, finally at low pressure, until the ether:beryllium ratio is only a little more than 1, leaving a moderately viscous liquid residue. No more ether could be separated even at 70° under reduced pressure. Tetrahydrofuran vapour is absorbed by beryllium borohydride with the formation of a crystalline complex of approximate composition  $\text{Be}(\text{BH}_4)_2(\text{THF})_4$ , which may reasonably be formulated as a salt  $[\text{Be}(\text{THF})_4](\text{BH}_4)_2$ . This has a negligible vapour pressure at room temperature. In contrast to the earlier statement<sup>2</sup> we find that beryllium borohydride is very soluble in tetrahydrofuran, and evaporation of a solution in an excess of tetrahydrofuran yields only glassy material. 1,2-Dimethoxyethane did not yield the analogous chelate complex,  $[\text{Be}(\text{MeOC}_2\text{H}_4\text{OMe})_2](\text{BH}_4)_2$ , but unexpectedly gave a crystalline complex, moderately soluble in the diether, in which the oxygen:beryllium ratio is about 3:1. At this stage we defer comment on the structures of this and the diethyl ether complex. Isobutylamine yields a 4:1 adduct,  $[\text{Be}(\text{Bu}^i\text{NH}_2)_4](\text{BH}_4)_2$ .

Those complexes which are formulated as salts have infrared absorptions in the 2200—2300  $\text{cm.}^{-1}$  region typical of the  $\text{BH}_4^-$  ion.<sup>3</sup> The diethyl ether complex has a more complex spectrum in the 2000—2500  $\text{cm.}^{-1}$  region, indicative, we believe, of the presence both of terminal  $\text{BH}_2$  and bridging  $\text{BH}_2\text{Be}$  groups since it resembles (in this region) the spectrum of the triphenylphosphine complex which is discussed below.

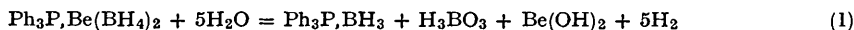
<sup>1</sup> A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1940, **62**, 3425.

<sup>2</sup> A. Brenner and B. Wood, *J. Electrochem. Soc.*, 1957, **104**, 33.

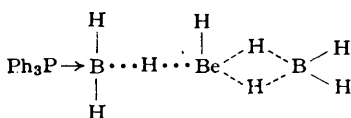
<sup>3</sup> W. C. Price, *J. Chem. Phys.*, 1949, **17**, 1044.

Since triphenylphosphine forms a particularly stable and unreactive borane complex,<sup>4</sup> it was of some interest to see if its complex with beryllium borohydride would decompose with elimination of  $\text{Ph}_3\text{P}\cdot\text{BH}_3$  and formation of beryllium hydride-rich material.

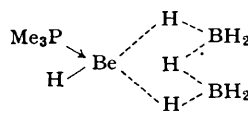
Beryllium borohydride, which is only sparingly soluble in benzene (0.8 g. l.<sup>-1</sup> at room temperature), dissolves in a solution of triphenylphosphine (1 mol.) in benzene and a 1:1 adduct can then be isolated. This is monomeric in benzene solution, and is quantitatively hydrolyzed according to the equation:



The triphenylphosphine adduct, when heated under nitrogen, becomes semi-liquid at about 122°, solidifies at a higher temperature, and then melts with apparent decomposition at 163°. Triphenylphosphine-borane may be separated from the residue. The nearly quantitative recovery (98.5%) of triphenylphosphine-borane, which is remarkably resistant to hydrolysis in contrast to the great sensitivity of beryllium borohydride, from the hydrolysis products suggests to us that the adduct  $\text{Ph}_3\text{P}\cdot\text{Be}(\text{BH}_4)_2$  contains a  $\text{Ph}_3\text{P}\cdot\text{BH}_3$  unit as part of the structure, as shown in the proposed formula (I) with a single hydrogen bridge similar



(I)



(II)

to that proposed<sup>5</sup> for the anion  $\text{B}_2\text{H}_7^-$ . The infrared spectrum of  $\text{Ph}_3\text{P}\cdot\text{Be}(\text{BH}_4)_2$  (as a Nujol mull) is complicated in the 2000—2500  $\text{cm}^{-1}$  region, and there are two main groups of strong absorptions. One of these contains four bands (2375, 2433, 2475, and 2500  $\text{cm}^{-1}$ ) which we attribute to terminal B-H stretching vibrations, and the second contains two strong bands (2114 and 2155  $\text{cm}^{-1}$ , with a considerably weaker absorption at 2252) which we attribute to bridging hydrogen atoms. These conclusions are based on similarities to the spectrum of beryllium borohydride also examined as a Nujol mull (two intense absorptions at 2415 and 2463  $\text{cm}^{-1}$ , and one even more intense absorption at 2174 with shoulders at 2141, 2096, and 2053). The spectrum of gaseous beryllium borohydride has already been examined; absorptions at 2440 and 2465  $\text{cm}^{-1}$  were attributed to terminal  $\text{BH}_2$  groups, and those at 1450 and 2180 to  $\text{BH}_2\text{Be}$  bridges.<sup>3</sup>

The <sup>11</sup>B magnetic resonance spectrum of  $\text{Ph}_3\text{P}\cdot\text{Be}(\text{BH}_4)_2$  in benzene solution (ca. 30%) appears to consist of a poorly defined broad band at 916 c./sec. to high field of trimethoxyborane (external reference). The complex is insufficiently soluble to allow a more detailed investigation of its <sup>11</sup>B resonance.\*

Attempts to prepare triphenylphosphine adducts with phosphorus:beryllium ratios greater than 1:1 failed, and resulted only in the isolation of the 1:1 complex and unreacted phosphine. The freezing points of dilute benzene solutions prepared from beryllium borohydride and 2 mol. of triphenylphosphine were those expected for equimolar mixtures of the 1:1 adduct and triphenylphosphine.

\* [Added, October 5th, 1964.] Since this paper was submitted we have examined the <sup>11</sup>B magnetic resonance spectrum of  $\text{Me}_3\text{P}\cdot\text{Be}(\text{BH}_4)_2$  (as pure liquid at room temperature). The spectrum consists of a well defined quintuplet, relative intensities 1:4:6:4:1; the chemical shift of the strongest resonance (measured by superimposition) was 995 c./sec. to high field of trimethylborane, the coupling constant being 84 c./sec. This spectrum suggests that the phosphorus atom is bound to beryllium, as in structure (II). We understand that the <sup>11</sup>B magnetic resonance spectrum of the ether complex  $\text{Et}_2\text{O}\cdot\text{Be}(\text{BH}_4)_2$  is very similar.<sup>6</sup>

<sup>4</sup> H. G. Heal, *J. Inorg. Nuclear Chem.*, 1961, **16**, 208.

<sup>5</sup> H. C. Brown, P. F. Stehle, and P. A. Tierney, *J. Amer. Chem. Soc.*, 1957, **79**, 2020.

<sup>6</sup> R. H. Kratzer and K. L. Paciorek, Naval Ordnance Laboratory, Corona, California, Navweps Report 8204, p. 27, August 1964.

Pyrolysis of a mixture of beryllium borohydride with 2 mol. of triphenylphosphine at 180° in a sealed tube under nitrogen results in the formation of a mixture of liquid and solid products. In one experiment, extraction of the cooled solid mixture with benzene gave triphenylphosphine-borane in 98.5% yield, and left a colourless insoluble residue consisting mainly (78 wt. % or 98.6 mole %) of beryllium hydride containing a small amount of triphenylphosphine-borane which did not dissolve in benzene. The beryllium hydride obtained in this way is hydrolyzed by water only very slowly, but dissolves readily in dilute aqueous acids, giving a slightly cloudy solution from which enough solid material could be separated to allow its identification as triphenylphosphine-borane by its infrared spectrum.

If the reaction is carried out in solution, the beryllium hydride content of the insoluble product is a little higher. Solutions of the 1:1 adduct in benzene containing an additional 1 mol. of triphenylphosphine slowly became turbid at 100°, and it was better to use xylene as solvent since reaction then was complete after 6 hours at 150°. At this temperature the density of the beryllium hydride appeared to be very close to that of the solution. After extraction of the insoluble product with benzene, on which it floats and in which triphenylphosphine-borane is considerably more soluble than in xylene, the residue contained 83 wt. % beryllium hydride, or 99 mole % on the assumption that the rest is triphenylphosphine-borane.

Nujol mulls of this product always scattered rather a high proportion of the incident infrared light, but prolonged grinding enabled us to obtain spectra consisting (apart from absorption due to Nujol) of only one major feature, namely, a rather broad band (width about 313 cm.<sup>-1</sup> at half-height) centred at 1758 cm.<sup>-1</sup>. There was also a relatively weak and extremely broad absorption between 880 and 660 cm.<sup>-1</sup>. No absorptions were observed that could be attributed to triphenylphosphine-borane, or indeed to anything but beryllium hydride and Nujol.

The main absorption at 1758 cm.<sup>-1</sup> is at a considerably higher frequency than those caused by the vibrations of BeH<sub>2</sub>Be bridges,<sup>7</sup> which are found in the region of 1340 cm.<sup>-1</sup> with another mode sometimes observed at about 1100 cm.<sup>-1</sup>. Absorptions due to terminal BeH bonds would be expected at frequencies greater than 2000 cm.<sup>-1</sup>.

The broad absorptions of our hydride, which is amorphous (by X-ray diffraction), must involve a range of beryllium-hydrogen bond types, in contrast to the relatively sharp absorptions of crystalline compounds containing BeH<sub>2</sub>Be bridges.

#### EXPERIMENTAL

Beryllium borohydride was prepared from lithium borohydride and beryllium chloride.<sup>8</sup> Infrared spectra were recorded with a Grubb-Parsons prism-grating Spectromaster. Volumes of gases are corrected to s.t.p.

*Ether Complexes.*—Diethyl ether was evaporated under reduced pressure (finally ~0.01 mm.) from a solution obtained by dissolving the borohydride (0.1 g.) in the ether (10 c.c.) (Found: hydrolysis of 0.0136 g. gave 20.8 c.c. H<sub>2</sub>. Calc. for the 1:1 adduct C<sub>4</sub>H<sub>18</sub>B<sub>2</sub>BeO: 21.6 c.c. H<sub>2</sub>).

Beryllium borohydride (~0.1 g.) was allowed to come to equilibrium with tetrahydrofuran vapour at room temperature. Excess tetrahydrofuran was then removed under reduced pressure, giving crystalline tetrakis(tetrahydrofuran)beryllium borohydride (Found: hydrolysis of 0.0586 g. gave 29.9 c.c. H<sub>2</sub>. Calc. for C<sub>16</sub>H<sub>40</sub>B<sub>2</sub>BeO<sub>4</sub>: 32.0 c.c. H<sub>2</sub>).

The 1,2-dimethoxyethane complex was prepared by adding the diether in excess to the cooled borohydride. The excess of solvent was then removed under reduced pressure (Found: hydrolysis of 0.0367 g. gave 40.3 c.c. H<sub>2</sub>. Calc. for the complex [C<sub>2</sub>H<sub>4</sub>(OMe)<sub>2</sub>]<sub>3</sub>[Be(BH<sub>4</sub>)<sub>2</sub>]<sub>2</sub>, 37.9 c.c. H<sub>2</sub>).

*Tetrakis(isobutylamine)beryllium Borohydride.*—Addition of the amine in excess to a solution of beryllium borohydride in diethyl ether resulted in immediate precipitation of the colourless complex, which was washed several times with ether and dried under reduced pressure (Found: hydrolyzable H, 2.38; isobutylamine, 88.8. C<sub>16</sub>H<sub>52</sub>B<sub>2</sub>BeN<sub>4</sub> requires hydrolyzable H, 2.43; isobutylamine, 88.3%).

<sup>7</sup> N. A. Bell and G. E. Coates, *J.*, 1965, 692.

<sup>8</sup> H. I. Schlesinger, H. C. Brown, and E. K. Hyde, *J. Amer. Chem. Soc.*, 1953, **75**, 212.

*Triphenylphosphineberyllium Borohydride.*—Beryllium borohydride (0.2659 g., 0.00687 mole) was condensed on to a frozen ( $-196^{\circ}$ ) solution of triphenylphosphine (1.75 g., 0.0067 mole) in benzene (20 c.c.). When the mixture had warmed to room temperature the borohydride slowly dissolved in the phosphine solution. Solvent and any excess of beryllium borohydride were then removed under reduced pressure, giving the colourless crystalline *complex* (1.9 g., 100%) [Found: Be, 2.9% and hydrolysis of 0.1105 g. gave  $H_2$ , 40.8 c.c.;  $H_3BO_3$ , 0.0234;  $Ph_3P, BH_3$ , 0.1000 g.; *M*, cryoscopically in 0.79, 1.58 wt. % benzene, 310, 323.  $C_{18}H_{23}B_2BeP$  requires Be, 3.0% and hydrolysis according to equation (1) requires  $H_2$ , 41.1 c.c.;  $H_3BO_3$ , 0.0228 g.;  $Ph_3P, BH_3$ , 0.1013 g.; *M*, 301].

*Reaction between Beryllium Borohydride and 2 Mol. of Triphenylphosphine.*—The borohydride (0.8465 g., 0.022 mole) was condensed on a frozen ( $-196^{\circ}$ ) solution of triphenylphosphine (11.48 g., 0.044 mole) in xylene (mixed isomers, 100 c.c.) contained in one limb of a double Schlenk tube.<sup>9</sup> After the mixture had warmed to room temperature and the borohydride had dissolved, it was heated to  $150^{\circ}$  (oil-bath temperature) for 6 hr. under a nitrogen atmosphere. The mixture was filtered while still hot, into the other limb of the Schlenk tube, and the residue was boiled with two 40 c.c. portions of dry benzene, the filtrate each time being added to the xylene solution from which triphenylphosphine-borane (11.6 g., 97% theoretical) was recovered (identified by m. p., mixed m. p., and i.r. spectrum). The insoluble residue (0.250 g.) consisted mainly of beryllium hydride (Found: Be, 63.2%; hydrolysis of 0.0193 g. gave 63.3 c.c.  $H_2$ . Calc. for  $BeH_2$ : Be, 81.9%; 78.4 c.c.  $H_2$ ).

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<sup>9</sup> E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. anorg. Chem.*, 1955, **282**, 47.