NNN'N'-Tetra-alkylethylenediamine Complexes of Some Alkyl- and Aryl-Beryllium Hydrides: the Reaction of Beryllium Hydride–Trimethylamine with Pent-1-ene

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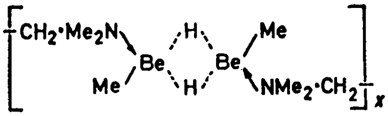
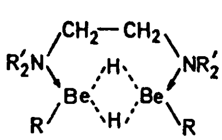
The complexes $(RBeH)_2$tmed (R = Et, Bu^s, Bu^t, n-C_5H_{11}; tmed = *NNN'N'*-tetramethylethylenediamine) are monomeric in benzene, as is the tetraethylethylenediamine (teed) complex of methylberyllium hydride, $(MeBeH)_2$teed. Modified preparations of $(PhBeH)_2$tmed, $(PhBeH)_2$teed, and $(BeH_2)_2$tmed are described. The tmed complexes of beryllium hydride and of methyl- and phenyl-beryllium hydride, which previously have been regarded as polymeric since they do not dissolve in non-polar solvents, are soluble in chlorobenzene or in dichloromethane. Thus all the RBeH complexes with chelate diamines are now believed to have a fused seven-membered ring structure, at least in solution. The rates of the reactions of $(BeH_2,NMe_3)_2$ and $(Bu^tBeH,NMe_3)_2$ with pent-1-ene are similar, and the former reaction gives the n-pentylberyllium hydride–trimethylamine complex rather than a mixture of $(n\text{-}C\text{-}H_{11})_2Be,NMe_3$ and unchanged $(BeH_2,NMe_3)_2$.

METHYLBERYLLIUM HYDRIDE, when first studied,[1] was found to form a tmed (tmed = *NNN'N'*-tetramethylethylenediamine) complex, $(MeBeH)_2$tmed, which was insoluble in benzene, ether, and carbon tetrachloride, nor did it sublime *in vacuo*. Thus the complex was believed to have a polymeric constitution (I), in which the diamine acts as a chain propagator rather than as a chelating ligand. When phenylberyllium hydride was prepared,[2] its tmed complex was also found to be insoluble and was believed to have a similar constitution. Later, the tmed complex of beryllium hydride,[3,4] $(BeH_2)_2$tmed, was also found to be insoluble and was considered to be polymeric, unlike the very soluble complexes of beryllium hydride with other tertiary amines.[3] At the same time, however, the isobutylberyllium hydride tmed complex was found to be very soluble in benzene, in which it is monomeric, and was thus assigned the structure (II, R = Bu^i; R' = Me).[4]



(I)



(II)

This, with the preparation of another monomeric hydride, $(Me_3CCH_2BeH)_2$tmed,[5] raised doubts whether the tmed complexes previously considered polymeric really are so, or whether their insolubility in benzene (and lack of volatility in the case of the methylberyllium hydride complex) is due to factors such as good crystal packing and high polarity. If all of these compounds have the chelate structure (II), then they all must have large dipole moments and the smaller the group R the greater will be the dipole interaction between neighbouring molecules in the crystal (because they will be nearer to each other).

Therefore we have prepared a series of RBeH–tmed complexes with the object of learning whether (I) or (II) is the normal structure. Though methyl- and ethylberyllium hydride can be obtained from the bromide and lithium hydride in ether, neither neopentyl- nor t-butylberyllium bromides react under similar conditions. t-Butyl- and n-pentyl-beryllium chlorides, however, and both phenyl- and *o*-tolyl-beryllium chlorides react readily with lithium hydride. We cannot explain these observations. One would expect bromides to react with lithium hydride in ether more readily than chlorides on account of the sparing solubility of lithium chloride compared with the relatively high solubility of lithium bromide.

The complexes, $(RBeH)_2$tmed (R = Et, Bu^s, Bu^t, and n-pentyl) are monomeric in benzene like the previously described complexes (R = Bu^i and neopentyl). Thus all of these can be assigned structure (II). If the low solubility of $(MeBeH)_2$tmed is indeed due to strong dipole interaction between neighbouring molecules in the crystal, then we reasoned that the complex might dissolve in a solvent that has a dielectric constant considerably higher than that of benzene. Since all solvents likely to react with metal–carbon or metal–hydrogen bonds must be excluded, we chose chlorobenzene (dielectric constant 5·6 at 25 °C[6]) on the grounds that its relatively low reactivity might allow a hydride to survive in it long enough to allow completion of a recrystallization procedure. The methylberyllium hydride–tmed complex crystallized from chlorobenzene, and both $(PhBeH)_2$tmed and (BeH_2)tmed were soluble in, and crystallized from, dichloromethane (dielectric constant 9·80 at 20°[7]). Thus it now appears likely that

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[1] N. A. Bell and G. E. Coates, *Proc. Chem. Soc.*, 1964, 59; *J. Chem. Soc.*, 1964, 692.

[2] G. E. Coates and M. Tranah, *J. Chem. Soc.* (*A*), 1967, 615; N. A. Bell and G. E. Coates, *J. Chem. Soc.* (*A*), 1966, 1069.

[3] L. H. Shepherd, G. L. TerHaar, and E. M. Marlett, *Inorg. Chem.*, 1969, **8**, 976.

[4] G. E. Coates and P. D. Roberts, *J. Chem. Soc.* (*A*), 1969, 1008.

[5] G. E. Coates and B. R. Francis, *J. Chem. Soc.* (*A*), 1971, 1305.

[6] A. A. Maryott and E. A. Smith, 'Table of Dielectric Constants of Pure Liquids,' NBS Circular 514, 10 Aug., 1951.

[7] Technique of Organic Chemistry, vol. VII, Organic Solvents, J. A. Riddick and E. E. Toops, Interscience, New York, 1955, p. 192.

all of the complexes of BeH_2 and RBeH with chelate diamines have structure (II), at least in solution. Some of these complexes could have the polymeric structure (I) in the crystalline state, as found in the case of the aluminium hydride–tmed complex $(\text{-}CH_2\cdot Me_2N \longrightarrow AlH_3 \longleftarrow NMe_2\text{-}CH_2\text{-})_x$.[8]

In further support of structure (II) we prepared the *NNN'N'*-tetraethylethylenediamine (teed) complexes of methylberyllium hydride, which is readily soluble in benzene, in which it is monomeric, with formulae (II, $R = Me$; $R' = Et$). In this instance the increase in molecular volume resulting from substitution of *N*-ethyl for *N*-methyl groups evidently reduces intermolecular dipole–dipole interaction enough to render the complex soluble in benzene. The teed complex of phenylberyllium hydride, though insoluble in benzene, can be crystallized from chlorobenzene (with addition of some hexane).

Attempts to prepare $(BeH_2)_2$teed and the analogous *NN'*-diethyl-*NN'*-dimethylethylenediamine (dedmed) complexes were not successful. Though beryllium hydride dissolved in benzene containing teed, no way could be found of purifying the complex by crystallization, *e.g.* addition of hexane to the solution resulted in separation of a viscous oil. The use of dedmed was somewhat more successful, in that the complex crystallized, but we were not able to dissolve it again for recrystallization. Possibly in this instance the complex existed as the monomer in solution and crystallized as the polymeric form analogous to (I).

In connection with these studies we found that the beryllium hydride–trimethylamine complex could conveniently be prepared using the beryllium hydride precipitated by the reaction between dimethyl- or diethylberyllium and lithium aluminium hydride in diethyl ether.[9] Since, in an earlier study,[4] we had found that isobutylberyllium hydride, its diethyl ether, and its trimethylamine complexes react with pent-1-ene (under similar conditions) at rates in the ratio 110 : 40 : 1, we thought that perhaps terminal Be–H groups, which might be present in base-free $(Bu^iBeH)_x$, are much more reactive to olefins than BeH_2Be bridging groups. To test this, the reaction between $(BeH_2,NMe_3)_2$ (which contains two terminal Be–H bonds as well as the BeH_2Be bridge) and pent-1-ene was followed by ^1H n.m.r. spectroscopy and the half-life was *ca.* 25 h under conditions similar to those in which the half-life of the reaction between $(Bu^iBeH,NMe_3)_2$ and pent-1-ene was found to be 20—25 h. This surprising result, indicating that terminal Be–H bonds are not significantly more reactive to pent-1-ene than bridging beryllium–hydrogen bonds, raised the possibility that the reaction between $(BeH_2,NMe_3)_2$ and pent-1-ene may take either or both the paths A or B.

$$(BeH_2,NMe_3)_2 + 2C_5H_{10} \longrightarrow (C_5H_{11}BeH,NMe_3)_2 \qquad A$$

$$(BeH_2,NMe_3)_2 + 2C_5H_{10} \longrightarrow (C_5H_{11})_2Be,NMe_3 + 1/2(BeH_2,NMe_3)_2 \qquad B$$

By examination of the ^1H n.m.r. spectrum of the reaction product, and comparison with spectra of $(n\text{-}C_5H_{11}BeH,NMe_3)_2$ and of $(n\text{-}C_5H_{11})_2Be,NMe_3$, it was established that A was the only reaction that took place to a significant extent. We conclude that the much faster reaction of base-free isobutylberyllium hydride (relative to its complexes) with pent-1-ene is not due to the presence of terminal Be–H bonds but to some other structural feature of which we at present know nothing.

EXPERIMENTAL

All manipulations were carried out with careful exclusion of air and moisture by use of Schlenk tube, vacuum-line, and glove-box techniques. Compounds were analysed by cautious hydrolysis followed by volumetric determination of beryllium by the fluoride method[10] under standardized conditions. Hydrogen and hydrocarbons were separated and measured with the use of the vacuum-line. All of the compounds described below are sensitive to air and to water, and to minimize the number of transfers from one apparatus to another, *e.g.* for weighing, yields were not recorded, but they appeared to be quantitative apart from crystallization and transfer losses.

NNN'N'-*Tetramethylethylenediamine Complexes*.—(a) *With beryllium hydride*, $(BeH_2)_2$tmed. Diethylberyllium (1·42 g) in diethyl ether (15 ml) was added dropwise to a filtered solution of lithium aluminium hydride (3·4 g) in ether (175 ml). The resulting white suspension was stirred overnight and then filtered. The precipitate was stirred for 24 h with more ether (15 ml), and the ether was then removed by filtration yielding the beryllium hydride–ether mixture[9] (0·405 g). A suspension of this product in toluene (8 ml) was frozen in liquid nitrogen and trimethylamine (about 10 ml) was condensed on to the mixture, which was then allowed to warm to room temperature. It was then stirred for ½ h and filtered. Addition of hexane (15 ml) with continued stirring results in the crystallization of beryllium hydride–trimethylamine as fine needles (identified by i.r. spectrum).

To a freshly prepared solution of $(BeH_2,NMe_3)_2$ (0·30 g) in benzene (8 ml) was added *NNN'N'*-tetramethylethylenediamine (1 ml), resulting in a white precipitate. After the mixture had been stirred ½ h volatile matter was removed under reduced pressure. Addition of dichloromethane (5 ml) to the residue gave a clear solution. Solvent was evaporated at room temperature until the diamine complex, $(BeH_2)_2$tmed, crystallized as colourless needles, identified by m.p. 206—209° (decomp.) (lit.,[4] 210—211° decomp.), and by i.r. spectrum.

(b) *With methylberyllium hydride*, $(MeBeH)_2$tmed. Addition of the diamine (1·3 ml, distilled from calcium hydride) to a solution of methylberyllium hydride diethyl ether complex[1] in benzene (10 ml), prepared from dimethylberyllium (0·319 g), beryllium bromide bisdiethyl ether complex (2·590 g), and lithium hydride (0·141 g), resulted in a white precipitate. After prolonged stirring the solvent and the excess of diamine were evaporated under reduced pressure. The residue was crystallized from chlorobenzene as needles, identified by i.r. spectrum.

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[8] G. J. Palenik, *Acta Cryst.*, 1964, **17**, 1573.

[9] G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1951, **73**, 4585.

[10] D. A. Everest, 'The Chemistry of Beryllium,' Elsevier, Amsterdam, 1964, p. 120.

(c) *With ethylberyllium hydride*, (EtBeH)$_2$tmed. Dropwise addition of the diamine (1·9 ml) to a solution of EtBeH,OEt$_2$ (0·491 g) in benzene (15 ml) prepared [1] from diethylberyllium, beryllium bromide, and lithium hydride, resulted in heat evolution. After stirring at room temperature for 24 h, volatile matter was removed under reduced pressure. The residue was recrystallized from toluene (8 ml) as colourless *needles*, m.p. 151° [Found: Be, 10·2; hydrolysable ethyl, 29·6; hydrolysable hydride, 1·02%; *M* (cryoscopic in benzene) 193. $C_{10}H_{28}Be_2N_2$ requires Be, 9·3; hydrolysable ethyl, 29·9; hydrolysable hydride, 1·03%; *M*, 194].

(d) *With sec-butylberyllium hydride*, (Bu^{s}BeH)$_2$tmed. After a solution of sec-butyl-lithium in benzene (200 ml of 2·0M solution) had been added to beryllium chloride bisdiethyl ether complex (45·6 g, 0·20 mol) in ether (200 ml), the mixture was boiled with reflux for 3 h and set aside overnight. The solution was then decanted from lithium chloride, concentrated by evaporation of solvents, and distilled at 10^{-3} mmHg (bath temp. 70—75°) giving di-sec-butylberyllium ether complex. An attempt to remove ether by reflux under reduced pressure (10^{-3} mmHg), in a way that succeeded for several other beryllium dialkyls [11] (even the di-isopropyl), resulted in loss of butene and the product gradually became viscous. After *ca.* 24 h the viscous product was dissolved in benzene, and analysis of a small sample yielded the ratio Be : Bu : H : Et$_2$O as 1·0 : 1·0 : 0·95 : 0·10.

To a solution of this hydride (0·60 g) in benzene (5 ml) was added the diamine (1·04 g), resulting in a mildly exothermic reaction. After evaporation of volatile matter the residue was recrystallized from benzene–hexane as *prisms*, m.p. 163—165° [Found: Be, 7·3; hydrolysable butyl, 45·3; hydrolysable hydride, 0·79%; *M* (cryoscopic, 0·58 and 0·87 wt. % in benzene) 248 and 256. $C_{14}H_{36}Be_2N_2$ requires Be, 7·2; hydrolysable butyl, 45·6; hydrolysable hydride, 0·80%; *M*, 250].

(e) *With t-butylberyllium hydride*, (Bu^{t}BeH)$_2$tmed. A mixture of lithium hydride (0·060 g), beryllium chloride bisdiethyl ether (0·85 g), a di-t-butylberyllium diethyl ether mixture Bu$^t_2$Be,0·6Et$_2$O (0·62 g), and diethyl ether (10 ml) was stirred at 60° for 24 h. Ether was then removed by evaporation and benzene (5 ml) was added. After stirring for 5 min, the benzene was evaporated and fresh benzene (10 ml) was added. The lithium chloride was then separated. After addition of the diamine (0·43 g) to the filtrate, and stirring for 15 min, all volatile matter was removed and the residue was crystallized from benzene–hexane as *prisms*, m.p. 195—196° (decomp.) [Found: Be, 7·3; hydrolysable butyl, 45·2; hydrolysable hydride, 0·81%; *M* (cryoscopic, 0·58 and 0·86 wt. % in benzene) 245 and 258. $C_{14}H_{36}Be_2N_2$ requires Be, 7·3; hydrolysable butyl, 45·6; hydrolysable hydride, 0·80%; *M*, 250].

An attempt to prepare t-butylberyllium hydride (as the diethyl ether complex) by a similar method, starting from beryllium bromide, gave only t-butylberyllium bromide–diethyl ether complex, which had m.p. 59° (lit.,[11] 55—56°) after sublimation at 50—60°, 10^{-3} mmHg.

(f) *With n-pentylberyllium hydride*, (n-C$_5$H$_{11}$BeH)$_2$tmed. A solution of n-pentylmagnesium bromide in diethyl ether (250 ml), prepared from magnesium (14·6 g) and n-pentyl bromide (90·6 g), was added to beryllium chloride bisdiethyl ether complex (42·97 g) in ether (500 ml) during 20 min causing the ether to boil. After the addition boiling with reflux was continued 45 min, then the solution was decanted from magnesium salts (which settled well). After evaporation of ether the di-n-pentylberyllium–ether mixture distilled at 50—105°, 10^{-5} mmHg, and amounted to 14 ml. Analysis of a sample gave the ratio C_5H_{11} : Be : Et$_2$O as 2·00 : 1·00 : 0·675.

A mixture of the above ether complex (1·10 g), beryllium chloride bisdiethyl ether complex (1·25 g), lithium hydride (0·060 g), and ether (10 ml) was stirred at 50° (bath temp.) for 30 h. After evaporation of ether, benzene (5 ml) was added and after stirring for 5 min the benzene was removed under reduced pressure. The addition of benzene (5 ml), stirring, and evaporation was repeated twice. Finally benzene (10 ml) was added and lithium chloride removed by filtration. Analysis of a small sample of the filtrate gave the ratio, Be : H as 1 : 1. Addition of the diamine (0·64 g) to the filtrate resulted in perceptible warming. When the mixture had been stirred $\frac{1}{2}$ h volatile matter was removed under reduced pressure leaving a viscous liquid which solidified under continuous vacuum after 2 days. The resulting solid was dissolved in hexane (5 ml), the solution filtered, concentrated to *ca.* 3 ml and kept at −5° overnight. The resulting *needles* were separated, washed with cold hexane (2 × 2 ml) and dried under reduced pressure for 24 h, m.p. 57—58° [Found: Be, 6·3; hydrolysable pentyl, 50·5; hydrolysable hydride, 0·69%; *M* (cryoscopic, 0·60 and 0·90 wt. % in benzene) 288 and 290. $C_{16}H_{40}Be_2N_2$ requires Be, 6·5; hydrolysable pentyl, 51·1; hydrolysable hydride, 0·72%; *M*, 278].

(g) *With phenylberyllium hydride*, (PhBeH)$_2$tmed. Lithium hydride (0·50 g) was stirred for 30 h at 40—50° (bath temp.) with diphenylberyllium (0·40 g) and beryllium chloride bisdiethyl ether complex (0·56 g) in ether (20 ml). Ether was then evaporated and was replaced by benzene (5 ml). After stirring for 5 min the solvent was removed under reduced pressure and the residue kept for $\frac{1}{2}$ h at *ca.* 10^{-3} mmHg. After addition of benzene (0·5 g) the mixture was filtered and the diamine (0·5 g) was added to the filtrate. The resulting white precipitate was separated, and was found not to be appreciably soluble in chlorobenzene at 80—90°. However, it dissolved in dichloromethane (10 ml). Solvent was evaporated until the *diamine complex* crystallized, m.p. 250—252° (decomp.) (lit.[2] *ca.* 245° (decomp.) (Found: Be, 6·15; hydrolysable hydride, 0·69%. Calc. for $C_{18}H_{28}Be_2N_2$: Be, 6·2; hydrolysable hydride, 0·69%).

(h) *With o-tolylberyllium hydride*, (*o*-CH$_3$C$_6$H$_4$BeH)$_2$tmed. This was similarly prepared from di-*o*-tolylberyllium (0·65 g), beryllium chloride ether complex (0·77 g), and lithium hydride (0·050 g) in ether (10 ml). After treatment with benzene as described above, addition of the diamine (0·40 g) yielded the diamine complex, decomp above 265° (Found: Be, 5·6; hydrolysable tolyl, 56·7; hydrolysable hydride, 0·62%. $C_{20}H_{32}Be_2N_2$ requires Be, 5·7; hydrolysable tolyl, 57·2; hydrolysable hydride, 0·63%).

NNN′N′-*Tetraethylethylenediamine Complexes*.—(a) *With methylberyllium hydride*, (MeBeH)$_2$teed. Addition of the diamine (1·95 ml) to methylberyllium hydride (0·43 g) as ether complex (prepared as described above) dissolved in benzene (18 ml) resulted in an exothermic reaction. After the mixture has been stirred for 2·5 h solvents were evaporated under reduced pressure and the residue was crystallized from toluene–hexane (3 : 1). The *adduct*, m.p. 125°, is rather soluble in this solvent and the yield was low, 0·39 g, 10% [Found: Be, 8·5%; methane plus hydrogen produced

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[11] G. E. Coates and F. Glockling, *J. Chem. Soc.*, 1954, 22; G. E. Coates and P. D. Roberts, *J. Chem. Soc.* (*A*), 1968, 2651.

by hydrolysis of 0·055 g, 23·2 ml at s.t.p., *M* (cryoscopic in benzene) 222 and 193. $C_{12}H_{32}Be_2N_2$ requires Be, 8·1%; methane plus hydrogen 22·2 ml at s.t.p.]. Methane and hydrogen could not be separated using available apparatus.

(b) *With phenylberyllium hydride*, $(PhBeH)_2$teed. This was prepared by the method described for the analogous tmed complex, and the *teed complex* crystallized from chlorobenzene after a little hexane had been added, m.p. 255—260° (decomp.) (Found: Be, 5·4; hydrolysable phenyl, 44·0; hydrolysable hydride, 0·57%. $C_{22}H_{36}Be_2N_2$ requires Be, 5·2; hydrolysable phenyl, 44·5; hydrolysable hydride, 0·58%).

*The Addition of Beryllium Hydride–Trimethylamine to Pent-*1-*ene.*—The olefin (0·344 g) and diphenylmethane (0·7306 g, to serve as a ^1H n.m.r. reference) were dissolved in benzene and made up to a volume of 10·0 ml. At time zero, 1 ml of the olefin solution was added to an n.m.r. tube which contained 0·0343 g of the beryllium hydride complex, and which was maintained at 33·5°, the ^1H n.m.r. spectrum being recorded at intervals up to 48 h. The area of the vinyl resonances, which slowly decreased, was compared to that of the methylene resonance of the diphenylmethane, giving 25 h as the time for half of the pent-1-ene to disappear. When the vinyl resonances had disappeared the spectrum was identical to that of the trimethylamine complex of n-pentylberyllium hydride (obtained by condensing the amine on the hydride, prepared as described earlier, then removing unreacted amine under reduced pressure) and different from that of $(n\text{-}C_5H_{11})_2Be,NMe_3$ which was similarly prepared from bis-n-pentylberyllium.

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