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SYNTHETIC STUDIES ON THE
ORGANIC COMPOUNDS OF BERYLLIUM

by

M. TRANAH.

A thesis submitted for the Degree of Doctor of

Philosophy in the University of Durham.

June 1966



Acknowledgements

The author wishes to express his sincere thanks to Professor G. E. Coates, M.A.,D.Sc.,F.R.I.C., under whose direction this research was carried out, for his constant encouragement and valuable advice.

The author is also indebted to the Science Research Council for a Research Studentship.

Memorandum

The work described in this thesis was carried out in the University of Durham between October 1963 and June 1966. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

SUMMARY

The reactions of beryllium dialkyls and diphenylberyllium with organo-tin hydrides have been investigated as preparative routes to alkyl and phenylberyllium hydrides.

The reaction between triethylstannane and dimethyl-beryllium in ether solution gave methylberyllium hydride, which was characterised as the known trimethylamine complex, $(\text{MeBeH.NME}_3)_2$. Similarly, diphenylberyllium and triphenylstannane react to give phenylberyllium hydride, but contamination of the product with tetraphenyltin prevent preparation of any pure coordination complexes.

Ether-free diethylberyllium and triethylstannane react, in 1:2 and 1:3 molar proportions, in hexane giving insoluble ethylberyllium hydrides (with $\text{Be:H} = 1.4 - 1.8$), hydrogen, and hexaethyl di-tin.

The reactions of ethylberyllium hydride-trimethylamine with dimethylamine, N,N,N',N' - tetramethyl-o-phenylenediamine and diethylmercury have been investigated. Reaction with diethylmercury yields ethane, diethylberyllium-trimethylamine and mercury, which contrasts with reaction of alane-trimethylamine alkylaluminium derivatives and mercury.

The coordination chemistry of diphenylberyllium has also been investigated. Reactions with the bi-dentate ligands N,N,N',N' - tetramethylethylenediamine, N,N,N',N' - tetramethyl-o-phenylenediamine, 1,2-dimethoxyethane and 2,5-dithiahexane yield well defined crystalline complexes, which are monomeric in benzene. The mono-dentate ligands, diethyl and dimethyl ethers, dimethyl and diethyl sulphides, trimethylamine and trimethylphosphine give 2:1 complexes. The formation of these complexes demonstrates the greater acceptor strength of diphenylberyllium compared to dimethylberyllium, which forms either no complex at all or a very unstable complex with these ligands. Several of the 2:1 complexes have an appreciable dissociation pressure of ligand at 0°C ; and consideration of this and measurements of the heats of dissociation of these and other 2:1 complexes shows that steric considerations are an important factor governing the stability of the complexes.

Reactions of diphenylberyllium with some donor molecules containing acidic hydrogen have been investigated. Diphenylamine yields a dimeric product, $(\text{PhBeNPh}_2)_2$, similar to the methylberyllium and methylzinc analogues. Reaction with dimethylamine yields a trimeric product, $(\text{PhBeNMe}_2)_3$ which is formulated as a six-membered ring, as is the methylberyllium derivative. A dimeric product $(\text{PhBeNMe}_2 \cdot \text{C}_2\text{H}_4\text{NMe}_2)_2$ is formed by reaction with N,N,N' - trimethylethylenediamine, and it is probably similar to the analogous methylberyllium and methylzinc derivatives. Phenylberyllium methoxide, $(\text{PhBeOMe})_4$, formed by reaction with methanol, has been found to be tetrameric and a cubic structure is proposed, similar to many tetrameric methylberyllium, methylcadmium and methylzinc alkoxides that have been observed.

Reaction of phenylberyllium chloride with sodium triethylboron hydride yields a solution from which the trimethylamine and trimethylphosphine adducts of phenylberyllium hydride have been prepared.

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INTRODUCTION

The work described in this thesis can be divided into two sections, (a) methods of preparation and reactions of organo-beryllium hydrides, and (b) a study of the co-ordination chemistry of diphenylberyllium. These topics overlap somewhat in respect of experiments on the preparation of phenylberyllium hydride complexes.

This introduction deals with the chemistry of compounds relevant to these topics. Firstly, the preparation, properties and co-ordination chemistry of the beryllium dialkyls and diphenylberyllium are reviewed. Preparative routes to and reactions of organo-beryllium hydrides and beryllium hydride are discussed, and finally the relevant chemistry of organic and hydride derivatives of other Group II elements is described.

Compounds of beryllium are almost exclusively covalent due to the small size and consequent high polarising power of the dipositive cation Be^{2+} . The atomic radius of beryllium is 0.89 \AA and the calculated ionic radius of Be^{2+} is 0.34 \AA . The first and second ionisation potentials are 215 and 420 Kcal./g.atom. respectively. Such high values would suggest that free divalent ions of beryllium are unlikely to exist in its compounds. Thus beryllium fluoride, which would be expected to be the most ionic compound of beryllium, is a poor conductor of electricity in the fused state ¹. and readily forms a glass.

Beryllium forms compounds with covalencies of two, three or four for the metal atom. The co-ordination number of two arises from the use of sp hybrid orbitals by the beryllium atom to give a linear molecule, as is found in beryllium chloride at high temperature when it exists as a monomer ². and, probably, in monomeric di-tertiarybutylberyllium ³. Dimethylberyllium-trimethylamine ⁴ and di-isopropylberyllium-trimethylamine ⁵ are



examples of the unusual co-ordination number of three, in which the beryllium atom must make use of sp^2 hybrid orbitals. However, beryllium has a very strong tendency to form four covalent compounds using sp^3 orbitals to give tetrahedral bonding around the beryllium atom. Studies on the viscosities, conductivities and freezing-points of solutions of beryllium salts⁶ show the beryllium ion to be more strongly hydrated than any other divalent cation, and beryllium salts commonly crystallise from aqueous solution with four molecules of water of crystallisation per beryllium atom. The equivalent ionic conductances at 25°C of Group II A divalent cations in water are:

Be	Mg	Ca	Sr	Ba	Ra	-1	2	-1
30	55.5	59.8	59.8	64.2	67	ohm.	cm.	equiv.

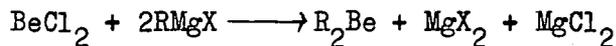
The phthalocyanine complex of beryllium is exceptional, it having a square-planar configuration due to the shape of the phthalocyanine molecule.⁷

There are no known compounds in which beryllium has a co-ordination number greater than four, since the atomic orbitals of principal quantum number three are of too high an energy to participate in bond formation and hybrid orbitals involving d-orbitals cannot be expected. However, it is possible that five or six coordinate beryllium compounds may be prepared since coordination numbers in excess of four are found both for boron (e.g. B_5H_9) and carbon (e.g. Me_2Be and the $MeLi$ tetramer). In such cases multicentre bonds still require the use of only 2s and 2p atomic orbitals.

Organo-Beryllium Compounds

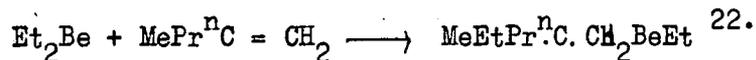
Dialkyls and diaryls of beryllium can be prepared in small quantities by reaction of beryllium metal and mercury dialkyls and diaryls at elevated temperatures, with small quantities of mercuric chloride used as catalyst⁸⁻¹⁷ For larger scale preparations the reactions of beryllium chloride and a Grignard^{17,18,19} or lithium reagent¹⁸ in ether are usually preferred, though complete

separation of the beryllium compound from ether is often difficult:



The action of free methyl or ethyl radicals on metallic beryllium²⁰ and thermal decomposition of alkylberyllium halides⁹ lead to the formation of dialkylberyllium compounds. The reaction of beryllium metal with alkyl halides, at elevated temperatures, has been used to prepare some organo-beryllium halides.^{9,21}

Alkylberyllium compounds react with ethylene in a step-wise manner, similar to aluminium and lithium alkyls, and have been used to polymerise other alkenes and for preparation of intermediates:



Dimethylberyllium

On a small scale dimethylberyllium is most conveniently prepared by reaction of dimethylmercury with excess beryllium powder^{12,13,15,16,17}. The product can be sublimed from excess beryllium under high vacuum, and trace quantities of mercury can be removed with gold foil¹⁵.

For larger scale preparations the reactions of beryllium chloride with Grignard or lithium reagents in ether are preferred. However, the isolation of a pure product presents some difficulties. Separation from dissolved salts by "ether distillation" at atmospheric pressure^{14,23,24} is possible, but complete separation from ether is very difficult. It has been suggested²⁵ that use of dimethyl sulphide as a solvent could facilitate isolation of a "solvent-free" dimethylberyllium, as dimethylsulphide does not coordinate to dimethylberyllium,⁴ but no experimental examination of this method has been published openly.

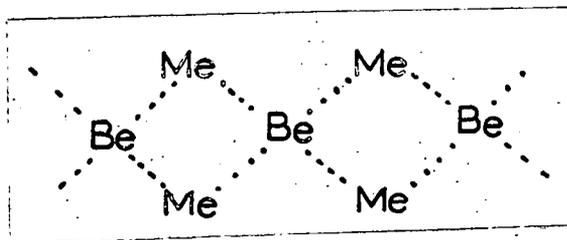
Dimethylberyllium forms colourless needles when condensed from the vapour phase, but has not been observed to melt. The vapour pressure of the solid²⁶ is given by the equations:

$$\begin{array}{l} 100-150^{\circ}\text{C} \quad : \quad \log_{10} P(\text{mm}) = 12.530 - 4771/T \\ 155-180^{\circ}\text{C} \quad : \quad \log_{10} P(\text{mm}) = 13.292 - 5100/T \end{array}$$

The extrapolated sublimation temperature is 217°C , and latent heat of sublimation is 23.5 Kcal./mole of monomer.

Independent observations²⁹ give a slightly different vapour pressure equation and sublimation temperature of 220°C .

X-Ray diffraction analysis²⁷ reveals a long chain polymeric structure, the interchain distances excluding an ionic structure (



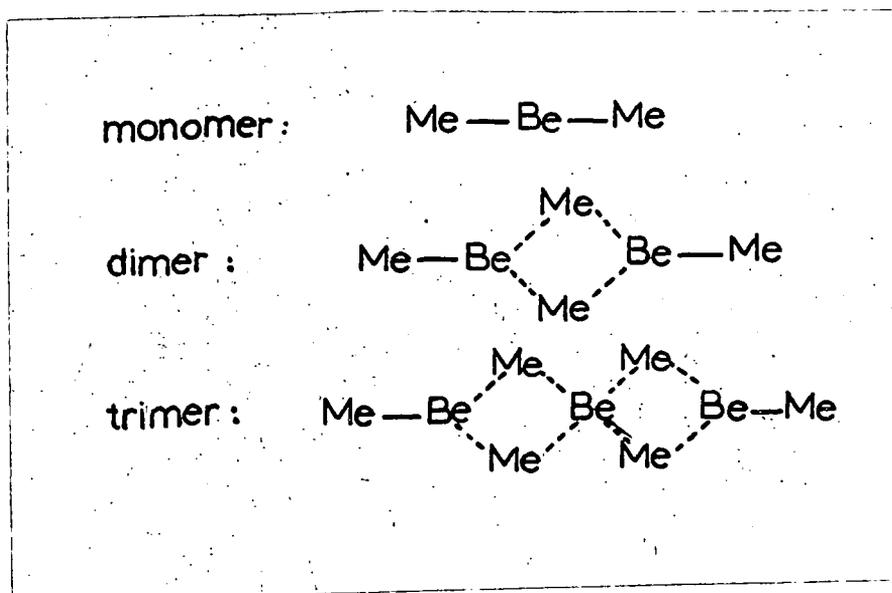
In the above formula dotted lines represent half-bonds.

Both beryllium and carbon atoms make use of four tetrahedral sp^3 atomic orbitals and it is probable that three-centre molecular orbitals $Be(sp^3) + C(sp^3) + Be(sp^3)$ are formed from these. Each molecular orbital would hold two electrons, giving a "bent bond", Be-C-Be. Alternatively each Be-C bond may be regarded as a half-bond. The Be-C-Be angle (66°) is small, but good overlap between tetrahedral atomic orbitals is possible. The C-Be-C angle (114°) is strained only slightly from the tetrahedral (109.5°). All Be-C distances are equal (1.92 \AA) and larger than the calculated value 1.73 \AA for a single bond, supporting half-bond formulation. The bond order (n) calculated from the Pauling equation:^{28.}

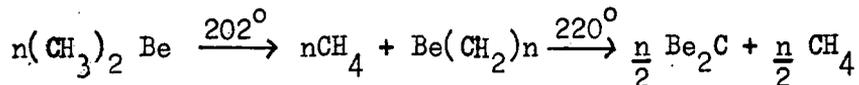
$$d = d_1 - 0.6 \log_{10} n.$$

is 0.48, or 0.5, within error of computing $d_1 = 1.73 \text{ \AA}$.

Vapour density measurements between 160° and 200°C , and a study of the pressure dependence of the vapour density show that the vapour consists of monomer, dimer and trimer molecules, together with higher polymers which are important only at near-saturation conditions. Structures have been proposed^{26.} for the first three:



Thermal decomposition of dimethylberyllium²⁹ starts at 200°C with formation of Be(CH₂)_n as an intermediate product. The end-product at 220-230°C is beryllium carbide:



Reaction of dimethylberyllium with diborane at elevated temperatures takes place in several stages⁸. An intermediate product (MeBeBH₄)_n can be detected, but the main products are trimethylborane and beryllium borohydride BeB₂H₈ together with an involatile solid, which is probably (BeBH₅)_n.

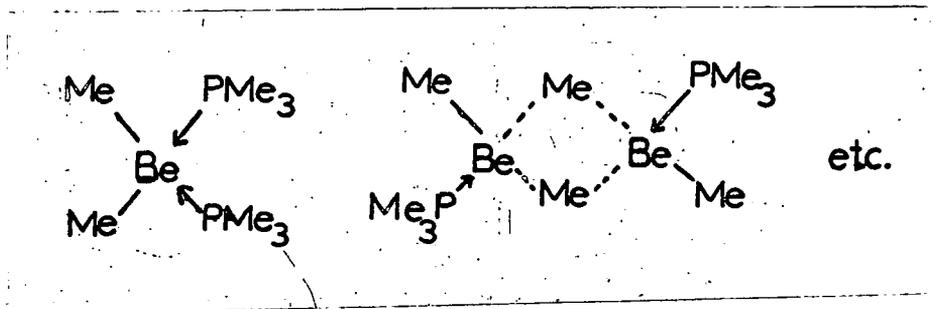
Oxidation of dimethylberyllium by oxygen has been studied under varying conditions.³⁰ The end-product was always beryllium methoxide (MeO)₂ Be, but containing varying amounts, 2.6 - 6.9%, peroxidic oxygen according to the method of preparation.

By electrolysis of an ethereal mixture of dimethylberyllium and beryllium chloride, beryllium metal can be deposited from solution²³.

Dimethylberyllium reacts with donor molecules and thus relieves its electron deficiency. However, only relatively strong donor molecules will coordinate, since the heat of coordination must exceed the heat of polymerisation or the polymeric structure is not broken down. Thus, it forms coordination compounds with trimethylamine, trimethylphosphine, dimethyl and diethyl ethers, but not with trimethylarsine or dimethyl sulphide. The properties of these compounds indicate that the order of heat of coordination is N > P > O > As, S.⁴ The same order is found with trimethylaluminium³¹ and trimethylgallium,³² when the acceptor atom is of the type that forms simple coordination links free from complications due to double bonding or any similar influence of d-orbitals, often found in transition metal compounds.

Dimethylberyllium forms a 1:1 compound ($\text{Me}_2\text{Be} \leftarrow \text{NMe}_3$) with trimethylamine. This melts at 36°C and is stable up to 180°C . Vapour density measurements show it to be monomeric in the gas phase,⁴ although cryoscopic measurements in benzene solution show it to be slightly associated.³³ An unstable compound $(\text{Me}_2\text{Be})_2 \cdot (\text{NMe}_3)_3$, dissociating about 10°C is described,⁴ but this has since been shown to be 2:1 complex, $\text{Me}_2\text{Be} \cdot (\text{NMe}_3)_2$.³⁴

Whereas trimethylamine coordinates so strongly to dimethylberyllium that is able to break down the polymeric structure, without difficulty, and form well-defined complexes, this is not true of trimethylphosphine. Complex equilibria result due to the similarity between the affinities of dimethylberyllium for trimethylphosphine and each other. A considerable range of compounds $(\text{Me}_3\text{P})_x (\text{Me}_2\text{Be})_y$, when $x = 2, 3, 1, 2, 2, 2$ and $y = 1, 2, 1, 3, 4, 5$ respectively are formed,⁴ each one being stable in a certain pressure of trimethylphosphine and temperature. All the trimethylphosphine can be removed in vacuo at room temperature. The suggested explanation is the successive formation of compounds of increasing chain length, with trimethylphosphine acting as a chain-ending group.

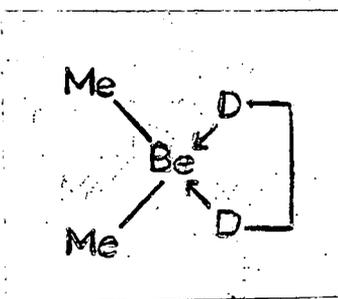


The recent correction³⁴ to the stoichiometry of the unstable dimethylberyllium-trimethylamine complex from 2:3 to 1:2 has accounted for a hitherto unexplained anomaly.

With dimethylether, the compounds $\text{Me}_2\text{Be} \leftarrow \text{OMe}_2$, (Me_2Be_2) $(\text{OMe}_2)_3$, $(\text{Me}_2\text{Be})_3$ $(\text{OMe}_2)_2$ and $(\text{Me}_2\text{Be}) \text{OMe}_2$ have been observed, but all are less stable than the phosphine complexes. There is no indication of a compound of any definite composition being formed with diethylether ⁴.

Colourless crystalline needles, m.p. 91-92°C, of dimethyldipyridine-beryllium have been isolated from the reaction of pyridine with ethered dimethylberyllium ³⁵.

Dimethylberyllium reacts with bidentate ligands to form very stable 1:1 chelate complexes of the type:

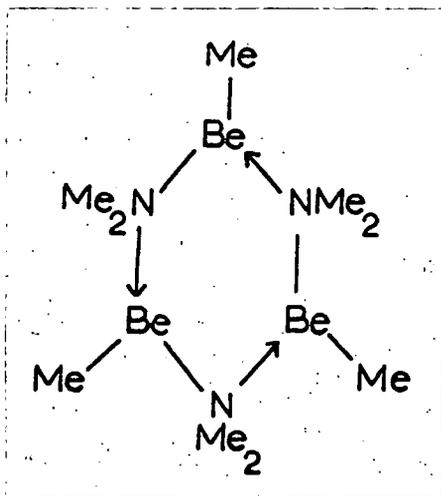


Thus, N,N,N',N' - tetramethylethylenediamine, N,N,N',N' - tetramethyl - o - phenylene-diamine and 1,2 - dimethoxyethane form well-defined complexes, both of which are claimed to sublime unchanged invacuo, ³⁵ but more recent work ³⁶ has shown the diether complex dissociates whilst subliming 55-60°C (0.001mm). The former amine complex is about ten per cent associated, whilst the latter complexes are monomeric.

Donor molecules containing reactive hydrogen atoms, e.g. alcohols, primary and secondary amines, also coordinate to dimethylberyllium, but there is a tendency to eliminate methane and form di-, tri- or polymeric products.

Dimethylamine forms an adduct, $\text{Me}_2\text{Be} \leftarrow \text{NHMe}_2$, which melts at 44°C with elimination of methane, leaving a white trimeric compound $(\text{MeBe.NMe}_2)_3$ ³⁷. This compound was originally described as

white crystals, m.p. 55-56°C. However, since dimethylaminodimethylaluminiumgallium and -indium have recently been found to be crystalline at room temperature and to undergo a transition to a glassy phase in the range 50-80°C, the transitions being attributed to a polymerisation process,³⁹ and since various dimethyl- and diethylphosphino and arsino-dimethyl derivatives of the same metals (e.g. Me₂GaPMe₂) have been found to be glassy in the condensed state at room temperature,⁴⁰ the aminoberyllium derivative has been re-examined.⁴¹ Though (MeBE.NMe₂)₃ may be sublimed at 50-80°C under reduced pressure, giving an apparently solid condensate, the latter is isotropic when examined in polarised light, and X-ray diffraction gives no lines. It is therefore amorphous, and, like some of the other compounds examined,^{39,40} appears to be a liquid of high viscosity, probably consisting of polymers and oligomers, (MeBeNMe₂)_n. When heated in a sealed capillary tube it softens and turns reversibly into a clearly recognisable liquid over the range 51-54°C. Corresponding changes occurred at 50-53°C for [(MeBeN(CD₃))]_{3,2,3}, and 48-54°C for (CD₃Be.NMe₂)₃.⁴¹ The original examination of MeBeNMe₂,³⁷ showed it to be trimeric both in benzene and as vapour, and a cyclic structure II was assigned:



II

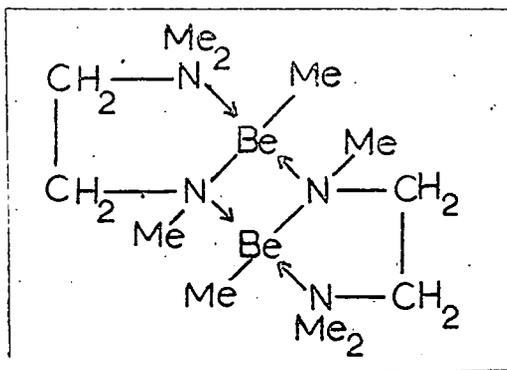
Such a structure would involve three-coordinate beryllium and four-coordinate nitrogen, and would not be planar. The observed proton magnetic resonance spectrum⁴¹ shows single resonances for both nitrogen and beryllium methyl protons, which do not change on cooling to -90°C. This is consistent with rapid interchange between possible conformations of the ring, remaining rapid even at the low temperature.

The secondary amines, diethylamine, di-n-propylamine and diphenylamine also react with dimethylberyllium with elimination of methane.³⁸ Diethylamine gives a trimeric product $(\text{MeBeNEt}_2)_3$ similar to methyl (dimethylamino) beryllium. However, di-n-propylamine and diphenylamine give dimeric products, $(\text{MeBeNPr}_2^{\text{n}})_2$ and $(\text{MeBeNPh}_2)_2$. The drop in degree of association from trimer to dimer is attributed to steric influences as the group bound to nitrogen becomes bulkier, since it has been shown by experiments with molecular models show there is less interference between alkyl groups in a dimeric structure than in a trimeric structure.

Di-iso-propylamine³³ and dimethylberyllium form a stable monomeric adduct $\text{Me}_2\text{Be} \leftarrow \text{NHPr}_2^{\text{i}}$, which eliminates methane at 100°C in the presence of excess amine. However, elimination of methane was not quantitative, even after refluxing with excess amine for several days; this is probably due to steric hindrance by the isopropyl groups.

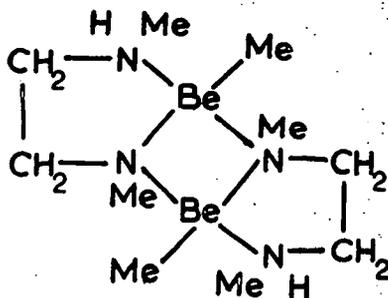
The reaction of dimethylberyllium with piperidine and morpholine⁴² gave 1:1 adducts $\text{Me}_2\text{Be} \leftarrow \text{NHC}_5\text{H}_{10}$ and $\text{Me}_2\text{Be} \leftarrow \text{NHC}_4\text{H}_8\text{O}$ respectively. In the presence of excess secondary amine at 40°C elimination of methane was quantitative after 24/25 hours, with formation of bis-N,N' - piperidylberyllium and bis-N,N' - morpholyberyllium. No information about the molecular complexity of the 1:1 adducts or the bis-derivatives is available.

N,N,N' - Trimethylethylenediamine ³⁵ reacts with dimethylberyllium at room temperature eliminating one mole of methane and forming a dimeric product III, which melts at 116-118°C.

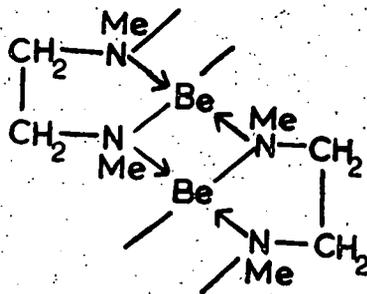


III

Similarly one mole of methane is liberated from a mixture of dimethylberyllium and N,N' - dimethylethylenediamine at low temperature. ³³ This product, probably has a structure IV similar to III, sublimes at 90°C and loses about eighty per cent of the methyl bound to beryllium as methane at 145°C. When IV is heated in tetralin at 150°C elimination of methane is quantitative, giving an insoluble polymeric product, probably having the structure V.



IV



V

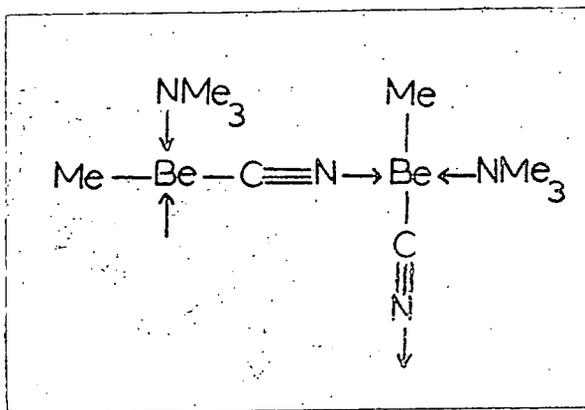
Reaction of unsymmetrical N,N-dimethylethylenediamine ³³ with dimethylberyllium involves elimination of one mole of methane

giving a product of structure similar to IV. When heated to 170°C the compound evolves methane, and, on cooling, a hard glass, evidently polymeric, is produced.

Ethylenediamine and dimethylberyllium³³ react at room temperature with elimination of about eighty per cent of the methyl as methane. The white, amorphous, polymeric product loses further methane at 45°C, but about six per cent of the methyl groups bound to beryllium are retained.

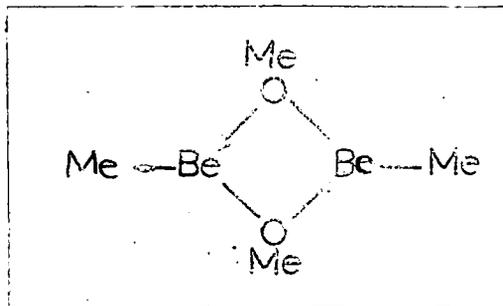
Methylamine and dimethylberyllium react with elimination of methane, but the other product has not been characterised.³⁷ Similarly, ammonia⁴³ liberates methane from dimethylberyllium at 0-20°C. Even at 50°C quantitative elimination of methane was not observed. The polymeric products, of the type $R-[Be-NH-Be]_n-NH_2$ were not characterised further. At low temperatures (-80°C) a 1:1 adduct $Me_2Be \leftarrow NH_3$ was observed but not isolated.

When dimethylberyllium is added to excess hydrogen cyanide in benzene, beryllium cyanide is precipitated⁴⁴. It will not react with trimethylamine or other donor molecules and is without doubt a cross-linked polymer. However, when equimolar quantities of dimethylberyllium and hydrogen cyanide are mixed, ether-soluble methylberyllium cyanide is formed with elimination of methane.⁴⁵ Separation of ether from methylberyllium cyanide can be achieved by pumping at 70°C, but the residue will not redissolve or react with trimethylamine and is obviously polymeric. The coordination complex of trimethylamine and methylberyllium cyanide was isolated from the reaction of dimethylberyllium-trimethylamine and hydrogen cyanide. It is an involatile amorphous solid and probably has a polymeric structure (fig. VI).



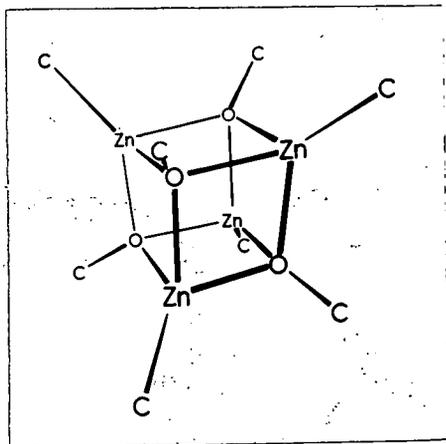
VI

Methanol and methanethiol³⁷ react with dimethylberyllium with immediate evolution of methane. The product from reaction with methanethiol has not been characterised, but methanol gives methylberyllium methoxide $(\text{MeBeOMe})_n$. It disproportionates at 120°C , presumably giving dimethylberyllium and beryllium methoxide $\text{Be}(\text{OME})_2$. Ebullioscopic measurements³⁷ in benzene showed methylberyllium methoxide to be dimeric for which structure VII was proposed.



VII

However, recent cryscopic measurements show it to be tetrameric, as are methylberyllium isopropoxide and Tert-butoxide prepared by reaction of dimethylberyllium with iso-propenol and tert-butand respectively.³⁸ The structure of these tetrameric alkoxides is probably similar to the cube-like structure of methylzinc methoxide, figure IX and proposed for other tetrameric alkylzinc alkoxides⁴⁶.



IX

The reaction of dimethylberyllium with phenol and substituted phenols has been studied.⁴⁷ The first mole of methane is liberated below -80° and in the presence of excess phenol the second mole of methane is liberated at about -30° c with precipitation of bis-phenoxy derivatives. No further characterisation of the bis-compounds is reported.

An unusual alkoxy derivative has been prepared by reaction of ethereal dimethylberyllium and benzhydrol³⁶. The product ($\text{MeBeOCH}_2\text{Ph} \leftarrow \text{OEt}_2$) is monomeric in benzene.

It is probable that the ether molecule, which can be displaced by stronger donors, such as tetrahydrofuran, is held to relieve the coordinative unsaturation of the beryllium atom. The expected association to give a tetrameric structure is probably prevented by steric interaction between groups on the α carbon atom.

The infrared and Raman spectra²⁹ of solid dimethylberyllium have shown that the polymer has D_{2h} symmetry with six vibrations active in the infrared and six in the Raman spectrum. There was no absorption in the region $1400-1500 \text{ cm}^{-1}$ where most compounds containing methyl groups absorb strongly due to methyl asymmetric deformations ($S_{\text{asym}} \text{CH}_3$). However, two very intense absorptions at 1243 and 1255 cm^{-1} have been identified as being due to deformation of the bridging methyl groups, and another absorption at 835 cm^{-1} as due to a rocking mode.

Absorptions at 535 and 567 ^{cm-1} were assigned as beryllium-carbon stretching vibrations. By comparison ^{41.} of the spectra of trimethylamine and N,N,N',N' - tetramethylethylenediamine complexes of $(\text{CH}_3)_2\text{Be}$ and $(\text{CD}_3)_2\text{Be}$ absorptions due to beryllium-methyl symmetric deformations ($\delta_{\text{sym}}\text{Be-CH}_3$) have been identified in the range 1186- 1206 cm^{-1} . Beryllium-methyl stretching vibrations could not be clearly identified but appeared to be in the range 700-900 cm^{-1} .

It is pointed out ^{41.} that the assignment of ($\delta_{\text{sym}}\text{Be-CH}_3$) in the region 1186-1206 cm^{-1} is supported by reference to the trimethylaluminium dimer, ^{48.} in which absorption due to terminal Al-CH₃ symmetric deformation is at 1206 cm^{-1} , and that due to bridging methyl being at 1255 cm^{-1} . Thus, in compounds containing terminal methyl groups, such as dimethylberyllium-tetramethylethylenediamine, symmetric methyl deformations would be expected to lie some 50 cm^{-1} below values obtained for bridging methyls, and these have been observed.

The proton magnetic resonance spectra of several dimethylberyllium complexes have been studied, ^{41.} and the chemical shifts of the methylberyllium protons, when the donor is trimethylamine, ether and N,N,N',N - tetramethylethylenediamine, have been compared with similar values obtained for compounds with methyl groups bound to other electropositive elements.

Diethylberyllium

Although diethylberyllium cannot be prepared by reaction of diethylmercury and beryllium metal, ^{14,17.} it is conveniently prepared from the reaction of ethylmagnesium bromide and beryllium chloride in ether. ^{14,19.} Difficulty is encountered in separation of the product from ether, but prolonged pumping and subsequent vacuum distillation gives a colourless liquid boiling at 63°C/0.3 m.m., which contains about two per cent ether. ^{19.} A more recent method of preparation involves treatment of beryllium chloride with triethylaluminium at 100°C. After one hour an electron-donor complexing

agent for the aluminium compound is added, and diethylberyllium separated by distillation.⁴⁹

The vapour pressure of diethylberyllium is given approximately by the equation: $\log_{10} P \text{ (mm)} = 7.59 - 220/T$. Whence the extrapolated boiling point is 194°C.

Molecular weight measurements show diethylberyllium to be monomeric in dioxan, but associated in cyclohexane and benzene, the values being time-dependant in the last two solvents (160 and 140 respectively after the solution had stood for two days, 212 and 224 respectively after 240 days)⁵⁰. These results could well be the subject of further experiments.

The apparent dipole moment in several solvents has been measured, it being 1.0 D in heptane, 1.69 D in benzene and 4.3 D in dioxan.^{51,52} It should be noted that diethylberyllium is associated in heptane and benzene, but monomeric in dioxan.

At temperatures above 80°C diethylberyllium undergoes a complicated decomposition, which is rapid at 190-200°C. Ethane, ethylene and butene are the main volatile products, with small amounts of benzene, 1,3-cyclohexadiene and 3-hexene. The residue is an oil, which can be distilled at 100°C/0.1-0.2 m.m. and analyses approximately to $[(H-Be-CH_2)_2]_n$, and a crystalline solid $[Be(CH_2)_3]_n$ ¹⁹.

The study of the coordination chemistry of diethylberyllium has not been as extensive as that of dimethylberyllium.

A volatile liquid 1:1 adduct,⁵³ stable up to 50°C, with trimethylamine $Et_2Be \leftarrow NMe_3$ has been prepared, which reacts with excess trimethylamine at low temperatures. A 2:1 adduct $Et_2(Be.(NMe_3))_2$ is formed at -65°C, at which temperature it is stable.

However, the second molecule of trimethylamine is lost at temperatures above -35°C. At -33°C and -16°C the dissociation pressures are 1.1 m.m. and 11.0 m.m. respectively.⁵³ An orange crystalline adduct Et_2BePy_2 is formed by reaction of diethylberyllium with pyridine.³⁵

Reaction of diethylberyllium with diethylamine and diphenylamine, in 1:1 molar quantities, gives dimeric products $(\text{EtBeNEt}_2)_2$ and $(\text{EtBeNPh}_2)_2$ respectively. ³⁸. When compared with the analogous methylberyllium derivatives it seems likely steric considerations are governing the molecular complexity of these derivatives. The dimethylamino- and diethylamino- derivatives $(\text{MeBeNMe}_2)_3$ and $(\text{MeBeNET}_2)_3$ are trimeric, ³⁸. whereas the di-n-propylamino- and diphenylamino- derivatives are dimeric. The drop in molecular complexity is explained by steric interference introduced as the alkyl groups bound to nitrogen becomes larger, similarly the steric interference introduced by changing the alkyl group bound to beryllium from methyl to ethyl must account for the ethylberyllium derivatives being dimeric.

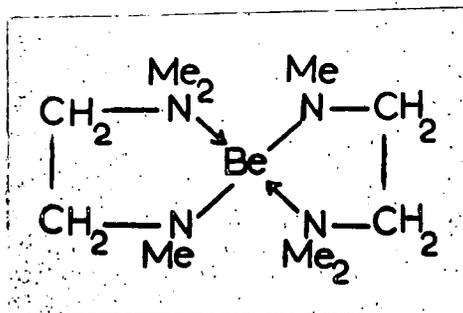
The reaction of diethylberyllium and its trimethylamine adduct with several methyl hydrazines has been investigated. ⁵⁴. In general, quantitative liberation of ethane was not observed and polymeric materials were formed. However, a 1:1 adduct $(\text{Et}_2\text{Be} \leftarrow \text{MEHNNMe}_2)$ was formed from trimethylhydrazine and a 1:2 adduct $[\text{ME}_2\text{NNMe}_2(\text{BeEt}_2)_2]$ from tetramethylhydrazine was isolated. It was found that the extent of replacement of ethyl by hydrazine was governed by steric considerations.

Methanol, isopropanol and hydrogen chloride all react explosively with diethylberyllium at room temperature. ¹⁹.

Addition of diethylberyllium to excess diphenylamine in benzene resulted in quantitative elimination of ethane and precipitation of polymeric material $[\text{Be}(\text{NPh}_2)_2]_n$ ⁵⁵.

Several other compounds obtained by displacement of both alkyl groups from diethylberyllium by piperidine, morpholine ⁴². and various substituted phenols ⁴⁷. are described, but nothing was reported concerning the molecular complexity of these compounds. Unlike dimethylberyllium, which loses only one mole of methane when heated with excess N,N,N' - trimethylethylenediamine at 60°C, ³⁵. the dimeric structure remains essentially intact, diethylberyllium

reacts with excess N,N,N' - trimethylethylenediamine ⁵⁶. in refluxing benzene. Elimination of ethane is complete after about three days reaction. The product, bis- 2-dimethylaminoethyl(methylamino-beryllium $(\text{Me}_2\text{N}.\text{CH}_2\text{CH}_2\text{NMe})_2\text{Be}$ is volatile and sublimes $40-45^\circ\text{C}/0.001$ m.m. Though expected to have a spiro-structure X, the infrared spectrum of the crystalline material (as a nujol mull) differs greatly from that of its solution in cyclohexane.

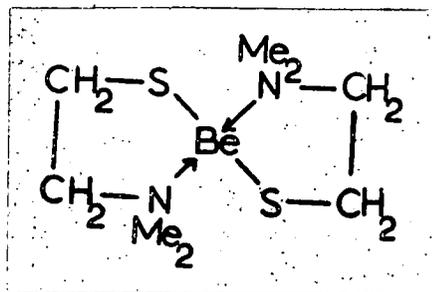


X

It has been suggested that steric interference between methylamino groups could lead to some of the dimethylamino becoming detached when the compound is in solution whereas in the crystalline state a single structure would be adopted. Detachment of dimethylamino groups would leave the central beryllium atom three-coordinate, examples of which have been established.⁴ The compound reacted rapidly at room temperature with methyl iodide forming a di-methiodide $[\text{Be}(\text{NMe}.\text{CH}_2\text{CH}_2\text{NMe}_3\text{I})_2]_x$, which is formulated as a coordination of polymer with bridging nitrogen atoms. The reactions of 2-methoxyethanol, 2-dimethylaminoethanol and 2-dimethylaminoethanethiol with diethylberyllium ⁵⁶ have also been investigated.

Bis-(2-dimethylaminoethylthio)beryllium, $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{S})_2\text{Be}$, was formed by reaction of excess 2-dimethylaminoethanethiol with diethylberyllium. The reaction was complete in one hour in boiling

benzene and the product crystallised from benzene as colourless needles and finally sublimed 120-130°C/0.001 m.m. It was found to be slightly associated in benzene (N = 1.1-1.3 in 0.09 -0.2 weight % solutions) but probably has the chelate structure XI:



XI

Since the space occupied by a sulphur atom is less than that required by a methylamino group, there would be less tendency for the dimethylamino groups to dissociate and leave three coordinate beryllium. Thus no dissimilarity is observed between the infrared spectra of a nujol mull and a cyclohexane solution of the compound.

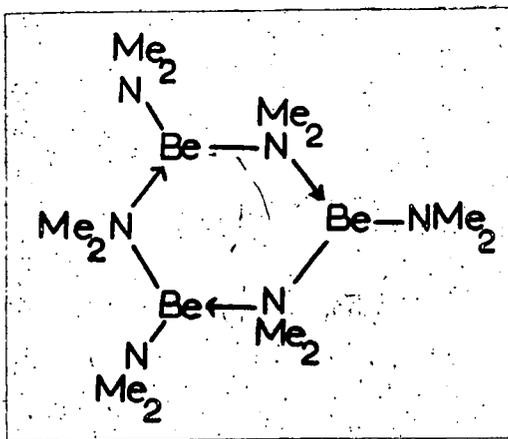
The product from dimethylberyllium and 2-dimethylaminoethanol, bis-(2-dimethylaminoethoxy)beryllium $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Be}$, was found to be crystalline and oligomeric in benzene ($n = 8-11$ in 1-2 weight % solutions).

In contrast, the products of reactions between diethylberyllium and 2-methoxyethanol can be regarded as polymers. An unusual feature of the reaction was that the product, bis-(2-methoxyethoxy)beryllium, differed in physical appearance according to the reaction conditions. In diethyl ether at -78°C a relatively dense material was formed, whereas in benzene at room temperature the product was a light porous, and rubbery mass. Both products were insoluble in all solvents with which they did not react, suggesting a highly polymeric structure, and they were amorphous (absence of lines in their X-ray powder diagrams.)

Magnesium isopropoxide, ⁵⁷ prepared from n-butylmagnesium isopropoxide and propan-2-ol, is apparently similar to the light, rubbery product isolated from reaction at room temperature, but, unlike the beryllium compound, loses its rubbery character when stored under dry nitrogen at room temperature.

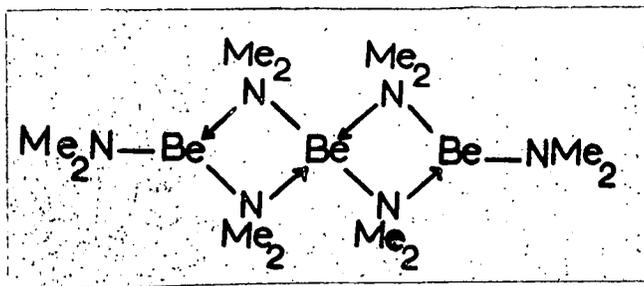
The extensive association of the above alkoxy-derivatives is to be contrasted with the monomeric amino- and thio- complexes. The donor strength of oxygen bond to an electropositive element is considerably greater than that of ether oxygen, as shown by the fact that the aluminium compound $(\text{Et}_2\text{AlOCH}_2\text{CH}_2\text{OEt})_2$ is dimeric, containing uncomplexed ether-oxygen atoms. ⁵⁸ In alkoxyberyllium compounds, association is likely to be propagated by means of the alkoxy-oxygen atoms, and the ether-oxygen is unlikely to compete successfully for coordination positions about the metal though the more basic dimethylamino groups in $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Be}$ may do so.

From reaction of diethylberyllium and excess dimethylamine ⁵⁹ at 25°C the product bis-(dimethylamino)beryllium, $[\text{Be}(\text{NMe}_2)_2]$, can be isolated. The same compound has been prepared ⁵ by reaction of di-isopropylberyllium and excess dimethylamine at just above room temperature. The compound is trimeric in both benzene solution and in vapour phase, and was originally assigned the cyclic structure XII.



XII

However, more recent investigations⁵⁹ do not agree with this. Differential thermal analyses indicate several different forms of bis-(dimethylamino) beryllium, and these observations together with proton magnetic resonance spectral data indicate a bridged trimeric structure XIII.



XIII

It is suggested that the other forms of $[\text{Be}(\text{NMe}_2)_2]_3$ may have different configurations of the trimer, e.g. cis/trans forms of the terminal dimethylamino-groups.

An interesting series of ether-free salts of diethylberyllium of the type $\text{MX}(\text{BeEt}_2)_n$, where M represents an alkali metal, X represents halide or cyanide and $n = 1, 2$ or 4 , have been prepared.^{60, 61, 62.}

Potassium fluoride dissolves in ethereal diethylberyllium at 65°C over three hours and the crystalline compound decomposes and ether-free diethylberyllium can be distilled from the compound. This reaction can be used as a method to prepare ether-free diethylberyllium, as can the decomposition of $\text{KF}(\text{BeEt}_2)_2$ in benzene at 70°C when the insoluble material (KFBeEt_2) and pure ether-free diethylberyllium, (soluble in benzene), are formed. Rubidium and caesium fluorides also form similar compounds but sodium cyanide, sodium fluoride, lithium fluoride, caesium chloride and potassium chloride either do not appear to react, or, no pure compound could be isolated from the reaction mixture. Tetra-ethylammonium chloride

forms a viscous liquid product at room temperature of the type Et_4NCl $(\text{BeEt}_2)_2$ and potassium cyanide forms a compound $\text{KCN}(\text{BeEt}_2)_4$ which loses pure diethylberyllium at $110-150^\circ\text{C}$ invacuo.

Di-isopropylberyllium⁵.

Di-isopropylberyllium has been prepared by reaction of isopropyl magnesium chloride and beryllium chloride in ether. An ether-free product can be obtained by refluxing with continuous pumping for several days. The ether-free product, a colourless and slightly viscous liquid, freezes at -9.5°C and 0.53 m.m. at 40°C , and extrapolated boiling point (280°C) are consistent with a dimeric structure.

When heated at 50°C di-isopropylberyllium decomposes slowly with the evolution of propene, which becomes rapid at 200°C . The non-volatile, viscous product is isopropylberyllium hydride $(\text{Pr}^i\text{BeH})_n$.

Thermal decomposition of this compound at $220-250^\circ\text{C}$ gives propane, propene, hydrogen, beryllium and an orange residue of unknown composition. Isopropylberyllium hydride reacts with dimethylamine at room temperature liberating propane and hydrogen in the ratio 2.5:1, the product probably being some kind of dimethylaminoberyllium hydride, but it was not investigated.

Trimethylamine and di-isopropylberyllium react to form a liquid 1:1 adduct $(\text{Pr}_2^i\text{Be} \leftarrow \text{NME}_3)$, which is monomeric in benzene solution and is thus an example of 3-coordinate beryllium. At 200°C di-isopropylberyllium-trimethylamine loses one mole of propene with the formation of isopropylberyllium hydride-trimethylamine $(\text{Pr}^i\text{BeH} \leftarrow \text{NME}_3)_n$. It is formed as feathery needle-like crystals which have not yet been further investigated.

The reaction of methanol of di-isopropylberyllium yields isopropylberyllium methoxide $(\text{Pr}^i\text{BeOME})_4$, with elimination of one mole of propane.

One mole of dimethylamine and di-isopropylberyllium react with the elimination of propane and formation of the liquid

dimethylaminoisopropylberyllium ($\text{Pr}^i\text{BeNME}_2$)_n which evolves propene at 100°C leaving a glassy residue of dimethylaminoberyllium hydride (ME_2NBeH)_n. This compound has not been further investigated.

Two moles of dimethylamine and di-isopropylberyllium react at just above room temperature with quantitative elimination of propane and formation of bis-(dimethylamino)beryllium $[\text{Be}(\text{NME}_2)_2]_3$, which is identical to the product obtained by reaction of excess dimethylamine and diethylberyllium.⁵⁹

Di-tertiary-butylberyllium.⁶³

Di-tertiary-butylberyllium has been prepared by reaction of tert-butylmagnesium chloride and beryllium chloride in ether. Distillation of the product, after removing as much ether as possible by pumping, yields a slightly viscous liquid boiling at about 60-65°C (0.1 m.m.), which has the approximate composition ($\text{Bu}_2^t\text{Be} \leftarrow \text{OEt}_2$). Refluxing with continuous pumping yields a product containing about 37 mole % ether. However, ether-free di-tert-butylberyllium can be prepared³ by treatment of the ether-containing product with beryllium chloride and subsequent distillation of the di-tert-butylberyllium. The pure, ether-free product is more volatile than the ether complex; it freezes at -16°C, has a vapour pressure of 35 m.m. at 25°C and is monomeric in benzene solution, in which case it is only the second known compound to contain beryllium in the two-coordinate state, the other being $[(\text{ME}_3\text{Si})_2\text{N}_2]_2\text{Be}$ which is also monomeric.¹⁰⁰

Both the ether complex and ether-free product decompose slowly at room temperature with the evolution of isobutene.

Pyrolysis of ethereal di-tert-butylberyllium at 150°C gave isobutene and a product corresponding to 89 mole % beryllium hydride, and pyrolysis at 200°C gave a product corresponding to 96.3 mole % beryllium hydride, the rest being tert-butyl groups.⁶³ The latter product is decomposed at 300°C, and was incompletely hydrolysed by water at room temperature.

When ether-free di-tert-butylberyllium was pyrolysed ^{3.} at 200°C a product corresponding to 97 mole % beryllium hydride was formed, it had a density 0.51 g./cc. and an X-ray powder photograph contained no lines attributable to a crystalline structure.

Di-tert-butylberyllium reacts with trimethylamine ^{63.} but the product has not been characterised and no other coordination compounds have been described.

Diphenylberyllium

Diphenylberyllium can be prepared by reaction of diphenylmercury and beryllium at 210-220°C for two hours, ^{64, 51, 14.} and more conveniently by heating the same two reagents in dry xylene in a sealed tube at 150°C for several days. ^{10.} It melts with decomposition at 244-248°C and its dipole moment is 1.64D in benzene, 4.33D in dioxan and zero in heptane. ^{51, 52.}

The crystalline product, m.p. 28-32°C, obtained from an ethereal solution of diphenylberyllium is claimed ^{65.} to be the dietherate $\text{Ph}_2\text{Be}(\text{OEt}_2)_2$. It is said not to lose ether until heated in vacuo at 130°C.

A complex salt $\text{Li}(\text{BePh}_3)$ ^{10.} has been isolated from the reaction of diphenylberyllium and phenyl-lithium in ether, followed by recrystallisation from xylene. Crystallisation from dioxan yields a product $\text{Li}(\text{BePh}_3)(\text{dioxan})_4$, containing four molecules of solvent. The diphenyl derivatives of magnesium, cadmium and zinc form similar compounds. ^{10.}

It has been shown by Dessey ^{66.} that there is no exchange between diphenylberyllium and beryllium bromide (with a Be^7 'tag') in ether solution and it is suggested that the complex formed may be formulated at $\text{Ph}_2\text{Be} \cdot \text{Be} \cdot \text{Br}_2$. Similar claims were made in respect of phenylmagnesium bromide, which is now known to exist as a monomer $\text{PhMgBr} \cdot (\text{OEt}_2)_2$, by X-ray diffraction, ^{67.} and there is now considerable doubt about the results obtained by isotopic exchange for both beryllium and magnesium compounds, .

Bipyridyl complexes 35.

An unusual series of coloured bipyridyl complexes of the organo and halide compounds of beryllium of the type, $X_2\text{Bebipy}$, has been prepared. These compounds, their colours, their long wave-length absorption bands (λ_{max}), and molar extinction coefficients are tabulated below:

<u>X in $X_2\text{Be.bipy}$</u>	<u>Colour</u>	<u>$\lambda_{\text{max.}}(\text{m}\mu)$</u>	<u>Molar extinction coefficient, $\times 10^{-3}$</u>
Cl.	White	352 infl.	1.2
Br.	Pale cream	364	2.4
I.	Yellow	368	7.0
Ph.	Yellow	353 infl.	0.5
Me.	Yellow	395	2.7
Et.	Red	461	3.7

Reaction of bipyridyl and di-isopropylberyllium, isopropyl-beryllium hydride, and di-n-butylberyllium gave coloured products which decomposed rapidly to brown tars.

The increase in molar extinction coefficient as the electronegativity of X decreases and their colours are explained by electron-transfer from the Be-X bonds to the lowest unoccupied molecular orbital of the bipyridyl.

Two black crystalline complexes of beryllium have also been prepared: bis-bipyridylberyllium, $(\text{bipy})_2\text{Be}$, from reaction of the dilithium adduct of bipyridyl and dichloro (bipyridyl)beryllium in 1,2-dimethoxyethane and subsequent crystallisation from benzene; lithium bis-bipyridylberyllate from lithiumbipyridyl and dichloro (bipyridyl)beryllium in ether. This latter product reacts with bromine to form dibromo (bipyridyl)beryllium.

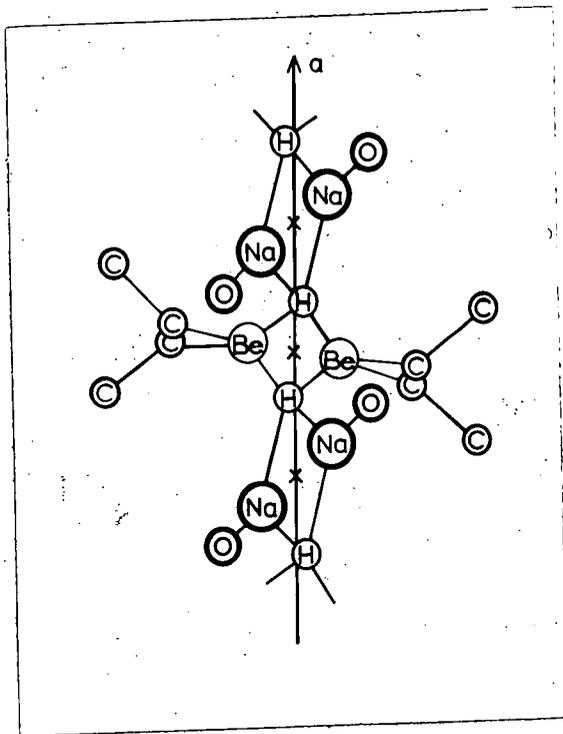
The magnetic properties of bipy_2Be and its deep colour are consistent with its formulation as a coordination complex of the bipyridyl

anion $(\text{bipy}^-)_2\text{Be}^{2+}$ This formulation has been confirmed by examination^{101.} of the electron spin resonance of the paramagnetic complex.

Hydride Chemistry of Beryllium

Many methods for preparing organo-beryllium hydrides have been investigated, but in only a few cases has a pure compound been isolated. However, coordination complexes of these hydrides with donor molecules have been prepared and examined in some detail.

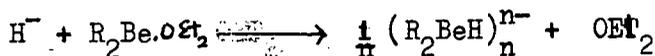
Alkali metal hydrides^{65,76,77.} react with beryllium dialkyls and diaryls with the formation of complex hydrides of the type $M\text{BeR}_2\text{H}$, where $M = \text{Na}$, $R = \text{Me}$, Et and $M = \text{Li}$, $R = \text{Et}$, Ph . Sodium hydride reacts with ethereal solutions of dimethyl-^{77.} and diethylberyllium^{76.} forming sodium hydridodimethyl- and hydridodiethylberyllates, reaction being complete after refluxing the ethereal solutions overnight. Lithium hydride reacts less readily with diethyl-^{76.} and diphenylberyllium^{65.} and requires a higher reaction temperature. The temperatures required for reaction are 110°C and 160°C respectively. Both lithium complexes crystallise from the reaction mixture with one molecule of ether, a pure sample of $\text{LiHEt}_2\text{Be}\cdot\text{OEt}_2$ having been only recently prepared.^{36.} Sodium hydridodiethylberyllate also crystallise with one molecule of ether per sodium atom, although it is easily removed during the normal process of drying at low pressure, (dissociation pressure of 17 m.m. at 25°C ^{77.}) The crystal structure of this etherate has been examined^{78.} by X-ray diffraction methods and the structure is shown, figure XIV.



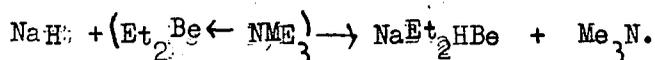
XIV

The arrangement of atoms shows the existence of centrosymmetric $\text{Et}_4\text{Be}_2\text{H}_2$ units with berylliums linked by hydrogen bridges. The mean beryllium-carbon bond length is 1.80\AA , compared with the value of 1.84\AA obtained by addition of covalent radii.⁷⁹ Above and below the plane which contains the beryllium atoms and the adjoining methylene carbons lie sodium atoms, and attached to each sodium is an etheroxygen. The beryllium-hydrogen distance is 1.40\AA compares with an average value of 1.33\AA found for bridging boron-hydrogens in a number of boronhydrides and the sodium-hydrogen distance is 2.40\AA , equal to that in sodium hydride.

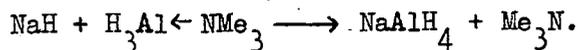
In the preparation of the sodium hydridodialkylberyllates it is probably that hydride ion displaces coordinated ether, (used as solvent):



It has been shown⁷⁷ that hydride ion will also displace trimethylamine:

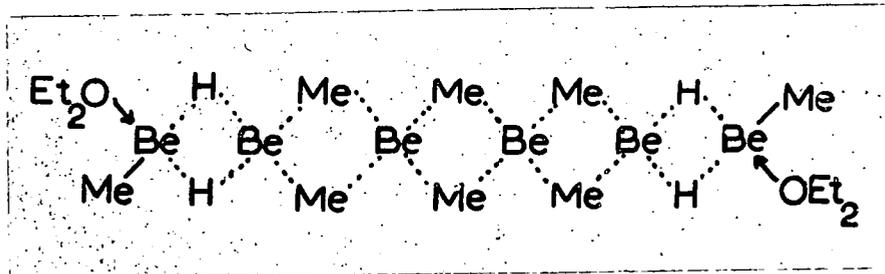


in a reaction very similar to the formation of sodium aluminium hydride from sodium hydride and trimethylamine-alane: ^{80.}



The reactions of some of the complex hydrides with beryllium chloride have been investigated ^{76,77.} and have enabled the preparation of various alkylberyllium hydrides to be carried out.

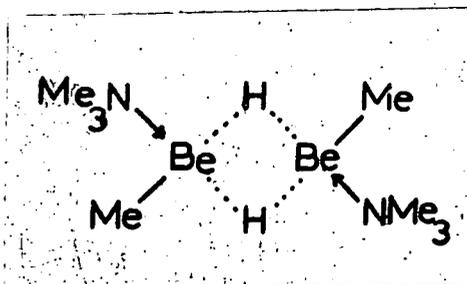
A preliminary investigation ^{76.} showed that ethereal solution containing lithium hydridodiethylberyllate reacted with a half molar proportion of beryllium chloride, precipitating lithium chloride. Evaporation of solvent from the solution left a viscous liquid of approximate constitution $\text{Et}_4\text{Be}_3\text{H}_2$. Similar reactions between NaR_2HBe , where R = Me, Et, and beryllium chloride have been investigated more fully. ^{77.} Thus reaction of the sodium hydridodialkylberyllates with half molar proportions of beryllium chloride yields species in solution of approximate constitution " $\text{R}_4\text{Be}_3\text{H}_2$ ". In the view of the reactions of the species " $\text{R}_4\text{Be}_3\text{H}_2$ ", R = Me, Et., with tertiary amines, it is probable that they consist of a mixture of solvated dialkylberyllium and solvated alkylberyllium hydride, though the existence of di- and tri- nuclear species cannot be disregarded. Evaporation of solvent from an ethereal solution of " $\text{Me}_4\text{Be}_3\text{H}_2$ " and prolonged pumping at room temperature gave an oily residue of approximate composition " $\text{Me}_4\text{Be}_3\text{H}_2 \cdot \text{OEt}_2$ ", which could be regarded as some kind of electron-deficient complex between dimethylberyllium and methylberyllium hydride, such as figure XV.



XV

In reaction with donor molecules solutions of " $R_4Be_3H_2$ " behave as a mixture of R_2Be and " $RBeH$ ", thus addition of trimethylamine to " $Me_4Be_3H_2$ " yields a mixture of the dimethylberyllium complex $Me_2Be \leftarrow NMe_3$ and the trimethylamine complex of methylberyllium hydride.⁸¹ The hydride complex being less volatile (vapour pressure is 1.8 m.m. at $60^\circ C$.) than the dimethylberyllium complex (vapour pressure is 1.8 m.m. at $30^\circ C$) separation by fractional condensation was possible.⁸¹ The pure complex, $(MeBeH \leftarrow NMe_3)_2$, melted at $73-74^\circ C$ and was found to be dimeric in benzene. From the vapour pressure equation:

$\log_{10} P(\text{m.m.}) = 7.483 - 2439/T$, for liquid $73-115^\circ C$ the latent heat of vapourisation is 11.2 Kcal. mole. the extrapolated boiling point is $257^\circ C$ and the Trouton constant 21.1. The normal Trouton suggests that there is no change in degree of association during the process of vapourisation; thus it is likely that the vapour, at least up to $110^\circ C$, consists mainly of dimer. Attempts to measure the molecular weight of the hydride as vapour at higher temperatures ($145^\circ-175^\circ C$) were not successful⁷⁷. due to some decomposition; however the vapour appeared to be monomeric at $175^\circ C$ and to become more associated at lower temperatures. The hydride dimer is formulated with a hydrogen rather than a methyl bridge, as shown in figure XVI, because the complex is not decomposed by excess trimethylamine whereas the methyl bridges between beryllium atoms in the dimethylberyllium polymer are cleaved by trimethylamine.⁴



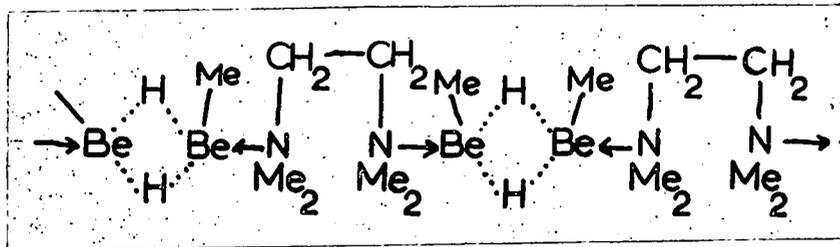
XVI

In addition, studies of reactions between dialkylaluminium hydrides and donor molecules have shown that hydrogen bridges in these compounds are less readily cleaved than are the methyl bridges in trimethylamine. ⁴⁸.

In attempt to prepare monomeric complexes, L_2BeMEH , of methylberyllium hydride, the reactions of " $Me_4Be_3H_2$ " with donor molecules which readily form chelate complexes were investigated, ^{77,81}. but with little success.

Thus addition of bipyridyl to ethereal " $Me_4Be_3H_2$ " resulted in precipitation of yellow Me_2Be bipy, ³⁵. leaving a deep red solution. Though the red colouration was probably due to $MeBeH$.bipy, the red colour soon turned to a dark brown and removal of solvent gave only an intractable tar. Evidently the Be-H groups had reacted with bipyridyl. A similar reaction is observed in the bipyridyl-aluminium hydride complex. ⁸².

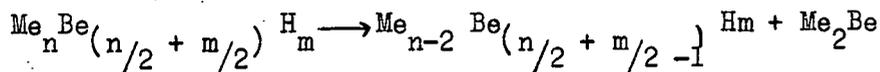
Reaction of " $Me_4Be_3H_2$ " with N,N,N',N' - tetramethylethylenediamine gave the known chelate complex of dimethylberyllium ³⁵. and a white, apparently amorphous precipitate which was insoluble in ether, benzene, carbon disulphide and carbon tetrachloride. It did not fume in air and analysis showed it to correspond to the formula $[(MeBeH)_2 Me_2NCH_2CH_2NMe_2]_n$. It appears that the hydrogen bridge is present, resulting in a polymeric constitution as shown in figure XVII.



XVII

Similarly, reaction with 1,2-dimethoxyethane gave a mixture of solid and liquid products. The solid was sublimed from the mixture at 50°C in vacuo, and shown to be the known chelate complex of 1,2-dimethoxyethane and dimethylberyllium.³⁵ The residue was a viscous oil, which corresponds to the formula $[(\text{MeBeH})_2 \text{MeOCH}_2\text{CH}_2\text{OME}]_n$ and its constitution is probably polymeric and similar to that suggested for the tetramethylethylenediamine complex.

Attempts to prepare alkylberyllium hydrides, RBeH , by sublimation of dialkylberyllium from the complex mixtures " $\text{R}_4\text{Be}_3\text{H}_2$ " were not successful. Thus sublimation of dimethylberyllium from the solid residue " $\text{Me}_4\text{Be}_3\text{H}_2$ " (from $2\text{NaMe}_2\text{HBe} + \text{BeCl}_2$) was apparent^{77,81} at 60°C/0.001 m.m. However, there was no indication of any pause in the evolution of dimethylberyllium at a stage corresponding to a residue of methylberyllium hydride. Sublimation in the range 170-210°C resulted in extensive disproportionation:

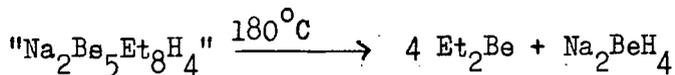
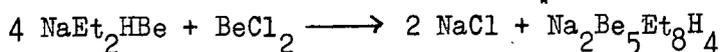


which continued until the hydride; methyl ratio was about 10:1. A greater hydride: methyl ratio was not achieved by reaction at higher temperatures on account of thermal decomposition of dimethylberyllium.

Diethylberyllium was found to separate more easily from " $\text{Et}_4\text{Be}_3\text{H}_2$ " and a glassy residue, consisting mainly of ethylberyllium hydride, was obtained by heating " $\text{Et}_4\text{Be}_3\text{H}_2$ " at 70-80°C for eight hours. The course of further reaction at higher temperatures was greatly affected by the composition of the ethylberyllium hydride - diethylberyllium solution.

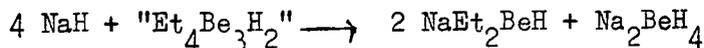
The composition of the ethylberyllium hydride - diethylberyllium mixture, " $\text{Et}_4\text{Be}_3\text{H}_2$ ", depended on the actual experimental technique used. It was found, during the course of several experiments,⁷⁷ that sodium entered the solution and was present in the residue after pyrolysis. This was confirmed by refluxing excess sodium hydride with solutions of

"Et₄Be₃H₂". The ethyl: hydride ratio (in solution) was always greater than 2:1 and concentration of the solution yielded NaEt₂HBe. It was assumed that sodium entered the solution as ether-soluble NaEt₂HBe and hydride was removed as an insoluble complex hydride. This was later confirmed by preparation⁸³ of sodium beryllium hydride, Na₂BeH₄, by reaction of sodium hydridodiethylberyllate and a quarter molar proportion of beryllium chloride, followed by pyrolysis at 180°C of the residue obtained by filtration and concentration of the solution.



The involatile residue was insoluble in ether and showed a clear X-ray pattern. It was more stable than beryllium hydride^{3,63}, decomposing to give hydrogen, sodium vapour and an involatile residue, presumed to be beryllium, at 380-400°C. Na₂BeH₄ was formulated⁸³ as an electron-deficient polymer, probably containing units similar to the Be₂HNa₂HBe₂ units shown to be present in the crystal structure of NaEt₂HBeOEt₂,⁷⁸ rather than a salt like NaBH₄.

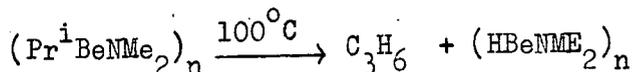
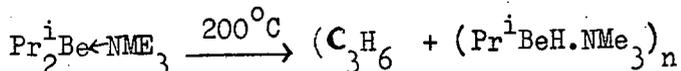
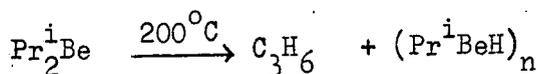
Thus, the entry of sodium into the "Et₄Be₃H₂" solutions was probably via a reaction of the type:



The presence of sodium in solution had a great effect on the extent of disproportionation of the residue during pyrolysis. Thus, in an experiment when excess sodium hydride, from the preparation of NaEt₂HBe, was allowed to react with the "Et₄Be₃H₂" solution before filtration the residue obtained by pyrolysis at 180°C.

corresponded approximately to a mixture of BeH_2 (5 mol.) + $\text{Na}_2\text{Be}_2\text{H}_6$ (3 mol.) or BeH_2 (8 mol) + Na_2BeH_4 (3 mol). Whereas, in another experiment, where excess sodium hydride was eliminated by modification of experimental technique, the residue obtained by pyrolysis at 180°C analysed to give a hydrogen: ethyl ratio of only 2.55:1. A trace of chloride (from a slight excess of beryllium chloride), but no sodium was detected in this product.

Unlike dimethyl- and diethylberyllium, which decompose at elevated temperature to give a complex mixture of products, di-isopropylberyllium and some of its derivatives⁵ decompose with evolution of propene at elevated temperatures and formation of "half-hydride" derivatives of beryllium:

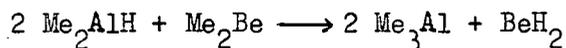


These compounds have not been further investigated and could well provide a useful preparative route to beryllium hydrides. A similar possible source of hydride derivatives is di-tertiary-butylberyllium and its derivatives. Pyrolysis of Bu_2^tBe ^{3,63} at 200°C provides beryllium hydride and it is reasonable to expect that controlled pyrolysis at lower temperatures could result in formation of "half-hydride" derivatives.

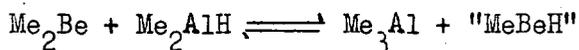
Alkyl-hydrogen exchange reactions have been investigated with a view to preparation of beryllium hydride derivatives, with varying degrees of success.

Dimethylberyllium reacts with dimethylaluminium hydride in the absence of solvent.⁸⁵ Although trimethylaluminium was formed

as indicated by the equation below, a product free from methyl groups could not be obtained.

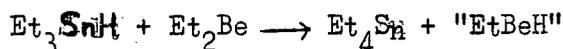


No better results could be obtained in isopentane solution, and it was suggested that the intermediate occurrence of reversible reaction:



could explain the results.

A more successful method involves reaction of diethylberyllium and triethylstannane in ethereal solution ⁷⁷. Tetraethyltin and ethylberyllium hydride are formed; hydrolysis of the involatile residue left after evaporation of the tetraethyltin yielded ethane and hydrogen in the ratio 1.016:1.



Ethylberyllium hydride prepared by this method was characterised by conversion into its trimethylamine complex, $(\text{EtBeH.NMe}_3)_2$, ⁷⁷ which is dimeric in benzene and is formulated with a hydrogen bridge, like its methyl analogue. A similar exchange takes place when triethylstannane is heated with triethylaluminium ⁸⁵ (giving Et_2AlH), though this reaction is inhibited by ethers and tertiary amines. Assuming exchange with Et_3Al involves an electron-deficient intermediate, it is reasonable to expect that exchange should be inhibited by reagents which remove the electron-deficiency of Et_3Al by formation of coordination complexes. Since there is evidence that electron-deficient bridges persist in dimethylberyllium in the presence of ethers and trimethylphosphine, ⁴ it is not surprising that the tin hydride-alkylberyllium exchange reaction takes place in the presence of diethyl ether.

Lithium aluminium hydride reacts with dimethylberyllium in ethereal solution with elimination of methane and precipitation of a white, insoluble, involatile solid. ⁸⁴ Although claimed to be beryllium hydride, the only impurity being ether, it was later shown to be inseparably contaminated with aluminium and lithium. ³

The reactions of bis-(dimethylamino)beryllium with several alkylaluminium hydrides, trimethylamine-alane and trimethylaluminium have been investigated.¹⁰² The studies indicate that dimethylamine-hydride exchange is complete between aluminium hydrides and bis-(dimethylamino)beryllium where as under similar experimental conditions, no exchange with trimethylaluminium and $\text{Be}(\text{NME}_2)_2$ was observed.

A surface reaction between lithium hydride and beryllium chloride has been reported, but no product was isolated.

Beryllium borohydride, $(\text{Be}(\text{BH}_4)_2)$, is most conveniently prepared by the reaction of lithium borohydride and beryllium chloride at elevated temperatures.⁸⁷ It is a white, volatile solid, monomeric in the vapour phase, and its vapour pressure is 760 m.m. at 91.3°C .⁸

The reactions of beryllium borohydride with ethers have been investigated. It is reported⁸⁸ to be soluble in anisole, diethyl ether and diphenyl ether, but insoluble in tetrahydrofuran, 1,2-dimethoxyethane, and some ethers. However, more recent investigations⁸⁹ have shown that beryllium borohydride reacts exothermically with diethyl ether, tetrahydrofuran and 1,2-dimethoxyethane. A 1:1 adduct, $\text{BeB}_2\text{H}_8\text{OEt}_2$, is formed with diethyl ether which is reported to be monomeric in benzene.⁹⁹ A convenient preparation of this is by the metathetical reaction between beryllium chloride and lithium borohydride in ether solution⁹¹. Tetrahydrofuran forms a crystalline 4:1 complex, soluble in tetrahydrofuran and is formulated as a salt $[\text{Be}(\text{THF})_4] (\text{BH}_4)_2$

Excess isobutylamine precipitates tetrakisisobutylamineberyllium borohydride from an ethereal solution of beryllium borohydride. It is formulated as a salt $[\text{Be}(\text{Bu}^i\text{NH}_2)_4] (\text{BH}_4)_2$, similar to the tetrahydrofuran complex. The complexes formulated as salts $[\text{BeL}_4] (\text{BH}_4)_2$ have infrared spectra typical,⁹¹ in the region $2200\text{--}2300\text{ cm}^{-1}$ of these compounds containing the borohydride ion.⁹²

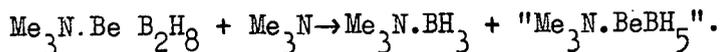
1,2-Dimethoxyethane reacts with beryllium borohydride in an unexpected manner.⁸⁹ It did not give the chelate complex $[\text{Be}(\text{MeOC}_2\text{H}_4\text{OME})_2] (\text{BH}_4)_2$, analogous to the tetrakis tetrahydrofuran complex, but gave a crystalline compound in which the O:Be ratio was about 3:1.

This compound has not been further investigated.

The reactions of beryllium borohydride with amines and phosphines have been studied. Trimethylamine reacts forming a 1:1 adduct, ⁸. $\text{Me}_3\text{N} \rightarrow \text{BeB}_2\text{H}_8$, which is monomeric in the vapour phase. Trimethyl-, ⁹³ triethyl-, ⁹³. and triphenylphosphine ⁸⁹. all react to form 1:1 adducts $\text{R}_3\text{P} \rightarrow \text{BeB}_2\text{H}_8$, which are monomeric in benzene. By various displacement reactions it was found that the donor strength ⁹¹. of ligands to beryllium borohydride was $\text{Me}_3\text{N} > \text{Me}_3\text{P}, (\text{Et}_3\text{P}, \text{Ph}_3\text{P}) > \text{Et}_2\text{O}$.

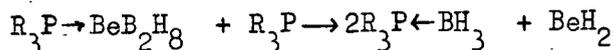
Reaction of the 1:1 adducts with excess ligand has been investigated and some unusual features have been discovered.

Trimethylamineberyllium borohydride reacts ⁸. with excess trimethylamine at 95°C over a period of thirty hours, with the formation of trimethylamine-borane:



The second product, $\text{Me}_3\text{N} \cdot \text{BeBH}_5$, although not fully characterised, reacts with diborane to give pure beryllium borohydride. Some trimethylamine could be removed from $\text{Me}_3\text{N} \cdot \text{BeBH}_5$ at 100°C, the process being reversible.

The phosphine adducts react with excess phosphine with formation of approximately 2 moles of phosphine-borane: ^{89,93}.



The extent of removal of borane as phosphine-borane was found to be dependant on experimental conditions. Thus, in absence of solvent beryllium borohydride reacts with excess trimethylphosphine at 70°C with approximately 80% removal of boron from the borohydride as trimethylphosphine-borane. In contrast, if triphenylphosphine and beryllium borohydride, in 2:1 molar quantities, are heated in xylene solution at 150°C for six hours, 97% of the boron content of the system was isolated as triphenylphosphine-borane. The other product was beryllium hydride, which was found to be 80.7 weight % pure, the impurity being identified as $\text{Ph}_3\text{P} \cdot \text{BH}_3$. Thus the beryllium hydride was the purest yet isolated, corresponding to 99.1 mole % BeH_2 .

It is interesting to note that although trimethylamine will displace trimethylphosphine from the complex $\text{Me}_3\text{P} \rightarrow \text{BeB}_2\text{H}_8$, in which the phosphine is bonded to the beryllium atom, trimethylphosphine is more efficient than trimethylamine⁸ in removing boron from the borohydride as the borane adduct.

Coates and Banford⁹³ point out that this is in agreement with the greater donor strength of Me_3P to boron in the adduct $\text{Me}_3\text{P} \rightarrow \text{BH}_3$, compared to that of the amine adduct, $\text{Me}_3\text{N} \rightarrow \text{BH}_3$ ⁹⁴. The unexpected reversal of donor strength of N, P, As, Sb in adducts of the type $\text{L} \rightarrow \text{BH}_3$, is explained by postulation that the σ bond is reinforced by back-coordination from BH_3 in a π type interaction with a vacant $d\pi$ orbital on the donor atom.

Infrared Spectra of Alkylberyllium Hydride Complexes

The $0 \rightarrow 1$ vibrational transition of the ground state ($^2\Sigma^+$) of the BeH molecule, derived from band heads and band origins in emission electronic spectra,⁹⁵ is at 2056.8 cm^{-1} and at 2087.7 cm^{-1} for the first excited $^2\Pi$ -state. Thus a terminal Be-H group could be expected to cause absorption near 2100 cm^{-1} and a similar conclusion is reached by considering the change with atomic number of the stretching frequencies of the hydrides of the other elements of the first short period. By analogy, with the vibrational modes of the BH_2B groups in diborane and the various methyl- and ethyl- diboranes, the vibrational modes of the bridging hydrogen atoms in a BeH_2Be group, of mainly stretching character, should cause absorption at frequencies well below 2100 cm^{-1} for, whereas, the terminal B-H bonds usually cause absorption in the $2200\text{--}2500 \text{ cm}^{-1}$ region, the two modes due to the BH_2B bridge in diborane are at 1915 (ν_{13} symmetrical out-of-phase) and 1606 cm^{-1} (ν_{17} asymmetric in-phase)⁹⁶. The alkylidiboranes provide a closer analogy to the beryllium compounds formulated as $(\text{MeBeH} \leftarrow \text{NMe}_3)_2$ with BeH_2Be bridges. In the former the weak absorption corresponding to ν_{13} is observed at 1972 ($\text{Me}_4\text{B}_2\text{H}_2$), 1880 ($\text{Me}_3\text{H}_2\text{H}_3$) and at 1852 cm^{-1} ($\text{Et}_4\text{B}_2\text{H}_2$), whereas the very strong absorption corresponding to ν_{17} is observed at 1605 , 1605 and 1582 cm^{-1} in the three compounds, changing to 1186 , 1183 , and 1166 cm^{-1} on deuteration.⁹⁷

A comparison ^{77.} of the infrared spectra of $(\text{MeBeH}\leftarrow\text{NMe}_3)_2$ and its deuterio-analogue, $(\text{MeBeD}\leftarrow\text{NMe}_3)_2$, shows that a strong absorption at 1344 cm.^{-1} in $(\text{MeBeH}\leftarrow\text{NMe}_3)_2$, which moves to about 1020 cm.^{-1} in the deuterio-analogue is due to one of the (BeH_2Be) stretching modes. The same absorption due to $\nu(\text{BeH}_2\text{Be})$ is found at 1333 cm.^{-1} in the spectrum of the ethyl derivative $(\text{EtBeH}\leftarrow\text{NMe}_3)_2$.

Similarly by comparison ^{77.} of the infrared spectra of $\text{Na}_2\text{Me}_4\text{H}_2\text{Be}_2$ and $\text{Na}_2\text{Me}_4\text{D}_2\text{Be}_2$, which are reasonably expected to contain $[\text{BeH}_2(\text{ or D}_2)\text{Be}]$ bridges are shown to occur in $\text{Na}_2\text{Et}_4\text{H}_2\text{Be}_2$ by X-ray diffraction analysis ^{78.}, it has been concluded that absorptions due to the (BeH_2Be) bridges are at 1325 and 1165 cm.^{-1} ; those due to (BeD_2Be) being at 917 and 869 cm.^{-1} . Comparison ^{77.} of infrared spectra of $\text{Na}_2\text{Et}_4\text{H}_2\text{Be}_2$ and $\text{Na}_2\text{Et}_4\text{D}_2\text{Be}_2$, although the spectra are more complicated as expected, shows $\nu(\text{BeH}_2\text{Be})$ at 1294 and 1065 cm.^{-1} and $\nu(\text{BeD}_2\text{Be})$ at 951 and 835 cm.^{-1} .

These assignments are confirmed by comparison ^{41.} of the spectra of $\text{Na}_2\text{Me}_4\text{H}_2\text{Be}_2$ and $\text{Na}_2(\text{CD}_3)_4\text{H}_2\text{Be}_2$. Thus it is concluded that absorptions due to $\nu(\text{BeH}_2\text{Be})$ are at 1325 and 1165 cm.^{-1} in $\text{Na}_2\text{Me}_4\text{H}_2\text{Be}_2$, at 1333 and 1164 cm.^{-1} in $\text{Na}_2(\text{CD}_3)_4\text{H}_2\text{Be}_2$, and at 920 and 870 cm.^{-1} in $\text{Na}_2\text{Me}_4\text{D}_2\text{Be}_2$.

As mentioned above, by comparison of the spectra of various neutral beryllium hydride complexes, absorptions due to $\nu(\text{BeH}_2\text{Be})$ have been identified at 1344 cm.^{-1} in $(\text{MeBeH}\leftarrow\text{NMe}_3)_2$, and at 1333 cm.^{-1} in $(\text{EtBeH}\leftarrow\text{NMe}_3)_2$. The absorptions expected at lower frequencies, corresponding to (asymmetric in-phase) vibrations of diborane, ^{96.} are now realised to be obscured by absorptions due to the amine.

The spectrum of $(\text{MeBeH}\leftarrow\text{NMe}_3)_2$ as saturated vapour has also been recorded, ^{77.} and at higher temperatures (80°) is dissimilar to the spectrum of a solution in cyclohexane, ~~and a $\nu(\text{Be-H})$ band~~ at 2141 cm.^{-1} appeared. This postulated as being due to terminal $\nu(\text{Be-H})$ in monomeric $\text{MeBeH}\leftarrow\text{NMe}_3$, since vapour density measurements indicated extensive dissociation with increasing temperature ($145\text{--}175^\circ\text{C}$). Thus between 65° and 80°C the concentration of monomer in the saturated vapour could begin to be significant. Experimental difficulties made study of the unsaturated vapour at higher temperatures impossible.

The infrared spectra of various samples of beryllium hydride, of varying purity, have been examined. Thus, the main feature of a sample, of approximate composition $[(\text{BeH}_2)_{34} \cdot \text{NaH}]$,⁹⁸ was rather broad absorption centred on 1750 cm^{-1} . The material was X-ray amorphous and regarded as a cross-linked disordered polymer. Similar absorptions, centred at $1750\text{--}1760 \text{ cm}^{-1}$, have been observed^{36, 91} and are due to (BeHBe) bonds in the cross-linked polymer.

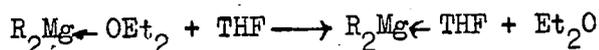
Coordination chemistry of the organo-derivatives of other Group II metals

The coordination chemistry of the organo-derivatives of calcium, strontium and barium has been little studied. The organic derivatives of these metals are highly reactive and resemble methyl lithium in many of their reactions. In contrast, the group IIB metals alkyls and their coordination chemistry have been studied in some detail. The large increase in electronegativity in going from the typical elements to those of the B sub-group is reflected in the properties of their organo-derivatives. Thus whereas, zinc, cadmium and mercury all form covalent organo-derivatives, the dialkyls being volatile liquids, easily soluble in hydrocarbon solvents, and monomeric in the liquid and vapour phase; the lower dialkyls of beryllium and magnesium reflect the lower electronegativities of the metals in being highly electron-deficient solids and liquids of polymeric constitution. The decrease of reactivity with increasing electronegativities in the sequence zinc, cadmium, and mercury is illustrated by the behaviour of the lower alkyls towards water; the dialkyls of zinc are hydrolysed with explosive violence, those of cadmium slowly and those of mercury not at all.

Magnesium

Apart from the extremely useful, and well-known Grignard reagents, magnesium forms dialkyl- and diaryl-derivatives. Like the analogous beryllium derivatives, the organo-derivatives of magnesium exhibit electron deficiency. Indeed, dimethylmagnesium is apparently a more strongly bound polymer than dimethylberyllium, since the former is only slightly soluble in diethyl ether,^{103, 104} whereas the latter

is easily soluble. The chemical evidence has found support in the recent X-ray structural analysis of dimethylmagnesium,¹⁰⁵ which reveals a long chain polymeric constitution. An unstable, crystalline mono-diethylether complex of diethylmagnesium has been reported,^{106.} and vapour pressure measurements of some solutions of diethyl- and dipropylmagnesium in ether-tetrahydrofuran mixtures show that an equilibrium exists in solution^{107.}



Dimethylmagnesium absorbs trimethylamine reversibly, in contrast to dimethylberyllium which forms a stable, volatile 1:1 complex^{4,} and an unstable 2:1 complex;^{34.} and several volatile, chelate complexes of R_2Mg with N,N,N',N' - tetramethylethylenediamine, (R = Et, Pr, Prⁱ, Buⁿ.) are also described.^{108.} The N,N,N',N' - tetramethylethylenediamine complexes of dimethyl and diphenylmagnesium are also described as crystalline solids, as are the 1,2- dimethoxyethane complexes, and a bis-tetrahydrofuran complex of diphenylmagnesium.^{109.}

Reactions of dialkylmagnesium derivatives with donor molecules containing active hydrogen atoms have not been fully investigated. However, N,N,N' - trimethylethylenediamine does react with dimethylmagnesium^{109.} in 1:1 proportions, with the elimination of methane, to give $(MeMgNMe.C_2H_4.NMe_2)_2$, which is dimeric in benzene, analogous to the corresponding beryllium compound.

Zinc

Due to the low polarity of the zinc-carbon bond, organo-zinc compounds had generally been thought of as being unable to form neutral electron donor-acceptor complexes; indeed trimethylamine and triethylphosphine have been reported as not reacting with diethylzinc.^{110.} It is only quite recently that the first examples of well-defined coordination complexes have been described. An indication of their existence was Frankland's observation^{111.} that the use of dimethyl or diethyl ether as a solvent greatly facilitated the formation

of dimethylzinc from zinc and methyl iodide, but that complete separation from the product was impossible. A recent reinvestigation^{112.} of the dimethyl ether-dimethylzinc system demonstrates the formation of a 1:1 complex, which could, however, be completely separated into the component compounds by distillation through an efficient fractionating column. A series of liquid adducts with cyclic ethers were also reported. The adducts could be distilled at atmospheric pressure without decomposition, but were found to dissociate in benzene solution. The strength of the bond between ether molecule and dimethylzinc, and possibility of coordination of a second ether molecule was found to increase from ethylene oxide to pentamethylene oxide. Thus, only 1:1 complexes were formed with ethylene oxide and trimethylene oxide, whereas tetrahydrofuran and pentamethylene oxide yielded 2:1 complexes. On steric grounds the reverse trend would be expected, and it was concluded that the major influencing factor was the orientation or the p-character of the oxygen orbitals, which would vary with the ring size of the ether.

Crystalline, and presumably chelate 1:1 complexes were formed by reaction of Me_2Zn with 1,4 - dioxan and 1,4 -thioxan.^{113.} These complexes can be distilled without decomposition, as can the liquid complexes, containing two ether molecules to one zinc atom, formed by reaction of aliphatic ethers, such as 1,2 - dimethoxyethane, with dimethylzinc. However, these 2:1 complexes dissociate in benzene solution into a 1:1 complex and free ether. Diarylzinc derivatives yield similar 1:1 complexes with 1,4-dioxan.^{114, 115.}

Dimethylzinc and tertiary amines yield definite coordination complexes,^{116.} one or two molecules of trimethylamine reacting with one molecule of dimethylzinc to give liquid adducts. The 1:1 complex distills at 84°C , whilst the 2:1 complex distills at 84.5°C , suggesting that dissociation into 1:1 complex and amine occurs during distillation, a process which is observed when the 2:1 complex is dissolved in benzene. Triethylamine and pyridine yield only 2:1 complexes, which are liquid and solid respectively; both dissociate in benzene solution yielding the 1:1 complex and free amine. N,N,N',N' - Tetramethylethylenediamine,

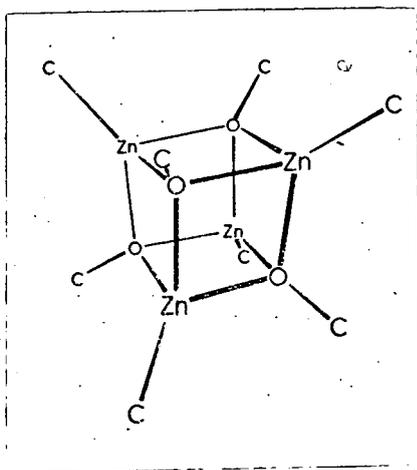
2,2'-bipyridyl and 1,10-phenanthracene react with dimethylzinc yielding chelate compounds, which may be sublimed without decomposition in vacuo. A series of 2:1 coordination complexes between dimethyl-, diethyl-, and dibutylzinc and the tertiary amines, pyridine, quinoline and isoquinoline have been examined,¹¹⁷ all dissociating when dissolved in benzene solution.

A pale yellow, chelate complex obtained from dimethylzinc and 2,2'-bipyridyl, and the orange compound, $\text{Et}_2\text{Zn}\cdot\text{bipy}$, have also been reported³⁵ in connection with a study of a series of coloured bipyridyl complexes of beryllium alkyls. The bipyridyl complex of diallylzinc is mentioned in connection with the preparation of diallylzinc.¹¹⁸ More recently the 1,10-phenanthracene and 2,2'-bipyridyl complexes of organozinc compounds have been prepared, and have been the subject of an ultra-violet and visible spectroscopic study.^{116,119} The colours of the complexes $\text{L}\cdot\text{ZnR}_2$ (L = bipy.or phena.: R = Et, Prⁱ, Buⁿ, C₆H₅ or C₆F₅), was found to depend on the electronegativity of the organic group R. It was concluded that the observed spectra are due to a charge-transfer process involving donation of electrons from the zinc-carbon bonds into the lowest, unoccupied molecular orbitals of the ligand. However, in contrast to the similar beryllium complexes,³⁵ the intensity of the charge-transfer bond increased with increasing electronegativity of R, and the authors suggest that participation of the 3d. orbitals of the zinc atom is important. A series of complexes of dibutyl-, diphenyl-, and bis-pentafluorophenylzinc with a variety of donor molecules has been described.¹²⁰ Chelate complexes with 1,2-dimethoxyethane, N,N,N',N' - tetramethylethylenediamine, 1,2-bis-diphenylphosphinoethane) and o-phenylene-bis(dimethylarsine) were prepared; as were the 2:1 complexes of triphenylphosphine and ZnR_2 . The increasing effect of increasing electronegativity of R was found to have a considerably effect on the stability of the complexes. Thus, dibutylzinc forms a complex with 1,2-dimethoxyethane, which

is thermally very unstable, (complete dissociation at 40°C and 0.01 m.m.), and fails to form a complex with triphenylphosphine. Similarly, the liquid complex formed by the chelating arsine slowly loses dibutylzinc when heated in vacuo. In contrast, the phenyl- and pentafluorophenyl-derivatives form very stable complexes, which are crystalline solids as opposed to liquids, and in all cases the melting-points of the complexes increased in the order: $Bu_2Zn < Ph_2Zn < (C_6F_5)_2Zn$. The increasing electronegativity of R brings about a corresponding increase in electron-affinity of the vacant orbitals of the zinc atom, causing the zinc atom, to become a stronger electron-acceptor. It is evident that stabilisation of complexes of phosphorus and arsenic ligands by $d\pi - d\pi$ back-coordination between the filled 3d orbitals of the zinc and the empty d orbitals on the ligands cannot be of great significance, as the increase in strength of the σ bond between zinc and ligand as the electronegativity of R increase necessarily decreases the possibility of back-coordination.

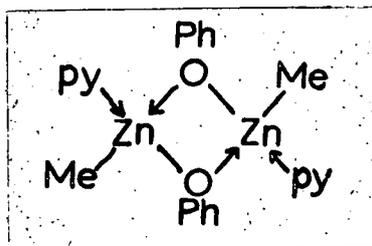
The reactions of zinc dialkyls and various alcohols, 121, 122. amines, 123, 132. and phosphines 125, 133. have been observed, but the complexes resulting from elimination of only one alkyl group was either not isolated, or if it was, very little information on its properties, apart from solubility in non-polar solvents, was reported. The acidolysis of zinc dialkyls by p-toluidine has been the subject of a kinetic study, but the intermediates $RZn.NHC_6H_4.CH_3$ were not isolated 124.

More recently the reactions of dimethyl- and diethylzinc with alcohols, thiols and secondary amines have been investigated. 46. The coordination complexes resulting from the displacement of one alkyl group were examined and found to have interesting structures. The reaction of dimethylzinc in 1:1 molar proportions with alcohols produced, in all cases examined, alkoxides which were tetrameric in benzene solution, $(MeZnOR)_4$. An X-ray diffraction study 99. on the methoxide $(MeZnOMe)_4$ has been revealed and cubic structure, fig. XVIII.



XVIII.

It is probable that the other methyl- and ethylzinc alkoxides have a similar structure, and also several tetrameric methylberyllium alkoxides, ³⁸. Only the phenoxide of the methylzinc alkoxide series formed a pyridine adduct, dimeric in benzene fig. XIX.

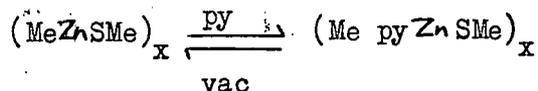


XIX.

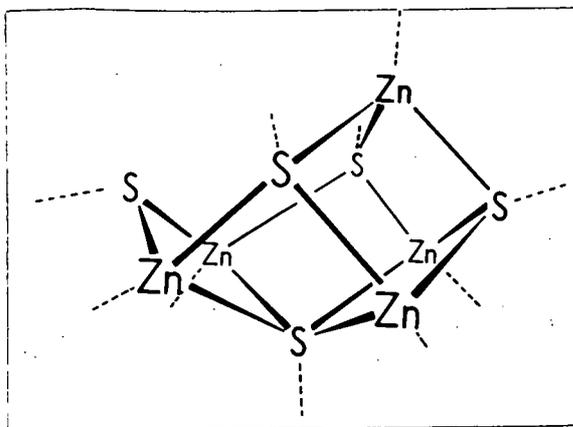
which suggests that the zinc atoms in these complexes have a substantial degree of coordinative saturation. It would be expected that the oxygen atom of a phenoxy group would show weaker donor character than that of an alkoxy group, accounting for the pyridine adduct.

Thiols, $R'SH$ ($R = Me, Pr^n$ and Ph), react with dimethylzinc to give apparently polymeric, insoluble solid $(MeZnSR)_x$, which do not

react with pyridine, although the methylthio-derivative dissolves in pyridine but loses pyridine under reduced pressure:

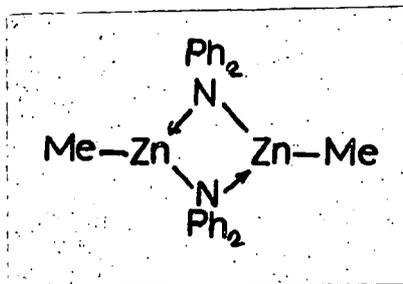


Branched chain thiols react yielding products soluble in benzene, Tertiary-butanethiol yields pentameric products, $(\text{RZnSBu}^t)_5$ (R = Me or Et), and iso-propanethiol gave a hexameric product $(\text{MeZnSPi}^i)_6$. The pyridine adduct of the tertiary-butylthio deriv, $(\text{Mepy Zn SBu}^t)_2$ was also prepared. X-Ray studies on the pentameric $(\text{MeZnSBu}^t)_5$ has revealed an unusual structure. ¹²⁶. The structure shown in fig. XX. could be described as two interpenetrating ~~square-based~~ pyramids of zinc and sulphurs respectively.



XX.

Reaction of dimethylamine with dimethylzinc gave only $[(\text{Me}_2\text{N})_2\text{Zn}]_x$ an insoluble, involatile and evidently polymeric solid. In contrast, diphenylamine gave a dimeric product $(\text{MeZnNPh}_2)_2$, which is formulated with 3-coordinate zinc, fig. XXI.



XXI.

Methylzinc diphenylamide reacts with pyridine in an unusual fashion. Thus, addition of pyridine in proportion of one g. mole of pyridine to one g. atom of zinc did not yield the diphenylamino analogue of $(\text{Me}_2\text{Zn}(\text{NPh})_2)$, but disproportionation took place giving Me_2Zn and $\text{py}_2\text{Zn}(\text{NPh}_2)_2$. Excess pyridine gave bright yellow crystals of $\text{Mepy}_2\text{ZnNPh}_2$.

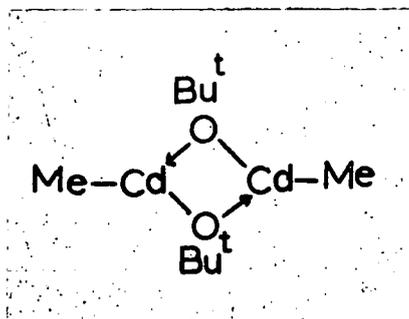
Reaction of dimethylzinc with N,N,N' - Trimethylethylenediamine gave a dimeric product, $(\text{Me}_2\text{ZnNMeC}_2\text{H}_4\text{NMe}_2)_2$, analogous to the beryllium derivative. 35.

Cadmium

Neutral coordination complexes formed by reaction of dialkyl and diarylcadmium derivatives with donor molecules are usually found to be considerably less stable than the corresponding zinc derivatives. A number of crystalline 1:1 complexes of diarylcadmium derivatives with 1,4 - dioxan have been described. ¹²⁷. The complexes lose dioxan when heated at 80°-100°C. Similar complexes of mixed cadmium aryls, $\text{Ar Cd Ar}'$ (Ar = phenyl, Ar' = 2-thienyl), have been reported. ¹¹⁵. Crystalline chelate complexes of dimethylcadmium with 1,4 -dioxan, N,N,N',N' - tetraethylethylenediamine, 2,2' - bipyridyl and 1,10 -phenanthracene are reported ¹²⁹. to be quite stable thermodynamically, whereas 1:1 complexes formed with unidentate donor molecules like tetrahydrofuran and pyridine are liquids which dissociate readily at room temperature and in benzene solution. In contrast to the above the yellow complex formed by reaction of dimethylcadmium and 2,2' -bypyridyl is reported to have an appreciable dissociation pressure of dimethylcadmium at room temperature, and is extensively dissociated in benzene solution. ³⁵.

Until quite recently the reactions of dialkylcadmium derivatives with molecules containing acidic hydrogen atoms had been little studied. A recent study ¹³⁰. has revealed some interesting alkoxy- and alkylthiomethyl cadmium derivatives. Methylcadmium methoxide was found to be too insoluble in benzene for molecular weight measurements, but the X-ray powder pattern was similar to that of the tetrameric methylzinc methoxide ⁹⁹. and a cubic structure is proposed for the methylcadmium methoxide.

The generality of the cubic structure for alkyl-metal alkoxides of beryllium, zinc and cadmium is reinforced by the fact that the methylcadmium ethoxide, iso-propoxide and phenoxide were found to be tetrameric in benzene solution. However, methylcadmium tertiary-butoxide was found to be anomalous in being ~~di~~meric. Any explanation involving steric interference must also explain why any such interference is more important around the larger cadmium atom when it would be expected to have more influence around the smaller zinc atom. It is also surprising that no pyridine adduct could be prepared from the tertiary-butoxide, which must be formulated with three-coordinate, and therefore coordinatively unsaturated, cadmium - fig: XXII.



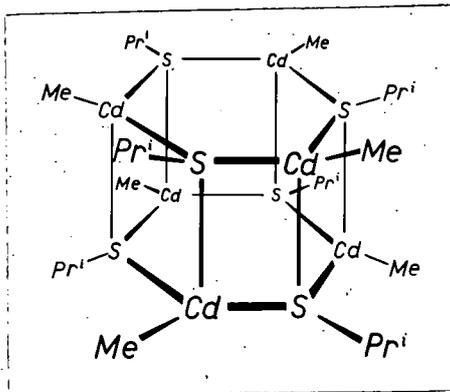
XXII.

The only derivative to yield a pyridine derivative was the phenoxide, as was found with the zinc analogue.

The reaction of dimethylcadmium with methanethiol and thiophenol gave ~~insoluble~~ products $(\text{MeCdSMe})_x$, $(\text{MeCdSPh})_x$, which are assumed to be polymeric. These products dissolve in pyridine, presumably as pyridine adducts, but pyridine is lost under reduced pressure.

As was found with the analogous zinc derivatives, branched-chain thiols gave derivatives soluble in benzene. Iso-propanethiol reacted with dimethylcadmium yielding a hexameric product, $(\text{MeCdSPr}^i)_6$, as was found with dimethylzinc, but tertiary-butanethiol gave a tetrameric product $(\text{MeCdSBu}^t)_4$, the analogous zinc compound being pentameric $(\text{MeZnSBu}^t)_5$.

The author suggests the tetrameric butylsulphide has a cubic structure, similar to the tetrameric alkoxides. A novel structure involving two six-membered rings is postulated for the methylcadmium (iso-propyl) sulphide, fig:XXIII.



XXIII.

As with the cubic structure, such an arrangement would have the effect of increasing the effective coordination number of the cadmium and sulphur atoms, which would oppose the formation of pyridine adducts. No pyridine adduct could be isolated.

Mercury

No coordination complexes of dialkyl- or diaryl- mercurials, with the exception of chlorinated and fluorinated derivatives, have been isolated. Indications of the formation of 1:1 and 2:1 compounds between such ligands as piperidine, triphenylphosphine and acetone respectively and diphenylmercury have been obtained by oscillometric titration in benzene solution but the concentration of such complexes if formed must be small and they dissociate very readily.¹³¹ The dialkyl- and diaryl- mercurials are unaffected by water or dilute acids and no compounds analogous to the alkoxy- and alkylthio- derivatives of beryllium and zinc are known.

Hydride Chemistry of the other Group II metals

In attempts to prepare Group II metal hydrides alkyl-hydrogen exchange reactions have been investigated, although the products obtained were rarely pure.

Thus dialkyl derivatives of magnesium, zinc and cadmium react in ether solution with lithium aluminium hydride⁸⁴ in a similar way to dimethylberyllium. The reactions appear to be more straightforward than found with dimethylberyllium, in that the products do not contain large quantities of lithium and aluminium. Zinc and cadmium hydrides are obtained as white, involatile, insoluble and ether-free solids, but do contain small amounts of impurities. Both decompose readily at ambient temperatures, (room temperature and 0°C respectively), into a metal and hydrogen. Dimethylmercury reacts with lithium aluminium hydride at 80°C yielding mercury and hydrogen; presumably the hydride, if formed, decomposes at the reaction temperature.

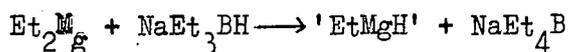
Diethylmagnesium reacts with lithium aluminium hydride to give magnesium hydride which contains ether and often aluminium, the amounts of impurities depending on the concentration of solutions, proportion of reactants, and order of addition.

Lithium aluminium hydride also reduces diphenylmercury,¹³⁴ and zinc,¹³⁵ cadmium¹³⁶ and mercury¹³⁶(II) iodides but pure hydrides have not been obtained, and the preparation of zinc hydride by reaction of zinc chloride with aluminium chlorohydride¹³⁵ was also found to give an impure product.

Alkyl-hydrogen exchange reactions between diethyl derivatives of magnesium, zinc, cadmium and mercury and diethylaluminium hydride, in the absence of solvent, have been investigated.¹²⁸ Triethylaluminium, indicating exchange had occurred, was isolated in every case, but the only hydride isolated was that of magnesium. The magnesium hydride isolated was 97% pure, although no mention of the impurity was made. Zinc and cadmium compounds reacted liberating hydrogen and depositing the metal in the temperature range 25°-50°C.

Diethylmercury reacted with the formation of hydrogen, ethane and mercury. The formation of ethane indicates the probably formation of ethylmercury hydride as an intermediate which breaks down into ethane and mercury. The formation of ethane indicates the probable formation of ethylmercury hydride as an intermediate which breaks down into ethane and mercury or reacts with diethylaluminium hydride to give mercury hydride which subsequently breaks down to mercury and hydrogen.

Ethylmagnesium hydride has been prepared by reaction of diethylmagnesium and sodium triethylboron hydride in ether: ¹⁵⁶.

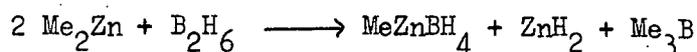


However, the product, isolated in solution only, is stable at low temperatures only, disproportionating into magnesium hydride and diethylmagnesium ~~at room temperature~~.

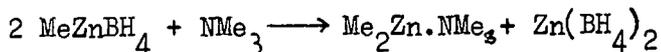
The reaction of ferric chloride, excess phenylmagnesium bromide and hydrogen has been studied as a possible method of producing Fe-H bonds, ¹⁵⁷ however, the infrared spectra and the chemical and thermographic analysis of the product supported the conclusion that it contained Mg-H bonds. No further description of the product is available

The reaction of diethylzinc and triethylstannane has been investigated ¹³⁷. and although tetraethyltin was isolated, indicating that alkyl-hydrogen exchange had taken place, the only other products were zinc metal and ethane. The ethylzinc hydride presumably decomposes under the conditions of reaction.

Dimethylzinc is reported ¹³⁸. to react with diborane with the formation of an apparently polymeric, mixed hydride-borohydride $(\text{HZnBH}_4)_n$, no experimental conditions being reported. However, a more recent investigation ¹³⁷. has shown that the two react with the formation of methylzinc borohydride and zinc hydride according to the equation:



The methylzinc borohydride formed is a volatile solid which reacts with trimethylamine ¹³⁷. with the formation of dimethylzinc-trimethylamine and zinc borohydride:

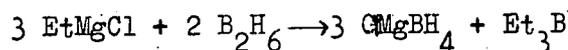


Some Organozinc compounds also form anionic hydride complexes in a way similar to the analogous beryllium compounds. Thus diphenylzinc ⁶⁵ forms the complex etherate, $\text{LiPh}_2\text{ZnH.OEt}_2$, with lithium hydride. The compound $[\text{NaH}(\text{Et}_2\text{Zn})_2]_n$, has been prepared by reaction of sodium hydride with diethylzinc in 'monoglyme' or 'diglyme', although attempts to isolate it resulted in its decomposition ¹³⁹. A similar compound $[\text{NaH}(\text{Bu}_2^t\text{Be})_2]_n$ has recently been prepared by reaction of sodium hydride with di-tertiary-butylberyllium in ether. ³⁶ Sodium hydride also reacts ¹³⁹. with zinc chloride in glycol ethers forming $[\text{NaH}(\text{ZnCl}_2)_2]_n$, which was not isolated. A competing reaction appeared to occur since sodium chloride and zinc metal were deposited, accompanied by some gas evolution.

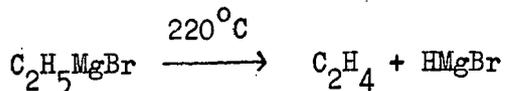
The original claim ¹⁴⁰. of the preparation of the Grignard reagent (HMgX) derived from hydrogen as bis-tetrahydrofuran and ether complexes from the reactions of ethylmagnesium halides with diborane at 25°C .



have since been disproved. A more recent work ^{137,141}. has shown that the bis-tetrahydrofuran complex of chloromagnesium borohydride is formed by reaction of ethylmagnesium chloride and diborane in tetrahydrofuran



It is also claimed that (HMgX) is formed by the pyrolysis of Grignard reagents:



However, this compound has been described ¹⁴⁴ by later workers as a mixture of magnesium hydride and bromide since at 300°-350°C it decomposes into magnesium, hydrogen and magnesium bromide.

Some dialkylmagnesium derivatives decompose at elevated temperatures evolving olefin and leaving magnesium hydride as the involatile residue, although side reactions are indicated by the formation of some paraffin. ^{144,145}.

The reactions between diethylmagnesium and diborane appear to be relatively complex, ^{145,146,147,148}. Excess diborane produces magnesium borohydride as a white microcrystalline precipitate. ¹⁴⁵. If excess diborane is not used, the reaction proceeds in several stages, and is affected by the presence of triethylaluminium which catalyses the reaction.

High pressure and temperature reactions of magnesium and hydrogen in the presence of magnesium iodide result in the formation of magnesium hydride. ¹⁴⁹.

EXPERIMENTAL

Apparatus and Techniques

Nitrogen Supply

Since most of the compounds studied react rapidly with oxygen and moisture, all the work described was carried out in an atmosphere of dry, oxygen-free nitrogen.

"White-spot" nitrogen was passed through a column of copper at 350° - 400° C to remove oxygen, and then through two traps cooled in liquid nitrogen to remove water.

The copper column was prepared by reducing copper oxide wire in a stream of hydrogen gas at 200° - 250° C, and was periodically regenerated in the same way.

Handling Techniques

The high toxicity of beryllium oxide means that beryllium compounds must be handled with extreme care, particularly when fumes of the oxide are formed on exposure to air.

Many reactions were carried out in a fume cupboard and transference of solids from one vessel to another was performed in a glove-box filled with dry, oxygen-free nitrogen.

Whenever convenient, starting materials were stored as solutions, such as diethylberyllium in ether and dimethylaluminium hydride in methylcyclohexane. Such solutions were conveniently transferred by using a hypodermic syringe and needle, thus minimising exposure to air.

Glove-box

The glove-box contained an atmosphere of dry, oxygen-free nitrogen. Purification of the nitrogen was achieved by the methods described above. A small circulatory pump, situated within the box, was employed to recycle the nitrogen atmosphere through the purification system whenever the box was not in use.

Due to the permeability of the tubing conventionally used for nitrogen systems (rubber, neoprene and P.V.C.) to oxygen, all nitrogen

supply and purification systems were fitted with glass or copper tubing (3/16" O.D.). Joints between glass and copper were made with thick-wall pressure tubing, the final joint being coated with a beeswax/vaseline mixture to minimise permeability to oxygen.

When fitted as described the glove-box was found to have an average oxygen content of 200-300 ppm, under which conditions the handling of extremely air-sensitive compounds without serious decomposition was possible.

Vacuum Apparatus:

A vacuum apparatus was available and consisted of three main sections:

(i) Storage

Volatile solids and liquids were stored in small tubes connected through mercury float valves to the main line. Gases were stored in large bulks (3 litre) fitted with a manometer and cold finger.

(ii) Gas Analysis

A Topley pump and gas burette were used to measure gases not condensed by liquid nitrogen. Two calibrated bulbs attached to a manometer were used for measurement of condensable gases. This system was calibrated with known quantities of carbon dioxide.

A combustion bulb for analysis of gaseous mixtures could be attached to the apparatus as required.

(iii) Fractionation

Three U-traps, connected by mercury float-valves to each other and separately to the main line, enabled separation of volatile mixtures to be achieved.

Tensimetric Titration Apparatus

A reaction tube, of small volume, and a double limb mercury manometer were connected through a mercury float valve to the main vacuum line. Non-volatile reactants were introduced into the reaction tube as pre-weighed samples (against a counter-current of nitrogen.) After sealing the apparatus

and evacuating it, volatile reactants, measured in the measuring bulbs, were condensed into the tube. Reactants were allowed to come to equilibrium, usually at 0°C, which often took several days, before further manipulations. When equilibrium had been reached, excess volatile reactants were removed step-wise from the system and measured. The pressure within system was plotted against the molar-ratio of reactants and the plot examined to determine the stoichiometry of the products.

Molecular weight measurements

Molecular weights were measured cryoscopically in benzene solution. The cryoscopic constant of the benzene, dried by standing over sodium wire before use, was determined using freshly sublimed biphenyl.

Infra-red Spectroscopy

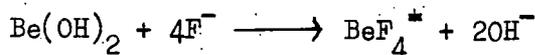
Infrared spectra were recorded on either a Grubb-Parsons GS2A or a Grubb-Parsons prism-grating Spectromaster.

Air sensitive solids were examined as nujol mulls, and liquids as contact films between potassium bromide discs. Spectra were recorded over the range 4000-400 cm.⁻¹

Analyses

Beryllium analyses

The method used to estimate beryllium was that developed, Dr. L. Branford, formerly of this department. It involves titration of the alkaline solution formed by addition of excess potassium fluoride to beryllium hydroxide.



The method requires standardisation under closely controlled conditions, and the calibration procedure described below must be strictly followed.

Aliquots of a standard beryllium solution, (0.01 M BeSO₄), were taken to cover the range 0-6 mg. Be²⁺. To each was added 5 cc. of a 0.5 M potassium sodium tartrate solution, 2 drops of a 0.1% alcoholic solution of bromothymol blue, and the solution titrated with dilute sodium hydroxide to

a green end-point. Then was added 5 cc. of a 1 M potassium fluoride solution, and the resulting blue solution set aside for about 2 minutes before titrating with 0.1 N sulphuric acid to a green end-point. A linear calibration graph of beryllium concentration against volume of acid-titrant was plotted. The solutions resulting from hydrolysis of the compounds to be analysed were treated in the same way, and very satisfactory results were obtained.

In some cases when bases (e.g. amines) were present in the hydrolysis solution, it was found necessary to remove them by ether extraction or oxidation by fuming to dryness with concentrated nitric acid.

Gas Analyses

Compounds evolving gases on hydrolysis were analysed by adding "degassed" 2-methoxyethanol to a weighed sample cooled with liquid nitrogen. The mixture was allowed to warm to the room temperature during which time gas evolution took place. The warming-up process was carefully controlled to ensure slow hydrolysis, as vigorous gas evolution often results in side reactions occurring. Hydrolysis was completed with dilute sulphuric acid and the gases liberated were fractionated, measured in the vacuumline, and identified by their infrared spectra.

Methane and hydrogen mixtures were often generated by hydrolysis of some of the compounds examined and the two gases cannot be separated by fractionation as neither is completely condensable in liquid nitrogen. The following procedure was therefore adopted.

A measured volume of the methane/hydrogen mixture was mixed with excess oxygen within a 200 cc. combustion bulb and ignited by passed an electric current through a platinum spiral inside the bulb. The products of the combustion, carbon dioxide and water were separated from excess oxygen and each other. The carbon dioxide was measured in the gas burette and the water condensed on to lithium aluminium hydride, the hydrogen produced being measured thus giving the quantity of water produced.

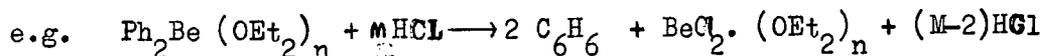
Phenyl analyses

Analysis of phenylberyllium derivatives is difficult, as benzene produced by normal hydrolysis techniques cannot readily be separated from the hydrolysis reagents, water and 2-methoxyethanol. The following method was therefore developed.

About 0.2 gm. of the compound to be analysed was weighed into a reaction tube in the glove box, the volume of the tube being about 200 cc. The tube was evacuated and an excess of dry hydrogen chloride, produced by reaction of concentrated sulphuric acid with dry sodium chloride, condensed into the tube. The tube was sealed at a constriction provided and allowed to warm slowly to -78°C . The tube was kept at -78°C for one hour, during which time the decomposition of the compound was almost complete. However, experience showed that to complete the reaction the reaction vessel must be heated in an oven at 160°C overnight for reliable results to be obtained.

The reaction tube was cooled in liquid nitrogen and opened to the vacuum line via a break-off sidearm provided. On warming to room temperature the benzene produced by the reaction was condensed into a trap cooled to -78°C , the excess hydrogen chloride being pumped away. The benzene was then estimated by condensing into a weighed V - tube and reweighing.

This method was found to be entirely satisfactory when the volatile products of the reaction were separable.



However, in some cases the products were found to be difficult to separate, e.g. benzene and methanol from phenylberyllium methoxide, and in other cases the hydrogen chloride produced decomposition of the products of the initial decomposition and the complicated mixture of final products was inseparable.

Amine analyses

These were estimated by steam distillation from an alkaline solution containing the amine into excess standard acid. The excess acid was determined by back-titration with standard alkali.

Preparation and Purification of Solvents and Starting Materials

Diethyl Ether

"Anhydrous Methylated Ether" was dried by standing over sodium wire for several days, and distilled from lithium aluminium hydride just before use.

Pentane and Hexane

These solvents were dried and purified by the same method used for diethyl ether.

Benzene

"Analar" benzene was dried by standing over sodium wire for several days before use.

Methylcyclohexane

This was purified and dried by twice distilling from sodium, the fraction boiling 101-102°C being collected. This was stored over sodium wire.

Xylene

Purification of this solvent was carried out by the method used for methylcyclohexane, the fraction boiling 138°-140°C being collected.

"Monoglyme"(1,2 - Dimethoxyethane or Ethylene glycol dimethyl ether)

The impure liquid was refluxed with potassium for several hours and distilled. After repetition of this process, final distillation from lithium aluminium hydride just before use was carried out.

Trimethylamine

Trimethylamine was dried by standing over phosphorus pentoxide and distilled from it as required.

N,N,N',N' - Tetramethylethylenediamine

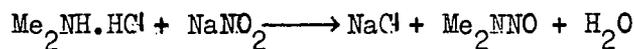
This chelating diamine was purified and dried by refluxing with sodium metal and distilling just before use

N,N,N',N' - Tetramethyl-o-phenylenediamine

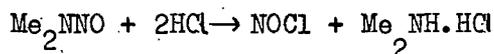
This was available in the department and had been prepared by Dr. N. A. Bell by the following method. *O*-phenylenediamine dihydrochloride⁶⁸ was treated with excess methanol at 175° - 185°C. The mixture of *N*-methylated *o*-phenylenediamines⁶⁹ obtained were treated with equal volumes of methyl-iodide at 180°-185°C from which reaction *N,N,N',N'* - tetramethyl-*o*-phenylenediamine⁷⁰ was isolated and distilled b.pt. 36°/10⁻³ m.m. The product was stored under nitrogen at -20°C in the absence of light, as it tends to decompose with the formation of dark-coloured product in air and light.

Dimethylamine

Since commercial dimethylamine hydrochloride usually contains traces of ammonium, methylamine and trimethylamine hydrochlorides, pure dimethylamine was prepared by the following method⁷¹.



An aqueous acid solution of commercial dimethylamine hydrochloride was heated at 75° - 80°C with excess sodium nitrite for three hours. The resulting solution, when cool, was saturated with sodium carbonate, the pale yellow oil which separated was isolated and combined with ethereal extracts of the aqueous layer. The mixture was dried over anhydrous potassium carbonate, and subsequent fractional distillation gave a 90% yield of pale yellow *N*-dimethylnitrosamine b.pt. 148°-150°C



The nitrosamine was refluxed with two moles of 4*N* hydrochloric acid until the solution was pale yellow. Treatment of the solution with excess aqueous potassium hydroxide liberated pure dimethylamine which was dried by passing through a column of potassium hydroxide pellets several times, and finally stored in the vacuum line.

Methanol

Methanol was refluxed with magnesium turnings for several hours. The fraction boiling 69.8 - 70.0°C was collected and used without further purification.

Diphenylamine

Crude diphenylamine was purified by boiling with animal charcoal in hexane and subsequently recrystallised from the same solvent twice before drying under reduced pressure, m.p. 52.8°C.

N,N,N', - Trimethylethylenediamine

The crude liquid was refluxed with a small amount of lithium aluminium hydride for twenty minutes, and subsequently fractionated. The fraction boiling 114 - 116°C was collected and used.

2,2' - bipyridyl

2,2' - Bipyridyl was available in the department and purified by vacuum sublimation (70-80°/0.1 m.m.) before use, as exposure to light and air results in brown decomposition products being formed.

Trimethylphosphine

This was stored in dilute sulphuric acid solution. Treatment of the solution with a concentrated solution of potassium hydroxide liberated the phosphine, which was dried over solid potassium hydroxide and measured in the vacuum line before use.

Dimethylsulphide and Diethylsulphide

Commercial samples of these sulphides were available, both of which purified by refluxing with sodium (to remove water) and copper powder (to remove thiols). Subsequent fractional distillation of each sample gave dimethylsulphide, b.pt. 36°-36.5°C, and diethylsulphide, b.pt. 92°C.

2,5 - Dithiahexane

Purification of this compound was achieved by refluxing with sodium and subsequent fractional distillation, b.pt. 181°C.

Dimethylether

A sample of this compound was available prepared by Dr. N. A. Bell by reaction of sodium methoxide and methyl iodide. It was stored and measured in the vacuum line.

Lithium Reagents

Methyl-, ethyl-, and phenyl-lithium were prepared in 80-90% yields from the corresponding alkyl or aryl halide and lithium shot in ether.

Grignard Reagents

These were prepared from the reaction of alkyl or aryl bromides with magnesium in about 90% yield in diethyl ether.

Beryllium chloride ^{2,19.}

This was prepared by heating beryllium powder in dry chloride gas. The product was sublimed from the reaction tube into a receiver flask which was then sealed from the reaction tube.

Dimethylberyllium

Solutions of dimethylberyllium in diethyl ether were prepared in 65 - 70% yield both by the addition of two moles of methylmagnesium bromide to one mole of beryllium chloride and addition of two moles of methyl-lithium to one mole of beryllium chloride in ether. The solution was decanted from precipitated halides, which were washed with ether and most of the ether removed by distillation. The dimethylberyllium was then purified by a process of continuous "ether distillation" at 180°-200°C to achieve separation from dissolved salts.^{14.} In general, a preparation yielding one half mole of dimethylberyllium required 24 hours distillation for complete transference of the beryllium compound. The solution was analysed by hydrolysis for hydrolysable methyl and beryllium.

Diethylberyllium ^{14.}

Ethereal solutions of diethylberyllium were prepared in 70-75% yield by addition of two moles of ethylmagnesium bromide to one mole of beryllium chloride in ether. The solution was decanted from precipitated salts, which were washed with ether, and distilled to low volume. The remaining ether was removed under vacuum and subsequent distillation gave diethylberyllium, a colourless liquid b.pt. 60° - 65°C/0.3 m.m.

Several reactions investigated required diethylberyllium completely ether-free. Since complete separation from ether is not achieved by vacuum distillation or even by prolonged pumping in high vacuum the following method, developed by Stöhmeier and co-workers,⁶⁰ was used:

Potassium fluoride (15g., 0.258 mole.), dried by grinding at 400°C, was added to 280 ml. of a 1.30 m. (0.464 mole) solution of ethereal diethylberyllium. The mixture was heated at 65°C with stirring for three hours. At fifteen minutes intervals the mixture was pumped to remove ether. After three hours nearly all the potassium fluoride had dissolved and slightly viscous mixture remained. When pumped in a high vacuum the solution slowly deposited a white crystalline solid as the last traces of ether were removed. After pumping at 40°C for fifteen minutes the white crystalline solid, $\text{KF}(\text{BeEt}_2)_2$ and some excess potassium fluoride, was transferred to a double Schlenk tube and washed with three 20 ml. portions of dry hexane. The solid was then transferred, under nitrogen, into a high vacuum distillation apparatus, designed so that the distillate did not come into contact with any greased ground-glass joints.

When heated in the high vacuum the solid melted in the range 85° - 90°C, the resulting liquid frothed vigorously in the range 105° - 120° and diethylberyllium distilled slowly from the mixture and solid residue remaining. The diethylberyllium was then redistilled and collected, in 60% yield as a colourless liquid boiling at 65°C/0.2 - 0.4 m.m.

A weighed sample (0.0501 g.) of diethylberyllium was analysed by hydrolysis; Found: Be, 13.4; Hydrolysable ethyl, 86.5; - hydride, none; ether, none. $\text{C}_4\text{H}_{18}\text{Be}$ requires Be, 13.5; Hydrolyzable ethyl, 86.5.)

The distillate was dissolved in 200 ml. of dry hexane, which was standardised by hydrolysis and found to be 0.815 M.

Diethylmercury

This compound was available in the department. Distillation before use, b.pt. 159°C was the only purification necessary.

Diphenylmercury

This was obtained in 90-95% yield by reduction ^{72.} of phenylmercury chloride with hydrazine hydrate in refluxing methanol, followed by crystallisation and sublimation of the product (as colourless needles, mpt. 123°-124°C.) As diphenylmercury is somewhat sensitive to light, turning yellow when exposed to light for several days, it was stored in the dark.

Diphenylberllium

Although reaction of diphenylmercury with beryllium powder at 200° - 220°C is claimed ^{64,51,14.} to give diphenylberyllium in good yield, it was found that some decomposition (charring) occurred which complicated purification of the product. A much cleaner reaction results when the same reagents are heated in xylene at 140°C for seventy-two hours. It was found that activation of the beryllium, by standing in ethereal diethylberyllium overnight before use or alternatively by addition of mercuric chloride to the reaction mixture, was imperative for good yields. Diphenylberyllium was isolated by filtration from the cooled reaction mixture and subsequent soxhlet extraction with benzene. Diphenylberyllium prepared in this way was a white solid, m.pt. 248° - 250°C with decomposition.

Attempts to prepare diphenylberyllium by reaction of two moles of phenylmagnesium bromide and one mole of beryllium chloride in ether and subsequent crystallisation from ether or benzene initially met with failure due to contamination of the product with magnesium halides, which are slightly soluble in ether and benzene/ether mixtures. However, this problem was overcome in a late stage in this work in the following way. Solutions of magnesium dialkyls and diaryls have been prepared ^{150,151,152.} by addition of dioxan to Grignard reagents which causes disproportionation and precipitation of magnesium halide dioxan complexes. Filtration yields a solution of the appropriate dialkyl or diaryl magnesium which requires no further purification.

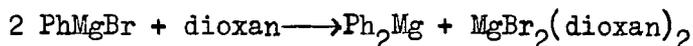
Thus by addition of dioxan to the solution obtained by addition of phenylmagnesium bromide (1.98 moles) to beryllium chloride (.1 mole) in ether, it was hoped to precipitate all magnesium halides and any excess beryllium chloride as insoluble dioxan complexes. A typical preparation is now described.

To a solution of beryllium chloride (6.81g; 0.0851 mole) in 150 ml. of ether phenylmagnesium bromide (0.162 moles, 168.0 ml. of a 0.96M solution in ether) was added. After the reaction mixture had been stirred for half an hour, dioxan (29.00 g., 0.34 moles) in 100 ml. of ether was added dropwise with vigorous stirring. The mixture was stirred overnight to ensure complete precipitation and coagulation of the precipitate, and then filtered.

The resulting solution was analysed for beryllium and hydrolysable-phenyl and found to be 0.54 M, the yield being about 60%. Purification was achieved by crystallisation of the bis-etherate $\text{Ph}_2\text{Be}(\text{OEt}_2)_2$ ⁶⁵ and redissolving this in ether to give a solution which was restandardised. Earlier observations during this work on the constitution of the so-called bis-etherate have shown it to have a dissociation pressure of ether (approx. 15 m.m. at 0°C) and the product obtained by pumping the crystals dry at room temperature had a variable constitution, $\text{Ph}_2\text{Be}(\text{OEt}_2)_n$ where $n < 2$, the actual composition depending on the length of time the product was pumped. Because of this uncertainty of composition only solutions of the etherate in ether were used.

Various points emerged from experiments in the preparation of diphenylberyllium by this method and the following instructions must be observed to obtain a product uncontaminated with magnesium and halide:

(a) A slight deficiency of grignard reagent must be used, otherwise diphenyl magnesium will contaminate the product:

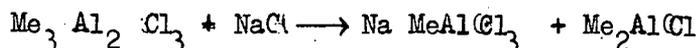


(b) The exact quantity of dioxan (2 moles for every mole of magnesium halide) to precipitate the magnesium halides as dioxan complexes

must be added. A deficiency or excess of dioxan causes the resulting solution to be contaminated with halogen.

Dimethylaluminium chloride

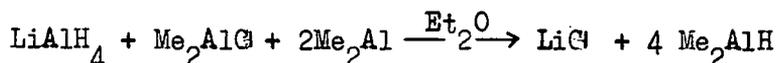
Methylaluminium sesquichloride, available in bulk in the department, was mixed with excess sodium chloride. The mixture was heated, with stirring, at 140°C for 3 hours. ^{73.}



The dimethylaluminium chloride was distilled from the involatile sodium methyl trichloroaluminate at atmospheric pressure. Redistillation of the distillate gave dimethylaluminium chloride, a colourless liquid b.pt. 125° - 126°C, in 80-85% yield.

Dimethylaluminium hydride

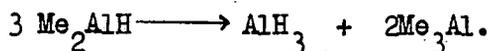
Several preparations of this compound were attempted by the following reaction:



Decantation of the solution from precipitated salts, evaporation of ether to low volume and high vacuum distillation of the resulting solution were carried out. Dimethylaluminium hydride is described ^{74.} as a colourless viscous liquid, distilling at 60° - 65°/0.005 m.m. and the product from the above reaction answered this description in all respects, but when allowed to warm to room temperature and dissolve in the solvent ether (the receiver was cooled to -196°C) the initially clear solution slowly deposited a voluminous white precipitate. The result of further distillations was the same, a clear solution being obtained at about -10° to 0°C which slowly deposited a white solid, slowly at 0°C and rapidly at ambient temperatures. Analysis of the solid showed it to contain hydrolyzable hydrogen and aluminium in the ratio 2.98 : 1 and no hydrolyzable methyl groups.

The solution was shown to contain hydrolyzable methyl, aluminium and hydrolyzable hydrogen in the approximate ratio 2.3: 1 : 0.7. It was also found that if the solution was filtered, the white solid being retained on a sintered disc, the filtrate, although initially clear, rapidly deposited further white solid.

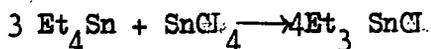
It is obvious from the above experimental observations that dimethylaluminium hydride disproportionates in ether solution.



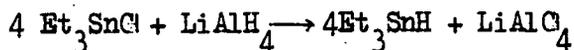
There is no mention of such a disproportionation of dimethylaluminium hydride in the literature, but diethylaluminium hydride is said to undergo a similar reaction in ether solution.⁷⁵ However, the deposition of solid is not significant unless the solution is allowed to stand for several days and the disproportionation is not considered to be of practical importance. Dimethylaluminium hydride was successfully prepared by reaction of trimethylaluminium with excess lithium aluminium hydride in methylcyclohexane at 70°C.

Triethyl-stannane

Triethyl-stannane had been prepared in this department by Dr. N. A. Bell. Triethyltin chloride was prepared by reaction of tetraethyltin and stannic chloride in the appropriate proportions. Distillation under reduced pressure gave a colourless liquid b.pt. 82° - 82.5°/10 m.m.¹⁵³.



Triethyltinchloride was then reduced with lithium aluminium hydride in ethereal solution. Subsequent removal of solvent and fractional distillation under reduced pressure gave a colourless liquid, b.pt. 44°/16 m.m.¹⁵⁴.

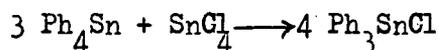


The product was stored under nitrogen at -20°C to inhibit any decomposition.

However, it was found necessary to distil under reduced pressure before use as in such a distillation a white involatile residue always remained. The composition of the residue is unknown.

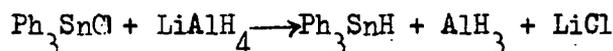
Triphenyltin chloride 153,155

A mixture of tetraphenyltin and stannic chloride, in appropriate proportions, were heated at 205° - 215°C for three hours at at 180° - 190°C for a further three hours.



The product was then crystallised by Soxhlet extraction with ether in 75% yield, m.pt. 106°C.

Triphenylstannane 152,159,160



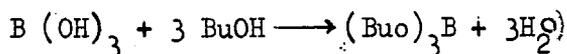
Triphenyltin chloride (12.50 g., 0.0324 mole,) was introduced, as an ethereal slurry, on to the sinter of a Soxhlet extraction apparatus. To the ether in the flask 23.1 ml. of a 1.39M (0.0321 mole.,) solution of lithium aluminium hydride in ether were added. The ether was heated to 60°C and the refluxing solvent slowly extracted the triphenyltin chloride into the solution. As the chloride was extracted into solution a white precipitate slowly appeared. After one hour all of the chloride had been extracted into solution and the mixture was refluxed for a further hour. The mixture was allowed to cool and 5 ml. of methanol in 100 ml. of ether was added slowly, followed by 100 ml. of a 2% solution of sodium potassium tartrate. The ether layer was separate from the aqueous layer, which was washed with two 50 ml. portions of ether, and the combined extracts dried with anhydrous magnesium sulphate. The ether was removed under reduced pressure and the oily residue distilled in vacuo. Triphenyltin hydride distilled as a colourless, slightly viscous liquid at 165° - 168°/0.1 - 0.3 m.m. in 60% yield.

Preliminary preparative experiments showed that the pressure in the apparatus during distillation was very important. Attempted distillation in high vacuum (0.001 m.m.) resulted in decomposition of the liquid into a yellowish solid and non-condensable gas, presumably hydrogen which was pumped away. The solid, when recrystallised from benzene, was shown to be tetraphenyltin, m.pt. 225° - 226°C and an identical infrared spectrum. This agrees with experiments^{160.} on the decomposition of triphenyltin hydride when heated or exposed to light.

Satisfactory results were obtained when the pressure was maintained at 0.1 - 0.3 m.m. The product was stored under nitrogen in the dark and found to be quite stable over a period of several weeks.

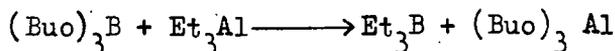
Tributylborate^{161.}

This compound was prepared by J. A. Heslop of this department by reaction of boric acid with butanol:



Triethylborane^{162.}

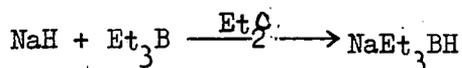
This was prepared in collaboration with J. A. Heslop by reaction of tributylborate with triethylaluminium:



Triethylaluminium was slowly added to tributylborate, with stirring, and triethylborane b.pt. 96°C was distilled from the mixture through a short fractionating column in 100% yield.

Sodium triethylborohydride

Triethylboron in ether solution was added drop-wise to excess sodium hydride suspended in boiling ether. The resulting solution was filtered from excess sodium hydride and analysed by hydrolysis for hydrolysable hydrogen, sodium, and boron.



EXPERIMENTAL RESULTS

Reaction of dimethylaluminium hydride and dimethylberyllium

Dimethylberyllium (4.13 ml. of a 2.42 M solution in ether, 0.001 mole.) was introduced by syringe into the cooled (-196°C) reaction bulb A of the high-vacuum reaction apparatus (diagram 1). Dimethylaluminium hydride (5.73 ml. of a 1.75 M solution in methylcyclohexane, 0.001 mole.) was similarly introduced, and the mixture allowed to warm to room temperature. The initially clear solution deposited a small amount of white precipitate at 0°C . No further precipitation was observed as the mixture was shaken and warmed to 40°C for one hour.

Receiver bulb B was cooled to -196°C and the apparatus evacuated. After the solvents had distilled into B, the oily residue in A was warmed to 40°C . The oily residue slowly turned solid over a period of fifteen hours, after which time the apparatus was filled with nitrogen. The distillate was removed as a solution in ether and methylcyclohexane by syringe.

Analysis of the distillate

The distillate was analysed, by hydrolysis with 2-methoxyethanol, for hydrolysable methyl- and hydrogen, and aluminium. (Found: hydrolysable methyl-, 604 N cc; hydrogen, none; aluminium, 0.000981 mole. Ratio of methyl; aluminium - 3.01:1)

Analysis of solid residue

Attempts to analyse the residue for beryllium by the usual procedure were complicated by the presence of aluminium, which interferes with the procedure adopted. The analysis was taken no farther.

Reaction of diethylberyllium with triethylstannane at 70°C

Triethylstannane (6.30g., 0.0327 mole.) was condensed into bulb A of the high vacuum reaction apparatus and 19.5 ml. of a 1.57 M solution of diethylberyllium in ether (0.0325 mole.) were added by syringe. The mixture was heated to 45°C for two hours, during which time most of ether distilled into receiver bulb B, and then at 75°C for a further two hours.

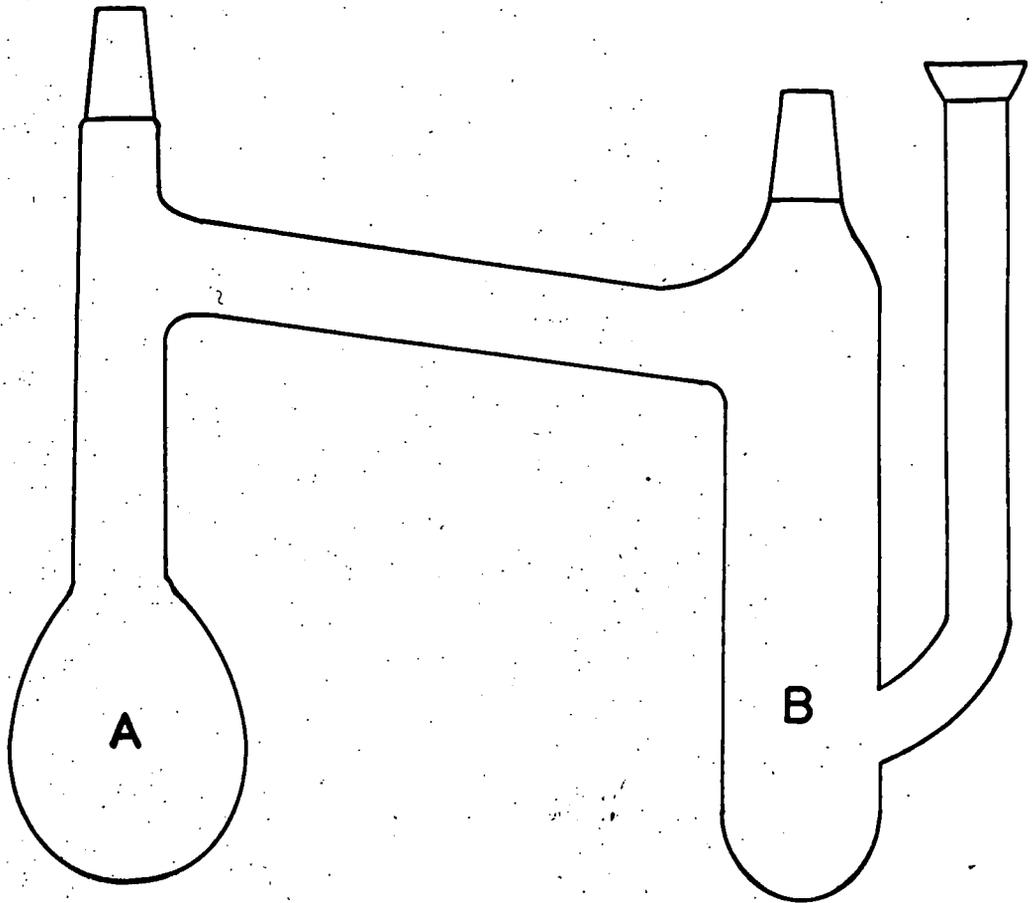


DIAGRAM I

After allowing the reaction mixture to cool to room temperature, bulb B was cooled to -196°C and the apparatus slowly evacuated. All volatile material was condensed into B over a period of fifteen hours, after which time bulb A was heated to 40°C for two hours. The initially mobile solution slowly turned to a viscous oil, which turned solid when heated at 40°C . Ether (100 ml.) was condensed on to the solid residue, and trimethylamine (850 Ncc., 0.038 mole.) added to the mixture, which was allowed to stand at room temperature for fifteen minutes. The solid slowly dissolved giving a clear, colourless solution. The solution was transferred by syringe into one arm of double Schlenk tube. On cooling the solution to -78°C a white solid slowly crystallised, which was filtered on to the sinter and pumped dry. The solid was then transferred into a sublimation apparatus and heated to $40-45^{\circ}\text{C}$ in high vacuum in an attempt to sublime the product $(\text{EtBeH.NMe}_3)_2$, as described in the literature.⁷⁷ However, even though a small amount of solid was sublimed as colourless prisms at $45^{\circ}/0.01$ mm., the major portion of the solid slowly changed to a viscous liquid. Trimethylamine (identified by its gas phase infrared spectrum) was found to be liberated during this change, and by condensing excess trimethylamine on to the viscous liquid a solid product was regenerated. Further attempts to sublime the solid at lower pressures and low temperatures ($35^{\circ}\text{C}/0.001$ m.m.) resulted in the same decomposition. It was concluded that ethylberyllium hydride-trimethylamine, $(\text{EtBeH.NMe}_3)_2$ has an appreciable dissociation pressure of trimethylamine at 45°C , and the liquid residue had a composition approximating to $(\text{EtBeH}).(\text{NMe}_3)_n$ where $0 < n < 1$. Attempted sublimation under a partial pressure of trimethylamine (1 mm.) was not successful and in further preparations isolation of the trimethylamine complex was achieved by low temperature crystallisation which gave very satisfactory results. The product was identified by its infrared spectrum and melting-point, $101-102^{\circ}\text{C}$ under nitrogen. 77.

Reaction of diethylberyllium with triethylstannane at 40°C

Triethylstannane (5.2g., 0.0252 mole.) and 16.0 ml. of a 1.57 M solution of diethylberllium (0.0250 mole.) were introduced into the reaction bulb A of the apparatus. The mixture was heated at 40°C for four hours. After allowing it to cool to room temperature, a small sample was removed by syringe and analysed by hydrolysis. (Found: hydrolysable ethyl, 18.95 Ncc: hydrogen, 10.4 Ncc: ratio of ethyl: hydrogen = 1.82:1.)

The amount of triethylstannane (2.98 g., 0.0144 mole.) required to bring the ethyl; hydrogen ration to 1:1 was added to the mixture. The mixture was then heated at 40°C for a further four hours. During this time a white precipitate was slowly formed.

The original aim of this experiment was to prepare ethylberyllium hydride by reaction at 40°C. The white precipitate was thought to indicate that exchange had occurred to such an extent that beryllium hydride, or some compound approximating to BeH_2 , had been formed. Such a reaction is investigated under slightly different conditions, and this reaction was investigated no further.

Reaction of dimethylberyllium with triethylstannane

Triethylstannane (5.49g., 0.0268 mole.) was condensed into the reaction bulb A, and 18.6 ml. of a 1.43 M solution of dimethylberllium (0.0267 mole.) were added by syringe. The solution was heated at 65-70°C for four hours. After the mixture had cooled to room temperature, receiver B was cooled to -196°C and the apparatus evacuated. Over a period of fifteen hours all volatile matter was collected in receiver B. The residue in bulb A was a viscous oil. Ether (100 ml.) was condensed on to the residue and the mixture allowed to stand at room temperature. A clear colourless solution was obtained, a small sample of which was analysed by hydrolysis (Found: Hydrolysablemethyl, 7.15 Ncc: hydrogen, 7.06 Ncc: ethyl, none: ratio methyl: hydrogen = 1.01:1)

The solution was used as a stock solution of methylberyllium hydride, $(\text{MeBeH})_n$, for the following reactions:

Reaction with trimethylamine

30 ml. of the solution were transferred by syringe into one arm of a double Schlenk tube. An excess of trimethylamine (400. Ncc.) was condensed on to the solution and the mixture allowed to warm to room temperature. Solvent was removed under reduced pressure and the solid residue heated at 45°C in high vacuum. Colourless prisms sublimed at 40°-45°C/0.001 m.m. (found: Be, 10.7; hydrolysable methyl, 17.6; hydrogen, 1.20%. $C_4H_{13}BeN$ requires Be, 10.7; hydrolysable methyl, 17.8; hydrogen, 1.20%) The solid melted at 70-72°C and its infrared spectrum was identical to that of $(MeBeH.NMe_3)_2$.⁷⁷

Reaction with trimethylphosphine

Methylberyllium hydride, 30 ml. of the stock solution, was transferred into one arm of a double Schlenk tube. An excess of trimethylphosphine (400 Ncc.) was condensed on to the solution. At low temperature (about -50°C) a white crystalline solid was observed, which dissolved as the solution warmed to room temperature. By crystallisation at low temperature a white crystalline product was produced, which was filtered on to the sinter and pumped dry at 0°C.

Attempts to handle the product in the glove-box for analysis and preparation of samples for infrared examined were complicated by the product slowly "losing weight," and turning to an oily liquid when ground. All observations indicated that the solid was losing trimethylphosphine, probably having a dissociation pressure of trimethylphosphine at ambient temperatures. A rough analysis was attempted, (Found: about 0.010 g. gave hydrolysable methyl, 16.4 Ncc., hydrogen, 16.3 Ncc.; trimethylphosphine, 10.4 Ncc.; ratio methyl; hydrogen; phosphine = 1: 1: 0.64.

By introduction of some of the solid into a small flask, and rapid evacuation with the solid frozen, it was estimated that the solid has a dissociation pressure of trimethylamine of about 2 cm. at 20-25°C.

No further investigation or purification of the compound were undertaken.

Solubility of methylberyllium hydride in hexane

30 ML. of the solution were transferred into a two-necked 100 ml. flask. The solvent ether was removed under reduced pressure and the oily residue pumped in high vacuum for two hours. Hexane (20 ml.) was added to the residue, and a clear solution was obtained on shaking. The hexane was removed under reduced pressure and a white solid residue remained¹, which was only partially soluble in hexane. By two successive additions and removals of hexane, a solid residue insoluble in hexane was obtained. When ether (2 ml.) was added to a suspension of the solid in hexane, a clear, colourless solution was obtained after five minutes shaking.

Reaction of diphenylberyllium with triphenylstannane (I)

Diphenylberyllium (2.06 g., 0.0134 mole.) was introduced in a small weighing-tube, into one limb of a double Schlenk tube. Triphenylstannane (4.50g. 0.0133 mole) was added in benzene (5ml.) by syringe. The mixture was stirred at room temperature for one hour. During this time the amount of solid in suspension had noticeably increased, however the solution was pale creamy yellow in colour. The mixture was heated at 70°C for a further hour during which time the colour deepened to a bright yellow. The benzene was removed under reduced pressure and ether (50 ml.) was condensed on to the lightbrown solid residue. On stirring for 30 minutes the mixture was filtered giving a bright yellow solution. A sample of the solution was analysed by hydrolysis (Found: hydrolysable hydrogen, 6.98 Ncc.;beryllium, 4.63 mg; ratio of beryllium: hydrogen = 1.65 : 1)

The experiment was investigated no further, as results indicate only partial exchange.

Reaction of diphenylberyllium with triphenylstannane (II)

Diphenylberyllium (1.84 g.; 0.0113 mole.) was introduced, as a solution in 15 ml. of ether, into one limb of a double Schlenk tube. Triphenylstannane (2.09g.; 0.0112 mole) in ether (20 ml.) was added by syringe. The mixture was heated and stirred at 35°-40°C for one hour.

The solution remained clear during the whole operation.

Benzene (10 ml.) was added and the mixture heated at 70°C for one hour. During this operation ether slowly distilled from the reaction mixture into the other limb of the double Schlenk tube and a white solid was slowly deposited, and a slight yellow colour developed. The temperature of the reaction mixture was raised to 75°C for a further hour. During the final 30 minutes no further solid was precipitated, and the colour deepened to a bright yellow. The mixture was filtered and ether (10 ml.) was added. A small sample of the solution was removed and analysed by hydrolysis (Found: hydrolysable hydrogen, 12.38 Ncc; Be, 5.40 mg.; ratio of beryllium: hydrogen = 1.02 : 1).

To the remainder of the solution 2.0 ml. of N,N,N',N' - tetramethylethylenediamine in 10 ml. of ether were added. A pale yellow solid was immediately precipitated. The solid was filtered on to the sinter, washed twice with ether and pumped dry. The solid obtained was creamy yellow in colour. (Found: hydrolysable hydrogen, 0.435; Be, 4.67; amine, 27.9; ratio hydrogen: beryllium: amine = 2:2:1. $C_{18}H_{27}Be_2N_2[(PhBeH)_2Me_2NC_2H_4NMe_2]$ requires hydrolysable hydrogen, 0.67; Be 6.04; amine, 39.0)

The solution remaining from hydrolysis was extracted with benzene before analysis for beryllium; a white solid (0.058 g.) was isolated on evaporation of benzene. The solid melted at 220°C and its infrared spectrum was similar to what would be expected for a mixture of tetraphenyltin and hexaphenyl di-tin.

The infrared spectrum of the hydride-containing product was identical to a spectrum of $[(PhBeH)_2Me_2NC_2H_4NMe_2]$ prepared in this department by an alternative method.³⁶

Reactions of triethylstannane with ether-free diethylberyllium

A. Triethylstannane (3.50 g., 0.0175 mole) was condensed into one limb of a double Schlenk tube. To the frozen hydride diethylberyllium (10.45 ml. of a 0.815M solution in hexane, 0.0086 mole.) was added, the mixture allowed to warm to room temperature. When the reaction mixture had warmed to 0°C, a cloudiness in the initially clear solution was observed.

On further standing gas evolution was observed, accompanied by precipitation of a white solid. The mixture was heated at 60° - 70° C for two hours. Gas evolution ceased after 30 minutes and after one hour no further solid was precipitated. However on filtering the solid from the solution, a further slow precipitation from the solution occurred. The solid that had been filtered from solution was pumped and analysed. (Found: hydrolysable ethyl, 46.8; hydrogen, 5.15; Be, 27.3%. Ratio of (H + Et)/Be = 1.99 : 1; and hydrolysable ethyl, 49.5; hydrogen, 3.62; Be, 23.1% Ratio (H + Et)/Be = 2.00 : 1.)

The figures correspond to compositions $\text{Et}_{0.54}\text{BeH}_{1.38}$ approximately 79 weight % pure, and $\text{Et}_{0.613}\text{BeH}_{1.41}$ approximately 76 weight % pure respectively.

B. Triethylstannane (1.08 g., 0.0052 mole.) was condensed into a reaction tube, fitted with break-off side-arm. 3.12 ML. of a 0.815M solution of diethylberyllium in hexane (0.00265 mole.) were added by syringe and the tube sealed at a constriction provided. The reaction mixture was warmed to 65° C; gas evolution and precipitation occurring as before. The reaction was allowed to proceed overnight. After 15 hours the tube was cooled to -196° C and opened via the break-off side-arm into a vacuum line and the gases evolved measured and identified.

(Found: Gas volatile at -196° C, 18.52 Ncc's. The gas, when ignited with excess oxygen, gave no carbon dioxide; and was thus shown to be hydrogen. Gas volatile at -78° C, none)

C. Triethylstannane (4.28 g, 0.021 mole.) was condensed into one arm of a double Schlenk tube and 12.8 ml. of 0.815M solution of diethylberyllium in hexane (0.0104 mole.) added by syringe. The double Schlenk tube was connected to a vacuum line, the apparatus evacuated and the reactants allowed to warm to room temperature and finally heated to 70° C. The double Schlenk tube was fitted with an "acetone/ CO_2 " cold-finger to condense reactants from the vapour phase back into the reaction mixture. The reaction was allowed to proceed over a period of 20 hours, the gas evolved being collected and measured in the Töpler pump. However, even after 20 hours gas evolution,

although very slow, had not ceased and as the problem of maintaining vacuum-tight system over such an extended period in the presence of solvent, was extremely difficult, the reaction mixture allowed to cool and the apparatus filled with nitrogen). Subsequent filtration of the reaction mixture yielded an initially clear solution which slowly deposited a white precipitate over a period of days, indicating the reaction is very slow to reach completion.

In view of the slowness of the reaction observed in the previous experiments, a piece of apparatus was designed to enable the following operations to be carried out: (a) to allow complete reaction in a vessel having no greased joints, (b) to allow measurement of gas produced at completion of reaction, (c) to allow separation of solid and solution. The apparatus shown in diagram III was used for all following reactions between triethylstannane and diethylberyllium:

D. Triethylstannane (2.71g., 0.13 mole.) was condensed into reaction bulb E of the apparatus. 8.1 ML. of a 0.815 M solution of diethylberyllium in hexane (0.0661 mole.) were added by syringe through constriction A, the apparatus evacuated and sealed at A. The reactants were allowed to warm to room temperature and the apparatus was maintained at 75°C for eight weeks. The reactants were cooled to -196°C, the apparatus opened via break-off side-arm F into a high vacuum line and gas that had been evolved collected and measured. The apparatus was sealed at constriction B and the solid filtered on the sinter. By condensing hexane from receive D into the reaction bulb E the solid was washed five times. The receiver D was cooled to -196°C overnight to ensure all volatile material was condensed into D, and finally constriction C was sealed to separate solid and solution.

Analysis of products

i) Gas

Found: Gas volatile at -196°C, 46.5 Ncc's. (Hydrogen). Gas volatile at -78°C, none.

ii) Solid

Found: Hydrokysable hydrogen, 3.77; ethyl, 18.4; Be, 19.4%

Figures correspond to "Et_{0.288} Be H_{1.71}" approximately 41 weight % pure.

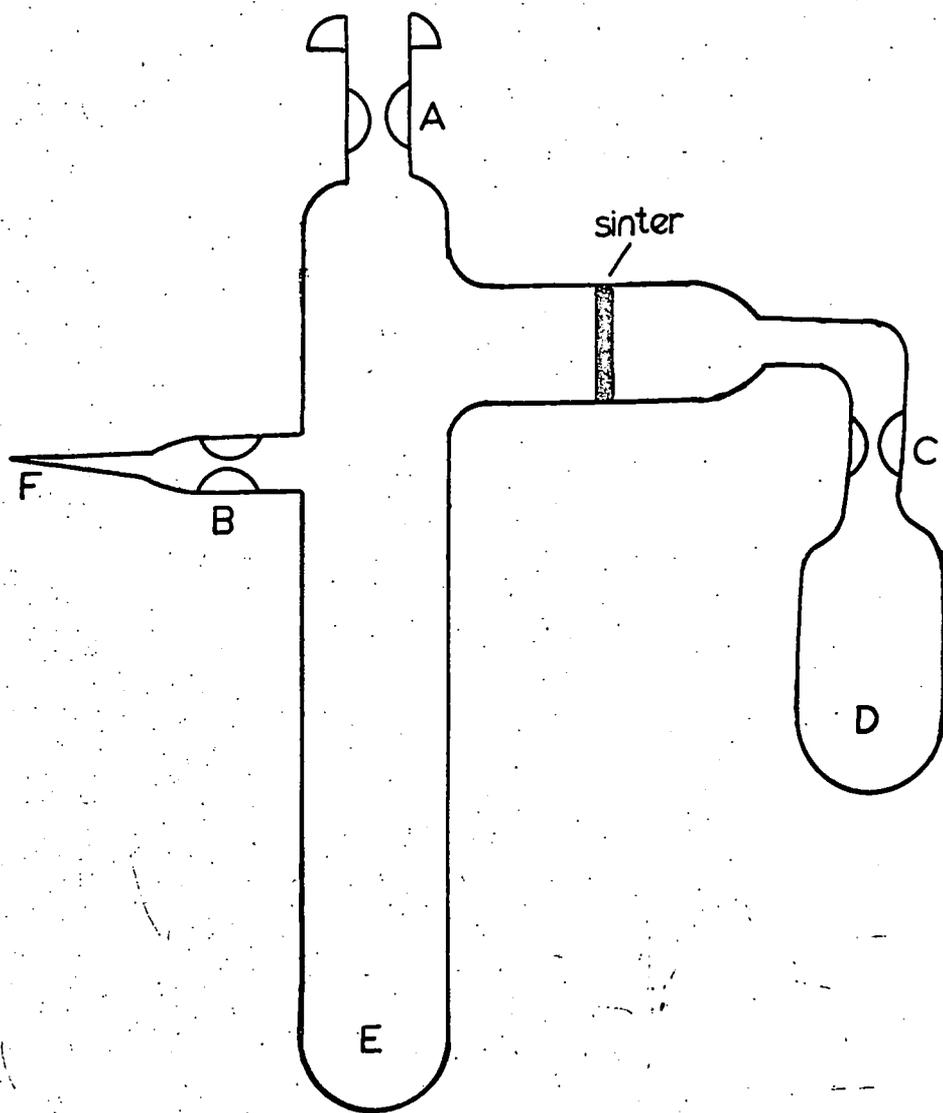


DIAGRAM. II.

Infrared examination of the solid showed the following features:

- (a) as a nujol mull: a broad absorption centered at 1742 cm.^{-1} ,
 - (b) as a perfluorokerosene mull: weak absorptions in the region $3100\text{--}2900 \text{ cm.}^{-1}$.
- iii) Solution

The solution was removed from bulb D by syringe and separated into three fractions by pumping through two traps, maintained at -50°C and -196°C respectively. The residue, involatile at room temperature was a colourless viscous oil. This, and the fractions involatile at -50°C and -196°C were identified by their infrared spectra.

Fraction involatile at -196°C

The infrared spectrum of this fraction, a colourless liquid, showed it to be hexane.

Fraction involatile at -50°C

This fraction was identified as tetraethyltin, on comparison of its infrared spectrum with published spectra. ^{164.}

Fraction involatile at 25°C

By comparison of its infrared spectrum with published spectra ^{164.} this fraction was shown to be hexaethyl di-tin. An attempt to weigh each individual fraction was made, but the results correspond to a 180% yield of tetraethyltin, and it was assumed an error had been made. The results were disregarded.

E. Triethylstannane (2.87g., 0.014 mole.) was condensed into bulb E of a reaction vessel as shown in diagram II. 5.70 ml. of a 0.815M solution of diethylberllium in hexane were added by syringe, the vessel evacuated and sealed at constriction A. The reactants were maintained at 75°C for 8 weeks, gas evolution and precipitation occurring as before, and the products separated and examined in exactly the same way as described in the previous experiment.

Analysis of products.

(i) Gas Gasvolatile at -196°C , 34.1 Ncc. (gave no carbon dioxide on ignition with excess oxygen. Therefore, it was hydrogen).

(ii) Solid

Found: hydrolysable hydrogen, 2.11; ethyl, 9.03; Be 11.2%
Figures correspond to $\text{Et}_{0.257}\text{Be.H}_{1.74}$ approximately 22 weight% pure.

The infrared spectrum of the solid recorded as a nujol mull, showed only one main feature, a broad absorption centred at 1743 cm.^{-1} .

(iii) Solution

The solution was separated into 3 fractions as previously described.

Fraction involatile -196°C :

This fraction was shown to be hexane by examination of its infrared spectrum.

Fraction involatile at -50°C :

This infrared spectrum of this fraction was similar to that of tetraethyltin, but showed absorptions at 1801 cm.^{-1} and 558 cm.^{-1} . The former is attributed to $\nu(\text{Sn-H})$ and the fraction assumed to be a mixture of tetraethyltin and triethylstannane.

Fraction involatile at 25°C

This fraction, a viscous, oily liquid, was shown, by examination of its infrared spectrum, to be mainly hexaethyl di-tin. However, a rather broad absorption at 1796 cm.^{-1} is attributed to an involatile tin hydride, probably a decomposition product of triethylstannane.

(iv) Examination of hydrolysis solution of solid

The solution resulting from hydrolysis of the solid product was extracted with three 5 ml. portions of ether. The combined extracts were dried over anhydrous magnesium sulphate and ether removed under reduced pressure. The infrared spectrum of the residue, a very small amount of white solid, was examined as a nujol mull. The spectrum was very similar to that of hexa-ethyl di-tin and the residue was assumed

to be an ethyltin derivative.

Thermal decomposition of triethylstannane

Triethylstannane (4.60g .) was condensed into a tube fitted with break-off side-arm. The tube was sealed and heated at 75°C for 36 hours. The tube was opened via the break-off side-arm into a high vacuum line and gas evolved collected, measured and identified. The residue, a colourless liquid, was pumped to remove all volatile components leaving a colourless viscous oil.

Analysis of products

- i) Gas involatile at -196°C , 107.4 Ncc. (Hydrogen, gave no carbon dioxide on igniting with excess oxygen)

Gas volatile at -78°C , none.

- ii) Volatile component of residue

Infrared examination of this fraction showed it to be triethylstannane.

- iii) Involatile residue

The infrared spectrum of this fraction showed absorptions attributable to hexa-ethyl di-tin and triethylstannane. However, since it is involatile at room temperature it is assumed to be a mixture of hexa-ethyl di-tin and an involatile ethyltin hydride derivative.

Reactions of ethylberyllium hydride-trimethylamine

Dimethylamine

Dimethylamine (33.1 Ncc., 0.00148 mole.) was condensed on to ethylberyllium hydride-trimethylamine (0.145g., 0.00148 mole.) in a 50 ml. two-necked flask connected to a high-vacuum line. The dimethylamine was apparently absorbed to give a solid product which melted with evolution of non-condensable gas. On warming to room temperature gas evolution was vigorous and complete in 15 minutes. All volatile products were collected and measured in the vacuum line.

Found: Gas volatile at -196°C , 15.7 Ncc's, (hydrogen, gave no carbon dioxide on igniting with excess oxygen)

Gas volatile at -96°C , 16.1 Ncc's (0.0074 mole)
(ethane, identified by infrared spectrum),

The infrared spectrum of the oily residue was recorded and showed a sharp absorption at 1340 cm.^{-1} . No further experiments were carried out on this product, since the elimination both hydrogen and ethane indicated that at least two products had been formed.

Diethylmercury

Trimethylamine-ethylberyllium hydride (0.0948g., 0.000968 mole.) was introduced into a reaction tube fitted with break-off side-arm. Diethylmercury (0.25g., 0.000968 mole.) was condensed into the tube; the tube evacuated, sealed and the reactants allowed to warm to room temperature. No visible signs of reaction were observed. However, on warming to 60°C gas evolution was observed and the mixture became liquid and gas evolution ceased. When cooled to room temperature the reaction mixture consisted of a colourless liquid and metallic mercury.

The tube was opened via the break-off side-arm and all volatile components collected. The residue was mercury.

Found: Gas volatile at -196°C , none.

Gas volatile at -78°C , 21.0 Ncc., 0.000968 mole.

(ethane, identified by infrared spectrum,)

The liquid product involatile at -78°C , but volatile at room temperature, was shown to be diethylberyllium-trimethylamine, $\text{Et}_2\text{Be.NMe}_3$, 98. by comparison of its infrared spectrum with that of a known sample.

N,N,N',N' - Tetramethyl-o-phenylene diamine

N,N,N',N' tetramethyl-o-phenylenediamine (0.17g., 0.001 mole) were added by syringe to ethylberyllium hydride-trimethylamine (0.0878g. 0.000896 mole.) in a 50 ml. two-necked flask. The mixture was allowed to stand at room temperature for 15 minutes, during which time no visible sign of reaction was observed. On heating at 50°C for one hour the hydride complex slowly dissolved in the amine and a gas was slowly evolved. The mixture was heated for a further 2 hours at 50°C , gas evolution, although very slow, continued throughout this period. The gas was collected, measured and identified in the vacuume line.

Found: Gas volatile -40°C , 14.5 Ncc., (trimethylamine, identified by infrared spectrum), 0.0006 mole.)

The residue was a viscous oil. The infrared spectrum of the oil showed an absorption at 1325 cm.^{-1} . No attempt to purify the oil was made.

Reactions of diphenylberyllium with donor molecules

N,N,N',N' - Tetramethyl-o-phenylenediamine

Tetramethyl-o-phenylenediamine (0.76g., 0.00457 mole.) was added, in 5 ml. of benzene, to diphenylberyllium (0.0767g, 0.00471 mole.) in 10 ml. of a 1:1 benzene/ether mixture contained in one limb of a double Schlenk tube. After complete mixing the solution was pumped to low volume when colourless crystals were deposited. The crystals were filtered on the sinter, washed with hexane and pumped dry.

On heating in a sealed tube, under nitrogen, the crystals melted irreversibly at 260-261°C, with shrinking at 248-249°C. When heated in high vacuum, amine was evolved at 70-75°C (identified by its infrared spectrum). If heated rapidly to 160-165°C the product sublimed slowly, accompanied by loss of amine. The product decomposed slowly in air and was slowly hydrolysed by water (Found: hydrolysable phenyl, 47.0; Be, 2.79; M, cryoscopically in benzene, 327, 324 in 1.06, 0.53 weight % solutions respectively. $C_{22}H_{26}BeN_2$ requires hydrolysable phenyl, 47.1; Be, 2.82; M 327)

The molecular weight measurements correspond to degrees of association of 1.00, 0.99 respectively.

N,N,N',N' - Tetramethylethylenediamine

A solution of diphenylberyllium (1.09g, 0.00667 mole.) in 10 ml. of a 1:1 benzene/ether mixture was transferred by syringe into one limb of a double Schlenk tube. Tetramethylethylenediamine (0.765g., 0.0067 mole.) was added in 5 ml. of benzene. A slightly exothermic reaction occurred, with deposition of a small amount of crystalline solid. Hexane 5 ml. was added and the mixture boiled giving a clear solution. On cooling colourless crystals (plates) were deposited. These were filtered on the sinter, washed with hexane and pumped dry.

When heated in a sealed tube, under nitrogen, the crystals decomposed at 150-156°C, with shrinking at 98-99°C.

The product slowly turned white in air and decomposed slowly in water. (Found: diamine, 41.0., Be, 3.25; M, cryoscopically in benzene, 284, 278 in 1.10, 0.55 weight % solutions. $C_{18}H_{26}N_2Be$ requires diamine, 41.6;; Be, 3.23%; M, 279)

The molecular weight measurements correspond to degrees of association of 1.02, 1.00 respectively.

1,2 - Dimethoxyethane

A solution of diphenylberyllium (1.36g., 0.00837 mole.) in ether (10 ml.) was transferred by syringe to one limb of a double Schlenk tube. Addition of 1,2-dimethoxyethane (0.88 g., 0.00979 mole.) in ether (5 ml.) resulted in warming of the reaction mixture. The clear solution was pumped to half-volume, whereupon crystals were deposited. The small, needle-like crystals were filtered on the sinter and pumped dry.

When heated in a sealed tube, under nitrogen, the crystals melted reversibly at 143-145°C, with shrinking at 130-135°C. When exposed to the air the crystals slowly turned liquid, and decomposed very slowly in water. (Found: hydrolysable, phenyl, 59.8; Be, 3.59; M, cryoscopically in benzene, 258, 241 in 1.11, 0.55 weight % solutions respectively. $C_{16}H_{20}BeO_2$ requires hydrolysable phenyl, 60.9; Be, 3.58; M, 253)

The molecular weight measurements correspond to degrees of association of 1.02, 0.97 respectively.

2,5 - Dithiahexane

Diphenylberyllium (1.39g., 0.00852 mole.) was transferred, in a small glass tube under nitrogen, to one limb of a double Schlenk tube, 2,5-Dithiahexane (1.04g., 0.00852 mole.) in benzene (15 ml.) was added by syringe. The reaction mixture was boiled and stirred for ten minutes during which time the diphenylberyllium dissolved giving a clear, colourless solution. Hexane (5 ml.) was added and the solution allowed to cool and stand overnight. Colourless crystals (needles) were slowly deposited, which were filtered on the sinter and pumped dry.

When heated in a sealed tube, the crystals melted reversibly at 127-128°C. When exposed to air the crystals turned white, and reacted slowly with dilute sulphuric acid, warming to 60°C being necessary to completely dissolve the solid. (Found: Be, 3.13; disulphide (weighed as the PdCl₂ complex), 41.9; M, cryoscopically in benzene, 279, 277 in 1.59, 0.80 weight % solutions respectively. C₁₆H₂₆S₂Be requires Be, 3.16; disulphide, 42.8; M, 285)

The molecular weight measurements correspond to degrees of association of 0.98, 0.97 respectively.

Diethyl ether

Diphenylberyllium (1.62g., 0.0099 mole.) was dissolved in diethyl ether (20 ml.) and the solution transferred to one limb of a double Schenk tube. On cooling to -78°C, long, needle-like crystals were deposited, which were filtered on the sinter and pumped dry.

When heated in a sealed tube, under nitrogen, the crystals melted irreversibly at 55.59°C. The crystals reacted slowly with water and were unaffected by short exposure to air. (Found: hydrolysable phenyl, 61.6; Be, 3.60 %; ratio of phenyl: beryllium = 2.00 : 1. C₂₀H₃₀O₂Be, Ph₂Be.(OEt)₂)₂, requires hydrolysable phenyl, 49.5; Be, 2.9 %. C₁₆H₂₀O Be, Ph₂Be.OEt₂, requires hydrolysable phenyl, 65.0; Be, 3.79%)

Trimethylamine

Diphenylberyllium (0.045g., 0.00518 mole.) was transferred to one limb of a double Schenk tube in a small weighing-tube. Benzene (15 ml.) was added and excess trimethylamine (400.Ncc) was condensed on to the mixture. On allowing to warm to room temperature and stirring for 15 minutes, the diphenylberyllium slowly dissolved. When hexane (10 ml.) was added and the solution allowed to stand, white, needle-like crystals were deposited. The crystals were filtered on the sinter and pumped dry.

When heated in a sealed tube, under nitrogen, the product melted at 65-67.5°C. (Found: hydrolysable phenyl, 64.8; Be, 3.88%; ratio of phenyl: beryllium = 1.99 : 1. C₁₈H₂₈N₂Be, Ph₂Be.(NMe₃)₂, requires hydrolysable phenyl, 56.8; Be, 3.21%. C₁₅H₁₉N Be, Ph₂Be.NMe₃, require hydrolysable phenyl, 69.4; Be, 4.06 %.)

Tensimetric titrations of diphenylberyllium with donor molecules

The reactions of diphenylberyllium with diethyl ether and trimethylamine resulted in the isolation of products, which correspond to compositions intermediate between the 2:1 and 1:1 coordination complexes. These unexpected results prompted the tensimetric investigations of various diphenylberyllium/ donor molecules systems. The equilibrium pressure (pmm.) at 0°C was plotted against the mole ratio of donor molecule against diphenylberyllium.

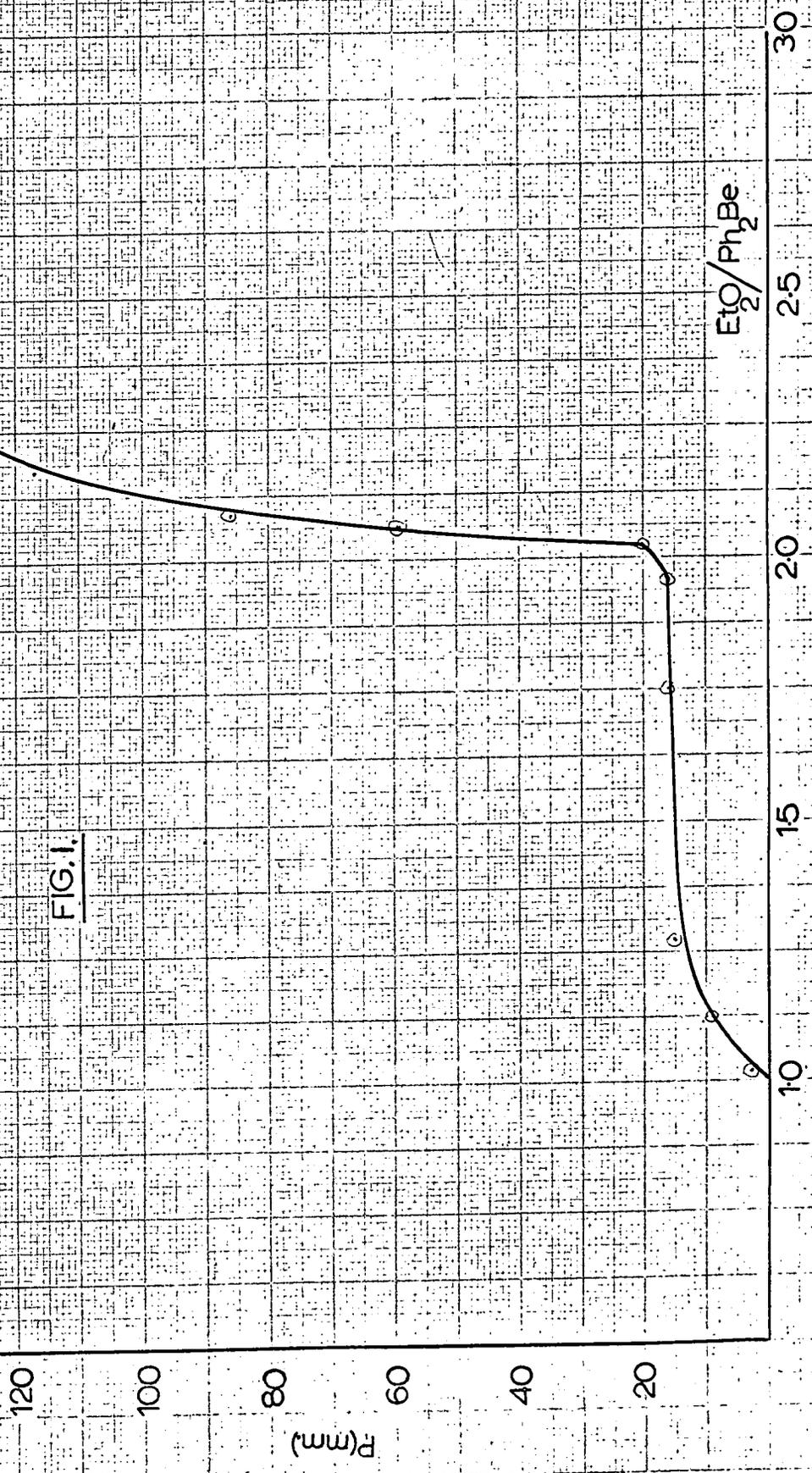
Tensimetric titration of diphenylberyllium with diethyl ether at 0°C

Weight of diphenylberyllium = 0.5539g. (75.9 Ncc.)

<u>Vol. Et₂O (cc)</u>	<u>P(mm)</u>	<u>Et₂O/Ph₂Be</u>
259.3	170.1	3.41
210.8	166.2	2.78
198.0	165.7	2.61
163.8	118.3	2.16
158.4	86.1	2.09
149.2	117.3	1.97
146.5	17.1	1.93
130.5	16.8	1.72
117.9	16.6	1.55
104.1	15.6	1.37
85.5	11.6	1.13
79.6	3.21	1.05
77.4	0.005	1.02
76.4	0	1.01

Tensimetric Titration of EtO_2
with PhBe_2 at 0°C .

FIG. 1.



The equilibrium pressure P(mm.)/mole ratio plot is shown in fig. I

Tensimetric titration of diphenylberyllium with diethyl sulphide at 0°C

Weight of diphenylberyllium = 0.7468g. (102.4 Ncc.).

<u>Vol. Et₂S (cc)</u>	<u>P(mm)</u>	<u>Et₂S/Ph₂Be</u>
274.0	19.1	2.68
238.0	17.8	2.32
226.4	17.2	2.21
202.9	16.2	1.98
190.0	14.8	1.86
182.0	13.8	1.78
172.5	11.4	1.68

<u>Vol. Et₂S (cc)</u>	<u>P(mm)</u>	<u>Et₂S/Ph₂Be</u>
167.5	10.2	1.64
162.0	6.93	1.58
160.0	1.56	1.56
157.8	0.01	1.54
157.0	0	1.53

The equilibrium pressure P(mm.)/mole ratio plot is shown in fig. II.

Tensimetric titration of diphenylberyllium with dimethyl ether at 0°C

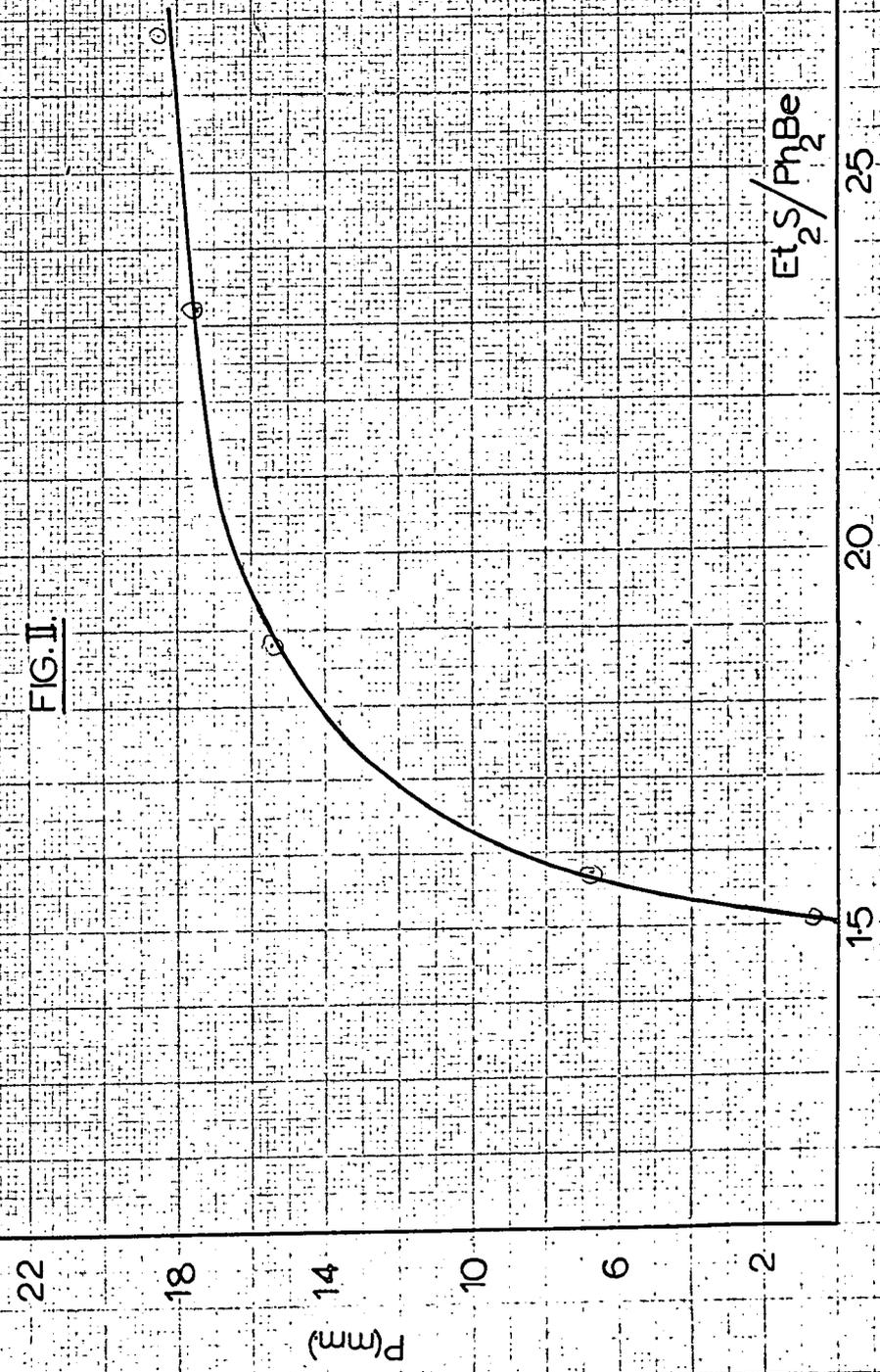
Weight of diphenylberyllium = 0.5229 g. (71.9 Ncc.)

<u>Vol. Me₂O (cc)</u>	<u>P(mm).</u>	<u>Me₂O/Ph₂Be</u>
164	74.3	2.28
148	31.1	2.06
144	0.53	2.00
141	0	1.98

The equilibrium pressure P(mm)/mole ratio plot is shown in fig. III.

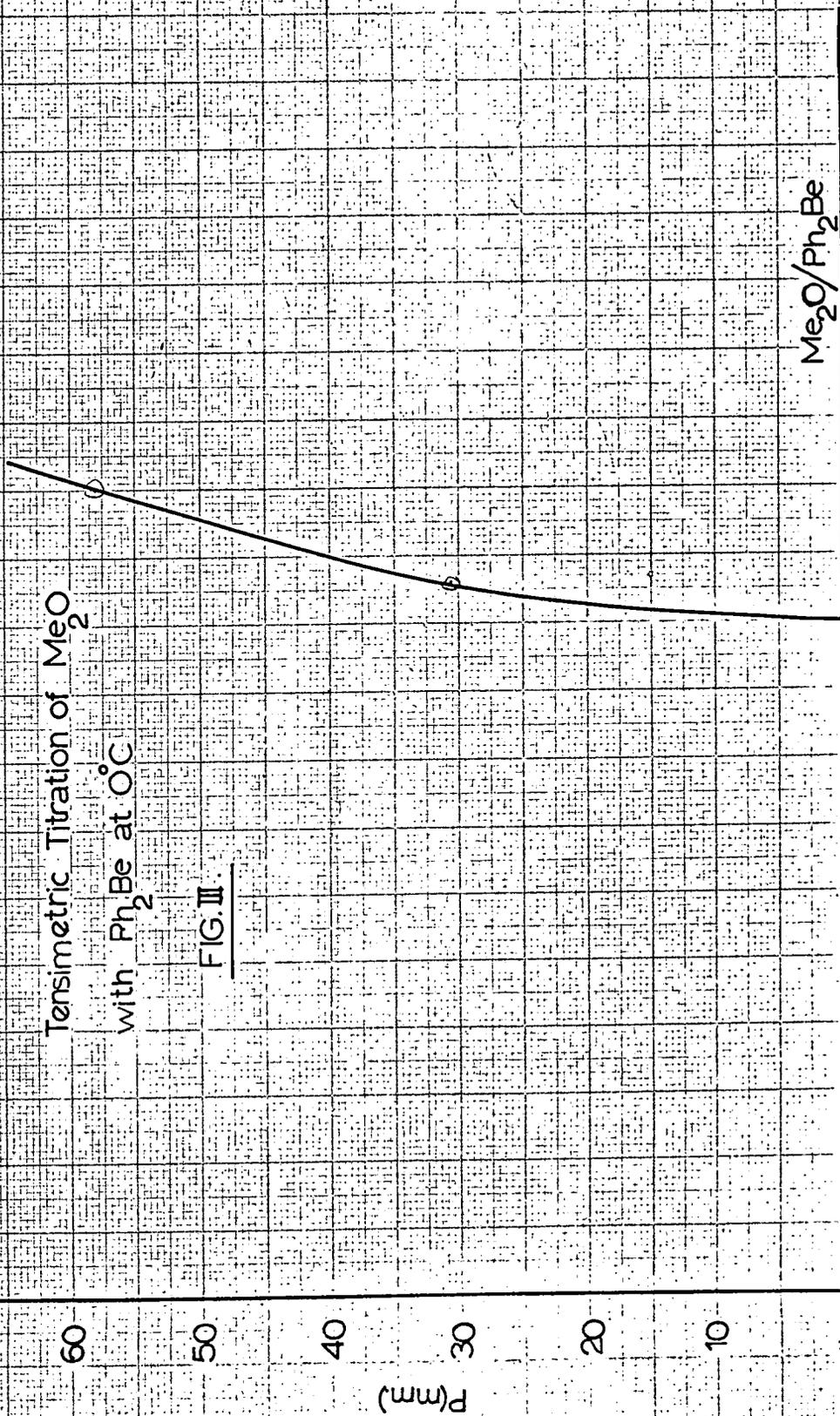
Tensimetric Titration of Et_2S
with Ph_2Be at 0°C

FIG. I



Tensimetric Titration of Me_2O
with Ph_2Be at 0°C

FIG. III



Tensimetric titration of diphenylberyllium with dimethyl-sulphide at 0°C

Weight of diphenylberyllium = 0.5509 g. (75.7 Ncc.)

<u>Vol. Me₂S(cc)</u>	<u>P(mm)</u>	<u>Me₂S/Ph₂Be</u>
224.1	142.5	2.96
203.6	141.5	2.69
188.5	124.8	2.49
182.5	113.0	2.41
173.3	78.6	2.29
169.8	58.1	2.24
167.8	46.8	2.22
163.7	20.4	2.16
160.7	15.0	2.12
158.5	6.05	2.09
155.0	0	2.03

The equilibrium pressure P(mm.)/mole ratio plot is shown in fig. IV.

Tensimetric titration of diphenylberyllium with trimethylamine at 0°C

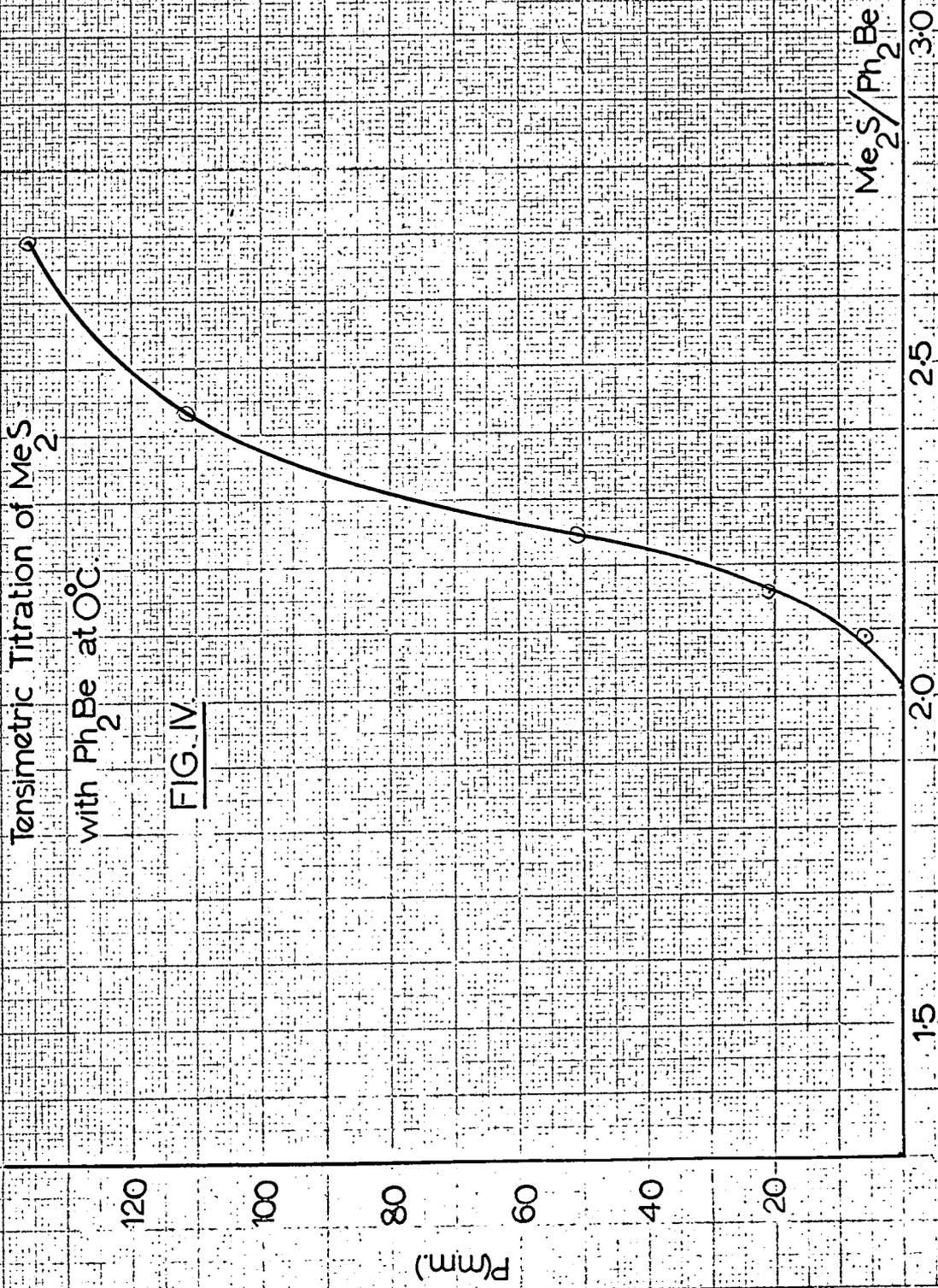
Weight of diphenylberyllium = 0.4674g. (64.2 Ncc.)

<u>Vol. Me₃N(cc)</u>	<u>P(mm)</u>	<u>Me₃N/Ph₂Be</u>
200.8	508.5	4.69
155.9	194.2	2.43
137.5	83.6	2.14
129.5	39.0	2.02
122.6	15.6	1.91
119.5	0.79	1.86
112.0	0.50	1.75
101.8	0.48	1.59
94.3	0.03	1.47
91.3	0.02	1.42
63.1	0	0.98

The equilibrium pressure P(mm)/mole ratio plot is shown in fig. V.

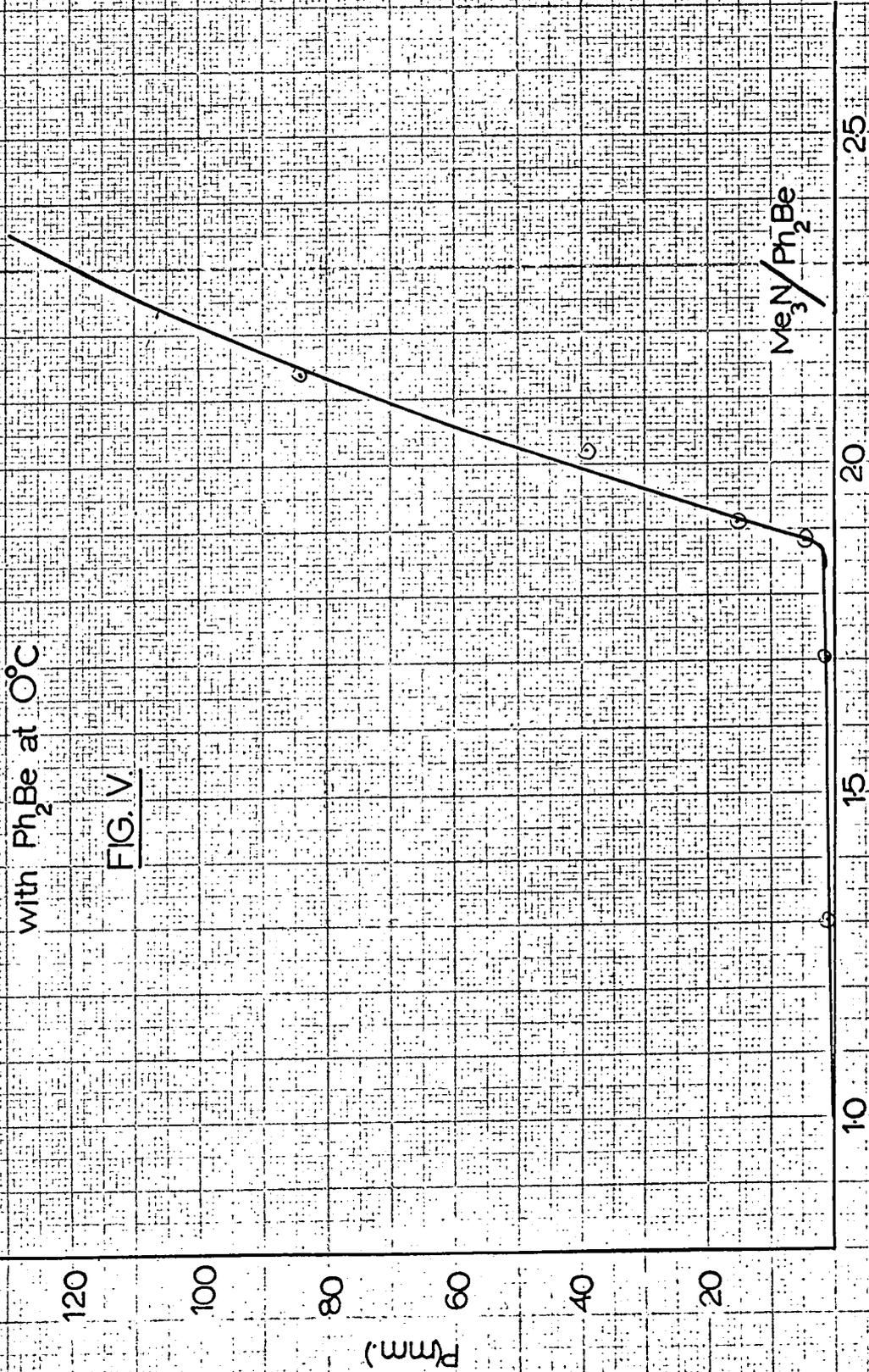
Tensimetric Titration of Me_2S
with Ph_2Be at 0°C .

FIG. IV



Tensimetric Titration of Me_3N
with Ph_2Be at 0°C

FIG. V.



Tensimetric titration of diphenylberyllium with trimethylphosphine at 0°C

Weight of diphenylberyllium = 0.6136g. (84.3 Ncc.)

<u>Vol. Me₃P(cc.)</u>	<u>P(mm.)</u>	<u>Me₃P/Ph₂Be</u>
196	73.6	2.33
179	28.7	2.12
170	1.65	2.02
168	0	1.99

The equilibrium pressure P(mm.)/mole ratio plot is shown in fig. VI.

Tensimetric Titration of MeP_3

with Ph_2Be at 0°C .

FIG. VI

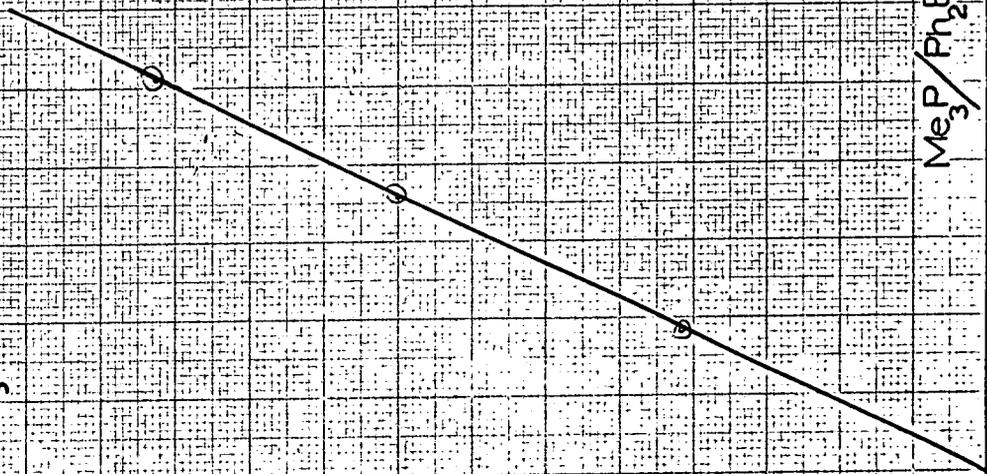
80
60
40
20
P(mm)

15

20

25

$\text{MeP}_3/\text{Ph}_2\text{Be}$



Preparation of diphenylberyllium-bis(trimethylphosphine)

Diphenylberyllium (15 ml. of a 0.51 M solution in ether, 0.00765 mole.) was transferred to one limb of a double Schlenk tube. The solvent ether was removed under reduced pressure and the white, crystalline residue was pumped at 50°C for two hours. Toluene (10 ml.) was added to the residue, and trimethylphosphine (800 Ncc., 0.0356 mole.) was condensed on to the mixture. On warming to room temperature, the solid slowly dissolved to give a clear, colourless solution. Hexane (10 ml.) was added and on cooling to -78°C a white crystalline solid (needles) was slowly deposited. The crystals were filtered on the sinter, washed once with hexane saturated with trimethylphosphine, and pumped dry at -15°C.

When heated in a sealed tube, under nitrogen, the crystals softened at 80-82°C and melted with decomposition at 132-134°C. (Found: Be, 2.90; phosphine, 47.8; M, cryoscopically in benzene, 271, 236 in 1.32, 0.66 weight % solutions respectively. $C_{18}H_{28}P_2Be$ requires Be, 2.86; phosphine, 48.3; M, 317)

Preparation of diphenylberyllium-bis(dimethyl sulphide)

3 Diphenylberyllium (15 ml. of a 0.51 M solution in ether) was transferred to one limb of a double Schlenk tube. The solvent ether was removed under reduced pressure and the residue pumped at 50°C for two hours. Dimethyl sulphide (10 ml.) was added and the mixture stirred at room temperature for one hour. The residue slowly dissolved to give a clear, colourless solution. The solution was cooled to -78°C and kept at this temperature overnight. Colourless, plate-like crystals were deposited, which were filtered on the sinter and pumped dry at -15°C.

The crystals melted at 111-113°C with decomposition, when heated in a sealed tube, under nitrogen. (Found: Be, 3.15; sulphide, 42.8; M, cryoscopically in benzene, 200, 181, in 1.48, 0.74 weight % solutions respectively. $C_{16}H_{22}S_2Be$ requires Be, 3.14; sulphide, 43.2; M, 287)

Measurement of the heats of dissociation of diphenylberyllium coordination complexes.

The investigation was confined to the bis-complexes formed by reaction of dimethyl ether, dimethyl sulphide, trimethylamine and trimethylphosphine with diphenylberyllium.

Excess donor compound was allowed to equilibrate with a known weight of diphenylberyllium over a period of several days. The excess donor compound was then removed from the mixture, cooled at -15°C until the mole ratio of donor/diphenylberyllium was 2:1. The remaining bis-complex was slowly heated from -15°C to about 70°C , the equilibrium dissociation pressure at various temperatures was measured.

A graph of $\log_{10} \text{Pmm.}$, dissociation pressure mm;1 versus $1/T$ ($^{\circ}\text{K}^{-1}$) was plotted for each complex. In each case a linear plot was obtained, and by measurement of the slope the heat of dissociation over the temperature range investigated was calculated:

$$\Delta H_{\text{DISS}} = 2.303 \times R \times \text{Slope} \quad \text{Kcal. mole.}^{-1}$$

Dimethyl ether

Weight of diphenylberyllium = 0.5229 g. (71.9 Ncc)

Volume of dimethyl ether = 141.0 Ncc.

Mole ratio dimethyl ether/diphenylberyllium = 1.97 : 1.

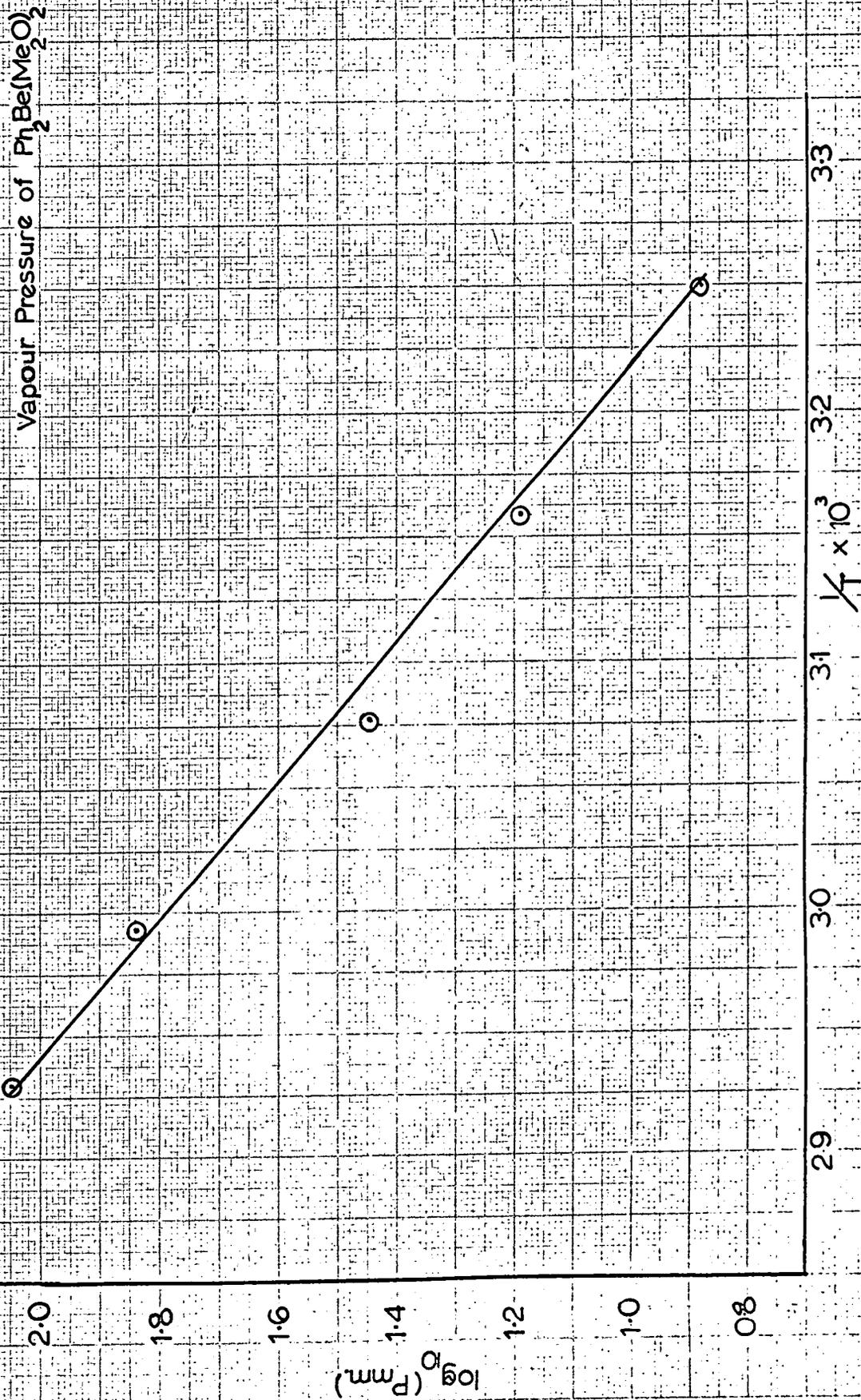
Pmm.	$\log (\text{Pmm.})$	T $^{\circ}\text{K.}$	$1/T$ $^{\circ}\text{K}^{-1}.$
7.6	0.8808	307.5	3.252×10^{-3}
13.1	1.1173	316.6	3.159×10^{-3}
26.9	1.4298	325.1	3.076×10^{-3}
69.2	1.8401	335.0	2.985×10^{-3}
111.2	2.0461	340.7	2.935×10^{-3}

The plot of $\log_{10} (\text{Pmm.})$ versus $1/T$ is shown in fig. VII

$$\text{Slope} = 3.941 \times 10^3 \quad ^{\circ}\text{K}$$

$$\text{Thus } \Delta H_{\text{DISS}} = 17.9 \text{ Kcal. mole}^{-1}. \quad (0-70^{\circ}\text{C})$$

FIG. VII



Dimethyl sulphide

Weight of diphenylberyllum = 0.4759 g. (65.4 Ncc)

Volume of dimethyl sulphide = 129.0 Ncc.

Mole ratio dimethyl sulphide/diphenylberyllum = 1.98 : 1

Pmm.	\log_{10} (Pmm)	T °K	$1/T$ °K ⁻¹ .
96.22	1.9833	307.0	3.257×10^{-3}
127.6	2.1058	311.4	3.210×10^{-3}
240.6	2.3813	322.4	3.102×10^{-3}
300.1	2.4772	326.4	3.064×10^{-3}

The plot of \log_{10} (Pmm.) versus $1/T$ is shown in fig VIII.

Slope = 2.619×10^3 °K

Thus $\Delta H_{DISS} = 12.0$ Kcal. mole.⁻¹ (0-50°C)

Trimethylamine

Weight of diphenylberyllum = 0.5624 g. (77.3 Ncc.)

Volume of trimethylamine = 155.0 Ncc.

Mole ratio trimethylamine/diphenylberyllum = 2.00 : 1.

Pmm.	\log_{10} (Pmm.)	T °K.	$1/T$ °K ⁻¹ .
1.52	0.1818	273.2	3.6605×10^{-3}
5.05	0.7033	299.1	3.343×10^{-3}
7.93	0.8993	304.1	3.288×10^{-3}
15.57	1.1923	312.2	3.204×10^{-3}
31.65	1.5004	322.1	3.105×10^{-3}
69.01	1.8389	331.0	3.021×10^{-3}
203.5	2.3086	344.8	2.901×10^{-3}

The plot of \log_{10} (Pmm.) versus $1/T$ is shown in fig. IX.

Slope = 3.656×10^3 °K

Thus $\Delta H_{DIS} = 16.7$ Kcal. mole.⁻¹ (0-70°C)

FIG. VIII

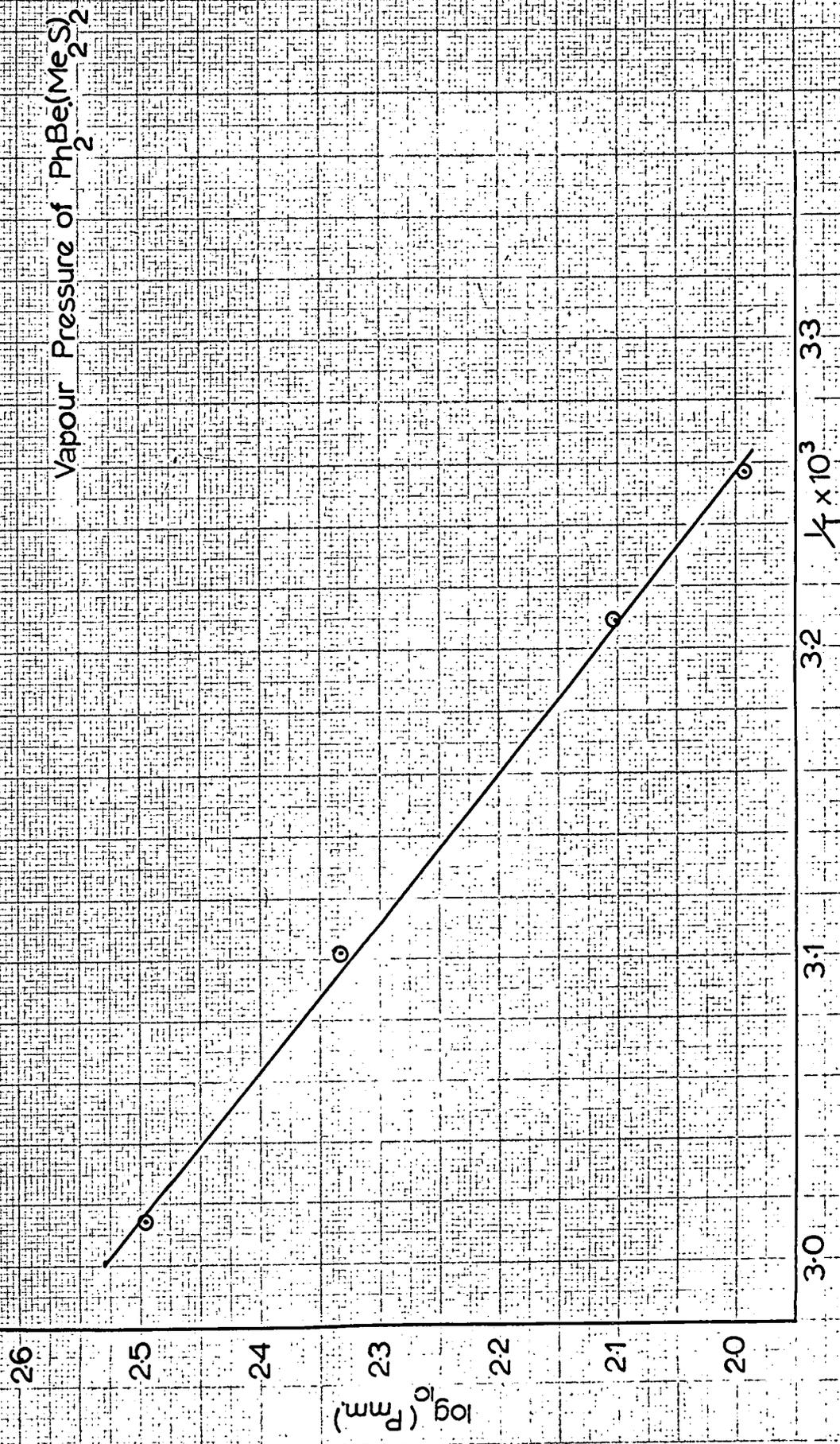
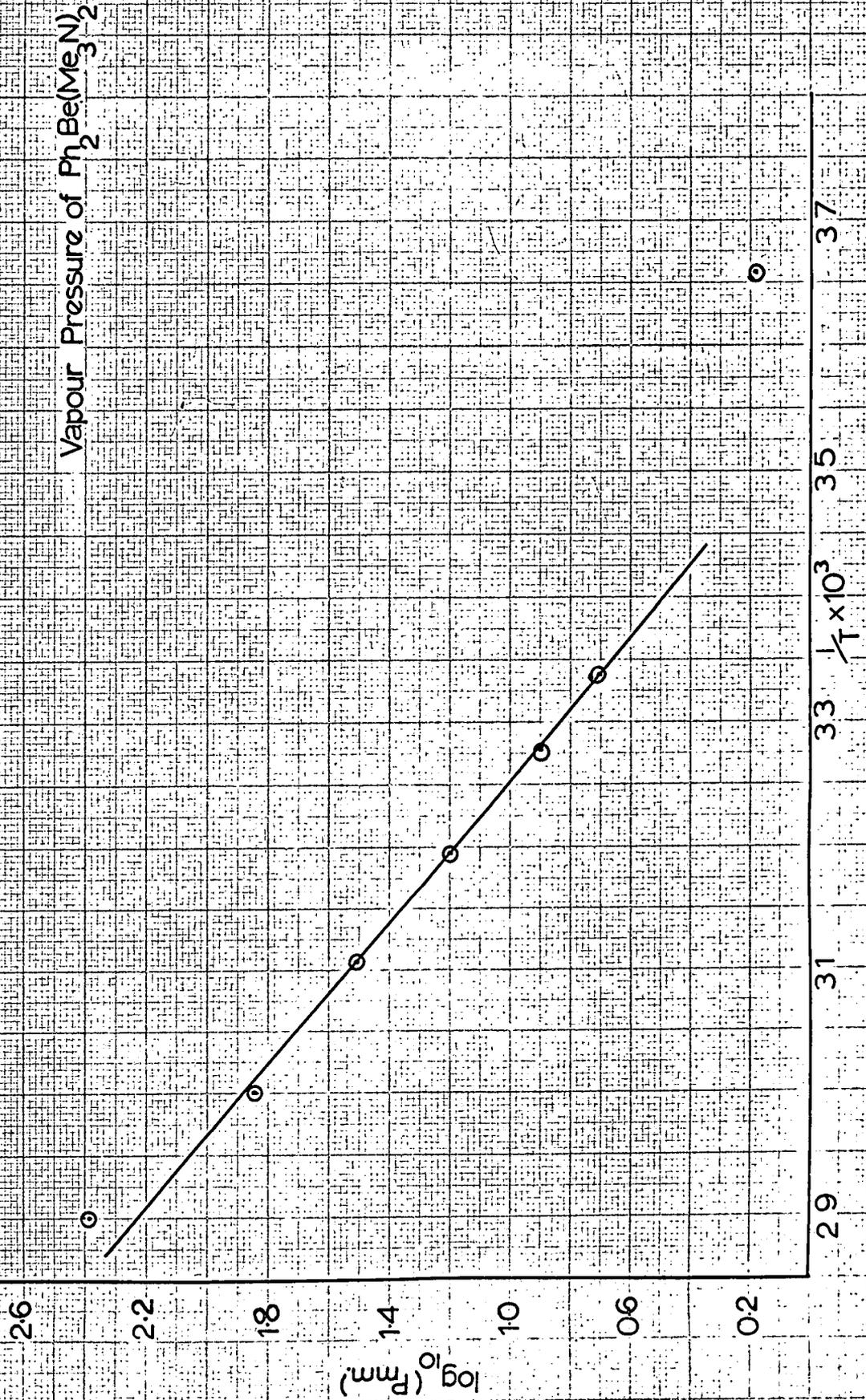


FIG. IX.



Trimethylphosphine

Weight of diphenylberyllium = 0.6136 g. (84.3 Ncc.)

Volume of trimethylphosphine = 168.0 Ncc.

Mole ratio trimethylphosphine/diphenylberyllium = 1.99 : 1.

Pmm.	Log ₁₀ (Pmm)	T °K	1/T °K. ⁻¹
5.51	0.7412	311.6	3.209 x 10 ⁻³
13.93	1.1440	330.7	3.024 x 10 ⁻³
22.89	1.3596	344.6	2.902 x 10 ⁻³
35.49	1.5501	359.7	2.788 x 10 ⁻³

The plot of log₁₀(Pmm) versus 1/T is shown in fig X.

Slope = 1.902 x 10³ °K

Thus $\Delta H_{DISS} = 8.68 \text{ Kcal. mole.}^{-1} (0-86^{\circ}\text{C})$

FIG. X.

Vapour Pressure $\text{PhBe}(\text{MeF})_3$

1.7

1.5

$\log_{10}(P_{\text{mm}})$

1.3

1.1

0.9

0.7

28

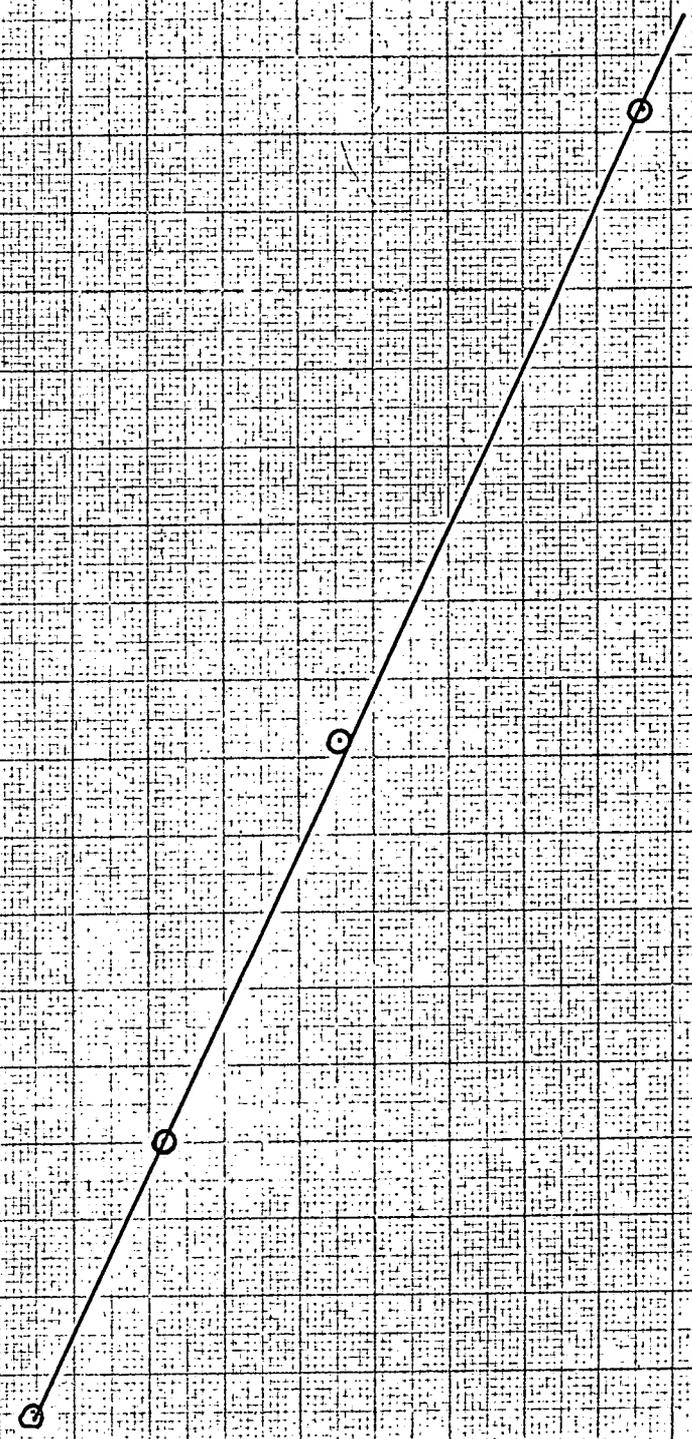
29

30

31

32

$\frac{1}{T} \times 10^3$



Reactions of diphenylberyllium with donor molecules containing active hydrogen

N,N,N' - Trimethylethylenediamine

Diphenylberyllium (2.402g., 0.0147 mole), dissolved in 10ml. of ether was transferred to one limb of a double Schlenk tube. N,N,N' - Trimethylethylenediamine (1.49g., 0.0146 mole), in 10ml. of ether, was added dropwise with shaking. An exothermic reaction was observed and a white crystalline solid was slowly precipitated. The solid was filtered from the solution and recrystallised from 15ml. of a 1:1 benzene/hexane mixture. The product which crystallised as small needles on cooling to room temperature, was filtered on the sinter and pumped dry.

On heating in a sealed tube, under nitrogen, the product decomposed at 255-256°C. The product reacted very slowly with water and it was found necessary to heat the product with dilute sulphuric acid to complete decomposition. (Found: Be, 4.80; diamine, 53.8; M, cryoscopically in benzene, 375,380 in 1.38, 0.69 weight % solutions. $C_{11}H_{20}N_2Be$ requires Be, 4.81; diamine, 54.0, M, 189).

The molecular weight measurements correspond to degrees of association of 1.99, 2.01 respectively.

Diphenylamine

A solution of diphenylberyllium (2.19g., 0.0135 mole), in 10ml. of diethyl ether, was transferred to one limb of a double Schlenk tube by syringe. Diphenylamine (2.27g., 0.0134 mole.), in 10ml. of toluene, was added slowly with stirring to the diphenylberyllium solution. An exothermic reaction was observed and it was found necessary to cool the reaction mixture during the reaction. The solution was pumped to low volume and hexane (10ml.) was added. On cooling to -78°C, a crystalline product was slowly precipitated. The crystals were filtered on the sinter and pumped dry.

The crystals were very sensitive to air and water. When exposed to air the crystals immediately turned green and the colour slowly deepened to a dark blue. Reaction with water was very vigorous, and it was found necessary to use 2 - methoxyethanol when hydrolysing for analysis. When heated in a sealed tube, under nitrogen, the crystals softened in the range 120-130°C and melted, with decomposition, at 260-262°C. (Found: Be, 3.52; amine, 66.20; M, cryoscopically in benzene, 500, (f₉₁ in 1.69, 0.85 weight % solutions. $C_{18}H_{15}BeN$ requires Be, 3.54; amine, 66.53; M, 254).

The molecular weight measurements correspond to degrees of association of 1.99, 1.98 respectively.

Reaction of phenyl(diphenylamino)beryllium with 2,2'-bipyridyl

Phenyl(diphenylamino)beryllium (0.914g., 0.0036 mole.) was transferred, as a solution in 20ml. of benzene, to one limb of a double Schlenk tube by syringe. A solution of 2,2'-bipyridyl (0.57g., 0.00358 mole) in 10ml of benzene was added slowly with stirring. A deep red colour was immediately formed and a deep red crystalline solid slowly precipitated. The solid was found to be moderately soluble in boiling benzene, and by several extractions with boiling benzene the product was extracted into the other limb of the double Schlenk tube. However, when the solution was allowed to cool, the crystals filtered on the sinter and pumped dry; the product was found to be a mixture of red crystals and pale cream crystals. Several attempts to obtain a pure product by recrystallisation from benzene were made, but the resulting product was always a mixture of red crystals and pale cream crystals. Analysis of solid suggested that the product was a mixture. (Found: Be, 2.69; bipy, 42.6; ratio Be: bipy = 1.2:1. $PhBe(Bipy)Nph_2$ requires Be, 2.15; bipy, 39.2%; ratio Be:bipy = 1:1).

Dimethylamine

Diphenylberyllium (2.15g., 0.0132 mole), dissolved in 20ml. of a 1:1 toluene/ether mixture, was transferred to one limb of a double Schlenk tube. The double Schlenk tube was attached to a high vacuum line, evacuated and dimethylamine (295.0 Ncc., 0.0131 mole) was condensed onto the diphenylberyllium solution cooled to -196°C . On allowing the solution to warm slowly to room temperature, a white solid was precipitated at -78°C . The precipitate slowly dissolved as the solution was stirred and warmed at 40°C . On cooling the solution to -78°C it remained clear and no solid precipitated. The solution was pumped to low volume (8ml.) and 10ml. of dry hexane were added. The solution was cooled to -78°C and on allowing to stand, at this temperature, overnight long needle-like, colourless crystals crystallised from the solution. The crystals were filtered onto the sinter and pumped.

On heating in a sealed tube, under nitrogen, the crystals melted at 154°C . The crystals decomposed quickly when exposed to air, and were hydrolysed quite vigorously by water. (Found: Be, 6.91: amine, 33.8: M, cryoscopically in benzene, 391,409 in 1.49, 0.174 weight % solutions respectively. $\text{C}_8\text{H}_{11}\text{BeN}_2$ requires Be, 6.92: amine, 33.9: M, 130). The molecular weight measurements correspond to degrees of association of 3.01, 3.14 respectively.

Methanol

A solution of diphenylberyllium (2.32g., 0.0143 mole) in 10ml. of a 1:1 benzene/ether mixture was transferred to one arm of a double Schlenk tube. Methanol (0.57ml., 0.0142 mole) in 5ml. of ether was added dropwise with stirring. An exothermic reaction was observed and it was necessary to cool the reaction mixture to prevent loss of solvent. On pumping the resulting clear solution to low volume a viscous oil was obtained. The oil was dissolved in 5ml. of

toluene and on addition of 10ml. of hexane and cooling to -78°C a white crystalline solid was precipitated. The solid was filtered onto the sinter and pumped dry.

When heated in a sealed tube, under nitrogen, the crystals melted reversibly at $53-55^{\circ}\text{C}$. When exposed to air the solid slowly decomposed, and reacted fairly vigorously with water. (Found: Be, 4.95; phenyl, 45.1; (ratio phenyl: Be, 1:1) $\text{C}_7\text{H}_8\text{BeO}$, PhBeOME , requires Be, ~~7.64~~: phenyl; ~~64.9~~).

On the basis of the analytical results, it was concluded that some ether is held by the phenylberyllium methoxide. This conclusion was confirmed by examination of the infrared spectrum of the solid. To overcome this complication the reaction was repeated in a non-etheral solvent.

A suspension of diphenylberyllium (3.81g., 0.023 mole) in 10ml. of benzene was transferred to one arm of a double Schlenk tube. Methanol (0.94ml., 0.023 mole) in 10ml. of benzene was added very slowly, with stirring. An exothermic reaction was observed and the diphenylberyllium slowly dissolved, eventually giving a clear solution. On addition of hexane, 15ml. a white crystalline solid was slowly precipitated which was filtered onto the sinter and pumped dry.

When heated in a sealed tube, under nitrogen, the solid melted reversibly at $177-178^{\circ}$, with shrinking at $168-170^{\circ}\text{C}$. The solid was decomposed violently by water and decomposed with immediate charring when exposed to air. (Found: Be, 7.76; phenyl, 64.7; M, cryoscopically in benzene, 450, 452 in 1.85, 0.93 weight % solutions respectively. $\text{C}_7\text{H}_8\text{BeO}$ requires Be, 7.69; phenyl, 64.9; M, 117.) The molecular weight measurements correspond to degrees of association of 3.85, 3.86 respectively.

Reaction of phenylberyllium chloride with sodium triethylboron hydride

Diphenylberyllium (63.0 ml. of a 0.51 M solution in ether, 0.0321 mole.) was transferred by syringe to one limb of a large Schlenk tube. A solution of beryllium chloride (2.570 g., 0.0322 mole.) in 50 ml. of ether was added. The mixture was vigorously stirred and a solution of sodium triethylboron hydride (95.6 of a 0.67 M solution in ether, 0.0641 mole) was slowly added. A white solid was immediately precipitated, accompanied by a slight warming of the reaction mixture. The solution was allowed to stand for one hour, during which time some of the precipitate settled. A small sample of the supernatant liquid was withdrawn by syringe and analysed by hydrolysis. The ratio of hydrolysable hydrogen to beryllium to chloride was found to be 0.98 : 1 : 0.03.

Addition of sodium triethylboron hydride, the quantity calculated to react with the excess chloride (3.0 ml.), resulted in immediate coagulation of the precipitate. The solution was filtered on the sinter and the filtrate analysed by hydrolysis of a small sample. The ratio of hydrolysable hydrogen to beryllium to sodium was found to be 1.01 : 1 : 0.002.

The reactions of the solution with trimethylamine and trimethylphosphine were then investigated.

Trimethylamine

A portion of the solution (60 ml.) was transferred to one limb of a double Schlenk tube. Trimethylamine (700 Ncc.) was condensed on to the solution and the mixture allowed to stand at room temperature for one hour. A small quantity of white solid was precipitated.

The mixture was filtered on the sinter, and ether was removed from the filtrate under reduced pressure. The oil obtained by removal of solvent was then pumped in high vacuum for one hour. (Found: hydrolysable hydrogen, 0.634; Be, 5.63; amine, 26.0; B, 23.2%. $C_9H_{15}BeN$, $PhBeH.NMe_3$, requires hydrolysable hydrogen, 0.685; Be, 6.16; amine, 40.4%.)

The analytical results shown an appreciable amount of boron is residue, the figures corresponding to the approximate composition $PhBeH.(NMe_3)_{0.7}(Et_3B)_{0.3}$. The reaction was repeated under different conditions in the attempt to obtain a product containing no boron.

A portion of the solution (60 ml.) was transferred by syringe to a reaction tube. The ether was removed under reduced pressure and the oily residue pumped in high vacuum for one hour. Benzene (20 ml.) was added and trimethylamine (3000 Ncc.) was condensed on to the mixture. The tube was sealed at the constriction and the reaction mixture allowed to stand at room temperature overnight. A white crystalline solid was slowly precipitated from the solution. The tube was opened to a high vacuum line via a break-off side-arm and the excess trimethylamine removed under reduced pressure.

The remaining mixture was transferred to one limb of a double Schlenk tube.

The solid was transferred by three extractions with benzene, to the other limb and allowed to crystallise from solution. The product crystallised slowly as white needles, which were filtered on the sinter and pumped dry.

The crystals, when heated in a sealed tube under nitrogen, did not melt below 300°C, but slowly charred in the range 180-230°C.

(Found: hydrolysable hydrogen, 0.69; Be, 6.14; amine, 40.3; M, cryoscopically in benzene, 285, 290 in 0.41, 0.42 weight % solutions respectively.

$C_9H_{15}BeN$ requires hydrolysable hydrogen, 0.685; Be, 6.16; amine, 40.4%; M, 146.)

The molecular weight measurements correspond to degrees of association of 1.96, 1.99 respectively.

The infrared spectrum of the compound, recorded as a nujol mull, showed two absorptions at 1342 and 1316 cm^{-1} in the 1300-1350 cm^{-1} region.

Trimethylphosphine

A portion of the solution (60 ml.) was transferred to a reaction tube and the ether removed under reduced pressure. The oily residue was pumped in high vacuum for one hour. Benzene (20 ml.) was added and trimethylphosphine (3000 Ncc.) was condensed on to the mixture. The tube was sealed at the constriction and the mixture allowed to stand overnight. The tube was opened to a high vacuum line via a break-off side-arm and the excess trimethylphosphine removed under reduced pressure. The remaining

clear, colourless solution was transferred by syringe to one limb of a double Schlenk tube. The solution was pumped to low volume and a colourless crystalline solid was slowly deposited. The solid was filtered on the sinter and pumped dry. (Found: hydrolysable hydrogen, 0.672; Be, 6.04; phosphine, 31.3)

The analytical results indicate on approximate composition $\text{PhBeH}(\text{PMe}_3)_{0.8}$ and the infrared spectrum of the compound showed, in addition to absorptions in the region $1300\text{--}1350\text{ cm.}^{-1}$ a broad absorption centred at 1754 cm.^{-1} indicating the presence of polymeric (Be-H-Be) units.

The solid was dissolved in toluene (10 ml.) and trimethyl-phosphine (1000 Ncc) was condensed on to the solution. On cooling to -78°C crystals were deposited, which were filtered on the sinter, washed with hexane saturated with trimethylphosphine and pumped dry at -15°C ,

When heated in a sealed tube, under nitrogen, it slowly charred in the range $190\text{--}220^\circ\text{C}$. (Found: hydrolysable hydrogen, 0.61; Be, 5.46; phosphine, 46.7; M, cryoscopically in benzene, 271 in 0.41 weight % solution. $\text{C}_9\text{H}_{15}\text{BeP}$ requires hydrolysable hydrogen, 0.62; Be, 5.49; phosphine, 46.9 % M, 163)

The infrared spectrum of the compound, recorded as a nujol mull, showed absorptions at 1356 and 1312 cm.^{-1} in the $1300\text{--}1350\text{ cm.}^{-1}$ region.

DISCUSSION

Alkyl-hydride exchange reactions of beryllium dialkyls and diphenylberyllium

The reaction of dimethylberyllium with dimethylaluminium hydride, in the absence of solvent, has been investigated⁸⁵ as a preparative route to beryllium hydride:

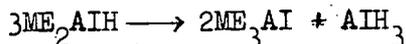


Although trimethylaluminium was formed, a product free from methyl groups could not be obtained and the product was often contaminated with aluminium. It was suggested the intermediate occurrence of a reversible reaction:



could explain the results.

However, reaction of dimethylberyllium and dimethylaluminium hydride in 1:1 molar proportions, in ether solution gives a product containing aluminium. Similar results were obtained in the attempted preparation of beryllium hydride by reaction of dimethylberyllium with lithium aluminium hydride^{84,3}. It is quite possible, as both beryllium and aluminium are electron deficient in their alkyl and hydride derivatives, that aluminium is bound into the polymer chain of the alkylberyllium hydride or beryllium hydride. Alternatively, it is possible that the dimethylaluminium hydride disproportionates.



during the reaction, thus contaminating the product with aluminium hydride. The reaction between dimethylberyllium and dimethylaluminium hydride was not investigated further as the reaction between dialkylberyllium and triethylstannane seemed more promising as a route to alkylberyllium hydrides.

Reaction of diethylberyllium with triethylstannane in ether

A preliminary investigation ⁷⁷ of the reaction of diethylberyllium with triethylstannane in ethereal solution has shown that tetraethyltin and ethylberyllium hydride are formed.



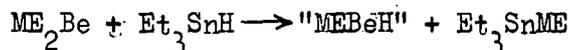
The conditions under which the reaction proceeds have now been investigated. A similar exchange between triethylstannane and triethylaluminium (giving Et_2AlH) is reported, ⁸⁵ and is inhibited by ethers and tertiary amines.

It is suggested ⁷⁷ in the preliminary report of the reaction of Et_2Be and Et_3SnH that, assuming exchange involves an electron-deficient intermediate, it is not surprising that exchange involving beryllium alkyls would proceed in the presence of ethers, as there is evidence that electron-deficient bridges persist in dimethylberyllium in the presence of ethers and trimethylphosphine. ⁴ In contrast, it is probable that the electron-deficiency of triethylaluminium would be removed under such conditions by formation of coordination complexes, and the reaction would be inhibited. However, reaction of diethylberyllium with triethylstannane results in complete exchange, but during the reaction most of the ether distills from the reaction mixture. Thus, it seems likely that the reaction is inhibited by a large excess of ether and will only proceed to completion when most of the ether has distilled from the mixture.

Reaction of dimethylberyllium with Triethylstannane in ether

The potentiality of reactions of beryllium dialkyls with triethylstannane as a preparative route to alkylberyllium hydrides was investigated by reaction of dimethylberyllium with triethylstannane.

Under exactly similar conditions, to those of the diethylberyllium reaction, dimethylberyllium gave an involatile residue, soluble in ether, which gave methane and hydrogen in the ratio 1:1.02 on hydrolysis,. Thus alkyl/hydrogen exchange takes place with no complications due to alkyl/alkyl exchange.



Reaction of the "MEBeH" solution with trimethylamine gave methylberyllium hydride - trimethylamine, $(\text{MEBeH} \leftarrow \text{NME}_3)_2$, which had previously been prepared by another method ⁸¹.

Addition of trimethylphosphine to the "MEBeH" solution gave a solid crystalline product. Although this product is, almost certainly, the phosphine analogue of $(\text{MEBeH} \leftarrow \text{NME}_3)_2$ no characterisation could be carried out as the solid has a high dissociation pressure of trimethylphosphine. Further experiments, designed to overcome this difficulty, have been postponed to a later date.

Several experiments on the solubility of "MEBeH" in hexane show that it is soluble as an etherate. Removal of the ether, by pumping the residue in high vacuum for an hour, or continued washing with hexane, renders the product insoluble in hexane.

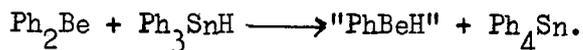
Reaction of diphenylberyllium with triphenylstannane

The reaction of diphenylberyllium with triphenylstannane has been investigated as a preparative route to phenylberyllium hydride. Reaction in benzene was not entirely successful. Exchange occurred to some extent, the ratio of beryllium: hydrolysable hydrogen being 1.65 : 1 after two hours reaction at 70°C. It is probable that the limited solubility of diphenylberyllium in benzene and possible insolubility of any beryllium-containing product contributed to the inhibition of total exchange.

Reaction in ether did not proceed at 40°C, as precipitation of tetraphenyltin, which is sparingly soluble in ether, did not occur.

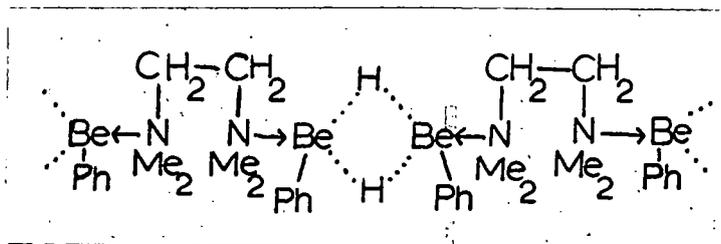


However, at 70-75°C, when most of the ether had distilled from the reaction mixture, exchange did take place and phenylberyllium hydride was formed.



However, a yellow colour produced during the reaction indicates that a side reaction also takes place. The attempted preparation of bis-(phenylberyllium hydride) - tetramethylethylenediamine, $[(\text{PhBeH})_2\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2]$, resulted in the isolation of an impure product. The yellow colour is probably due to a decomposition product of triphenylstannane, which is known to be quite unstable.¹⁶⁰ No gas evolution was observed, however, and the mechanism of the decomposition remains obscure.

The structure of the phenylberyllium hydride complex is probably similar to that proposed for the analogous methylberyllium hydride derivative:⁷⁷



The infrared spectrum of the complex, recorded as a nujol mull, showed a broad absorption, centred at 1754 cm.⁻¹ which has been observed in other beryllium hydride derivatives^{36,91,98}, and is due to $\nu(\text{BeHBe})$ in a disordered polymer.

The tetraphenyltin impurity in the product is probably held in the polymer, it being physically trapped during the precipitation of the hydride complex.

The observation that exchange does not proceed in ether solution at 40°C agrees with results observed for exchange between diethylberyllium and triethylstannane. Thus, it seems that exchange will not take place with a large excess of ether present. Although the results could be explained by proposing that exchange does not proceed to completion below 70°C. experiments discussed in the following section show that exchange will proceed at room temperature, in the absence of ether.

Reactions of ether-free diethylberyllium with triethylstannane

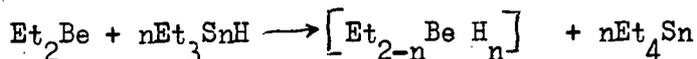
A preliminary investigation showed that reaction at room temperature between ether-free diethylberyllium and triethylstannane, in 1:2 molar ratio, resulted in gas evolution and precipitation of a white solid. Analysis of the precipitate showed it to be an ethylberyllium hydride of variable composition and purity. The beryllium to hydrogen ratio was found to be 1.38 and 1.41 for two different samples of the same product. The gas evolved was shown to be hydrogen, by an additional small scale experiment.

These unexpected results, coupled with the fact that the reaction is not complete after 224 hours, led to a further investigation of the system.

Two experiments, in which diethylberyllium and triethylstannane were allowed to react, in molar ratios of 1:2 and 1:3, at 70°C over a period of eight weeks were performed. An additional "control" experiment, in which triethylstannane was maintained under the same conditions, was also carried out.

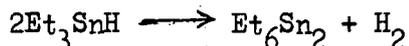
The results show that two reactions are taking place,:

- (a) ethyl/hydrogen exchange takes place, resulting in formation and precipitation of an ethylberyllium hydride:



where $1 < n < 2$.

- (b) some triethylstannane decomposes to give hydrogen and hexaethyl di-tin;



However, a detailed examination of the results shows that the system is rather more complicated than the two equations indicate.

The solid product was, in both cases, extremely impure. The impurity, released only by hydrolysis, was shown to be an ethyltin derivative, the constitution of which is not known. In addition, even when excess triethylstannane was used, the product still contained hydrolysable ethyl groups (the beryllium to hydrogen ratio being 1.74) and some triethylstannane was recovered unchanged. It is probable that ethyl/hydrogen exchange proceeds in solution until the ethylberyllium hydride is precipitated; then, exchange continues on the surface of the precipitated ethylberyllium hydride until further removal of ethyl groups by exchange becomes physically impossible. The recovery of unchanged triethylstannane from the reaction mixture indicates that such a limiting factor does exist. Infrared examination of the solid showed a broad absorption, centred at 1743 cm^{-1} indicating a random polymeric constitution containing (Be-H-Be) groups. It is not unreasonable to assume that ethyltin derivatives could be trapped within the polymer network as it is formed during the precipitation of the ethylberyllium hydride, thus explaining the impurity of the products. It is significant that the product of the reaction in which an excess of triethylstannane was used contained much more ethyltin impurity than when two moles of triethylstannane were used.

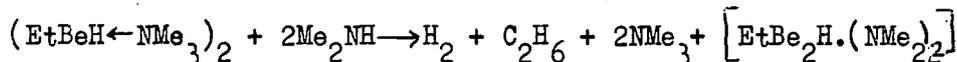
The mechanism by which the triethylstannane decomposed is not known, and no mention of such a decomposition is to be found in the literature. Triethylstannane does not spontaneously evolve hydrogen at room temperature, and experience shows that decomposition of the compound at room temperature is very slow. However, an experiment showed that it does decompose at 70°C to give hydrogen, hexaethyl di-tin and an involatile ethyltin hydride of unknown constitution. But, in all the experiments performed gas evolution, indicating decomposition of the triethylstannane, was significant at or just below room temperature.

Thus, it seems that the decomposition is somehow catalysed by diethylberyllium or by the ethylberyllium hydride precipitated from solution.

Reactions of ethylberyllium hydride-trimethylamine

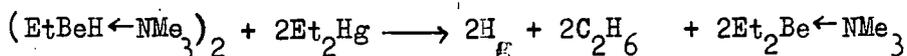
Dimethylamine

Ethylberyllium hydride-trimethylamine reacts with dimethylamine with formation of ethane, hydrogen and trimethylamine, in the ratio 0.98 : 1 : 2, as gaseous products. Similar reactions have been observed between dimethylamine and isopropylberyllium hydride,⁵ which evolved propene and hydrogen in the ratio 2.5 : 1, and methylberyllium hydride-trimethylamine and dimethylamine.⁹⁸ Evolution of both ethane and hydrogen indicates the formation of a mixture of products, and the reaction was investigated no further.

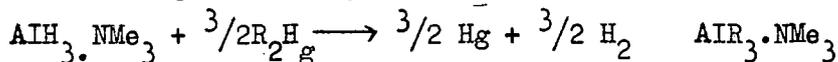


Diethylmercury

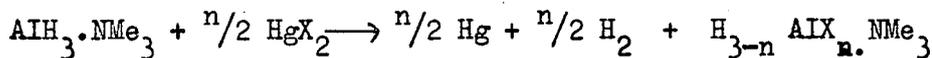
Reaction of ethylberyllium hydride-trimethylamine and diethylmercury, in the absence of solvent, resulted in quantitative elimination of ethane, and formation of diethylberyllium-trimethylamine and mercury.



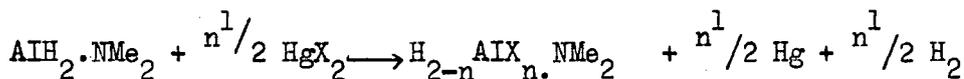
Similar reactions have been observed between aluminium hydride derivatives and organo mercury derivatives and mercury halides:¹⁶⁵



where R = Ph, nC₄H₉, (CH₂ = CH), and (C₃H₇C = C).



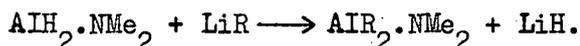
where n = 1, 2 or 3; BX = Cl, Br.



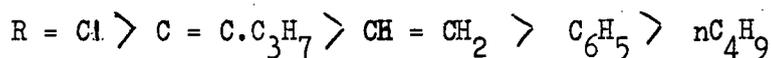
where n = 1, 2.

The reactions were carried out in benzene or ether solvent, and the time taken for complete reaction varied between thirty minute and twelve hours.

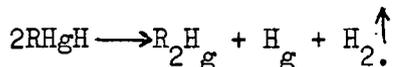
Exchange between dimethylaminoalane and mercury dialkyls did not take place, but reaction with the more reactive alkyl lithium derivatives did result in exchange.



On the basis of time taken to complete the reaction an order of reactivity of R_2H_g to alane-trimethylamine was obtained.



The author suggested, on the basis of these results, that the mechanism was via electrophilic attack by the aluminium on the aryl/alkyl/halogen group of the mercurial. The author also suggested that a probable intermediate was an organo mercury hydride, which decomposed giving hydrogen.



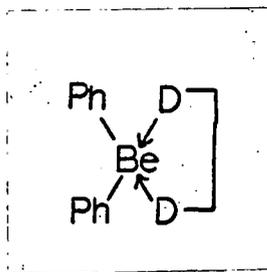
The result obtained from the beryllium derivative does not seem compatible with an ethylmercury hydride intermediate. Elimination of ethane was quantitative, no hydrogen being observed, and it is unlikely that an ethylmercury hydride intermediate would decompose to give ethane quantitatively. If such a decomposition did occur, it must take place via a one-stage process

Further experiments on the exchange between alkylberyllium hydride complexes and mercury dialkyls, and possibly a reinvestigation the alane-trimethylamine/mercury dialkyls systems are necessary before the apparent anomalies can be explained.

The coordination chemistry of diphenylberyllium

Reactions with bidentate ligands

Diphenylberyllium forms well defined, monomeric, crystalline coordination complexes with N,N,N',N' - tetramethylethylenediamine, N,N,N',N' - tetramethyl-o-phenylenediamine, 1,2 - dimethoxyethane and 2,5 - dithiahexane. Analogous complexes with the first three compounds have also been prepared from dimethylberyllium.^{34,35} Since the complexes are monomeric in benzene, they are formulated as shown in fig. I.



I.

As dimethyl sulphide does not coordinate to dimethylberyllium⁴, the formation of a stable chelate complex with 2,5-dithiahexane, MeSCH₂CH₂SMe, stands in contrast, but work described in the following sections shows that diphenylberyllium is a better acceptor than dimethylberyllium.

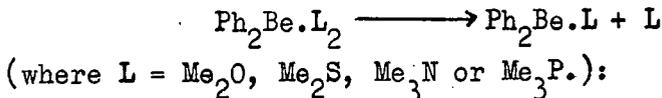
Reaction with monodentate ligands

Preliminary experiments show that diphenylberyllium-bis(diethyl ether) is not stable as had originally been claimed. Indeed, tensimetric observations show that the 2:1 complex has an appreciable dissociation pressure of ether at 0°C, and ether can be removed until the mole ratio of diethyl ether/diphenylberyllium is 1:1.

The results of several tensimetric observations involving simple monodentate ligands as tabulated as follows:-

Ligand	Compound stable at 0°C	Dissociation pressure of 2:1 complex at 0°C.
Me ₂ O	Ph ₂ Be.(Me ₂ O) ₂	-
Me ₂ S	Ph ₂ Be.(Me ₂ S) ₂	-
Et ₂ O	Ph ₂ Be.Et ₂ O	17.0 mm.
Et ₂ S	(Ph ₂ Be) ₂ (Et ₂ S) ₃	-
Me ₃ N	Ph ₂ Be.NMe ₃	0.8 mm.
Me ₃ P	Ph ₂ Be.(PMe ₃) ₂	-

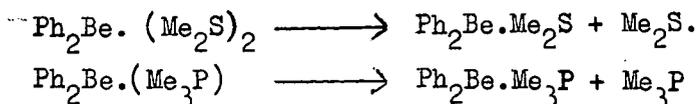
Further observations on the dependence of the dissociation pressure with temperature, for several compounds, have enabled measurement of the heat of dissociation for:



Ligand	Me ₂ O	Me ₂ S	Me ₃ N	Me ₃ P	Kcal. mole ⁻¹ .
Δ H _{DISS.}	17.9	12.0	16.7	8.68	

Several interesting facts emerge from consideration of these results.

Diphenylberyllium might be expected to be better acceptor than dimethyl- or diethylberyllium, as the inductive withdrawal of the phenyl groups would render the central beryllium atom more positive. Thus, whereas dimethyl and diethyl ethers form no definite coordination complexes with dimethylberyllium and trimethylphosphine forms a series of unstable complexes,⁴ diphenylberyllium forms well defined complexes with these and related ligands. The 2:1 coordination complexes between dimethyl sulphide, trimethylphosphine and diphenylberyllium have been prepared. Cryoscopic molecular weight measurements in benzene show the complexes to be somewhat dissociated in solution:



the results indicating a higher degree of dissociation as the solution is diluted, as would be expected.

The results of the tensimetric observations on the various ligand / diphenylberyllium systems lead to conclusions which emphasize steric effects.

Thus, at 0°C the 2:1 trimethylamine complex has a dissociation pressure of ligand, and ligand can be removed until a 1:1 complex is formed. In contrast, the 2:1 trimethylphosphine complex is stable and does not dissociate at this temperature. Experiments with molecular models indicate that when the donor atom is nitrogen, there is considerable steric interaction between the methyl hydrogens of the amine and the phenyl hydrogen. When the donor atom is phosphorus, the much larger phosphorus atom has the effect of pushing the methyl groups farther from the central beryllium atom and so reducing the steric interactions.

In the same way, molecular model experiments show there is more interaction when the ligand is diethyl ether than when it is dimethyl ether. Thus, one important feature governing the formation of coordination complexes appears to be steric interactions. This feature goes a long way to explaining the reaction of dimethyl-³⁴ and diethylberyllium ⁵³ with excess trimethylamine. Both form 2:1 coordination complexes, which are unusually unstable and the stable compound at room temperature is the 1:1 complex, involving 3-coordinate beryllium. In the light of the results obtained with diphenylberyllium it is not unreasonable to assume that steric considerations are very important in the formation of the 2:1 complexes.

The compound $(\text{Et}_2\text{S})_3 \cdot (\text{Ph}_2\text{Be})_2$ indicated by the tensimetric titration of diethyl sulphide with diphenylberyllium is extremely unusual. It is possible that this system is similar to the trimethylphosphine / dimethylberyllium system,⁴ where a considerable range of compounds, each one stable in a certain pressure of trimethylphosphine and temperature, is formed. The complex equilibria are due to the similarity between the affinities of dimethylberyllium for trimethylphosphine and for each other. A more elaborate investigation of the diethyl sulphide / diphenylberyllium system must be carried out before anything definite as to the structure of $(\text{Et}_2\text{S})_3 (\text{Ph}_2\text{Be})_2$ can be proposed.

The measurements of the heats of dissociation of several bix-complexes provide some interesting features. On the basis of the values obtained the following facts emerge:

- (a) dimethyl ether is a stronger donor to diphenylberyllium than dimethyl sulphide.
- (b) trimethylamine is a stronger donor to diphenylberyllium than trimethylphosphine.

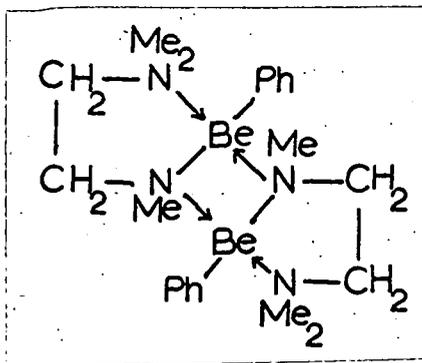
This agrees with previous observations of donor strengths to dimethylberyllium⁴. N>P and O>AS,S. However, the values indicate an overall order of heat of coordination O>N>S>P. This is not the order normally observed for 'A' type acceptors and it is probable that the results are much affected by steric considerations. Thus, the heat of coordination of a ligand or heat of dissociation of a 2:1 complex is dependant both on the donor strength of the donor atom and steric considerations.

Reactions of diphenylberyllium with donor molecules containing acidic hydrogen.

The reactions of dimethylberyllium,^{33, 35, 37, 38} dimethylzinc⁴⁶ and dimethylcadmium¹³⁰ with donor molecules, containing acidic hydrogen, involving elimination of one methyl group as methane have been extensively studied. The general effect of replacing one of the alkyl groups (by an atom such as oxygen or sulphur) is to enhance the acceptor properties of the metal atom and also to increase the donor characteristics of the oxygen or sulphur. Thus, in general such derivatives are associated by relatively strong coordination.

Reaction with N,N,N' - trimethylethylenediamine

N,N,N' - Trimethylethylenediamine reacts with diphenylberyllium in 1:1 molar proportions, with elimination of one mole of benzene and formation of a product, $(\text{PhBeNMeCH}_2\text{CH}_2\text{NMe}_2)_2$, which is dimeric in benzene and, beyond reasonable doubt, has a structure shown in fig. II.

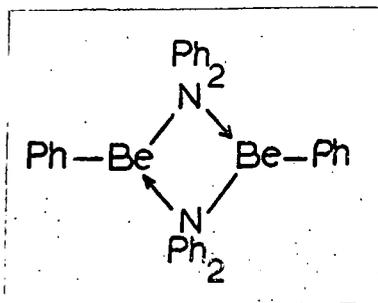


II.

Analogous dimeric compounds are formed by reaction of dimethylberyllium³⁵ and dimethylzinc⁴⁶ with trimethylethylenediamine.

Reaction with diphenylamine

Reaction of diphenylberyllium with diphenylamine leads the formation of a dimeric product, phenyl (diphenylamino)beryllium $(\text{PhBeNPh}_2)_2$. This compound is formulated with 3-coordinate beryllium, as shown in fig. III.



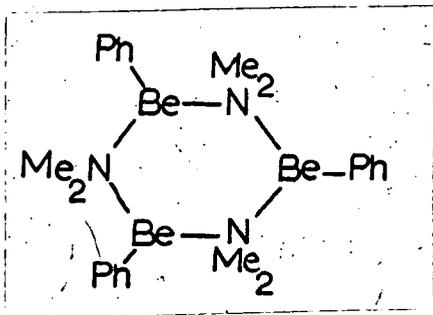
III.

Although, in general, the formation of a dimer would be favoured on entropy grounds, relative to more associated species (greater number of independent molecules per unit mass), when the association of various alkyl derivatives of beryllium, zinc and cadmium is considered; this consideration cannot be of great importance in the view of the many trimers, tetramers and higher oligomers that have been observed.

Thus, $(\text{MeCdOBu}^t)_2$ ¹³⁰, $(\text{MeZnNPh}_2)_2$ ⁴⁶ and $(\text{MeBeNPh}_2)_2$ ³⁸ all are dimeric in benzene, and are formulated with 3-coordinate metal; and angular strain cannot be of overwhelming importance in the formation of these compounds. In contrast, many tetrameric and oligomeric structures have been observed and are discussed elsewhere.

Reaction with dimethylamine

Dimethylberyllium reacts with dimethylamine forming an adduct, $\text{Me}_2\text{Be} \cdot \text{NMe}_2\text{H}$, which melts at 44°C , eliminating methane and forming a trimeric compound $(\text{MeBe} \cdot \text{NMe}_2)_3$ ³⁷. Similarly there is indication of an adduct, formed between dimethylamine and diphenylberyllium, which is sparingly soluble in ether and slowly decomposes at room temperature. The product, $(\text{PhBeNMe}_2)_3$, is trimeric in benzene and is formulated with a structure similar to the methylberyllium analogue, fig. IV.

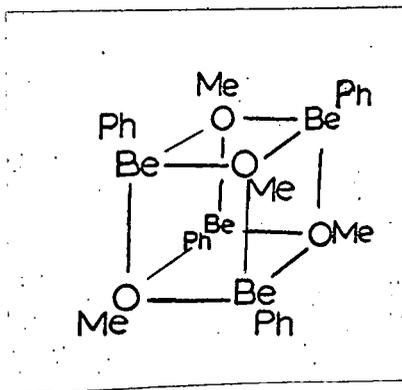


IV.

Recent experiments³⁸ have shown that the size of the alkyl groups attached to beryllium and nitrogen govern the degree of association. Thus, $[\text{MeBeNR}_2]_n$ is trimeric when $R = \text{Me}, \text{Et.}$, and dimeric when $R = \text{Pr}^n, \text{Ph.}$ Similarly $(\text{EtBeNEt}_2)_2$ is dimeric in benzene solution. In the light of these observations it is not surprising that phenyl (dimethylamino)beryllium is a trimer.

Reaction with methanol

Phenylberyllium methoxide, formed by reaction of methanol with diphenylberyllium is tetrameric in benzene. A whole series of tetrameric methylberyllium,³⁸ zinc⁴⁶ and cadmium¹³⁰ alkoxides is now known; and an X-ray diffraction study⁹⁹ on methylzinc methoxide has revealed a cubic structure. It is probable that all the tetrameric alkoxides have a similar structure, and that proposed for phenylberyllium methoxide is shown in fig. V.



V.

All alkylberyllium alkoxides, RBeOR' , so far examined are tetrameric except when $R = R' = \text{Bu}^t$, $(\text{Bu}^t\text{BeOBu}^t)_2$ being dimeric in benzene.

Reaction of phenylberyllium chloride with sodium triethylboron hydride

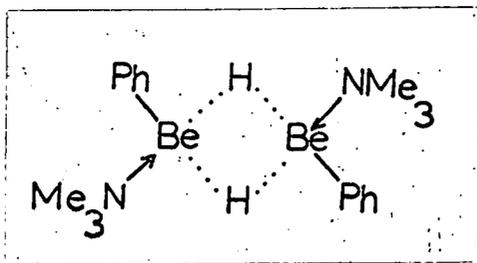
Reaction of phenylberyllium chloride with sodium triethylboron hydride in ether results in precipitation of sodium chloride. The solution obtained after filtration has been used to prepare the trimethylamine and trimethylphosphine complexes of phenylberyllium hydrides. The analogous reaction between ethylberyllium chloride and sodium triethylboron hydride gives a solution which contains hydrolysable ethyl: beryllium: hydrogen in the ratio 1: 1: 1³⁶. The trimethylamine adduct of ethylberyllium hydride, $(\text{EtBeH.NMe}_3)_2$ has been prepared by addition of trimethylamine to the solution. Similar reactions between ethyl- and methylmagnesium chlorides with sodium triethyl- and trimethylboron hydrides respectively have been investigated¹⁵⁶. Sodium chloride was precipitated, but isolation of alkylmagnesium hydrides was not possible. It was difficult to remove all of the trialkyl borane from the residue, indicating the existence of alkylmagnesium trialkylboron hydrides, $\text{RMg R}_3\text{BH}$. Various attempts to remove trialkylborane by pumping or heating resulted in formation of magnesium hydride, indicating the disproportion of any alkylmagnesium hydride formed:



There is some indication that a large excess of ligand is required to effect complete displacement of triethylborane from the phenylberyllium hydride, the first preparation of $(\text{PhBeH.NMe}_3)_2$ resulting in isolation of an oil containing both trimethylamine and boron. When a large excess of trimethylamine or trimethylphosphine is used, no boron is found in the product.

Phenylberyllium hydride-trimethylamine. $(\text{PhBeH.NMe}_3)_2$

The molecular weight measurements show it to be dimeric in benzene, and its structure is probably similar to that proposed for the analogous methyl-⁸¹ and ethyl-⁷⁷ derivatives:



The infrared spectrum of the compound show absorptions in the region $1350-1300 \text{ cm.}^{-1}$. The spectra of the analogous methyl- and ethyl- derivatives show absorption in this region and the absorptions have been assigned to vibrations of the (BeH_2Be) bridge on the basis of the effect of substituting bridging denterium for bridging by hydrogen.

Phenylberyllium hydride - trimethylphosphine ($\text{PhBeH} \cdot \text{PMe}_3$)

The first attempted preparation of this compound resulted in isolation of a product, $\text{PhBeH} \cdot (\text{PMe}_3)_{0.8}$, which showed absorptions in the region $1350-1300 \text{ cm.}^{-1}$ and at 1752 cm.^{-1} . The latter absorption indicates polymeric $(\text{Be}-\text{H}-\text{Be})$ units. A later successful preparation, achieved by low temperature crystallisation and pumping dry at -15°C , indicates that the adduct has an appreciable dissociation pressure of trimethylphosphine. The molecular weight measurement would seem to indicate dissociation of the adduct, but the compound was not soluble enough for accurate measurement.

The adduct is probably dimeric, having an analogous structure to the trimethylamine complex:

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