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ORGANIC AND HYDRIDE CHEMISTRY OF MAGNESIUM

by

J.A. HESLOP, B.Sc.

A thesis submitted for the Degree of Doctor of Philosophy in the University of Durham.

July 1967.

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Memorandum.

The work described in this thesis was carried out in the University of Durham between September 1964 and June 1967. The work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of the work has been the subject of a publication in the Journal of the Chemical Society, [J.C.S. (A), 1966, 26.]

Summary.

Coordination complexes of some magnesium dialkyls and of diphenylmagnesium with bidentate and unidentate ligands have been prepared. The complexes all contain four coordinate magnesium and where molecular weights have been measured they are monomeric in benzene. The dissociation of $Bu^t{}_2Mg(C_4H_8O)_2$ in benzene has been studied.

The action of donors on some alkylmagnesium halides has been investigated. The complex $MeMgBr.Me_2NC_2H_4NMe_2$ and a dimeric (in benzene) alkylmagnesium chloride $(Bu^tMgCl.OEt_2)_2$ have been isolated.

N,N,N'-Trimethylethylenediamine and some magnesium dialkyls ($R = Me, Pr^i, Bu^t$) give dimeric products, the t-butyl complex showing some tendency to dissociate.

The products formed from magnesium dialkyls and thiols depend both on the nature of the alkyl group attached to the magnesium and on that attached to the thiol. Methylmagnesium alkyl sulphides disproportionate on the addition of non-donor solvents and a mechanism for the disproportionation has been suggested. Addition of tetrahydrofuran gives the dimeric complexes $(MeMgSR.THF)_2$ ($R = Bu^t, Pr^i$). Similar complexes $(EtMgSBu^tTHF)_2$, $(Bu^tMgSPr^i.OEt_2)_2$ have been isolated. Disproportionation occurs on addition of t-butylthiol to di-t-butylmagnesium in ether and in the presence of tetrahydrofuran. Magnesium t-butylsulphide is a polymeric solid which does not form any simple

coordination complexes. Methylmagnesium 2-dimethylaminoethyl sulphide is tetrameric in benzene and the t-butyl magnesium analogue is dimeric.

Attempts to prepare complexes of the type $MMgR_2H$ (M = alkali metal, R = alkyl group) failed. The preparation of an alkylmagnesium hydride has, so far, not been achieved. In any system likely to generate the system RMgH only the disproportionation products magnesium hydride and magnesium dialkyl are produced. The exchange reaction between sodium trimethylboron hydride and dimethylmagnesium was investigated by p.m.r. methods at low temperature.

The crystalline complex $NaBMe_3H$ which is tetrameric in benzene has been isolated and characterised.

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INTRODUCTION

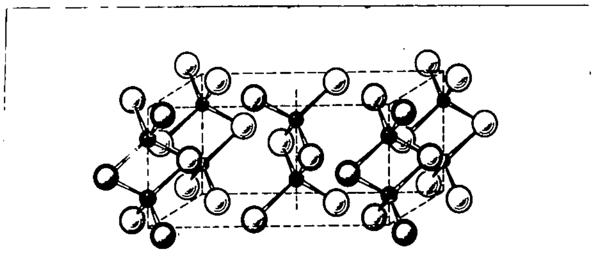
INTRODUCTION

This thesis is concerned with the organic chemistry of magnesium, especially that of the dialkyl- and diaryl- compounds, and with experiments aimed at the preparation and properties of magnesium hydrides.

Although organomagnesium compounds, usually as Grignard reagents, have an extensive chemistry and have been the subject of several reviews [1,2,3], the mode of action of these extremely useful reagents is still not altogether clear. In the same way the chemistry of the dialkyl- and diaryl- compounds has been relatively little studied. This second item will make up the major part of this thesis and the reactions of Grignard reagents will not be discussed at any length.

Magnesium differs from all the other elements of group II in that it forms both covalent and ionic compounds. Beryllium, on the other hand, forms almost exclusively covalent compounds while the heavier members, calcium, strontium, barium and radium, form mainly ionic compounds. Magnesium has an ionic radius of 0·65Å which leads to a charge-to-radius ratio of 3:1 and thus according to Fajans' rules there is a considerable tendency to form covalent compounds. The first and second ionisation potentials of magnesium are 7·64 and 15·3 eV respectively, thus because of the much increased lattice energy resulting from the formation of Mg^{2+} compounds, magnesium exists only in the divalent state.

The ground electronic state of magnesium is $1s^2 2s^2 2p^6 3s^2$, the promotion energy to the state $3s^1 3p^1$ is relatively low and thus magnesium would perhaps be expected to form linear covalent compounds utilising sp hybrids. No compound of this type is known as a co-ordination number of two leaves two low lying unoccupied orbitals which can be used in bonding. The use of these orbitals results in the formation of an sp^3 hybrid and the two unoccupied orbitals will be filled by the formation of an electron deficient bridging bond, as in dimethylmagnesium[4] (fig 1.),



or by co-ordination with an electron donor, for example $PhMgBr.(Et_2O)_2$.[5] In both cases the dominant tendency is for magnesium to use all its low energy orbitals in bonding and become four-co-ordinate.

In aqueous solution the magnesium cation becomes six-co-ordinate and hydrates such as $MgCl_2.6H_2O$ can be readily crystallised. Anhydrous magnesium chloride absorbs ammonia to give $MgCl_2.6NH_3$ which has a high dissociation pressure. It is likely that the bonding in $Mg(Donor)_6^{2+}$ is essentially electrostatic as a degree of covalent bonding would involve using 3d orbitals of Mg which are probably of too high an energy. Thus in any covalent compound of magnesium a maximum co-ordination number of four is to be expected.

A few examples of magnesium compounds with a co-ordination number of three are known, $(Pr^iMgNPr^i_2)_2$, $[EtMgN(Et)CH_2Ph]_2$.[6] The alkylmagnesium alkoxide $(Bu^{n}MgOPr^{i})_3$ [7] is reported to contain 3-coordinate magnesium but the authors suggest that π-bonding between an oxygen lone pair and a vacant magnesium orbital occurs to account for the lack of acceptor properties of the magnesium (fig 1). In the case of the amines, the low coordination number of the magnesium is undoubtedly accounted for by steric factors.

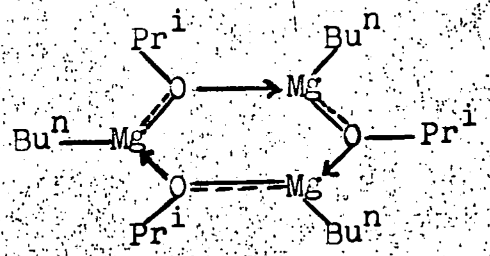
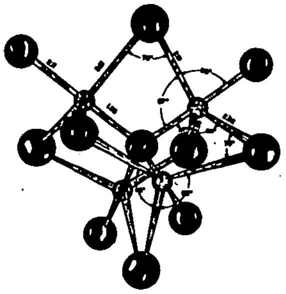


Fig. 1a



Structure of magnesium, bromine, and oxygen atoms in crystals of $Mg_4Br_6O{\cdot}4C_4H_{10}O$: spheres represent bromine, oxygen, and magnesium atoms in order of decreasing size.

One example of five coordinate magnesium is known. Partial oxidation of a Grignard solution results in the crystallisation of a compound $Mg_4Br_6O.4Et_2O$. The ether can be replaced by tetrahydrofuran but the resulting product is not isomorphous with the ether complex which has the structure shown, (fig 2.). Tetrahydrofuran is probably too strong a donor to allow the presence of bromine bridges (alkylmagnesium bromides are monomeric in THF).[11]

Preparation of organomagnesium compounds.

One of the factors which accounts for the extensive use of Grignard reagents is that they can easily be prepared from readily accessible materials. Almost all organomagnesium compounds can be prepared directly from metallic magnesium.

Historically, dialkylmagnesium compounds were prepared before the better known Grignard reagents but were usually not obtained in a pure state or even recognised as such. Cahours [8] prepared diethyl- and dimethylmagnesium by heating the alkyl iodide with magnesium in a sealed tube. In 1891, Lohr [9] using the same method correctly described dimethyl-, diethyl- and dipropylmagnesium as white, air-sensitive solids. This method of preparation did not give pure products or good yields and thus organomagnesium compounds remained curiosities until the first preparation of organomagnesium halides by Grignard in 1900. [10]

The methods of preparation of Grignard reagents are now well known [1] and in their simplest form involve the slow addition of an alkyl or aryl halide to magnesium turnings in a donor solvent.

$$RX + Mg \xrightarrow{\text{Donor Solvent}} \text{`}RMgX\text{'}$$

The donor solvent is an integral part of the Grignard reagent and although organomagnesium halides can be prepared in the absence of donors their properties are considerably modified. Although diethyl ether is the commonly used donor medium other ethers, such as tetrahydrofuran, dibutylether [12], anisole, and non-ethereal solvents, such as tertiary amines (dimethylaniline [13], heterocyclic amines [14]) and formals,[15] have been used also. Hydrocarbon solvents to which small amounts of donor compounds are added are also used. The donor compounds are usually added so as to form 1:1 complexes with the organomagnesium compounds.[16,17]

The use of hydrocarbon solvents containing no donor molecules as media for the preparation of organomagnesium compounds was first extensively studied by Schlenk [18] but he obtained either no reaction or very low yields. Bryce-Smith and co-workers [19,20,21] found that isopropylbenzene and other hydrocarbon media gave good yields of organomagnesium compounds from the alkyl or aryl-halide and magnesium turnings. The product was an alkylmagnesium halide in which R:Mg:X (X = halide, R = alkyl or aryl) = 3:2:1, a similar type of compound is obtained on the removal of ether from a normal Grignard reagent. The composition of the unsolvated organomagnesium halides may change with time but the alkyl content is always greater than the halide and in some cases approaches that of the dialkylmagnesium. [22]

Alkylmagnesium alkoxides have recently been prepared by direct synthesis in hydrocarbon solvents in which they are readily soluble. [23]

$$2Bu^{n}Cl + 2Mg + Pr^{i}OH \longrightarrow Bu^{n}MgOPr^{i} + MgCl_2 + Bu^{n}H$$

$$Bu^{n}Cl + Mg + NaOPr^{i} \longrightarrow Bu^{n}MgOPr^{i} + NaCl$$

There are two main methods for the preparation of dialkylmagnesiums, 1) From the Grignard reagent by precipitation of magnesium halide with 1,4-dioxan and 2) from magnesium metal and dialkylmercurials.

The latter method is limited to those organomagnesium compounds for which the corresponding dialkylmercury is available e.g. methyl,[24] ethyl, phenyl [25] etc., but the method is ideal for small scale preparations and preparation of halide-free dialkyl- or arylmagnesium compounds.

The most widely applicable synthesis of di-organomagnesium compounds is precipitation of magnesium halide by addition of 1,4-dioxan. In 1929 [26] Schlenk and Schlenk found that addition of 1,4-dioxan to a Grignard reagent precipitated all the halide and some of the magnesium leaving the di-organomagnesium compound in solution. They therefore proposed the now famous Schlenk equilibrium for the constitution of the Grignard reagent in solution.

$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$

It was at first thought that the 1,4-dioxan precipitated both MgX_2 and RMgX and that the amount of magnesium left in solution represented the amount of dialkyl(aryl)magnesium present in the Grignard solution. [27,28] Later, however, it was found that the composition of the solution produced after precipitation of the Grignard reagent changed rapidly on standing in contact with the precipitate and that the yield of dialkylcompound could be improved by shaking.[29,30] A later investigation[31] showed that 1,4-dioxan precipitated $MgBr_2 \cdot 2$-dioxan from ethylmagnesium bromide. Rapid addition of the dioxan gave a 55-60% yield of dialkylmagnesium which improved to 70-75% if the solution remained in contact with the precipitate. The best yields, 93-97%, of diethylmagnesium were obtained by extremely slow addition of the dioxan to a stirred solution of the Grignard reagent. The addition of more than one mole of dioxan per mole of ethylmagnesium bromide is necessary to ensure complete precipitation of all the halide. A detailed description of the preparation of a typical di-organomagnesium compound is given by Strohmeier.[32] If an excess of dioxan is used then the magnesium alkyl is generally isolated from ethereal solution as the dioxan complex and the dioxan removed by heating in vacuo. This procedure fails when the alkyl chain is branched as heating *in vacuo* then decomposes the dialkylmagnesium.

Long chained dialkylmagnesiums can be prepared by heating the alkyl halide with magnesium. Addition of benzene gives a solution containing largely dialkylmagnesium.[94]

The structure of organomagnesium compounds.

The structures of some dialkylmagnesium compounds in the solid phase have been recently determined by X-ray powder diffraction methods.[33,34]

It has been shown that dimethyl- and diethylmagnesium have a polymeric chain structure similar to that established for dimethylberyllium.[35] (fig 1) The polymeric chains consist of straight lines of magnesium atoms with tetrahedrally disposed alkyl groups, in planes perpendicular to the C-crystallographic axis, placed symmetrically between. The alkyl groups, have one tetrahedral sp^3 orbital directed symmetrically between two magnesiums, this forms a three centre bond with two magnesium sp^3 orbitals $Mg^1(sp^3) + C(sp^3) + Mg^2(sp^3)$. The C - Mg - C angle in the four-membered ring of Me_2Mg is 105 ± 2°, i.e. quite near the expected tetrahedral angle of 109° while the Mg - C - Mg angle in the ring is 75 ± 2°. This small angle is caused by the requirement that the overlap between the magnesium and carbon orbitals is large. The magnesium-carbon bond distances are 2·24Å and 2·26Å in dimethylmagnesium and diethylmagnesium respectively, while the Mg - Mg distances are 2·73Å in the former and 2·79Å in the latter. These distances indicate that the magnesium-carbon bonds have a bond order of less than one, again indicative of electron deficient molecules, while the metal-metal distances show that some degree of metal-metal bonding may be present.

Single crystal X-ray diffraction work has shown that bis-cyclopentadienylmagnesium is essentially ionic and possesses the antiprismatic structure similar to ferrocene.[38]

Stucky and Rundle[36] have shown that the compound obtained on crystallising a diethylether solution of diphenylmagnesium is the dietherate $Mg(C_6H_5)_2.2C_4H_{10}O$ which is monomeric in the crystalline phase and tetrahedrally coordinated.

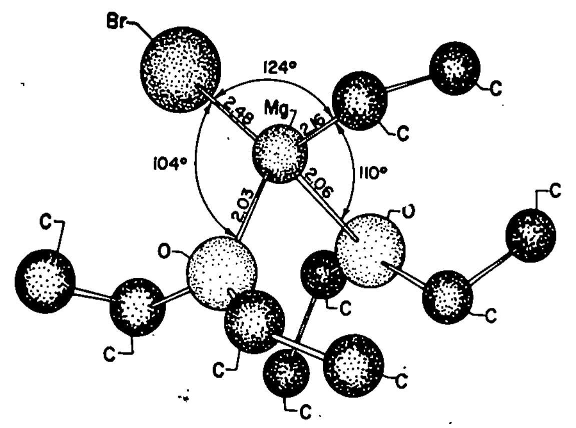
The polymeric nature of the magnesium dialkyls and, presumably, the diaryls accounts for their general involatility and their insolubility in non-donor solvents, [37] i.e. those which do not disrupt the polymer chain.

Little is known about the structure of the dialkyl- and arylmagnesiums in donor solvents but they are presumably monomeric at sufficiently low concentrations with two or more solvent molecules coordinated. Proton magnetic resonance studies have shown that the τ value of the methyl protons in dimethylmagnesium falls from 11·58 at very low dilutions to 11·42 in solutions in which the Me_2Mg/OEt_2 ratio is 0·06, this has been interpreted as being due to the dissociation of a polymeric species present in the more concentrated solutions. [39] This is consistent with the strong polymeric nature of dimethylmagnesium and its low solubility (0·8M solution is saturated) in diethyl ether. Molecular weight measurements in diethyl ether [40] and tetrahydrofuran [41] solution have shown that diethylmagnesium is monomeric in dilute solution.

The structure of the Grignard reagent, organomagnesium halide, has been the subject of controversy since its first discovery. [10] The facts which must be explained are briefly as follows, a) structure in the crystalline phase, b) molecular weights in solution, c) exchange reactions, d) the ionic nature of the Grignard. These headings will be discussed in turn.

a) Structure of Grignard reagents in the solid phase.

Crystallisation of Grignard reagents from diethyl ether solutions gives compounds of the type $RMgX.2Et_2O$ (R = alkyl or aryl, X = halide). Single crystal diffraction data have been obtained for $PhMgBr.2C_4H_{10}O$ [36] and $EtMgBr.2C_4H_{10}O$. [41] Both of these compounds consist of alkyl or aryl group, bromine atom, and two ether molecules forming a distorted tetrahedron around the magnesium atom (fig 3.), which is four coordinate.



The molecular configuration of $EtMgBr \cdot 2Et_2O$.

Ether can be removed from $RMgX.2Et_2O$ by heating in vacuo to give syrupy liquids and finally solid solvent-free Grignard reagent. Removal of ether from CH_3MgCl, C_2H_5MgCl and C_2H_5MgBr gave solid products which contained, as shown by X-ray powder photographs, dimethylmagnesium in the first case and diethylmagnesium in the two latter cases. It was concluded from this that solvent-free Grignard reagents consist of dialkylmagnesium and magnesium halide. [43]

Crystallisation of Grignard reagents from tetrahydrofuran solution does not lead to compounds of the type $RMgX.(C_4H_8O)_2$ but to halide-rich crystals in which R:Mg:X = 1:2:3 i.e. RMg_2X_3 leaving R_2Mg in solution, despite the fact that Grignard reagents are monomeric in tetrahydrofuran solution. [44] Halide rich phases also separate out on crystallising solutions in other ethers e.g. MeOPh, $Pr^i{}_2O$ and $Bu^n{}_2O$. [45]

Addition of triethylamine to a diethyl ether solution of ethylmagnesium bromide followed by crystallisation results in the formation of a compound in which Mg:Br:N = 1·0:1·0:1·0 which is monomeric in trimethylamine over a large concentration range and dimeric in benzene. [17]

Although the structure of the Grignard reagent in the solid phase does not necessarily correspond to the nature of the solution it would seem that the two should be closely related. The original equilibrium proposed by Schlenk [26] to explain the precipitation of magnesium halides by dioxan is adequate to explain the facts presented above,

$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$

with the equilibrium well to the left except on removal of the solvent. The equilibrium can be extended to RMg_2X_3 [44]

$$3RMgX \rightleftharpoons {}^3/{}_2R_2Mg + {}^3/{}_2MgX_2 \rightleftharpoons R_2Mg + RMg_2X_3$$

Degress of association in ethereal solution.

The measurement of the degrees of association of Grignard reagents mainly in diethyl ether and tetrahydrofuran was the first result to throw doubt on the simple formula RMgX for the reagent.[46] Much of the early work was clouded by the non-realisation of the effects of oxygen[47] and excess magnesium halides on the degree of association.[48] Table 1 summarises the results obtained for Grignard reagents in diethyl ether and tetrahydrofuran.

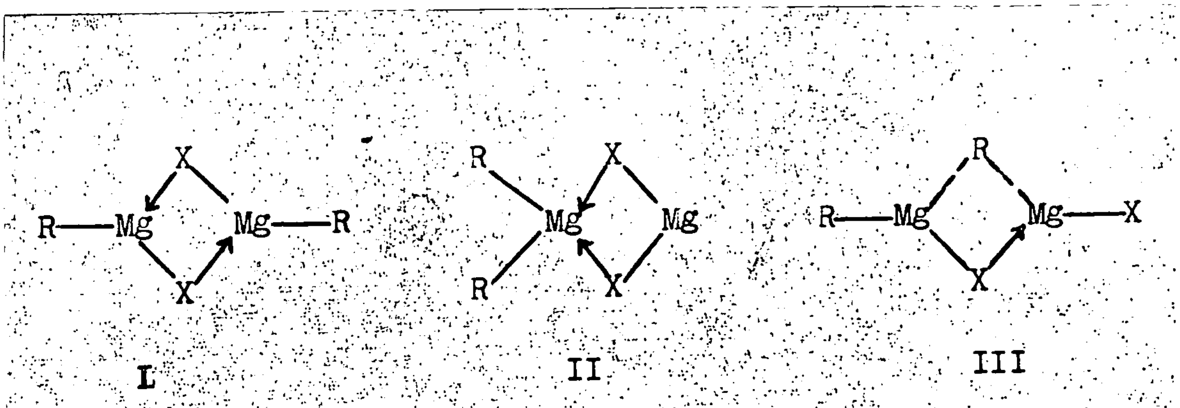
The following generalisations can be made.

a. In dilute diethyl ether solutions ($<0{\cdot}06$ moles of RMgX per litre) alkyl- and arylmagnesium bromides and iodides are monomeric but tend to associate at higher concentrations.

b. Alkylmagnesium chlorides tend to be dimeric in diethyl ether at all concentrations even up to 0·04 molar.

c. All Grignard reagents, so far studied, are monomeric in tetrahydrofuran.

It is possible that in very concentrated Grignard solutions, especially in diethyl ether, the degree of association may increase.[73] The structure of Grignard reagents which are monomeric in solution is probably similar to that established for the solid phase i.e. RMgX.2S, where S is a solvent molecule, while there are several possible structures for the dimeric species (fig 4.).



IV V

Fig. 4

Solvent molecules are not shown in the formulae, but they will be present in such numbers as to make each magnesium atom, at least, four coordinate. Structures III, IV and V seem unlikely as it is known[49] that in most cases bridging will occur via the halogen atoms rather than the alkyl groups. The choice, therefore, seems to lie between structures I and II.

c) Equilibria in solution.

In order to explain the precipitation of magnesium halides on the addition of dioxan to Grignard solutions, Schlenk[18] and later workers proposed the following equilibria

$$2RMgX \rightleftharpoons R_2Mg.MgBr_2 \rightleftharpoons R_2Mg + MgX_2$$

This phenomenon does not allow a choice to be made between the structures I and II as the equilibria involved could be very rapidly established.

It has been shown by means of several experiments such as kinetic studies on the reaction with hex-1-yne[50] and the dielectric constants of mixtures of Et_2Mg and $MgBr_2$, which show a break at a 1:1 mixture indicating compound formation,[51] that a 1:1 mixture of Et_2Mg and $MgBr_2$

is equivalent to the classical Grignard reagent. Conductance studies, however, show significant deviations between the conductances of synthetic mixtures and the normal Grignard at concentrations below 0·4M and it is concluded that at low concentrations the synthetic mixtures are more associated than the normally prepared Grignard reagent. [52]

A number of exchange reactions have been investigated using radioactive tracers. Radioactive magnesium bromide (labelled magnesium) was mixed with an equal quantity of Et_2Mg and allowed to equilibrate for 36 hours. Dioxan precipitation showed that all the radioactivity remained in the magnesium bromide. This was taken to indicate that the equilibrium shown was the only one taking place and that RMgX was not a significant constituent of the Grignard solutions. [58]

$$Et_2Mg \quad + \quad MgBr_2 \rightleftharpoons \quad Et_2Mg{:}MgBr_2 \qquad 2RMgX$$

Later experiments concerning the same equilibrium [53] and the equilibrium between a Grignard reagent and magnesium bromide [54] or diethyl magnesium [55] show that statistical exchange takes place and thus that RMgX must play a significant part in the equilibrium. Similarly, association studies [40,41,44,56] have shown that mixtures of Et_2Mg and $MgBr_2$ can produce monomeric species i.e. RMgX showing that alkyl exchange does take place in ethereal solution and that RMgX is a significant species in solution. It is probable, therefore, that the dimeric species has the structure shown (fig 5.).

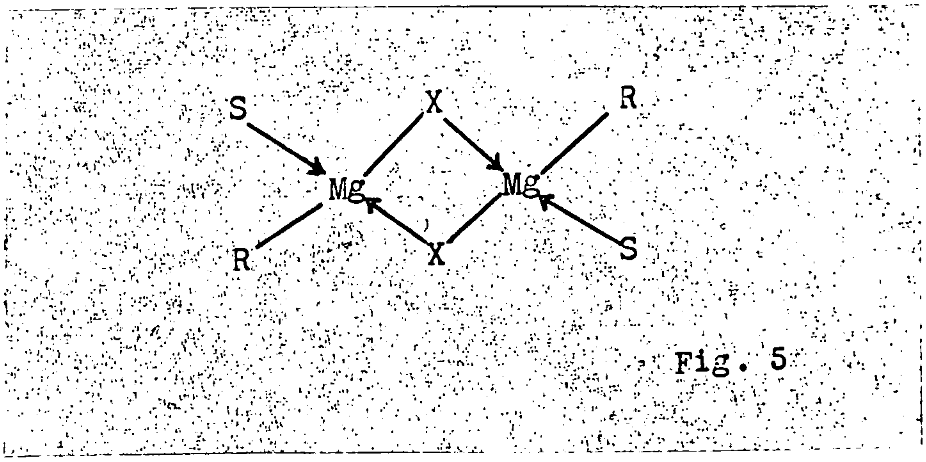


Fig. 5

No evidence for the equilibrium

$$Et_2Mg \quad + \quad MgBr_2 \rightleftharpoons Et_2Mg : MgBr_2$$

was obtained in these experiments.

c) The ionic nature of Grignard reagents.

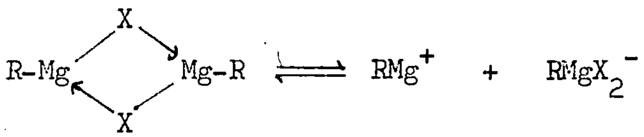
Grignard solutions are known to possess a significant conductivity and although ionic species need not be present to a large extent any theory on the structure of Grignard solutions must be able to explain the observations.

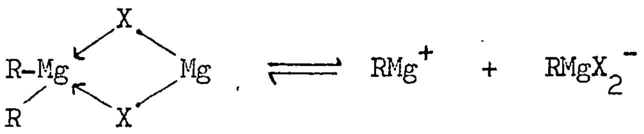
Electrolysis of a Grignard solution under controlled conditions i.e. the middle compartment of a transference cell has constant composition, shows that magnesium metal plates out at the cathode, hydrocarbons are evolved at the anode and the magnesium concentration in the anode compartment increases.[57] This indicates that magnesium is present both in the anion and cation. The following equilibria have been postulated.

At cathode
$$2RMg^{+} + 2e^{-} \longrightarrow Mg + MgR_2$$
$$2MgX^{+} + 2e^{-} \longrightarrow Mg + MgX_2$$

At anode
$$R_2MgX^{-} \longrightarrow R' + RMgX + e^{-}$$
$$R_3Mg^{-} \longrightarrow R' + MgR_2 + e^{-}$$
$$RMgX_2^{-} \longrightarrow R' + MgX_2 + e^{-}$$

Dessy *et al* have essentially confirmed the above observations. On mixing diethylmagnesium and labelled magnesium bromide ($Mg^{*}Br_2$), however, they found the magnesium plating out at the cathode, contained no activity when Mg ^{28} was used. This essentially confirmed their findings with the dioxan precipitation of labelled mixtures of Et_2Mg and $MgBr_2$, although use of Mg ^{25} resulted in complete exchange, and they took this as supporting evidence for their model of the Grignard reagent i.e. $R_2Mg : MgBr_2$,[58] since it has been shown that the lack of exchange in the above system depends on the type of magnesium used[53] some doubt must be thrown on the electrolysis results. It is probably easier to envisage the necessary ions being produced from the RMgX or $(RMgX)_2$ formulation of the Grignard than from $R_2Mg : MgBr_2$ as this would require the breaking of bonds other than bridge bonds.[59]





Measurement of specific conductivities of Grignard reagents has shown that the conductivities of the normally prepared Grignard reagent differ from that of a synthetic mixture of Et_2Mg and $MgBr_2$, [60] but later work has shown that this is only significant at concentrations below 0·4M. [52]

Electrolysis of aromatic Grignard reagents [57] has shown that they have a colloidal nature although association studies demonstrate that they are dimers on solution.

There is no evidence for the existence of carbanions in ethereal solutions of either Grignard reagents or dialkylmagnesium compounds, [62,63] On adding tris(dimethylamino)phosphine oxide to an ethereal solution of benzyl Grignard reagent a red colour develops which has been attributed to the $C_6H_5CH_2^-$ anion. [64]

The coordination chemistry of organomagnesium compounds.

Very few organomagnesium coordination compounds have been isolated. They do, however, obviously exist as the easy preparation of organomagnesium reagents requires the use of donor media. Ether complexes of organomagnesium halides, RMgX.2Ether (R = Et, Ph; X = Br; Ether = $C_4H_{10}O$, C_4H_8O) have been isolated and their structures determined. [36,41] The ether complex $EtMg_2Cl_3$.THF has been isolated from a THF/benzene solution of a Grignard, Et_2Mg being left in solution. [44] There is more evidence for the formation of coordination compounds in Grignard solutions.

The following equilibria have been proposed to take place in Grignard solutions:

$$RMgXnOEt_2 + rTHF \rightleftharpoons RMgX(n-r)Et_2O.rTHF + rEt_2O$$

$$RMgX.OEt_2 + C_4H_8O_2 \rightleftharpoons RMgX.C_4H_8O_2 + Et_2O$$

The value of this work is doubtful as in all cases some precipitation occurred and measurements were carried out on heterogenous systems.[65] Complex formation in solution is also indicated by the change of reactivity of a Grignard with solvent. Thus the nucleophilic activity of organomagnesium compounds was found to depend on the solvating medium, which for RMgX [66] follows the order:

$$(CH_3OCH_2CH_2OCH_3) > THF > Et_3N > Et_2O$$

This would also be the order of increasing stability of the coordination compound. Other reactions, e.g. reaction of Grignards with hex-1-ynes,[67,68,69,70] reaction with benzonitrile,[71] have been shown to be affected by the presence of donor molecules showing that coordination in Grignard solutions plays an important part in the reaction path.

The preparation of ethylmagnesium bromide in triethylamine followed by fractional crystallisation from benzene, gives the product $C_2H_5MgBr.Et_3N$ which is monomeric in boiling triethylamine. The product initially crystallises as $C_2H_5MgBr.2Et_3N$ but loses triethylamine on drying in high vacuo.[72,17]

Coordination complexes of dialkyl- and diarylmagnesium have not been definitely characterised until recently. The formation of coordination complexes relieves the electron deficiency of the magnesium alkyls, however the polymeric nature of the dialkylmagnesium compounds means that before coordination compounds can be formed the polymer chain must be broken and thus the free energy change on coordination must be greater than that of polymerisation. It has been shown that the magnesium alkyls are stronger polymers than the corresponding beryllium compounds and thus it is to be expected that the corresponding coordination compounds of magnesium will not form as readily as those of beryllium.

The existence of a crystalline etherate $(C_2H_5)_2Mg.OEt_2$ was reported by Schlenk as being prepared during the formation of Et_2Mg from Et_2Hg and Mg in ether.

Measurements of partial pressures in mixed solvents have led to the following equilibrium being proposed for dialkylmagnesium solutions,

$$R_2Mg.OEt_2 + THF \rightleftharpoons R_2Mg.THF + OEt_2 \qquad (R = Et, Pr^n, Pr^i)$$

The experiments do not rule out the possibility that the actual complexes in solution are $R_2Mg.OEt_2,THF$ (i.e. contain 4-coordinate Mg) but suggest that the rate constant for the reaction shown below is small

$$R_2Mg.OEt_2.THF \rightleftharpoons R_2Mg(THF)_2 + OEt_2$$

The bis-etherate of diphenylmagnesium, $Mg(C_6H_5)_2.2Et_2O$ can be crystallised from an ethereal solution. Removal of some of the ether gives a sticky liquid $Ph_2Mg.nEt_2O$ where $1 < n < 2$.[36,5]

Experiments on the preparation of dialkyl- and diarylcompounds of magnesium have shown that dioxan forms a 1:1 complex of the type $R_2Mg.C_4H_8O_2$. This is presumably a chelate complex containing 4-coordinate magnesium. In some cases (R = Et, Pr, Pr^i, Bu^n) the dioxan can be removed on heating in vacuo at 115-170°C.[32] The compound obtained on adding dioxan to a methyl Grignard reagent is said to be $(CH_3)_2Mg.\frac{1}{2}$dioxan, for which the structure, containing 3-coordinate magnesium, shown below was proposed.[75] (fig 6.)

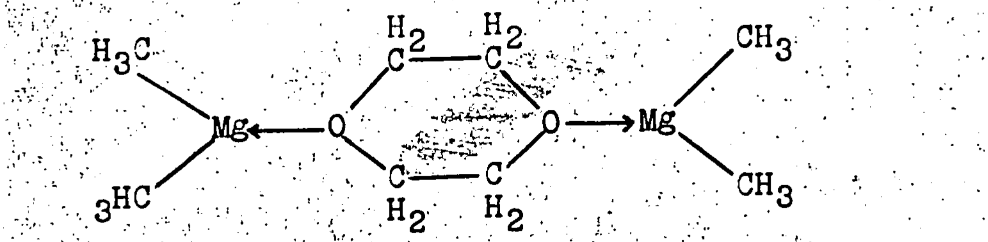


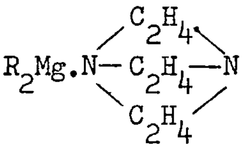
Fig. 6

This 3-coordination could be removed if the oxygen atom utilised its second lone pair and cross linking with another magnesium atom occurred.

Coordination complexes with nitrogen as donor are also known. Dimethylmagnesium absorbs trimethylamine reversibly but no stoichiometric complex was isolated.[76] Measurements of the dissociation pressure follow the equation,

$$\log_{10}P(mm) = 11{\cdot}66 - 3316/T^{o}K$$

corresponding to a heat of dissociation of 15·2 kcal./mole of $N(CH_3)_3$. This is in sharp contrast to dialkylberylliums which form both 1:1, $R_2Be(NMe_3)$, and 2:1, $R_2Be(NMe_3)_2$ complexes.[76,77,78] Stable, volatile complexes with the chelating amine, N, N, N', N'-tetramethylethylenediamine (T.M.ED) of the type $R_2Mg.TMED$ have been prepared where R = Et, Pr^n, Pr^i, Bu^n these are crystalline solids except for $Bu^n{}_2Mg.TMED$ which is liquid.[79] Triethylenediamine, $C_6H_{12}N_2$, gives a white precipitate with both Grignard reagents and dialkylmagnesiums. No details of preparation or analytical data are given. The dialkylmagnesium complexes are presumably 1:1 chelated complexes of the type,



Coordination compounds with magnesium present in an anion also exist. Phenyl-lithium reacts reversibly with an ethereal solution of diphenylmagnesium and addition of xylene causes a crystalline solid $Li^+[MgPh_3]^-$ to separate. If dioxan is present then the complex $LiMgPh_3.4$dioxan is formed.[80] Recently N.M.R. studies have shown the existence of two interesting anionic complexes of magnesium in ethereal solution.[81] Studies of the temperature dependance of the proton and ^7Li spectra of mixtures of methyl-lithium and dimethylmagnesium show that both 2:1, Li_2MgMe_4 and 3:1, Li_3MgMe_5 complexes exist in solution at low temperatures, the amount of 3:1 complex increasing with temperature. The following structures have been proposed for these complexes. (fig 7.)

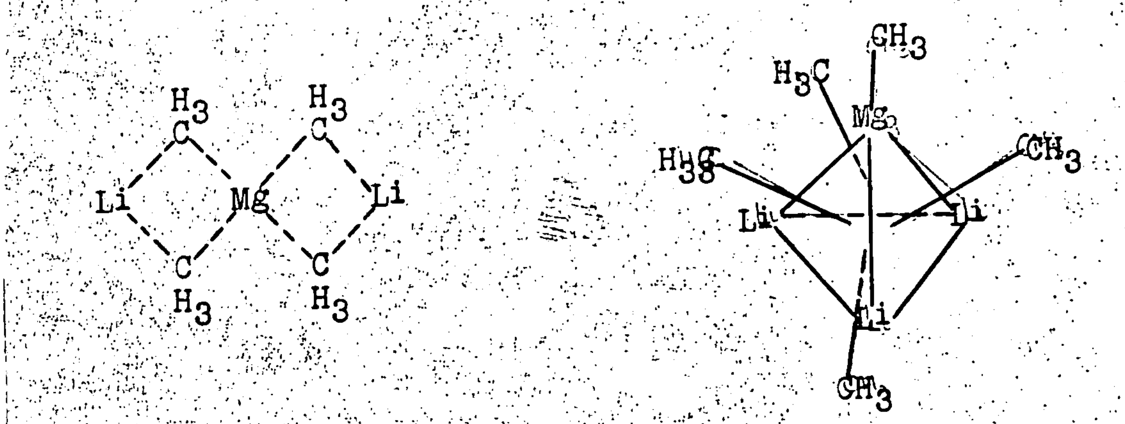


Fig. 7.

The structure of the 3:1 complex is similar to that of the methyllithium tetramer with one of the lithium atoms replaced by a magnesium atom. No evidence for a 1:1, $LiMgMe_3$, complex was obtained.

Properties of organic compounds and coordination of the other Group II elements.

Few organometallic coordination complexes of the elements of Group IIA, Ca, Sr, Ba are known. The organic compounds of these metals are presumably highly ionic and their behaviour will parallel that of the Group I metals for which, with the exception of lithium, no coordination complexes have been prepared.

In contrast the coordination chemistries of beryllium, zinc and cadmium are well documented.[82]

Beryllium

The dialkyl- and diaryl-compounds of beryllium are, like those of magnesium, electron deficient molecules. Dimethyl beryllium has a polymeric chain structure, analogous to dimethylmagnesium, in the solid phase.[35] The higher alkyls, however, are liquids and are obviously less associated. Molecular weight studies have shown that diethylberyllium has a molecular weight of 160 and 140 in cyclohexane and benzene respectively i.e. is approximately dimeric, but the value is time-dependant and increases to 212 and 240 respectively after 240 days.[83] Di-isopropylberyllium is also a liquid, its physical properties being consistent with a dimeric structure. These alkyls possess three coordinate metal atoms, a striking difference from magnesium caused by the much smaller size of the beryllium atom, steric effects preventing the formation of more associated species. The steric situation is more extreme in the case of di-tertiarybutylberyllium which is a liquid with a fairly high vapour pressure, 35mm. at 25°C. Cryscopic molecular weight measurements have shown that it is monomeric in benzene and this has been confirmed for the molecule in the gas phase by a recent infrared study.[84] The beryllium atom in this molecule is two-coordinate, only one other beryllium compound of this type, $Be[N(SiMe_3)_2]_2$,[85] is known.

Diphenylberyllium is a high melting solid with a low solubility in non-donor solvents and is thus probably an electron deficient chain polymer similar to dimethylberyllium.[86]

Because of their electron-deficient nature organoberyllium compounds readily form coordination complexes with donor molecules. Studies on dimethylberyllium indicated that the order of the heat of coordination of donors is $N > P > O \gg As, S$ in fact no coordination compounds of dimethylberyllium with trimethylarsine or dimethylsulphide are known.[76] This same order is shown by trimethylaluminium[88] and trimethylgallium[89] when no complicating factors such as double or d-π bonding are present. Organoberyllium compounds form stable 1:1 complexes with bidentate ligands which are generally monomeric, crystalline solids.

Group V donors.

Compounds formed by bidentate nitrogen donor species are usually simple crystalline, monomeric 1:1 complexes. Thus 1,2-(NN-dimethylamino)ethane forms the complex $R_2Be(Me_2NCH_2CH_2NMe_2)$ where $R = CH_3$,[90] $C_3H_7{}^i$,[84] $C_4H_9{}^t$.[84] The di-tertiarybutylberyllium complex is interesting in that, at room temperature the p.m.r. spectrum shows a single line for the $N(CH_3)_2$ resonance but at low temperatures this line is split indicating two distinct types of NMe_2 group. Thus it is suggested that $Bu^t{}_2Be.(NMeCH_2CH_2NMe_2)$ contains only 3-coordinate beryllium with one NMe_2 group attached to the metal atom and the other free. Rapid exchange will occur at room temperature but this will be frozen at -25°C.[84]

N, N, N', N'-tetramethyl-o-phenylenediamine forms similar complexes with dimethyl-[77] and diphenylberyllium.[91] Diethyl- and di-isopropylberyllium form both 1:1 and 2:1 complexes with tetramethyl-tetrazene (TMT) i.e. $R_2Be.TMT$ and $(R_2Be)_2TMT$. [93] On heating the 1:1 complex an exothermic reaction occurs producing the 2:1. Di-tert-butylberyllium forms only a complex which on heating gives $Bu^t{}_2Be.Me_2NN{=}NNMe_2.Bu^tBeH$

$$R_2Be{:}Me_2NN{=}NNMe_2 \xrightarrow{\Delta} (R_2Be)_2Me_2NN{=}NNMe_2 + Me_2NN{=}NNMe_2.$$

It is suggested that the 2:1 complexes contain 4-coordinate beryllium although molecular weight data show they are somewhat associated. (fig 8.)

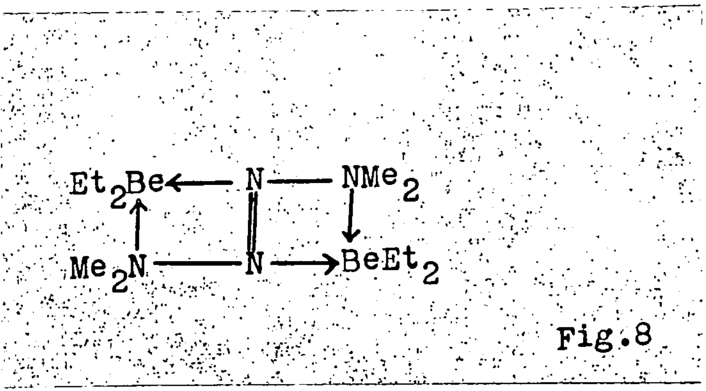


Fig. 8

Similar complexes are formed between diethylberyllium and tetramethylhydrazine. [92] No 2:1 complex could be isolated with $Bu^t{}_2Be$ and 1,2-NN-(dimethylamino)ethane. [84]

Bipyridyl reacts with dimethyl-, diphenyl- and diethylberyllium forming yellow, yellow, and red crystalline, 1:1 complexes respectively. Studies on these and the beryllium halide complexes have shown that the molar extinction coefficient of these compounds increases as the electronegativity of the group attached to beryllium decreases and the colours are explained by electron transfer from the beryllium-halide or beryllium-carbon bond to the lowest unoccuped molecular orbital of the bipyridyl-π-systems.[90]

Uni-dentate donor molecules can react with organoberyllium complexes to form two main types of complex $R_2Be.L$ and $R_2Be.L_2$ (L = ligand). Thus trimethylamine reacts with dimethylberyllium to form a stable compound $Me_2Be \leftarrow NMe_3$ [87] and the less stable $Me_2Be.(NMe_3)_2$ [94] which has recently been shown to be the 2:1 complex and not $(Me_2Be)_2(NMe_3)_3$ as first thought. [87] Diphenylberyllium [91] and diethylberyllium [95] also form stable 1:1 complexes and less stable 1:2 complexes with trimethylamine. Only 1:1 complexes are known between di-isopropyl-, di-t-butylberyllium [84] and trimethylamine another example of the importance of steric effects in beryllium chemistry. The 1:1 complexes are monomeric in the vapour phase when volatile [87] and either monomeric or slightly associated in benzene solution and thus possess 3-coordinate beryllium. Studies on the trimethylamine and 1-,2-dimethylamino ethane complexes of $Be(CH_3)_2$ and $Be(CD_3)_2$, have allowed the $Be-CH_3$ symmetric deformations to be identified as occurring in the range $1186\ cm^{-1} - 1206\ cm^{-1}$ and the $Be-CH_3$ stretching vibrations in the range $700 - 900\ cm^{-1}$. The $Be-CH_3$ p.m. resonances occur at $11{\cdot}19\tau$ and $11{\cdot}52\tau$ for $Me_2Be:NMe_3$ and $Me_2Be(CH_3)_2NCH_2CH_2N(CH_3)_2$ respectively. A solution of $Be(CH_3)_2 2N(CH_3)_3$ in cyclohexane containing free trimethylamine, to suppress dissociation, shows a sharp $Be-CH_3$ resonance at $11{\cdot}28\tau$. The small variations in the chemical shift for different donor atoms are explained by the spatial arrangement about the beryllium atom. [97]

Pyridine forms stable, coloured crystalline, 2:1 complexes with organoberyllium compounds (R = Me, Et,[90] Pr^i, Bu^t [96]).

In order to form stable complexes with dimethylberyllium the donor molecules must break up the polymer. Trimethylamine does this easily, in the case of trimethylphosphine, however, the situation is more complex in that the heat of coordination of the phosphine with dimethylberyllium is of a magnitude comparable to the heat of polymerisation of the dimethylberyllium. Thus a complex set of equilibria are set up and a considerable range of compounds $(Me_3P)_x(Me_2Be)_y$, where x = 2,3,1,2,2,2 and y = 1,2,1,3,4,5, respectively are formed. These differ from each other only in the length of the Be-Me polymer chain left intact.[76] All the trimethylphosphine can be removed in vacuo. Trimethylphosphine complexes with di-t-butylberyllium [84] and diphenylberyllium [91] are known. The former forms only a 1:1 complex, presumably for steric reasons, while the latter forms both 2:1 and 1:1 complexes, although the latter was not isolated. The complex $Ph_2Be(PMe_3)_2$ has a vapour pressure of 35·49 mm. at 86°C and is slightly dissociated in benzene solution.

No organoberyllium trimethylarsine complexes have been isolated.[76]

Group VI complexes.

The ready solubility of organoberyllium compounds in ethers indicates that the polymeric chain must be broken down by the ethers.

Chelated 1:1 complexes are formed between dimethylberyllium and 1,2-dimethoxyethane.[90] The compound is monomeric in benzene solution and the ether can be removed by heating (55-60°C) in vacuo.

Molecular weight studies [83] and the high dipole moment of diethyl- and diphenylberyllium in dioxan [86] indicate that complex formation takes place in this solvent. The complex is probably $Et_2Be.C_4H_8O_2$.

Although organoberyllium compounds are soluble in diethylether no definite coordination compounds have been isolated, except for diphenylberyllium where an ether complex is formed on crystallising an ethereal solution. This low melting crystalline complex was claimed to be $Ph_2Be.(OEt_2)_2$ which did not lose ether until heated in vacuo at 130°C. [99] More recent work has shown that the bis-etherate has a considerable vapour pressure of ether at room temperature (17mm. at 0°C) and cannot be isolated without the loss of some ether, and ether can be removed until the 1:1 complex is left. [91] The alkyls of beryllium all retain ether on isolation from ethereal solution to some extent. Di-t-butylberyllium on removal of ether by pumping yields a viscous liquid in which the ratio $Be:OEt_2$ is approximately 1:1. If the liquid is refluxed while pumping a product containing 37 mole % ether is obtained. Ether can be removed from diisopropylberyllium by refluxing with continuous pumping for several days.[100] Diethylberyllium retains about 2% ether even after this treatment.

Dimethylberyllium and dimethylether form a series of complexes similar to those with trimethylphosphine. [76] The compounds $(Me_2Be)_2(OMe_2)_3$, $Me_2Be.OMe_2$, $(Me_2Be)_2OMe_2$ and $(Me_2Be)_3OMe_2$ are formed, they are much less stable and dissociate at lower temperatures than the trimethylphosphine complexes. Diphenylberyllium forms a stable complex $Ph_2Be(OMe_2)_2$ which has no appreciable vapour pressure of ether at 0°C. [91]

No coordination compounds are known between dialkylberyllium compounds and donor atoms containing sulphur. Diphenylberyllium, which is a stronger acceptor due to the electron withdrawing effect of the phenyl groups, forms a chelate, 1:1 complex with 2,5-dithiahexane, a 2:1 complex with dimethylsulphide, $Ph_2Be.(Me_2S)_2$, which is somewhat dissociated in solution.

$$Ph_2Be.(Me_2S)_2 \rightleftharpoons Ph_2Be.Me_2S \quad + \quad Me_2S$$

and there is some evidence, based on tensimetry, for a complex with diethylsulphide $(Ph_2Be)_2(Et_2S)_3$. [91] This latter situation may be similar to the trimethylphosphine and dimethylether with dimethylberyllium systems.

No coordination complexes of organoberyllium compounds with other members of group VI have been isolated.

It seems from these studies, that strength of the group V and VI elements as donors to beryllium are in the order N>P>O>>As, S. Measurement of the heat of dissociation in the system

$$Ph_2Be.L_2 \rightleftharpoons Ph_2Be.L \quad + \quad L$$

have indicated that in this case the order is O>N>S>P. No explanation of this order is given. [101]

Anionic complexes.

Complexes in which the beryllium atom is present in an anion are known for a variety of systems.

Diphenylberyllium reacts with phenyl-lithium in ether to give the complex salt $Li[BePh_3]$ which can be recrystallised from xylene, or dioxan in which case $Li[BePh_3].4$dioxan is isolated. Magnesium, cadmium and zinc form similar compounds.[80]

Diethylberyllium forms a series of salts of the type $(MX).(BeEt_2)_n$, where M = alkali metal or Et_4N^+, X = halogen or cyanide and n = 1, 2, 4. Reactions have so far been carried out with Et_2Be and KF, RbF, CsF, $(Et_4N)Cl$, KCN in which n = 1 or 2, 2, 2, 2 and 4 respectively.[102, 103, 104]

Alkalimetal hydrides react with beryllium dialkyls and diaryls to form complex hydrides of the type $MBeR_2H$ where M = Na, R = Et,[105] Me[106] and M = Li, R = Et[105] and Ph.[99] These will be discussed in more detail later.

Zinc.

Because of the large increase in electronegativity in going from the elements of the first two rows to the B-subgroup, which have a complete d^{10} shell, the organic derivatives show vastly modified properties. Thus the dialkylcompounds of zinc are volatile liquids easily soluble in non-polar solvents and are monomeric in the liquid and vapour phase.[83, 107] The dialkylzincs ignite in air and are vigorously hydrolysed by water. Spectroscopic evidence, especially the infrared[108] and Raman[109] spectra, is interpreted in terms of a linear structure ($C - \widehat{Zn} - C = 180^\circ$) for the dialkyls. The formation of sp hybrids has been explained solely in terms of the more covalent nature of the zinc compounds but may also be due to the larger separation of the s and p orbitals of zinc which will favour the formation of hybrid orbitals with a larger amount of s-character.

The acceptor properties of the alkyl-metal compounds of group II depend to some extent on the electronegativity difference between R and M in R_2M. Because of the low polarity of the zinc-carbon bond organo-zinc compounds were thought for a long time not to form electron donor-acceptor complexes. In recent years however a full range of coordination compounds have been prepared.

Group V complexes.

Chelated crystalline complexes of the type $R_2Zn.(CH_3)_2NCH_2CH_2N(CH_3)_2$ are formed where R = Ph, C_6F_5, $C_4H_9{}^n$, [110] Me and a similar complex $R_2Zn.(Et)_2NCH_2CH_2NEt_2$ is formed between dialkylzincs and NNN'N'-tetraethylethylenediamine where R = Me,[112] Et. [117] Tetramethyltetrazene also forms 1:1 crystalline complexes with Ph_2Zn, $(C_6F_5)_2Zn$, $Bu^n{}_2Zn$. [110] The chelated complexes are much less sensitive to air than the original organo-zinc compounds.

2-2'-Bipyridyl forms a series of highly coloured 1:1 complexes of the type R_2Zn.bipy (R = Me, Et, Pr, Bu^n, pentyl, hexyl, heptyl, octyl,[113] Pr^i, Ph, C_6F_5, [114] Me, [112] allyl [116]). Studies on some of these and on the corresponding 1,10-phenanthroline complexes $R_2Zn.C_{14}H_8N_2$ (R = Bu^n, Et, C_6F_5,[114] Me[112]) have shown that the colour of the complex depends on the electronegativity of R and the intensity of the absorption bond drops as the electronegativity of R decreases. This is in contrast to the analogous beryllium compounds where the intensity drops as the electronegativity of the attached group increases.[90] It is suggested that the absorption band in the zinc complexes involves the π-system of the donor molecule as an acceptor and the 3d-orbitals of the zinc as donor. The energy of the 3d-orbitals will vary in the required manner with variation of R. [114]

Trimethylamine reacts with dimethylzinc to form both $Me_2Zn:NMe_3$ and $Me_2Zn(NMe_3)_2$. The 1:1 complex distils at 85° without decomposition while the 1:2 complex distils at this temperature suggesting dissociation into the 1:1 complex and free trimethylamine. Triethylamine and pyridine form only 2:1 complexes with dimethylzinc but these dissociate in benzene solution into free amine and the 1:1 complex. [112] A 2:1 pyridine complex of di-n-butyl zinc is also known. [117]

A yellow crystalline, 1:1 complex is formed between diethylzinc and isoquinoline. The complex is monomeric in benzene, presumably containing 3-coordinate zinc, but dissociates on heating alone above 60°. The colour is probably due to a mechanism similar to that discussed for the bipyridyl complexes. [115] A series of 1:2 complexes of dialkylzincs (R = Me, Et and Bu^n) with quinoline and isoquinoline have been prepared. [117] The complex $Me_2Zn(quinoline)_2$ is said to form the 1:1 complex in benzene solution whereas the corresponding diethylzinc complex is said to be completely dissociated; this contrasts with the work of Pajaro et al who states that the complex $Et_2Zn(isoquinoline)$ is monomeric in benzene.[115]

Coordination complexes containing phosphorus and arsenic as electron donors have been found to form only when the group attached to the zinc atom is strongly electron withdrawing. Thus diphenylzinc and di(pentafluorophenyl)zinc both form a 1:2 complex with triphenylphosphine while $Bu^n{}_2Zn$ forms no complex. With 1,2-bisdiphenylphosphinoethane and tetramethyl-o-phenylenediarsine, however, diphenyl-, di(pentafluorophenyl)- and di(n-butyl)-zinc all form 1:1 complexes, although the di(n-butyl)-zinc complex with the chelating arsine is a liquid which slowly loses dibutylzinc on heating in vacuo, in all cases the melting points of the complexes increase in the order $Bu^n{}_2Zn < Ph_2Zn < (C_6F_5)_2Zn$. It is suggested that the phosphine and arsine complexes do not involve dπ-dπ back bonding as a major stabilising influence but simply that increasing the electronegativity of R causes the zinc to become a stronger acceptor.

Group VI.

Although complexes of organozinc compounds with ethers have not been isolated until recently their existence could have been postulated from a number of previous experiments. In 1859, Frankland [118] found that the use of dimethyl- or diethylether facilitated the formation of dimethylzinc from zinc and methyl iodide and the ether cannot be removed. A recent investigation of this system demonstrated the existence of a 1:1 complex $ZnMe_2:OMe_2$. [119] A series of liquid adducts $Me_2Zn.xO(CH_2)_n$ where n = 2,3,4,5 and x = 1 or 2, which can be distilled at room temperature are known. The strength of the $Zn \leftarrow O$ coordinate bond and thus the possibility of the coordination of a second ether molecule increases from n = 2 to n = 5. Thus tetrahydrofuran and pyran form 1:2 complexes while $O(CH_2)_3$ forms both

1:1 and 1:2 complexes. The apparent extent of dissociation in benzene and cyclohexane depends on the concentration and the donor properties of the solvent. The cause of the stability difference for ethers of different ring size is thought to be the orientation and character of the oxygen lone pair orbitals which are affected by the ring size of the ether. Tetrahydrofuran does not form a stoichimetric complex with diethylzinc.[117] P.m.r. studies[120] have enabled equilibrium constants for the reaction,

$$R_2Zn \quad + \quad \text{ether} \rightleftharpoons R_2Zn\text{:ether}$$

where R = Me or Ph and ether = $O(CH_2)_2$, $C_4H_8O_2$, $CH_3O(CH_2)_2OCH_3$, to be calculated.

Strohmeier's experiments on organozinc compounds provided good evidence for the formation of dioxan complexes. Thus diphenyl- and diethylzinc are monomeric in dioxan[83] and they have a non-vanishing dipole moment in dioxan (2·7D[121] and 1·68D,[122] respectively) which is attributed to electron-acceptor-donor complex formation. Several 1:1 dioxan complexes of organozinc compounds have in fact been isolated. These are especially stable for diarylzincs but lose dioxan on heating in vacuo.[123,130] Dialkylzincs do not readily form dioxan complexes, thus dimethylzinc forms a stable 1:1 compound with 1,4dioxan, but no compound with 1,3dioxan.[124] Diethylzinc does not give a stoichiometric compound, the adduct having the empirical formula $Et_2Zn(\text{dioxan})_{0\cdot7}$.[117] Di-n-butyl- and di-iso-butylzinc are reported not to form dioxan complexes.[123]

1,2-Dimethoxyethane and 1,3-dimethoxypropane forms 2:1 complexes with dimethylzinc which can be distilled without decomposition, on cooling below 0°C however the 1:1 complexes can be separated.

Only one complex of organozinc compounds with the higher members of group VI is known. Dimethylzinc forms a crystalline chelate complex with 1,4-thioxan, $Me_2ZnC_4H_8S_2$.

Anionic complexes.

Until recently the only complexes of organozinc known were those in which the zinc atom was part of a complex anion. Sodium and diethylzinc react to give a low melting crystalline solid which analysed as sodium triethylzincate $NaZnEt_3$,[125] this can also be prepared by dissolving ethylsodium in diethylzinc. As the complex is associated in benzene the formula $Na_2[Zn_2Et_6]$ has been proposed[126] and this has been supported by a dipole moment study.[127] Lithium tetramethylzincate diethyletherate has been obtained by addition of methyl-lithium to an excess of dimethylzinc and removing volatile material.[128] A 1:1 complex is formed between diethylzinc and alkyl lithium reagents the reaction being completely reversible.[99]

$$R^-Li^+ \quad + \quad Et_2Zn \rightleftharpoons (RZnEt_2)^-Li^+$$

Phenyl-lithium also adds reversibly to diphenylzinc in ether solution to give a crystalline 1:1 complex $LiZnPh_3$ and a less stable complex $Li_3Zn_2Ph_7$ which is highly dissociated in boiling ether whereas the 1:1 complex is essentially monomeric.[80] Addition of dioxan to $LiZnPh_3$ allows the crystallisation of $LiZnPh_3.4C_4H_8O_2$.

The hydride anionic complexes of organo-zinc compounds will be discussed later.

Cadmium.

The trends which first showed themselves in the chemistry of organozinc compounds i.e. linear structure of the alkyls and the lessened tendency to expand coordination number above 2 become even more pronounced for cadmium. The liquid cadmium alkyls are monomeric in benzene and cyclohexane and the infrared spectra have been interpreted in terms of a linear C-Cd-C structure. The linear structure may again be due to the larger separation of the 5s and 5p orbitals of cadmium which will favour the formation of a small number of bonds, with a large s contribution. A second factor may be d-s mixing, although this is more likely for mercury compounds than for cadmium.[131] In the case of cadmium the complete $4d^{10}$ electron shell will provide a less effective screening to outer electrons and thus increase the electronegativity of cadmium. This phenomenon becomes still more pronounced in the case of mercury.

Few coordination compounds of cadmium dialkyls and diaryls are known. A crystalline chelate complex is formed between dimethylcadmium and N,N,N',N'-tetraethylethylenediamine.[132] This can be sublimed in vacuo at 50°C but is slightly dissociated in benzene. The yellow bipyridyl complex of dimethylcadmium is much more extensively dissociated in benzene solution and loses dimethylcadmium on pumping.[90] The 1,10-phenanthroline complex is, however, monomeric in benzene.[132]

Pyridine forms a 1:1 liquid adduct which dissociates into its components at low temperatures and is thus difficult to isolate. Similar behaviour is shown by tetrahydrofuran. Because of this no reliable molecular weight data are available for these compounds.[132] 1,4-Dioxan forms a crystalline complex with dimethylcadmium which can be sublimed in vacuo but is completely dissociated at room temperature in benzene solution.[132] Diarylcadmium compounds also form 1:1 chelated complexes with 1,4-dioxan but no molecular weight data are vailable for these.[134] Dipole moment measurements also indicate the formation of a complex between dioxan and diphenylcadmium.[121]

Mercury.

Mercury is the least electropositive metal in Group II and thus organomercury compounds show relatively little tendency to form neutral coordination complexes. The large separation of the 6s and 6p orbitals causes the dialkylmercury compounds to have a linear structure containing two coordinate mercury.

The organomercury compounds do not expand their coordination number above two, as evidenced by the low dipole moment of diphenylmercury in dioxan solution,[121] unless the organic group attached to the mercury is chlorinated or fluorinated. Oscillometric techniques have detected 1:1 and 2:1 complexes between piperidine, pyridine, triphenylphosphine, triphenylarsine, acetone, ethanol, dimethylsulphoxide, pyridine N-oxide, tri(p-tolyl)thiophosphate, dimethylsulphide and various fluorinated alkyl- and arylmercury compounds. Diphenylmercury also forms similar compounds.[133] The existence of all these compounds depends on very weak interactions, however, $(C_6F_5)_2Hg.bipy$, $(C_6F_5)_2Hg.[P(C_6H_5)_2]_2C_2H_4$,[207] $(CF_3)_2Hg.bipy$, $(CF_3)_2Hg.phen$, $(C_2F_5)_2Hg.bipy$, $(C_3F_7)_2Hg.bipy$,[208] and $(CCl_3)_2Hg.bipy$ are all known as crystalline complexes.

Phenyl-lithium does not form any complex with diphenylmercury.

Reaction of organometallic compounds with acidic hydrogen.

Reaction of a dialkyl- or arylmetal compound of Group II with a substance (HA) containing an acidic hydrogen, in 1:1 molar proportions normally gives a product of the type RMA. These compounds, if monomeric, would be coordinately unsaturated at the metal atom, which would itself have enhanced acceptor characteristics due to being attached to the more electronegative entity A, (i.e. more electronegative than R in R_2M). If the residue A possesses any lone pair electrons on the atom attached to the metal then their donor properties will be increased, again because of the polarity of the M - A bond. In order to remove the coordinative unsaturation of the metal atom the RMA species may be expected to undergo some associative process. The factors which affect the degree of association of this type of compound are now beginning to be understood, though their relative importance is sometimes obscure.[135]

The association process can be written,

$$n\text{RMA} \rightleftharpoons (\text{RMA})_n$$

$$\Delta G = \Delta H - T.\Delta S$$

The factors affecting n are summarised as follows:

1. Entropy - for association to occur as shown in the above equation ΔG must be negative. This will be achieved if ΔS can be positive. Association will be favoured by a positive value of ΔS, thus entropy factors will favour small values of n i.e. if entropy were the only factor involved then the likelihood of association would be

$$\text{dimers} > \text{trimers} > \text{tetramers} \gg \text{polymers.}$$

2. Steric interference - by the use of models it can be shown that there is less interference between bulky substituents in dimers than in trimers. Steric interference (minimal in the monomer) will cause ΔH to become more positive and thus steric interference will favour low association numbers.

3. Valency angle strain - the associated compound formed will tend to have the least possible strain. If some strain is present then this will be more easily tolerated by the heavier elements. Valency angle strain will decrease as n increases from 2 to 3.

4. Nature of reaction intermediates - polymeric intermediates formed by an inter-molecular condensation will favour polymers, tetramers and trimers as the isolated species. A monomeric intermediate will favour a dimer as the associated species.

Most of the work on the factors affecting the degree of association has been done on the organic compounds of Group III. Enough work has now been done, however, on the Group II elements, especially beryllium and zinc, for a representative picture to be given.

Reaction of organomagnesium compounds with acidic hydrogen.

Amines.[136]

The products $RMgNR_2$ formed by the displacement of one alkyl group R by reaction of secondary amines with a dialkylmagnesium can associate with both the alkyl groups and the nitrogen atom acting as possible bridging groups.

Reaction between equimolar proportions of diethylmagnesium and dimethylamine gives the polymeric, insoluble bis-dimethylaminomagnesium, $Mg(NMe_2)_2$. If the intermediate $EtMgNMe_2$ shows any tendency to disproportionate then the process will proceed to completion due to the insoluble nature of the product. When amines with larger organic groups are used disproportionation does not take place but the products, which are prepared in ethereal solution, cannot be freed from diethylether. When tetrahydrofuran is added to a hexane solution of $EtMgNEt_2$ and $EtMgNPr^i_2$ removal of the solvent leaves viscous liquids with the formulae $(EtMgNEt_2)_2THF$ and $(EtMgNPr^i_2)_2THF$. The liquids are associated to some extent in benzene solution. Monomers would contain one 3-coordinate and one 4-coordinate magnesium atom unless both lone pairs of the THF are used for coordination. The dimer $[(EtMgNR_2)_2THF]_2$ has been formulated, (figure 9) as shown, with four-coordinate magnesium.

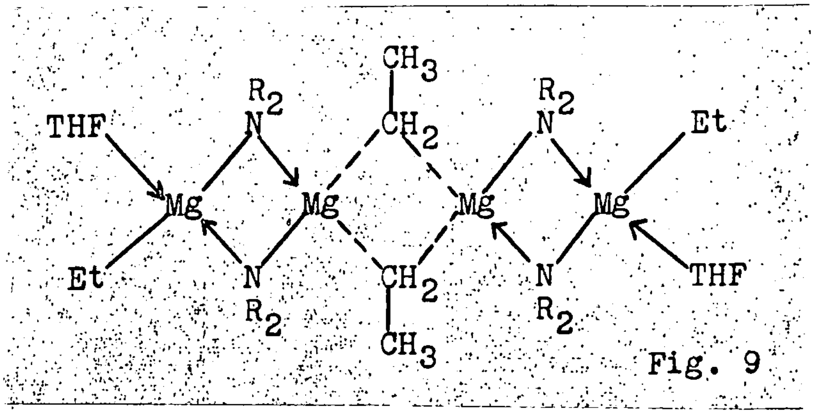


Fig. 9

The p.m.r. spectrum shows only one type of Mg-Et group so there is rapid exchange between the bridging and terminal ethyl groups. The formation of these compounds is somewhat surprising in view of the fact that diethylmagnesium is monomeric in tetrahydrofuran.

Reactions with diphenylamine give simpler products. Diethylmagnesium gives an ether-free, insoluble, presumably polymeric product $(EtMgNPh_2)_x$ with both bridging nitrogens and bridging ethyl groups. Addition of tetrahydrofuran gives the monomeric complex $EtMgNPh_2(THF)_2$, Di-iso-propylmagnesium and diphenylamine in diethylether gives the bis-ether complex $Pr^iMgNPh_2.(OEt_2)_2$ which dissociates in toluene giving the polymeric $(Pr^iMgNPh_2)_x$. The phenylgroups in the NPh_2 residue are electron withdrawing this decreases the donor capacity of the nitrogen atom and increases the acceptor properties of the magnesium atom thus allowing the formation of the ether complexes. Diphenylamine will eliminate both ethyl groups from diethylmagnesium giving $Mg(NPh_2)_2$ which is insoluble in ether but can be recrystallised from tetrahydrofuran.[138]

Di-isopropylamine reacts with di-isopropylmagnesium to form $Pr^{i}MgNPr^{i}_{2}$ which is dimeric in benzene and must be formulated with three coordinate magnesium. (fig 10)

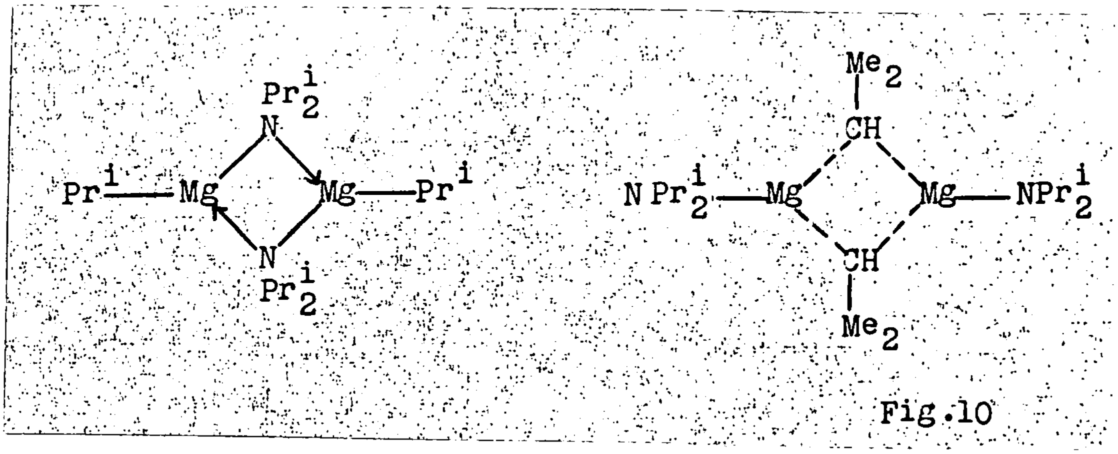
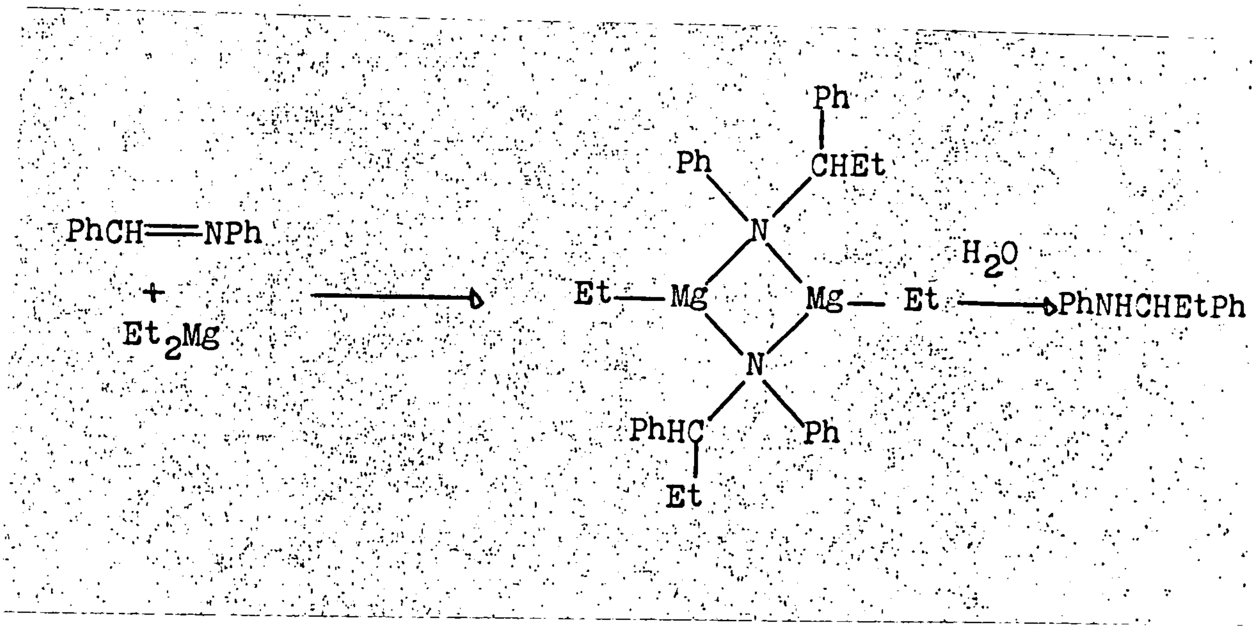


Fig.10

Of the two possible structural formulae the first with bridging nitrogen is preferred.

Reaction of diethylmagnesium with an equimolar amount of 2,2,6,6 tetramethylpiperidine also yields a crystalline dimer and again there are two possible structures, one with bridging nitrogens and the other with bridging ethyl groups.

Benzylideneaniline and diethylmagnesium form a crystalline ether-free product, which is dimeric in benzene. Hydrolysis yields the amine PhCHEt.NHPh.



The product formulated with 3-coordinate magnesium in benzene solution may be more associated in the crystalline state although an analogous zinc compound $MeZnNPh_2$, which is dimeric in solution, consists of dimer molecules in the crystalline state.[187]

Phosphines.[138]

The reactions of diethylmagnesium with various phenylphosphines have been studied by Issleib and Deylig. Diethylmagnesium reacts with an excess of diphenylphosphine in ether to give the insoluble $Mg(PPh_2)_2$ which is presumably polymeric but can be recrystallised from tetrahydrofuran as $Mg(PPh_2)_2.4THF$. In equimolar proportions diphenylphosphine reacts with ethereal diethylmagnesium to eliminate one ethyl group and give crystalline $EtMgPPh_2.OEt_2$. Although no molecular weight data are given the compound may well be dimeric with 4-coordinate magnesium. (fig 11)

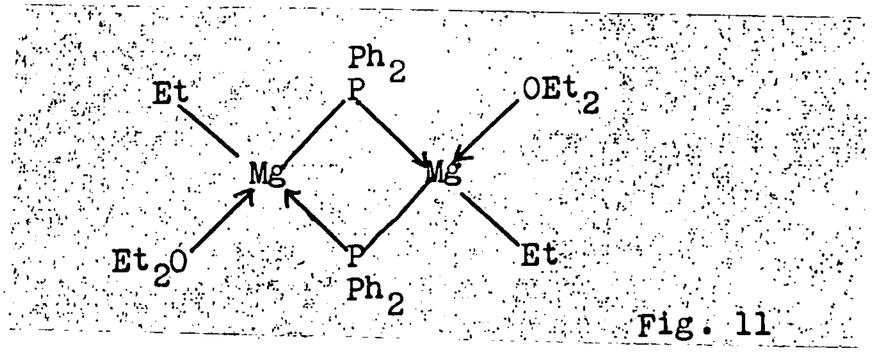


Fig. 11

The ether can be removed by heating in vacuo at 100°C.

Diethylmagnesium reacts with an equimolar amount of phenylphosphine to give $EtMgPHPh_2$ from which the second ethyl group can only be removed by heating for 2 - 3 hours at 160°.

$$Et_2Mg \quad + \quad PhPH_2 \longrightarrow (EtMgPHPh)_n \xrightarrow[\Delta]{160^\circ} (MgPPh)_x$$

An excess of phenylphosphine produces bis-phenylphosphinomagnesium at room temperature.

The chelating phosphine, P,P'-phenyl-1,3-diphosphinopropane $(CH_2)_3(PPhH)_2$ removes both ethyl groups from diethylmagnesium in butylether to form a chelate compound $Mg(PPh)_2(CH_2)_3$ which is monomeric in tetrahydrofuran. Higher homologues of the diphosphine produce polymeric compounds.

Alcohols.

Although organomagnesium alkoxides have long been proposed as intermediates in the reaction between organomagnesium compounds and ketones it is only recently that they have been isolated.[146,147]

Ethylmagnesium ethoxide can be prepared by the pyrolysis of diethylmagnesium which retains some solvent diethyl ether.[139] Pyrolysis causes cleavage of the solvent molecules giving EtMgOEt which sublimes out of the pyrolysis mixture, and not MgC_2H_4 as first thought.[140]

Bryce-Smith and co-workers,[23] have developed several methods for the direct preparation of alkylmagnesium alkoxides from magnesium, alkyl halide and alcohol in hydrocarbon media. It is reported that n-butylmagnesium isopropoxide prepared by this procedure is trimeric.[7] The structure proposed (fig.1a) contains 3-coordinate magnesium and some Mg-O π-bonding arising from overlap of the pπ component of the occupied <u>n</u>-orbital on oxygen with a vacant orbital on the adjacent magnesium is suggested to account for the weak acceptor properties of the alkoxide. A trimeric alkoxide $(EtMgOEt)_3$ is also reported to be present in ethereal solution. The alkoxide was formed by the absorption of oxygen by a diethylmagnesium solution.[47]

The degree of association of alkylmagnesium alkoxides has been shown to depend on the nature of the alkoxide group.[6] If there is chain branching at the carbon α to oxygen then only tetramers (cryoscopically in benzene) $[(EtMgOPr^i)_4$, $(EtMgOBu^n)_4$ and $(Pr^iMgOPr^i)_4]$ are formed. These compounds probably have a cubane structure (diagram 12) similar to MeZnOMe [143] and $EtZnOBu^t$.[144] When no branching occurs at carbon atom α to the oxygen then the species formed are more associated in benzene e.g. $EtMgOPr^n$, Pr^iMgOMe, Pr^iMgOEt are oligomers all having degrees of association in the range 7-8·4, EtMgOEt is too insoluble in benzene to allow its degree of association to be determined. All the alkoxides mentioned were prepared by reaction of the appropriate alcohol with the appropriate dialkylmagnesium.

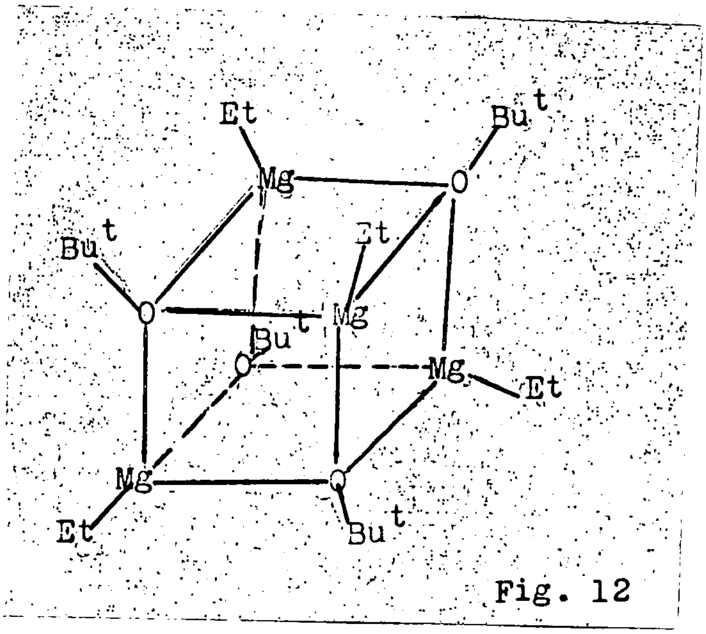


Fig. 12

The p.m.r. spectra of $(EtMgOBu^t)_4$, $(Pr^iMgOMe)_{7\cdot8-8\cdot4}$, and $(Pr^iMgOEt)_{7\cdot5-8\cdot1}$ are interesting in that the alkoxy and in the case of $(EtMgOBu^t)$ the metal alkyl resonances are split into two components of unequal intensities. This indicates that, for example in $(EtMgOBu^t)_4$, that there are two types of Mg - Et and OBu^t group and that any exchange between them is slow enough for them to appear magnetically different.[145]

Addition of benzophenone to diethylmagnesium gives $EtMgOCPh_2Et$ which cannot be freed from diethylether. Diethylketone and ethereal diethylmagnesium give a crystalline solid $EtMgOCEt_3.OEt_2$ which is either monomeric in benzene or decomposes in benzene with loss of ether forming an associated, probably tetrameric, ether-free alkoxide.

$$2(EtMgOCEt_3.OEt_2)_2 \rightleftharpoons 4Et_2O + (EtMgOCEt_3)_4$$

Reaction between acetone and methylmagnesium halides (Halide = Cl, Br, I) gives the interesting compound $BrMgOBu^t.OEt_2$ which is dimeric in benzene. A possible structure is [6] (fig 13).

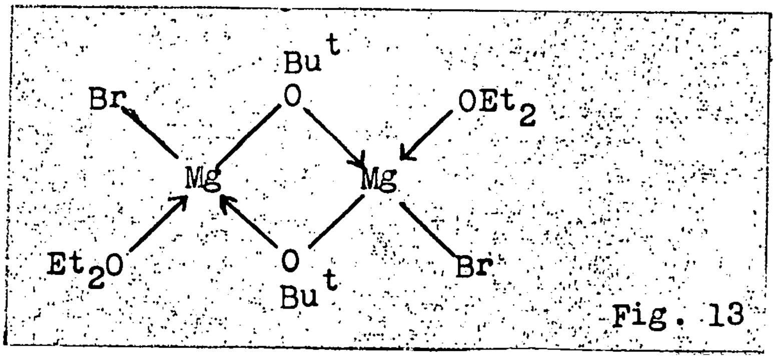


Fig. 13

Reactions of organoberyllium compounds with acidic hydrogen.

Amines.

Compounds of the type $RBeNR'_2$ have been known for some time.[160] The usual method of preparation is

$$R_2Be + HNR'_2 \longrightarrow (RBeNR'_2)_x$$

It is the value of x which provides the main area of interest.

From Table 2 it can be seen that in the majority of cases the value of x is three except when R' is a bulk group when the less sterically hindered dimer is formed. Although entropy effects would favour dimers over trimers, in both cases the beryllium is three coordinate, (fig 13), rough calculations show that the effect of angular strain, less for trimers than dimers, will be the most important factor except where large steric effects are involved. Thus, as found, trimers will be favoured for small R' groups and dimers for larger ones.

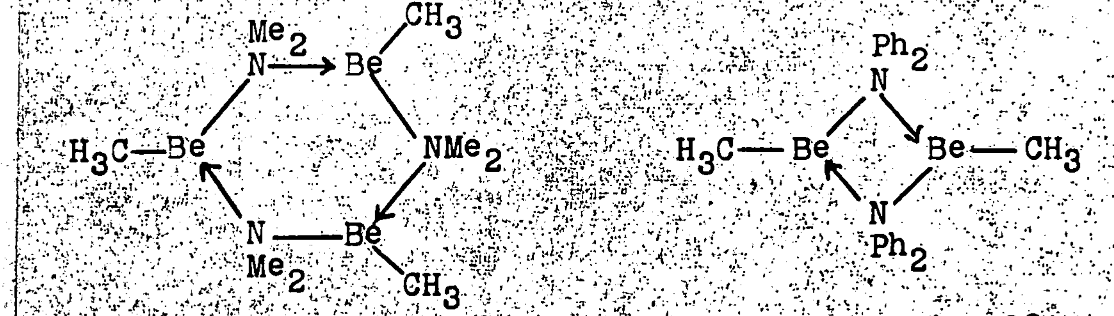


Fig. 13

Normally the nature of R does not affect the degree of association, however, when R = Bu^t, steric hindrance prevents the easy formation of Bu^tBeNMe_2, giving $Bu^t{}_2Be.HNMe_2$ which eliminates butane only slowly and incompletely, and causes $Bu^tBeN(Me)CH_2CH_2NMe_2$ to be monomeric instead of dimeric like the corresponding methyl- and phenylberyllium compounds. (fig 14.)

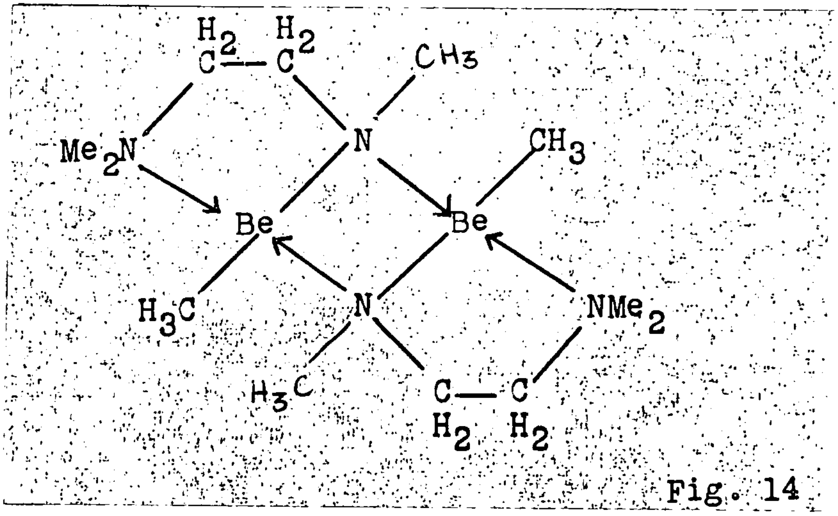


Fig. 14

As the compounds mentioned above contain 3-coordinate, coordinatively unsaturated beryllium they react easily with pyridine and bipyridyl to give complexes. With excess of ligand the $Be(NR_2)_2Be$ bridge is broken. (Table 3)

Reaction of dimethylberyllium with various ethylenediamines gives either dimeric or polymeric products depending on the extent of reaction. (Table 4) Similar reactions have been done between diethylberyllium and various methylhydrazines,[92] and it is suggested that the amount of alkane elimination is determined by steric factors.

Both alkylgroups are normally replaced when an excess of a simple secondary or primary amine is used. Ammonia forms an adduct with dimethylberyllium at -80°C which on warming evolves methane, but even at 50°C elimination is not quantitative, polymeric products of the type $R-[Be-NH-Be]_n-NH_2$ being formed. Piperidine and morpholine with dimethylberyllium give 1:1 adducts $Me_2Be\leftarrow NHC_5H_{10}$ and $Me_2Be\leftarrow NHC_4H_8O$ which, in the presence of excess amine at 40°C, eliminate methane quantitatively forming $Be(NC_5H_{10})_2$ and $Be(NC_4H_8O)_2$ respectively.[163]

The presence of an adduct has also been observed between dimethylberyllium and di-isopropylamine, $Me_2Be \leftarrow HNPr^i{}_2$, methane evolution is, however, not quantitative even up to 100°C in refluxing solvent. Diphenylamine eliminates both ethyl groups from diethylberyllium giving $Be(NPh)_2$.[164] Diethylberyllium also reacts, eliminating both ethyl groups, with N, N, N'-trimethylethylethylenediamine, giving the monomeric $Be(MeNCH_2CH_2NMe_2)_2$.[165] Excess dimethylamine forms $[Be(NMe_2)_2]_3$ with diethyl- and di-isopropylberyllium, for which two possible structures have been proposed.[100] (fig 15.)

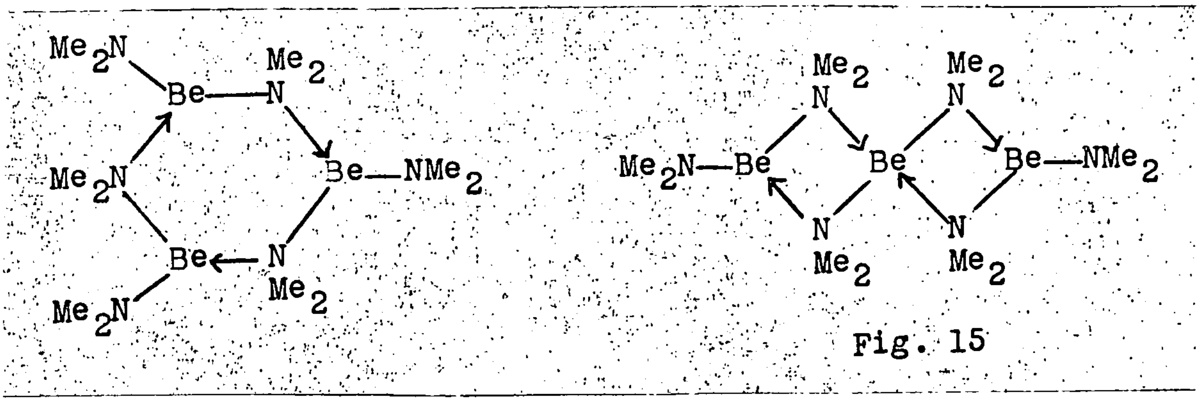
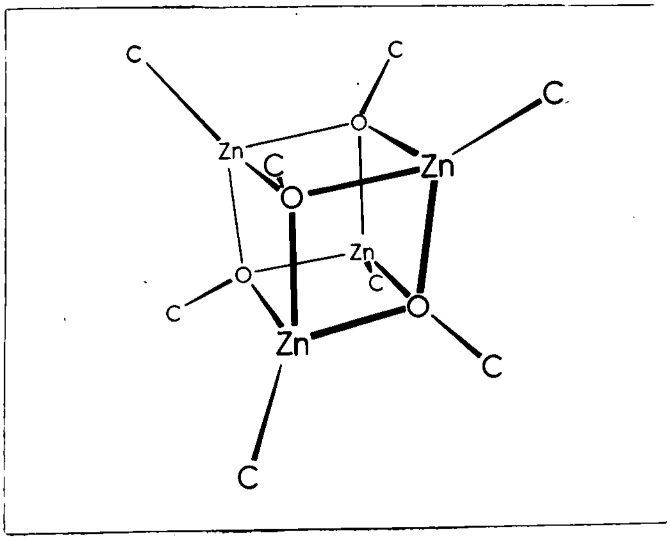


Fig. 15

Alcohols. (Table 5)

The alkoxides so far prepared illustrate quite effectively the effect of steric hindrance on the degree of association. For the methylberyllium alkoxides the degree of association is 4 in all compounds so far prepared except for the very sterically hindered alkoxy groups $-O-CHPh_2$ and $-OCPh_3$. The structure of the tetrameric alkoxides is probably similar to that of $(MeZnOMe)_4$ (fig. 16).



and that of the dimers probably contains 3-coordinate beryllium (fig.17). The series of compounds $(MeBeOCH_2Ph)_4$, $(MeBeOCHPh_2)_2$, $(MeBeOCPh_3)_2$ also illustrates the effect of increasing steric hindrance. That the alkyl group attached to beryllium also plays a part in determining the association number is illustrated by $MeBeOBu^t$ which is tetrameric whereas Bu^tBeOBu^t is dimeric. (fig. 17)

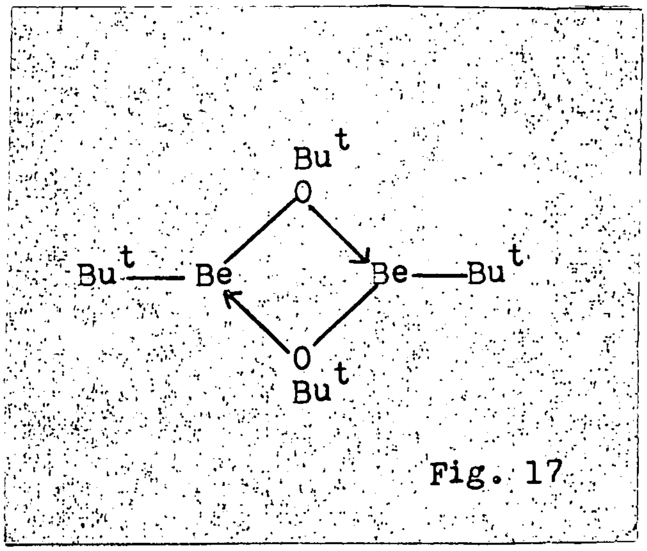
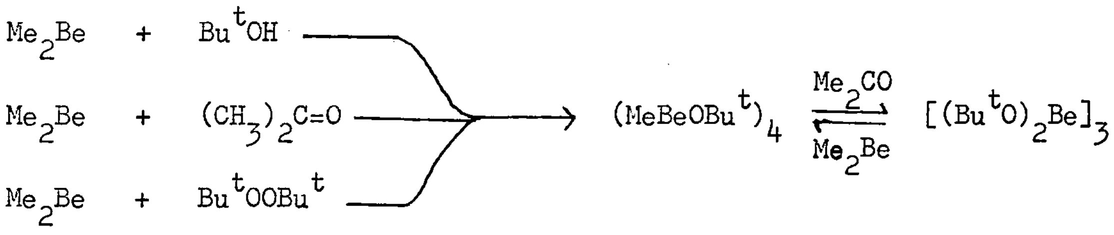


Fig. 17

The alkoxides were generally prepared from equimolar amounts of a dialkylberyllium and an alcohol. Methylberyllium t-butoxide was prepared by four methods,



The reaction with aldehydes and ketones seems to be a general one.

The p.m.r. spectra of the alkylberyllium alkoxides are of interest in that they present some evidence for some of the alkoxides [$(MeBeOMe)_4$, $(MeBeOBu^t)_4$,] possessing alkoxy groups in at least two environments.[96]

The alkoxides often form less associated complexes with pyridine (Table 6) and if the alkoxide is sterically hindered ether complexes are often formed.

The bis-alkoxyberyllium compounds are formed on reaction of a dialkylberyllium with excess alcohol. The sterically hindered alkoxides have low degrees of association. (Table 7) Studies with various substituted phenols have shown that the first alkyl (Me_2Be and Et_2Be) group is eliminated below -80° and the second starts to react between -55° and -30°. [167]

Di-methoxyberyllium, which is polymeric, dissolves in an ethereal solution of dimethylberyllium producing methylberyllium methoxide whose infrared and n.m.r. are identical with a sample prepared by the usual method.[96]

Thiols

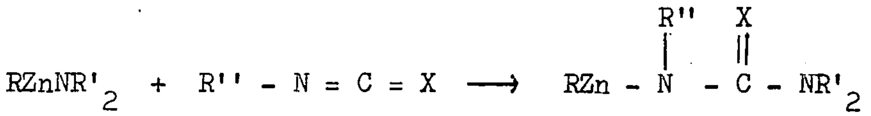
The reaction of dialkylberyllium compounds with thiols is at present under investigation. Preliminary results again show a tendency towards the formation of tetramers.

Reactions of organozinc compounds with acidic hydrogen.

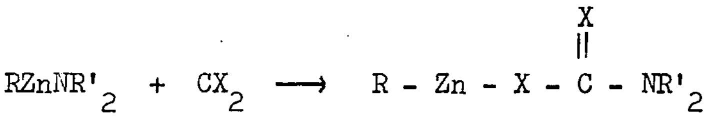
Amines

The compounds shown in Table 8 are formed by the reaction between a secondary amine and dialkylzinc. $(MeZnN(Me)CH_2CH_2NMe_2)_2$ is thought to have a structure similar to the analogous beryllium compound. [149] The compound $(RZnNPh_2)_2$ is formulated with 3-coordinate zinc as evidenced by its ready reaction with pyridine and its tendency to disproportionate. Noltes[150] has prepared the crystalline dimers $RZnNPh_2$ (where R = Et, Pr^i

Bu^n, Ph) which again must be formulated with three coordinate zinc. These compounds and the liquid $EtZnNEt_2$ react rapidly and quantitatively with R''NCO, R''NCS, CO_2, CS_2 as follows:



$$RZnNR'_2 + R''-N=C=X \longrightarrow RZn-\overset{\overset{R''}{|}}{N}-\overset{\overset{X}{\|}}{C}-NR'_2 \qquad (X = O, S)$$



$$RZnNR'_2 + CX_2 \longrightarrow R-Zn-X-\overset{\overset{X}{\|}}{C}-NR'_2 \qquad (X = O, S)$$

The nature of the compounds was not examined.

The rates of acidolysis of various alkylzincs in Pr^i_2O with a number of amines viz. p-toluidine, cyclohexylamine, diphenylamine has been examined but the intermediates were not isolated.[151] It appears, however, that the compound $RZnNR'_2$ once formed is inert to excess amine and shows no tendency to form $Zn(NR'_2)_2$.

Dimethylzinc and an equimolar amount of dimethylamine gives only $(Me_2N)_2Zn$ as an insoluble, involatile, presumably polymeric white solid. No evidence was obtained for the existence of $(MeZnNMe_2)_x$.[149]

Phosphines [152]

Only a few reactions between phosphines and dialkylzincs are known. When the two are mixed in equimolar proportions compounds of the type $RZnPR'_2$ (R = Et, R' = Ph; R = R'=Ph; R=Et, R'=Bu^n; R=R'=Bu^n) are formed. $EtZnPPh_2$ is apparently polymeric and insoluble in most solvents once it has been isolated. $EtZnPBu^n_2$ and $Bu^nZnPBu^n_2$, the latter being a liquid, are associated in benzene but the extent is not known. $(PhZnPPh_2)_n$ has $n = 7{\cdot}2$ in 1·1 wt.% benzene. The polymeric compound $EtZnPPh_2$ reacts with an equal amount of methyliodide to give $[EtZnPPh_2Me]^+I^-$ and with excess methyliodide giving EtZnI and $[PPh_2Me_2]^{++}2I^-$.

Insertion reactions with RNCO, RNCS and CS_2, similar to those of the amino compounds are undergone by the phosphines.

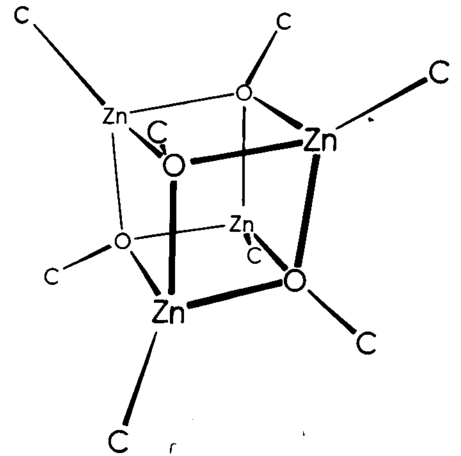
Unlike the corresponding aminocompounds, $RZnPR'_2$ react with a second mole of phosphine.

$$RZnPR'_2 + HPR'_2 \longrightarrow RH + Zn(PR'_2)_2$$

Alcohols (Table 9)

The reaction between zinc dialkyls and alcohols has been known for some time[153,154] but it is only recently that a detailed investigation has been carried out.

Most of the alkylzinc alkoxides so far described are tetramers.[149] X-ray-crystallographic examination of MeZnOMe and $EtZnOBu^t$ has shown that they possess the cubane structure illustrated.



The tetrameric structure allows the alkoxides to become coordinately saturated so that only the less basic phenoxide forms a pyridine adduct although the use of a stronger Lewis base 4-dimethylaminopyridine causes $(MeZnOMe)_4$ to form an adduct $(Me_2NC_5H_4NZnMeOMe)$ which is dissociated very largely in benzene solution to free base and the tetramer.

The p.m.r. spectra of the alkylzinc alkoxides are interesting in that the O-CH_3 and Zn-CH_3 resonances of $(MeZnOMe)_4$ are split at low and room temperatures, although the latter collapses at about 40°C, whereas the -OBu^t and Zn-CH_3 resonances of $(MeZnOBu^t)_4$ are both singlets. It was thought that isomeric forms of the cubane structure are available to the methoxy compound which are denied the butoxy compound for steric reasons. An alternative explanation, involving equilibria between various alkylzinc alkoxide species e.g. $Me_6Zn_7(OEt)_8$ has been put forward on the basis of the p.m.r. spectra of dimethyl- and diphenylzinc which have reacted with varying amounts of alcohol.[155,156]

Alkylzinc alkoxides are fairly resistant to further alcoholysis and even with water the EtZnOH (the kinetics indicate the EtZnOH is a dimer) produced by $Et_2Zn + H_2O$ eliminates the second mole of ethane only very slowly.[157]

The siloxy compound $CH_3ZnOSiMe_3$ is also tetrameric in non-acidic solvents.[158] Trimers are produced in the reaction between alkylzincs and 2-dimethylaminoethanol, and the products do not react with excess methyl iodide. The following structure is therefore proposed.[142] (fig 18.)

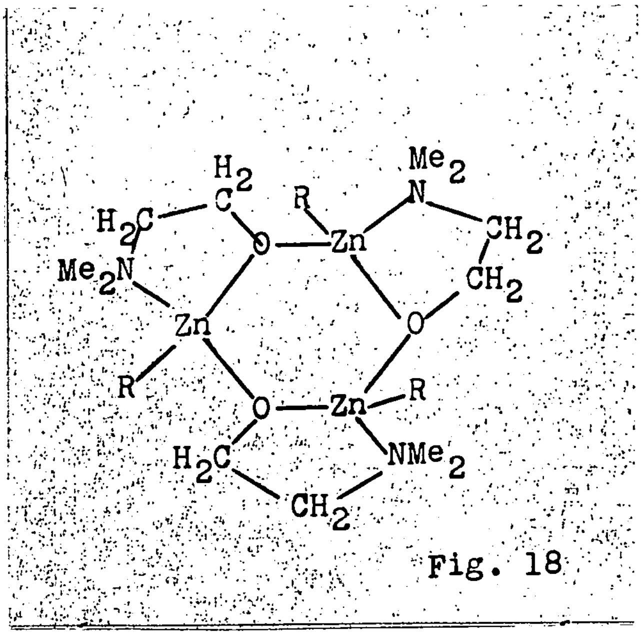
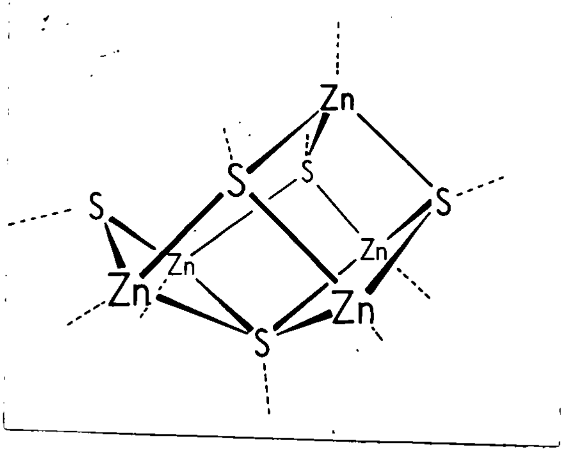


Fig. 18

The reaction between benzophenone and dialkylzincs is interesting. Dimethylzinc forms only a complex from which Me_2Zn can be easily recovered. Diethylzinc reacts with the formation of ethylene and ethylzinc diphenylmethoxide trimer quantitatively. Diphenylzinc reacts to give the normal addition product $(PhZnOCPh_3)_2$. The effect of increasing steric hindrance in reducing the degree of association is illustrated by these compounds.[142]

Thiols.[149] (Table 10)

Equimolar amounts of thiol and dialkylzincs give compounds of the type $(RZnSR')_x$. When R' = Ph or an unbranched alkyl group the products are polymers. With R' = Pr^i, Bu^t, however, very unusual degrees of association are found. No trend with concentration has been found in the molecular weight and additional evidence is provided by an X-ray crystallographic study on $(MeZnSBu^t)_5$, confirming the pentameric structure.



Addition of pyridine causes the thio-compounds to depolymerise but only in one case $(MepyZnSBu^t)_2$ was a crystalline pyridine derivative isolated.

The compounds mentioned above and also polymeric $(MeZnSPh)_x$ all evolved dimethylzinc on heating.

Reactions of organocadmium compounds with acidic hydrogen.

The reactions of organocadmiums with acidic hydrogen have received very little attention until recently.

Alcohols.[159] (Table 11)

The nature of the alkylcadmium alkoxides is very similar to those of zinc with one striking difference, namely methylcadmium t-butoxide dimer.

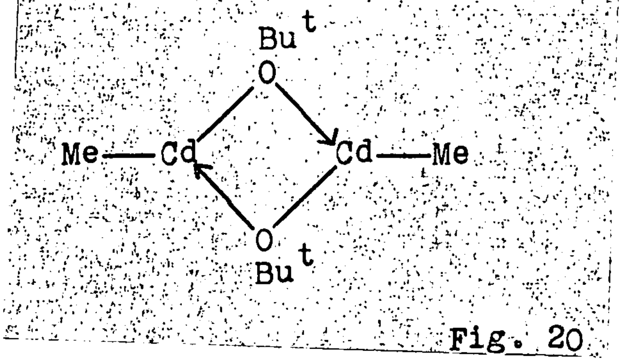


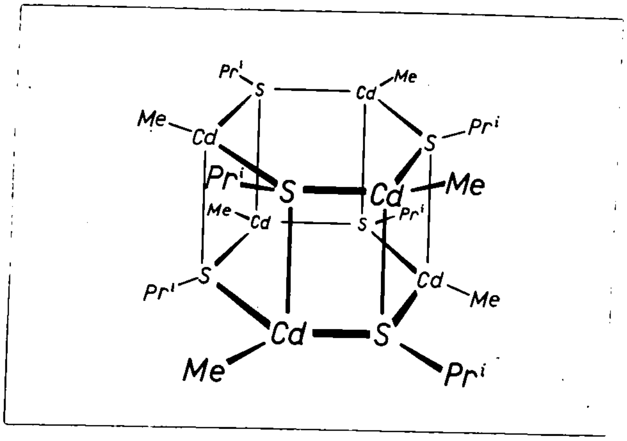
Fig. 20

The tetrameric compounds probably have a cubane structure similar to $(MeZnOMe)_4$, as the X-ray powder pattern for $(MeCdOMe)_4$ is similar to that of MeZnOMe. The reason for the formation of a dimeric species $(MeCdOBu^t)_2$ is somewhat obscure, entropy would favour the formation of dimers, but the isolation of $(RCdOR')_4$ in all other cases seems to indicate that it is not of major importance. The presence of a bulky t-butyl group would favour smaller degrees of association but the existence of $(MeZnOBu^t)_4$ where steric crowding is more pronounced shows that this cannot be the most important factor. Large atoms can cope with angular strain more easily than smaller ones. As the angular strain in a dimer is no greater than that in a tetramer there is no reason why the difference in size between zinc and cadmium should allow the formation of dimeric $(MeCdOBu^t)_2$, especially as zinc forms $(MeZnNPh_2)_2$. An important factor may be the greater energy difference between the outer s and p orbitals as compared with those of zinc. A large s-p energy separation will favour the formation of orbitals with a large amount of s-character and thus the formation of sp^2 hybrid orbitals, as would be present in $(MeCdOBu^t)_2$, may be favoured for sterically hindered cadmium. No pyridine adduct is formed by $(MeCdOBu^t)_2$. The pyridine adduct of MeCdOPh i.e. $(MepyCdOPh)_2$ is partially dissociated in benzene solution unlike the corresponding zinc compound.

The siloxy derivative, $MeCdOSi(CH_3)_3$, is also tetrameric.[158] This compound is an analogue of $(MeCdOBu^t)_2$ but the greater size of the Si atom will remove some of the steric hindrance.

Thiols. (Table 12)

Polymeric products are obtained from Me_2Cd and RSH unless R is a branch chained alkylgroup. Thus $MeCdSPr^i$ is hexameric (fig 21) whereas the more sterically hindered $MeCdSBu^t$ is tetrameric.



Again for the t-butyl compound the cadmium compound is less associated than the zinc analogue. No stoichiometric pyridine adducts are formed but the compound $(MeCdSBu^t)_4$ does retain pyridine to some extent at room temperature.

Mercury.

The dialkyl- and diaryl-mercurials are unaffected by water and dilute acids, concentrated acids being required to decompose them. Thus no compounds analogous to the compounds of zinc, cadmium and beryllium previously discussed are formed. It is worth noting, however, that organomercury alkoxides, are trimeric.

Hydrides of Group II elements.

Magnesium hydrides.

Only the binary hydride of magnesium (MgH_2) has been well characterised although the literature contains a few references to other hydrides e.g. HMgX (X = halogen) and RMgH (R = Et and Ph).

The binary hydride, MgH_2, represents a borderline hydride i.e. on the borderline between a typical ionic saline hydride (NaH) and a typical covalent metal hydride $(AlH_3)_x$.

The hydride has been prepared, in varying degrees of purity, by several different methods. Historically, it was first prepared by the pyrolysis of diethylmagnesium,[168] which loses ethylene at 170° and by the pyrolysis of ethylmagnesium iodide at 175°C. This method has been investigated by later workers[169,170,171,172] who essentially confirmed these results,

$$Et_2Mg \text{ or } (EtMgI) \xrightarrow{175-280^\circ} MgH_2 + 2C_2H_4$$

It was found that some other reaction was taking place during the pyrolysis,[171] as the gas evolved contained 20% ethane and a white crystalline solid sublimed from the pyrolysis vessel. This was given the formula MgC_2H_4 and thought to be a polymer of the type (fig 22.)

$$(Mg - CH_2 - CH_2 - Mg - CH_2 - CH_2-)_x \qquad \text{(fig 22.)}$$

It was later shown, however, that the compound was ethylmagnesium ethoxide[139] produced by cleavage of the ether present by diethylmagnesium

$$Et_2Mg \quad + \quad O(C_2H_5)_2 \quad \xrightarrow{175^\circ C} \quad EtMgOEt \quad + \quad C_2H_6$$

Variation of the alkyl group attached to the magnesium produced no general change in the reaction scheme except in the case of phenyl when although diphenyl, benzene and a little ethylene were evolved the brown pyrolysis residue gave no hydrogen on hydrolysis showing that no magnesium hydride had been formed.[171]

The preparation of hydrohalides of magnesium ($HMgX.xEt_2O$, $x < 1$) by the hydrogenation of 0·5 - 1·0M solutions of ethylmagnesium halide at 100-150°C has been reported.[173] The products were insoluble in organic solvents but on stirring with aluminium chloride in boiling ether gave AlH_2Cl by hydride/halide exchange. All other pyrolyses of alkylmagnesium halides had given a mixture of magnesium hydride and magnesium halide from which the halide could be removed by extraction with ether.

The preparation of $HMgX.2C_4H_8O$ as a crystalline solid has been reported.[174] This was prepared by bubbling diborane through a solution of a Grignard reagent in THF or ether, in either case the dietherate crystallised out. Later work [175] has shown that these compounds are not the hydrohalides but halo-magnesiumborohydrides, formed as shown,

$$3C_2H_5MgCl \quad + \quad 2B_2H_6 \quad \xrightarrow[25^\circ C]{THF} \quad 3ClMgBH_4 \quad + \quad B(C_2H_5)_3$$

from which $ClMgBH_4.2THF$ crystallises; the compound is a dimer in benzene.

The reaction of dialkylmagnesiums with diboranes can, under some conditions, produce MgH_2. The reaction scheme is complex and has been investigated by R. Bauer.[176,177] Diethylmagnesium (free from aluminium) absorbs diborane at room temperature,

$$Et_2Mg + B_2H_6 \longrightarrow \overset{\text{I}}{MgH_2(BEtH_2)_2} \underset{B_2H_6}{\overset{MgEt_2}{\rightleftarrows}} \overset{\text{II}}{2EtMgH_2BEtH}$$

and this reacts with more diethylmagnesium. This second reaction can be reversed by reaction with diborane. Products I and II are air sensitive colourless liquids, which decompose above 80°C,

$$MgH_2(BEtH_2)_2 \longrightarrow MgH_2 + 2BEtH_2$$

$$EtMgH_2BEtH \longrightarrow MgH_2 + BEt_2H.$$

Products I and II also react with diethylboron hydride, dealkylation occurring,

$$MgH_2(BEtH_2)_2 + Et_2BH \longrightarrow Mg(BH_4)_2 + 2BEt_3$$

$$EtMgH_2BEtH + 6Et_2BH \longrightarrow 2MgH_2(BEtH_2)_2 + 4Et_3B$$

When trimethylaluminium is present more complete disproportionation is catalysed giving ethylmagnesium borohydride and MgH_2BEt_3. Ethylmagnesium borohydride decomposes above 100°C to give diethylmagnesium and magnesium borohydride which recombine to form MgH_2,

$$MgEt_2 + Mg(BH_4)_2 \longrightarrow 2MgH_2 + 2EtBH_2$$

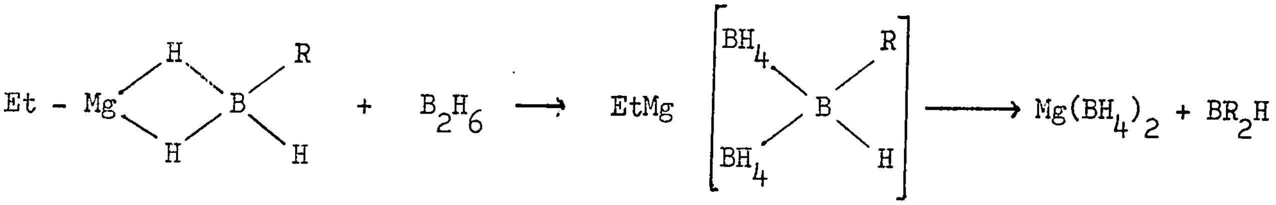
or, if sufficient diethylmagnesium is present,

$$Mg(BH_4)_2 + 3Et_2Mg \longrightarrow 4MgH_2 + 2Et_3B.$$

MgH_2BEt_3 decomposes above 80°C

$$MgH_2BEt_3 \xrightarrow{\Delta} MgH_2 + BEt_3$$

If triethylaluminium is added to a stable solution of product I then reaction occurs and the same products are obtained as if aluminium were present during the reaction of diethylmagnesium and diborane. Product II reacts with diborane to produce magnesium borohydride and diethylboron hydride



If aluminium alkyls are present then magnesium borohydride is formed at 250°C.[177]

Alkyl-hydride exchange has been used in the preparation of magnesium hydride. The reaction between diethylmagnesium and lithium aluminium hydride [178] has been shown to give products which depend markedly on the reaction conditions. Thus on adding diethylmagnesium to an excess of lithium aluminium hydride in ether no precipitate forms even in concentrated solution. Addition of benzene gives a solid of empirical formula $MgAlH_5.xEt_2O$, which could be $HMgAlH_4$ or $MgH_2 + AlH_3$. If the excess lithium aluminium hydride is added to the diethylmagnesium a white precipitate initially forms which redissolves on standing and on reprecipitation the solid has an aluminium to magnesium ratio greater than

1:1. Magnesium hydride, of about 75% purity (impurities mainly ether with some aluminium and some ethyl groups) can be obtained only by the addition of an ether solution of lithium aluminium hydride to a large excess of diethylmagnesium.

Exchange also occurs between diethylmagnesium and diethylaluminium hydride,[179] giving magnesium hydride and triethylaluminium. The magnesium hydride obtained was 97% pure, when reaction was carried out in the absence of a solvent.

Magnesium metal absorbs hydrogen directly at high temperatures and pressures producing magnesium hydride. A variety of conditions have been used, and many catalysts. Studies of the magnesium/hydrogen system[180,181,182] have shown that for magnesium hydride to be formed the decomposition pressure of the solid must be less than the pressure of hydrogen used in the system at a given temperature. If this condition is met then the use of a hydrogen transfer agent, MgI_2, as described in the original preparation,[183] is unnecessary. If a catalyst, such as a mixture of allyl iodide, propargyl bromide and iodine is used, then magnesium hydride can be prepared under much milder conditions, 5atm. hydrogen pressure and 175°C, [184] as opposed to 70atm. hydrogen and 450°C without catalyst.[180]

Hydrogen also reacts directly, under pressure, with an ethereal solution of a Grignard reagent producing magnesium hydride. [185]

$$2RMgX + 2H_2 \xrightarrow{Et_2O} 2RH + MgX_2 + MgH_2$$

The properties of MgH_2 vary with the method of preparation, thus the product formed by direct union of the elements is described as [180] a grey solid inert to air which reacts slowly with water, while the magnesium hydride prepared by pyrolysis of a dialkylmagnesium [171] is said to react immediately in air and to catch fire on addition to water. This difference in properties may be due simply to the differing particle sizes of the magnesium hydride.

The structure of magnesium hydride has been shown by X-ray diffraction [172,180] to be of rutile type with a Mg-H distance of 1•95Å and unit cell dimensions, a = 4•517Å, c = 3•020Å, there being two molecules in the unit cell. A neutron diffraction study of MgD_2 [186] has also been carried out.

The infrared spectrum of magnesium hydride has been studied in the 400-5000 cm^{-1} region.[22,23] The only feature is a very broad band from 1600-900 cm^{-1} with a maximum at 1160 cm^{-1}. It is thought that the absorbtion is due to valence vibrations of the Mg-H bond and the following structure is suggested.

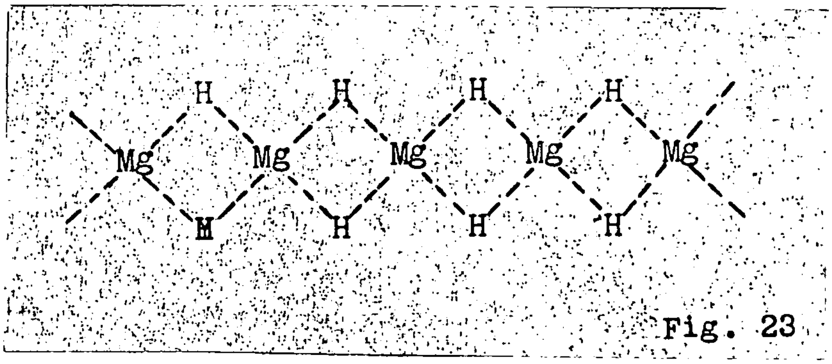


Fig. 23

The available evidence, however, does not rule out an ionic structure for MgH_2 as the Mg-H distances available can be fitted both to an ionic or covalent bridging structure. The actual situation no doubt lies between the two extremes.

The reaction between magnesium hydride and olefins [187] gave products containing only about 4% Mg-Et and traces of higher magnesium alkyl bonds. All attempts to prepare Et-MgH failed. Addition of a catalyst, such as $AlMe_3$, raises the amount of Mg-alkyl products about 17%. The preparation of phenylmagnesium hydrides has been claimed by reaction of phenylmagnesium bromide with lithium aluminium hydride. When the ratio of Grignard to $LiAlH_4$ was 6:1 the product was $Ph_2Mg.PhMgH.3Et_2O$ while when the same ratio was 10:1 $PhMgBr.PhMgH.3Et_2O$ was isolated. [188]

Ethoxymagnesium hydride has been prepared by bubbling silane into an ethereal solution of diethylmagnesium. The suggested reaction is,

$$yMgR_2 + SiH_4 \longrightarrow yHMgR + SiH_{(4-y)}Ry$$

$$HMgR + Et_2O \longrightarrow HMgOC_2H_5 + C_4H_{10}$$

Ethoxymagnesium hydride is an insoluble solid. [205,206]

Hydrides of other Group II elements.

Beryllium hydrides.

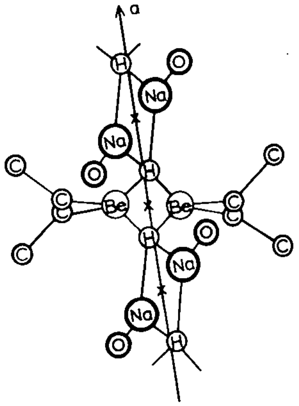
The binary hydride BeH_2 has been obtained in varying degrees of purity by a variety of methods. [189] Pyrolysis of di-t-butylberyllium etherate gives a product containing 96·5 mole per cent BeH_2 [190] and the purity has been improved (98·0 mole per cent BeH_2) by the use of ether free $Bu^t{}_2Be$.[191] A product containing 99·5 mole per cent BeH_2 has been made by removing BH_3 from $Be(BH_4)_2$ with triphenylphosphine.[192]

$$2Ph_3P \quad + \quad Be(BH_4)_2 \quad \longrightarrow \quad 2Ph_3PBH_3 \quad + \quad BeH_2$$

The action of lithium aluminium hydride on ethereal dimethylberyllium gives BeH_2 which retains a good deal of ether[78] and also some aluminium and ether.[191]

Alkali metal hydrides react with dialkyl- and di-arylberyllium[105,106,129] compounds to give complexes of the type $MBeR_2H$ (M = Na, R = Me and Et; M = Li, R = Et, Ph). Di-t-butylberyllium etherate, however, reacts with sodium hydride to give the 1:2 compound $Na(Bu^t{}_2Be)_2H.OEt_2$.[98]

The reactions involving NaH are generally easier to carry out. Both sodium hydridodiethylberyllate and the corresponding lithium compound crystallise with one molecule of ether per sodium (lithium) atom, although the ether is easily removed at low pressures (dissociation pressure of 17 mm. at 25°C).[106] X-ray diffraction has shown that $NaBeEt_2H.OEt_2$ has the structure shown (fig. 24).[193]



The structure shows the existence of $Et_4Be_2H_2$ units with the beryllium atoms linked by hydrogen bridges. The sodium hydrogen distance is 2·40Å, equal to that in sodium hydride.

Ethereal lithium hydridodiethylberyllate reacts with a half molar proportion of beryllium chloride, precipitating lithium chloride and giving a beryllium hydride '$Et_4Be_3H_2$' which is left as a viscous liquid on evaporation of the solvent.[105] This reaction has been more fully investigated for other systems [106] and in each case the species left in solution has the approximate composition $R_4Be_3H_2$ (R = Me, Et). Evaporation of the solvent from an ethereal solution of '$Me_4Be_3H_2$' gives an oily residue of approximate composition "$Me_4Be_3H_2.OEt_2$" which is regarded as an electron deficient complex of the type (fig 25.)

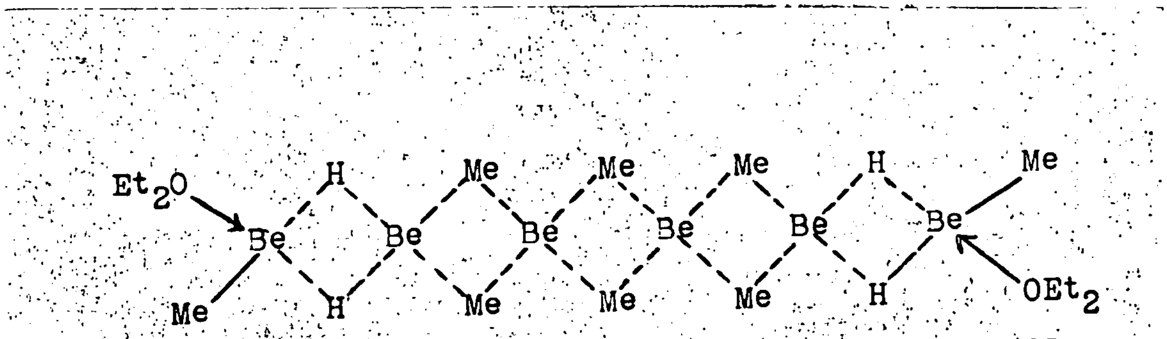


Fig. 25

Addition of donor molecules to '$R_4Be_3H_2$' solutions causes them to behave as mixtures of R_2Be and RBeH, thus addition of trimethylamine gives $Me_2Be.NMe_3$ and the hydride complex $RBeH.NMe_3$ which can be separated by fractional sublimation.[194] The pure hydride complex is dimeric in benzene and the normal Trouton constant (21·1, from vapour pressure data) suggests that, at least up to 110°C, the molecules in the vapour are mainly dimeric. The compound is formulated with hydrogen rather than methyl bridges as it is not decomposed by an excess of trimethylamine which readily breaks the methyl bridges in dimethylberyllium (fig 26).

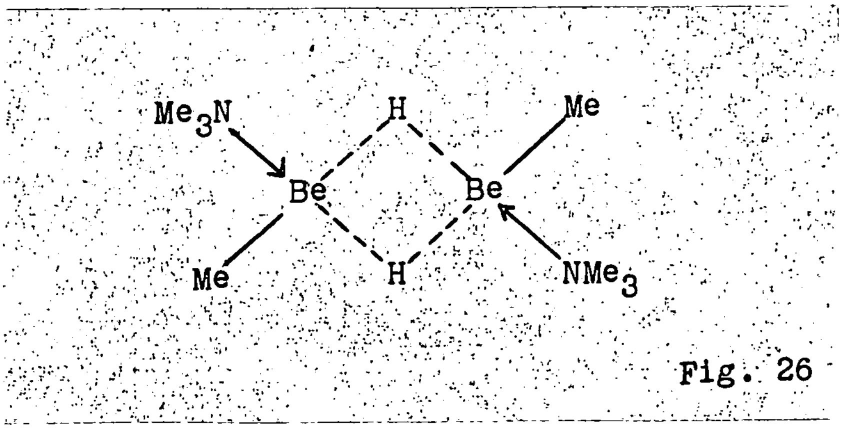


Fig. 26

A study of the infrared spectra of $MeBeH.NMe_3$ and various deuterated species provides further evidence for the above formulation.[106] A terminal Be-H may be expected to cause an absorbtion near 2100 cm^{-1} whereas the absorbtions due to BeH_2Be, by analogy to diborane and the alkyldiboranes, may be expected at approximately 1900 cm^{-1} (ν_{13}, symmetrical out of phase) and 1600 cm^{-1} (ν_{17}, asymmetric in phase). Accordingly a peak at 1344 cm^{-1} (1020 cm^{-1} in $(MeDBe.NMe_3)_2$) has been assigned to a BeH_2Be vibration. On heating a sample of $(MeBeH.NMe_3)_2$ to 80° an absorbtion occurs at 2141 cm^{-1} which is assigned to terminal Be-H in monomeric $MeBeH.NMe_3$. In the compounds $Na_2Be_2Me_4H_2$ and

$Na_2Be_2Et_4H_2$ which are known to possess BeH_2Be bridges infrared absorbtions due to this group have been identified at 1300-1400 and 1060-1170 $cm.^{-1}$

The p.m.r. spectra of $(EtBeH.NMe_3)_2$ and $(MeBeH.NMe_3)_2$ and of some deuterated species in cyclohexane provide evidence for the existence of cis-trans isomerism about the BeH_2Be bridge.[195] Thus the resonance due to the $N\beta CH_3$ protons in the above compounds is split at 25°C and the relative intensities of the two peaks varies with temperature, and the peaks coalesce at about 40°C. Calculations show that trans isomer is more stable at high temperatures.

The p.m.r. spectra of other dimeric hydride complexes $(Et_2OMeBeH)_2$ and $(pyMeBeH)_2$ are consistent with the compounds being either a single geometrical isomer or a mixture of rapidly interconverting cis and trans forms.

Attempts to prepare monomeric complexes L_2BeMeH of MeBeH by the use of chelating donors have not been successful. N,N,N',N'-tetramethylethylenediamine with '$Me_4Be_3H_2$' gives the known Me_2Be complex and a white amorphous insoluble substance $[(MeBeH)_2Me_2NC_2H_4NMe_2]_n$, the BeH_2Be bridge is still present and the complex has been formulated. accordingly (fig 27).

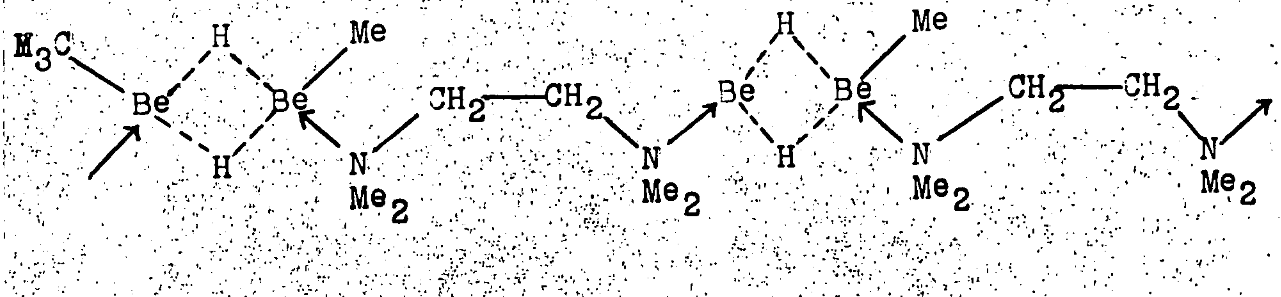


Fig. 27

1,2-Dimethoxyethane gives a similar product.

Ethylberyllium hydride may be produced by hydride/alkyl exchange

e.g. $Et_2Be + Et_3SnH \longrightarrow Et_4Sn + EtBeH$

The ethylberyllium hydride has been characterised by its trimethylamine complex.[105] The trimethylamine complex has also been prepared by the reaction sequence [98]

$$NaBEt_3H + EtBeCl \longrightarrow NaCl + EtBeBEt_3H$$

$$EtBeEt_3BH + 2NMe_3 \longrightarrow EtBeHNMe_3 + Et_3B{:}NMe_3$$

The trimethylphosphine complex of phenylberyllium hydride has been prepared in a similar manner.[101]

The simplest method of making alkylberyllium hydrides is by refluxing an ethereal solution of alkylberyllium bromide (R = Me, Et, Ph; from $R_2Be + BeBr_2$) with lithium hydride.[196]

$$LiH + RBeBr \longrightarrow LiBr + EtBeH$$

The ether is evaporated under reduced pressure precipitating lithium bromide and addition of benzene completes this process leaving the alkylberyllium hydride in solution as an ether complex.

Heating the solid residue from '$Me_4Be_3H_2$' solutions at reduced pressure causes sublimation of dimethylberyllium from the mixture but there is no indication of a pause at a stage corresponding to a residue of methylberyllium hydride. Extensive disproportionation occurs at 170-210° until the hydride:methyl ratio is a little more than 10:1.

$$Me_nBe_{(n/2+m/2)}H_m \longrightarrow Me_{n-2}Be_{(n/2+m/2-1)}H_m + Me_2Be$$

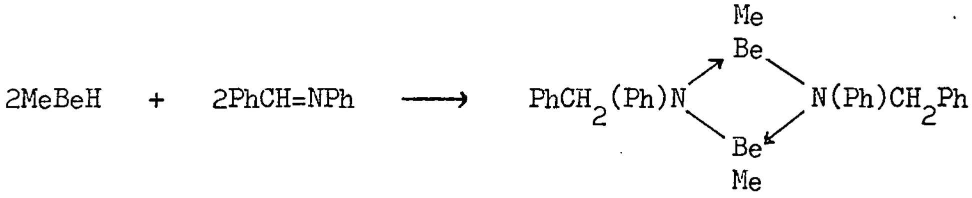
Heating $Et_4Be_3H_2$ for 8 hours at 70-80° leaves a glassy residue consisting mainly of ethylberyllium hydride. If a solution of sodium hydridodiethylberyllate is prepared from excess sodium hydride and diethylberyllium and a half molar proportion of beryllium chloride is added without removing excess sodium hydride, then more sodium hydride dissolves and the filtrate contains a mixture of '$Et_4Be_3H_2$' and $NaBeEt_2H$. Pyrolysis of this mixture at 180° leaves a residue of BeH_2(5 mol.) + $Na_2Be_2H_6$(3 mol.) or BeH_2(8 mol.) + Na_2BeH_4(3 mole.). Further evidence for an ether insoluble sodium beryllium hydride is obtained by boiling ethereal solutions of '$Et_4Be_3H_2$' with excess sodium hydride. The Et:H ratio in solution is always at least 2:1 but $NaEt_2BeH$ is isolated from the solution showing the sodium hydride has dissolved and that hydride has left solution as beryllium hydride or as a complex sodium salt.[106] Ether insoluble lithium salts of the type $nLiH.BeH_2$ have been reported. The ether insoluble hydride Na_2BeH_4 has now been prepared.

$$4NaEt_2BeH + BeCl_2 \longrightarrow 2NaCl + \text{"}Na_2Be_5Et_8H_4\text{"}$$

$$\text{"}Na_2Be_5Et_8H_4\text{"} \longrightarrow 4Et_2Be\uparrow + Na_2BeH_4$$

The involatile residue shows a clear X-ray diffraction pattern. It is more stable thermally than beryllium hydride and is regarded as an electron-deficient polymer with polarised metal-hydrogen bonds rather than a salt $Na_2[BeH_4]$ analogous to $NaBH_4$.[197]

Ethylberyllium hydride reacts with various unsaturated compounds, addition of hydride across the double bond taking place.[196] Addition across carbonyl and azomethine groups is rapid at room temperature. Thus methylberyllium hydride and benzaldehyde form tetrameric methylberyllium benzyl oxide $(MeBeOCH_2Ph)_4$. Methylberyllium hydride and benzophenone in ether solution give the ether complex $Me(Et_2O)BeOCHPh_2$. Reaction between methylberyllium hydride and benzylideneaniline rapidly produces N,N'-phenylbenzyl(methyl)beryllium which is dimeric in benzene solution,



The addition of olefins to what effectively was an alkylberyllium hydride solution has been described in the patent literature.[198] Recently it has been shown that terminal olefin react fairly readily with alkylberyllium hydrides. The reactions were followed by p.m.r. methods and the following degree of reactivity with ethylberyllium hydride was observed,[196] Pent-1-ene >> pent-2-ene.

Bromination of the product from ethylberyllium hydride and pent-2-ene shows that migration of the beryllium to the end of a carbon chain occurs as 1-bromopentane is produced. Beryllium hydride in the presence of a small amount of ethylberyllium hydride reacts quantitatively with pent-1-ene at 84° after 160 hours.

Iso-propylberyllium hydride has been prepared by the pyrolysis of di-_iso_-propylberyllium at 200°C and the corresponding trimethylamine complex by pyrolysis of $Pr^i_2Be.NMe_3$.[100] It is probable that _tert_-butylberyllium hydride has been produced as a viscous liquid by the controlled pyrolysis of di-_tert_-butylberyllium hydride but that isomerisation occurs during the pyrolysis giving a mixture of _iso_-butyl- and _tert_-butylberyllium hydride.[84] Pyrolysis of the di-_tert_-butylberyllium complex with tetramethyltetrazine (TMT) at 90°C gives $Bu^t_2Be.Me_2NN{=}NNMe_2.Bu^tBeH$.[93]

Pyrolysis of dimethylamino(isopropyl)beryllium at 100°C gives dimethylaminoberyllium hydride (Me_2NBeH).[100] A similar type of compound is produced by the reaction of beryllium hydride with an equimolar quantity of N,N,N'-trimethylethylenediamine in hydrocarbon solution. The crystalline compound $HBeN(Me)C_2H_4NMe_2$ is trimeric in benzene [98] and preliminary X-ray data show that the crystal is triclinic.[199] Reaction of beryllium hydride with other compounds containing acidic hydrogen (2-dimethylaminoethanol, 2-dimethylaminoethanethiol, _tert_-butanol, _iso_-propylamine) does not result in the formation of a hydride derivative. Dimethylamine gives a viscous liquid which analyses as $Be(NMe_2)_2.(HBeNMe_2)$.[98]

The reactions of bis-(dimethylamino)beryllium with some alkylaluminium hydrides, trimethylamine-alane and trimethylaluminium have been investigated. Dimethylamino-hydride exchange is complete in the cases investigated, but no methyl-dimethylamino exchange is described.[200]

Hydrides of zinc, cadmium and mercury.

Zinc and cadmium hydrides can be prepared by reaction of dimethyl-metals with lithium aluminium hydride at low temperatures.[178]

$$\mathrm{MMe_2} \quad + \quad \mathrm{2LiAlH_4} \quad \longrightarrow \quad \mathrm{MH_2} \quad + \quad \mathrm{2\,`LiAlH_3X'}$$

The nature of the aluminium compound, which remains in solution, is unknown. In the case of zinc, zinc iodide may be used. A later study[201] of the zinc iodide reaction with lithium aluminium hydride, by conductimetric titration, showed two discontinuities in the titration curve at $\mathrm{ZnI_2:LiAlH_4}$ ratios of $\frac{1}{4}:1$ and $\frac{1}{2}:1$. The conductivity rose towards the first point and fell towards the second, leading to the interpretation.

$$\begin{tikzcd}
\mathrm{4LiAlH_4} \quad + \quad \mathrm{ZnI_2} \quad = & \mathrm{Li_2[Zn(AlH_4)_4]} \arrow[d, "+\mathrm{ZnI_2}"] \\
& \mathrm{2Zn(AlH_4)_2} \quad + \quad \mathrm{2LiI} \arrow[d] \\
& \mathrm{ZnH_2} \quad + \quad \mathrm{2AlH_3}\text{(in solution).}
\end{tikzcd}$$

The conductivity curve showed further reactions between the $\mathrm{Li/AlH_3/I}$ species and $\mathrm{ZnI_2}$.

Zinc and cadmium hydrides are white, non-volatile, insoluble materials which decompose at normal temperatures, zinc hydride slowly and cadmium hydride rapidly at 0°C, giving the metals and hydrogen.[202]

Alkyl-hydrogen exchange takes place between diethylzinc and diethylcadmium with diethylaluminium hydride but no metal hydrides were isolated.[179]

Evidence for the existence of methylzinc hydride is reported in the observations that zinc hydride dissolves in ether containing a large excess of dimethylzinc.[203] Attempts to isolate this compound by the equilibration of equimolar quantities of lithium aluminium hydride and dimethylzinc-trimethylamine, and between diethylzinc and trimethylstannane failed. The former gave zinc hydride and the latter zinc, ethane and hexaethyldi-tin and tetraethyltin. Attempts to repeat the dissolution of zinc hydride in ethereal dimethylzinc also failed.[111]

Diborane reacts with dimethylzinc forming methylzinc borohydride and zinc hydride, not $(HZnBH_4)_n$ as previously reported.

$$2Me_2Zn + B_2H_6 \longrightarrow MeZnBH_4 + ZnH_2 + Me_3B$$

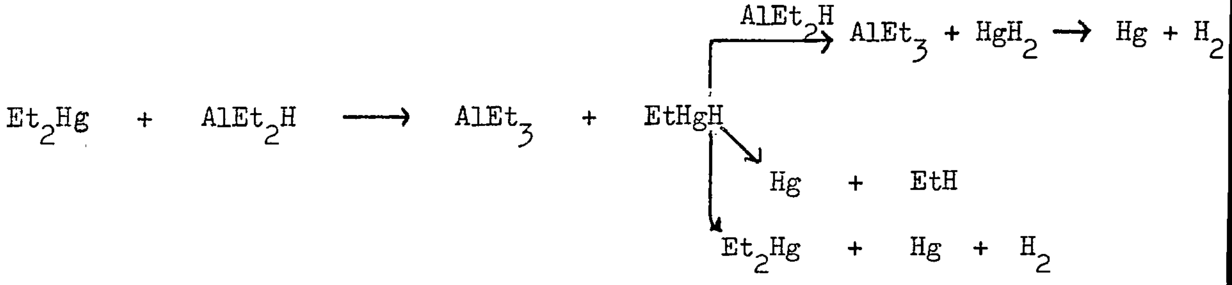
The methylzinc borohydride is a volatile crystalline solid.[111]

Zinc hydride reacts with N,N,N'-trimethylethylenediamine liberating hydrogen and forming $HZnN(Me)C_2H_4NMe_2$, a crystalline complex which is dimeric in benzene solution.[98]

Anionic hydride complexes of zinc are known. Lithium hydride dissolves in an ethereal solution of diphenylzinc and the complex etherate $LiZnPh_2HnOEt_2$ can be crystallised. Diethylzinc and zinc chloride form 2:1 complexes $Na(ZnX_2)_2X$ (X = Cl or Et) with sodium hydride in monoglyme or diglyme, but not in ether solvents.[204] Attempts to isolate these compounds led to decomposition.[204] These compounds are similar to the beryllium complex hydride $[Na(Bu^tBe)_2H]_n$.[98]

Attempts to prepare mercury hydride by alkyl-hydride exchange have generally failed, even at low temperatures, only mercury and hydrogen being produced.[178] A solid supposed to be mercury hydride has been prepared at -135° by Wiberg and Henle. This decomposed rapidly above -90°C.[202]

Diethylaluminium hydride and diethylmercury react in the absence of a solvent giving mercury, hydrogen and ethane. The presence of ethane in the gas mixture was taken to indicate the transitory formation of ethylmercury hydride.[179]



The reaction of ethylberyllium hydride-trimethylamine and diethylmercury in the absence of solvent resulted in quantitative evolution of ethane, and the formation of diethylberyllium-trimethylamine and mercury.

$$(EtBeH{:}NMe_3)_2 \quad + \quad 2Et_2Hg \quad \longrightarrow \quad 2Hg \quad + \quad 2C_2H_6 \quad + \quad 2Et_2Be{:}NMe_3$$

These results are not compatible with an ethylmercury hydride intermediate.[101]

The decrease in stability of the binary hydrides of Group II metals with increasing molecular weight is very marked.

EXPERIMENTAL

Apparatus and Techniques.

Most of the compounds studied were sensitive to both oxygen and moisture and therefore almost all the work was carried out in an atmosphere of oxygen- and moisture-free nitrogen.

The nitrogen was B.O.C. 'White Spot' which was further purified by passing over heated copper, to remove the last traces of oxygen, and through a molecular sieve and a liquid nitrogen trap, to remove the last traces of water.

The compounds used were usually not volatile enough to be handled on a vacuum line and were generally prepared and purified in a double-limbed Schlenk tube. Whenever possible the air sensitive materials were transferred under nitrogen on the bench, when this was not possible materials were handled in a nitrogen-filled glove box fitted with a recirculating gas purifying system. The nitrogen in the box was continuously recycled, using a small mechanical pump, passing through two heated (350°C) copper towers and a liquid nitrogen trap. All connections were made using either copper or butyl rubber tubing. The gloves were of the 'Buta-sol' type with a low permeability to both oxygen and moisture.

The vacuum apparatus used had two main sections. (i) Fractionation train - consisting of three U-traps connected by mercury float valves, in which volatile compounds could be purified. (ii) Gas analysis system - gases which were not condensable by liquid nitrogen were measured by using a Topler pump and gas burette. Condensable gases were measured by a calibrated bulb system attached to a manometer. Gaseous mixtures were analysed by the use of a combustion bulb which could be attached to the gas analysis system. Facilities were also available for attaching an infra-red gas cell to the apparatus.

Infra-red spectra.

Infra-red spectra were recorded using either a Grubb-Parsons "Spectromaster" or GS2A prism-grating spectrophotometer, both of which had a range of 4000-400 $cm.^{-1}$ Routine low resolution spectra were recorded on a Perkin Elmer 'Infracord' with a 4000-666 cm^{-1} range.

The spectra of solid compounds were generally recorded as nujol mulls pressed between KBr discs and, where solubility allowed, as a solution in 'Spectrosol' cyclohexane using a compensated cell.

Nuclear magnetic resonance spectroscopy.

Proton and ^{11}B resonance spectra were recorded on a Perkin Elmer R10 spectrometer operating at $33{\cdot}5^{\circ}C$, and 60 Mc/s for protons and 19·75 Mc/s for ^{11}B nuclei. Chemical shifts were measured relative to tetramethylsilane, or benzene for protons and trimethylborate for ^{11}B nuclei.

Variable temperature studies were carried out on a A.E.I. RS2 spectrometer operating at 60 Mc/s.

Analyses.

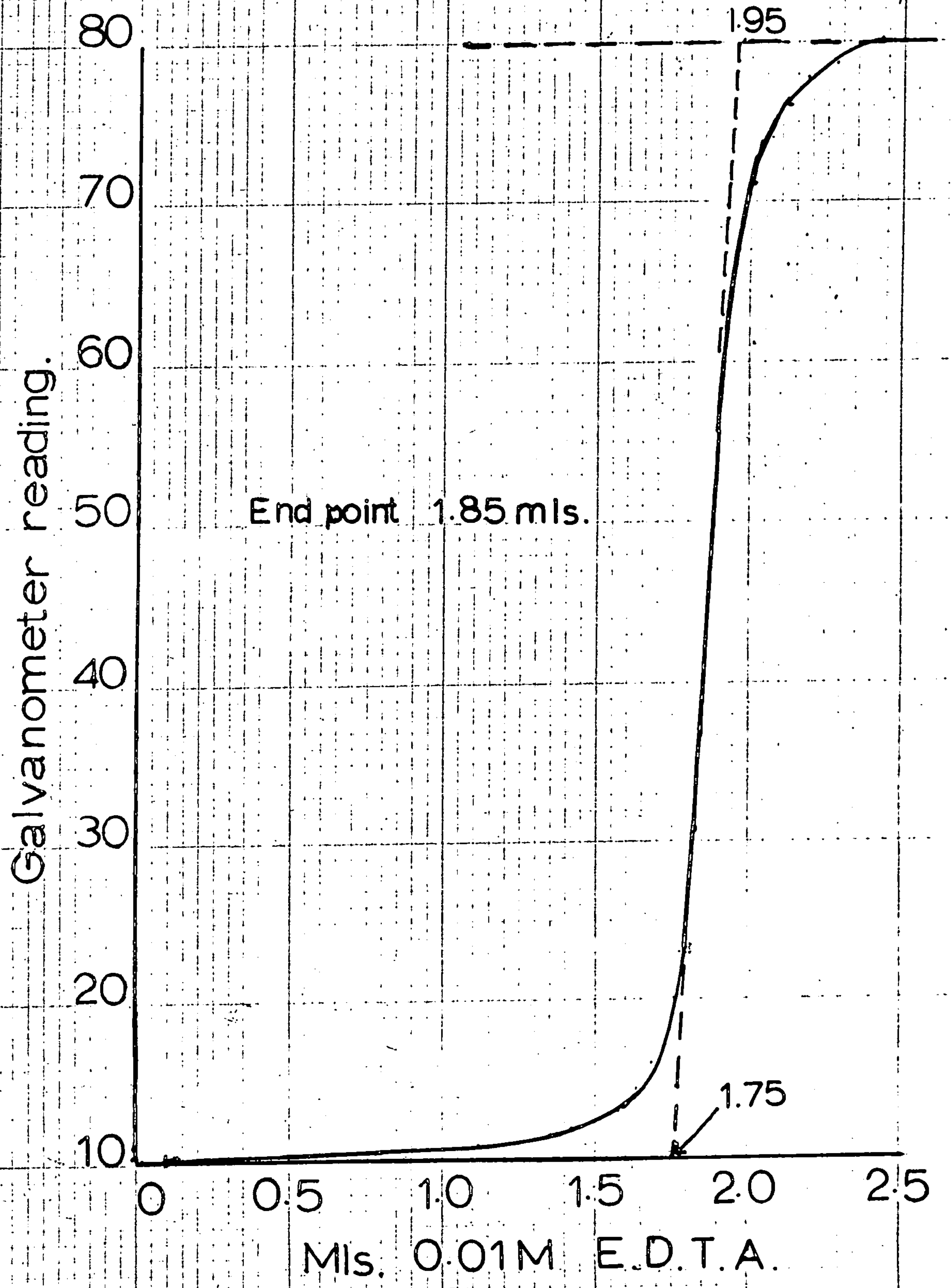
Magnesium analyses.

After a study of the various known methods for the determination of magnesium (as pyrophosphate, colo~~r~~rimetrically using Titan Yellow, flame photometry) the metal was determined volumetrically using EDTA and eriochrome black T. The main interference encountered was organic matter which was removed by fuming with concentrated nitric acid. When sulphur compounds, thiols, were used concentrated nitric acid did not remove the interference. It was found, however, that the thiol could be removed by pumping an acid solution almost to dryness.

The magnesium determination was carried out using an 'Eel' titrator. Aliquots of the magnesium solution (10 mls. containing about 5×10^{-5} moles of magnesium) were neutralised with dilute sodium hydroxide, buffered to pH 10 using an ammonia/ammonium chloride buffer (5 mls.) and after addition of the indicator (~10 drops) titrated with 0·01M EDTA. The indicator solution consisted of 0·1g. of eriochrome black T dissolved in 14 mls. of distilled water and 6 mls. of propanol. A fresh indicator solution was prepared daily.

A typical plot of mls. of EDTA added against galvanometer reading is shown in fig.28. It was found by studies on standard solutions that the best end point was obtained by using the construction shown in figure 28.

Fig. 28.


80
70
60
50
40
30
20
10
Galvanometer reading.
1.95
End point 1.85 mls.
1.75
0
0.5
1.0
1.5
2.0
2.5
Mls. 0.01M E.D.T.A.

Gas analyses.

Compounds which evolved gas on hydrolysis were analysed by adding 'degassed' 2-methoxyethanol to a weighed sample contained in a flask attached to the vacuum system previously described. The samples were initially held at liquid nitrogen temperature, allowed to warm to room temperature and the hydrolysis completed by the addition of dilute (2N) sulphuric acid. Unless the hydrolysis is carefully controlled some carbon is formed resulting in low values for the amount of hydrolysed gas. After fractionation and measurement the gases were identified either by their vapour pressure at liquid nitrogen temperature or more usually by their infra-red spectrum. All gas volumes were corrected to N.T.P.

Mixtures of methane and hydrogen were determined by combustion with an excess of oxygen followed by measurement of the carbon dioxide produced which could be simply separated from the other product, water, and the excess of oxygen. The amount of carbon dioxide produced is equivalent to the amount of methane present in the initial mixture.

Halide analyses.

Halide determinations were carried out in the analytical section of the department, generally on the acid solutions available after the determination of magnesium. The method used depended on the release of hydroxyl ions, equivalent to the halide present, on the addition of mercury oxycyanide,

$$\mathrm{Hg(OH)(CN)} + \mathrm{Cl^-} \longrightarrow \mathrm{Hg(CN)Cl} + \mathrm{OH^-}$$

Amine analyses.

Volatile amines were estimated by steam distillation from an alkaline solution of the amine into an excess of standard acid. The excess acid was determined by titration with standard alkali.

Boron analyses.

Whenever possible boron was determined as boric acid by titration with standard alkali, in the presence of mannitol using a methylene blue indicator. Organoboron compounds were converted into boric acid by making a cooled 'solution' of them alkaline with 3N sodium hydroxide and adding approximately 5 mls. of 100 volume hydrogen peroxide. The solution was left for one hour to complete the oxidation and then the excess hydrogen peroxide destroyed with a small amount of platinum black.

It was found that magnesium interfered with the boron titration and the following procedure was adopted. A weighed sample was placed in a two necked flask under nitrogen and cooled to liquid nitrogen temperature. Dry methanol was added to the flask which was allowed to warm up. The flask was cooled again in liquid nitrogen and a few drops of concentrated sulphuric acid carefully added. The flask was connected to a distillation apparatus and the boron distilled from the solution as trimethoxyborane which was led into distilled water where it immediately hydrolysed to boric acid. The boric acid was determined in the usual manner.

$$\begin{tikzcd}
\mathrm{BR_3} + 3\mathrm{MeOH} \arrow[r, "H^+"] & \mathrm{B(OMe)_3} \arrow[dr, "H_2O"'] & + \quad 3\mathrm{RH} \\
& & \mathrm{B(OH)_3} + 3\mathrm{MeOH}
\end{tikzcd}$$

Sodium and lithium.

Sodium and lithium were estimated using an 'Eel' flame photometer Mark II, calibrated with standard sodium or lithium solution over a concentration range in which the calibration curves were linear, i.e. from 0·001 to 0·01g. of alkali metal per litre.

Molecular weight measurements.

Molecular weights were determined cryoscopically in 'Analar' benzene which had been carefully dried with sodium wire and calibrated with sublimed diphenyl. All molecular weight determinations were carried out under a static nitrogen atmosphere.

Purification of solvents and preparation of starting materials.

Solvents.

The following solvents were dried by standing over sodium wire - diethyl ether, pentane, hexane, methylcyclohexane, benzene, toluene and xylene.

1,2-Dimethoxyethane and tetrahydrofuran.

These solvents were purified and dried by distillation from lithium aluminium hydride immediately prior to use.

1,4-Dioxan.

Dioxan was available as the 'technical' grade and required extensive purification. 'Technical' dioxan (200 mls.) was refluxed with 200 mls. of 1N hydrochloric acid for 24 hours, with nitrogen continuously blowing through the apparatus to remove the large amount of acetaldehyde produced. Stannous chloride (0·2g) was added, to remove peroxides, and the dioxan separated from the aqueous layer and distilled (b.pt. 88°C). The distilled dioxan was then refluxed with sodium for 6 hours and distilled from molten sodium. More sodium was added and the dioxan refluxed again until a blue colour developed on addition of benzophenone. The dioxan was distilled and stored over sodium wire.

Amines.

All amines were either available in the pure state or were purified by distillation from an appropriate drying agent.

Alcohols.

Alcohols were normally purified by distillation after refluxing with magnesium turnings or magnesium hydride.

Thiols.

The thiols were normally available in a pure dry state. N,N-Dimethylaminoethanethiol was prepared from the corresponding hydrochloride by addition of less than one molar equivalent of sodium hydroxide to an aqueous solution. The thiol was extracted with ether and purified by fractional distillation followed by a final distillation.

Grignard reagents.

These were prepared by the standard procedure from alkyl bromides and magnesium turnings in diethyl ether or tetrahydrofuran. The yields obtained varied with the nature of the organic group - MeMgBr, EtMgBr (80-90%); Pr^iMgBr (60-70%); Bu^tMgCl (50-60%). The drop in yield is due mainly to the formation of magnesium halide via a coupling reaction.

Magnesium bromide was prepared in an analogous manner using 1,2-dibromoethane and magnesium turnings.

Dimethylmercury.

Dimethylmercury was prepared by reaction of mercuric chloride with two molar equivalents of methylmagnesium bromide. The product was separated from ether by fractional distillation and final purification effected by distillation, b.pt. 92-93°/760mm. Yield 66%.

Diethylmercury.

Diethylmercury was prepared by a similar method to that outlined for dimethylmercury. An 80% yield was obtained on a two molar scale. Et_2Hg b.pt. 152°/760mm.

Diphenylmercury.

This was obtained by the reduction of phenylmercury chloride (available commercially) with hydrazine hydrate in refluxing methanol.

The product was purified by crystallisation as colourless needles (m.pt. 124-125°C) from methanol. Yield 85%. The compound was stored in the dark as it deposits mercury on exposure to light.

Triethylboron.

Tributoxyborane was prepared by refluxing n-butanol with boric acid and purified by distillation.

$$B(OH)_3 \quad + \quad 3Bu^nOH \longrightarrow \quad B(OBu^n)_3 \quad + \quad 3H_2O$$

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

Sodium triethylboron hydride.

Triethylboron in ether solution was added dropwise to a refluxing, vigorously stirred suspension of sodium hydride in diethyl ether. The sodium hydride readily dissolved producing sodium triethylboron hydride.

$$NaH \quad + \quad Et_3B \xrightarrow{Et_2O} NaBEt_3H$$

The ethereal solution was standardised by a complete analysis, for hydrolysable hydrogen, boron and sodium.

Trimethylboron.

Trimethylaluminium (10·3g) was run into a 500 ml., two-necked flask fitted with a dropping funnel and attached to the vacuum system. Tributoxyborane was slowly added and a vigorous reaction ensued. As the trimethylboron was produced it was fractionated through a trap at -30°C and finally collected in a liquid nitrogen trap. The reaction flask was heated to 100°C to complete the reaction and remove all the trimethylboron. The trimethylboron was refractionated and stored in the vacuum system.

The use of this method of preparing trimethylboron avoided the difficult separation of trimethylboron from ether encountered in the normal preparation by the Grignard method.

Dialkylmagnesium compounds.

Two methods of preparation were used for these compounds, (a) Dimethyl- and diethylmagnesium were prepared by reaction of magnesium turnings with the corresponding mercury alkyl, (b) dimethyl-, diethyl-, di-isopropyl- and di-t-butylmagnesium were prepared from the corresponding Grignard reagent by precipitation of magnesium halide with 1,4-dioxan.

(a) From dialkyl mercury.

$$Mg + HgMe_2 \longrightarrow MgMe_2 + Hg$$

Magnesium turnings (12·2g) were placed in a pyrex Carius tube and dimethylmercury (58g) added to them. The tube was cooled in liquid nitrogen, evacuated and sealed. Heating at 100°C in an oven overnight caused the formation of a voluminous grey powder. The tube was opened in a dry box and the contents transferred to a Soxhlet extractor. The solid was first extracted with hexane to remove any excess dimethylmercury and the hexane solution discarded. Ether extraction followed giving a dimethylmagnesium solution which was standardised by analysis for hydrolysable methyl and magnesium.

Diethylmagnesium was prepared in a similar manner except that Soxhlet extraction was unnecessary and the product could be obtained simply by adding ether and filtering from the excess magnesium.

Attempts to scale up this reaction led, for both dimethyl- and diethylmagnesium to the explosion of the reaction vessel. It is, therefore, recommended that the reaction should only be performed on a small scale ($<$ 0·25Molar) and that the heating of the reaction tube should be carried out in a well ventilated, isolated fume cupboard.

(b) Dioxan method.

This method involves the preparation of a Grignard compound and the addition of enough 1,4-dioxan to precipitate all the halide present.

$$2Mg \quad + \quad 2RX \quad \longrightarrow \quad 2RMgX \quad \xrightarrow{2(1,4\text{-dioxan})} \quad R_2Mg \quad + \quad MgX_2.2\text{dioxan}$$

There are two main difficulties to the preparation,

(a) Removal of the precipitated magnesium halide dioxan complex.

It was found that if the Grignard solution was vigorously stirred during the very slow addition of the dioxan and stirring continued for 24 hours after addition was complete then in the case of dimethyl- and diethylmagnesium the magnesium halide could be easily filtered or decanted from the dialkylmagnesium solution. For the branched chain alkyls, however, in general the precipitate was not filterable, a method involving centrifuging the precipitate was, therefore, devised.

(b) Presence of excess dioxan.

It was found that all the methods for preparing dialkylmagnesium compounds described in the literature ensured complete removal of halide by the addition of an excess of dioxan ($>$ 2 molar equivalent). This excess dioxan forms a complex with the dialkylmagnesium (see later experimental). The dioxan complexes of dimethyl- and diethylmagnesium lose dioxan on heating but di-isopropyl- and di-t-butylmagnesium do not lose their dioxan on heating before they start to decompose. As the presence of dioxan would affect the course of a number of the reactions studied the effect of dioxan on a Grignard solution (t-butylmagnesium chloride) was investigated.

Tert-butylmagnesium chloride was prepared in the usual way and the solution analysed for hydrolysable butane, magnesium and chlorine. Four, ten ml. samples were taken and different amounts of dioxan added to each, the solutions centrifuged and the supernatent liquor analysed. Each sample contained Grignard reagent which could be regarded as 0·0144 moles of Bu^tMgCl and 0·0038 moles of $MgCl_2$.

Sample	Amount of dioxan added	Bu^t : Mg	Mg : Cl
Initial	-	1 : 1·25	1 : 1·15
A	$6{\cdot}5\times10^{-3}$ moles	1 : 0·78	1 : 0·74
B	$8{\cdot}8\times10^{-3}$ moles	1 : 0·70	1 : 0·72
C	$1{\cdot}4\times10^{-2}$ moles	1 : 0·66	1 : 0·42
D	$2{\cdot}2\times10^{-2}$ moles	1 : 0·53	1 : 0·04

Although the results are not intended to be accurate, as some time dependency was found, they show that the 1:2 magnesium chloride - dioxan complex is formed, but that not all the chloride (~4-5% remains) was precipitated at the 'equivalence' point. The proton magnetic resonance spectrum of solution D was recorded. This showed that dioxan was present in the solution. The reaction,

$$2Bu^tMgCl + 2C_4H_8O_2 \rightleftharpoons Bu^t{}_2Mg + MgCl_2.(C_4H_8O_2)_2$$

is an equilibrium with the reaction well over to the right but an excess of dioxan must be added to remove all the chloride and some of this dioxan will remain in solution. The di-t-butylmagnesium solutions used therefore contain small amounts of both dioxan and halide. The following description is a typical preparation of di-isopropyl- or di-t-butylmagnesium.

The tert-butyl- Grignard reagent was prepared in the usual way. Analysis showed that the solution was 1·0M with respect to hydrolysable 2-methylpropane, 1·29M in magnesium and 1·43M in chloride. Thirty mls. of the Grignard solution were syringed into a centrifuge tube through a rubber serum cap and 30 mls. of dry ether added. Dry dioxan (3·7g, 0·042 moles) was added to the vigorously stirred solution producing an immediate white precipitate. Three similar centrifuge tubes were prepared and rotated at 3000 r.p.m. for thirty minutes on a M.S.E. 'Multex' centrifuge. The supernatant di-t-butylmagnesium solution was transferred by syringe to a nitrogen filled two-necked flask. The solution was 0·18M with respect to hydrolysable iso-butane, 0·177M with respect to magnesium and 0·007M with respect to chloride.

The procedure for dimethyl- and diethylmagnesium was as follows. The Grignard reagent was prepared in the usual way and completely analysed. Two molar equivalents of 1,4-dioxan were added to the stirred solution and the slurry stirred for 24 hours. On standing the slurry for 24 hours the precipitate settled out and the dialkylmagnesium solution decanted from it.

Experimental Results.

Unless otherwise stated all reactions were carried out under dry nitrogen in a double-limbed Schlenk tube.

Reaction between dimethylmagnesium and N,N,N',N'-tetramethylethylenediamine.

The ditertiary amine in slight excess (1·2g., 0·0103 mole) was added to dimethylmagnesium (0·01 mole) in diethyl ether (20 cc.). Slight heat evolution occurred and a white precipitate formed which dissolved on boiling the ether. A crystalline compound was obtained on cooling the ether solution to -78°C. On heating in vacuo the solid sublimed at 65-75°/0·01mm., m.pt. 97-98°. [Found: Mg, 14·3; hydrolysable methyl, 17·6%; M(cryoscopically, 0·22 and 0·33 wt.% in benzene, 178-181. $C_8H_{22}MgN_2$ requires Mg 14·3; hydrolysable methyl, 17·6%; M, 171].

The infrared spectrum recorded as a nujol mull had absorptions at; 2941s(sh), 2915s, 2849s, 2770m(sh), 1466s, 1451s, 1410m, 1377s, 1353m, 1287m, 1261w, 1250m, 1189w, 1163m, 1126m, 1099s, 1091s, 1064m, 1043m(sh), 1031s, 1017s, 947m, 794m, 769w, 721w, 581m, 541s.

The spectrum of a saturated solution in cyclohexane (1mm. spacer) was essentially similar, the 600-400 cm^{-1} region was however, more resolved; 582w, 544s, 516m.

Reaction between dimethylmagnesium and N,N,N',N'-tetramethyl-o-phenylenediamine.

Addition of the diamine (1·49g, 0·0085 moles) to dimethylmagnesium (0·01 mole) in diethyl ether (30cc.) at room temperature resulted in heat evolution sufficient to boil the solution. A solid crystallised when the solution was concentrated, and after removal by filtration, was washed with pentane (10cc.) and dried under reduced pressure at room temperature. The complex decomposed when heated above 70°. [Found: Mg, 11·1; hydrolysable methyl, 14·0%; M(cryoscopically, 0·64 wt.-% in benzene) 212. $C_{12}H_{22}MgN_2$ requires Mg, 11·1; hydrolysable methyl, 13·75%; M, 219].

The infrared spectrum of the complex as a nujol mull contained absorptions at; 3058m(sh), 2890s(sh), 2849s, 2778s(sh), 1443s, 1372m, 1316w, 1282w, 1247m, 1205w, 1189m, 1183m(sh), 1151m, 1145m, 1089s, 1044m, 1012s, 989w, 952w, 924s, 916m(sh), 870vw, 771s, 745m, 683m, 595m(sh), 583m, 489s.

The p.m.r. spectrum contained three resonances at 3.15τ, 7·38τ, 11·29τ relative to T.M.S. as an internal standard. These are assigned on the bases of relative intensity and position to aromatic protons, nitrogen-methyl protons, and magnesium methyl protons respectively.

Reaction between dimethylmagnesium and 1,2-dimethoxyethane.

Addition of 1,2-dimethoxyethane in excess (2cc.) to dimethylmagnesium (0·01 mole) in diethylether (20cc.) gave an immediate white precipitate which was soluble enough to allow its recrystallisation from the warm ether/monoglyme mixture. The complex did not melt when heated under nitrogen at atmospheric pressure but decomposed by dissociation from about 120°C. On heating in vacuo the solid began to lose monoglyme at about 105° and 0·1mm. pressure, at 160° a white solid sublimed which was shown by its infrared spectrum to be uncoordinated dimethylmagnesium. [Found: Mg, 17·2, hydrolysable methyl 20·0%. $C_6H_{10}MgO_2$ requires Mg, 16·8, hydrolysable methyl 20·8%]. The complex was insoluble in benzene and no molecular weight was determined.

The infrared spectrum recorded as a nujol mull contains absorptions at; 2899s, 2786m(sh), 1453s, 1368m, 1282w, 1248m, 1100s, 1051s, 1022s, 1010m(sh), 867s, 831w, 798vw, 578s, 562s(sh), 476s.

Reaction between dimethylmagnesium and 2,2'-bipyridyl.

Addition of sublimed bipyridyl (0·005 moles) in ether solution (10 mls.) to dimethylmagnesium (0·0045 moles) in diethyl ether (10 mls.) gave an immediate bright yellow crystalline material which turned brown and then black after about one hour. The bright yellow material gave a red benzene solution which is more stable than the solid but eventually became brown. Even the black tarry material reacted violently with water evolving methane. No pure complex could be isolated.

Crystallisation of dimethylmagnesium.

Dimethylmagnesium (0·0089 moles) in diethyl ether was cooled to -78°C when colourless needlelike crystals formed. These were filtered from excess ether and allowed to warm to room temperature. At room temperature the solid was white and powdery. No attempt was made to dry the product. A small amount of the solid was mounted in a pyrex tube and its X-ray diffraction pattern recorded. This was compared with published values and with that of another sample which had been thoroughly dried in vacuo and whose analysis showed that it was ether-free dimethylmagnesium. [Found: Mg, 44·62; hydrolysable methyl, 55·80%. C_2H_6Mg requires Mg, 44·72, hydrolysable methyl 55·28%].

d-values for sample (calc.)	d-values for Me_2Mg
5·79	5·76
5·33	5·34
3·304	3·302
2·652	2·666
2·425	2·430
2·074	2·074
2·014	2·017
1·969	1·971
1·900	1·903

N,N,N',N'-Tetramethylethylenediamine - Diphenylmagnesium.

The di-tertiary amine (5cc.) was added to a solution of diphenylmercury (purified by sublimation; 5·73g, 0·0162 mole) in benzene (10cc.) to which magnesium turnings (0·8g, 0·33 mole) had been added. The mixture was boiled under reflux and with continuous stirring for 24 hours, after which the remaining metal was observed to be amalgamated and no soluble mercury compound could be detected in the pale yellow supernatant solution. The supernatant liquid was transferred (N_2 atmosphere) to a double Schlenk tube, and, after filtration, solvent was removed under reduced pressure until crystallisation began. The complex was separated by filtration and dried at low pressure, m.p. 170-172°. [Found: Mg, 8·3; amine, 38·9%. M(cryoscopically, 0·45 and 0·89 wt.-% in benzene), 312 and 319. $C_{18}H_{26}MgN_2$ requires Mg, 8·25; ditertiary amine, 39·4%; M, 295].

The infrared spectrum of the complex, recorded as a nujol mull, contained absorptions at; 3215m, 2933s(sh), 2906s, 2841s, 2747w, 1592m, 1466s, 1412m, 1381s, 1346m(sh), 1291m, 1269w, 1250w, 1232m, 1192w, 1164m, 1151w(sh), 1127w, 1099w, 1056m, 1046m, 1030m, 950m, 935w(sh), 794m, 766w, 736w, 718m, 709s, 704s, 675s, 640w, 633w, 430m.

The complex was also prepared by the following method. An excess of the di-tertiary amine (0·005 moles) was added to a solution of bis-(tetrahydrofuran)-diphenylmagnesium (see later for preparation, 0·95g, 0·003 moles) in benzene (15 mls.). Some solvent was removed and methylcyclohexane added, from which the complex was crystallised m.p. 169-171°C. The infrared spectrum of the complex as a nujol mull was identical to that of the complex prepared as outlined above.

1,2-Dimethoxyethane - Diphenylmagnesium.

A mixture of diphenylmercury (7g.), 1,2-dimethoxyethane (4cc.), benzene (50cc.) and magnesium (0·6g.) in a tube was frozen, evacuated, sealed, and then heated for seven days at 100°. The tube was opened in a glove box and its contents transferred to a double Schlenk tube. After addition of hexane to the filtered solution, the complex crystallised and it was recrystallised from a 2:1 benzene-hexane mixture. The complex decomposed without melting when heated. [Found: Mg, 9·2%; M(cryoscopically, 0·58 and 0·88 wt.-% in benzene), 274 and 272. $C_{16}H_{20}MgO_2$ requires Mg, 9·05%; M, 269].

The infrared spectrum of the complex as a nujol mull contained absorptions at; 3030w, 2941s(sh), 2915s, 2849s, 1590m, 1490s, 1462s, 1408w, 1376m, 1368m(sh), 1299m, 1247vw, 1225vw, 1203vw(sh), 1188w, 1163w, 1111m, 1089m, 1066m, 1053m, 1043m, 1024m(sh), 922w, 864m, 848m, 830w, 761m, 736w, 718m(sh), 711m, 700m, 675m, 571m, 529m, 438m.

Bis-(tetrahydrofuran) - Diphenylmagnesium.

Diphenylmercury (25g., 0·089 mole) in tetrahydrofuran (100cc.) was boiled overnight with magnesium turnings (2·4g., 0·0098 moles). After filtration and evaporation of a little solvent, the complex crystallised as long needles. It was separated by filtration and dried under reduced pressure at room temperature, m.p. 105-106°. [Found: Mg, 7·7%; M(cryoscopically, 0·47 and 0·93 wt.-% in benzene), 303 and 306. $C_{20}H_{26}MgO_2$ requires Mg, 7·55%, M 323].

The infrared spectrum of the complex as a nujol mull contains absorptions at; 3012m(sh), 2941s(sh), 2906s, 2841s(sh), 1565w, 1466s, 1410w, 1376m, 1263m, 1143w(sh), 1081m(sh), 1055m, 1022m, 917w, 877w, 817w(sh), 798m, 734w(sh), 719w(sh), 704m, 675w, 641w, 400m.

The complex possessed a measurable vapour pressure at temperatures a little above room temperature (25^o). The vapour pressures were measured in the apparatus shown (fig 29). A sample of the complex was loaded into A, attached to the apparatus, cooled in liquid nitrogen, and the whole evacuated with taps B and C open. Tap B was then closed and the sample allowed to warm. The vapour pressure was measured by finding the difference in the mercury levels, h. The results shown in the table are a combination of three separate runs.

Temperature.	Vapour Pressure cm.
25·3	0·108
43·0	0·160
47·8	0·261
54·0	0·330
63·5	0·530
71·0	0·801
74·6	1·081
81·8	1·503
90·0	2·467
96·6	3·742
104·5	5·729

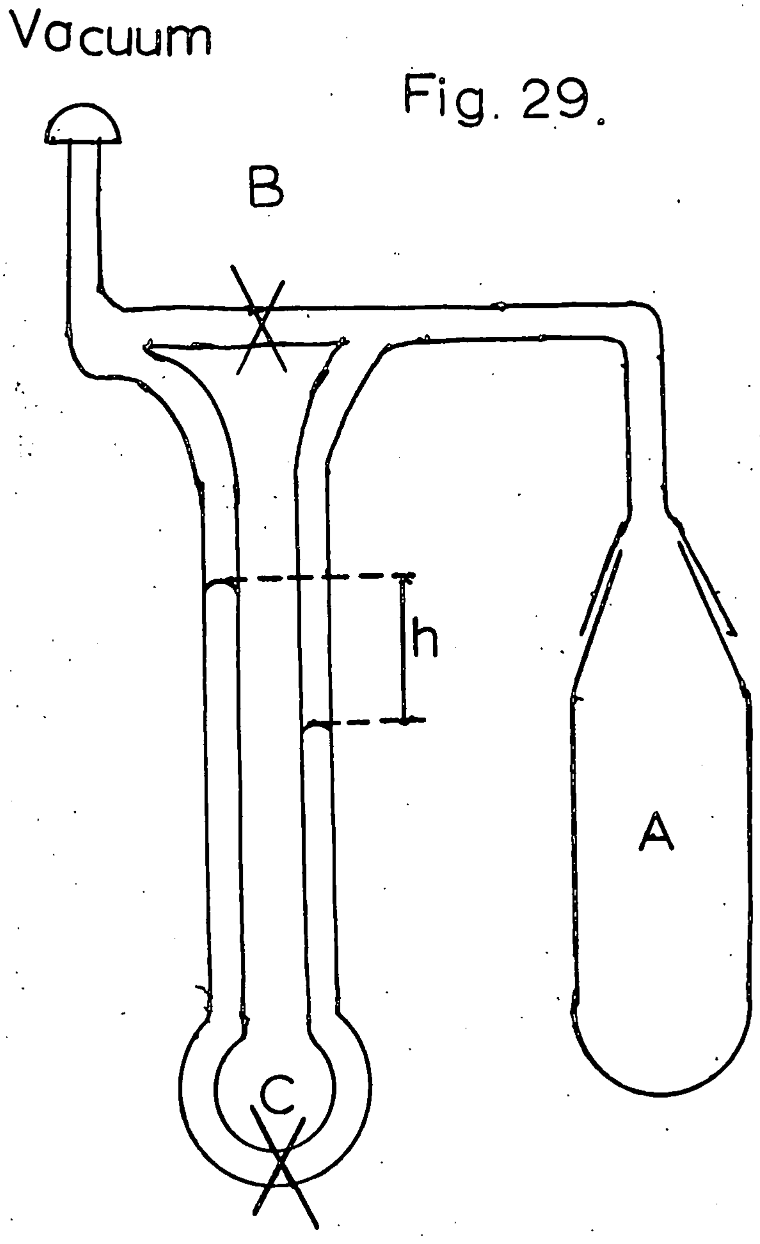


Fig. 29.

The recombination of the tetrahydrofuran vapour with the residual solid was very slow and thus no measurements were taken of the vapour pressure with falling temperature. Above the melting point of the solid recombination was much quicker.

An attempt was made to form $Mg(C_6H_5)_2$.THF by the removal of tetrahydrofuran from bis-(tetrahydrofuran)-diphenylmagnesium. A weighed sample of the complex (1·232g, 0·0038 moles) was placed in a flask and heated to 100°C in vacuo while attached to a vacuum line. The volatile product (shown by I.R. to be tetrahydrofuran) was collected in a liquid nitrogen trap. From time to time the amount of tetrahydrofuran was measured (as a gas) and when 94N ccs. were obtained, corresponding to removal of 54% of the total tetrahydrofuran content of the original complex, heating was stopped. Dry benzene (20 mls.) was added to the yellow residue and the mixture boiled, not all the solid dissolving. The supernatant solution was transferred to a double Schlenk tube and recrystallisation attempted. No solid product could be obtained except by complete removal of the solvent which left a sticky yellow solid.

The infrared spectrum of this solid showed that it still contained coordinated tetrahydrofuran. Absorptions were located at; 2985m, 2924s, 2849s, 2825s(sh), 2688m, 1587m, 1563m, 1553m(sh), 1488m(sh) 1468m, 1451m, 1408s, 1370w, 1342m, 1333w, 1290m(sh), 1274m(sh), 1261m, 1222m, 1185m, 1174m(sh), 1153m, 1087m(sh), 1055s(sh), 1038s(sh), 1015s, 988s, 953w, 915m, 866s, 797m, 763m, 736m, 699s, 680m(sh), 667m(sh), 638m, 627m, 400s.

No further attempt was made to obtain a crystalline product.

N,N,N',N'-Tetramethylethylenediamine - di-isopropylmagnesium.

The diamine (1·16g, 0·01 moles) was added dropwise to di-isopropylmagnesium (0·01 moles) in diethylether at room temperature giving a clear solution. On cooling to -78°C white crystalline needles were obtained. The compound is soluble in hydrocarbon solvents and can be crystallised from hexane. The complex was dried in vacuo at room temperature, m.p. 86-87°.

The infrared spectrum of the complex as a nujol mull and as a cyclohexane solution were identical. Absorptions were located at; 2985s, 2958s, 2915s, 2845s, 2770s, 2725s, 2679m, 2660w(sh), 1587s, 1570s, 1431s, 1408m(sh), 1372m, 1353s, 1284s, 1256m, 1239m, 1183m, 1156m, 1124m, 1094m, 1058m, 1040m(sh), 1028s, 1009s, 983m, 963m, 946m, 902m, 895m(sh), 848m, 829w(sh), 790s, 766m, 579m, 476s.

The p.m.r. spectrum of the complex in a 5% benzene solution contained the following resonances (chemical shifts quoted relative to tetramethylsilane τ = 10).

τ value		Coupling constant J	Assignment
8·10	Singlet		$N\text{-}C\underline{H_3}$
8·18 8·32	Doublet	0·14 ppm	$Mg\text{-}CH\text{-}(C\underline{H_3})_2$
8·32	Singlet		$N\text{-}C\underline{H_2}$
9·69 9·80 9·94 ....? 10·05 10·19 10·33	Septet	0·14 ppm	$Mg\text{-}C\underline{H}$

Removal of ether from di-isopropylmagnesium.

The removal of ether from di-isopropylmagnesium in vacuo at room temperature (18·2°) for one hour left a viscous liquid whose analysis corresponded to $Pr^{i}_{2}Mg.(Et_{2}O)_{1\cdot05}$. This liquid had a dissociation pressure of ether of 3·34mm. at room temperature. Further pumping of the product for fourteen hours left a white solid which was di-isopropylmagnesium containing 3·7% ether by weight.

N,N,N',N'-tetramethylethylenediamine di-tert-butylmagnesium.

Addition of the diamine (1·16g, 0·01 mole) in 5 mls. of diethyl ether to a vigorously stirred solution of di-t-butylmagnesium and removal of most of the solvent resulted in the crystallisation of the complex. On heating under nitrogen the compound did not melt but decomposed over the range 90-120°. On heating in vacuo (0·002mm.) the solid sublimed at 130-140°. [Found: magnesium 9·55, hydrolysable butane, 43·58%, M(cryoscopically in 0·88 and 0·44 wt.-% in benzene) 256 and 243. Required for $C_{14}H_{25}N_{2}Mg$, magnesium 9·55, hydrolysable butane 44·82%, M 254].

The infrared spectrum recorded as a nujol mull contained absorptions at; 2857s, 2740s, 2660s, 2597m, 2551w(sh), 1462s(sh), 1437s, 1425s(sh), 1332s, 1282sm 1255m(sh), 1242m, 1195m, 1161m, 1131s, 1122s, 1097w, 1060m, 1042m, 1024s, 1009s, 996s, 947s, 931m, 886vw, 877w, 826w, 790s, 768s, 749w(sh), 772w(sh), 615w, 582s, 500-400s.

The p.m.r. spectrum of the complex in benzene solution was recorded at three different temperatures. Chemical shifts relative to TMS.

Temperature	τ (Bu^t)	τ ($N-CH_3$)	τ ($N-CH_2$)
20°C	8·71	8·24	7·98
-60°C	8·68	8·17	7·89
-70°C	8·60	8·20	7·89

As can be seen the spectrum shows no marked change with temperature. In d_8-toluene, however, the resonances occur as follows ($Mg-\underline{Bu}^t$) 8·79, ($N-\underline{CH_2}$) 8·17, ($N-\underline{CH_3}$) 8·00 τ.

1,4-Dioxan di-t-butylmagnesium.

During the first preparations of di-t-butylmagnesium no attempt was made to control the amount of dioxan added to the Grignard reagent. Removal of the ether from a 0·3M solution gave a white solid which was refluxed with 10 mls. of hexane and extracted with toluene. Square prismatic crystals were obtained from the toluene but the majority of material was insoluble. Analysis of the toluene-soluble material showed it to be t-butylmagnesium t-butoxide. [Found: magnesium 15·75, hydrolysable butyl, 36·71%. Required for $C_8H_{18}OMg$; Mg, 15·74, hydrolysable butyl, 36·95%]. Only 0·08g. of the butoxide were isolated from a total amount of solid of 2·4g.

The toluene insoluble material was dissolved in ether and precipitated and washed with hexane. [Found: magnesium 10·80, hydrolysable butyl 48·5%. Required for $C_{12}H_{26}O_2Mg$, Mg, 10·74; hydrolysable butyl, 50·30%].

The infrared spectrum is mainly that of coordinated dioxan:

2907s, 2849s, 2762s, 2721s, 2667m, 2604w, 2500w, 1466s, 1451s, 1379s, 1366s, 1297m, 1261s, 1238m, 1227m, 1203m, 1166w, 1130s, 1105s, 1073s, 1041m, 1025w, 998m, 989m, 960m, 934w, 930w(sh), 892s, 875s, 860s, 826w, 795s, 765w, 722w, 621s, 616s, 576s, 512s, 491s.

Trimethylamine (0·03 moles) was condensed on to an ethereal solution of the dioxan complex (0·01 mole) which was vigorously stirred while it was warming. The solvent was removed and fresh diethyl ether condensed on to the white solid. A p.m.r. spectrum of this solution contained no resonance attributable to N-CH_3.

τ value	Assignment
6·79	-O-C$\underline{H_2}$ of dioxan and O-C$\underline{H_2}$ of ether
6·93	-O-C$\underline{H_2}$ of ether
7·04	-O-C$\underline{H_2}$ of ether
7·17	-O-C$\underline{H_2}$ of ether
9·23	-C$\underline{H_3}$ of ether
9·36	-C$\underline{H_3}$ of ether
9·48	-C$\underline{H_3}$ of ether and -$\underline{\mathrm{Bu}}^t$ of $\mathrm{Bu}^t{}_2\mathrm{Mg}$.

Bis-(tetrahydrofuran) di-t-butylmagnesium.

Addition of excess tetrahydrofuran (1·51g, 0·021 moles) to an ethereal solution of di-t-butylmagnesium (0·01 moles) resulted in a small evolution of heat but the solution remained clear. Removal of the solvent left a crystalline solid which was soluble in aromatic hydrocarbons but effectively insoluble in aliphatic. Crystallisation was thus effected using a toluene/hexane (1/5) mixture and cooling to -78°. The complex was filtered from excess solvent and dried in vacuo.

On heating under nitrogen slow decomposition appears to set in at about 90° but the solid melted at 132-135° giving a clear viscous liquid, which formed a glass on cooling. The liquid bubbled at 160° and a grey-white solid was gradually deposited which charred at 210°. [Found: magnesium, 8·98; hydrolysable butyl, 38·81%. Required for $C_{16}H_{34}O_2Mg$; magnesium 8·61, hydrolysable butyl, 40·39%].

The molecular weight determinations (cryoscopically in benzene) are tabulated below. Required for $C_{16}H_{34}O_2Mg$; M, 283.

wt.-% in C_6H_6	Mol. wt.	Degree of Association.
1·599	266	0·94
1·066	248	0·877
0·799	230	0·813
0·533	223	0·788
0·400	215	0·76
0·267	213	0·753

The infrared spectrum recorded as a nujol mull contained absorptions at; 2899s, 2732s, 2667s, 2611m, 2506w, 1466s(sh), 1453s, 1447s, 1429m(sh), 1372s, 1355m(sh), 1346m(sh), 1311w, 1294w, 1252m, 1233m, 1220m, 1200m, 1176m(sh), 1133s, 1071m, 1038s, 996s, 958m, 993w, 917s , 875s, 831w, 796s, 766w, 722w, 673m, 571s, 500s.

The p.m.r. spectrum was recorded in benzene solution. Chemical shifts are quoted as p.p.m. upfield from benzene (calculated values, τ values-benzene = 2·73τ - are in brackets).

Peak position		Coupling constant J	Assignment
3·59 (6·32)	Triplet	0·1 p.p.m.	-O-$\underline{CH_2}$ of THF
3·69 (6·43)			
3·80 (6·53)			
5·80 (8·53)			-$\underline{CH_3}$ of t-butyl
5·91 (8·64)	Multiplet	0·06 p.p.m.	-$\underline{CH_2}$ of THF
5·97 (8·70)			
6·03 (8·76)			

Reaction between N,N,N',N'-tetramethylethylenediamine and methylmagnesium bromide.

Methylmagnesium bromide was prepared by the usual Grignard method. Analysis showed that the solution was 2·5M and the hydrolysable methyl:magnesium:bromide ratio was 0·99:1:1.

Addition of an excess of N,N,N',N'-tetramethylethylenediamine (6·0g.) to 20 mls. of this solution (0·05 moles) resulted in the evolution of heat and the immediate formation of a white precipitate. Excess ether, which contained no soluble material, was removed by filtration, and the precipitate washed with dry hexane and dried *in vacuo*.

The complex was purified by sublimation 100–110°/0·01mm. m.pt. 125-6°. Analysis for hydrolysable methyl, magnesium, bromide and amine gave a Me:Mg:Br:amine ratio of 1·03:1:0·98:0·97 i.e. $CH_3MgBr.(NMe_2)_2C_2H_{14}$. All the precipitate would not sublime the residue gradually turning yellow.

The infrared spectrum of the sublimed material as a nujol mull was identical with that of dimethylmagnesium N,N,N',N'-tetramethylethylenediamine.

N,N,N',N'-Tetramethylethylenediamine magnesium bromide.

Magnesium bromide was prepared as a solution in diethyl ether from 1,2-dibromoethane and magnesium turnings,

$$Mg \quad + \quad BrC_2H_4Br \quad \xrightarrow{Et_2O} \quad MgBr_2 \quad + \quad C_2H_4$$

N,N,N',N'-Tetramethylethylenediamine (2g.) was added to the ethereal magnesium bromide (0·014 moles) giving an immediate white precipitate which was filtered from excess solvent. Purification was effected by sublimation at 160–165°/0·005mm. [Found: Mg, 7·98%; Br, 55·20%. Required for $C_6H_{16}Br_2N_2Mg$; Mg, 8·10; Br, 53·2%].

The complex was insoluble in all solvents with which it did not react.

The infrared spectrum was recorded as a nujol mull.

Tert-butylmagnesium chloride diethyl etherate.

The t-butylmagnesium chloride was prepared by the usual Grignard method giving a solution containing t-butylmagnesium chloride. Thus removal of the ether from a small sample of the solution at 60° in vacuo resulted in a viscous liquid which analysed as $C_4H_9{}^tMg_{1\cdot18}Cl_{1\cdot22}.OEt_2$.

Di-t-butylmagnesium (0·0012 moles) was added to 10 mls. of the ethereal Grignard solution (0·011 moles of Bu^tMgCl and 0·00124 moles of $MgCl_2$). A slight precipitate formed, probably the dioxanate of magnesium chloride, produced from the small amount of dioxan which the di-t-butylmagnesium contains. The solution was filtered and the ether removed in vacuo at room temperature leaving a viscous liquid. Addition of hexane, boiling, followed by removal of the solvent resulted in the formation of a white solid. [Found: hydrolysable butyl, 30·29; magnesium, 12·86; chloride, 18·35%; M(cryoscopically in 1·61, 1·07 wt.-% benzene) 388, 390. Required for $C_{16}H_{38}Cl_2O_2Mg_2$ i.e. $(C_4H_9MgCl.OEt_2)_2$; hydrolysable butyl, 29·91; magnesium, 12·74; chloride, 18·54%, M, 382].

The infrared spectrum as a nujol mull contained absorptions at; 2985s, 2915s, 2857s, 2770s, 2681m, 2618w, 1639w, 1490m(sh), 1473m(sh), 1464m, 1399s, 1385m(sh), 1370m(sh), 1331w, 1295w, 1266w, 1247w, 1195m, 1152s, 1096s, 1047s, 1000s, 953w, 935w, 901m, 835m, 805s, 781s, 587m, 512m.

The p.m.r. spectrum of the complex in benzene solution contains the following absorptions. Chemical shifts are quoted as p.p.m. upfield from benzene and as shifts from benzene equals 2·73 p.p.m. (bracketed quantities).

Chemical Shift		Coupling Constant	Assignment
3·57 (6·30)	Quartet	·12 p.p.m.	$-O-C\underline{H_2}$ of Et_2O
3·69 (6·42)			
3·81 (6·54)			
3·92 (6·65)			
6·02 (8·75)			$-C_4\underline{H_9}$ of Bu^t-Mg
6·20 (8·93)	Triplet	·12 p.p.m.	$-C\underline{H_3}$ of Et_2O
6·32 (9·05)			
6·44 (9·17)			

It is hoped to obtain crystals of this complex for examination by X-ray diffraction.

Reaction between dimethyl ether and tert-butylmagnesium chloride.

An excess of dimethyl ether was condensed on to an ethereal solution of t-butylmagnesium chloride (0·012 mole). A white precipitate was present at -78° which dissolved on warming and did not reappear on subsequent recooling. Removal of the solvent gave a viscous liquid which was miscible with hydrocarbon solvents but no solid product could be obtained.

The p.m.r. spectrum of the viscous liquid in benzene solution showed that it contained both dimethyl and diethyl ether, each line in the spectrum being slightly split.

The experiment was repeated using t-butylmagnesium chloride diethyl etherate. A large excess of dimethyl ether was condensed on to solid t-butylmagnesium chloride etherate (0·12 mole) giving a white precipitate which was soluble in excess dimethyl ether but can be crystallised at -78°. The white solid so formed was filtered, the excess dimethyl ether removed <u>in vacuo</u> at room temperature leaving a viscous liquid which was not further investigated. The white solid produced did not inflame in air but reacted violently with water.

Analysis showed that the ratio of hydrolysable gas (2-methylpropane + dimethyl ether) to magnesium was 1·46:1 and not 2:1 as expected for $Bu^tMgCl.OMe_2$. The p.m.r. spectrum in benzene solution consisted of two single peaks at 4·16 p.p.m. upfield from benzene (6·89 p.p.m. taking benzene as 2·73 p.p.m.) assigned to the $O\text{-}C\underline{H_3}$ resonance and at 5·73 p.p.m. upfield from benzene (8·46 p.p.m. taking benzene as 2·73 p.p.m.) assigned to the $MgC_4\overset{t}{\underline{H_9}}$ resonance. The integrated spectrum gave 1·27:1 as the ratio of the $-OCH_3$:$-C_4H_9$ peaks. The complex $C_4H_9Mg_2Cl_3.(OMe_2)_2$ would require a hydrolysable gas:magnesium ratio of 1·5:1 and a ratio of 1·33:1 in the integrated spectrum of the $-OCH_3$ and $-Mg\text{-}C_4H_9$ peaks.

The infrared spectrum of the complex was recorded as a nujol mull; 2899s, 2770m, 2732m, 2674w, 2611w(sh), 1471s, 1460s, 1385m, 1370m(sh), 1264w, 1203w, 1176w(sh), 1163m, 1088w(sh), 1063s, 1022w(sh), 1005w, 960w, 908s, 802m, 768w, 722w, 595m, 500m(sh), 469-400m.

Reactions with weak acids.

Amines.

Reaction between dimethylmagnesium and N,N,N'-trimethylethylenediamine.

N,N,N'-Trimethylethylenediamine (0·0098 mole) was added slowly to dimethylmagnesium (0·010 mole) in diethyl ether (20 ml.). Vigorous gas evolution (methane identified by infrared spectrum) occurred. After the solvent had been removed under reduced pressure, the white solid product was sublimed at 80-90°/0·005mm. The sublimed complex had m.p. 116-118°. [Found: Mg, 17·5; hydrolysable methyl, 10·65%; M(crycoscopically 0·43 and 0·68 wt.-% in benzene), 265 and 280. $C_{12}H_{32}Mg_2N_4$ requires Mg, 17·3; hydrolysable methyl, 10·7%; M, 281].

The p.m.r. spectrum of the complex was recorded in benzene solution. Chemical shifts are given as τ values.

Chemical shift		Assignment
7·42		N-$\underline{CH_3}$
7·81	multiplet	$C_2\underline{H_4}$
8·14		N-$(\underline{CH_3})_2$
11·06		Mg-$\underline{CH_3}$

The infrared spectrum of the complex recorded as nujol mull and as a solution in cyclohexane are essentially similar. Absorptions are located at; 2740w, 1339w, 1274m(sh), 1256m, 1192w, 1149s, 1111s, 1094s(sh) 1042m(sh), 1018m, 1008m(sh), 980m, 939m, 933m(sh), 841m, 780m, 597m, 528s(sh), 514s, 495s(sh), 465m(sh), 435m.

Reaction between N,N,N'-trimethylethylenediamine and di-isopropylmagnesium.

Slow addition of N,N,N'-trimethylethylenediamine (0·0099 moles) to di-isopropylmagnesium in diethyl ether (53 mls.) at room temperature caused the evolution of heat and slow evolution of propane on vigorously stirring. Gas evolution continued for two hours on keeping the solution at 30°. Removal of the solvent under reduced pressure produced a white solid which was purified by recrystallisation from ether. The complex was soluble in hydrocarbon solvents and sublimed at 80°/0·002mm. On heating under nitrogen the complex did not melt but shrank at 80-81° and began to decompose in the range 100-110°. [Found: hydrolysable propyl, 26·23; magnesium 14·47%; M(cryoscopically, 0·64 and 1·27 wt.-% in benzene) 360, 369. Required for $C_{16}H_{40}N_4Mg_2$; hydrolysable propyl, 25·56; magnesium, 14·43%; M, 337].

The infrared spectrum of the complex was recorded as a solution in cyclohexane and as a nujol mull. Cyclohexane solution - 0·01mm. spacer, saturated solution; 2985m, 2793m, 2747s, 2720s, 2674m, 2618w, 2564w, 1471s, 1408w, 1379m, 1350s, 1297s, 1263m(sh), 1252s, 1192m, 1166s, 1148s, 1125s(sh), 1112s, 1100s(sh), 1057s, 1029s, 1006s, 987s, 951s(sh), 938s, 908s, 876m, 853s, 829w, 805w(sh), 793m, 786s, 596m, 579m, 561m, 530m, 493s, 456s.

Nujol mull; 2985m, 2717m, 2674m, 2604w, 2564w, 1460s, 1418w, 1410w, 1377s, 1370m(sh), 1350s, 1295w(sh), 1280s, 1252s, 1242m, 1192m, 1172m, 1163m, 1148s, 1110s, 1055m, 1029s, 1006s, 985m, 969w, 936s, 908s, 855s, 797w(sh) 779s, 721w, 595m, 578m, 576m, 490s, 463s.

The p.m.r. spectrum of the complex was recorded in cyclohexane and perdeuterocyclohexane. Peaks were recorded at 8·75, 8·62, 8·52, 7·76, 7·66, 7·53, 7·36 relative to T.M.S. (10). No assignments were made. The solution was too dilute to detect the expected septet due to the Mg-CH resonance.

Reaction between N,N,N'-trimethylethylenediamine and di-t-butylmagnesium.

N,N,N'-Trimethylethylenediamine (0·096g., 0·0093 moles) was added dropwise to di-t-butylmagnesium (0·01 moles) in diethyl ether at -78°. Gas evolution began just below room temperature (21°) and was complete after one hour at room temperature, during which time a white solid was produced. The solid was purified by recrystallisation from ether. On heating under nitrogen the solid began to decompose at 100° but decomposition was not rapid until 150° when a sudden shrinking and moistening occurred. [Found: hydrolysable t-butyl, 30·46; magnesium, 13·16%; M(cryoscopically, 2·34, 0·90 and 0·67 wt.-% in benzene) 316, 306 and 300. Required for $C_{18}H_{44}N_4Mg_2$; hydrolysable t-butyl, 31·27; magnesium 13·31%; M, 365].

The infrared spectrum recorded as a nujol mull has absorptions at; 2899s, 2809s, 2755s, 2725s, 2703m, 2674m, 2611w, 1490m, 1445s, 1437s, 1427w, 1412w, 1383s, 1350m, 1312w, 1282m, 1253m, 1241w, 1208w, 1192w, 1175w, 1148m, 1140m, 1122m, 1110s, 1056w, 1032s, 1028s, 1007m, 1000m, 985w, 973w, 936m, 876w, 852m, 800m, 781m, 735w, 723w, 595w, 508m, 462m, 436m, 422m.

Alcohols.

Reaction between 2-dimethylaminoethanol and dimethylmagnesium.

Slow addition of 2-dimethylaminoethanol (0·99 mls., 0·01 moles) to dimethylmagnesium (0·01 moles) in diethyl ether, at -50°, caused immediate evolution of methane. Removal of the solvent left a white solid which was crystallised from a toluene/hexane (1/15) mixture. The solid was dried *in vacuo* m.p. 160° (dec.). [Found: hydrolysable methyl, 12·13; magnesium 20·01%; M(cryoscopically in 0·966 wt.-% in benzene) 535. Required for $C_{20}H_{52}O_4Mg_4N_4$; hydrolysable methyl, 11·79; magnesium, 19·07%; M, 510].

In some preparations of this compound analyses much higher than those quoted were obtained and difficulty with precipitation occurred during the molecular weight determinations.

The infrared spectrum of the complex as a nujol mull has absorptions at; 2941s(sh), 2915s, 2849s, 2786s(sh), 2710w(sh), 1445s, 1406w, 1379m, 1357w(sh), 1274m, 1267m(sh), 1253m(sh), 1186m, 1172m, 1099s, 1079s, 1030s, 950m, 895m, 858w, 785m, 727w, 605s, 520s.

Reaction between t-butanol and dimethylmagnesium.

t-Butanol (0·736g., 0·00991 moles) was slowly added to a cold (-96°), vigorously stirred solution of dimethylmagnesium (0·01 moles) in diethyl ether (32 mls.). Evolution of methane occurred at about -70° giving a clear solution. Removal of the solvent left a white foam which was soluble in pentane and hexane but could not be crystallised.

A white solid was obtained by the removal of solvent from a pentane solution and heating the solid in vacuo at 50° for two hours. On heating under nitrogen the solid decomposed at about 270°. On heating in vacuo the solid slowly sublimed at 200°. [Found: hydrolysable methyl, 13·50; magnesium, 21·59%. Required for $C_5H_{12}MgO$; hydrolysable methyl 13·36; magnesium 21·62%].

Attempts to measure the molecular weight cryoscopically in benzene failed due to the precipitation of a white solid during the determination.

The p.m.r. spectrum consisted of two broad peaks centred at 8·06 p.p.m. (10·79τ) and 5·94 p.p.m. (8·67τ) upfield from the benzene standard, the former is assigned to the Mg-$C\underline{H_3}$ resonance and the latter to the O-$C_4\underline{H_9}^t$. The benzene solution used was extremely viscous which may be the cause of the broadened peaks. Recorded at 100° the spectrum is much sharper, the Mg-$C\underline{H_3}$ resonance is still single but the O-$C_4\underline{H_9}^t$ resonance is split into two components, separation 0·07 p.p.m., the one at low field being the most intense.

Thiols.

Reaction between t-butylthiol and dimethylmagnesium.

t-Butylthiol (1·13 mls., 0·01 moles) dissolved in 10 mls. of ether, was added dropwise to an ethereal solution of dimethylmagnesium (0·01 moles) at -78° with vigorous stirring. Methane evolution began at about -60° and continued smoothly until the system reached room temperature. Removal of the ether left a white foam which was insoluble in hexane and

and toluene. The foam was redissolved in ether, the solution filtered and a white solid precipitated by addition of hexane. The solid was dried in vacuo. The solid reacted vigorously with water but gave only small amounts of methane. [Found: hydrolysable methyl, 1·89; magnesium, 14·21%. Calculated for $C_8H_{18}S_2Mg$ i.e. $Mg(SBu^t)_2$: hydrolysable methyl, zero; magnesium 12·0%]. Heating the solid under nitrogen produced no visible change up to 200°.

The infrared spectrum of the solid was recorded as a nujol mull, 2959s, 2924s, 2849s, 1453s, 1372m, 1263w, 1218w, 1163m, 1149m, 1099m, 1028m, 820w, 800w, 720w, 578m.

The reaction was repeated in the presence of tetrahydrofuran.

Addition of t-butylthiol (1·13 mls., 0·01 moles) dissolved in diethyl ether (10 mls.) to dimethylmagnesium (0·01 mole) at -78° in the presence of an excess of tetrahydrofuran (2·5 ml., 0·025 mole) causes evolution of methane on slight warming producing a clear solution. Removal of a small amount of the solvent caused a white solid to crystallise. The solid was filtered and dried in vacuo. On heating under nitrogen the white crystalline solid, shrank rapidly and became amorphous, presumably with loss of tetrahydrofuran at 107-109° and then remained unchanged up to 250°. [Found: hydrolysable methyl, 7·37; magnesium 12·30%; M(cryoscopically 1·69, 1·13, 0·85 wt.-% in benzene) 410, 410 and 408. Required for $C_{18}H_{40}Mg_2O_2S_2$; hydrolysable methyl, 7·49; magnesium, 12·12%; M, 401].

The p.m.r. spectrum was recorded as a ~30% solution in benzene. Chemical shifts are quoted as p.p.m. shift upfield from benzene with τ values in brackets.

Chemical shift		Coupling constants J c.p.s.	Assignment
3·24 (5·97) 3·34 (6·07) 3·44 (6·17)	Triplet	6·0	O-$CH_{\underline{2}}$ of THF
5·53 (8·26)			S-$\underline{Bu}^t$
5·83 (8·56)	Multiplet	2·4	O-CH_2-$CH_{\underline{2}}$ of THF
7·98 (10·71)			Mg-$CH_{\underline{3}}$

The infrared spectrum recorded as a nujol mull contained absorptions at; 2941s(sh), 2899s, 2849s, 2778m, 2703w(sh), 2667w(sh), 1456s, 1379m, 1364m, 1348w, 1299w, 1263w, 1250w(sh), 1215w, 1170m, 1153m, 1106s, 1074m, 1022s, 952w, 917m, 880m, 821m, 800m, 733w(sh), 721w, 680w, 669w(sh), 579m, 491s.

Reaction between dimethylmagnesium and isopropylthiol.

Isopropylthiol (0·762g., 0·01 mole) in ether (15 mls.) was added dropwise to a solution of dimethylmagnesium (0·01 mole) in diethyl ether (32 mls.), cooled to -78°. Methane evolution occurred almost immediately and continued smoothly on warming giving a clear solution. Removal of the solvent left a white foam which was heated at 100° in vacuo for one hour to ensure complete solvent removal. The resulting solid was insoluble in non-donor solvents and was purified by redissolving in a small volume of ether and precipitating with hexane. The solid was filtered and dried in vacuo. [Found: The compound obtained had a hydrolysable methane:magnesium ratio of 1:1•22. This was taken as evidence for disproportion and the product was not investigated further].

The reaction was repeated in the presence of excess tetrahydrofuran.

Addition of isopropylthiol (0•01 mole) to an ethereal solution of dimethylmagnesium in the presence of tetrahydrofuran (0•03 mole) results in the immediate evolution of methane giving a clear solution. Removal of the solvent gave a viscous liquid which could not be further purified. [Found: hydrolysable methyl, 9•19; magnesium, 15•14%. Required for $C_8H_{18}MgOS$; hydrolysable methyl, 8•05; magnesium, 13•04%. The hydrolysable methyl:magnesium ratio is 1:1•02 and the liquid has the empirical formula $MeMgSPr^i\ 0{\cdot}78\ (C_4H_8O)$].

The infrared spectrum of the liquid contains absorptions at; 2950s, 2890s, 2857s, 2825m(sh), 2778m, 1468m, 1456m, 1387m, 1370m, 1253m, 1200m, 1142m, 1107m, 1054s, 1031s, 957w, 918m, 881s, 678w, 621m, 500s.

Reaction between dimethylmagnesium and 2-dimethylaminoethanethiol.

Dropwise addition of 2-dimethylaminoethanethiol (1•05g., 0•01 mole) at -60° caused immediate evolution of methane and the formation of a white precipitate which was sparingly soluble in ether. The solvent was removed and the solid purified by recrystallisation from toluene at room temperature. On heating the crystals under nitrogen they shrank at 180° and melted with decomposition at 193°. [Found: hydrolysable methyl, 10·46; magnesium 16·54%; M(cryoscopically 1·84 and 1·22 wt.-% in benzene) 552, 569. Required for $C_{20}H_{52}Mg_4N_4S_4$; hydrolysable methyl, 10·47; magnesium, 16·93%; M, 574].

The p.m.r. spectrum of a benzene solution of the complex was recorded. Chemical shifts relative to TMS.

Chemical shift (τ)		Assignment
10·82		$\text{Mg-CH}_{\underline{3}}$
7·82		$\text{N-(CH}_{\underline{3}})_2$
7·33 7·58 7·93 8·05 8·14	Multiplet	$\text{-S-CH}_{\underline{2}}\text{-CH}_{\underline{2}}\text{-N}$

The infrared spectrum of the solid was recorded as a nujol mull, 2933s(sh), 2907s, 2859s(sh), 2778m(sh), 2725w(sh), 1605w, 1462s(sh), 1449s, 1408w(sh), 1372m, 1302m(sh), 1297m, 1255m(sh), 1248m, 1229w(sh), 1220w, 1164m, 1121m, 1096m, 1089m(sh), 1050m, 1032m, 997m, 946m, 894m, 799w, 766m, 762m, 728m, 667m, 657m, 510s.

Reaction between di-t-butylmagnesium and t-butylthiol.

Tert-butylthiol (0·902g., 0·01 mole) in ether (12 mls.) was added dropwise to an ethereal solution of di-t-butylmagnesium (0·01 mole) at -78°. On stirring vigorously a white precipitate appeared at about -50° which did not redissolve on boiling the ether. The precipitated solid was filtered and dried in vacuo. On heating the solid under nitrogen the compound decomposed above 315°. [Found: hydrolysable butyl, 0·70; magnesium, 11·36%. Required for $C_8H_{18}S_2Mg$; magnesium 12.00%].

The infrared spectrum of the solid contained absorptions at; 2915s, 2778s, 2740m, 2710m, 2674m, 1471s, 1464s, 1406s, 1399s, 1307w, 1266w, 1248w, 1221w, 1205w, 1172s, 1160s, 1133m, 1096w, 1074w, 1052m, 1030w, 1000w, 943m, 893w, 876m, 824m, 800m, 781w, 765w, 724w, 613m, 580s, 400s.

The reaction was repeated using the same quantities but adding an excess (1·29g., 0·18 moles) of tetrahydrofuran to the solution. On warming the reaction mixture a white precipitate again formed which did not redissolve at room temperature. The solid was filtered and dried in vacuo. The total weight of solid obtained was 0·822g. The theoretically required amount of magnesium t-butylsulphide was 0·912g. [Found: magnesium, 11·84%. Required for $C_8H_{18}S_2Mg$; 12·00%].

The infrared spectrum of the solid contains absorptions at; 2899vs, 2762m, 2725w, 2674w, 1460s, 1374s, 1304w, 1261w, 1238w, 1215w, 1199m, 1163m, 1152m, 1107w, 1074w, 1028w, 952m, 875m, 820m, 799w, 758w, 734w(sh), 723w, 577s.

Reaction between di-t-butylmagnesium and iso-propylthiol.

Addition of iso-propylthiol (0·94 mls.) in ether (10 mls.) to a solution of di-t-butylmagnesium in diethyl ether caused a transitory yellow colour followed by evolution of butane and the formation of a white precipitate. On warming the precipitate gradually dissolved. Removal of the ether gave a white solid which was purified by recrystallisation from pentane at low temperature. On heating under nitrogen the compound shrank at 85°, and melted with gas evolution from 170–180° giving a viscous semi-solid material which darkened when heated up to 320°. [Found: hydrolysable butyl, 25·02; magnesium, 10·52; ether (as vapour) 33·20%; M(cryoscopically, 1·67, 1·12, 0·73 wt.-% in benzene) 485, 483, 460. Required for $C_{22}H_{52}S_2O_2Mg_2$; hydrolysable butyl, 24·77; magnesium, 10·54; ether, 32·14%; M, 461].

The p.m.r. spectrum of a benzene solution was recorded. Chemical shifts are quoted as τ values. The expected septet due to S-CH$<$ was not positively identified.

Chemical Shift		Coupling constant J c.p.s.	Assignment
6·36 6·47 6·58 6·69	quartet	6·6	$O\text{-}CH_{\underline{2}}$
8·58 -	doublet	-	$S\text{-}CH(CH_{\underline{3}})_2$
8·69		-	$Mg\text{-}C_4H_{\underline{9}}{}^t$
8·90 9·30 9·16	triplet	7·2	$O\text{-}CH_2\text{-}CH_{\underline{3}}$

The infrared spectrum (nujol mull) contained absorptions at; 2950s(sh), 2915s, 2857s, 2770m, 2710w(sh), 2674w, 1462s, 1383s, 1368m, 1299w, 1263m, 1247m(sh), 1202m, 1151m, 1125m, 1100m, 1074m, 1053m, 1020m, 1000w, 891w, 870m, 829w(sh), 801s, 765w, 722w, 614m, 581m, 500m.

Reaction between di-t-butylmagnesium and 2-dimethylaminoethanethiol.

Addition of 2-dimethylaminoethanethiol (1·04g., 0·01 mole) in diethyl ether to di-t-butylmagnesium (0·01 mole) in diethyl ether (33 ml.) produced a white precipitate which dissolved almost immediately. As the reaction mixture warmed a white precipitate began to form which did not redissolve in boiling ether but could be recrystallised from toluene m.p. 212-215 (dec.). [Found: hydrolysable butyl, 32·23; magnesium, 13·8%; M(cryoscopically 2·4, 2·59 wt.-% in benzene) 390, 390. Required for $C_{16}H_{38}Mg_2N_2S_2$; hydrolysable butyl, 30·79; magnesium 13·1%; M, 371].

The p.m.r. spectrum of the solid in benzene solution was recorded. It contained two singlets at 8·52τ and 8·12τ, relative to TMS, assigned to the $Mg-C_4H_9$ and $N(CH_3)_2$ resonance respectively.

The infrared spectrum of the complex as a nujol mull contained absorptions at; 2941s(sh), 2906s, 2857s(sh), 2747s, 2732s, 2703m(sh), 2667m(sh), 2604s, 1464s, 1441s(sh), 1410w, 1377m, 1370m, 1351w(sh), 1300s, 1261w(sh), 1250w, 1221w, 1203w, 1166m, 1145m, 1122w, 1100w, 1063w(sh), 1047m, 1030s, 1000s, 990m(sh), 950m, 939w(sh), 899w, 891w, 876w, 801s, 763m, 727w, 672w, 668w(sh), 610w, 581w, 532m, 507m, 459m.

Reaction between diethylmagnesium and t-butylthiol.

Tert-butylthiol (0·01 mole) in ether was slowly added to an ethereal solution of diethylmagnesium (0·01 mole) at -78° producing an immediate white precipitate. On warming a clear solution was obtained, ethane being evolved just below room temperature over a period of thirty minutes. To complete the reaction the ether was boiled. On removal of the solvent colourless crystals appeared. During the drying process the crystals became white and slightly powdery. On heating the solid under nitrogen no appreciable change occurred up to 300°. [Found: The analysis figures were found to vary in different preparations. Two representative figures are given; Ratio (1) hydrolysable ethyl:magnesium: ether was 1:1:0·63; (2) hydrolysable ethyl:magnesium:ether was 1:1·02:0·73].

The infrared spectrum of the solid was recorded as a nujol mull; 2924s, 2857s, 2717w, 1462s, 1381s, 1368s, 1263m, 1220w, 1171m(sh), 1156s, 1121m, 1096m, 1065m(sh), 1045s, 1019s, 927w, 887w, 814m(sh), 799m, 722w, 599w(sh), 575m(sh), 557m, 488m(br).

The experiment was repeated in the presence of an excess of tetrahydrofuran (2 mls., 0·025 mole). No product could be crystallised from ether. Removal of the solvent and recrystallisation from hexane gave a white crystalline solid m.pt. 72-74°. [Found: hydrolysable ethane, 13·74; magnesium, 11·37%; M(cryoscopically 1·36, 0·68 wt.-% in benzene) 442 and 434. Required for $C_{20}H_{44}Mg_2O_2S_2$; hydrolysable ethyl, 13·54; magnesium, 11·32%; M,429].

The p.m.r. spectrum of a benzene solution of the solid was recorded. Chemical shifts are quoted as p.p.m. upfield from benzene, τ values are given in brackets.

Chemical shift		Coupling constants J c.p.s.	Assignment
3·37 (6·10)	triplet	7	$O-CH_{\underline{2}}-CH_2$
5·51 (8·24)			$S-C_4\overset{t}{H}_{\underline{9}}$
5·35-5·85 (8·08-8·58)			$O-CH_2-CH_{\underline{2}}$ and $Mg-CH_2-CH_{\underline{3}}$
7·00 (9·73) 7·13 (9·86) 7·27 (10·00) 7·40 (10·13)	quartet	13	$Mg-CH_{\underline{2}}$

The infrared spectrum of the solid was recorded as a nujol mull; 2941s(sh), 2907s, 2841s, 2755m(sh), 2688m(sh), 1449s, 1374m, 1359m, 1294w, 1258m, 1209w, 1163m(sh), 1149m, 1117m(sh), 1095m, 1067s, 1022s, 972w, 917m, 876m, 820m, 719w, 575m.

Preparation of magnesium t-butylsulphide.

The thiol (0·02 mole) in ether (10 mls.) was added to diethylmagnesium (0·01 mole) in ether (30 ml.) depositing a white precipitate at -60°. The precipitate did not redissolve and was insoluble in all solvents with which it did not react. The solid was filtered, washed twice with hexane and dried *in vacuo*. On heating under nitrogen no visible change took place up to 300°. [Found: Magnesium, 11·82%.

Required for $C_8H_{18}S_2Mg$; magnesium, 12·00%.]

The infrared spectrum of the solid as a nujol mull contains absorptions at; 1453s, 1376s, 1366s, 1297w, 1263w, 1218w, 1167s, 1153s, 1126m, 1110m, 1064m, 1028w, 955w, 891w, 875w, 822m, 800w, 733w, 721w, 613w, 579s.

Reaction between magnesium t-butylsulphide and excess pyridine.

Magnesium t-butylsulphide (1·07g., 0·0053 mole) was suspended in toluene (30 ml.) and an excess of pyridine (0·021 mole, 1·676g.) added to the vigorously stirred suspension. No visible reaction took place but on boiling the toluene the precipitate became a pale yellow colour. The solid was filtered, washed with hexane and dried in vacuo during which time it became white once again.

The infrared spectrum of the solid recorded as a nujol mull contained no bands attributable to coordinated pyridine; 1464s, 1379s, 1368s, 1264w, 1220w, 1170s, 1159s, 1101w, 1068w, 1042w, 1024w, 957w, 893w, 821m, 800w, 723w, 700w, 579s.

Hydride Chemistry.

Reactions of alkali metal hydrides with diethylmagnesium.

The reaction between the alkali metal hydrides and diethylmagnesium was studied in various solvents, namely diethyl ether, tetrahydrofuran and 1,2-dimethoxyethane (abbreviated to monoglyme in the table below). The course of the reaction, if any, was followed by hydrolysis of aliquots of solution and the measurement of any hydrolysable gases. In a typical experiment diethylmagnesium (0·1 moles) in 100 mls. of ether was refluxed with a large excess of hydride (500%) in a nitrogen-filled two-necked flask fitted with reflux condenser. Samples were withdrawn by syringe from time to time. The results are tabulated below.

Alkali metal hydride	Solvent	Time (hrs.)	Result	Conclusion
NaH	Et_2O	72	(i) No drop in hydrolysable ethyl. (ii) No hydrolysable hydrogen	No reaction
NaH	THF	72	(i) Hydrolysable Et drops by 80%. (ii) No hydrolysable H appears (iii) No compound extracted from solid, which contains no hydrolysable Et	Reaction with solvent

Alkali metal hydride	Solvent	Time (hrs.)	Result	Conclusion.
NaH	Monoglyme	12	(i) 100% loss of hydrolysable ethyl. (ii) No hydrolysable hydrogen (iii) Solid residue contains Mg but no hydrolysable ethyl.	Reaction with solvent.
-	Monoglyme	24	(i) No loss of hydrolysable ethyl.	
LiH	Et_2O	26	(i) No loss of hydrolysable ethyl. (ii) No hydrolysable hydrogen.	No reaction
LiH	(i) Et_2O		(i) Small loss of hydrolysable ethyl.	No reaction
	(ii) Remove most of solvent (100°C)	12	(ii) No hydrolysable hydrogen	No reaction
KH	Et_2O	24	(i) Small loss of hydrolysable ethyl (ii) No hydrolysable hydrogen	No reaction

Attempted preparation of lithium dimethylmagnesium hydride.

The proposed route was as follows,

$$Me_2Mg \quad + \quad LiBu^n \quad \longrightarrow \quad Li[Me_2MgBu^n] \quad \xrightarrow{\Delta} \quad LiMg(CH_3)_2H \quad + \quad C_2H_5CH{=}CH_2$$

A clear yellowish solution of n-butyl-lithium (0·01 mole) in hexane (5·2 mls.) was slowly added to a solution of dimethylmagnesium (0·01 mole) in diethyl ether (23 mls.) with the evolution of heat. Removal of the solvent left a viscous liquid which could not be purified. [Found: hydrolysable methyl, 15·04; hydrolysable butyl, 28·64; magnesium, 12·60%. Required for $C_{10}H_{25}OLiMg$ i.e. $Li[Mg(CH_3)_2(C_4H_9)].O(C_2H_5)_2$; hydrolysable methyl, 15·61; hydrolysable butyl, 29·66; magnesium, 12·63%].

The infrared spectrum of the liquid contained absorptions at; 1486m, 1462s, 1449s, 1387s, 1370m, 1333w, 1325w, 1304m, 1285m, 1263w, 1182s, 1151s, 1092s, 1057s, 1019s, 1000s, 979s, 936m, 901m, 864m, 834m, 786s, 548-500s.

The viscous liquid was heated at 130° for 14 hours. During this time a gas was steadily evolved which was shown by its infrared spectrum to be ether (215N ccs., 0·0096 mole) with a little butene (27N ccs.). A pale yellow solid remained which analysed correctly for $Li[Mg(CH_3)_2(C_4H_9)]$ by hydrolysable methyl and butyl but contained a little hydrolysable hydrogen. This product was heated to 170° for 16 hours during which time 198N ccs. (0·0088 moles) of butene were evolved leaving an off-white solid. (Total amount of butene evolved is 225N ccs. which was the theoretically required amount). The infrared spectrum of the solid contained the following absorptions, 1205, 1190 and continuous absorption from 1075 $cm.^{-1}$ This is consistent with the solid being a mixture of dimethylmagnesium and lithium hydride.

Extraction of the solid with diethyl ether gave a solution of dimethylmagnesium proved by analysis (95% yield) and left lithium hydride as a solid (identified by infrared spectrum).

The p.m.r. spectrum of the liquid $Li[MgMe_2Bu^n].OEt_2$ in benzene solution was as follows. Chemical shifts are quoted as p.p.m. upfield from the benzene resonance.

Chemical shift		Coupling const. p.p.m.	Assignment
3·71 (6·44) 3·82 (6·55) 3·94 (6·67) 4·05 (6·78)	Quartet	0·11	$O\text{-}CH_{\underline{2}}$ of ether
5·52 (8·25)	Multiplet		$CH_{\underline{2}}\text{-}CH_{\underline{2}}\text{-}CH_{\underline{3}}$ of butyl
6·11 (8·84) 6·22 (8·95) 6·33 (9·06)	Triplet	0·11	$O\text{-}CH_2\text{-}CH_{\underline{3}}$ of ether
7·38 (10·11) 7·51 (10·24) 7·63 (10·36)	Triplet	0·12	$Mg\text{-}CH_{\underline{2}}\text{-}CH_2$
8·37 (11·10)		-	$Mg\text{-}CH_{\underline{3}}$

Integration of the p.m.r. spectrum gives the following relative intensities Mg-C$\underline{H_3}$ (3·5), Mg-C$\underline{H_2}$ (1·2), O-C$\underline{H_2}$ (2·7), C$\underline{H_2}$-C$\underline{H_2}$-C$\underline{H_3}$ + (O-CH$_2$)-C$\underline{H_3}$ (8·7). Using the first three figures this gives a methyl:butyl:ether ratio of 1:0·51:0·56. Required for $LiMg(CH_3)_2C_4H_9.OEt_2$, methyl:butyl:ether ratio of 1:0·5:0·5.

Reactions between alkali metal hydrides and ethylmagnesium bromide.

Lithium hydride and ethylmagnesium bromide in ether.

Lithium hydride (0·26g., 10% excess) in a finely powdered form was placed in a 250 ml. two-necked flask and covered with 200 mls. of diethyl ether. Ethylmagnesium bromide (3·99g.) in diethyl ether (17 mls.) was added to this and the solution made up to 250 mls. The solution was refluxed and continuously stirred, the course of the reaction being followed by hydrolysis of samples taken at various times. After refluxing for a total of 20 hours the composition of the solution showed no change.

A similar result was obtained on using a large excess of lithium hydride, removing the ether and heating to 90°.

Potassium hydride and ethylmagnesium bromide in ether.

A large excess of potassium hydride (5·12g.) in powder form was covered with 150 mls. of diethyl ether in a 250 ml. two-necked flask and ethylmagnesium bromide (3·99g.) in diethyl ether added. After three days of continuous stirring and refluxing the magnesium content of the solution had dropped to 55% of its original value and the hydrolysable ethyl content remained constant. Further refluxing did not change the composition of the solution.

Potassium hydride and ethylmagnesium bromide in 1,2-dimethoxyethane.

When this reaction was attempted it was found that addition of the ethylmagnesium bromide caused an immediate white precipitate and that the magnesium:hydrolysable ethyl ratio rose from 1:1 to 1:1·22. On refluxing the mixture overnight all the hydrolysable ethyl and 95% of the magnesium content disappeared from solution.

Reaction between ethylmagnesium bromide and 1,2-dimethoxyethane.

Addition of 1,2-dimethoxyethane (0·9g.) to ethylmagnesium bromide (1·33g.) in diethyl ether (20 mls.) gave an immediate white precipitate with the evolution of heat. Extraction with diethyl ether and crystallisation gave a white crystalline solid m.p. 147-149°. [Found: Mg, 6·62, bromine, 43·2%. Required for $C_8H_{20}O_4MgBr_2$; Mg, 6·67; Br, 43·86%].

The infrared spectrum of the solid was essentially that of coordinated 1,2-dimethoxyethane.

Reaction of sodium trimethylboron hydride with diethylmagnesium.

Sodium triethylboron hydride (0·01 moles) in diethyl ether (13 mls.) was slowly added to a solution of diethylmagnesium (0·824g., 0·01 mole) in diethyl ether cooled to -30°. No immediate precipitate was produced but on warming to approximately 0° a precipitate suddenly formed. The reaction mixture was stirred at room temperature for one hour. Removal of the solvent at 50° *in vacuo* left a white solid.

Analysis of the white solid precipitated at 0° gave a hydrolysable hydrogen:magnesium:ethyl ratio of 1·45:1:0·55. A qualitative test showed that no boron was present.

Analysis of a sample (0·04527g.) of the white solid produced by removal of the solvent gave the results indicated below;

Hydrolysable hydrogen	$7{\cdot}895\times10^{-5}$ moles	$7{\cdot}955\times10^{-5}$g.
Hydrolysable ethyl (H_2O)	$1{\cdot}392\times10^{-4}$ moles	$4{\cdot}042\times10^{-3}$g.
Hydrolysable ethyl (acid)	$2{\cdot}328\times10^{-4}$ moles	$6{\cdot}768\times10^{-3}$g.
Magnesium	$1{\cdot}748\times10^{-4}$ moles	$4{\cdot}250\times10^{-3}$g.
Sodium	$2{\cdot}924\times10^{-4}$ moles	$6{\cdot}722\times10^{-3}$g.
		$2{\cdot}258\times10^{-2}$g.

This left 0·02269g. of the sample unaccounted for. This could be triethylboron which was the only species not determined. Thus, triethylboron (by difference) amounted to $2{\cdot}318\times10^{-4}$ moles.

It was noticed that all the hydrolysable ethyl present was not released by water alone, even on boiling. Addition of dilute sulphuric acid was necessary to release the remaining ethane. These two quantities are reported as 'hydrolysable ethyl (H_2O)' and 'hydrolysable ethyl (acid)' respectively. Total amount of hydrolysable gas - $4{\cdot}510\times10^{-4}$ moles.

Magnesium content should produce two molar equivalents of gas i.e. $3{\cdot}496\times10^{-4}$ moles.

Sodium content should produce one molar equivalents of gas i.e. $2{\cdot}924\times10^{-4}$ moles.

Therefore total amount of hydrolysable gas required - $6{\cdot}420\times10^{-4}$ moles.

The experiment was repeated in order to investigate the stability of the solution at low temperatures.

A solution of diethylmagnesium (0·01 mole) in diethyl ether (40 mls.) was cooled to -78° and sodium triethylboron hydride (1·22g., 0·01 mole) added to it as a diethyl ether (15·3 ml.) solution. The solution remained clear when maintained at -78° for five hours. Analysis of samples of the solution at various times remained constant. [Found: ratio of hydrolysable ethyl (H_2O):hydrolysable hydrogen is 1·01:1. If acid was added more ethane was evolved. The ethane came off fairly slowly but the amount evolved did not account for all the ethyl groups believed present. In a typical sample the ratio, hydrolysable ethyl (H_2O):hydrolysable hydrogen:hydrolysable ethyl (acid) was 1·01:1:0·48].

N,N,N',N'-Tetramethylethylenediamine (1·16g., 0·01 mole) was added to the solution obtained above and the reaction mixture allowed to warm to room temperature. No precipitate appeared, even on boiling the ether, in the presence of the diamine. Removal of the ether left a sticky white solid which was soluble in aromatic hydrocarbons but not in aliphatic. No pure products could be obtained from the reaction mixture which was not further investigated.

It was decided to repeat the series of reactions with the methyl analogues of the compounds mentioned above in the hope that they would provide more tractable products and be more amenable to spectroscopic studies.

Preparation of sodium trimethylboron hydride.

Methylmagnesium bromide was prepared in the usual way from magnesium turnings (20g.) and methyl bromide (68g.). Addition of n-butylborate dropwise to the stirred Grignard solution produced trimethylboron which was bubbled directly into a vigorously stirred suspension of excess sodium hydride (0·3 mole) in diethyl ether, where it was immediately absorbed. The reaction was completed by gently warming the Grignard solution to release all the trimethylboron and finally refluxing the sodium hydride suspension for two hours. The solution was standardised by determination of the sodium, boron and hydrolysable hydrogen content.

Removal of the solvent from a sample of the sodium trimethylboron hydride (0·015 mole) *in vacuo* yielded after prolonged pumping a crystalline substance which was soluble in hydrocarbon solvents and could be crystallised as long colourless needles from hexane m.p. 46·5-47°. [Found: hydrolysable hydrogen, 1·25; boron, 13·50; sodium, 28·75%. M(cryoscopically 1·83, 0·598 wt.-% in benzene) 324 and 323. Required for $C_{12}H_{40}B_4Na_4$; hydrolysable hydrogen, 1·26; boron, 13·54, sodium, 28·76%. M, 320].

The infrared spectrum of the solid was recorded both as a nujol mull and as a cyclohexane solution.

Nujol mull: 1905m(sh), 1876m, 1468s(sh), 1451s, 1379m, 1266s, 1130s(br), 1098s, 1043s(sh), 1018s, 971m(sh), 835w(sh), 797w, 769w, 719w.

Cyclohexane solution: 1968m, 1876m, 1429m, 1364w, 1351w(sh), 1294s(sh), 1282s, 1176s, 1151s, 1126s, 1096s, 1064m, 1017w(sh), 1002m, 877w, 791w.

The p.m.r. spectrum recorded in benzene solution contains a single peak, assigned to the B-$\underline{CH_3}$ resonance, at 10·30τ. In ether the peak is found at 10·35τ. The ^{11}B spectrum of the compound in benzene solution relative to an external trimethylborate standard contains a broad single resonance 234 c.p.s. upfield from the $B(OMe)_3$ resonance.

Reaction between sodium trimethylboron hydride and dimethylmagnesium.

Addition of sodium trimethylboron hydride (0·01 mole) in hexane solution to a stirred solution of dimethylmagnesium (0·01 mole) in diethyl ether at -78° produced an initially clear solution which began to deposit a white solid just below room temperature. After stirring at room temperature the solid was filtered. Analysis of the solid gave the empirical formula $MgH_{1\cdot9}Me_{0\cdot1}$.

The p.m.r. spectrum of the clear solution at room temperature contained a complex of peaks centred at 10·55τ which corresponded with the known spectrum of sodium tetramethylboron and a single peak at 11·6τ which was due to the methyl groups attached to magnesium.

It was decided to attempt to follow the reaction at low temperatures by recording the change in the p.m.r. spectrum with temperature.

An equimolar mixture of sodium trimethylboron hydride and dimethylmagnesium was prepared at -78° and a sample quickly transferred to a p.m.r. tube also maintained at -78°.

At -78° the spectrum consisted of two single peaks at 10·48τ and 11·62τ attributable to the boron-methyl and magnesium-methyl resonances respectively. The results are tabulated below.

Temp.	δ(Mg-$\underline{\text{Me}}$)-δ(B-CH$_{\underline{3}}$)p.p.m.	Peak width at half height p.p.m.		Intensity ratio
		B-Me	Me-Me	B-Me/Mg-Me
-70°	1·14	0·113	0·057	2·09
-60°	1·20	0·12	0·057	2·07
-50°	1·15	0·139	0·044	1·95
-40°	1·25	0·157	0·050	2·36
-30°	1·26	0·195	0·050	2·00
-20°	1·32	0·22	0·057	2·33
-10°	1·27	0·246	0·057	3·14
0°	1·27	0·327	0·063	5·16

Only gross changes in the intensity ratio are significant as the data were collected simply by tracing the line shapes on constant weight paper and weighing these.

Precipitation begins to occur at -20° and is significant at 0°.

The line shape of the B-Me resonance changes from a singlet at -70°, gradually broadening until it is a complex peak at 0°.

Reaction between sodium trimethylboron hydride and dimethylmagnesium in the presence of N,N,N',N'-tetramethylethylenediamine.

It is known that in the case of the corresponding ethyl compounds the diamine prevented the precipitation of a magnesium hydride species.

N,N,N',N'-Tetramethylethylenediamine (0·01 mole) was added to an ethereal solution containing an equimolar mixture of dimethylmagnesium (0·01 mole) and sodium trimethylboron hydride at -78°. On warming no precipitate formed, unlike the system in the absence of amine. Removal of some solvent caused the formation of a white crystalline solid m.pt. 96-98°. The infrared spectrum of the solid was identical with that of N,N,N',N'-tetramethylethylenediamine-dimethylmagnesium.

Reaction between ethylmagnesium chloride and sodium triethylboron hydride.

Addition of an ethereal solution of ethylmagnesium chloride (1·77g., 0·02 mole) to a solution of sodium triethylboron hydride (2·44g., 0·02 mole) in diethyl ether gave an immediate precipitate of sodium chloride. The solution was allowed to settle and an aliquot of the solution analysed. Addition of water to the sample released all the hydrolysable hydrogen but only part of the hydrolysable ethyl e.g. for a 0·7 ml. sample, found hydrolysable hydrogen:hydrolysable ethyl (H_2O) was 1:0·85. Addition of acid brought the ratio to 1:1·02. Thus for the sample the ratio total hydrolysable ethyl:hydrolysable hydrogen: magnesium:boron was 1:0•98:1•01:0•98.

An aliquot of the solution was concentrated and the p.m.r. spectrum recorded. The spectrum contains, besides the resonances due to ether, peaks at 9•02, 919, 9•28 and a broad peak centred at 9•60. No resonances due to the ethyl group attached to magnesium could be detected.

The infrared spectrum contains absorptions at; 1887w, 1456m, 1395m, 1292w, 1266w, 1190w, 1153m, 1093s, 1067s, 1046s, 1002m, 926w, 896w, 864w, 833w, 793w, 779w, 508w.

An aliquot of the filtered solution was taken and the solvent removed at -30°. On warming the remaining viscous liquid was pumped for 20 hours and the volatile components trapped in liquid air.

Analysis of the remaining viscous liquid showed that it had a hydrolysable ethyl:hydrolysable hydrogen:magnesium ratio of 1•0:1•1:1•0 and that 25% of the boron had been removed. Once again the addition of acid was necessary to release all the hydrolysable ethyl.

A second aliquot of the solution was taken and the ether removed leaving a viscous liquid. Excess trimethylamine was condensed on to the liquid and kept at -78° overnight. Removal of the excess trimethylamine left a viscous liquid which on heating to 110° became a white solid. The infrared spectrum of this solid consisted simply of the peaks due to nujol and a continuous absorption from 1379 cm^{-1}.

The white solid was extracted with benzene and the benzene solution analysed. The solution contained only hydrolysable ethyl and magnesium in the ratios 2:1. A p.m.r. spectrum of the solution showed the presence of diethyl ether. An unknown amount of boron was also present.

Reaction between sodium trimethylboron hydride and methylmagnesium bromide.

Immediate precipitation of sodium bromide occurred when sodium trimethylboron hydride (0·04 moles) was added to methylmagnesium bromide (0·04 moles) in diethyl ether. After filtration an aliquot of the solution was analysed. [Found: hydrolysable methyl:magnesium:hydrolysable hydrogen was 0·95:1:1·02. Once again all the hydrolysable methyl was not released by water and boiling with acid was necessary. As the analyses show the ratios are not exactly correct, but as only a little sodium (the ratio, magnesium:sodium was 1:0·015) was present it was assumed that the hydrolysable methyl was difficult to release].

Ten mls. of the filtered solution (containing 0·0054 moles of magnesium) were taken and an excess of trimethylamine condensed on to it. The reaction mixture was allowed to remain at -78° overnight. A white solid appeared which dissolved on warming. At almost room temperature a greyish precipitate began to form which did not dissolve on boiling. The precipitate was filtered and dried in vacuo. [Found: hydrolysable hydrogen, 2·35; magnesium, 31·9%; hydrolysable methane, 0·56%].

This corresponds to a H:Mg:Me ratio of 1·76:1:0·25.

Removal of the solvent from the filtrate left a white solid which lost weight in vacuo and trimethylboron was collected. The infrared spectrum of the solid showed it to be dimethylmagnesium although hydrolysis gave a small amount of hydrogen.

Pyrolysis of di-isopropylmagnesium.

An ethereal solution of di-isopropylmagnesium (50 mls., 5·86 millimoles) was made ether-free by removal of the solvent in vacuo, initially at room temperature and finally at 70° overnight. During this time 5·3N ccs. of propane and 18·24N ccs. of ether were collected. The temperature was increased to 130-140° when rapid gas evolution began to take place. The heat was removed when 65N ccs. of gas had been evolved. Analysis of the gas mixture by bromination of the olefin content and remeasurement showed that it contained 93·4% propene, 5·2% propane and a little (~0·7%) ethane. The solid remaining was sticky and yellowish in colour. The solid was refluxed with ether. The insoluble residue was shown to be magnesium hydride by analysis and infrared spectrum while analysis of the solution showed that it contained di-isopropylmagnesium (0·48 millimoles of magnesium, 0·90 millimoles of propane and 0·02 millimoles of hydrogen) with a small hydrolysable hydrogen content.

Pyrolysis of di-isopropylmagnesium containing some ether.

An ethereal solution of di-isopropylmagnesium (18 mls., $2{\cdot}1\times10^{-3}$ moles) was placed in a tube, attached to a vacuum system and the bulk of the ether removed. When a sticky solid was obtained the tube was heated to 140°. Almost immediately a colourless sublimate formed in a cooler part of the tube. After heating overnight only 13% of the expected amount of gas had been evolved. The temperature was raised to 200° for twenty four hours after which time 32% of the total possible gas had been evolved. Heating for a further twenty four hours raised the total gas evolved to 46% at which point the heat was removed. Analysis of the evolved gas showed it to be a mixture of 18% propane and 82% propene. The solid product left was a dark brown glue which was not investigated further.

Only a small amount of the colourless sublimate could be removed from the tube. The infrared spectrum showed similarities to those of isopropylmagnesium ethoxide and isopropylmagnesium isopropoxide but was identical to neither.

Pyrolysis of [2-dimethylaminoethyl(methyl)amino]isopropylmagnesium.

A weighed amount of the complex (0·1394g., 0·827 millimoles) was placed in a two-necked flask, dissolved in 10 mls. of a high boiling paraffin oil (purified by distillation from lithium aluminium hydride followed by fractionation on a vacuum line), and heated *in vacuo* at 130° for 12 hours after which time 50% of the expected amount of gas had been evolved. The infrared spectrum of the gas showed it to be only propane and not propene as expected. No product could be isolated from the oil and the experiment was abandoned at this stage.

Pyrolysis of solid [2-dimethylaminoethyl(methyl)amino]-t-butylmagnesium at 170° for 17 hours gave a similar dark brown solid product which evolved no gas on hydrolysis.

DISCUSSION

Discussion.

Dimethyl- and diethyl-magnesium have been shown, by X-ray powder diffraction methods, to be polymeric solids containing magnesium-alkyl-magnesium bridges.[33,34] The higher alkyls which have been prepared have similar physical properties i.e. they are white solids, insoluble in non-donor solvents, and it is a reasonable assumption that they too consist of long linear polymeric chains. This situation contrasts markedly with that of beryllium where only dimethylberyllium has a similar structure,[35] the higher alkyls having a much lower degree of association.[83,84] The smaller size of the beryllium atom must be the main contributing factor to this situation, steric hindrance preventing the formation of a linear polymer in all but the least hindered beryllium alkyls. Although no gross change in structure occurs in the magnesium alkyls as the size of the alkyl group increases it is likely that the strength of the bridge bond will be affected. The following order is suggested for the strength of the Mg-C-Mg bridging bond with changing alkyl group,

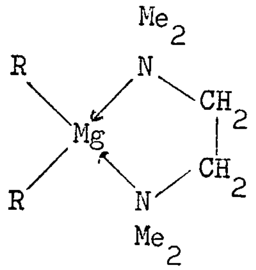
$$\text{Me} > \text{Et} > \text{i-Pr} > \text{t-Bu}$$

This order is substantiated by the nature of the coordination complexes prepared and by the ease of removal of diethyl ether from an ethereal solution of the alkyls. Thus on cooling a solution of dimethylmagnesium in diethyl ether long needle-like crystals form (at -78°) but on warming the product, ether is readily lost. If crystallisation is carried out at room temperature by partial removal of the solvent, solvent-free dimethylmagnesium is obtained. Diethylmagnesium behaves in an analagous fashion, crystallisation at room temperature gives the uncoordinated metal-alkyl while at low temperature a crystalline solid, reported to be $MgEt_2.OEt_2$, is formed, which loses ether at about 0^o. Removal of the ether from di-isopropylmagnesium is more difficult. Pumping in vacuo, at room temperature, leaves a viscous liquid $Pr^i{}_2Mg.(Et_2O)_{\sim 1}$ which loses ether only very slowly, the process being almost complete after 14 hours. So far, complete removal of the diethyl ether from di-t-butylmagnesium, without decomposition, has not been achieved.

Reaction with donor molecules.

Because of the polymeric nature of the dialkyl- and diarylmagnesium compounds coordination complexes with donor molecules are only formed when the free energy of coordination of the donor is greater than the free energy of polymerisation of the organomagnesium compound. X-Ray data show that the bonds in the polymer chains are stronger in the case of magnesium than those of the beryllium polymer.[33,34] Thus it is to be expected that the coordination complexes of dialkylmagnesium compounds will lose the donor molecule more readily than the corresponding beryllium compounds. Reactions between organomagnesium compounds and various chelating ligands were investigated first as these were considered most likely to give stable crystalline products.

N,N,N',N'-Tetramethylethylenediamine reacts with dimethyl-, di-isopropyl, di-t-butyl- and diphenylmagnesium to give crystalline coordination complexes $R_2Mg.(Me_2N)_2C_2H_4$ which are all monomeric in benzene. They most probably have the structure,

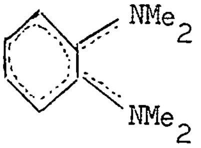


(R = Me, Ph, i-Pr, t-Bu)

The complexes all sublime in vacuo although both $Pr^i{}_2Mg.(Me_2N)_2C_2H_4$ and $Bu^t{}_2Mg.(Me_2N)_2C_2H_4$ decompose slowly on heating and the diphenylmagnesium complex sublimes only at high temperatures (~250°).

The p.m.r. spectra of the di-isopropyl- and di-t-butylmagnesium complexes contain single resonances due to the N-CH_3 and N-CH_2 groups of the ligand indicating the presence of only one type of nitrogen atom and therefore four-coordinate magnesium. Cooling to -70° produces no change in the spectrum of $Bu^t{}_2Mg.(Me_2N)_2C_2H_4$. This contrasts with the behaviour of $Bu^t{}_2Be.(Me_2N)_2C_2H_4$ in which the N-CH_3 and N-CH_2 resonances both split at low temperatures indicating the presence of two types of nitrogen atom and hence three coordinate beryllium.[84]

Dimethylmagnesium also forms a crystalline complex with N,N,N',N'-tetramethyl-o-phenylenediamine, which is monomeric in benzene. In contrast to the N,N,N',N'-tetramethylethylenediamine complex, this loses ligand on heating above 70°. This is probably due to the lower basicity of N,N,N',N'-o-phenylenediamine where there is a possibility of delocalisation of the nitrogen lone pairs with the π-electrons in the phenyl ring (fig.30).



The 1,2-dimethoxyethane complex of dimethylmagnesium also loses ligand on warming. The corresponding beryllium compound behaves similarly although it can be sublimed unchanged in the presence of a low partial pressure of ligand.[98]

Dimethylmagnesium does not form a stable complex with bipyridyl, the initially formed yellow crystalline complex rapidly darkens. It is thought that this is due to addition of the magnesium-methyl group across the C=N bond of the bipyridyl.

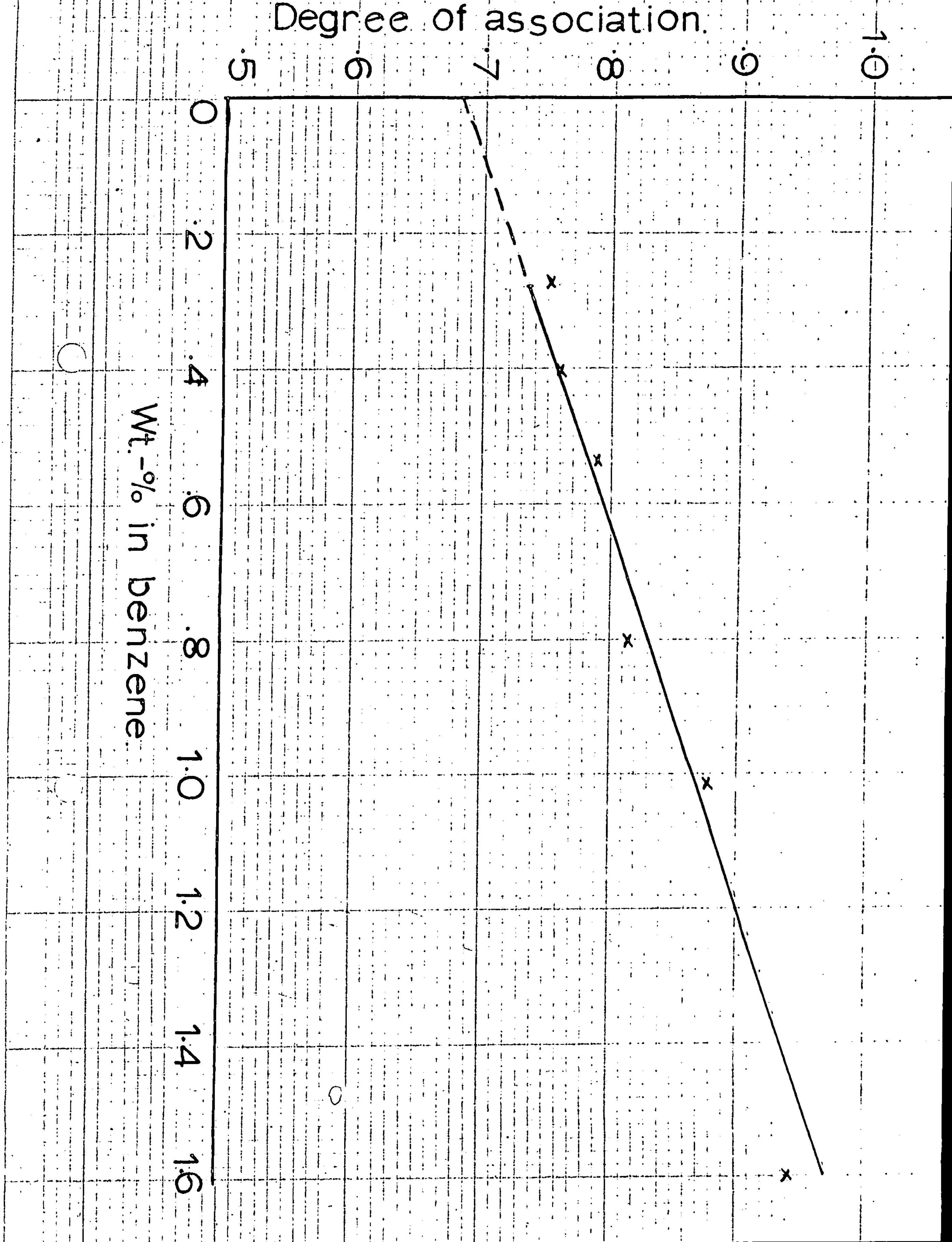
Complexes of diphenylmagnesium are generally more stable than the corresponding dialkylmagnesium complexes as the electron-withdrawing nature of the phenyl group increases the acceptor properties of the magnesium atom. Thus diphenylmagnesium forms a 1:1 complex, presumably chelated, with 1,2-dimethoxyethane and a 1:2 complex with the monodentate ligand, tetrahydrofuran. The tetrahydrofuran complex, $Mg(C_6H_5)_2$, $(C_4H_8O)_2$ posesses a measurable vapour pressure at 25°. Vapour pressure measurements give a value of ~9 kcals./mole for the heat of coordination of tetrahydrofuran. This value must be treated with caution as the measurements of the vapour pressure were made only for ascending temperature. The recombination could not be studied as the reaction between vapour and solid is too slow. The vapour pressure increases markedly above the melting point (7·43cm. at 126·2°, 9·00cm. at 138°, 10·93cm. at 151·5° and 15·42cm. at 160°) and recombination is faster.

Removal of half of the tetrahydrofuran from $Mg(C_6H_5)_2.(C_4H_8O)_2$ leaves a yellow residue which cannot be purified. The infrared spectrum of the residue contains all the absorptions present in a spectrum of bis-tetrahydrofuran-diphenylmagnesium and many others. It is possible, therefore, that removal of half the tetrahydrofuran leaves a mixture of diphenylmagnesium and the bis-tetrahydrofuran complex.

Di-t-butylmagnesium forms a crystalline complex with 1,4-dioxan which decomposes on heating before losing dioxan. The dioxan is not displaced from the complex by tetrahydrofuran nor by trimethylamine, but is displaced by N,N,N',N'-tetramethylethylenediamine.

Tetrahydrofuran forms a 2:1 complex with di-t-butylmagnesium which is crystalline m.p. 132-5°. The complex dissociates in benzene solution. A plot of degree of association against concentration is shown in figure 31. Various dissociation schemes are possible:

(i) $Bu^t{}_2Mg(C_4H_8O) \rightleftharpoons Bu^t{}_2Mg.C_4H_8O + C_4H_8O$

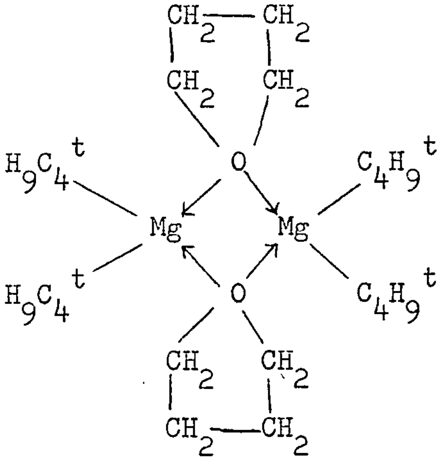

Degree of association.
·5
·6
·7
·8
·9
1·0
0
·2
·4
·6
·8
1·0
1·2
1·4
1·6
Wt.-% in benzene.

(ii) $x\mathrm{Bu}^{t}{}_{2}\mathrm{Mg}(\mathrm{C}_4\mathrm{H}_8\mathrm{O})_2 \rightleftharpoons (\mathrm{Bu}^{t}{}_{2}\mathrm{Mg})_x + 2x\mathrm{C}_4\mathrm{H}_8\mathrm{O}$

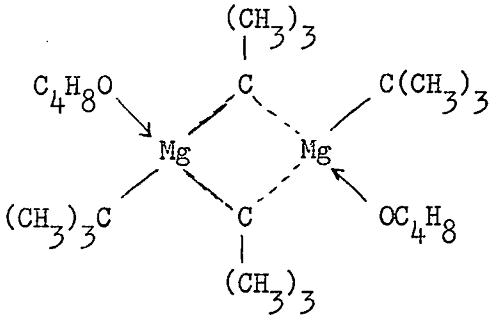
(iii) $2\mathrm{Bu}^{t}{}_{2}\mathrm{Mg}(\mathrm{C}_4\mathrm{H}_8\mathrm{O})_2 \rightleftharpoons (\mathrm{Bu}^{t}{}_{2}\mathrm{Mg.C}_4\mathrm{H}_8\mathrm{O})_2 + 2\mathrm{C}_4\mathrm{H}_8\mathrm{O}$

(iv) $n\mathrm{Bu}^{t}{}_{2}\mathrm{Mg}(\mathrm{C}_4\mathrm{H}_8\mathrm{O})_2 \rightleftharpoons (\mathrm{Bu}^{t}{}_{2}\mathrm{Mg.C}_4\mathrm{H}_8\mathrm{O})_n + n\mathrm{C}_4\mathrm{H}_8\mathrm{O}$

If dissociation according to the above schemes becomes complete (i.e. reaction goes completely to the right) at infinite dilution, then the degree of association ought to reach a limiting value at this point. For schemes (i) and (ii) this will be 0·5, for scheme (iii) 0·66 while for scheme (iv) the value will be n/(n+1) where n is an integer equal to the degree of association of the magnesium species formed on dissociation. Figure 31 shows that the degree of association at infinite dilution for $\mathrm{Bu}^{t}{}_{2}\mathrm{Mg}(\mathrm{C}_4\mathrm{H}_8\mathrm{O})_2$ is ~0·68 which indicates that scheme (iii) is the probable method of dissociation. The product $(\mathrm{Bu}^{t}{}_{2}\mathrm{Mg.C}_4\mathrm{H}_8\mathrm{O})_2$ has a number of possible structures. The two most likely are shown (I and II).



I



II

A structure with a mixed alkyl, oxygen bridge can also be drawn. Although no real choice can be made between the two structures, the use of the bulky t-butyl group to form an electron deficient bridge in structure II would seem to be less likely on steric grounds.

Reaction between alkylmagnesium halides and donor molecules.

Organomagnesium halides show no general reaction in the presence of donor molecules. Thus in diethyl ether the species $RMgX.(Et_2O)_2$ is normally obtained on crystallisation.[36,41] In tetrahydrofuran and other ethers however, RMg_2X_3, species can be obtained [44,45] while addition of the chelating ether, 1,4-dioxan causes a complete disproportionation into dialkyl(aryl)magnesium and magnesium halide.[26]

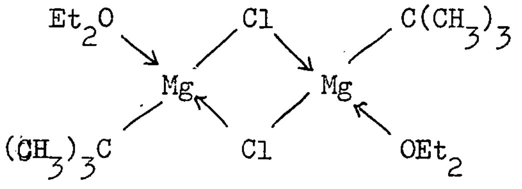
Addition of the chelating diamine, N,N,N',N'-tetramethylethylenediamine to methylmagnesium bromide does not cause disproportionation but gives an immediate white precipitate from which a crystalline solid, m.p. 125-126° which has the empirical formula $CH_3MgBr.(NMe_2)_2C_2H_4$. $CH_3MgBr.(NMe_2)_2C_2H_{14}$, can be sublimed. This solid is not a mixture of dimethylmagnesium N,N,N',N'-tetramethylethylenediamine and the magnesium bromide complex as the melting point is sharp and distinct from those of the symmetrical complexes and the infrared spectrum is identical to that of the dimethylmagnesium complex and contains no absorptions due to the magnesium bromide complex, $MgBr_2(NMe_2)_2C_2H_4$.

After this work had been completed, Ashby published some work on the addition of triethylamine to ethylmagnesium bromide and isolated a similar complex with a Mg:Br:N ratio of 1:1:1.

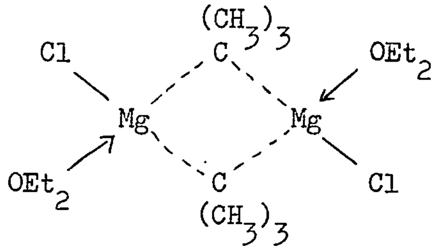
Measurement of the molecular weights of organomagnesium halides in diethyl ether solution have shown that the degrees of association increase well above dimers at higher concentrations.[73] t-Butylmagnesium chloride, however, did not increase its degree of association above two at high concentrations.

Removal of all the diethyl ether from a solution of t-butylmagnesium chloride and recrystallisation from hexane gives a crystalline solid, $Bu^tMgCl.OEt_2$, which is dimeric in benzene. In order to prepare crystals of this compound two conditions are necessary, (i) the t-butyl:magnesium: chloride ratio in the original ether solution must be exactly 1:1:1 and (ii) as much diethyl ether as possible must be removed before the addition of hexane.

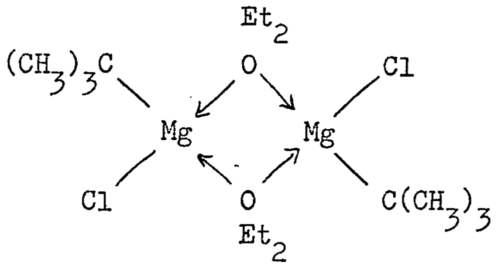
There are three possible structures for the complex,



I



II

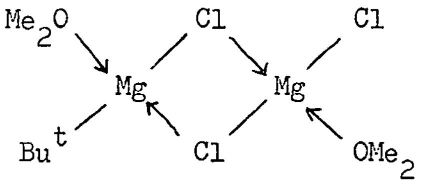


III

Structures with mixed halide-alkyl, halide-oxygen and alkyl-oxygen bridges can also be drawn. Of these structure I is the most likely as it is known that the tendency of chlorine atoms to act as bridges is greater than that of alkyl groups and it is almost certainly greater than that of ether molecules.

It is hoped to obtain crystals of this complex for X-ray examination to settle the question of the structure.

It has not proved possible to prepare the analagous dimethyl ether complex, which would be a simpler X-ray problem, as crystallisation from dimethyl ether yields a halide-rich phase $Bu^tMg_2Cl_3.(OMe_2)_2$, which probably has the structure,

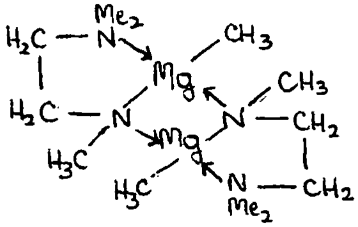


The products obtained on crystallisation of alkylmagnesium halides from solutions containing donor molecules do not seem to form any simple pattern e.g. variation with donor strength, and it is probable that the species obtained is simply the least soluble of those present in the complex equilibria which occur in alkylmagnesium halide solutions.

Reactions with weak acids.

Amines.

N,N,N'-trimethylethylenediamine reacts with dimethyl-, di-isopropyl-and di-t-butylmagnesium to give solid crystalline products. The methyl- and isopropylmagnesium compounds sublime <u>in vacuo</u> and are dimeric in benzene while the t-butylmagnesium compound does not sublime before decomposing and dissociates somewhat from a dimer in benzene solution. This dissociation is probably caused by the increased steric hindrance of the t-butyl group. This behaviour is shown to an even greater extent by the corresponding beryllium compounds where the methyl-[90] and di-isopropylberyllium compounds are dimeric while the t-butylberyllium complex shows no tendency to associate, is monomeric and is formulated with three coordinate beryllium.[84] The structure of the dimer is probably as shown in fig. 32.



The p.m.r. spectrum of [2-dimethylaminoethyl(methyl)amino]methyl magnesium shows that whereas the $N(CH_3)_2$ resonance of the amine moves to higher field compared to the free amine by 0·3 p.p.m. the $N\text{-}CH_3$ resonance moves to lower field by 0·21 p.p.m. and the $Mg\text{-}CH_3$ (11·06τ) is in fact lower than that recorded for dimethylmagnesium in diethyl ether (~11·5τ).

The situation with regard to the amine is complicated by the fact that on complex formation the spatial orientation about the nitrogen atoms is radically changed from those of the free amine so it is difficult to predict by how much and in which direction shifts will occur. The shift to higher field for N-CH_3 groups attached to magnesium and participating in a ring structure may be fairly general as in the complexes $Pr^i{}_2Mg.(Me_2N)_2C_2H_4$ and $Bu^t{}_2Mg(Me_2N)_2C_2H_4$ the N-Me resonances moves from 7·83τ in the free amine to 8·10τ and 8·20τ respectively in the complexes. There will probably be a net withdrawal of electrons from the magnesium atoms due to the polarity of the magnesium nitrogen bonds, which will not be compensated by the coordinate links to magnesium and will account for the lower chemical shift of the Mg-CH_3 protons in the complex.

Thiols.

The dialkyls of beryllium, zinc and cadmium react with equimolar proportions of thiols in non-donor media to give compounds which have interesting, and in some instances unexpected, degrees of association. All the beryllium compounds of the type RBeSR' so far isolated have been tetramers[96] while $Me(Et)ZnSBu^t$ is a pentamer, $MeZnSPr^i$ is a hexamer,[149] $MeCdSBu^t$ is a tetramer and $MeCdSPr^i$ is a hexamer.[159] The other zinc and cadmium compounds which are known have less sterically hindered groups attached to the sulphur and are all polymeric.

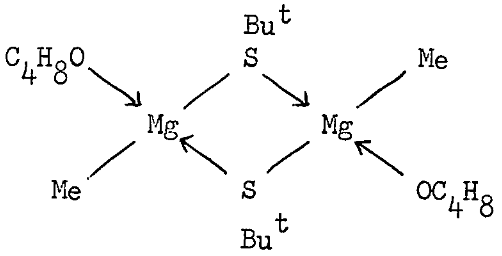
No successful preparations of alkylmagnesium alkylsulphides have been carried out in hydrocarbon reaction media (in which the magnesium dialkyls used are insoluble). Such experiments resulted in R:Mg ratios exceeding 1:1.

t-Butylthiol reacts with dimethylmagnesium in diethyl ether to give a clear solution which, on addition of hexane, gives a white solid consisting mainly of magnesium t-butylsulphide, i.e. disproportionation has occurred:

$$\mathrm{MeMgSBu^{t}(xOEt_2)_2} \xrightarrow[\text{ether}]{\text{hexane}} \mathrm{Mg(SBu^{t})_2} + \mathrm{Me_2Mg}$$

A similar reaction takes place between dimethylmagnesium and iso-propylthiol although addition of hexane does not cause such a complete disproportionation since the product obtained still contains a substantial amount of hydrolysable alkyl.

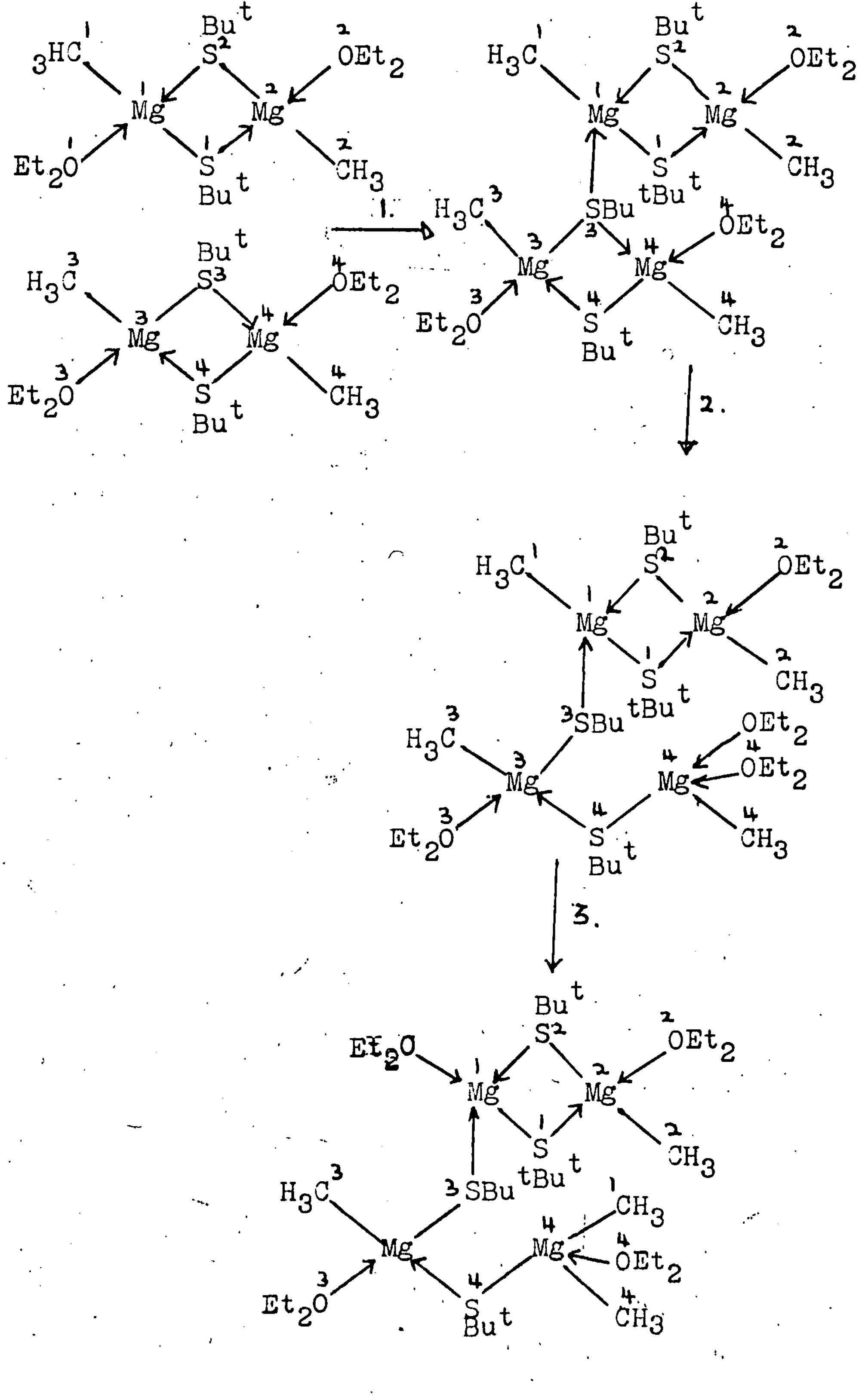
In the presence of tetrahydrofuran, however, disproportionation does not occur and the complexes $(\mathrm{MeMgSBu^{t}.C_4H_8O})_2$ and $(\mathrm{MeMgSPr^{i}.0.78C_4H_8O})_x$ are isolated. The dimeric complex is formulated as shown,

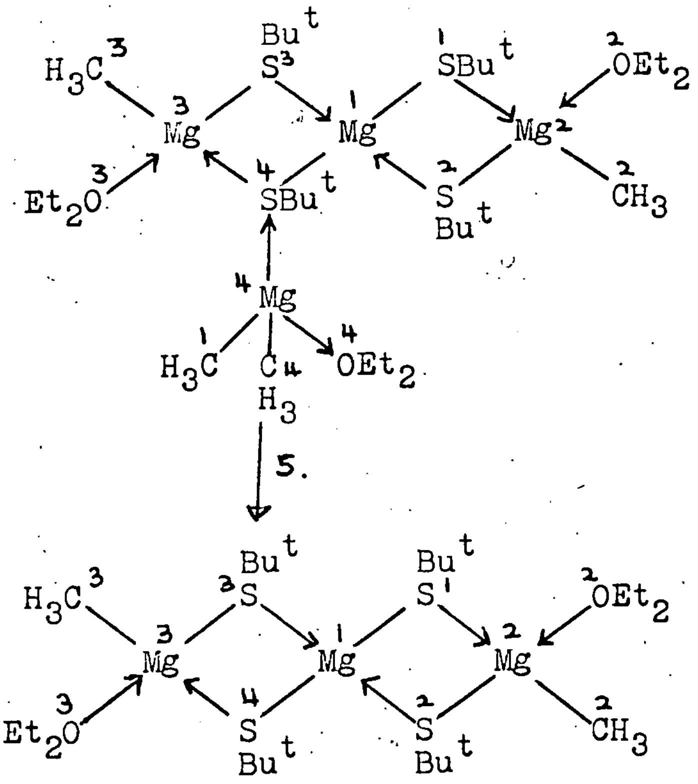


It is probable that in ethereal solution the methylmagnesium t-butyl sulphide will be complexed with the diethyl ether forming a compound of the type shown above.

In order to formulate a disproportionation mechanism it would seem that two conditions are necessary, (a) that the formation of methyl bridges between two magnesium atoms is possible in the presence of the donor solvent (that this is the case is shown by the fact that dimethyl-

Disproportionation Scheme for Methylmagnesium Alkylsulphides.





$\overset{4}{\mathrm{Mg}}(\mathrm{CH_3})^{1}(\mathrm{CH_3})^{4}(\mathrm{OEt_2})_2$

magnesium crystallises from ether solution at room temperature in a solvent-free state) and (b) that the second lone pair on the sulphur atom is of comparable donor strength to the solvent. If this occurs then the following disproportionation mechanism can be formulated (fig.33)

1. The second lone pair on S^3 displaces an ether molecule from Mg^1.
2. An ether molecule breaks the bond between S^3 and Mg^4.
3. The methyl group on Mg^1 transfers to Mg^4 (probably via an electron deficient bridge) displacing one of the ethers on Mg^4 and being replaced by another ether on Mg^1.
4. The second lone pair on S^4 displaces the ether on Mg^1.
5. An ether molecule breaks the bond between S^4 and Mg^4 releasing dimethylmagnesium and leaving the beginning of the $Mg(SBu^t)_2$ polymer.

This polymer will grow by a similar mechanism until it becomes insoluble and is precipitated. The hydrolysable methyl content of the polymer will depend upon the length of the polymer chain.

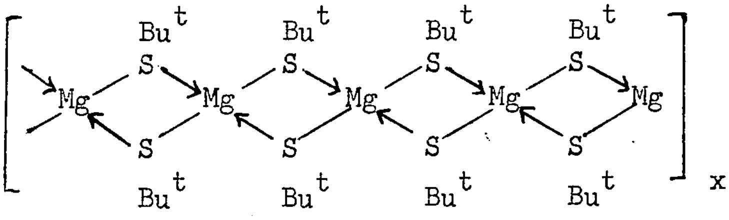
That an ether solution of $MeMgSPr^i$ does not contain simply dimer molecules $(MeMgSPr^i.OEt_2)_2$ is shown by the fact that the methyl-magnesium resonance in ether solution is found at 11·34τ, much nearer the position of the methyl resonance in ethereal dimethylmagnesium, than that of a known dimeric methyl-magnesium alkylsulphide, $MeMgSBu^t.THF$, 10·71τ and $MeMgSPr^i.THF$, 10·71τ.

Addition of tetrahydrofuran will make both conditions (a) and (b) invalid and disproportionation will not occur, as is observed.

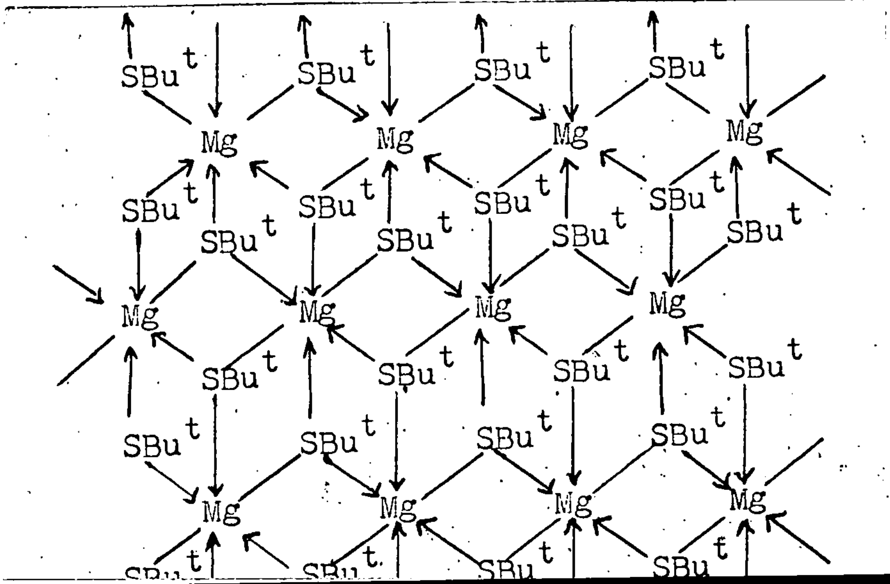
Reaction between diethylmagnesium and t-butylthiol is not accompanied by disproportionation but a stoichiometric diethyl ether complex is not isolated some ether being lost *in vacuo*. The second lone pair on the sulphur atoms must be of a similar donor character to that in the corresponding methyl compounds, and thus it would seem that disproportionation is inhibited because of the inability of ethyl bridges to compete with the donor properties of the solvent. The complex isolated probably contains some degree of cross-linking via the two lone pairs on the sulphur atom. Addition of tetrahydrofuran again produces a crystalline dimeric (in benzene) complex whose structure is probably similar to that of the analagous methyl compound.

Di-t-butylmagnesium and t-butylthiol react eliminating butane with extensive disproportionation. As the reaction between di-t-butylmagnesium and isopropylthiol gives a crystalline diethyl etherate which shows no tendency to disproportionate and is dimeric in benzene, it is possible that steric factors may play some part in causing the disproportionation of the more sterically hindered t-butylsulphide. It is somewhat surprising however that there is such a striking difference in behaviour between the t-butylsulphide and the isopropylsulphide especially in view of the fact that attempts to make a model of t-butylmagnesium t-butylsulphide diethyl etherate showed no serious effect from steric hindrance. The mechanism of the disproportionation is unlikely to be closely similar to that considered for methylmagnesium t-butylsulphide. Condition (b), concerning the donor properties of the second lone pair on the sulphur atom, should still be true but the likelihood of t-butyl bridges competing with the donor solvent is relatively low. The factors causing disproportionation in this case are thus somewhat obscure.

Magnesium t-butylsulphide is formed directly on reaction of diethylmagnesium with two molar proportions of t-butylthiol. Elimination of both hydrolysable ethyl groups seems to take place at about -60°. The magnesium t-butylsulphide is undoubtedly polymeric and probably has the linear structure shown (fig. 34)



It is possible that the magnesium atoms in magnesium t-butylsulphide have a coordination number greater than four. This can be achieved by cross-linking of the linear polymer chains (fig. 35) using the second lone pair on the sulphur atoms.

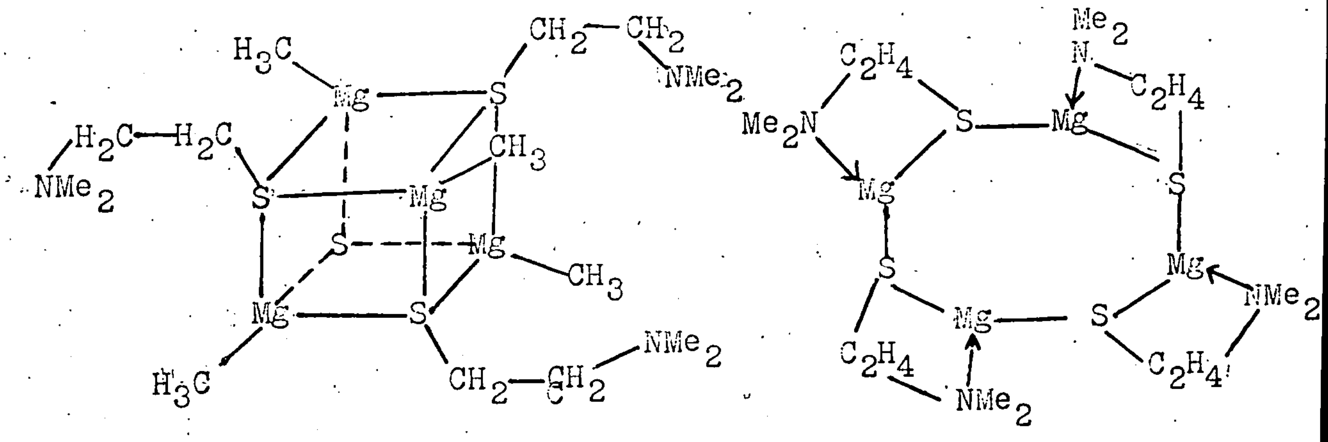


If cross-linking is complete as shown in fig.35 then the coordination number of the magnesium is 6 and an infinite 3 dimensional polymer is produced.

This structure could account for the stability, towards donors, of magnesium t-butylsulphide which is insoluble both in tetrahydrofuran and in pyridine although with pyridine the precipitate does become a pale yellow colour, which may be indicative of coordinated pyridine. This colour disappears on drying in vacuo. It is possible that the pyridine may become coordinated by breaking the cross-linking of the polymer without rupturing the linear polymeric chain. In which case the coordination number of the magnesium will again be greater than four, in the pyridine adduct. Pyridine coordinated in this fashion will be weakly held and could easily be removed in vacuo.

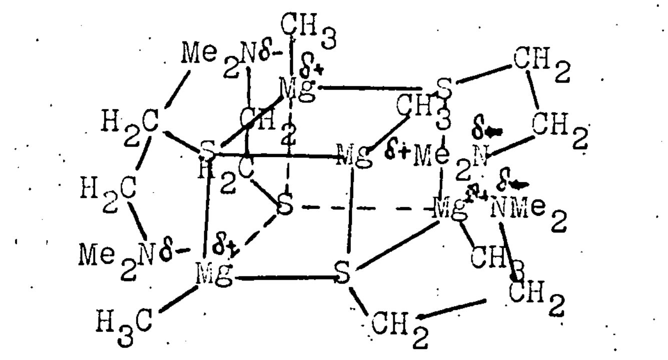
Magnesium t-butylsulphide is obviously a more stable polymer towards donor molecules than beryllium t-butylsulphide which readily forms a bis-pyridine adduct which is only slightly dissociated in ether solution.

Dimethyl- and di-t-butylmagnesium both react with 2-dimethylaminoethane thiol in diethyl ether to form complexes which contain no coordinated diethyl ether. The methyl-magnesium complex is tetrameric in benzene solution while the t-butylmagnesium complex is dimeric. Two structures are possible for $(MeMgSC_2H_4NMe_2)_4$ involving either a cubane structure, similar to that postulated for the alkylmagnesium alkoxides,[6] or an open ring structure of a similar type to that suggested for the trimeric $MeZnOC_2H_4NMe_2$.



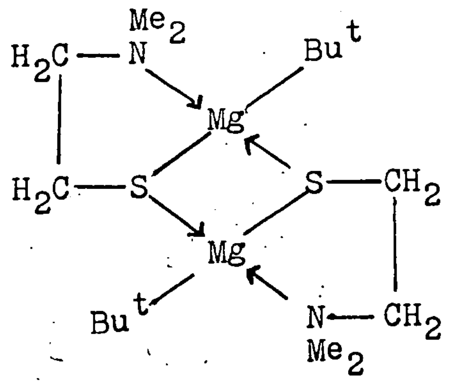
The cubane structure involves postulating the use of the second lone pair on the sulphur atoms as a donor even in the presence of free dimethylamino groups. The work with alkylmagnesium alkylsulphides has shown that in preference to associating by use of the second lone pair the molecules become coordinatively saturated by coordination with a donor solvent molecule. The ring structure does not make use of the second lone pair on the sulphur atoms and allows the dimethylamino groups to be coordinated. Against this formulation the p.m.r. spectrum shows that the NMe_2 resonance occurs at $7{\cdot}82\tau$ which is almost the same as the position of the NMe_2 resonance in pure 2-dimethylaminoethane thiol. In all other compounds containing coordinated NMe_2 groups the NMe_2 resonance moves to higher field on coordination viz. from $7{\cdot}84\tau$ to

8·14τ in $(CH_3MgN(Me)C_2H_4NMe_2)_2$, from 7·83τ to 8·10τ in $Pr^i_2Mg.(NMe_2)_2C_2H_4$ and from 7·83τ to 8·20τ in $Bu^t_2Mg.(Me_2N)_2C_2H_4$. The p.m.r. evidence indicates, therefore, that the cubane structure is the most likely, although this is somewhat of an anomaly in view of the other evidence. If the open ring structure is the correct one it is not immediately apparent why a tetramer is the preferred degree of association. An alternative based on the cubane structure is shown in fig. 36.



In this structure the dimethylamino groups are attached to the magnesium by a simple electrostatic attraction. This method of bonding will not greatly change the electron density at the dimethylamino-group and the p.m.r. signal of the group will be similar to that of the free amine. The coordination number of the magnesium becomes 5.

The t-butylmagnesium complex $(Bu^tMgSCH_2CH_2NMe_2)_2$ is dimeric in benzene and is formulated as shown in fig.37 with coordinated NMe_2 groups.



This is supported by the fact that the NMe_2 resonance in the p.m.r. spectrum is found at 8·12τ which is similar to all the other complexes containing coordinated NMe_2 groups.

Summary.

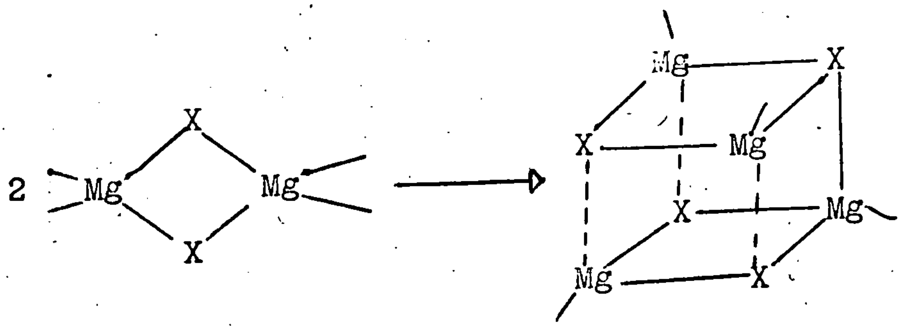
The work described in the first part of this discussion again shows the tendency of organomagnesium compounds to utilise all the available low energy orbitals of the magnesium atom causing it to become four coordinate. Only a few alkylmagnesium amino complexes are thought to contain three coordinate magnesium, which has not been found in any other complexes. Even the complexes of the extremely sterically hindered di-t-butylmagnesium, so far prepared, contain four coordinate magnesium. This situation contrasts strongly with the other members of Group II where the existence of three coordinate species seems much more common.

The differences in behaviour between beryllium and magnesium seems to be entirely attributable to steric factors, the small size of the beryllium atom in many cases preventing the formation of a four coordinate species. The differences in behaviour between magnesium and the elements of group IIB zinc, camium and mercury probably depends on several factors. The increased electronegativity of the atoms of Zn, Cd and Hg, which possess filled, d^{10}, electron shells, causes their acceptor properties to be much reduced while the increasing energy separation between the s and p orbitals of the valence shell with increasing atomic number makes the formation of compounds in which the orbitals used by the metal atoms have a large degree of s character much more likely. This will tend to reduce the coordination number of the metal.

Thus it seems that the tendency to form compounds containing four coordinate metal atoms is at its greatest in group II at magnesium. The magnesium atom is large enough to prevent steric factors playing a large part, except in the most extreme cases, while the electronegativity of magnesium indicates that its acceptor properties are probably greater than those of Be, Zn, Cd or Hg. The energy separation between the 3s and 3p orbitals of magnesium is small enough to allow the easy formation of sp^3 hybrids and hence of four coordinate magnesium.

There seems to be little tendency for magnesium to increase its coordination number above four in compounds which possess magnesium-carbon bonds. In only one case, $[MeMgSC_2H_4N(CH_3)_2]_4$, was any possibility of the magnesium becoming more than four coordinate envisaged.

The dominant feature of the degrees of association of the complexes produced by reacting magnesium dialkyls with weak acids is the preponderance of dimeric and tetrameric species. The tetramers are invariably formed by the superimposition of two dimers.



The tendency to form tetramers will depend on the availability of lone pair on X. In the alkoxides the utilisation of the second lone pair on the oxygen allows the easy formation of tetramers. In the case of the sulphides, however, the donor properties of the second lone pair on the sulphur are much reduced and cannot effectively compete with the lone pair in, say, tetrahydrofuran. Thus dimers are the predominant species in the alkylmagnesium sulphides with the magnesium atom achieving coordinative saturation by incorporating a donor solvent molecule in the complex.

The large numbers of dimers and tetramers known (only two trimers Bu^nMgOPr^i and EtMgOEt in ether are known) attests to the stability of the four membered ring containing two magnesium atoms and two more electronegative atoms. In a ring of this type steric hindrance will be at a minimum while the angular strain will be greatest. The latter must obviously be of least importance.

Hydride chemistry.

Of the main group elements beryllium[105,106] and zinc alkyls[204] in Group II and boron[209,210] and aluminium alkyls[211] in Group III are known to react with alkali metal hydrides to form addition compounds of the type $MM'R_nH$ (where M = alkali metal, M' = B,Be,Al, n = 2(Be) or 3(B,Al) and R is an alkyl group). In the case of zinc only one compound of this type $NaH.2Et_2Zn$ has been described and this is stable only in a glycol ether solution.[204]

It was hoped that it would be possible to extend this reaction to the magnesium alkyls. With sodium hydride and diethylmagnesium addition of the sodium hydride does not occur in any of the solvents used (diethyl ether, tetrahydrofuran and 1,2-dimethoxyethane) even over prolonged periods of refluxing. With tetrahydrofuran and 1,2-dimethoxyethane there is an almost total loss of hydrolysable ethyl from the solution but no hydrolysable ethyl appears in the solid matter present indicating some type of reaction with the solvent. A control experiment in which diethylmagnesium refluxed for a comparable period of time in 1,2-dimethoxyethane gave no indication of any reaction with the solvent. It is possible, therefore, that the presence of sodium hydride is necessary for the loss of the hydrolysable ethyl content, either itself reacting with the solvent to form a compound which then reacts with the dialkylmagnesium or by forming a complex sodium alkylmagnesium hydride which cleaves the solvent. The nucleophilic character of ethyl bound to magnesium in such a complex would be expected to exceed that of ethyl in diethylmagnesium.

No reaction is detected between either lithium hydride or potassium hydride in diethyl ether although a small loss of hydrolysable ethyl does occur. It may be that any sodium alkylmagnesium hydride formed is completely insoluble in the solvents used and forms a protective coating on the alkali metal hydride preventing further reaction.

An attempt was made to prepare lithium dimethylmagnesium hydride by the pyrolysis of lithium dimethyl(n-butyl)magnesium. The latter is prepared simply by the addition of n-butyl lithium to a diethyl ether solution of dimethylmagnesium, followed by removal of the solvent. This leaves a viscous liquid which has the empirical formula $Li[Mg(CH_3)_2(C_4H_9)^n].OEt_2$. It is difficult to purify this complex. That the liquid is a complex and not simply a mixture of n-butyl lithium and dimethylmagnesium is shown by the much enhanced solubility of the dimethylmagnesium in the diethyl ether (a 0·8M solution of dimethylmagnesium alone in ether is saturated) and by the Metal-CH_2 resonance of the n-butyl in the p.m.r. spectrum which is centred at $10{\cdot}24\tau$ i.e. it is probably attached to the magnesium (τ value of Mg-CH_2 in an ethereal solution of diethylmagnesium, 10·55) rather than the lithium atom (τ value for Li-CH_2 in $(n\text{-}BuLi)_2OEt_2$, 10·98 [212]). The O-CH_2 resonance is centred at $6{\cdot}6\tau$ which is similar to the O-CH_2 resonance in free diethyl ether, indicating that there is little change

change in the electron density at the CH_2 group of the ether on complex formation. Pyrolysis of the complex in vacuo is slow at 130° but the ether is completely removed. At 170° pyrolysis is complete in 16 hours (pyrolysis of n-butyl-lithium is complete after a few hours at 80°). Extraction of the pyrolysis product with diethyl ether gives a solution of dimethylmagnesium and leaves lithium hydride.

$$[LiMgMe_2(C_4H_9)^n] \xrightarrow[16\text{ hrs.}]{170^\circ} Me_2Mg + LiH + C_4H_8$$

The lithium dimethyl(n-butyl)magnesium complex may fall apart on removal of the ether although the pyrolysis temperature indicates that the n-butyl group is still attached to the magnesium at this stage. Thus either pyrolysis gives lithium hydride and dimethylmagnesium directly or the ether solvent breaks up the lithium dimethylmagnesium hydride complex. The first alternative seems more likely as the infrared spectrum of the pyrolysis product contains no absorptions attributable to any Mg-H vibration and is in fact a simple superimposition of the spectra of dimethylmagnesium and lithium hydride.

Reactions between alkali metal hydrides and ethylmagnesium bromide.

The use of alkali metal hydrides in carrying out hydride/halogen exchange is now well established. Thus sodium hydride reacts with an equimolar mixture of diethylberyllium and beryllium chloride in diethyl ether, giving a solution of ethylberyllium hydride,[196] lithium hydride reacts with aluminium chloride giving lithium aluminium hydride and in

Group IV sodium hydride reduces silicon tetrachloride to silane in 95% yield using a zinc compound as catalyst.[213]

It was, therefore, expected that halide/hydride exchange of a similar type would occur between alkali metal hydrides and ethylmagnesium bromide.

Lithium hydride either in large or small excess does not react with ethyl magnesium bromide on refluxing for twenty hours or even on removal of the solvent and heating to 90°.

Potassium hydride reduces the magnesium content of an ethylmagnesium bromide solution to approximately half its original value after refluxing for three days, while the hydrolysable ethyl content remains constant and eventually becomes twice the magnesium content. The following reaction must take place

$$2EtMgBr + 2KH \longrightarrow MgH_2\downarrow + Et_2Mg. + 2NaBr$$

The reaction may well go via ethylmagnesium hydride although no evidence was obtained for the existence of this species.

$$EtMgBr + NaH \longrightarrow EtMgH + NaBr$$

$$2EtMgH \longrightarrow Et_2Mg + MgH_2$$

In 1,2-dimethoxyethane addition of the ethylmagnesium bromide to the solvent caused an immediate loss of about 20% of the magnesium content and the formation of a white precipitate and refluxing overnight caused all of the hydrolysable ethyl content and 95% of the magnesium content to be lost from the solution.

Addition of 1,2-dimethoxyethane to ethylmagnesium bromide, in fact precipitates $MgBr_2(C_4H_{10}O_2)_2$ and leaves diethylmagnesium solution.

$$2EtMgBr \xrightarrow{CH_3OCH_2CH_2OCH_3} MgBr_2.(C_4H_{10}O_2)_2 + MgEt_2$$

Refluxing overnight in the presence of sodium hydride presumably causes reaction with the solvent as previously described.

Reactions between organomagnesium compounds and sodium trialkylboron hydrides.

Sodium trimethylboron hydride.

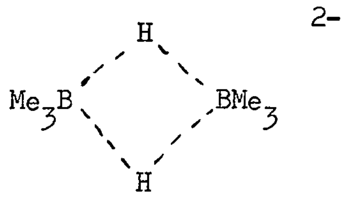
Sodium trialkyl(aryl)boron hydrides have been known for some time,[214,210] but except in the case of the phenyl complex, $NaBPh_3H$, have never been isolated in a pure state.

Sodium hydride reacts directly with trimethylboron in an ether solvent and the complex produced can be recrystallised, after removal of the ether, from hexane as solvent-free $NaBMe_3H$.

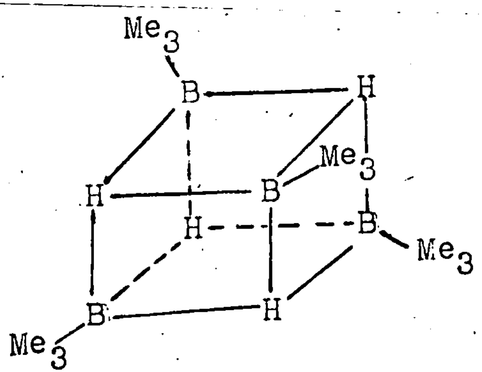
The complex is tetrameric in benzene and the degree of association in the solid phase could also be four as determined by a preliminary X-ray diffraction study. The crystals are monoclinic, a = 10·19, b = 10·92, c = 13·20Å, $\beta = 98^\circ\ 5'$ and the space group is either $p2_1$ or $p2_1/m$ with 8 monomer units in the unit cell.

The infrared spectrum of the complex as a nujol mull has absorptions at 1905 and 1876 cm^{-1} and as a cyclohexane solution at 1968 and 1876 $cm.^{-1}$

This would suggest a dimer structure

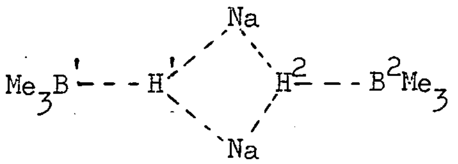


for the anion which could presumably associate to form a tetramer as shown



The position of the sodium atoms is unknown, but the above structure implies a fairly ionic compound which is not in accordance with the known properties of the complex e.g. solubility in hydrocarbons, low melting point.

A structure can be drawn in which the sodium atoms are involved in the bonding scheme. Thus the dimeric species,



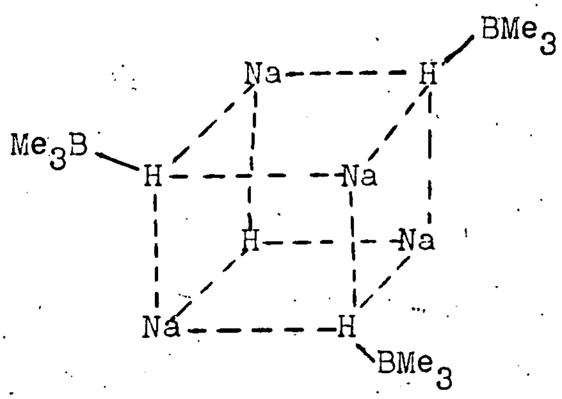
can be formulated using the orbitals

$B^1(sp^3) \quad + \quad H^1(1s) \quad + \quad 2Na(3s) \quad + \quad H^2(1s) \quad + \quad B^2(sp^3)$

$B^1(sp^3) \quad + \quad H^1(1s) \quad + \quad 2Na(3p) \quad - \quad H^2(1s) \quad - \quad B^2(sp^3)$

each containing two electrons.

The tetramer can thus be drawn



The properties of this compound are more likely to be those of a typical covalent complex than those expected from the other formulation.

The n.m.r. spectra of the complex were recorded in benzene solution. The ^{11}B spectrum consists of a broad singlet 234 c.p.s. upfield from a trimethylborate external reference. The high quadrupole moment of ^{23}Na probably prevents the formation of the expected doublet by eliminating coupling between the boron and hydrogen. A rapid exchange of the methyl-boron protons with a small amount of free trimethyl boron would also eliminate the B-H coupling.

$$NaBMe_3H + BMe_3 \rightleftharpoons NaBMe_3H + BMe_3$$

This has been observed for sodium triethylboron hydride where the ^{11}B spectrum was initially a singlet which became a doublet with the same chemical shift on standing over sodium hydride for several months.[216]

The p.m.r. spectrum of the complex contains a single resonance at 10·30τ which is assigned to the B-CH_3 group. No coupling is observed between the boron and methyl groups. There is no tetrahedral symmetry about the boron in the BMe_3H so a large effective field gradient is experienced by the central atom and the quadrupole relaxation time of the nuclear spin is large. Thus scalar coupling between the boron and methyl protons is eliminated.

Reactions between sodium trialkylboron hydrides and magnesium dialkyls.

Diethylmagnesium and sodium triethylboron hydride react at 0°C precipitating a solid which has the empirical formula $Mg_1H_{1\cdot45}Et_{0\cdot55}$ while the soluble material contains only a small amount of hydrolysable hydrogen. The analysis figures are inconclusive in that the liberation of ethane on hydrolysis of a sample of the solution is slow even on addition of acid and does not seem to be complete even after an hour. This is consistent with the production of sodium tetraethylboron which is only slowly hydrolysed even by dilute acids.[210]

At low temperatures and in the presence of the chelating diamine N,N,N',N'-tetramethylethylenediamine no precipitation occurs. The solutions in the absence of the amine have a hydrolysable hydrogen: hydrolysable ethyl (H_2O) ratio of 1:1. Addition of acid slowly releases more ethane.

These results indicate that sodium tetraethylboron is present even at low temperatures. The results are inconclusive in that the exchange reaction may take place during transfer of the sample for analysis as it is not possible to ensure that a low temperature is maintained during the sampling process. The overall reaction at room temperature is, however, almost certainly

$$2Et_2Mg \quad + \quad 2NaBEt_3H \longrightarrow MgH_2\downarrow \quad + \quad Et_2Mg \quad + \quad NaBEt_4$$

The precipitated material contains a considerable amount of ethyl groups attached to the magnesium. The evidence for an intermediate ethylmagnesium hydride, EtMgH, is based on the fact that no precipitation occurs at low temperatures as the analytical data show, with the reservations made above, that exchange is complete at -78°,

$$NaBEt_3H \quad + \quad Et_2Mg \longrightarrow NaBEt_4 \quad + \quad \text{'EtMgH'}.$$

Sodium trimethylboron hydride and dimethylmagnesium react just below room temperature precipitating a white solid, with the empirical formula $MgH_{1.9}Me_{0.1}$, and leaving dimethylmagnesium and sodium tetramethylboron only in solution. The two latter compounds were identified by their p.m.r. spectra.

The reaction was followed by n.m.r. at variable temperatures by comparing the intensity ratios of the $B-CH_3$ and $Mg-CH_3$ peaks. At -78° the spectrum consists of two single peaks assigned to the $B-CH_3$ and $Mg-CH_3$ resonances. It is not possible to assign the $B-CH_3$ peak to a single species i.e. either $NaBMe_3H$ or $NaBMe_4$ as it has recently been shown that the spectrum of $NaBMe_4$, which is a complex peak at room temperature, collapses to a singlet at low temperatures (-50°).[215] The ratio of $B-CH_3$ to $MgCH_3$ resonances should be 1·5:1 in the absence of exchange and 4:1 if total exchange has taken place.

At -78° the $B-CH_3$:$Mg-CH_3$ ratio is 2:1 and remains at this value until the temperature rises to -10° when the value becomes 3·14:1 (from 2·33:1 at -20°). At 0° the ratio is 5:1. Precipitation begins to occur at -20° and is significant above this temperature.

The results show that as soon as exchange occurs a precipitate is formed and provides no evidence for the formation of an intermediate ethylmagnesium hydride stable at low temperatures. If this species does exist then its lifetime, with respect to disproportionation into dimethylmagnesium and magnesium hydride, must be short.

Addition of N,N,N',N'-tetramethylethylenediamine to a 1:1 mixture of sodium trimethylboron hydride and dimethylmagnesium prevents the formation of magnesium hydride. In this case, however, the coordination complex of dimethylmagnesium with N,N,N',N'-tetramethylethylenediamine is isolated. Thus the amine must completely inhibit the alkyl/hydrido exchange in the system.

Reaction between sodium triakylboron hydrides and alkylmagnesium halides.

Sodium chloride is immediately precipitated on adding sodium triethylboron hydride to ethylmagnesium chloride in 1:1 proportions.

Analysis of a sample of the filtered solution shows that the ratio, hydrolysable ethyl (H_2O):hydrolysable hydrogen is 0·85:1. Addition of acid releases more ethane bringing the hydrolysable ethyl (total): hydrolysable hydrogen up to 1:0·98. The p.m.r. spectrum of the solution contains only two sets of resonances centred at 9·19 and 9·60 τ assigned to the B-CH_2-CH_3 and B-CH_2 groups respectively. No peak due to the Mg-CH_2 resonance (expected above 10·0) is present.

The initial reaction must be

$$NaBEt_3H \quad + \quad EtMgCl \quad \longrightarrow \quad NaCl\downarrow \quad + \quad EtMgBEt_3H$$

The nature of the magnesium containing species in solution is open to speculation. The properties on hydrolysis, slow evolution of the hydrolysable ethyl and the p.m.r. spectrum which contains no readily identifiable Mg-CH_2 resonance indicate the possibility of the equilibrium,

$$EtMgBEt_3H \quad \rightleftharpoons \quad HMgBEt_4$$

with the equilibrium well over to the right.

The BEt_4 group would only release all the hydrolysable ethyl on addition of acid and the $HMgBEt_4$ species would show no Mg-CH_2 resonance. The infrared spectrum of the liquid, ether-containing product, obtained on removal of most of the solvent contains an absorption at 1887 cm^{-1} which is similar to that in sodium triethylboron hydride. As the position of the Mg-H absorption is unknown it is not possible to draw any certain conclusions about the species present, from this evidence.

When a sample, obtained from the solution, is maintained at 0·005 mm/Hg for 20 hours the hydrolysable ethyl (acid):magnesium: hydrolysable hydrogen ratio remains at 1:1:1 but about 25% of the boron is removed, presumably as triethylboron. Addition of trimethylamine and heating to 110° leaves a white solid which on extraction with benzene gives a solution with a hydrolysable ethyl: magnesium ratio of 2:1. The solution contains both boron and diethyl ether.

The reaction between sodium trimethylboron hydride and methylmagnesium bromide was investigated in the hope that trimethylboron would be easier to remove than the triethylboron in the experiment just discussed.

Addition of the two reactants immediately produces a precipitate of sodium bromide and the filtered solution has a hydrolysable methyl (acid):magnesium:hydrolysable hydrogen ratio which is effectively 1:1:1. Once again the presence of acid is necessary to release all the hydrolysable methyl.

Addition of trimethylamine to the solution gives a grey precipitate which has the empirical formula $MgH_{1\cdot76}Me_{0\cdot25}$ and leaves dimethylmagnesium in solution. The solid obtained on removal of the solvent contains some boron but this is easily removed *in vacuo* leaving dimethylmagnesium.

Trimethylamine forms a weak coordination complex with boron alkyls and facilitates removal of the boron from the solution

$$\text{'MeMgBMe}_3\text{H'} \quad + \quad \text{NMe}_3 \quad \longrightarrow \quad \text{'MeMgH'} \quad + \quad \text{BMe}_3.\text{NMe}_3$$

If methylmagnesium hydride is produced it undergoes immediate disproportionation to magnesium hydride and dimethylmagnesium.

Pyrolysis of isopropylmagnesium compounds.

Pyrolysis of branched chain magnesium alkyls and of diethylmagnesium is a well known route to magnesium hydride. It was hoped that it would be possible to stop the pyrolysis at the half way point leaving an alkylmagnesium hydride.

The presence of any organic material, other than alkyl groups attached to magnesium, raises the temperature required for pyrolysis and results in the formation of large amounts of the saturated alkane. Thus the pyrolysis of di-isopropylmagnesium containing some ether produces a gas containing 18% propane and results in the sublimation of a white solid which is probably an ether cleavage product cf. ethylmagnesium ethoxide which is produced on the pyrolysis of diethylmagnesium containing some ether. Pyrolysis of [2-dimethylaminoethyl-(methyl)amino]isopropylmagnesium at 130° gave no propene, only propane being produced.

Pyrolysis of ether-free di-isopropylmagnesium produces a gas containing 93·4% propene, 5·2% propane and a little ethane and leaves a sticky solid. Extraction of this solid with ether gives a solution containing di-isopropylmagnesium and leaves magnesium hydride as the insoluble material.

Summary.

The experiments discussed show that magnesium dialkyls show no tendency to form complexes with alkali metal hydrides and that systems in which the formation of an alkylmagnesium hydride is possible result only in the disproportionation products, magnesium hydride and magnesium dialkyls. The tendency for complex equilibria to exist in some organomagnesium compoundsof the type RMgX is well known (witness the Grignard controversy). Thus if an alkylmagnesium hydride is formed in solution and the equilibrium between the various possible species e.g.,

$$2RMgH \rightleftharpoons \text{'}MgH_2\text{'}(sol) + MgR_2$$

is liable, then the complete insolubility of magnesium hydride in ether will result in the equilibrium being forced completely over to the right.

This situation could be taking place in the following systems, a) $KH + EtMgBr$ in Et_2O, b) $NaBR_3H + R_2Mg$ in Et_2O, c) $RMgX + NaBR_3H + NMe_3$ in Et_2O and d) on extraction of the pyrolysis product of $Pr^i{}_2Mg$ with ether.

TABLE 1.

Degree of Association of Grignard reagents (RMgX) in solution.

R	X	Conc. moles/l	Degree of Assocn.	Solvent	Reference
Me	I	0·037	1·09	Ether	49
Me	I	0·245	1·59	Ether	49
Et	Cl	0·086	1·87	Ether	49
Et	Cl	0·196	1·92	Ether	49
Et	Cl	2·5	2·7	Ether	87 *
Et	Br	10^{-2}–10^{-3}	1·01	Ether	40
Et	Br	0·035	1·00	Ether	49
Et	Br	0·249	1·37	Ether	49
Et	Br	2·2	2·7	Ether	87 *
Et	I	0·055	1·00	Ether	49
Et	I	0·204	1·36	Ether	49
Et	I	2·5	2·5	Ether	87 *
Pr^i	Cl	0·042	1·85	Ether	49
Pr^i	Cl	0·260	2·02	Ether	49
Cyclohexyl	Br	0·324	2·05	Ether	48
Ph	Br	0·042	1·07	Ether	49
Ph	Br	0·326	1·71	Ether	49
Ph	Br	0·331	1·67	Ether	48
Ph	Br	1·1	3·2	Ether	87 *
p-tolyl	Br	0·566	1·65	Ether	48
Mesityl	Br	0·059	1·06	Ether	49
Mesityl	Br	0·275	1·77	Ether	49
Bu^t	Cl	0·1	1·9	Ether	87 *
Bu^t	Cl	2·0	2·1	Ether	87 *

TABLE 1. (contd.)

R	X	Conc. moles/l	Degree of Assocn.	Solvent	Reference
Et	Cl	0·1-0·3	1·01	THF	41
Et	Br	10^{-2}-10^{-3}	1·01	THF	44
Et	Br	0·1-0·3	1·04	THF	41
Et	Br	0·7	1·05	THF	87 *

* Numerical values taken from graph.

TABLE 2.

Compounds produced from reaction R$_2$Be + R'$_2$NH.

Compound	State (at R.T.)	Solvent	Conc.	Degree of Association
MeBeNMe$_2$ [160]	Glass	Benzene	0·37,0·75	3
EtBeNMe$_2$ [148]	Liquid	Benzene	0·37,0·75	3
Pr^{i}BeNMe$_2$ [148]	Liquid	Benzene	0·76,1·07	3
PhBeNMe$_2$ [91]	Solid	Benzene	0·74,1·49	3
MeBeNEt$_2$ [148]	Liquid	Benzene	0·51,1·02	3
EtBeNEt$_2$ [148]	Liquid	Benzene	0·49,0·98	2
MeBeNPh$_2$ [148]	Solid	Benzene	1·37,2·06, 4·12	2
EtBeNPh$_2$ [148]	Solid	Benzene	0·76,1·53	2
PhBeNPh$_2$ [91]	Solid	Benzene	0·85,1·69	2
MeBeNPr$^n{}_2$ [148]	Liquid	Benzene	0·97,1·08	2
MeBeNPhBz [161]	Liquid	Benzene	0·99,1·48	2
Bu^{t}BeN(Me)(CH$_2$)$_2$NMe$_2$ [148]	Liquid	Benzene	0·97,1·29 1·93	1
PhBeN(Me)(CH$_2$)$_2$NMe$_2$ [91]	Solid	Benzene	0·69,1·38	2

TABLE 3.

Pyridine and bipyridyl adducts of aminoberyllium alkyls. [148]

Compound	State (at R.T.)	Solvent	Concn.	Degree of Association
Me(py)BeNMe$_2$	Solid	C_6H_6	0·303,0·606	2
Me(py)$_2$BeNMe$_2$	Solid	C_6H_6	0·71,0·76	1
Me(py)BeNPh$_2$	Solid	-	-	-
Me(py)$_2$BeNPh$_2$	Solid	C_6H_6	0·58	1
Et(py)$_2$BeNPh$_2$	Solid	C_6H_6	0·52,1·04	1
Me(bipy)BeNPh$_2$	Solid	-	-	-
Et(bipy)BeNPh$_2$	Solid	C_6H_6	0·35,0·69	1

TABLE 4.

Amine	Product	Temp. of elimination of alkyl groups	
		1	2
$HN(Me)CH_2CH_2NMe_2$ [90]	$(MeBeN(Me)CH_2CH_2NMe_2)_2$	20°C	-
$H_2NCH_2CH_2NMe_2$ [90]	$(MeBeHNCH_2CH_2NMe_2)_2$	20°C	
	$(BeN(CH_2)_2NMe_2)_n$		170°C
$HN(Me)(CH_2)_2NHMe$ [90]	$(MeBeN(Me)(CH_2)_2NHMe)_2$	>0°C	
	$(BeN(Me)(CH_2)_2NMe)_x$		150°C
$H_2NCH_2CH_2NH_2$ [90]	Polymeric product	45°C	45°C

TABLE 5.

Organoberyllium alkoxides

Compound	State (at R.T.)	Solvent	Concn.	Degree of Association
MeBeOMe	Solid	C_6H_6	0·49,0·99	4
MeBeOEt	Solid	C_6H_6	0·31,0·47 0·94	4
$MeBeOPr^n$	Solid	C_6H_6	0·64,1·28	4
$MeBeOPr^i$	Solid	C_6H_6	0·30,0·60	4
$MeBeOBu^t$	Solid	$C_6H_6(Et_2O)$	0·43,0·86	4 (3·8)
$MeBeOCH_2Ph$	Solid	C_6H_6	0·78,1·28	4
$MeBeOCHPh_2$	Solid	C_6H_6	0·87,1·73	2
$MeBeOCPh_3$	Solid	C_6H_6	0·54,1·08	2
$EtBeOCEt_3$	Liquid	C_6H_6	0·45,0·90	3
Pr^iBeOMe	Solid	C_6H_6	0·49,0·97	4
Bu^tBeOMe	Solid	C_6H_6	0·35,0·70	4
Bu^tBeOBu^t	Solid	C_6H_6	0·49,0·98 1·36	2
PhBeOMe	Solid	C_6H_6	0·93,1·85	4
$MeBeO(CH_2)_2OMe$	Solid	C_6H_6	0·42,0·85	4

TABLE 6.

Coordination compounds of alkylberyllium alkoxides.

Compound	State (at R.T.)	Solvent	Concn.	Degree of Association
$MeBeOCHPh_2.OEt_2$	Solid	C_6H_6	0·38,0·86	1
$MeBeOCHPh_2.THF$	Solid	C_6H_6	0·40,0·57	1
$MeBeOCPh_3.OEt_2$	Solid	C_6H_6	1·15,1·50	1
$PhBeOMe.OEt_2$				
$MeBeOPh.OEt_2$	Solid	C_6H_6	0·59,1·19	1·21,1·41
$Me(MeO)Bepy_2$	Solid	C_6H_6	0·61,1·21	1
$Me(Bu^tO)Bepy$	Solid	C_6H_6	0·35,0·70	1·23,1·41

TABLE 7.

Compound	State (at R.T.)	Solvent	Concn.	Degree of Association
$Be(OC_6H_4X)_2$ [167] X=H,OH,Cl,Me,NO_2	Solid	-	-	Polymeric
$Be(OBu^t)_2$ [96]	Solid	C_6H_6	0·53,1·06	3
$Be(OMe)_2$ [96]	Solid	-	-	Polymeric
$Be(OCEt_3)_2$ [96]	Solid	C_6H_6	0·36,0·72	2
$Be(OCH_2CH_2OCH_3)_2$ [165]	Solid	-	-	Polymeric
$Be(OCH_2CH_2N(CH_3)_2)_2$ [165]	Solid	C_6H_6	0·99,1·32 1·97	8 - 11

TABLE 8.

Amino zinc alkyls.

Compound	State (at R.T.)	Solvent	Concn.	Degree of Association
$MeZnNPh_2$	Solid	C_6H_6	0·74,1·48	2
$EtZnNPh_2$	Solid	C_6H_6	1·5, 1·79	2
Pr^iZnNPh_2	Solid	C_6H_6	-	2
Bu^nZnNPh_2	Solid	C_6H_6	-	2
$PhZnNPh_2$	Solid	C_6H_6	-	2
$EtZnNEt_2$	Liquid	C_6H_6	-	2
$MeZnNPh_2py_2$	Solid	C_6H_6	1·26,1·58 1·66	1
$MeZnN(Me)(CH_2)_2NMe_2$	Solid	C_6H_6	1·22,2·43	2

TABLE 9.

Compound	State (at R.T.)	Solvent	Concn.	Degree of Association
MeZnOMe	Solid	C_6H_6	1·12,1·69	4
$MeZnOBu^t$	Solid	C_6H_6	1·71,2·43	4 (concn. dependant)
$EtZnOBu^t$	Solid	C_6H_6	1·43,2·86	4
Bu^tZnOBu^t	Solid	C_6H_6		2
$EtZnOPr^i$	Solid	C_6H_6	1·51,2·26	4
MeZnOPh	Solid	C_6H_6	1·77,3·05	4
MepyZnOPh	Solid	C_6H_6	1·10,1·11 1·34	2
$EtZnOCHPh_2$	Solid	C_6H_6	2·15,3·08	3
$PhZnOCPh_3$	Solid	C_6H_6	2·98,4·18	2
$MeZnO(CH_2)_2NMe_2$	Solid	C_6H_6	1·14,1·60	3
$EtZnO(CH_2)_2NMe_2$	Solid	C_6H_6	1·98,2·24	3
$MeZnO(CH_2)_2OCH_3$	Liquid	C_6H_6	1·83,2·29	4

TABLE 10.

Compound	State (at R.T.)	Solvent	Concn.	Degree of Association
$MeZnSMe$	Solid	-	-	Polymer
$MeZnSPr^n$	Solid	-	-	Polymer
$MeZnSPh$	Solid	-	-	Polymer
$MeZnSPr^i$	Solid	C_6H_6	1·66,1·97, 2·03,2·49	6
$MeZnSBu^t$	Solid	C_6H_6	2·49,3·05 3·47	5
$EtZnSBu^t$	Solid	C_6H_6	2·67,3·64	5
$MepyZnSBu^t$	Solid	C_6H_6	0·87,1·75	2

TABLE 11.

Alkylcadmium alkoxides.

Compound	State (at R.T.)	Solvent	Concn.	Degree of Association
MeCdOMe	Solid	-	-	4
MeCdOEt	Solid	C_6H_6	1·67, 1·95, 2·33	4·3
$MeCdOPr^i$	Solid	C_6H_6	1·27, 1·57, 1·83	4
$MeCdOBu^t$	Solid	C_6H_6	1·95, 1·74, 1·08, 0·74	2
MeCdOPh	Solid	C_6H_6	1·66, 1·93, 2·31, 2·87, 3·78	3·38-4
MepyCdOPh	Solid	C_6H_6	2·15, 4·13	1·40-1·52

TABLE 12.

Compound	State (at R.T.)	Solvent	Concn.	Degree of Association
MeCdSMe	Solid	-	-	Polymeric
$MeCdSPr^i$	Solid	C_6H_6	3·75,4·33, 5·11,6·24	6
$MeCdSBu^t$	Solid	C_6H_6	2·23,2·63, 2·92	4
MeCdSPh	Solid	-	-	Polymeric

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