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COMPLEXES OF UNSATURATED AND OTHER ORGANOBERYLLIUM COMPOUNDS

BY

B. R. FRANCIS, B.Sc.

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

JANUARY 1970

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Memorandum

The work described in this thesis was carried out in the University of Durham between September 1966 and August 1968, and in the University of Wyoming between August 1968 and January 1970. The work is the original work of the author except where acknowledged by reference.

Summary

A number of 2:1 complexes of diphenylethynylberyllium and dimethylethynylberyllium with monodentate ligands are described. The bis-tetrahydrofuran complexes are monomeric in benzene solution. Primary and secondary amines give 2:1 complexes in addition to tertiary amines. Several 1:1 complexes with monodentate and bi-dentate ligands have also been prepared. Diphenylethynylberyllium diethyl etherate is slightly associated in benzene, the association being thought to involve phenylethynyl bridges.

Uncomplexed dimethylethynylberyllium is a solid, insoluble in benzene and extremely reactive towards hydrolysis. A polymeric electron-deficient structure is proposed for the compound.

Reactions of diphenylethynylberyllium complexes with alcohols and thiols have given the following compounds, $PhC{\equiv}CBeOBu^t,THF$, $PhC{\equiv}CBeOPh,THF$, $PhC{\equiv}CBeOBu^t$, $(PhC{\equiv}C)_2Be_3(OBu^t)_4$ and $(PhC{\equiv}CBeSBu^t,THF)_2$. The first two compounds are slightly associated in benzene, while the third is an insoluble, presumably polymeric, solid with a remarkable stability towards hydrolysis.

The coordination complexes Me_2Be,NEt_3 , $(benzyl)_2Be,OEt_2$, (*neo*-pentyl (*neo*-pentyl)$_2$Be,OEt_2 , (*neo*-pentyl)$_2$Be,NMe_3 , (*neo*-pentyl)$_2$Be,TMED , and *neo*-pentyl(methyl)Be,TMED are all monomeric in benzene solution. Variable temperature p.m.r. studies establish the existence of *neo*-pentyl(methyl)Be,TMED in solution rather than a mixture of Me_2Be,TMED and (*neo*-pentyl)$_2$Be,TMED. Evidence is presented for the following equilibrium in solution,

$$Me_2Be,NMe_3 \quad + \quad (\underline{neo}\text{-pentyl})_2Be,NMe_3 \rightleftharpoons \quad 2MeBe\underline{neo}\text{-pentyl},NMe_3$$

and an equilibrium constant of 170 at -40° is calculated.

EtBeBr,TMED and *neo*-pentylBeBr,TMED are monomeric in benzene, but EtBeCl,TMED is slightly disproportionated. The bromides have temperature

dependent p.m.r. spectra. Addition of NMe_3 to *neo*-pentylBeBr,etherate causes quantitative disproportionation, whereas addition to *neo*-pentylBeCl,etherate gives partial disproportionation.

The trimer, $(Bu^iBeOBu^i)_3$, is described and a complex of it, $(i\text{-}BuBeOBu^i)_2$, TMED, has been crystallised. This latter compound and $(\textit{neo}\text{-pentylBeH})_2$,TMED are believed to contain the TMED acting as a bridge between the beryllium atoms.

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Abbreviations

The following abbreviations have been used during this thesis:

M = metal atom, of group I unless otherwise specified.

L = D = monodentate ligand.

R = organic or alkyl group.

THF = tetrahydrofuran.

en = ethylenediamine.

TMED = N,N,N',N'-tetramethylethylenediamine.

TEED = N,N,N',N'-tetraethylethylenediamine.

py = pyridine.

bipy = bipyridyl.

DME = 1,2-dimethoxyethane.

X = halogen.

glyme = ethyleneglycol dimethylether.

Francis

Introduction

Although the organometallic chemistry of beryllium has not received as much attention as that of many other metals, it has shared in the rapid growth of organometallic chemistry and is now beyond the stage where an introduction could reasonably include a detailed review even if such a review were necessary. Hence there follows a brief survey of those aspects of organometallic chemistry which have direct relevance to the author's own work. Even so, to keep the thesis to a reasonable length many preparative details have had to be omitted. Recent literature articles and past theses provide an adequate source for those experimental techniques and synthetic methods which are not covered here.[1,2,3,4,5,6]

Valency, Coordination Number and Stereochemistry

Beryllium has an electron configuration $1s^2 2s^2$. The 2s electrons feel a strong nuclear charge with the result that the beryllium atom has high first and second ionisation potentials and small size. The ionisation potentials are sufficiently high that the formation of Be^{2+} ions is prevented and all beryllium compounds have bonds to beryllium which have a significant degree of covalent character.

In its covalent bonding beryllium might be expected to use *sp* hybridised orbitals and hence form linear molecules containing two-coordinate beryllium. Indeed some examples of this are known but most beryllium compounds have the atom making use of all its valence 2*s* and 2*p* orbitals in a four-coordinate state. A few compounds are also known where the beryllium is three-coordinate and uses only three valence orbitals for bonding. In view of the great tendency to involve all four valence orbitals in bonding, two- and three-coordinate beryllium atoms are thought of as coordinatively unsaturated.

As would be expected if hybridised *s* and *p* orbitals are used for bonding, the approximate stereochemistries are, four-coordinate, tetrahedral, three-coordinate, planar trigonal, and two-coordinate, linear, at least in those compounds so far investigated.

The increase in coordination number above two may be achieved by a number of ways including, the formation of donor-acceptor complexes, the formation of oligomers and polymers, and the formation of electron-deficient bridges. This last method has so far been observed only in the organic and hydride derivatives of beryllium. In some cases, for which Me_2Be is a good example, polymerisation by formation of coordinate bonds as in the case of $BeCl_2$ is not possible since carbon and hydrogen do not possess lone pairs of electrons. Nevertheless, polymerisation does take place and it does so by the formation of three-centre, two-electron bonds involving $\underline{sp}^3$ hybridised orbitals of beryllium and 1s orbitals of hydrogen or $\underline{sp}^3$ hybridised orbitals of carbon.

The next member of group II, magnesium is considerably more electropositive (1.23) than beryllium (1.47) and has much greater size. As a result magnesium forms ionic as well as covalent compounds. The covalent compounds have very polar bonds and indeed some compounds may be considered as ionic or covalent, e.g. $Mg(OMe)_2$, $Mg(NMe_2)_2$. In the ionic solvates, such as $Mg(OH_2)_6^{2+}.2Cl^-$, the coordination number of magnesium is six and in other compounds, e.g. $MgCl_2(THF)_4$, it is also six. It is rare to find coordination numbers greater than four for the more covalent compounds like the Grignard reagents, but it is also rare to find magnesium less than four-coordinate. Many of the covalent magnesium compounds exist as polymers where the beryllium and zinc compounds are less associated. This may well be because of increased lattice energy for the solid magnesium compounds through magnesium increasing its coordination number above four.

The elements of group IIA show an increasing electropositive character and form essentially ionic compounds even with organic groups. In contrast the elements of group IIB have an increasing electronegativity and a decreasing tendency to increase their coordination numbers above two. Beryllium and zinc have similar electronegativities (1·47 and 1·66Å), but zinc is considerably larger. Their organometallic chemistries have much in common except for the much greater ability of beryllium to form electron-deficient bonds.

Steric effects

An important consequence of the small size of the beryllium atom (covalent radius 0·90Å) is the increased prominence of steric effects of groups attached to beryllium compared with those attached to magnesium (1·30Å) or zinc (1·31Å). The influence of steric effects may be seen in both structural and reactivity terms, where lower degrees of association or reduced reaction rates are observed. These effects are exemplified by the properties and reactions of di-t-butylberyllium.

Disproportionation

The disproportionation reaction is an important feature of group II organometallic chemistry. It is a redistribution reaction (1), in which symmetrical species are produced from unsymmetrical species, as when the equilibrium moves from right to left below.

$$R_2M + MA_2 \rightleftharpoons 2\ RMA \qquad (1)$$

M=Be, Mg, Zn. A=X, OR', SR', NR'_2, H, R'

Although disproportionation is not predictable it appears to be particularly important when a.) insoluble products can be formed, and b.) very stable coordination complexes can be formed. With the exception of the thiometalalkyls, disproportionation reactions to form uncomplexed metal dialkyls or diaryls are quite rare. Some examples are shown below:

$$EtMgNMe_2 \longrightarrow Et_2Mg + Mg(NMe_2)_2 \qquad (2)^7$$

$$MeZnNMe_2 \longrightarrow Me_2Zn + Zn(NMe_2)_2 \qquad (3)^8$$

$$(MeZnOMe)_4 \rightleftharpoons Me_2Zn + Me_6Zn_7(OMe)_8 \qquad (4)^9$$

Degree of Association

The strong driving force for beryllium compounds to increase their coordination number above two was mentioned earlier. One of the most common methods of achieving this is through association of monomer units to oligomers or polymers. This process is particularly noticeable for the organoberyllium compounds RBeA, where A = NR', OR', or SR', (and will be for A = PR'_2, X, when they are prepared). Similar compounds of many other group II and group III metals show comparable tendencies to associate. 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.

The following three factors appear to be most significant in determining the degree of association of compounds RMA (M = group II metal, A = alkoxide, amide, sulphide, phosphide, halide), (5)

$$nRMA \rightleftharpoons (RMA)_n \quad \Delta G = \Delta H - T.\Delta S \qquad (5)$$

a.) Entropy will favour the formation of small units since these will contribute the greatest translational entropy per mole of monomer and hence make S more positive. So dimers will be favoured over higher degrees of association.

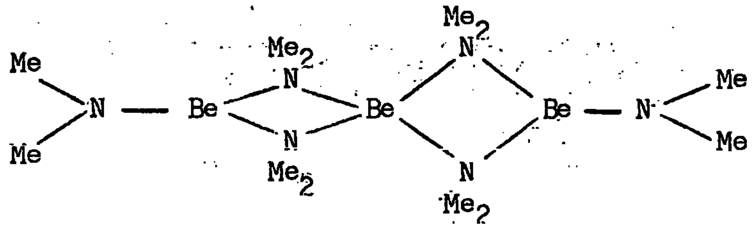
b.) That degree of association will be favoured which requires least valence angle strain. In a dimer the average angle must be 90°, but puckered ring trimers could be relatively strainless. In this case trimers will be preferred over other degrees of association. Ring strain should be more easily tolerated by the heavier elements.

c.) Steric interaction between groups in RMA increase as the ring size increases, so it is to be expected that as the volume of R and A increases dimers will become the favoured species.

π- Bonding

The importance of π-bonding in boron-nitrogen and boron-oxygen chemistry is well documented and has been demonstrated by n.m.r. studies which have measured the barrier to rotation about the B-N bonds of RR'B-MR"R" (10-20 kcals/mol)[10] and RR'B-OR" (8·5 kcals/mol).[11] Boron-carbon π-bonding is found in the heteroaromatic boron compounds such as the borazaronaphthalenes and a recent n.m.r. study of phenyl(vinyl)dimethylaminoborane suggests restricted rotation about both the B-N and the $B\text{-}C_{vinyl}$ bonds so that only one isomer is present in solution.[10]

On the other hand, the importance of π-bonding from beryllium to nitrogen, oxygen or carbon is still not understood. An X-ray diffraction determination of the structure of the bis-dimethylaminoberyllium trimer, (I), found that a.) the terminal Be-N distance (1·57Å) was considerably shorter than those of the four-membered ring (1·65 and 1·78Å) and b.) the terminal nitrogen was coplanar with the two carbon atoms and the beryllium atom to which it is bound. This was taken as evidence of Be-N π-bonding.[12] Any compound containing three-coordinate beryllium bonded to nitrogen or oxygen with a lone pair of electrons or to an unsaturated carbon atom has the possibility of π-bonding. N.m.r. experiments of the type used for boron are likely to provide more definitive evidence.



(I)

Dialkyl- and diaryl-metal compounds of Group II

The dialkyl- and diaryl- derivatives of Be, Mg, Zn, Cd, and Hg have two-coordinate metal atoms. Association through electron-deficient bonding can increase the coordination number and this takes place for the beryllium and magnesium compounds giving dimers and polymers, but does not for the remaining elements. Formation of coordination complexes with bases also increases the coordination number of the metal. It is seen that the acceptor strength of the R_2M compounds decreases as the electronegativity of the metal increases:

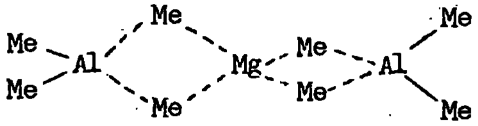
$$R_2Be < R_2Mg > R_2Zn > R_2Cd > R_2Hg.$$

Studies show that these compounds behave as hard acids or class A acceptors towards bases, so that in general nitrogen and oxygen bases form stronger complexes than phosphorus, arsenic or sulphur bases. Mercury compounds are exceptional in forming stronger complexes with phosphines than with amines.

Beryllium and Magnesium

Dimethylberyllium and dimethyl- and diethyl-magnesium have been shown to have polymeric chain structures consisting of straight lines of metal atoms with tetrahedrally disposed alkyl groups.[13,14] The metal-carbon distances indicate that the M-C bond order is less than one, as is expected for electron deficient bonding. All other dialkyls of beryllium studied so far are liquids and are dimeric in solution with the exception of $t\text{-}Bu_2Be$ which is monomeric in solution and in the gas phase. The decrease in association of these compounds is attributed mainly to steric effects caused by the small size of the beryllium atom.[15] A complete infrared, Raman and electron diffraction study of $t\text{-}Bu_2Be$ has shown the molecule to be linear.[16] Magnesium being substantially larger and more electropositive, it forms strong electron deficient bonds for a number of different alkyl groups and hence tends to form polymeric compounds. Steric effects become important for di-n-amylmagnesium and di-s-butylmagnesium.[17,18] These compounds show an increased solubility in hydrocarbon solvents and are dimeric in solution. Both Me_2Mg and $i\text{-}Bu_2Mg$ are insoluble in hydrocarbons but dissolve in solutions containing $s\text{-}Bu_2Mg$. However, the compositions of the species in solution were not investigated. Dimethylmagnesium and dimethylberyllium dissolve in trimethylaluminium to give species $Mg(AlMe_4)_2$ and $Be(AlMe_4)_2$. The magnesium compound may be isolated and an X-ray analysis shows it has structure (II)[19].

Both diphenylberyllium and diphenylmagnesium have low solubilities in hydrocarbon solvents and are presumably electron-deficient polymers.

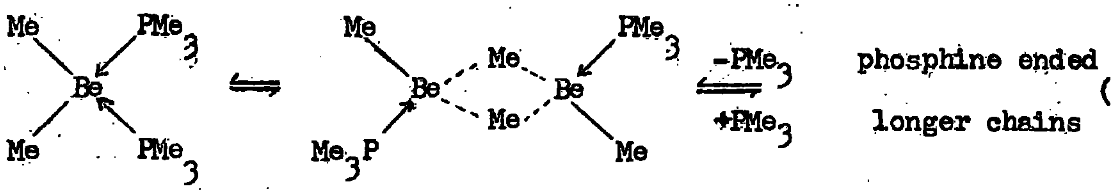


(II)

The coordination chemistries of R_2Be and R_2Mg compounds are now relatively extensive. Formation of a complex will only take place when the coordinate bond formed is stronger than the electron deficient bonding of the polymer or dimer. Since magnesium alkyls have stronger bridge bond than the beryllium alkyls, coordination complexes of magnesium do not form as readily as those of beryllium. The diphenyl compounds have increased acceptor character compared with the dialkyl compounds due to the electron-withdrawing phenyl groups. This shows itself in the greater stability of $Ph_2Be,2L$ compared with say, $Et_2Be,2L$.

Trimethylamine is absorbed reversibly by Me_2Mg but no stoichiometric complex is obtained.[20] This contrasts with the beryllium dialkyls and diaryls which form stable 1:1 complexes R_2Be,NMe_3 and less stable 1:2 complexes $R_2Be(NMe_3)_2$.[21,22,23] For steric reasons i-Pr_2Be and t-Bu_2Be only form 1:1 complexes with NMe_3.[24,25] The 1:1 complexes are monomeric in the vapour phase and in solution and so contain three-coordinate beryllium. Pyridine, a stronger base, forms 1:2 complexes with a number of dialkyls (R = Me, Et,[26] Pr^i, Bu^t,[27] Bu^i [28]) which are coloured.

Trimethylphosphine is a weaker base than trimethylamine to beryllium and forms a coordinate bond of comparable strength to the electron deficient methyl bridge bond so that the following equilibrium is set up,



(6)

The only firmly established phosphine complexes are *t*-Bu_2BePMe_3[15] and $Ph_2Be(PMe_3)_2$[21], the latter being slightly dissociated in benzene.

The etherates Et_2Mg,OEt_2 and $Ph_2Mg,2OEt_2$ are reported to crystallise from ether solution[30,31] and Me_2Mg crystallises ether-free[32]. Molecular weight measurements show that Et_2Mg and particularly Me_2Mg retain some association in diethylether[33]. Although organo-beryllium compounds including Me_2Be are soluble in diethylether the only etherate isolated so far is $Ph_2Be,2OEt_2$ and this has a considerable dissociation pressure of ether so that the 1:1 complex is obtained on pumping[21]. The ether cannot be completely removed from the dialkyls by pumping, but it may be removed by refluxing under high vacuum. Dimethylether and dimethylsulphide appear to act towards Me_2Be in a similar way to PMe_3.[29,34] Towards Ph_2Be they react to give 1:2 complexes. Measurement of the heat of dissociation in the system

$$Ph_2Be,L_2 \rightleftharpoons Ph_2Be,L + L \qquad (7)$$

have indicated an order $O > N > S > P$.[35] This contrasts with the order normally found for class A acceptors such as Me_3Al, *viz*, $N > P > O > S$, and is probably the result of increased importance of steric interactions in the 1:2 complexes. An earlier study of the heats of coordination of donors to Me_2Be indicated an order , $N > P > O > As, S$.[29]

Some of the most important chelating ligands are TMED, bipyridyl, 1,2-dimethoxyethane and dioxan. Complexes of these ligands with R_2Be or R_2Mg have always been found to be monomeric, and can normally br formulated with four-coordinate metal atoms.[21,26,36,37,22,38,39,40] However a low temperature n.m.r. study of *t*-Bu_2Be,TMED showed that only one dimethylamino group of TMED is coordinated to the beryllium and that complexed and free amino groups change places rapidly at room temperature.[15] While the bipyridyl adducts of R_2Mg decompose rapidly, those of R_2Be are stable and many of them are brightly coloured. Electron transfer from the Be-C bond into the lowest unoccupied molecular orbital of the heterocyclic system is thought to give rise to the colours. The absorption moves to the red for electron releasing groups and to the blue for electron attracting groups.[26]

Ionic complexes with magnesium or beryllium in the anion are known. From ether $LiMgPh_3$ and $LiBePh_3$, and from dioxan $LiMgPh_3,4C_4H_8O_2$ and $LiBePh_3,4C_4H_8O_2$, may be isolated from the reaction of PhLi with Ph_2Mg or Ph_2Be.[41] The base-free compounds may have polymeric structures like $LiAlEt_4$ rather than ionic structures. N.m.r. studies on $MeLi/Me_2Mg$ mixtures have shown the presence of Li_2MgMe_4 and Li_3MgMe_5 in ether solution but not the presence of $LiMgMe_3$.[42] Recently an X-ray diffraction study of Li_2BeMe_4 has found it to be ionic with a tetrahedral anion.[43] Diethylberyllium forms a series of salts $(MX)(BeEt_2)_n$ where M = Li, Na, K, Et_4N, X = halogen or cyanide and n = 1,2,3,4.[44] Complexes of R_2Be with alkali metal hydrides are discussed later.

Zinc, Cadmium and Mercury.

Zinc, cadmium and mercury dialkyls are volatile liquids, soluble in non-polar solvents and monomeric in solution and in the vapour phase. Their infrared and Raman spectra are consistent with a linear R - M - R structure and sp hybridised orbitals may be thought to be used by the metal. It is believed that formation of electron-deficient bridge bonds is prevented mainly because of the large metal-metal repulsions that would exist in an associated species. Diphenyl-, divinyl-, and dicyclopropyl-zinc are all apparently monomeric. Some mixed compounds R'ZnR and R'HgR have been prepared by the reaction of RLi or RMgX on the organometallic halides.[45,46,47,48] The zinc compounds slowly disproportionate to the symmetrical compounds (8), but for the mercury compounds an equilibrium mixture of symmetrical and unsymmetrical species is established containing annearly statistical distribution when the organic groups are not very different.

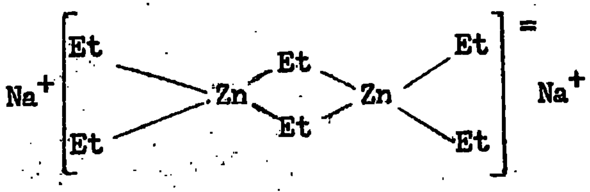
$$2RZnR' \longrightarrow R_2Zn + R'_2Zn \qquad (8)$$

The coordination chemistry of R_2Zn compounds is now an extensive subject. It resembles that of the corresponding beryllium compounds in many respects. With monodentate ligands the 1:2 complexes are often considerably dissociated into the more stable 1:1 complexes. Diphenylzinc forms more stable 1:2 complexes and forms more stable complexes with ligands of lower donor strength such as the phosphines. Chelating ligands, such as 1,2-dimethoxyethane, TMED, bipyridyl and 1,4-dioxan, as expected form very stable complexes and even chelating diphosphine and diarsine adducts have been isolated.[49]

Using a dielectric constant titration technique the stability of R_2Zn complexes with TMED and bipyridyl, is compared for various R groups. A decrease in order of stability for R_2Zn, TMED is found, Me>Et>i-Pr>t-Bu, but the decrease for R_2Zn, bipy is t-Bu>i-Pr>Et>Me. The change in order is attributed to the π-bonding ability of the bipyridyl ligand.[50]

Coordination complexes of dialkyl- and diaryl-cadmium compounds are much less stable towards dissociation than their zinc analogues, while the mercury compounds do not form complexes unless the organic groups are very electron withdrawing, e.g. C_6F_5-, CF_3-.

A number of anionic complexes of zinc have been reported. They generally fall into three types, $MZnR_3$, M_2ZnR_4 and M_3ZnMe_5. Those of the first type are probably electron-deficient polymers in the solid state but are thought to contain ions of the following type in solution,[51]



whereas those of the M_2ZnR_4 type are ionic in both phases. X-ray studies on Li_2ZnMe_4 show it to be a salt with the zinc tetrahedrally surrounded by methyl groups in the anion.[52] The last type has been shown to be present in ether solutions of MeLi and Me_2Zn by n.m.r. studies. It is believed to have the structure of the tetramer, $(MeLi)_4$, but with one MeLi replaced by Me_2Zn.[53]

Alkynyl- lithium, -sodium, and potassium compounds

Alkynyl-sodium and -potassium compounds, $RC{\equiv}CM$, may be prepared by the action of the metal on the 1-alkyne in liquid ammonia, ether, or tetrahydrofuran. Alkynyl derivatives of lithium are better made, however, from alkyl-lithium reagents. (8)

$$RLi + HC{\equiv}CR' \longrightarrow R'C{\equiv}CLi + RH \qquad (8)$$

These compounds must be regarded as essentially ionic, although there is no information concerning the structures of $RC{\equiv}CLi$ derivatives. The crystal structure of $LiC{\equiv}CLi$ is found to be ionic.[54] Recently lithium acetylides were shown to be the principal products of the reactions of lithium with some 1-alkenes, and of lithium with substituted vinylbromides in tetrahydrofuran.[55,56]

There is no definitive information about structures of the polylithiated acetylenes but they are thought to contain allene units of the type $Li_2C{=}C{=}CLi_2$. A lithium acetylide complex with ethylenediamine can be crystallised, $(LiC{\equiv}CH.\ en)$; its structure also remains unknown.[57,58]

Alkynyl derivatives of Group II

Uncomplexed compounds containing alkynyl-metal bonds are not known for beryllium and magnesium. Those of zinc and cadmium are electron-deficient polymers and those of mercury monomeric. A few complexes of $(RC{\equiv}C)_2M$ with amines have been reported for M = Be, Zn, Cd, while dialkynylmercury compounds do not form complexes.

In a report given a few years ago the complexes $(PhC{\equiv}C)_2Be.OEt_2$,

$[(PhC\equiv C)_2Be]_2$,bipy and $[(PhC\equiv C)_2Be]_2$,o-phenanthroline were thought to have been prepared. The mono-etherate was monomeric cryoscopically in benzene.[59]

Information on the structures of the $RC\equiv CMgX$ and $(RC\equiv C)_2Mg$ compounds whose preparation in donor solvents is described later (page 34) is restricted to one reference. Partial evaporation of a THF solution of the solid prepared from $PhC\equiv CH$ and EtMgBr yields a mixture of $MgBr_2,(THF)_4$ and two types of triclinic needles of $(PhC\equiv C)_2Mg,(THF)_4$ which may well be cis and trans octahedral complexes, like the halide complexes.[60]

The metalation reaction (9) has been realised in a few cases,[61,62,63,] the rate of reaction increasing enormously as the base strength of the solvent increases.[64] Addition of M-C carbon bonds does not take place simultaneously.

$$R_2M \quad + \quad R'C\equiv CH \quad \longrightarrow \quad R'C\equiv CMR \quad + \quad RH \qquad (9)$$

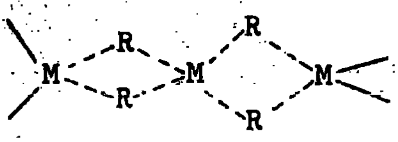
$$R'C\equiv CMR \quad + \quad R'C\equiv CH \quad \longrightarrow \quad (R'C\equiv C)_2M \quad + \quad 2RH$$

M = Zn,Cd; R = Me,Et,Ph; R' = Ph,octyl.

Phenyl(phenylethynyl)zinc slowly disproportionates in ether (10)

$$2PhZnC\equiv CPh \quad \longrightarrow \quad (PhC\equiv C)_2Zn \quad + \quad Ph_2Zn \qquad (10)$$

Both diphenylethynyl-zinc and -cadmium are white solids, practically insoluble in non-polar organic solvents, but di-1-octynyl-zinc and -cadmium are soluble in hot benzene and molecular weight data suggest that they are linear polymers(III)[65]



(III)

M = Zn,Cd

R = PhC≡C-

Diphenylethynyl-zinc and -cadmium dissolve in liquid ammonia and crystallise as ammines, $M(C\equiv CPh)_2.xNH_3$. Similar ethynyl derivatives have been made from the metal amide and acetylene in liquid ammonia.[66] These ammines are non-electrolytes but compounds $K_2M(C\equiv CR)_4$ are three-ion electrolytes and have ionic crystal structures[67] (11). The Zn-C≡ bond

$$M(SCN)_2.2NH_3 \quad + \quad 4RC\equiv CK \quad \xrightarrow{\text{liq. } NH_3} \quad K_2M(C\equiv CR)_4 \quad + \quad 2KSCN \qquad (11)$$

R=H,Ph ; M=Zn,Cd.

length is slightly shorter than that in Li_2ZnMe_4 (2·0 vs. 2·07Å). Dialkynylmercury compounds are easily prepared by adding the 1-alkyne in ethanol to an alkaline solution of K_2HgI_4.[68]

$$2RC{\equiv}CH \quad + \quad K_2HgI_4 \quad + \quad 2KOH \longrightarrow (RC{\equiv}C)_2Hg \quad + \quad 2H_2O \qquad (12)$$

Variations lead to other alkynylmercury compounds,[69] or Grignard

$$2RHgX \quad + \quad C_2H_2 \quad + \quad 2KOH \longrightarrow RHgC{\equiv}CHgR \quad + \quad 2KX \quad + \quad 2H_2O \qquad (13)$$

$$PhHgBr \quad + \quad PhC{\equiv}CH \quad + \quad Et_3N \longrightarrow PhHg{\equiv}CPh \quad + \quad Et_3NHBr \qquad (14)$$

reagents may be used.[70]

$$MeHgI \quad + \quad HC{\equiv}CMgBr \longrightarrow MeHgC{\equiv}CH \quad + \quad MgBrI \qquad (15)$$

Alkynyl derivatives of Group III

The last few years have seen a large increase in the number of compounds containing an alkynyl group directly bonded to a group III metal. It has been demonstrated that the alkynyl group has superior bridging ability to an alkyl group and dimeric compounds of aluminium, gallium and indium have been prepared, all of which are believed to contain electron-deficient alkynyl bridges. Although analogous boron compounds are known, there are no molecular weight data available to show if electron-deficient bridges are formed in this case. A large number of coordination and ionic complexes for boron and aluminium have been described and in certain cases, particularly for the trialkynylmetal derivatives complexation is necessary to enable the compounds to be isolated (otherwise they would decompose too rapidly).[71,72]

Alkynylboron compounds are prepared by the action of alkali metal acetylides or alkynyl Grignard reagents on boron halides, organoboron halides, or borates. The reactions are often carried out in the presence of a complexing agent because complexation increases the stability of the products. Trialkynylboranes polymerise during their preparation if a strong base is not present. The types of compounds synthesised in this way are listed in the table below.

$(RC\equiv C)_3B.D$	73,85	$MB(C\equiv CR)_4$	86, 87
$(RC\equiv C)_2BR'$	88	$R'_2NB(C\equiv CR)_2$	74, 91
$(RC\equiv C)BR'_2$	88, 78, 90	$(R'O)_2BC\equiv CR$	75, 76, 79, 90
$(RC\equiv C)BR'_2.D$	82, 83, 89	$X_2BC\equiv CH$	80
$R_2BC\equiv CBR_2$	81	$M(R'O)_3C\equiv CR$	73, 77
$(RC\equiv C)_2BR'.D$	89	$RC\equiv CB(NR'_2)_2$	90

Others have been prepared by metalation and redistribution reactions,[84] e.g.

$$MBR'_3H \quad + \quad HC\equiv CR \quad \longrightarrow \quad MR'_3BC\equiv CR \quad + \quad H_2 \qquad (16)$$

The best general method for the preparation of alkynylaluminium compounds is the reaction between aluminium halides and sodium acetylides.[92,93,94,95]

$$R_2AlX \quad + \quad R'C\equiv CNa \quad \longrightarrow \quad R_2(R'C\equiv C)AL \quad + \quad NaX \qquad (17)$$

$$AlX_3 \quad + \quad 3R'C\equiv CNa \quad \xrightarrow{D} \quad (R'C\equiv C)_3Al.D \quad + \quad 3NaX \qquad (18)$$

Reaction (17) may be carried in hydrocarbon solvents to obtain the uncomplexed compounds or in a donor solvent in which case coordination complexes are obtained. The uncomplexed compounds $R(R'C\equiv C)_2Al$ and $(R'C\equiv C)_3Al$ are unstable towards decomposition and indeed some uncomplexed trialkynyl compounds decompose violently on warming to 100°. A weak donor D may be displaced by a stronger donor D' (19).

$$R_2(R'C\equiv C)Al.D \quad + \quad D' \quad \longrightarrow \quad R_2(R'C\equiv C)Al.D' \quad + \quad D \qquad (19)$$

Alkynyl-aluminium compounds may also be prepared by the reaction of R_3Al or R_2AlH with terminal alkynes (20), (21), (see page 35).[96,97,98,99,100,102,103]

$$R'C\equiv CH \quad + \quad R_3Al \quad \longrightarrow \quad R_2(R'C\equiv C)Al \quad + \quad RH \qquad (20)$$

$$R'C\equiv CH \quad + \quad R_2AlH \quad \longrightarrow \quad R_2(R'C\equiv C)Al \quad + \quad H_2 \qquad (21)$$

A transmetalation reaction involving dialkynylmercury compounds has also yielded a trialkynylaluminium complex. (22)[93,101]

$$3Hg(C\equiv CR)_2 \quad + \quad 2Al \quad \xrightarrow{D} \quad 2Al(C\equiv CR)_3.D \quad + \quad 3Hg \qquad (22)$$

Several salts have been isolated in which alkynyl-aluminium bonds are found in the anion. The principal synthetic route is the reaction of 1-alkynes with compounds of general formula $MAlR_nH_{4-n}$ (MLi,Na; n0,1,2,3,4) e.g.[93,103,104,105,106]

$$MAlH_4 \quad + \quad 4R'C{\equiv}CH \quad \longrightarrow \quad MAl(C{\equiv}CR')_4 \quad + \quad 4H_2 \qquad (23)$$

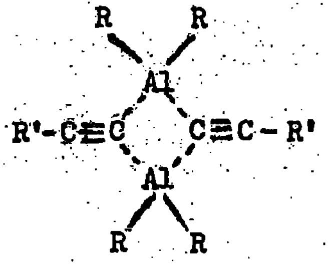
Other salts are more conveniently prepared by redistribution reactions (24),(25).

$$MAlR_4 \quad + \quad MAl(C{\equiv}CR')_4 \quad \longrightarrow \quad 2MAlR_2(C{\equiv}CR')_2 \qquad (24)$$

$$MAlH_4 \quad + \quad MAl(C{\equiv}CR')_4 \quad \longrightarrow \quad 2MAlH_2(C{\equiv}CR')_2 \qquad (25)$$

The products isolated may be solvated, e.g. $NaAlMe_2(C{\equiv}CPh)_2.THF$, in which case they are more likely to be ionic than the unsolvated ones which may have constitutions like $LiAlMe_4$.

The more symmetrical $R_2AlC{\equiv}CR'$ compounds are solids (e.g. $Me_2AlC{\equiv}CPh$, $Ph_2AlC{\equiv}CPh$) while the remainder are liquids which may be distilled at low pressure. They are all extremely air and moisture sensitive. Compounds of the type $R_2AlC{\equiv}CH$ have not been isolated since polymerisation occurs during their formation. They are dimeric in benzene and unlike trialkylaluminiums do not tend to become monomeric as R gets larger.[65,94,95] P.m.r. measurements have established that the bridge bonds are formed exclusively by the α-carbon of the alkynyl group (IV).[107] This bridge bond is stronger than the alkyl, alkenyl, or aryl bridge bonds. While complexes $R_2(R'C{\equiv}C)Al.D$ and $R(R'C{\equiv}C)_2Al.D$ are said to be stable, few have been well characterised, the diaryl(alkynyl)aluminium complexes being the best known.[92,103,108,109] For the weaker donor complexes such as the diethyletherates, the strength of the coordinate bond is about the same as that of the bridge bond of the uncomplexed form so that an equilibrium exists (26) and it is possible to remove the ether by distillation at reduced pressure.[94]



(IV)

$$(R_2AlC{\equiv}CR')_2 \quad + \quad 2Et_2O \quad \rightleftharpoons \quad 2R_2Al(C{\equiv}CR').OEt_2 \qquad (26)$$

This equilibrium probably accounts for the low stability of $R_2Al(C{\equiv}CH).OEt_2$

complexes. N.m.r. evidence suggests that $Me_2AlC\equiv CPh$ disproportionates significantly in ether or THF into $Me_3Al.D$ and $MeAl(C\equiv CPh)_2.D$.[97,65] The number of trialkynylaluminium complexes, $(RC\equiv C)_3Al.D$ is quite large although many have not been adequately characterised. $Al(C\equiv CH)_3.C_4H_8O_2$ and $Al(C\equiv CBu)_3.C_4H_8O_2$ are monomeric in dioxan and $Al(C\equiv CBu)_3.C_4H_8O_2$ is monomeric in benzene.[92,109,93,95]

The $C\equiv C$ stretching frequencies do not appear to be particularly significant. Values for phenylethynyl-bridged dimers, $(R_2AlC\equiv CPh)_2$ are lower, 2050-2100 cms^{-1}, than for alkylethynyl-bridged dimers, 2100-2170 cms^{-1}. Complexation appears to raise the frequency of these compounds and successive replacement of alkyl groups by alkynyl groups raises the frequency slightly.

$(Me_2AlC\equiv CPh)_2$	2050 cms^{-1}	$Me_2AlC\equiv CPh, THF$	2110 cms^{-1}
$(Me_2GaC\equiv CPh)_2$	2050 cms^{-1}	$Me_2GaC\equiv CPh, THF$	2110 cms^{-1}
$(Et_2AlC\equiv CMe)_2$	2110 cms^{-1}	$EtAl(C\equiv CMe)_2.OEt_2$	2150 cms^{-1}
$Et_2AlC\equiv CMe,OEt_2$	2150 cms^{-1}	$Al(C\equiv CMe)_3,OEt_2$	2165 cms^{-1}

Dialkyl(alkynyl) compounds of gallium and indium have been prepared by the reaction of the trialkyls with 1-alkynes (27). Unlike the reaction with R_3Al there appears to be very little addition of metal-carbon bonds to the alkyne. Metalation is the predominant reaction and it proceeds at lower temperatures than for aluminium.[111,110,65]

$$R_3M \quad + \quad R'C\equiv CH \longrightarrow R_2MC\equiv CR' \quad + \quad RH \qquad (27)$$

$$R{=}Me,Et;\ R'{=}Ph,H,Bu^n;\ M{=}Ga,In.$$

Both $Me_2GaC\equiv CPh$ and $Me_2InC\equiv CPh$ are dimeric in benzene solution and the similarity of spectroscopic data to those of $Me_2AlC\equiv CPh$ suggest that they too have bridging phenylethynyl groups. Two trialkynylgallium dioxan complexes have been prepared from gallium trichloride and sodium acetylides, $(HC\equiv C)_3Ga,C_4H_8O_2$ and $(CH_3C\equiv C)_3Ga,C_4H_8O_2$.[92]

Dimethylthallium alkynyls may be prepared from Me_2TlNH_2 and 1-alkynes in liquid ammonia (28), and complex salts, $MTl(C\equiv CR)_4$, from alkali metal alkynes and $TlCl_3,4NH_3$ in liquid ammonia (29).

$$Me_2TlNH_2 \quad + \quad HC{\equiv}CR \quad \longrightarrow \quad Me_2TlC{\equiv}CR \quad + \quad NH_3 \qquad (28)$$

$$R = Ph, Me, TlMe_2$$

$$TlCl_3,4NH_3 \quad + \quad RC{\equiv}CM \quad \longrightarrow \quad MTl(C{\equiv}CR)_4 \quad + \quad 3MCl \qquad (29)$$

$$R = Ph, Me; \; M = Na, K, Ph_4P$$

The $Me_2TlC{\equiv}CR$ compounds are water sensitive but are soluble as monomers in liquid NH_3, pyridine and aniline.[112,113]

Organometallic halides of Group II.

The organomagnesium halides, organozinc halides and organomercury halides have received a great deal of attention and are among the earliest and best known organometallic compounds. On the other hand there is almost no information about the beryllium and cadmium compounds. Surprisingly, it is only for zinc and mercury that the composition of the unsolvated compounds is known, and it is only recently that light has been shed on the solid state and solution properties of the solvated magnesium compounds. The fluorides are likely to have very interesting structures but at present have not been studied.

Many years ago alkylberyllium halides were prepared by heating an alkyl halide with beryllium in ether in a sealed tube but the constitution of the products was not established.[114,115] More recently some complexes of alkylberyllium halides have been made. As a by-product of the removal of ether from $t\text{-}Bu_2Be,OEt_2$ using $BeCl_2$ or $BeBr_2$, the corresponding ether complexes of t-butylberyllium halides were prepared. Both were dimeric in benzene and since the bridging properties of halogen are undoubtedly better than those of t-butyl, they are formulated in the same way as $(t\text{-}BuMgCl,OEt_2)_2$, (V). In diethyl ether the chloride is monomeric and must be $t\text{-}BuBeCl,(OEt_2)_2$.[15]

A bipyridyl complex, EtBeCl,bipy, is described as a yellow-orange crystalline compound which disproportionates on prolonged extraction with benzene.[116] The complexes $KF.Et_2Be$ and $KF.(Et_2Be)_2$, formed by the addition of potassium fluoride to diethylberyllium almost certainly contains fluorine bridges, and the latter may have a linear fluorine bridge as found in KEt_6Al_2F.[44]

Dimethyl-, diethyl-, and diphenylberyllium were found to redistribute rapidly with $BeCl_2$ and $BeBr_2$ in diethylether so that equilibrium (30) lies predominantly if not entirely to the right.

$$R_2Be + BeX_2 \rightleftharpoons 2RBeX \qquad (30)$$

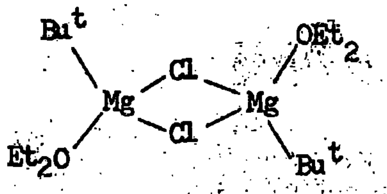
This was established by a combination of experiments:

1.) molecular weight measurements show that the beryllium containing species of a 1:1 $R_2Be:BeX_2$ mixture in diethyl ether is monomeric, 2.) addition of 1,4-dioxan to a 1:1 $R_2Be:BeX_2$ mixtures results in precipitation of the RBeX, dioxan, 3.) the low temperature p.m.r. spectra of Me_2Be and 1:1 $Me_2Be:BeX_2$ in ether show a single resonance 4 c.p.s. apart. That of a 2:1 mixture of $Me_2Be:BeX_2$ showed two resonances, one characteristic of Me_2Be, and the other of the 1:1 mixture. Since the signals bear a 1:2 ratio this is evidence for the formation of MeBeX.[40]

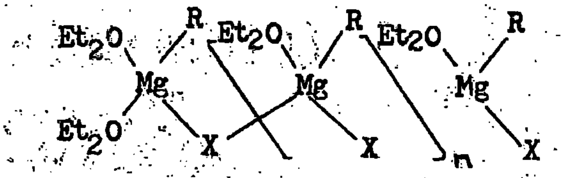
The alkylmagnesium halides, called Grignard reagents after their discoverer, have an interesting history, which cannot adequately be discribed in this brief introduction.[117,118] They are usually prepared by the direct reaction between an alkyl or aryl halide and magnesium in a basic solvent such as diethylether and this easy and versatile preparation has led to their widespread use as synthetic reagents.

Two important problems have been recognised. The solution of the first, an understanding of the composition of Grignard reagents in solution, is necessary for the solution of the second, an understanding of the mechanisms of their reactions. Considerable effort has been devoted to the first problem but the position is still not entirely clear, while studies of the second problem have proved very difficult.

Reliable molecular weight determinations have shown that in THF solution the Grignard reagents are monomeric over a wide range of concentration and that they approach a monomeric consitution in diethyl ether with increasing dilution.[119,33] These solutions presumably contain $RMgX(D)_n$ species with n probably equal to two. More concentrated solutions in diethyl ether show increasing association and are, usually at least dimeric in 1 molar solution. Comparison of molecular weight data with those of R_2Mg and MgX_2 compounds shows that the association takes place through halogen bridges. Species like (V) and/or (VI) must be present. t-Butylmagnesium chloride etherate is dimeric in ether and in benzene and is reasonably thought to have structure (V).



(V)



(VI)

The changing degree of association of Grignard reagents in Et_2O arises because the halogen is able to compete with the solvent molecules for coordination positions about magnesium whereas it cannot displace the more basic THF. Some alkylmagnesium bromides and chlorides are monomeric in NEt_3 but the situation is more complicated for iodides or aryl compounds.[120]

The disproportionation equilibrium (31) is suggested by the precipitation of magnesium halides by the addition of bases such as dioxan to Grignard reagents. Molecular weights do not give information on the position of equilibrium. Radioactive tracer studies of 1:1 mixtures of ether solutions containing $MgBr_2$ (labelled with radioactive magnesium) and Et_2Mg (not labelled) have shown that the exchange reaction (32) does take place.[121,122]

$$R_2Mg \quad + \quad MgX_2 \quad \rightleftharpoons \quad 2RMgX \qquad (31)$$

$$Et_2Mg \quad + \quad {}^*MgBr_2 \quad \rightleftharpoons \quad EtMgBr \quad + \quad Et^*MgBr \qquad (32)$$

X-ray diffraction studies of the crystalline Grignard reagents $EtMgBr(Et_2O)_2$, $PhMgBr(OEt_2)_2$, and $PhMgBr(THF)_2$, show each to contain RMgX units with tetrahedrally bonded magnesium.[123,124,125] A similar study on the dimeric Grignard, $(EtMgBr,NEt_3)_2$ indicated halogen bridges and a trans disposition of ligands.[126]

P.m.r. Studies have demonstrated that there is rapid exchange of alkyl groups among the various magnesium species in ether solvents and that the p.m.r. spectra of RMgX and the corresponding R_2Mg compounds are essentially the same. Fluoroaryl groups do not exchange so rapidly, and using the chemical shifts of ^{19}F it has been possible to obtain the ratio $RMgX:R_2Mg$ for a number of phenyl Grignard reagents containing a para fluorine atom.[127]

Grignard reagents are reported to react with other ligands which precipitate the halide as a magnesium halide complex, apart from 1,4-dioxan. These include 1,2-dimethoxyethane and TMED. In contrast TEED and an ether solution of a Grignard reagent (EtMgBr, PhMgBr, $p\text{-}FC_6H_4MgBr$) give the corresponding RMgBr,TEED adduct. In benzene $p\text{-}FC_6H_4MgBr$,TEED is monomeric and shows no tendency to disproportionate. It has a p.m.r. spectrum at room temperature with broad resonances for the TEED which were not investigated.[128] However, addition of TMED to MeMgBr in ether gives MeMgBr,TMED, a sharp-melting, sublimable solid.[3]

Although Grignard reagents complexed with bases have received a great deal of attention, knowledge of the unsolvated compounds is very limited. It has been found that alkyl and aryl halides will react with magnesium in a hydrocarbon solvent if the conditions are right. The compositions of these unsolvated organomagnesium halides vary, especially with time, but often for freshly prepared solutions they correspond closely to R_3Mg_2X.[129]

Several donor solvents have been used for the preparation of alkylzinc halides from zinc and an alkyl halide.[130,131] The unsolvated ethylzinc halides (Cl, Br, I) have been prepared by dissolving the zinc halide in excess diethylzinc and evaporating the excess. Ethylzinc chloride and ethylzinc bromide are tetrameric in benzene and do not disproportionate in non-polar solvents. A structure similar to that of methylzinc methoxide has been proposed for them.[133] Ethylzinc iodide does disproportionate in benzene, precipitating zinc iodide but may be crystallised from ethyl iodide. In the crystalline state it is a coordination polymer with zinc and iodine atoms forming a sheet-like layer lattice[132,134]

A number of studies have shown that the equilibrium (33) in ether solvents lies well to the right. But in contrast to the magnesium and beryllium cases the equilibrium may not be established rapidly.[135,136,137]

$$R_2Zn + ZnX_2 \rightleftharpoons 2RZnX \qquad (33)$$

If TMED is added to a 1:1 $Et_2Zn:ZnI_2$ mixture in THF soon after preparation, ZnI_2,TMED crystallises, but if it is added after a week at 25° then EtZnI,TMED crystallises. Other coordination complexes that have been isolated include EtZnCl,TMED, $EtZnCl(py)_2$ and a series of arylzinc halide complexes with 1,4-dioxan or diethyl ether.[130,138]

There is no information on the constitution of organocadmium halides. The ethyl compounds, EtCdX, are described as insoluble in hydrocarbons and in ether, and so must be highly associated. From ether n-BuCdBr and PhCdBr have been crystallised but no molecular weights were reported.[139]

A survey of organomercuric halides is found in reference 1, p. 148-157. The chlorides, bromides, and iodides are linear, monomeric, crystalline compounds. The stability of the RM^+ unit towards water and oxygen appears to increase down the group but not so markedly as that of the R_2M^+ unit of group IIIb. Alkylmercuric chlorides ionise in the presence of triphenylphosphine to give $(RHgPPh_3)^+Cl^-$ and RHgF compounds behave largely as salts, dissolving in water as $(RHgOH_2)^+F^-$.

Organometallic amides of Group II

In general the reaction between secondary amines and the metal dialkyls produces $RMNR'_2$ compounds that are associated to polymers (Mg), dimers (Be,Mg,Zn) or trimers (Be). The zinc compounds require heating at 50-70° for reaction to take place while the beryllium and magnesium compounds react at about room temperature. Adducts of $RMNR'_2$ with strong bases have been isolated. They show a greater tendency to disproportionate than the uncomplexed species. No mercury or cadmium compounds have been reported.

Of the factors discussed earlier concerning the degree of association of compounds formed by the reaction of metal dialkyls with weak acids, steric effect effects are most important for the aminoberyllium alkyls. Where bulky organic groups are present dimers become more stable than trimers as illustrated by the series $(MeBeNEt_2)_3$, $(EtBeNMe_2)_3$, $(EtBeNEt_2)_2$.[140,143,24] Reaction takes place readily with the exception of di-t-butylberyllium. The complex $t\text{-}Bu_2Be,NHMe_2$ is easily prepared but elimination of iso-butane is not complete even at 70°. This is believed to be because the amino hydrogen is well shielded and would find it difficult to come within reaction distance of the Be-C bond. In a similar way to some group III dimethylamino derivatives, $MeBeNMe_2$ is polymeric in the solid state but trimeric in solution and in the vapour phase.

The primary amine, $t\text{-}BuNH_2$, in reaction with Me_2Be gives a trimeric compound (34), which apparently does not react with more Me_2Be to give $(MeBe)_2NBu^t$ (35) nor does it eliminate methane quantitatively on heating.[141]

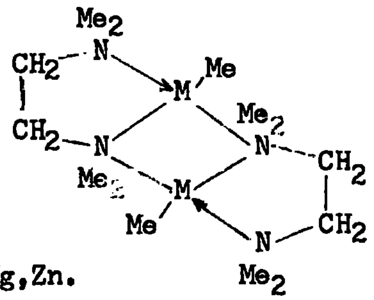
$$Me_2Be \quad + \quad Bu^tNH_2 \longrightarrow \tfrac{1}{3}(MeBeNHBu^t)_3 \quad + \quad MeH \qquad (34)$$

$$2Me_2Be + Bu^tNH_2 \longrightarrow \frac{1}{3}(MeBeNHBu^t)_3 + Me_2Be + MeH \qquad (35)$$

One mole of methane is evolved from the reaction of Me_2Be (1 mole) and $MeNH_2$ (1 mole) between -90° and -10°, and another 0·5 moles on heating to high temperatures. No products from the reaction were characterised.[142]

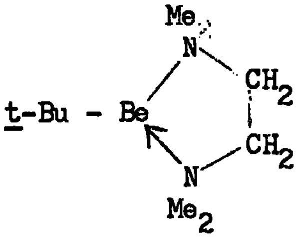
In the compounds described above the beryllium atoms of the four and six membered rings are still only three coordinate and therefore they should react with bases. Complexes with pyridine and bipyridyl have been obtained, e.g. $(MeBeNMe_2,py)_2$, colourless; $MeBeNPh_2.2py$, deep yellow; $MeBeNPh_2.bipy$, brick red. The colours in this case may be due to electron transfer from the Be-C bonds or from the nitrogen lone pair into the heterocyclic π-system. Disproportionation sometimes complicates the reaction with bases, e.g. $MeBeNPr^n_2$ and pyridine produce Me_2Be,py_2.[140]

Trimethylethylenediamine, $MeHNCH_2CH_2NMe_2$, gives dimeric complexes with Me_2Be, Et_2Be, Ph_2Be, Me_2Mg, and Me_2Zn by elimination of hydrocarbon, (VII). But with $t\text{-}Bu_2Be$ steric congestion forces a unique monomer to be formed, (VIII).[26,8,21,36]



M=Be,Mg,Zn.

(VII)



(VIII)

Aminomagnesium alkyls tend to be polymeric unless the organic groups on nitrogen are large. Both nitrogen and alkyl bridges must be present in these polymeric compounds. Ether from the reaction solvent could not be completely removed from $(EtMgNEt_2)_n$ or $(EtMgNPr^i_2)_n$, but it may be separated from the crystalline complexes $EtMgNPh_2.(OEt_2)_2$ and $iPrMgNPh_2(OEt_2)_2$ leaving polymeric materials. More sterically hindered amines do yield dimers such as $(Pr^iMgNPr^i_2)_2$ which are among the few compounds which contain magnesium in the three coordinate state.[7]

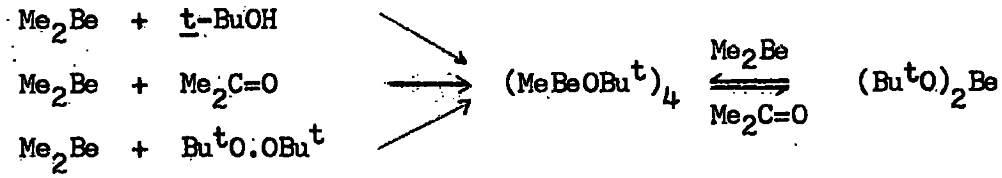
Examples are known of the addition of R_2Mg to C=N and -C≡N to give amino and imino derivatives, but $i\text{-}Pr_2Mg.N{\equiv}CBu^t$ is a stable complex.

In the case of zinc alkyls no amino trimers have yet been prepared. The compound most likely to be trimeric, $MeZnNMe_2$, is unfortunately unstable to disproportionation. Other derivatives have been obtained though, and are dimeric in benzene.[8,145] An X-ray diffraction study of $MeZnNPh_2$ has shown that it is dimeric in the solid state also, with three-coordinate zinc.[146] This coordination unsaturation can be relieved by complexing with pyridine, e.g. $Me(py)_2ZnNPh_2$, yellow.

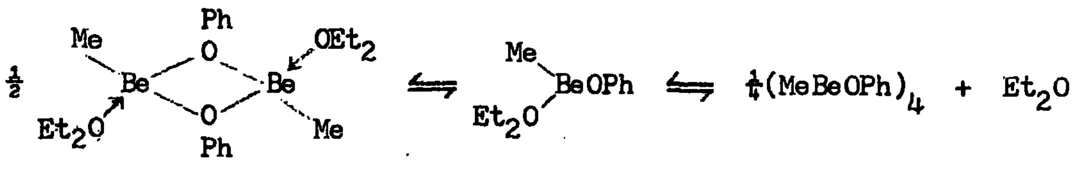
Organometallic alkoxides and phenoxides of Group II

By elimination of a hydrocarbon, compounds RMOR' may be prepared from alcohols and metal dialkyls. The coordination unsaturation of the metal may be relieved by association. Tetramers are the most common species formed for beryllium, zinc and cadmium, while generally the magnesium compounds are polymeric or oligomeric. Lower degrees of association result when steric interference between the organic groups becomes significant. Bases are capable of competing in donor strength with the second coordinate bond of oxygen and so form dimeric coordination complexes, but rarely compete with the first coordinate oxygen bond.

Alcohols react rapidly with R_2Be compounds except for $t\text{-}Bu_2Be$ which reacts slowly, probably for steric reasons. RBeOR' compounds may also be prepared by other methods as illustrated for $(MeBeOBu^t)_4$.[147,21,148]



Many RBeOR' compounds are tetrameric in benzene solution and $Me_3SiOBeMe$ is tetrameric in the solid state with a cubic arrangement of beryllium and oxygen atoms.[149] When the organic groups are bulky the degree of association becomes two or three, e.g. $(Bu^tBeOBu^t)_2$, $(MeBeOCPh_3)_2$, and $(EtBeOCEt_3)_3$, and may even crystallise from ether solvents as monomeric complexes, e.g. $MeBeOCPh_3.OEt_2$ and $MeBeOCHPh_2.THF$. The complex $PhBeOMe.OEt_2$ is also monomeric, but $MeBeOPh.OEt_2$ is slightly associated in benzene. Equilibria of the following kind may exist in the solution.



(IX)

Several compounds have been found to be dimeric in diethylether and probably oxygen-bridged as in (IX).

Methyl beryllium methoxide forms a bis pyridine adduct, MeBeOMe,2py, but addition of 1 mole of pyridine per beryllium causes disproportionation to $Me_2Be.2py$ and insoluble $(MeO)_2Be$. A 1:1 complex of pyridine with methylberyllium t-butoxide, $MeBeOBu^t.py$ is slightly associated like $MeBeOPh.OEt_2$.

Other examples of disproportionation have been encountered. Both MeBeOPh and EtBeOPh disproportionate in the absence of ether giving insoluble $(PhO)_2Be$, and $(MeBeOMe)_4$ disproportionates on heating above 120°. Addition of bipyridyl to $(MeBeOCH_2Ph)_4$ gives Me_2Be,bipy.

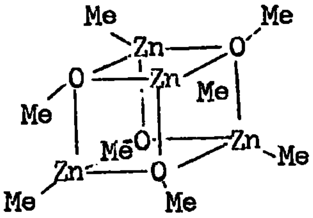
The p.m.r. spectra of $(MeBeOMe)_4$ and $(MeBeOBu^t)_4$ show some features which have not yet been explained. In benzene the $C\underline{H}_3O$ resonance of the methoxide is a doublet instead of the expected singlet whereas the t-butoxide does show a singlet for the $(C\underline{H}_3)_3CO$ resonance. However, the t-butoxide in perdeuteromethylcyclohexane shows doublets both for the butoxy and the $C\underline{H}_3$-Be resonances, these being temperature and concentration independent.

Aside from the reaction between R_2Mg and R'OH, alkyl magnesium alkoxides may be prepared by the direct synthesis (36) in hydrocarbon solvents.[32,150]

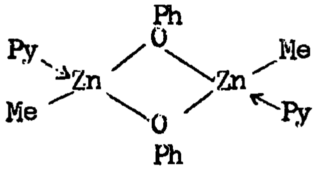
$$2Bu^nCl \quad + \quad 2Mg \quad + \quad Pr^iOH \longrightarrow Bu^nMgOPr^i \quad + \quad MgCl_2 \quad + \quad Bu^nH \qquad (36)$$

In general the alkylmagnesium alkoxides are more highly associated then the beryllium and zinc compounds. Some of them are insoluble polymers, e.g. EtMgOEt, and others, while probably polmeric in the solid state, are oligomeric in benzene, e.g. Pr^iMgOMe and $EtMgOPr^n$. Tetramers result when there is chain branching at the α-carbon atom of the alkoxy group, e.g. $(EtMgOBu^t)_4$ and $(Pr^iMgOPr^i)_4$. No dimeric alkoxides have yet been found and only one trimer, $(Bu^nMgOPr^i)_3$.[151] Since ether is not easily removed from the RMgOR' compounds, the second lone pair of the oxygen must have similar donor strength to magnesium as ether. Some of the alkoxides are tetrameric in diethyl ether, such as $(EtMgOEt)_4$ and $(MeMgOBu^t)_4$, and are presumably not complexed with it, but others like $(EtMgOCEt_3)_2$ are dimeric and crystallise as etherates that lose ether readily. Of the compounds studied only methylmagnesium t-butoxide was observed to disproportionate in hydrocarbon solution.

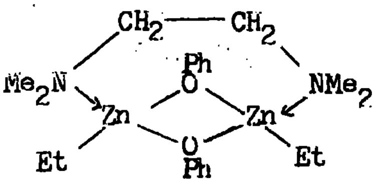
A number of crystalline compounds RZnOR' have now been obtained from zinc dialkyls and alcohols. Most of them are tetrameric in benzene, e.g. $(MeZnOMe)_4$, $(EtZnOPr^i)_4$, $(MeZnOPh)_4$ and $(MeZnOSiMe_3)_4$, but when there are large steric requirements for the organic groups trimers and dimers may be formed,e.g. $(Bu^tZnOBu^t)_3$, $(PhZnOCPh_3)_2$ and $(EtZnOCHPh_2)_3$.[152,153,154] The mean degree of association of $MeZnOBu^t$ changes from four to less than three as the concentration is reduced from 0·7M to 0·12M in monomer. X-ray diffraction studies of MeZnOMe and$EtZnOBu^t$ have shown them to be tetrameric in the solid state also and to have a cubic arrangement of zinc and oxygen atoms, (X).[155,156] The tetramer arises because dimerisation or trimerisation would leave the metal three-coordinate and the oxygen with a remaining lone pair. In the tetramer both the metal and the oxygen are four coordinate. Very electron withdrawing groups can reduce the donor character of the oxygen so that only dimers are formed, e.g. $(EtZnOC_6F_5)_2$ and $(EtZnOC_6Cl_5)_2$.



(X)



(XI)



(XII)

The tetramers do not form adducts with pyridine or TMED except where the second lone pair of oxygen is not such a good donor to three-coordinate zinc as these bases. Pyridine forms dimeric 1:1 adducts, $(MeZnOPh,py)_2$, (XI), $(EtZnOC_6F_5,py)_2$ and TMED a 2:1 adduct, $(EtZnOPh)_2$,TMED (XII) and a 1:1 adduct $EtZnOC_6F_5$,TMED. The dimeric and trimeric compounds contain three-coordinate zinc. Pyridine is found to give an unstable 1:1 complex with Bu^tZnOBu^t but does not form a complex with TMED.[157]

Most of the alkylzinc alkoxides disproportionate on heating, and p.m.r. studies suggest that $(MeZnOMe)_4$ disproportionates in solution.[9] On the other hand $(MeZnOPr^i)_4$, $(MeZnOBu^t)_4$ and $(Bu^tZnOBu^t)_3$ are quite stable in solution. The alkoxides $(MeZnOMe)_4$ and $(MeZnOBu^t)_4$ have p.m.r. spectra in benzene which show peculiarities in the same way as the beryllium compounds. The t-butoxide has two singlets as expected but the methoxide shows doublets for both methyl groups.

Alkylzinc alkoxides can also be made by the addition of R_2Zn to aldehydes or ketones. Below is shown the interesting reactions of benzophenone.[153]

$$\begin{array}{llll} & + \ \text{Me}_2\text{Zn} & \longrightarrow & \text{yellow; Me}_2\text{Zn recovered 100\%.} \\ \text{Ph}_2\text{C=O} & + \ \text{Et}_2\text{Zn} & \longrightarrow & (\text{EtZnOCHPh}_2)_3 \ + \ \text{C}_2\text{H}_4 \qquad (37) \\ & + \ \text{Ph}_2\text{Zn} & \longrightarrow & (\text{PhZnOCPh}_3)_2 \end{array}$$

Those alkylcadmium alkoxides known are analogous to the corresponding zinc compounds with the notable exception of $(MeCdOBu^t)_2$. Two trimeric mercury compounds, $(PhHgOMe)_3$ and $(PhHgOBu^n)_3$, and a compound, MeHgOSiMe, which is monomeric in solution are the only mercury derivatives so far prepared.[159,153] This last compound which contrasts with the tetrameric zinc and cadmium compounds is found to be tetrameric in the crystalline state.[160,161]

Organometallic sulphides of Group II

The RMSR' compounds with M = Be, Mg, Zn, and Cd, show substantial changes from the alkoxides. Formation of tetramers for beryllium and magnesium seems to be somewhat more difficult because of a.) the lower donor strength of the second sulphur lone pair, b.) the greater tendancy to form coordination polymers especially with straight chain sulphides and c.) the greater tendancy to form disproportionation products. The formation of uncomplexed alkylberylkium sulphide dimers and trimers is restricted to a single example of a dimer $(MeBeSPh)_2$. RZnSR' and RCdSR' compounds with chain branching at the α-carbon of the R' group disproportionate only on heating but do show peculiar degrees of association.

The methylberyllium- and i-propylberyllium sulphides with the exception of $(MeBeSBu^t)_4$ disproportionate. For some reason the ethylberyllium sulphides form stable tetramers which presumably have a cubic Be_4S_4 structure. Complexation with bases can stop disproportionation and a number of monomeric RBeSR'.2D, and dimeric $(RBeSR'.D)_2$ compounds have been prepared.[162]

Only tetrameric $(EtMgSBu^t)_4$ is known as an uncomplexed alkylmagnesium sulphide. Some dimeric coordination complexes such as $(MeMgSBu^t.THF)_2$ and $(Bu^tMgSPr^i.OEt_2)_2$ have been described. Removal of ether from a solution of $MeMgSBu^t$ does not give $(MeMgSBu^t.OEt_2)_2$ but causes disproportionation to insoluble Me_2Mg and $Mg(SBu^t)_2$. Here apparently ether cannot compete with bridging methyl in donor strength to magnesium nor can it compete in donor strength with the sulphur attached to magnesium. On the other and THF competes successfully for a coordination position about magnesium and prevents disproportionation. Ether can compete for coordination positions with ethyl or t-butyl bridging groups which are much poorer than methyl and so $(Bu^tMgSPr^i.OEt_2)_2$ does not disproportionate. By the same reasoning $(t\text{-}BuMgSBu^t.OEt_2)_2$ ought to be stable but, inexplicably, both in ether and in the presence of THF disproportionation does take place.[143]

Polymeric products $(RMSR')_x$ are obtained from the reactions of R_2Zn or R_2Cd with MeSH, n-BuSH, or PhSH. The coordination polymers MeZnSMe and MeBeSMe are probably similar to that of crystalline Me_2AlSMe with the possibility of cross-linking between chains through the second sulphur lone pair and the three-coordinate metal atom.[164] Branching at the α-carbon of the R' group gives the following compounds in benzene solution: $(MeZnSPr^i)_6$, $(MeZnSBu^t)_5$, $(MeCdSPr^i)_6$, $(MeCdSBu^t)_4$.[8,158] The structures of $MeZnSBu^t$ (pentameric) and $MeZnSPr^i$ (octameric) in the crystalline state have been determined by X-ray diffraction methods.[165,166]

Organometallic hydrides of Group II

The chemistry of these compounds, RMH, is not as well developed as that of the Group III organometallic hydrides, but certain general features have begun to appear. Compounds RBeH are probably stable although only one member of the series has been prepared so far. The BeH_2Be electron deficient bridge is an important feature of the chemistry of the coordination complexes of RBeH compounds and is likely to be an important feature of the uncoordinated compounds. Terminal Be-H bonds have been found for a few compounds although not for certain in RBeH compounds. It does not seem possible to prepare RMgH compounds, principally because the high lattice energy of the essentially ionic MgH_2 causes disproportionation to occur. Although RZnH compounds have not yet been isolated, the greater electronegativity of zinc compared with magnesium would indicate that they might be stable to disproportionation.

However, in the same way that Et_2GaH is less stable than Et_2AlH, RZnH compounds may decompose to metal and alkane.

At present little is known about donor-free alkyl- or aryl-beryllium hydrides. Iso-butylberyllium hydride, prepared by careful pyrolysis of $i\text{-}Bu_2Be$, is oligomeric in benzene solution. Pyrolysis of $t\text{-}Bu_2Be$ does not give t-BuBeH but a mixture of it with i-BuBeH.[167] A similar attempted preparation of i-PrBeH from $i\text{-}Pr_2Be$ gave a glassy, presumably polymeric, material which was not further investigated.[144] Alkylberyllium hydrides prepared in donor solvents always retain some coordinated solvent even after prolonged pumping.[148]

Complexes of RBeH with donor molecules have been prepared by several routes.[167,168] These methods are the two most important:

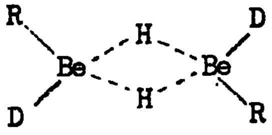
a.) $RBeCl + NaEt_3BH \xrightarrow{Et_2O} NaCl + Et_3B + RBeH,OEt_2$ (38)

The soldium chloride is removed by filtration, the triethyl borane by pumping at 60°, leaving $RBeH,(Et_2O)_x$. Addition of NMe_3 gives $RBeH,NMe_3$.[169]

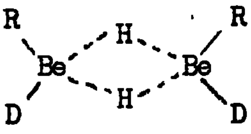
b.) $LiH + RBeBr \xrightarrow{Et_2O} LiBr + RBeH$ (39)

Evaporation of ether at reduced pressure and addition of benzene precipitates the LiBr and leaves $RBeH.(Et_2O)_x$ in benzene solution. This works well for MeBeH and EtBeH only.

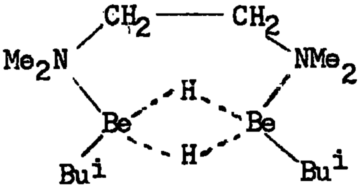
Several complexes RBeH,D with monodentate ligands such as NMe_3 are now known. They are dimeric in solution and are believed to contain hydrogen bridges.



(XIII)



(XIV)



(XV)

The hydrogen bridge is evidently stronger than the methyl bridges of Me_2Be or the BH_2B bridge of borane since excess NMe_3 will not break the bridge to give $RBeH,(NMe_3)_2$. In the p.m.r. spectra of these compounds the absorption due to the BeH_2Be protons is only rarely observed. The splitting of the NMe_3 resonance of $(MeBeH.NMe_3)_2$ has been attributed to the presence of <u>cis</u> and <u>trans</u> isomers (XIII), (XIV).[170]

The chelating ligand TMED when added to solutions of RBeH where R = Me,Et or Ph, does not give monomeric complexes RBeH,TMED, but gives an insoluble material $(RBeH)_2TMED$. These compounds are believed to be coordination polymers with TMED-linked dimer units of $(RBeH)_2$. However, with i-BuBeH, addition of TMED gives monomeric $(i\text{-}BuBeH)_2TMED$ which is though to have structure (XV). Models show that the TMED is capable of bridging, particularly if it is twisted out of planarity.

A number of complex hydrides, MR_2BeH, have been described where M = Li,Na and R = Me,Et,[171,172] Pr^i,Bu^i.[28] Sometimes they are isolated as etherates. The crystal structure of $NaEt_2BeH.OEt_2$ has been determined and has shown the presence of $Et_2BeH_2BeEt_2$ units.[173]

Early qualitative investigations of the addition reactions of both complexed and uncomplexed alkylberyllium hydrides with olefins have been reported.[174,148] A recent kinetic study of the reaction between 1-decene and $(MeBeH.NMe_3)_2$ has shown the reaction to proceed through a monomer-dimer equilibrium followed by rate determining addition of the monomer to the 1-decene.[175]

All attempts to prepare RMgH compounds by methods analogous to the preparation of RBeH compounds have resulted in no reaction or in the precipitation of MgH_2. No alkali metal diethylmagnesium hydride complexes were produced by the reaction of Et_2Mg with LiH,NaH or KH in ether solvents. Pyrolysis of $LiBu^nMe_2Mg.OEt_2$ prepared from Bu^nLi and Me_2Mg, gives a mixture of LiH and Me_2Mg.[176]

Organozinc hydride compounds have not yet been made but it may be possible to make them. Zinc-hydride terminal bonds have been found in $(HZnNMeC_2H_4NMe_2)_2$.[177,178] Anionic hydride complexes such as $LiPh_2ZnH.OEt_2$ have also been prepared.[179,180] It seems that RHgH if ever formed is very unstable towards decomposition to R_2Hg, RH, H_2, and Hg.

Reactions of Organolithium compounds with alkynes.

It has been known for some time that organolithium reagents can metalate the terminal hydrogen of 1-alkynes but recent studies stimulated by developments in the stereoregular polymerisation of alkenes, have demonstrated that the reaction can give rise to a large number of products.

Depending on the reagents and the conditions, metalation, isomerisation, addition and reductive dimerisation have all been observed as in the case of the aluminum alkyls and aryls.

For terminal acetylenes metal-hydrogen exchange occurs readily in diethyl ether or hydrocarbon solvents at about -78° to form alkynyl-lithium compounds (40). However, recently a number of examples have been found where an increased quantity of RLi and increased temperatures results in further metalation to give polylithiated species (41-43)

$$R'C{\equiv}CH + RLi \longrightarrow R'C{\equiv}CLi + RH \qquad (40)$$

$$CH_3C{\equiv}CH + \underset{\text{excess}}{\underline{n}\text{-BuLi}} \longrightarrow CLi_3C{\equiv}CLi + 4Bu^nH \qquad (41)^{181}$$

$$C_2H_5C{\equiv}CH + \underset{\text{excess}}{n\text{-BuLi}} \longrightarrow CH_3CHLiC{\equiv}CLi + 2Bu^nH \qquad (42)^{182}$$

$$C_2H_5C{\equiv}CH + \underline{t}\text{-BuLi} \longrightarrow CH_3CLi_2C{\equiv}CLi + 3Bu^nH \qquad (43)^{183}$$

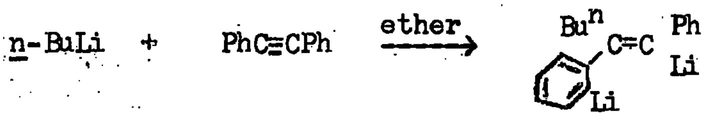
Of the non-terminal alkynes MeC≡CMe does not appear to react with alkyl-lithium reagents, but PhC≡CMe undergoes isomerisation (1:1 ratio) or metalation (1:6 ratio).[184]

$$\mathrm{PhC{\equiv}CMe} \quad + \quad \underline{\mathrm{n}}\text{-}\mathrm{BuLi} \longrightarrow \;?\; \xrightarrow{H_2O} C_6H_5CH_2C{\equiv}CH \qquad (44)$$

$$\mathrm{PhC{\equiv}CMe} \quad + \quad 6\underline{\mathrm{n}}\text{-}\mathrm{BuLi} \longrightarrow C_6H_5C_3Li_3 \quad + \quad \underset{\text{small quantity}}{C_6H_4LiC_3Li_3} \qquad (45)$$

Only PhC≡CPh has been found to react by addition and even then metalation often occurs at the same time. Ether solvents appear to allow addition to take place more readily than hydrocarbons and the order of reactivity appears to be PhLi, Bu^tLi Bu^nLi MeLi, as illustrated by reactions (46-50) [185,186,187]

$$\underline{\mathrm{n}}\text{-}\mathrm{BuLi} \quad + \quad \mathrm{PhC{\equiv}CPh} \xrightarrow[40^{\circ}]{\text{hydrocarbon}} \text{no reaction} \qquad (46)$$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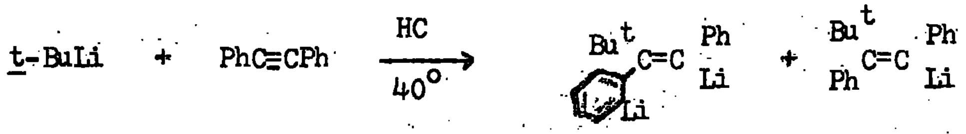

(48)

$$\mathrm{MeLi} \quad + \quad \mathrm{PhC{\equiv}CPh} \xrightarrow[50^{\circ}]{\text{glyme}} \text{no reaction} \qquad (49)$$

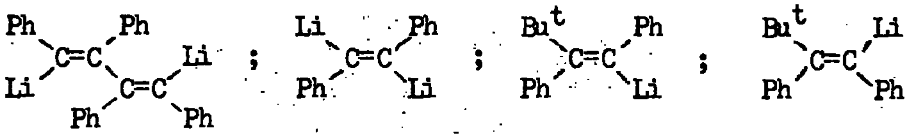
$$\mathrm{PhLi} \quad + \quad \mathrm{PhC{\equiv}CPh} \longrightarrow (Ph)_2C{=}CPhLi \qquad (50)$$

It is not known whether the <u>trans</u> addition observed reflects the stereochemistry of the reaction or whether the <u>cis</u> compound initially formed has isomerised. In those cases where metalation and addition have been observed the evidence supports the conclusion that addition preceded metalation.

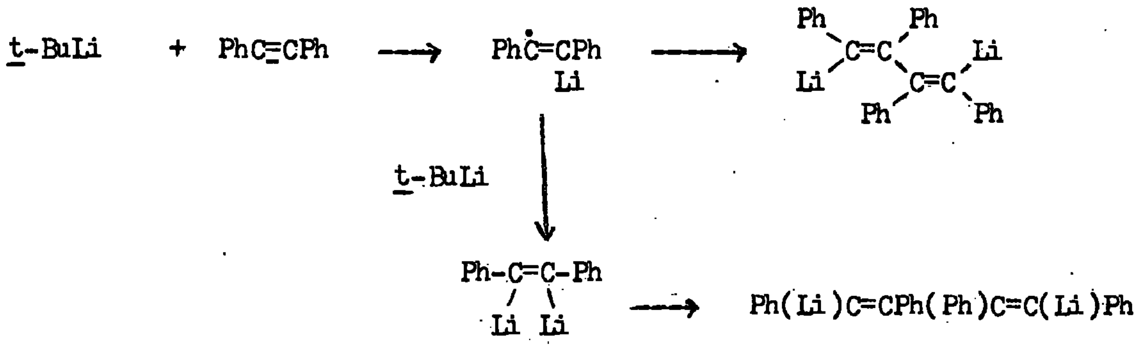
Both reactions (47) and (48) procede rapidly in the presence of TMED.[188] (Recent evidence from n.m.r. and molecular weight studies indicate that <u>n</u>-BuLi,TMED is not an accurate representation of the reacting species in this solution since the smallest aggregate of <u>n</u>-BuLi found in the solution is the tetramer).

When <u>t</u>-BuLi and PhC≡CPh react in hydrocarbon solution at 90° instead of 40°, the reaction takes a different course. Among the products isolated are

are those below,



The 1,3-butadiene derivative is believed to arise *via* an electron transfer process from *t*-BuLi to PhC≡CPh, (51), rather than insertion of PhC≡CPh into an alkenyl-lithium bond[186].



(51)

Reactions of Organomagnesium compounds with alkynes.

Neither Grignard reagents nor diorganomagnesium compounds have been found to add to alkynes in ethereal solvents but they metalate terminal alkynes fairly rapidly and in special cases cause the trimerisation and tetramerisation of internal alkynes.

Many kinetic studies have been carried out on the systems (52) and (53) and yet the mechanism of the reaction is still not understood.

$$RMgX + R'C{\equiv}CH \longrightarrow R'C{\equiv}CMgX + RH \qquad (52)$$

$$R_2Mg + 2R'C{\equiv}CH \longrightarrow (R'C{\equiv}C)_2Mg + 2RH \qquad (53)$$

It is generally agreed that in ether solution (52) is a second order reaction, first order in each reactant (R=Et, R'=Et [189,190]; R=Ph, R'=Ph; R=Benzyl, R'=Ph [191]). At the concentrations most frequently used (1 molar) EtMgBr is approximately dimeric and PhMgBr approximately trimeric. So the reaction probably involves cleavage of these units by the alkyne. A large deuterium isotope effect on substituting RC≡CH by RC≡CD implies considerable ≡C-H bond breaking in the transition state and so a four-centre type transition state is not unreasonable.

The effect on the rate and order of reaction (52) of changing solvent from diethyl ether to tetrahydrofuran is interesting. For the system R=Et, R'=Et, the rate hardly changes but the order changes to three (first in alkyne, secon in Grignard),[190,192] but for the systems, R=Ph,R'=Ph and R=Benzyl, R'=Ph, there is a great increase in rate (3×10^4) but no change in order.[191] The deuterium isotope effect does not appear to be quite as important in THF as in Et_2O.

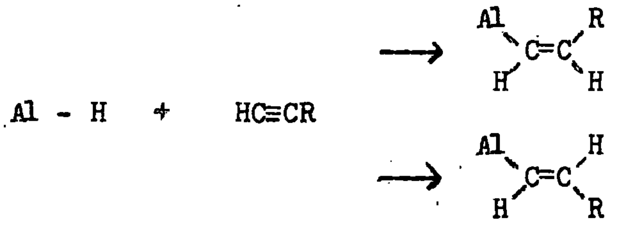
Reaction (53) is bound to be more complicated; a consecutive competitive, second order reaction is proposed for the case R=Et, R'=Et in ether.

One of the most remarkable reactions in main group organometallic chemistry occurs between Ph_2Mg, PhMgBr or BenzylMgCl and PhC≡CPh. Trimerisation of the alkyne to hexaphenylbenzene and tetramerisation to octaphenylcyclo-octatetraene are observed. With MeC≡CPh and MeC≡CMe trimerisation is seen but no tetramerisation. No reactions have been observed with any other organomagnesium compounds[193]

Reactions of Alumium-hydrogen bonds with alkynes

This reaction has been studied in some detail but as much from the point of view of organic synthesis as the study of aluminium containing species.[194-198] Hydroalumination has been shown to depend upon the solvent, the temperature, the reaction time, the acidic properties of the alkyne, and the nature of the Al-H containing species. *Cis*-addition of the Al-H bond to the alkyne, *trans*-addition, bi-addition and metallation have all been observed. By controlling the conditions a pathway involving exclusively one of these reations may be provided.[199]

For terminal alkynes in a hydrocarbon solvent with R_2AlH, addition takes place at about 50° stereospecifically <u>cis</u> (55), in high yield except for the more acidic 1-alkynes like phenylacetylene when metalation (57) is a competing reaction.[94,98,95,102]



trans addition (54)

cis addition (55)

$$\text{Al - H} + \text{HC}\equiv\text{CR} \longrightarrow (\text{Al})_2\text{-CH-CH}_2\text{R} \quad \text{bi-addition} \qquad (56)$$

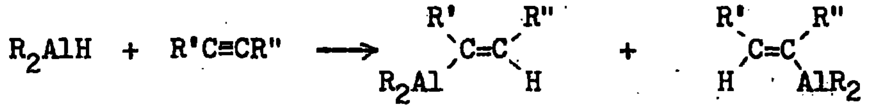
$$\text{Al - H} + \text{HC}\equiv\text{CR} \longrightarrow \text{AlC}\equiv\text{CR} + \text{H}_2 \quad \text{metalation} \qquad (57)$$

It appears that addition of Al-H to 1-alkynes, including $PhC\equiv CH$, always proceeds to put the aluminium on the terminal carbon.[94,95,198] Ether solvents considerably inhibit the mono-addition of R_2AlH and suppress the metallation reaction, but promote the bi-addition (56), so that in THF this is almost quantitative.[200] The metallation reaction (57) can be made practically quantitative by using the complex $R_2AlH.NR'_3$ or by using NEt_3 as the reaction solvent.[103] If hydride and 1-alkyne are used in a 2:1 ratio at about 90° then bi-addition is again the principal reaction path.[201]

Hydrides of the type $MAlH_4$ and $MAlR_{4-n}H_n$ have been employed to prepare alkynyl derivatives by metallation.[104,93,202,203] No addition is observed for the $MAlH_4$ compounds in hydrocarbons, ethers or pyridine.

Amines are reported to catalyse the metallation, while the presence of R_2AlH or R_3Al apparently catalyses the addition reaction at the expense of metallation. The reaction of $MAlR_{4-n}H_n$ takes place easily and in high yield in hydrocarbons but is accompanied by considerable addition in ether solvents.

Hydroalumination of internal alkynes in hydrocarbon solvents or in the absence of solvent is also stereospecifically cis but is more difficult than for 1-alkynes.[94,95] Using unsymmetrical alkynes, there is also the possibility of two orientations.[100]

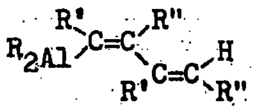

(XVI) (XVII)

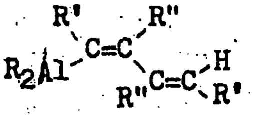
cis addition (58)

The ratio of (XVI) to (XVII) formed in some reactions with i-Bu_2AlH are:

R'=Ph, R"=Me	82	18
R'=Ph, R"=CPh_3	56	44
R'=Ph, R"=CMe_3	100	0
R'=Ph, R"=H	0	100

For the 1:1 reaction (58) minor products arise from the cis-addition of the vinyl-Al bond to another molecule of alkyne giving substituted 1,3-butadienes, and for the 1:2 reaction they are the major products. Only isomer (XIX) has been observed from the 1:1 reactions (R'=Ph,R"=Me; R'=Ph,R"=CMe_3) and only isomers (XVIII) and (XIX) from the 1:2 reaction (R'=Ph,R"=Me) in a ratio C:D = 9:91.

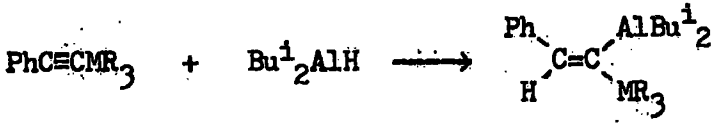

(XVIII)

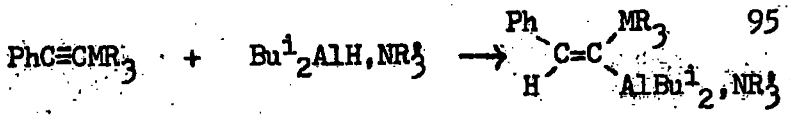

(XIX)

From the results it is seen that the ability to undergo insertion by alkyne is Al-H > Al-C=C > Al-C-C > Al-C≡C, the last being deduced from the fact that insertion into these bonds has never been observed.

If the proportion of alkyne is increased further then hexa-substituted benzenes are produced.[94]

The cis-vinyl products (XVI, XVIII) have been shown to undergo slow thermal isomerisation to the trans-vinyl systems, and it has been suggested that this occurs via a geminal di-addition intermediate. Stereospecific trans-addition has been achieved by using other reagents such as $LiAlH_4$ and $LiBu^i_2MeAlH$ in donor solvents (THF, monoglyme)[197,204] and by using R_2AlH with other alkynes in hydrocarbon solvents (59).[205,206]


95% trans addition (59)


95 % cis addition (60)

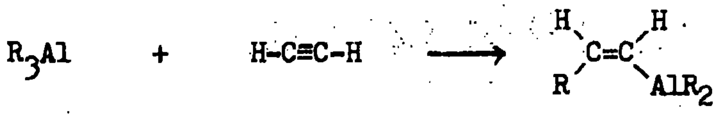
$MR_3 = SiMe_3, GeMe_3, GeEt_3$.

Surprisingly, use of the tertiary amine complex of R_2AlH completely reverses the stereochemistry giving the cis derivatives, (60). In both these cases (59), (60), it was shown that the aluminium atom was attached solely to the same carbon atom as the silicon or germanium groups. This contrasts with case above where $MR_3 = CMe_3$, in which the aluminium was attached only to the same carbon as the phenyl group. Finally in this section, it is reported that bi-addition to internal acetylenes occurs in good yield in refluxing toluene with $LiAlH_4$.[204]

Reactions of Aluminium-carbon bonds with alkynes.

Cis-addition of the Al-C bond of R_3Al to alkynes has been observed in a number of cases when the reaction has been carried out in a hydrocarbon solvent or in the absence of solvent. Comparable reactions in donor solvents and reactions involving $MAlR_4$ species have briefly been mentioned. Metalation is a competing reaction of variable importance depending on the reactants and the conditions.

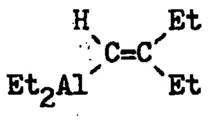
Towards acetylene itself, $i\text{-}Bu_3Al$ adds more readily (20°) than Et_3Al (40-50°), while Me_3Al reacts only by metalation. This reflects the fact that monomeric aluminium species are involved in the addition, (61).[94,95]

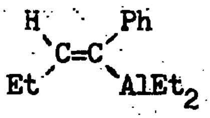

(61)

The addition to 1-alkynes takes place at 40-70° giving vinyl aluminium compounds as the major products. However, metalation is a competing reaction which becomes more important with increasing temperature and increasing acidity of the 1-alkyne (62).[97,98]

$$R_3Al \quad + \quad HC{\equiv}CR' \longrightarrow R_2AlC{\equiv}CR' \quad + \quad H_2 \qquad (62)$$

At 110° for 1-2 hours, the yields of metalated products with phenylacetylene in toluene solution were 60, 45, 40, and 20% for Me_3Al, Et_3Al, n-Pr_3Al, and i-Bu_3Al.[96] The yield of $Ph_2AlC{\equiv}CPh$ by metalation of $PhC{\equiv}CH$ with Ph_3Al (1 hour, benzene, 75-80°) was 86%. For Me_3Al metalation is the predominant course of reaction, and for the complexes $R_3Al.NR'_3$ it is essentially quantitative.[97,99,103] 1-Hexyne and phenylacetylene are reported to combine with Et_3Al in different orientations, (XX) and (XXI), while $PhC{\equiv}CH$ with Ph_3Al gives a mixture of both <u>cis</u> addition products.


(XX)


(XXI)

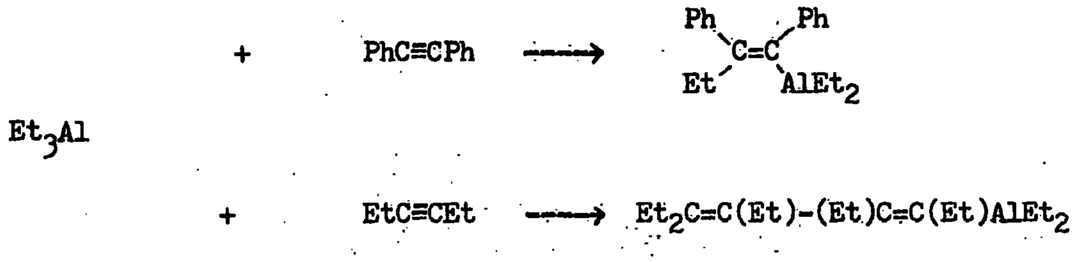
Furthermore, it has been shown for the phenylacetylene reactions that the vinyl-aluminium bonds formed are capable of metalating more $PhC{\equiv}CH$, as in (63).

$$EtHC{=}C(Ph)AlEt_2 \quad + \quad HC{\equiv}CPh \quad \text{----} \quad EtHC{=}CHPh \quad + \quad Et_2AlC{\equiv}CPh \qquad (63)$$

Evolution of i-butene accompanies the reaction of i-Bu_3Al and $PhC{\equiv}CH$ and the product is mainly that formed by addition of i-Bu_2AlH.

In the reactions of salts $MAlR_4$ with phenylacetylene much higher temperatures are required than for reactions with $MAlR_{4-n}H_n$. One alkyl group (R=Me,Et) is displaced at 140-150°, two at 160-180°, and three at 180-200°. No addition of Al-R to the triple bond is noticed.[105]

As for hydroalumination, disubstituted acetylenes are less reactive towards Al-C addition than monosubstituted acetylenes. But above 100° reaction occurs fairly rapidly, Ph_3Al giving <u>cis</u>-addition products with PhC≡CPh, MeC≡CPh, and $Me_3CC{=}CPh$, and Et_3Al giving a <u>cis</u>-addition product with PhC≡CPh. (64) Strangely, for Et_3Al and EtC≡CEt only a 1,3-butadiene compound could be dete detected (65).[94,207]

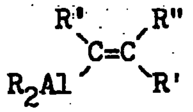


(64)

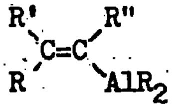
(65)

Heating the addition product $Ph_2AlC(Ph){=}CPh_2$ eliminates benzene and allows the isolation of an aluminium heterocycle.

Unsymmetrical alkynes can give two <u>cis</u> addition products,



(XXII)



(XXIII)

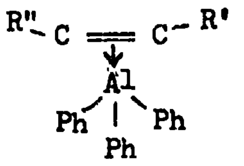
The ratio (XXII) to (XXIII) in reactions involving Ph_3Al shows interesting changes.

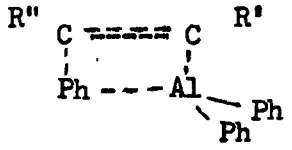
	(XXII)	(XXIII)
R' = Ph, R" = Me	98	2
R' = Ph, R" = CMe_3	5	95
R' = Ph, R" = CPh_3	no reaction at 110°	
R' = Ph, R" = H	37	63

In a kinetic study of the reaction PhC≡CPh/Ph_3Al in hydrocarbon solvents the reaction order was found to be three halves, first order in acetylene and half order in dimer. This corresponds to a reaction involving a monomer-dimer equilibrium followed by rate-determining addition to the acetylene.(66)[208] Ether solvents strongly retard the rate presumably because complex formation makes it more difficult for the alkyne to attain a coordination position about the metal.

$$\begin{aligned} Ph_6Al_2 &\rightleftharpoons 2Ph_3Al \\ Ph_3Al + PhC{\equiv}CPh &\longrightarrow Ph_2Al(Ph)C{=}CPh_2 \end{aligned} \qquad (66)$$

It has been proposed that the second stage proceeds, first via an intermediate π-complex, then via a four-centre transition state, the direction of addition being determined primarily by steric differences between R and R'.[206] Electronic effects have been demonstrated for the Ph_3Al reaction with $ArC{\equiv}CAr'$, but are considered less important.





In view of the fact that the addition reactions of Et_3Al and $i\text{-}Bu_2AlH$ to alkenes and Ph_3Al to alkynes all show similar kinetics, it is to be expected that the addition of R_2AlH to acetylenes will be analogous.[100,209] However, for the hydride additions steric effects do not completely explain the results with $PhC{\equiv}CMe$ and $PhC{\equiv}CCPh_3$, and so electronic effects must be invoked. It is hard to predict the direction of addition that will be preferred by electronic effects, since the polarization of the π-electrons is not known.

Hydroboration of alkynes.

This subject has been described in a book and in several recent articles.[210,211,212] Insertion of alkynes into B-H bonds takes place easily in ether solvents at about 0°. Good yields of vinyl boranes may be obtained from diborane and internal alkynes in a 1:3 ratio $BH_3{:}RC{\equiv}CR$ (67), but the predominant reaction for terminal alkynes involves dihydroboration, (68).

$$R\text{-}C\equiv C\text{-}R \quad + \quad H\text{-}B \longrightarrow (RCH{=}CR)B \qquad (67)$$

$$R\text{-}C\equiv C\text{-}H \quad + \quad H\text{-}B \longrightarrow (RCH{=}CH)B \xrightarrow{H\text{-}B} \text{dihydroboration} \qquad (68)$$

However, use of bis-(3-methyl-2-butyl)-borane, disiamylborane, which has large steric requirements, allows the quantitative monoaddition process to proceed for both internal and terminal alkynes, (69).

$$R\text{-}C\equiv C\text{-}E \quad + \quad (Me_2CHCHMe)_2BH \longrightarrow (RCH{=}CE)B(CHMeCHMe_2) \qquad (69)$$

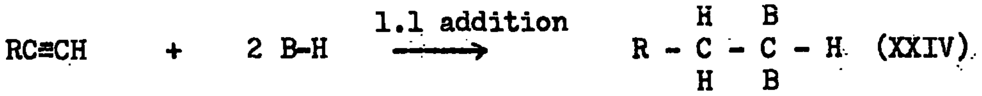
$$E = R, H$$

Monohydrobaoration of terminal alkynes is also achieved using t-$BuBH_2NMe_3$ as the source of hydride but with lower yields, (70).[213]

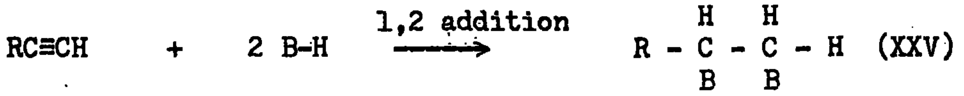
$$2R\text{-}C\equiv C\text{-}H \quad + \quad Me_3N.BH_2Bu^t \longrightarrow (RCH{=}CH)_2BBu^t \quad + \quad NMe_3 \qquad (70)$$

The addition of two B-H bonds to alkynes has been looked at in some detail. It has been found that dihydroboration cannot be taken to completion using diborane. Some of the C=C bonds are believed to become buried in a cross-linked polymer so that they are shielded from the hydride. By making use of the much larger hydrides (2,3-dimethyl-2-butyl)BH_2 or (cyclo-$C_6H_{11})_2BH$, the uptake of B-H bonds per alkyne approaches two.[214,212]

There has been some dispute over the relative quantities of the 1,1-diboro derivatives formed during dihydroboration of 1-hexyne. Now it has been shown conclusively by deuteration and oxidation studies that isomer (XXIV) is by far the most important, accounting for at least 85% of the reaction with diborane and 90-96% of the reaction using 2,3-dimethyl-2-butylborane or dicyclohexylborane.[211,212]



$$RC\equiv CH \quad + \quad 2\ B\text{-}H \xrightarrow{1.1\ \text{addition}} R-\overset{H}{\underset{H}{C}}-\overset{B}{\underset{B}{C}}-H \quad (XXIV) \qquad (71)$$



$$RC\equiv CH \quad + \quad 2\ B\text{-}H \xrightarrow{1,2\ \text{addition}} R-\overset{H}{\underset{B}{C}}-\overset{H}{\underset{B}{C}}-H \quad (XXV) \qquad (72)$$

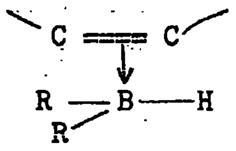
The proportion of the 1,2-diboro compound is reported to be greater than that of the 1,1-diboro compound for other alkynes including acetylene itself.[215]

Unlike the addition reactions exhibited by trialkyl- and triaryl-aluminium derivatives towards acetylenes, the reaction of trialkylboranes results in displacement of alkene in an irreversible step.

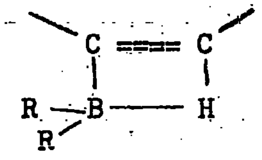
$$3RC\equiv CR \quad + \quad i\text{-}Bu_3B \quad \longrightarrow \quad B(CR{=}CHR)_3 \quad + \quad 3H_2C{=}CMe_2 \qquad (73)$$

This reaction proceeds well for disubstituted acetylenes but gives polymeric products with monosubstituted ones.[216]

Mechanistically, the addition of B-H bonds to olefins and acetylenes is still being investigated. At the present time the evidence is that a.) it involves cis-addition, b.) it involves one molecule of olefin or acetylene and one molecule of hydride dimer,[217] and c.) the orientation of addition is predominantly determined by steric effects rather than electronic effects, the boron being directed to the least substituted carbon atom. It is not yet known if the reaction proceeds via an intermediate π-complex but it is being debated whether the transition state resembles such a complex (XXVI) or whether it resembles more closely the four-centre condition (XXVIII). (For convenience the transition states are shown with hydride monomer rather than dimer.)



(XXVI)



(XXVIII)

Although trialkylboranes do not add to acetylenes, addition of the phenyl-boron bonds of the halides, $PhBX_2$ and Ph_2BX, has been found to occur.[221,222]

Experimental

Apparatus and techniques.

Because most of the compounds studied in this work were sensitive both to oxygen and to moisture, many of the tehniques and most of the apparatus employed were those which enabled work to be carried out in an atmosphere of oxygen- and moisture-free nitrogen or argon.

The compounds were not volatile enough to be handled on a vacuum line and were nearly always prepared and purified in a double-limbed Schlenk tube. The weighing and transfering of air sensitive materials was sometimes carried out on the bench and sometimes in an inert gas-filled glove box, fitted with a recirculation system for purification of the inert gas by removal of oxygen and water. Three methods of purification have been used:

a.) Copper needles at 350° were used to remove oxygen and liquid nitrogen was used to remove moisture. Oxidised copper was regenerated by passing hydrogen through it at 120° and then blowing out the water produced with a stream of nitrogen.

b.) Manganous oxide at 25° supported on vermiculite was used to remove oxygen and molecular sieves (4A and 13X) to remove water. Regeneration of the manganous oxide was achieved by passing hydrogen through at 350°. Water was removed from the molecular sieves by pumping at 200°.

c.) An automatic system was employed (Vacuum Atmospheres Corporation) which used heated copper to remove oxygen and molecular sieves to remove moisture. A 95%:5% mixture of argon:hydrogen was circulated through the box and the purification system. In this way oxidised copper was regenerated during normal use. An atmosphere containing less than 1 p.p.m. oxygen or water was easily maintained.

In all the three cases connections were made wherever possible using copper tubing and the gloves were made of butyl rubber to minimise permeability to to oxygen and water.

Vacuum line techniques were employed for the separation, purification and measurement of gases. The vacuum line was divided into two parts: a.) A fractionation train consisting of U-traps connected by mercury float valves, used for the separation and purification of gases, and a Topler pump used for the measurement of gases. This section of the vacuum line was particularly important for the analysis of gases produced by the hydrolysis of organometallic compounds. b.) A number of storage bulbs for gases and volatile liquids each connected to the main line by a mercury float valve, and a standard bulb for measurement of larger quantities of gas. At the top of the Topler pump was a connection whereby a combustion bulb or an infrared gas cell could be attached.

Analyses a.) Gas Analyses

Compounds which evolved gas on hydrolysis were analysed by adding 2-methoxyethanol to a weighed sample contained in a flask attached to the vacuum line and frozen at -196°. The mixture was allowed to warm up slowly and hydrolysis was completed by the addition of water followed by 2N sulphuric acid. The 2-methoxyethanol, water, and 2N sulphuric acid were degassed prior to use. After fractionation and measurement the gases were identified by their i.r. spectra. All gas volumes were corrected to N.T.P.

b.) Beryllium Analyses

The solution from hydrolysis was made up to a standard volume and then aliquots containing 3-5 mg. of beryllium were treated as follows. To each aliquot was added 5 ml. of 0•5M potassium sodium tartrate, 4 drops of a 1% solution of bromothymol blue in 50:50 water:ethanol, and sufficient 1M sodium hydroxide to give a blue colour to the solution. Each solution was then made green by the addition of 0•1N sulphuric acid. This was the end point for this indicator. Addition of 5 ml. of 1M KF solution caused the solution to become blue. Finally the blue solution was titrated accurately with 0·1N sulphuric acid until the same green colour as had been obtained earlier, returned and persisted. The essence of the method is the formation of a tartrate complex of beryllium hydroxide which is destroyed by the addition of fluoride ions liberating hydroxide ions in proportion to the beryllium in the solution. The tartrate is necessary to keep the $Be(OH)_2$ in solution.

$$\text{complexed } Be(OH)_2 \quad + \quad 4F^- \quad \longrightarrow \quad BeF_4^{2-} \quad + \quad 2OH^-$$

Because the reaction is not stoichiometric, standard beryllium solutions must be used to make a calibration graph plotting milligrams of beryllium versus ml. 0·1N sulphuric acid. From the volume of 0·1N H_2SO_4 required for the final titration, any unknown quantity of beryllium can then be found.

The presence of amines or of large concentrations of ions was found to cause drifting of the end point. The quantity of acid used in the hydrolysis was kept to a minimum and where possible amines were removed berfore beryllium analysis by pumping the alkaline solution.

c.) Analysis of lithium alkyls.

Solution of lithium alkyls in hydrocarbon solvents were analysed by the method of Watson and Eastham[229] whereby the concentration of hydrolysable alkyl groups was measured, and by syringing a known volume into distilled water and titrating the hydroxide produced against standard acid, whereby the concentration of lithium was measured. Any difference between the two values was a measure of the alkoxide content in the solution. The method of Watson and Eastham involves titrating the lithium alkyl with a standard (approx. 1M) solution of sec-butanol in xylene using 1,10-phenanthroline as the indicator.

d.) Lithium analyses.

Lithium solutions were analysed using an 'Eel' flame photometer, calibrated over a concentration range in which the calibration curve was approximately linear, i.e. 0·0001 - 0·001 moles Li per litre.

e.) Amine analysis

Volatile amines were estimated by taking an aliquot of the acid solution from hydrolysis, adding excess sodium hydroxide and then steam distilling the amine into an excess of standard acid. The excess acid was titrated with standard alkali. For TMED both nitrogens remain protonated if screened methyl orange is used as the indicator.

f.) Analysis for phenylacetylene.

Phenylacetylene produced by hydrolysis was extracted with hexane. The hexane solution was made up to 100 ml. and then 1 ml. of this solution was diluted ca. 125 times. The UV spectrum of this solution was recorded and the absorbance at 240 mμ measured. The value obtained allowed the concentration of phenylacetylene in the solution to be read from a calibration graph plotting concentration (gms litre^{-1} x 10^{3}) versus absorbance at 240 mμ.

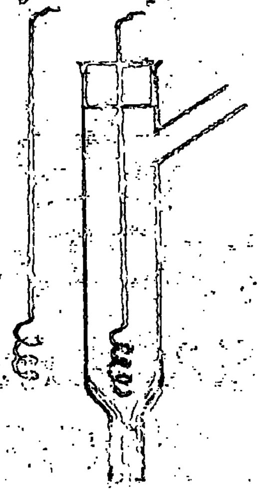
It was found that over the concentration range 2-10 x 10^{-3} gm. litre^{-1} phenylacetylene obeys Beer's Law. The path length was 1 cm. and the reference was hexane.

g.) Pyridine analysis.

Pryidine was estimated by a method analogous to that for phenylacetylene. The acid solution from hydrolysis was diluted ca. 100 times and the absorbance at 256 mμ was measured. A calibration graph enabled the concentration of pyridine to be found. The path length was 1 cm. and the reference was distilled water.

h.) Halide analyses.

Chloride and bromide in acid solution were determined by a potentiometric technique. The cell, shown below, contains a Ag,AgCl or a Ag electrode separated from another silver electrode except for a capillary tube. Since both electrodes are sensitive to the concentration of silver ions, any difference in concentration of silver ions between the solution inside the tube and the solution outside the tube will be reflected in a difference in electrode potential between the electrodes. The end-point of the titration is the time when the concentration of silver ions in the solution is undergoing its greatest change per unit volume of added silver nitrate solution. Thus the position of greatest difference in electrode potential will be the end-point. Successive equal portions of 0•01M $AgNO_3$ are added to the halide solution, each time having the composition of the solution inside the tube the same as that outside before the addition. After each addition the difference in potential between the electrodes is measured. Decreasing the volume of 0•01 $AgNO_3$ added each time increases the sensitivity and improves the accuracy of the titration.



i.) Molecular Weights.

Cryoscopic molecular weights were determined in benzene solution where solubility permitted. The benzene was dried over sodium wire and the cryscopic constant was determined by calibration using solution of freshly sublimed biphenyl.

Spectra a.) Infrared spectra.

Infrared spectra were recorded using a Grubb-Parsons Spectromaster or a Perkin-Elmer 621 instrument in the region 4000-400 cm^{-1}. The spectra of solids were recorded an Nujol mulls between KBr plates, those of liquids as a liquid film between KBr plates, and those of gases using a 10 cm. cell with KBr windows and a gas pressure of 1-3 cm.Hg. Specimens of air sensitive materials were prepared in a glove box.

b.) Ultraviolet spectra.

The ultraviolet (UV) spectra of solutions containing phenylacetylene or pyridine were recorded on a Unicam SP 800 spectrophotometer in the range 225-350 m .

c.) Proton magnetic resonance spectra.

Proton magnetic resonance spectra (p.m.r. spectra) were recorded at 60 MH_z on a Perkin-Elmer R10 spectrometer operating at 33·5° or at 100 MH_z on a Varian HA100 instrument operating at 25-30°. Tetramethylsilane (TMS), benzene, and cyclopentane were the most commonly used internal standards. The samples were usually prepared as 10-15 wt.% solutions.

Chromatography. Gas-liquid chromatography.

This was used occasionally to find out the number of products formed during certain reaction products. Carbowax and apiezon colums were used at temperatures of about 50°. The instruments used were a Pye 104 chromatograph and a Perkin-Elmer 154.

Purification and preparation of starting materials.

Solvents

Pentane, hexane, benzene, toluene, methylcyclohexane, diethyl ether and tetrahydrofuran were dried over sodium. Diethyl ether, tetrahydrofuran, benzene and 1,2-dimethoxyethane were also dried in solvent stills over lithium aluminium hydride. The solvent was refluxed in the still for about 30 min. prior to use.

Amines, pyridine and 2,2'-bipyridyl

Monomethylamine, dimethylamine, ammonia, and trimethylamine were dried over phosphorus pentoxide or calcium hydride and then stored on the vacuum line.

Triethylamine was distilled from $LiAlH_4$ just before use, as was TMED. Pyridine was distilled from potassium hydroxide on to potassium hydroxide under nitrogen. 2,2'-Bipyridyl, m.p.t. 72°, was sublimed at $70^{\circ}/10^{-2}$ mm on to a -78° cold finger, leaving the major impurity, terpyridyl, unsublimed. Diphenylamine was purified by sublimation at $70^{\circ}/10^{-3}$ mm, m.p.t., 53°. Aniline was distilled from zinc dust to give a colourless luquid, b.pt., 184°.

Alcohols

Methanol was refluxed over magnesium turnings and then distilled, and t-butanol was refluxed over aluminium turnings activated with a trace of mercuric chloride before it was distilled. Phenol, m.pt. 43°, was sublimed at $40\text{-}50^{\circ}/10^{-3}$ mm.

Alkyl halides

Methyl bromide, ethyl bromide, neo-pentyl chloride and benzyl chloride were used without purification.

Alkynes

Propyne was purified by fractionating the gas through a -96° bath, and 2-butyne was purified by fractionation through a -78° bath. Phenylacetylene and methyl(phenyl)acetylene were purified by distillation under reduced pressure before use. Diphenylacetylene was used without further purification.

Lithium Alkyls

n-Butyl-lithium was purchased from Pfizer Co. or Foote Chemical Co. Methyllithium in ether was prepared by the reaction of methyl chloride with lithium metal.

Grignard Reagents

These were prepared by the standard method from magnesium turnings and an alkyl halide in diethylether. The yields varied with the nature of the alkyl group. The solutions were analysed for hydrolysable alkyl before further use.

Beryllium Chloride and Beryllium Bromide

These compounds were prepared by heating beryllium powder in a stream of chlorine or bromine vapour diluted with nitrogen. The products were sublimed into a receiver flask. Yield 80-90%.

Beryllium Dialkyls

The preparation of beryllium dialkyls was normally carried out on a 0·5 molar scale. Ether was added to a known quantity of beryllium chloride cooled to -78°. When the beryllium chloride was covered with ether, the mixture was allowed to warm up to room temperature. More ether was added and the mixture warmed so that the ether was refluxing. With vigorous stirring the beryllium chloride dissolves giving two liquid layers. The upper layer is a dilute solution of beryllium chloride in ether while the lower layer is predominantly an ether complex of beryllium chloride. The required quantity of Grignard reagent is then added fairly rapidly (30 mins.) to the beryllium chloride solution with vigorous stirring. After the final addition the ether solution of beryllium dialkyl and the precipitated magnesium halide are stirred for a further 30 mins. The ether solution is decanted off, concentrated to about 200 ml. and then transferred to a distillation flask. The dialkyls can be distilled as the etherates at about $70^{\circ}/10^{-2}$ mm. Hg.

Dimethylberyllium is a polymeric solid. This product is purified either by continuous 'ether distillation'[223], or by sublimation.

Triethylboron

This was prepared from triethylaluminium and trimethylboroxine according to a published procedure.[224] The product was distilled from the reaction mixture, b.pt. 89-90°.

Sodium triethylboron hydride

Sodium hydride (excess) was stirred with triethylboron in hexane to give sodium triethylboron hydride in solution. Excess sodium hydride was filtered off and the solution analysed for hydrolysable hydrogen.[225]

Lithium hydride

Lithium hydride was available commercially. It was hydrolysed to determine the weight per cent purity from the quantity of hydrogen produced.

Methyl- and ethyl-beryllium hydride trimethylamine complexes

These complexes were prepared by the reaction of lithium hydride with methyl- or ethyl-beryllium bromide in ether. Addition of benzene, removal of ether, and filtration from the lithium bromide precipitate, left a solution of the hydride in benzene/ether. On removal of the solvent, addition of excess trimethylamine and then removal of the excess a white solid was obtained. Sublimation of the solid at $50^{\circ}/10^{-3}$ mm. Hg. gave the pure methyl- or ethylberyllium hydride trimethylamine complexes.

Experimental Results

1. Coordination complexes of diphenylethynylberyllium

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

Preparation of diphenylethynylberyllium N,N,N',N'-tetramethylethylenediamine. To a solution of methyl-lithium (18•70 millimoles) in ether, a solution of phenylacetylene (2•05 mls, 18•70 millimoles) in ether (10 mls) was added slowly. A gas evolved leaving a clear solution. Beryllium chloride (0•751 gms, 9•38 millimoles) was dissolved in ether (20 mls) and syringed into the solution. An exothermic reaction took place and a white precipitate of lithium chloride was produced. Removal of ether left a yellow oil. 20 mls of ether were added to dissolve the oil and TMED (1•38 mls, 9•35 millimoles) added slowly. A white precipitate was produced which was filtered and washed with ether. Recrystallisation from a benzene/hexane mixture gave small colourless needles. The needles melted in a sealed tube under nitrogen at 168-170° giving a colourless liquid. The complex could also be formed by addition of TMED to diphenylethynylberyllium bis-(tetrahydrofuran) in benzene and subsequent recrystallisation from benzene/hexane. Found: hydrolysable phenylethynyl, 61•2%; Be, 2•72%; TMED, 35•1%; M(cryoscopically in 0•82,1•24 wt.% in benzene), 320,333. $C_{22}H_{26}BeN_2$ requires hydrolysable phenylethynyl, 61•8%; Be, 2•75%; TMED, 35•5%: M, 327. The infrared spectrum, recorded as a Nujol mull contained absorptions, below 20000 cms^{-1} at: 509 m; 536 m; 547 w; 608 m; 680 s,br; 699 s; 724 w; 760 s; 800 s; 868 s; 919 m; 953 m; 990 w; 1026 m; 1042 m; 1071 w; 1105 w; 1124 w; 1153 vw; 1176 w; 1210 s; 1284 m; 1350 w; 1488 m; 1592 m; cm^{-1}. s - strong, m - medium, w - weak, v - very, br - broad, sh - shoulder. These abbreviations are used throughout for i.r. spectra.

The p.m.r. spectrum was recorded as a solution in d_6-benzene with TMS as internal standard. The spectrum showed:

Type	τ	Assignment	Relative Intensity
Multiplets	Centered at 2·30 and 2·85	$C_6\underline{H}_5C\equiv C$	5
Singlet	8·09	$N-C\underline{H}_2$	2
Singlet	7·71	$N-C\underline{H}_3$	6

Sublimation of the complex was attempted. With a cold finger at -78° and an adjacent trap at -196°, the complex was heated at 110-120°/10^{-3}mm. There was slow depostion of a white solid on the cold finger. At 150-160°/10^{-3}mm it was only a little faster. Some decomposited material remained in the tube. The melting point and infrared spectrum were identical to that of the starting material showing that some of the complex had sublimed unchanged. No volatile material was collected in the -196° trap.

Preparation of diphenylethynylberyllium bis-(tetrahydrofuran).

Phenylacetylene (2·05 mls, 18·70 millimoles) was added in ether solution to methyl-lithium (18·70 millimoles) in ether. A solution of beryllium chloride (0·747 g., 9·34 millimoles) in ether was added slowly and the lithium chloride was filtered leaving a pale yellow clear solution. On removal of most of the ether an oil remained to which was added excess tetrahydrofuran (10 ml.). When the oil had dissolved hexane was added slowly. A white precipitate was produced which recrystallised from THF/hexane mixture as colourless needles, which melted at 138-140° to give a red liquid. The compound could also be recrystalised from benzene/hexane. Found: hydrolysable phenylethynyl, 56·7%; Be, 2·52%; M(cryoscopically in 0·49, 0·84 wt.% in benzene), 352,365. $C_{24}H_{26}BeO_2$ requires hydrolysable phenylethynyl, 56·9%; Be, 2·55%; M, 355. The infrared spectrum was recorded as a Nujol mull: 493 m,br; 515 w,br; 550 m,br; 620 m,br; 635 m,br; 694 s; 709 s,sh; 722 m; 757 s; 795 m; 813 w,sh,br; 873 s; 894 m,sh; 921 m; 961 w; 995 w; 1037 s; 1070 m; 1176 w; 1209 s; 1490 s;

1594 w. Even when the spectrum was recorded as a very thick mull there was no peak in the 2000-2500 cm^{-1} region. The p.m.r. spectrum was recorded as a solution in d_6-benzene with TMS as the internal standard.

Type	τ	Assignment	Relative Intensity
Multiplets	Centered at 2·30 and 2·86	$C_6\underline{H}_5{\equiv}C$	1·5
Distorted triplet	Centered at 6·02	$O{-}C\underline{H}_2$	1
Distorted triplet	Centered at 8·59	$O{-}CH_2{-}C\underline{H}_2$	1

Preparation of diphenylethynylberyllium bis-(pyridine).

Following the same procedure as for the preparation of the THF complex, a solution of diphenylethynylberyllium in tetrahydrofuran was obtained to which was added excess pyridine. A white precipitate was produced insoluble in THF, hexane and toluene at room temperature and insoluble in toluene at 80°. After filtering and washing well with hexane the white precipitate was pumped dry. A sample of the compound in a sealed tube under nitrogen melted at 226-230° giving a black liquid. Found hydrolysable phenylethynyl, 53·9%; Be, 2·43%. $C_{26}H_{20}BeN_2$ requires hydrolysable phenylethynyl, 54·8%; Be, 2·44%. The infrared spectrum recorded as a Nujol mull showed: 501 m; 513 m; 535 w; 562 s; 618 m; 657 s; 66 m; 690 s; 698 s; 706 s,sh; 727 w; 756 s; 799 m; 809 m; 869 s; 913 w; 1021 m; 1050 s; 1074 s; 1158 w; 1212 s; 1490 s; 1569 vw; 1597 m; 1616 s.

Preparation of diphenylethynylberyllium bipyridyl.

$(PhC{\equiv}C)_2Be(THF)_2$ (0·894 g., 2·52 millimoles) was dissolved in 10 mls. THF. Freshly sublimed bipyridyl (0·393 gms, 2·53 millimoles) was dissolved in 10 mls. THF and added slowly to the first solution. A white precipitate formed which was filtered washed with hexane and dried. The solid appeared to consist of fine white plates, which melted to a black liquid 295-302°. It was insoluble in benzene. Found: hydrolysable phenylethynyl 53·3%; Be, 2·41%. $C_{26}H_{18}BeN_2$ requires hydrolysable phenylethynyl, 55·0%; Be, 2·45%. The infrared spectrum recorded as a Nujol mull showed absorptions: 511 w,br; 535 w; 560 m; 635 m; 666 m; 671 m; 693 m; 707 m; 718 m; 745 m; 757 s; 780 m; 800 s; 813 s,sh; 873 s,br; 913 m; 1026 s; 1041 s; 1062 s; 1069 s; 1092 m; 1104 s; 1162 w; 1180 w; 1208 m; 1264 m; 1317 m; 1492 s; 1574 w; 1605 m; 1618 s.

Preparation of diphenylethynylberyllium 1,2-dimethoxyethane.

1,2-dimethoxyethane (1 ml.) in benzene (5 ml.) was added slowly to $(PhC\equiv C)_2Be(THF)_2$ in benzene (10 ml.). A clear colourless solution was formed. On addition of a few mls. hexane a precipitate of white feather-like crystals was formed that would not redissolve in benzene. The precipitate was filtered, washed with hexane and pumped dry. A sample of the compound was found to melt to a red liquid at 190°. Found: hydrolysable phenylethynyl, 67·1%; Be, 3·02%. $C_{20}H_{20}BeO_2$ requires hydrolysable phenylethynyl 67·1%; Be, 2·99%. The infrared spectrum recorded as a Nujol mull contained absorptions: 506 m; 517 m; 540 m; 602 m; 647 w; 667 sh,m; 675 s; 695 s; 720 w; 757 s; 798 m; 812 w; 876 s; 916 w; 1016 w; 1026 w; 1050 s; 1075 m,sh; 1081 s; 1191 w; 1213 m; 1234 w; 1267 w; 1490 m; 1568 vw; 1597 w.

Dissociation of diphenylethynylberyllium bis-(trimethylamine).

a.) 0·240 G., 0·730 millimoles, of the complex were pumped at 20-25°/ 10^{-3}mm for 24 hours. After this time 0·3 N ccs of a gas was collected in an adjacent -196° trap. This amounts to about 1% of the complexed trimethylamine.

b.) 0·243 G., 0·739 millimoles, of the complex were heated at 70°/10^{-3}mm for 24 hours. 13·5 N ccs of trimethylamine were collected, corresponding to 40·9% of the complexed trimethylamine.

c.) 0·248 G., 0·754 millimoles, of the complex were heated at 90-100°/10^{-3}mm for 24 hours and 15·45 N ccs of trimethylamine were collected, corresponding to

45·7% of the complexed trimethylamine.

Preparation of diphenylethynylberyllium diethyletherate.

A standard solution of diphenylethynylberyllium in ether was prepared in the following way. 27·8 mls of 2·17M n-BuLi in hexane (62·3 millimoles) were put into one arm of a large double Schlenk tube. The hexane was removed leaving a brown liquid. This was cooled to about -20° and 30 mls ether added slowly. To the solution of n-BuLi in ether at -10°, phenylacetylene (6·80 ml.) was added dropwise. A gas was evolved on addition of each drop. When all the phenylacetylene had been added the solution was allowed to warm up to room temperature and to filter through the sinter into a solution of $BeCl_2$ in ether (2·481 G., 31 millimoles). A white precipitate of LiCl immediately formed which was filtered to leave a clear brown solution. Analysis of the solution showed it to be 0·410M in beryllium and 0·845M in phenylethynyl.

8 ml. of the ether solution (3·28 millimoles) were filtered and white crystalline needles were obtained from the filtrate. In another experiment the ether was removed and white crystalline needles were obtained by recrystallisation from benzene. The crystals went yellow on standing for a few days, and a solution in benzene went orange on standing for a few weeks. On heating the crystals redden and darken from about 120°, finally melting to a dark red liquid at 149-151°. Found: hydrolysable phenylethynyl, 69·5; Be, 3·19. $C_{20}H_{20}BeO$ requires hydrolysable phenylethynyl, 71·5%; Be, 3·16%. Found: M(cryoscopically in 0·93, 0·63 wt.% in benzene), 496,451. $C_{20}H_{20}BeO$ requires M, 285. This corresponds to degrees of association of 1·74 and 1·58. The infrared spectrum showed: 536 w; 558 m; 673 m; 690 s; 695 s; 719 w; 761 s; 776 m; 797 m; 811 w; 838 m; 876 m; 904 s; 913 m; 1000 m; 1031 s; 1067 w; 1090 m; 1150 w; 1176 vw; 1190 vw; 1212 w; 1485 w; 1595 w. It also had an absorption at 2105 cms^{-1} of medium strength. The p.m.r. spectrum in d_6-benzene with TMS as internal reference showed the following resonances:

Type	τ	Assignment	Relative Intensity
Multiplets	Centered at 2·29 and 2·91	$C_6\underline{H}_5C\equiv C$	5
Quartet	5·75, 5·87, 5·99, 6·11	$O\text{-}C\underline{H}_2\text{-}CH_3$	2
Triplet	8·78, 8·90, 9·02	$O\text{-}CH_2\text{-}C\underline{H}_3$	3

Preparation of diphenylethynylberyllium triethylamine.

10 Mls. of the 0·41M solution of diphenylethynylberyllium in ether were taken and the ether removed to leave a white solid. The solid was dissolved in benzene (10 ml.) and excess triethylamine (6 ml.) added. Removal of the solvent left a white solid. Recrystallisation from benzene/hexane left large colourless prisms. Yield 65%. Melting point, 102-6°. Found: hydrolysable phenylethynyl, 66·1%; Be, 2·88%; M(cryoscopically in 0·74, 1·11 wt.% solution in benzene), 304, 315. $C_{22}H_{25}BeN$ requires hydrolysable phenylethynyl, 64·8%, Be, 2·88%; M, 312. The infrared spectrum recorded as a Nujol mull, showed: 513 w; 524 vw; 537 m; 557 m; 586 m,br; 637 s,br; 693 s; 701 m,sh; 746 m; 760 s; 786 m,br; 810 m; 838 s; 899 m; 907 m; 913 w; 999 w; 1015 m; 1028 m; 1039 m; 1049 m; 1068 m; 1086 m; 1102 w; 1165 m; 1183 w; 1209 m; 1257 vw; 1300 vw; 1485 m; 1567 vw; 1592 w. There was an absorption at 2090 of medium strength. The p.m.r. spectrum recorded in d_6-benzene with TMS as internal standard showed the following resonances:

Type	τ	Assignment	Relative Intensity
Multiplets	Centered at 2·36 and 2·94	$C_6\underline{H}_5C\equiv C$	10
Quartet	7·23, 7·35, 7·47, 7·59	$N\text{-}C\underline{H}_2\text{-}CH_3$	6
Triplet	9·07, 9·19, 9·31	$N\text{-}CH_2\text{-}C\underline{H}_3$	9

In another experiment 1·4 ml. excess triethylamine was added to 3·28 millimoles of diphenylethynylberyllium in ether (8 ml.). The solvent and excess triethylamine was removed and colourless prisms were obtained from benzene solution. Analysis showed that there remained about 2-3% ether in the product.

Addition of NEt$_3$, (2 ml., excess), to a solution of $(PhC{\equiv}C)_2Be(THF)_2$ (0·918 G., 2·59 millimoles) in 20 ml. benzene. The solvent was removed and the solid remaining crystallised from benzene/hexane as colourless needles, whose m.pt. and i.r. spectrum were identical with those of the bis-tetrahydrofuran complex.

Attempted preparation of diphenylethynylberyllium mono-pyridine.

8·0 Ml. of the ether solution of diphenylethynylberyllium (0·41M) were taken and the solvent removed giving a brown oil. 5 Ml. hexane were added and the ether/hexane solvent evaporated to leave a brown solid. This was dissolved in benzene and pyridine (0·26 ml., 3·27 millimoles) added slowly. When the solution was reduced in volume a precipitate appeared, that would not redissolve in benzene. The m.pt. and i.r. spectrum of the solid were identical to those of $(PhC{\equiv}C)_2Be,py_2$.

Preparation of diphenylethynylberyllium trimethylamine.

A solution of diphenylethynylberyllium etherate (3·71 millimoles) in benzene was frozen in liquid nitrogen and trimethylamine (82·5 N ccs, 3·69 millimoles) was condensed on. On warming the mixture under vacuum in a closed system a white precipitate was seen. Another 5 ml. benzene was added and the solution warmed. The precipitate dissolved at about 60-80° and slow cooling gave small white needles, which melted at 186-188° to give a red liquid. The compound was only sparingly soluble in benzene at room temperature.

Found: hydrolysable phenylethynyl, 73·1%; Be, 3·25%; NMe$_3$, 20·0%.
$C_{19}H_{19}BeN$ requires hydrolysable phenylethynyl, 74·8%; Be, 3·33%; NMe$_3$, 21·9%.
Infrared spectrum recorded as a Nujol mull showed: 519 vw; 527 vw; 535 w; 555 w; 606 s,br; 638 s,br; 673 m,sh; 687 s; 706 s; 762 s; 783 s; 826 s; 836 s; 914 w; 967 vw; 939 s; 1022 w; 1030 w; 1068 w; 1107 w; 1149 vw; 1156 vw; 1173 vw, 1200m;

1237 w; 1477 m; 1562 vw; 1587 w. There was also a medium strength band at 2085 cms^{-1}.

<u>Reaction of $(PhC{\equiv}C)_2Be(THF)_2$ with dimethylamine.</u> <u>Preparation of diphenylethynylberyllium bis-(dimethylamine).</u>

a.) 1:1 ratio.

The tetrahydrofuran complex $(PhC{\equiv}C)_2Be(THF)_2$ (1·4kk G., 4·19 millimoles) was dissolved in benzene (16 ml.). The solution was frozen in liquid nitrogen and $NHMe_2$ (94·0 N ccs, 4·20 millimoles) was condensed on. On warming to room temperature in a closed system, a white precipitate was observed. The solution was warmed to dissolve the solid and filtered hot. Long thin needles crystallised on cooling, which were filtered, washed with hexane and dried. From the filtrate more solid was produced when the hexane mixed with the benzene solution. The m.pt. and infrared spectrum of the solid from the filtrate were the same as those of the bis-tetrahydrofuran complex. The first crystalline compound melted, 152-158°, and analysed: hydrolsable phenylethynyl, 66·1; Be, 2·70%; $NHMe_2$, 25·2%. $(PhC{\equiv}C)_2Be(NHMe_2)_2$ (= $C_{20}H_{24}BeN_2$) requires hydrolysable phenylethynyl, 67·1%; Be, 2·99%; $NHMe_2$, 29·9%. These analysis figures were not good so the experiment was repeated using a 1:2 ratio.

b.) 1:2 ratio.

The tetrahydrofuran complex $(PhC{\equiv}C)_2Be(THF)_2$, (0·683 G., 1·92 millimoles) was dissolved in benzene and $NHMe_2$ (106 N ccs, 4·73 millimoles) condensed on as before. A precipitate was formed which recrystallised from benzene as colourless needles. After washing and drying, a flaky white solid remained, m.pt. 151-153° without dec. The compound was not appreciably soluble in benzene at room temperature. Found: hydrolysable phenylethynyl, 67·3%; Be, 2·94%; $NHMe_2$, 29·1%. This corresponds to $(PhC{\equiv}C)_2Be(NHMe_2)_2$. The infrared spectrum recorded as a Nujol mull showed; 518 w; 533 w; 655 m; 792 s; 719 m; 754 s; 796 m; 806 w,sh; 841 s; 901 m; 909 m; 1025 s; 1039 m; 1062 w; 1070 w; 1123 w; 1176 w;

1206 w; 1219 w,sh; 1274 w,br; 1468 m; 1595 w; there were also bands at 3225 w, 3257 w,sh.

Reaction of $(PhC{\equiv}C)_2Be(THF)_2$ with monomethylamine. Preparation of diphenylethynylberyllium bis-(monomethylamine).

a.) 1:1 ratio.

The tetrahydrofuran complex $(PhC{\equiv}C)_2Be(THF)_2$, (1·757 G., 4·95 millimoles) was dissolved in benzene (15 ml.). The solution was frozen in liquid nitrogen and NH_2Me (111 N ccs., 4·96 millimoles) was condensed on. On allowing the solution to warm to room temperature a white precipitate was observed. Warming to 60-80° dissolved the precipitate and the solution was then filtered hot. Removal of some solvent allowed the isolation of a small quantity of colourless needles, m.pt. 85-86°. No more solid was precipitated from the filtrate until very little solvent remained. More solid was obtained by adding a little hexane to the filtrate. An infrared spectrum of this solid showed it to contain mainly the starting material with a small quantity of another compound.

b.) 1:2 ratio, without heating.

The tetrahydrofuran complex $(PhC{\equiv}C)_2Be(THF)_2$, (0·621 G., 1·75 millimoles) and $MeNH_2$ (97 N ccs, 4·33 millimoles) were mixed in benzene (8 ml.) as above. A white precipitate was formed which was filtered, washed, and dried without heating. The melting point of the solid was 86-7°, and the infrared spectrum was identical to that of the colourless needles from the 1:1 reaction. Found: hydrolysable phenylethynyl, 72·3%; Be, 3·32%; NH_2Me, 22·2%. $C_{18}H_{20}BeN_2$ requires hydrolysable phenylethynyl, 74·0%; Be, 3·30%; $MeNH_2$, 22·7%. The infrared spectrum recorded as a Nujol mull showed: 523 w; 536 w; 650 w,br; 666 w; 675 w; 694 s; 702 s,br; 761 s; 796 m; 858 s; 913 w; 1016 s; 1029 w; 1049 s; 1070 m; 1156 vw; 1178 vw; 1205 m; 1238 m; 1259 w,sh; 1336 w; 1485 m; 1588 m; there were also bands 3145 w, 3230 m, 3285 w, and a very weak band at 2100 cm^{-1}.

c.) 1:2 ratio, with heating.

The tetrahydrofuran complex $(PhC{\equiv}C)_2Be(THF)_2$, (1·41 G., 3·97 millimoles) and $MeNH_2$ (190 N ccs, 8·48 millimoles) were mixed in benzene as above. A white precipitate was obtained again, which would not dissolve in 35 ml. benzene at room temperature. However, it dissolved in about 15 minutes in benzene at about 80°. No solid came out of solution on cooling. Solvent was removed until about 4 ml. were left, and then solid started to be seen. Addition of a little hexane (4 ml.) produced a white solid, which was filtered, washed with benzene, and dried. It would not redissolve in benzene and did not melt below 300°. Found: hydrolysable phenylethynyl, 38·9%; Be, 6·94%; Amine, 45·8%. Ratio Be:N:PhC≡C = 1·0:1·92:0·49.

Reaction of $(PhC{\equiv}C)_2Be(THF)_2$ with aniline. Preparation of diphenylethynylberyllium bis-(monophenylamine).

The tetrahydrofuran complex $(PhC{\equiv}C)_2Be(THF)_2$ (1·088 G., 3·07 millimoles) was dissolved in benzene (15 ml.) and aniline (0·285 G., 3·06 millimoles) in benzene (5 ml.) was added slowly with stirring. There was immediate precipitation of a white solid. Without attempting to recrystallise it, the solid was filtered, washed with benzene, and dried. It was insoluble in benzene at room temperature. On heating it softened at 204–7° but did not melt below 310°. Found: hydrolysable phenylethynyl, 52·0%; Be, 2·28%; $PhNH_2$, 47·4%. $C_{28}H_{24}BeN_2$ requires hydrolysable phenylethynyl, 52·6%; Be, 2·35%; $PhNH_2$, 48·6%. The infrared spectrum recorded as a Nujol mull showed: 492 w; 516 w; 534 w; 543 w; 550 w; 622 w; 631 w; 687 s; 723 w,br; 752 s; 760 s; 794 w; 802 w; 816 w; 825 w,sh; 885 s; 893 m,sh; 1003 w; 1030 w; 1067 m; 1096 s; 1149 w; 1176 w; 1211 w; 1350 w; 1493 m; 1501 m; 1587 s; 1637 m. There were also bands at 3139 w, 3226 m, and 3268 w, and a very weak band at 2114 cm^{-1}.

Reaction of $(PhC{\equiv}C)_2Be(THF)_2$ with diphenylamine.

Diphenylamine (0·435 G., 2·57 millimoles) in benzene (6 ml.) was added with stirring to a solution of $(PhC{\equiv}C)_2Be(THF)_2$, (0·915 G., 2·58 millimoles) in benzene (8 ml.). The addition of the amine turned the pale yellow solution slowly green, but produced no precipitate. The solvent was removed until about four ml. remained, and then 5 ml. hexane was added slowly giving a white precipitate. Warming the solution to about 50° to dissolve the solid led to the disappearance of the green colour as well. On cooling, colourless needles were obtained and the green colour returned to the solution. The melting point of the crystals was 135-139° and a red liquid was formed. Analysis and the i.r. spectrum confirmed that it was the starting material.

Reaction of $(PhC{\equiv}C)_2Be(THF)_2$ with ammonia.

The complex $(PhC{\equiv}C)_2Be(THF)_2$ (0·7945 G., 2·24 millimoles) was dissolved in benzene (10 ml.) and put into one limb of a double Schlenk tube. The solution was frozen and ammonia (115 N ccs, 5·13 millimoles) condensed onto it. On allowing the mixture to warm up to room temperature a white precipitate was found. Heating a sample of the solid showed that some melting took place 30-50°, but the bulk did not melt below 300°. The i.r. spectrum indicated that the solid was not a pure compound. Found: hydrolysable phenylethynyl, 58·6%; Be, 9·32%; NH_3, 32·5%. Ratio - $PhC{\equiv}C-$: NH_3: Be = 0·56:1·0:1·84.

2. Coordination complexes of dimethylethynylberyllium. Preparation of dimethylethynylberyllium bis-(tetrahydrofuran).

Methylacetylene (980 N ccs, 43·6 millimoles) was condensed onto ether (30 ml.) in a large Schlenk tube at -78°. n-Butyl-lithium (19 ml. of 2·25M soln. in hexane, 42·7 millimoles) was added with stirring at -78° giving a white precipitate. After allowing the mixture to warm up to room temperature, beryllium chloride (1·755 G., 21·9 millimoles) in ether (30 ml.) was added by syringe and the mixture stirred well. Lithium chloride was produced as a white precipitate which differed considerably from the previous precipitate, being far more granular. The solution was filtered and ether pumped off to leave a white crystalline solid. This solid was dissolved in THF and crystallised from THF/hexane as colourless needles. Found: hydrolysable methylethynyl, 33·8%; Be, 3·97%; M, (cryoscopically in 0·58, 0·87 wt.% solution in benzene) 235, 244. $C_{14}H_{22}BeO_2$ requires hydrolysable methylethynyl, 34·1%; Be, 3·90%; M, 231. The infrared spectrum recorded as a Nujol mull showed the following absorptions: 549 m,br; 610 s,br; 713 m,sh; 725 m,br; 750 m; 777 m; 855 m,sh; 882 s; 917 m; 991 m; 1017 m; 1040 s; 1184 w; 1197 w,sh; 1254 vw,br; 1347 w. There was also an absorption at 2137 cm^{-1} of weak strength. The p.m.r. spectrum as a 10% solution in d_6-benzene with TMS as internal standard showed resonances as follows:

Type	τ	Assignment	Relative Intensity
Distorted triplet	Centered at 6·05	$O-\underline{CH_2}-CH_2$	4
Singlet	8·06	$\underline{CH_3}-C\equiv C$	3
Distorted triplet	Centered at 8·66	$O-CH_2-\underline{CH_2}$	4

Preparation of dimethylethynylberyllium bis-(trimethylamine).

Trimethylamine (500 N ccs, 22·3 millimoles) was condensed onto dimethylethynylberyllium bis-(tetrahydrofuran) (1·81 G., 8·05 millimoles) dissolved in 10 ml. benzene and frozen at -196°. The frozen mixture was allowed to warm up to room temperature under vacuum in a closed system. A precipitate was obtained which dissolved on heating. On cooling colourless crystalline needles came out of solution. Heating a sample of the crystals caused some melting between 172-177°; further heating caused the compound to decompose but it never completely melted. Found: hydrolysable methylethynyl, 38·3%; Be, 4·44%. $C_{12}H_{24}BeN_2$ requires hydrolysable methylethynyl, 38·0%; Be, 4·39%. The infrared spectrum recorded as a Nujol mull showed: 690 s,br; 709 w,sh; 733 m,br; 784 m,br; 826 s,sh; 831 s; 980 m; 1005 s; 1112 m; 1233 w; 1247 m; 1352 w,sh; 1400 w; 1445 s; 1474 s; there was also a sharp weak absorption at 2123 cm^{-1}.

Attempted sublimation of $(MeC\equiv C)_2Be(NMe_3)_2$ at 110°/10^{-3} mm. results in considerable decomposition. However, some white solid is sublimed. It analysed as $(MeC\equiv C)_2Be(NMe_3)_{1\cdot5}$.

Preparation of dimethylethynylberyllium.

If a solution of dimethylethynylberyllium in a mixed ether/hydrocarbon solvent is evaporated almost to dryness, a white solid is produced which is readily soluble in benzene, but insoluble in hexane. When the solid is filtered and pumped dry (30 min.) it is no longer soluble in benzene, even at 70-80°. Hydrolysis of this compound by 2-methoxyethanol at about -60° was very vigorous, giving small deposits of carbon. The analysis showed the solid to be $(MeC\equiv C)_2Be(OEt_2)_{0\cdot37}$. After further pumping (25°/10^{-3} mm.) for 18 hours, the solid was hydrolysed extremely vigorously (almost explosively) by 2-methoxyethanol at -60°. Large deposits of carbon were formed. The ether and beryllium analyses indicated a ratio $(MeC\equiv C)_2Be$: Et_2O = 20:1. Found: Be, 9•9%; ether, 4•0%; hydrolysable methylethynyl, 46•7%. A melting point was not attempted in light of the tendency of $(MeC\equiv C)_3Al$ to explode. The infrared spectrum recorded as a Nujol mull was very simple showing the following bands: 473 s; 494 s; 703 m; 976 m; 994 m; 1032 w; 1360 w. There was also a strong, sharp peak at 2119 cm^{-1}.

Preparation of dimethylethynylberyllium N,N,N',N'-tetramethylethylenediamine.

The amine TMED, (1•0 ml., 6•72 millimoles) in benzene (5 ml.) was added slowly to a solution of $(MeC\equiv C)_2Be(THF)_2$ in benzene (10 ml.). A precipitate formed immediately. The precipitate dissolved on warming and gave colourless crystalline needles on cooling. The crystals were filtered, washed with benzene, and dried. A sample melted 196-201° to give a clear liquid. Found: hydrolysable methylethynyl, 28•5%; Be, 3•29; TMED, 44•4%. $C_{12}H_{22}BeN_2$ requires hydrolysable methylethynyl, 38•4%; Be, 4•43%; TMED, 57•2%. This large difference between the observed and expected analysis figures led to a second recrystallisation of the compound from benzene. Found: hydrolysable methylethynyl, 28·7%; Be, 3·36%; TMED, 43.3%. These figures were essentially the same as the previous ones.

A sample of the compound (0·307 G.) was heated in a sublimation tube at 100°/10^{-3} mm. with the cold finger at -78° and an adjacent trap at 196°. A white solid condensed onto the cold finger, and some volatile material was colected in the trap. An attempt to collect the volatile material in the Topler pump showed that one of the components did not have a high vapour pressure at room temperature since it liquified in the pump. The i.r. spectrum of the gas showed it to be a mixture of benzene and methylacetylene. $(MeC\equiv C)_2BeTMED.C_6H_6$, (= $C_{18}H_{28}BeN_2$) requires hydrolysable methylethynyl, 27·8%; Be, 3·20%; TMED, 41·3%, which corresponds closely to the analysis figures found above. The sublimate analysed: hydrolysable methylethynyl, 38·0%; Be, 4·43%; TMED, 56·5%. $(MeC\equiv C)_2BeTMED$ (= $C_{12}H_{22}BeN_2$) requires hydrolysable methylethynyl, 38·4%; Be, 4·43%; TMED, 57·2%. The melting point of the sublimate was the same as that of the crystallised compound. The infrared spectrum recorded as a Nujol mull showed: 538 m; 608 m; 664 s; 671 s,sh; 730 w; 770 w; 782 m; 814 m; 954 m; 990 m; 1015 s; 1029 s; 1042 m; 1106 w; 1124 w; 1176 vw; 1200 vw; 1250 vw; 1282 w; 1346 vw; there was also a weak band at 2128 cm^{-1}.

3. Coordination complexes of phenylethynyl(methyl)beryllium. Attempted preparation of phenylethynyl(methyl)beryllium tetrahydrofuran.

2·28 Ml. of a 1·79M solution of Me_2Be in ether were put into one limb of a double Schlenk tube and the ether removed to leave the solid Me_2Be. A 50° oil bath was used to heat the solid and a ring of solid CO_2 was constructed further up the tube. After about 5 mins. under 10^{-3} mm. pressure the solid began to sublime, and it was presumed that very little ether remained. Benzene (8 ml.) was added to the solid, followed by a solution of $(PhC\equiv C)_2Be(THF)_2$

(1·451 G., 4·09 millimoles) in benzene (20 ml.). After about an hour of stirring at room temperature, the Me_2Be had dissolved. The solution was pale yellow. The solvent was slowly removed without heating until about 2-3 remained. When the whole entity solidified. A further 10 ml. benzene was added but the solid would not completely dissolve even when heated. The mixture was allowed to cool and then filtered. The filtrate was transfered to another Schlenk tube and hexane was added. A white precipitate was deposited from the solution which was now orange due to some decomposition. Recrystallisation of the solid from benzene/hexane as colourless needles, which were shown to be $(PhC\equiv C)_2Be(THF)_2$ by i.r. spectrum and m.pt.

Attempted preparation of phenylethynyl(methyl)beryllium.triethylamine.

2·67 Ml. of a 1·79 solution of Me_2Be in ether (4·78 millimoles) were taken and treated as above to obtain solid Me_2Be with very little coordinated ether. Toluene (5 ml.) and NEt_3 (0·67 ml., 4·81 millimoles) were added and a clear solution resulted. $(PhC\equiv C)_2BeNEt_3$ (1·492 G., 4·78 millimoles) was dissolved in toluene (6ml.) and added slowly with stirring to the Me_2BeNEt_3 solution to give a pale yellow solution. A sample was taken for p.m.r. study and the remainder was filtered. Some of the toluene was pumped off but no precipitate was seen. When the volume of the solution was about 5 ml. hexane (10 ml.) was added but still no solid appeared. Cooling the solution produced two liquid layers. Finally, vigorous stirring in the presence of hexane as the only solvent gave a white precipitate, which was shown by i.r. spectrum and m.pt. to be $(PhC\equiv C)_2BeNEt_3$.

The p.m.r. spectrum of the mixture at +30° showed the following resonances:

Type	τ	Assignment	Relative Intensity
Quartet	7·27, 7·40, 7·53 7·66	$N-\underline{CH_2}-$	6
Triplet	9·13, 9·26, 9·39	$N-CH_2-\underline{CH_3}$	9
Singlet	10·65	$Be-\underline{CH_3}$	3

Lowering the temperature of the sample showed changes in the chemical shifts and at about -60° the $\mathrm{NEt_3}$ resonances broadened because of the slowing down of the exchange process of $\mathrm{NEt_3}$ groups.

4. Anionic Complexes

Reaction of $(\mathrm{PhC{\equiv}C})_2\mathrm{Be(THF)}_2$ with $\mathrm{PhC{\equiv}CLi}$. Preparation of $\mathrm{Li_2Be(C{\equiv}CPh)_4}$.

a.) 1:1 ratio.

Phenylethynyl-lithium (0·611 G., 5·66 millimoles) in THF (10 ml.) was added slowly to a solution of $(\mathrm{PhC{\equiv}C})_2\mathrm{Be(THF)}_2$ (2·004 G., 5·64 millimoles) in THF (15 ml.) to form a pale yellow solution. The THF was pumped away to leave an oil. The oil dissolved in benzene but addition of hexane produced two liquid layers. Pumping off the hydrocarbon solvents produced a white solid, which would not completely redissolve in toluene. The solid which did not dissolve was filtered, washed with toluene and dried (30 min.). A sample of the solid did not melt below 300°. Found: hydrolysable phenylethynyl, 90·0%; Be, 1·91%; Li, 2·80%. $\mathrm{Li_2Be(C{\equiv}CPh)_4}$ (= $\mathrm{C_{32}H_{20}BeLi_2}$) requires hydrolysable phenylethynyl, 94·6%; Be, 2·11%; Li, 3·28%. Ratio of Li:Be:C≡CPh found by analysis = 1·89: 1·00: 4·16, and the analysis accounted for 94·7% of the weight taken.

b.) 1:2 ratio.

Phenylethynyl-lithium (1·06 G., 9·82 millimoles) in THF (12 ml.) was added to $(\mathrm{PhC{\equiv}C})_2\mathrm{Be(THF)}_2$ (1·736 G., 4·89 millimoles) in THF (20 ml.) giving a pale yellow solution. The solution was concentrated to about 5 ml. and then 15 ml. hexane added slowly. No precipitate formed so the solvent was removed and a foam was left. The foam was boiled with 10 ml. hexane to produce a yellow solid. Benzene (5 ml.) was added and the solid dissolved on warming. Hexane was now added and a white solid was formed, which was no longer soluble in benzene, and which had no melting point below 300°. Its infrared spectrum was the same as that of the solid isolated from the 1:1 reaction. Found: hydrolysable phenylethynyl, 91·5%; Be, 1·93%; Li, 2·83%. The ratio Li:Be: PhC≡C = 1·91: 1·00: 4·24. The analysis accounted for 96·3% of the weight taken. A sample of the compound was heated at 50° for 16 hours at 10^{-3} mm. pressure and any volatile material was collected in a -196° trap. No volatile material was colected. The infrared spectrum of the compound recorded as a Nujol mull showed: 499 w; 532 w; 538 w; 545 w; 667 m; 673 m; 682 m; 694 s; 699 m,sh; 751 s; 757 s; 770 m; 790 m; 803 m; 817 m; 840 vw; 895 w; 913 w; 1028 w; 1045 m; 1070 w; 1090 vw,br; 1202 w; 1484 w; 1618 w; there was also a very weak broad band centred at 2080 cm^{-1}.

5. Phenylethynylberyllium alkoxides and phenoxide.

Reaction of $(PhC\equiv C)_2Be(THF)_2$ with methanol.

Methanol (0·19 ml., 4·69 millimoles) in benzene (6 ml.) was added to $(PhC\equiv C)_2Be(THF)_2$ (1·672 G., 4·71 millimoles) in benzene (12 ml.). A clear solution at first became a little cloudy as a colourless gelatinous precipitate was formed, and the solution became slightly warm. The precipitate was quite small in quantity. It was filtered off and the filtrate reduced in volume. Hexane was added to the filtrate when the volume was about 3 ml. and a white precipitate was produced. This product was found to have a m.pt. and i.r. identical with those of the starting beryllium compound. The first compound had an i.r. spectrum identical with that of $(MeO)_2Be$.

Reaction of $(PhC\equiv C)_2Be(THF)_2$ with tertiary butanol. Preparation of $PhC\equiv CBeOBu^t.THF$.

To $(PhC\equiv C)_2Be(THF)_2$ (1·446 G., 4·07 millimoles) dissolved in benzene (12 ml.) was added t-BuOH (0·302 G., 4·08 millimoles) in benzene (6 ml.) with stirring. Immediately after the addition there was a clear solution but within about 30 secs. a precipitate had appeared. On warming to about 80° the precipitate dissolved, and on cooling small colourless needles were formed, which were not observed to melt on heating to 300°. The compound was fairly soluble in benzene at room temperature. Found: hydrolysable phenylethynyl, 40·6%; Be, 3·58%; M (cryoscopically in benzene, 0·60 and 0·91 wt.% solution) 311, 364. $C_{16}H_{22}BeO_2$ requires hydrolysable phenylethynyl, 39·6%; Be, 3·53%; M, 255. Observed molecular weight corresponds to degrees of association of 1·22 and 1·43. The infrared spectrum recorded as a Nujol mull showed: 508 m; 531 m; 631 m; 687 s; 697 s; 758 m; 768 m; 802 s; 858 s; 886 m; 917 m; 957 m; 975 s; 999 m; 1031 s; 1067 w; 1176 w; 1205 m; 1230 w; 1247 w; 1277 w; 1592 w.

Reaction of $(PhC\equiv C)_2Be(THF)_2$ with phenol. Preparation of PhC≡CBeOPh,THF.

Phenol (0·171 g., 1·82 millimoles) in benzene (5 ml.) was added to $(PhC\equiv C)_2Be(THF)_2$ (0·648 g., 1·82 millimoles) in benzene (6 ml.) giving a pale yellow solution. Solvent was removed till the volume was about 6 ml.. Hexane (3 ml.) was added slowly and a white precipitate formed which on crystallisation from benzene/hexane produced colourless needles, which melted 203-6° to give a red liquid. Found: hydrolysable phenylethynyl, 37·3%; Be, 3·27%; M, (cryoscopically in 1·04, 1·54 wt.% solution in benzene) 440, 473. $C_{18}H_{18}BeO_2$ requires hydrolysable phenylethynyl, 36·7%; Be, 3·27%; M, 275. Observed molecular weight corresponds to degrees of association of 1·60 and 1·72. The infrared spectrum recorded as a Nujol mull showed: 506 m; 531 w; 536 w; 611 w; 651 w; 695 s; 707 s; 757 s; 633 m,sh; 826 w,br; 862 s; 873 s; 882 s; 889 s,sh; 915 m; 966 w; 1000 w; 1022 m; 1068 w; 1169 w; 1176 w,sh; 1210 w; 1264 s; 1484 m; 1591 m.

Reaction of $(PhC\equiv C)_2Be,NEt_3$ with tertiary butanol.

a.) 1:1 ratio. Preparation of polymeric $PhC\equiv CBeOBu^t$

t-Butanol (0·159 ml., 1·68 millimoles) in benzene (4 ml.) was added slowly to $(PhC\equiv C)_2Be,NEt_3$ (0.525 g., 1·68 millimoles) dissolved in benzene (6 ml.). A white precipitate slowly formed which was filtered, washed with hexane and dried. It was insoluble in hydrocarbons, in 2N H_2SO_4 , in H_2SO_4/MeOH, in NaOH/EtOH, and in acetic acid. It was soluble in warm concentrated nitric acid. Gravimetric analysis for Be, 4·89%. $PhC\equiv CBeOBu^t$, (= $C_{12}H_{14}BeO$) requires Be, 4·92%. The compound did not melt below 300°. Its infrared spectrum recorded as a Nujol mull showed: 525 w; 535 w; 693 s,br; 754 m,sh; 762 s; 766 m,sh; 884 m,br; 866 s; 893 br, sh; 915 m; 931 m; 1030 w; 10 1045 w; 1072 w; 1110 w,br,sh; 1171 w; 1179 w,sh; 1219 w; 1264 m; 1399 w; 1493 w; 1595 vw; there was also a weak, broad absorption band at 2118 cm^{-1}. The reaction between $(PhC\equiv C)_2Be,OEt_2$ and t-butanol in a 1:1 ratio gives the same product.

b.) 3:4 ratio. Preparation of $(PhC\equiv C)_2Be_3(OBu^t)_4$.

t-Butanol (1·04 ml., 11·0 millimoles) in benzene (5 ml.) was added to $(PhC\equiv C)_2Be,NEt_3$ (2·58 g., 8·27 millimoles) dissolved in benzene (12 ml.). The solution became warm during the addition and a white precipitate formed. The solid only dissolved when the benzene was heated to its boiling point. On cooling no solid came out of solution. The benzene was pumped off and the solid that remained was crystallised from hexane as colourless needles, m.pt. 210°. Found: hydrolysable phenylethynyl, 39·2%; Be, 5·14%. $C_{32}H_{46}Be_3O_4$ requires hydrolysable phenylethynyl, 38·8%; Be, 5·18%. The infrared spectrum recorded a as a Nujol mull showed: 534 w; 541 w; 619 w; 692 m; 709 vw; 756 s; 785 w; 820 s; 839 s; 861 m,sh; 913 vw; 989 vs,br; 1031 m; 1072 w; 1081 w; 1196 m; 1227 m; 1241 m; 1255 m; 1326 w; 1368 s; 1490 w,sh; 1595 vw; there was also a sharp weak band at 2131 cm-1.

The p.m.r. spectrum in d_6-benzene with TMS as internal standard showed the following resonances.

Type	τ	Assignment	Relative Intensity
Multiplets	Centred at 2·34 and 2·89	$C_6H_5C{\equiv}C$	5
Singlet	8·51	$(CH_3)_3CO$	9

Preparation of $(PhC{\equiv}C)_2Be_3(OBu^t)_4$ using $Be(OBu^t)_2$.

To Bu^nLi (1·55 ml., of 3·38M solution in benzene) dissolved in benzene (10 ml.) was added PhC≡CH (0·57 ml., 5·22 millimoles) dissolved in benzene (5 ml.). A white precipitate of PhC≡CLi was formed, to which was added $BeCl_2$ (0·209 g., 2·61 millimoles) in ether (15 ml.). Lithium chloride was precipitated ans filtered from the remaining solution. Then $Be(OBu^t)_2$ (0·808 g., 5·22 millimoles) in benzene (10 ml.) was added. The solvent was removed leaving a white solid. Hexane (20 ml.) was added and most of the solid dissolved. After filtration, colourless needles were crystallised from hexane, m.pt. 212°. The infrared spectbrum of the compound was the same as that of the compound formed from $(PhC{\equiv}C)_2Be,NEt_3$ and t-BuOH. A cryoscopic molecular weight determination in 1·27 and 1·67 wt.% solution in benzene gave values of 532 and 540. $C_{32}H_{46}Be_3O_4$ requires 521.

6. Phenylethynylberyllium sulphides.

Reaction of $(PhC{\equiv}C)_2Be(THF)_2$ with t-BuSH. Preparation of $(PhC{\equiv}CBeSBu^t,THF)_2$.

a.) without heating.

The thiol (0·50 ml., 4·41 millimoles) was dissolved in benzene (5 ml.) and added to $(PhC{\equiv}C)_2Be(THF)_2$ (1·564 g., 4·41 millimoles) dissolved in benzene (15 ml.). A clear pale yellow solution was produced. The solvent was removed till about 5 ml. remained and then hexane was added dropwise to produce a white precipitate. Recrystallisation from benzene/hexane left colourless needles, identified by infrared spectrum and m.pt. to be the starting material. From the filtrate a white solid was obtained which crystallised as colourless prisms from hexane, m.pt. 132-135°(dec). The infrared spectrum showed that it was not all starting material. The reaction was not fast and some t-BuSH was probably pumped away.

probably pumped away.

b.) heating at 50°.

The reaction above was repeated using 1·376 g., 3·88 millimoles, $(PhC\equiv C)_2Be(THF)_2$ and 0·44 ml., 3·88 millimoles t-BuSH. After addition of the t-BuSH, the solution was heated under a closed system at 50° for an hour. Most of the benzene was pumped away and 5 ml. hexane was added. No precipitate was seen. Pumping all of the solvent away left a white solid, which was crystallised from hexane as colourless needles, m.pt. 150-155°(dec). Found: Be, 3·31%; M, (cryoscopically in 0·67, 1·01 wt.% solution in benzene) 523,529. Analysis for phenylethynyl was upset by the presence of another peak in the uv spectrum, which must arise from the t-BuSH. It was estimated to be 33-35%. $C_{16}H_{22}BeOS$ requires hydrolysable phenylethynyl, 37·3%; Be, 3·32%; M, 271. The observed degrees of association are 1·93 and 1·95. The infrared recorded as a Nujol mull showed: 500 w; 515 w; 539 m; 545 m; 568 w; 595 m; 694 s; 717 m; 763 s; 853 s; 873 s,br,sh; 913 m; 922 m,sh; 954 w,sh; 1000 m; 1026 s; 1042 m; 1070 m; 1164 m; 1176 m; 1215 m; 1366 m; 1484 m; 1595 w; there was also a very weak band at 2118 cm^{-1}. The p.m.r. spectrum in d_6-benzene with TMS as internal standard showed the following resonances:

Type	τ	Assignment	Relative Intensity
Multiplets	Centred at 2·30 and 2·90	$C_6\underline{H}_5C\equiv C$	7
Distorted triplet	Centred at 5·95	$O-C\underline{H}_2-CH_2$	6
Singlet	7·91	$S-C(C\underline{H}_3)_3$	14

Reaction of $(PhC\equiv C)_2Be(THF)_2$ with thiophenol.

Thiophenol (0·41 ml., 4·00 millimoles) in benzene (8 ml.) was added to a solution of $(PhC\equiv C)_2(THF)_2$ (1·420 G., 4·00 millimoles) in benzene (15 ml.). A clear solution resulted. The solvent was removed to leave an oil. Boiling with two successive 10 ml. portions of hexane failed to solidify the product but caused the oil to go brown. Cooling the oil or its solution in toluene failed to produce a solid. The reaction was abandoned at this point.

7. Phenylethynylberyllium halides.

Reaction of PhC≡CLi with $BeCl_2$.

Phenylethynyl-lithium (1·041 G., 9·64 millimoles) dissolved in ether was added to $BeCl_2$ (0·778 G., 9·70 millimoles) in the same solvent. The precipitated LiCl was filtered off leaving a clear yellow solution. Removal of the solvent left an oil which was stirred vigourously with several portions of hexane eventually to produce a solid which was pumped dry. The solid was soluble in benzene but addition of hexane only produced an oil at room temperature. Cooling and stirring the benzene/hexane mixture at about 0° caused the oil to change to a light-brown precipitate, that could then be filtered, washed, and dried at room temperature. Found: hydrolysable phenylethynyl, 44·8%; Be, 3·52%; Cl, 9·00%. Ratio PhC≡C : Be : Cl = 1·12 : 1·00 : 0·65. The reaction was not investigated furter.

Reaction of $(PhC{\equiv}C)_2Be(THF)_2$ with $BeCl_2$.

Beryllium chloride (0·368 G., 4·60 millimoles) dissolved in warm THF (50°) was added to a solution of $(PhC{\equiv}C)_2Be(THF)_2$ (1·634 G., 4·61 millimoles) in THF (30 ml.). A clear solution was formed which was concentrated to about 10 ml. Hexane (8 ml.) was then added slowly to produce a white precipitate. Attempted crystallisation of the solid from THF/hexane or from benzene/hexane always produced two liquid layers. The precipitate could be recovered by cooling the solution to about 0° and stirring well. It was filtered without crystallisation, washed with hexane, and dried. A sample of the solid melted at 85-87°. Found: hydrolysable phenylethynyl, 37·1%; Be, 3·27%; Cl, 13·5%. If the remaining weight is assumed to be THF, then the ratio PhC≡C : Be : Cl : THF = 1·01 : 1·00 : 1·05 : 1·75. These analysis figures would suggest that the compound was a mixture of $\mathrm{PhC{\equiv}CBeCl.THF}$ and $\mathrm{PhC{\equiv}CBeCl(THF)_2}$ rather than a mixture containing $\mathrm{(PhC{\equiv}C)_2Be(THF)_2}$ and $\mathrm{BeCl_2.2THF}$. It was not possible by comparison of infrared spectra to say that $\mathrm{BeCl_2.2THF}$ was not present but the absence in the spectrum of the solid of bands at 620 and 625 $\mathrm{cm^{-1}}$ showed that no $\mathrm{(PhC{\equiv}C)_2Be(THF)_2}$ was present.

0·8812 G. of the compound isolated above were dissolved in benzene. Pyridine (0·51 ml.) was added to the solution and since no precipitate was produced, the solvent was pumped off. A solid formed at low volume which could not be completely redissolved in benzene even at 80°. The solid was filtered off for analysis. Found: a.) hydrolysable phenylethynyl, 28·4%; Be, 3·04%; Cl, 14·8%; py., 57·5%. b.) hydrolysable phenylethynyl, 27·4%; Be, 3·18%; Cl, 14·7%; py., 55·9%. Average ratio: $\mathrm{PhC{\equiv}C}$: Be: Cl: py = 1·00: 1·25: 1·50: 2·62.

8. Coordination complexes of beryllium dialkyls.

Preparation of dimethylberyllium triethylamine.

8 Ml. of an ether solution of $\mathrm{Me_2Be}$ (1·79M) were syringed into one limb of a double Schlenk tube and the ether evaporated to leave a white solid. Benzene (12 ml.) and triethylamine (4 ml.) were added to give, on stirring, a colourless liquid, which was transfered to a distillation apparatus. With the receiver at -30 - -40° and a pressure of 10^{-2}mm a liquid slowly distilled over. Found: hydrolysable methyl 21·2%; Be, 6·44%; M (cryscopically in 0·45 and 0·68 wt.% solution in benzene), 134,138. $\mathrm{C_8H_{21}BeN}$ requires hydrolysable methyl, 21·4%; Be, 6·43%; M, 140. The infrared spectrum of the liquid showed the following bands: 619 w,br; 707 s; 748 s; 806 s; 837 m; 910 m; 940 s; 1016 m; 1035 m; 1068 w; 1090 m; 1110 w; 1164 m; 1194 m; 1299 vw; 1330 w; 1355 w; 1391 m; 1456 m; 1481 m. The p.m.r. spectrum in d_6-benzene with TMS as internal standard showed the following resonances:

Type	τ	Assignment	Relative Intensity
Quartet	7·44,7·56,7·68,7·80	$N{-}C\underline{H}_2$	6
Triplet	9·26,9·38,9·50	$N{-}CH_2{-}C\underline{H}_3$	9
Singlet	10·59	$C\underline{H}_3{-}Be$	6

Preparation of di-neo-pentylberyllium diethyl etherate.

0 To 8·0 G., 0·1 moles, of $BeCl_2$ dissolved in 500 ml. ether was added 260 ml. 0·80M <u>neo</u>-pentylmagnesium chloride (0·21 mole). The ether solution was decanted from the magnesium halides and concentrated to about 100 ml. The solution was then put into the reflux-distillation apparatus (see page) and refluxed for 21 hours at 50°/10^{-3} mm. before distillation at 50°/10^{-3} mm. Hydrolysis of a small sample showed the presence of a considerable quantity of ether in the liquid so it was distilled back into the reflux-distillation apparatus and then refluxed for 29 hours at 50°/10^{-3} mm. The liquid was distilled again at about 30°/10^{-3} mm. Found: Be, 4·07%; M (cryoscopically in 0·61, 0·91 wt.% solution in benzene) 206, 216. $C_{14}H_{32}BeO$ requires Be, 4·00%; M, 225. 0·845 G., of the compound produced on hydrolysis 1·11 millimoles of <u>neo</u>-pentane plus ether. $C_{14}H_{32}BeO$ requires 1·13 millimoles. The infrared spectrum of the liquid shows the following bands: 530 w,br; 656 m; 715 m,sh; 728 m; 754 s; 779 m; 835 m; 875 w; 903 m; 910 m; 920 vw; 955 m; 994 m; 1010 m; 1033 s; 1090 m; 1128 m; 1152 m; 1192 m; 1221 s; 1238 m; 1355 s; 1390 m; 1448 m; 1468 s. The p.m.r. spectrum in benzene with benzene as the reference showed:

Type	τ	Assignment	Relative Intensity
Quartet	5·21, 5·28, 5·35 5·42	$O{-}C\underline{H}_2{-}CH_3$	2
Singlet	8·70	$(C\underline{H}_3)_3CCH_2Be$	9
Triplet	9·00, 9·07, 9·14	$O{-}CH_2{-}C\underline{H}_3$	3
Singlet	9·81	$(CH_3)_3CC\underline{H}_2Be$	2

Preparation of di-neo-pehtylberyllium N,N,N',N'-tetramethylethylenediamine.

Di-neo-pentylberyllium (0·978 G., 4·35 millimoles) in benzene (5 ml.) and TMED (0·65 ml., 4·46 millimoles) in benzene (10 ml.) were mixed to produce a clear solution. Removal of the solvent left a white solid which was recrystallised from hexane as colourless prisms, m.pt. 78°-80°. Found: hydrolysable neo-pentyl, 53·9%; Be, 3·32%; M (cryoscopically in 0·74, 1·11 wt.% in benzene) 256, 256. $C_{16}H_{38}BeN_2$ requires hydrolysable neo-pentyl, 53·2%; Be, 3·37%; M, 267. The infrared spectrum recorded as a Nujol mull showed: 462 w; 480 w; 560 vw; 620 m; 674 s; 723 m; 747 m; 770 vw; 802 m; 834 s; 900 vw; 938 m; 948 m; 1002 m; 1009 m; 1020 s; 1038 w; 1053 w; 1091 w; 1105 m; 1116 s; 1157 w; 1181 w; 1199 m; 1207 m; 1235 w; 1275 s; 1344 s. The p.m.r. spectrum in benzene solution with benzene as the internal reference showed the following resonances at room temperature:

Type	τ	Assignment	Relative Intensity
Singlet	8·00	$C\underline{H}_3$-N	3
Singlet	8·17	$C\underline{H}_2$-N	2
Singlet	8·47	$(C\underline{H}_3)_3CCH_2$	9
Singlet	9·92	$(CH_3)_3C\underline{CH}_2$	2

Preparation of dibenzylberyllium diethyl etherate.

A solution of dibenzylberyllium in ether was prepared by adding benzylmagnesium chloride to beryllium chloride in a 2:1 molar ratio, and then decanting the ether solution from the precipitated magnesium halides. Pumping off the ether cooled the solution and a large quantity of solid came out of solution. At about 5-10° it went back into solution. Pumping at 50-70° led to the solution turning dark brown in colour. Since the resulting liquid could not be refluxed in the reflux-distillation apparatus, an attempt was made to remove any remaining ether by successive addition and evaporation of 20 ml. aliquots of methylcyclohexane. Finally 30 ml. of methylcyclohexane were added and the solution filtered to remove some precipitated magnesium halides. A sample of the filtrate showed on hydrolysis a ratio Be:OEt$_2$ = 1·00:0·97. The methylcyclohexane was evaporated from the solution to leave a viscous liquid. This was transfered to a short path distillation apparatus and a little ether added. With a pressure of 10^{-3} mm and a bath temperature of 120-150°, white crystalline needles collected in the receiver (-10°). There was a great deal of decomposition in the distillation flask. The crystals had a melting point of 50-51°. Found: diethyl ether, 27·5%; Be, 3·38%; M, (cryoscopically in 1·00, 1·51 wt.% solution in benzene) 245, 259. $C_{18}H_{24}BeO$ requires diethyl ether, 27·9%; Be, 3·40%; M, 265. The infrared spectrum recorded as a Nujol mull showed: 452 w; 472 w; 494 m; 510 w; 570 w; 610 s; 720 m; 745 s,br; 787 m; 800 m; 835 m; 899 m; 990 m; 1023 s; 1062 s,br; 1146 m; 1172 w; 1197 s; 1281 w; 1447 s; 1483 s; 1490 s,sh; 1590 s; 1737 w,br; 1797 w,br; 1864 w,br; 1940 w,br. The p.m.r. spectrum in benzene solution showed the following resonances:

Type	τ	Assignment	Relative Intensity
Quartet	6·55,6·62,6·69,6·76	$O\text{-}C\underline{H_2}CH_3$	2
Singlet	8·25	$Be\text{-}C\underline{H_2}$	2
Triplet	9·29,9·39,9·43	$O\text{-}CH_2C\underline{H_3}$	3

Preparation of neo-pentyl(methyl)beryllium N,N,N',N'-tetramethylethylenediamine.

In one arm of a double Schlenk tube was put (neo-pentyl)$_2$Be,OEt$_2$ (0·801 g., 3·56 millimoles), Me$_2$Be (0·140 g., 3·60 millimoles) and benzene (10 ml.). On stirring some of the Me$_2$Be dissolved. Then TMED (1·06 ml., 7·13 millimoles) was added slowly, causing the solution to get warm. The solution was filtered and the benzene pumped off to leave a liquid. Pentane (5 ml.) was added and pumped off. When there was practically no solvent left the liquid crystallised as colourless prisms, m.pt. 41°. Found: hydrolysable methyl, 7.15%; Be, 4·25%; hydrolysable neo-pentyl, 33·2%; M (cryoscopically in 0·69, 1·04 wt.% solution in benzene) 204, 212. $C_{12}H_{30}BeN_2$ requires hydrolysable methyl, 7·11%; hydrolysable neo-pentyl, 33·7%; Be, 4·27%; M,211. The infrared spectrum recorded as a Nujol mull showed: 572 w; 583 w; 670 s; 720 s; 744 s; 770 w; 803 m; 850 s; 905 vw; 938 m; 949 m; 1000 m; 1024 s; 1042 m; 1053 w; 1096 w; 1113 m; 1120 s; 1162 m; 1173 s; 1188 m; 1215 m; 1233 w; 1240 w; 1278 m; 1284 m; 1346 s; 1405 vw; 1445 s; 1471 s; The p.m.r. spectrum in benzene at 30° was as follows:

Type	τ	Assignment	Relative Intensity
Singlet	7·98	$N-C\underline{H}_3$	12
Singlet	8·07	$N-C\underline{H}_2$	4
Singlet	8·55	$(C\underline{H}_3)_3CCH_2Be$	9
Singlet	10·12	$(CH_3)_3CC\underline{H}_2Be$	2
Singlet	10·88	$C\underline{H}_3-Be$	3

The spectrum in TMS at 30° was as follows:

Singlet	7·48	$N-C\underline{H}_2$
Singlet	7·72	$N-C\underline{H}_3$
Doublet	9·06, 9·08	$(C\underline{H}_3)_3CCH_2Be$
Singlet	10·62	$(CH_3)_3CC\underline{H}_2Be$
Singlet	11·35	$C\underline{H}_3-Be$

The spectrum in TMS at -40° was as follows:

Multiplet	Centred at 7·45	$N-C\underline{H}_2$
Doublet	7·67, 7·70	$N-C\underline{H}_3$
Singlet	9·07	$(C\underline{H}_3)_3CCH_2Be$

Reaction of Me_2Be,NMe_3 with (neo-pentyl)$_2Be,NMe_3$.

Evidence for the formation of neo-pentyl(methyl)Be,NMe_3.

Some dimethylberyllium trimethylamine was prepared by condensing NMe_3 (excess) onto Me_2Be and subliming the solid that remained after evaporating the excess. The sublimate had a melting point of 36°. In benzene solution the p.m.r. spectrum shows two single resonances, one at 8·15 and the other at 10·59 , in an area ratio of 3:2. The low field resonance is assigned to the NMe_3 protons and the high field resonance to the Me_2Be protons.

Solutions in cyclopentane were prepared containing 1.) Me_2Be,NMe_3, 2.) (<u>neo</u>-pentyl$)_2Be,NMe_3$, 3.) an approximately 1·0:1·0 molar ratio of Me_2Be,NMe_3: (<u>neo</u>-pentyl$)_2Be,NMe_3$, and 4.) an approximately 2·5:1·0 molar ratio of Me_2Be,NMe_3: (<u>neo</u>-pentyl$)_2Be,NMe_3$. The p.m.r. spectra of these solutions were taken at or below room temperature. Interest was directed towards the methyl and methylene groups bonded to beryllium.

Chemical Shifts. a.) 30°

1) Me_2Be,NMe_3	$C\underline{H}_3$-Be	11·00			
2.) (neo-pentyl$)_2Be,NMe_3$			-$C\underline{H}_2$-Be	10·05	
3.) 1·0 : 1·0 mixture	$C\underline{H}_3$-Be	11·02	-$C\underline{H}_2$-Be		10·18
4.) 2·5: 1·0 mixture	$C\underline{H}_3$-Be	11·00	-$C\underline{H}_2$-Be		10·21

b.) -16°

1.) Me_2Be,NMe_3	$C\underline{H}_3$-Be	11·00			
2.) (neo-pentyl$)_2Be,NMe_3$			-$C\underline{H}_2$-Be	10·04	
3.) 1·0 : 1·0 mixture	$C\underline{H}_3$-Be	10·99	-$C\underline{H}_2$-Be	10·05	10·21
4.) 2·5 : 1·0 mixture	$C\underline{H}_3$-Be	11·01	-$C\underline{H}_2$-Be		10·21

c.) -40°

1.) Me_2Be,NMe_3	Me_2Be,NMe_3 crystallises out of solution.				
2.) (neo-pentyl$)_2Be,NMe_3$			-$C\underline{H}_2$-Be	10·05	
3.) 1·0 : 1·0 mixture	$C\underline{H}_3$-Be	11·02	-CH_2-Be	10·06	10·21
4.) 2·5 : 1·0 mixture	Me_2Be,NMe_3 crystallises out of solution.				

Relative Intensities.

The methylene resonances of the neo-pentyl groups in the 1·0:1·0 mixture showed a single peak at room temperature which changed to two peaks on lowering the temperature. Accurate area measurements were carried out on the CH_3-Be and -CH_2-Be resonances of the 1·0:1·0 mixture at 30° and -40°.

Ratio of CH_3-Be to -CH_2-Be at 30° = 1·00 : 1·01.

Ratio of CH_3-Be to -CH_2Be (at 10·05) to -CH_2Be (at 10·21) at -40°
= 1·00 : 0·14 : 0·87 .

Coordination complexes of alkylberyllium halides.

Preparation of neo-pentylberyllium bromide N,N,N',N'-tetramethylethylenediamine.

The reaction between LiH and neo-pentylberyllium bromide does not proceed to give neo-pentylberyllium hydride and lithium bromide. Thus, when this reaction was attempted there remained a solution of neo-pentylberyllium bromide in benzene containing a little ether. A portion of the solution containing about 10 millimoles of neo-C_5H_{11}BeBr was taken and excess TMED (5 ml.) was added. On removal of the solvent a white solid was obtained which was crystallised from benzene/hexane (1:2) as colourless plates, m.pt. 104-6°. Found: hydrolysable neo-pentyl, 25·6%; Be, 3·26%; M (cryoscopically in 0·64, 0·96 wt.% solution in benzene) 264, 286. $C_{11}H_{37}BeN_2Br$ requires hydrolysable neo-pentyl, 25·7%; Be, 3·26%; M, 276. The infrared spectrum recorded as a Nujol mull showed: 462 m; 482 w; 550 m; 593 m; 675 s; 712 m; 760 w; 800 s; 932 m; 945 m; 985 m; 1002 m; 1012 s; 1034 m; 1051 vw; 1094 w; 1113 m; 1120 m; 1162 w; 1189 w; 1215 m; 1232 m; 1270 m; 1281 m; 1342 m; 1348 m; 1400 vw; 1427 m. The p.m.r. spectrum of the compound in benzene solution with benzene as the internal standard showed the following resonances at 30°:

Type	τ	Assignment	Relative Intensity
Multiplet	Centered at 7·83	N-CH_2	4
Doublet	7·65, 8·12	N-CH_3	12
Singlet	8·46	$(CH_3)_3CCH_2Be$	9

Singlet	10·02	$(CH_3)_3CC\underline{H}_2Be$	2

As the temperature was raised the spectrum changed, so that at 90°:

Singlet	7·76	$N-C\underline{H}_3$	12
Singlet	7·96	$N-C\underline{H}_2$	4
Singlet	8·46	$(C\underline{H}_3)_3CCH_2Be$	9
Singlet	10·02	$C\underline{H}_2-Be$	2

<u>Preparation of ethylberyllium bromide N,N,N',N'-tetramethylethylenediamine.</u>

In an attempt to remove the last traces of ether from diethylberyllium, beryllium bromide was added to the diethylberyllium. After distilling the diethylberyllium (which retained the ether), a residue remained which was mainly solid. Benzene (40 ml.) and TMED (3 ml.) were added and the solid dissolved. Removal of the solvent gave a white solid which was difficult to crystallise. It was very soluble in benzene but only sparingly soluble in hexane. The compound was finally crystallised from benzene/hexane as long, colourless needles, m.pt. 107-9°. Found: hydrolysable ethyl, 12·7%; Be, 3·87%; M (cryscopically in 0·62, 0·92 wt.% solution in benzene) 221, 228. $C_8H_{21}BeN_2Br$ requires hydrolysable ethyl, 12·4%; Be, 3·85%; M, 234. The infrared spectrum recorded as a Nujol mull showed: 448 w; 477 w; 500 w; 561 m; 598 s; 657 s; 758 m; 781 s; 801 s; 910 w; 942 s; 986 m; 994 m; 1016 s; 1031 m; 1101 w; 1117 m; 1169 w; 1190 m; 1194 m,sh; 1238 m; 1278 s; 1342 w; 1402 w. The p.m.r. spectrum of the compound in benzene solution with benzene as the internal standard showed the following resonances at 30°:

<u>Type</u>	<u>τ</u>	<u>Assignment</u>	<u>Relative Intensity</u>
Multiplet beneath the $N-CH_3$ peaks		$N-C\underline{H}_2-$	- 16
Doublet	7·58, 7·91	$N-CH_3$	-
Triplet	8·27, 8·35, 8·43	$C\underline{H}_3-CH_2Be$	3
Quartet	10·01, 10·09, 10·17, 10·25	$CH_3-C\underline{H}_2Be$	2

The spectrum changed on heating so that at 95°:

Singlet	7·68	$N-C\underline{H}_3$	-	16
Singlet	7·81	$N-C\underline{H}_2-$	-	
Triplet	8·39, 8·47, 8·55	$C\underline{H}_3-CH_2Be$	3	
Quartet	10·06, 10·14, 10·22, 10·30	$CH_3-C\underline{H}_2Be$	2	

Attempted preparation of ethylberyllium chloride N,N,N',N'-tetramethylethylenediamine.

A solution of $BeCl_2$ (0·306 G., 3·81 millimoles) in ether (15 ml.) was added to diethylberyllium (0·265 G., 3·80 millimoles) in benzene, and the clear solution which resulted was reduced to about 10 ml. To this solution was added TMED (1·14 ml., 7·62 millimoles) and the solvent was pumped off leaving a white solid. Recrystallisation from benzene/hexane gave colourless needles. Found: hydrolysable ethyl, 10·4%; Be, 4·83%; Cl, 25·0%. $C_8H_{21}BeN_2Cl$ requires hydrolysable ethyl, 15·3%; Be, 4·75%; Cl, 18·7%. The ratio of Et:Be:Cl found was 0·67:1·00:1·32. A second recrystallisation led to essentially the same result. The p.m.r. spectrum of the compound as a solution in benzene showed a doublet at 7·68 and 7·93 which is due to the $N-C\underline{H}_3$ of EtBeCl.TMED by analogy with the bromide above. The ratio of ethyl groups to TMED groups was 1·0 to 1·7. The solid appears to be a mixture of EtBeCl.TMED and a TMED complex of $BeCl_2$ in approximately a 2:1 ratio.

Reaction of neo-pentylberyllium bromide etherate with trimethylamine. Preparation of di-neo-pentylberyllium trimethylamine.

In an attempt to prepare neo-pentylberyllium bromide trimethylamine, excess trimethylamine was condensed onto a benzene solution containing about 10 millimoles of neo-pentylberyllium bromide and a little ether. On warming the mixture to room temperature, a precipitate was obtained, which dissolved in benzene at 80° to give on cooling colourless needles. This compound gave no *neo*-pentane on hydrolysis. The filtrate from the reaction could not be pumped dry, so it was transfered to a distillation apparatus. With the receiver at -78° and the heating bath at 50° a colourless liquid distilled at 10^{-3} mm. pressure. Found: hydrolysable *neo*-pentyl, 67·4%; Be, 4·32%; M, (cryoscopically in 0·58, 0·86 wt.% solution in benzene) 203, 197. $C_{13}H_{31}BeN$ requires hydrolysable neo-pentyl, 67·6%; Be, 4·29%; M, 210. The infrared spectrum of the liquid showed: 512 m; 594 w; 650 m; 719 m; 753 s; 815 m; 871 m; 903 w; 919 w; 947 m; 998 s; 1090 m; 1097 m; 1121 s; 1231 m; 1238 m; 1349 s; 1375 w; 1401 w; 1445 m; 1463 s; 1476 s. The p.m.r. spectrum as a solution in benzene showed the following resonances:

Type	τ	Assignment	Relative Intensity
Singlet	8·17	$N{-}\underline{CH}_3$	9
Singlet	8·57	$(\underline{CH}_3)_3CCH_2Be$	18
Singlet	9·74	$(CH_3)_3C\underline{CH}_2Be$	4

Reaction of neo-pentylberyllium chloride with trimethylamine.

A solution of (*neo*-pentyl)$_2$Be.OEt$_2$ (0·672 G., 2·99 millimoles) in benzene (8 ml.) was added to a solution of $BeCl_2$ (0·239 G., 2·99 millimoles) in ether (10 ml.). A clear solution resulted which was concentrated to remove most of the ether. The solution was then frozen and excess NMe_3 condensed on. Warming the mixture to room temperature showed a light precipitate to have been formed. Excess NMe_3 was removed and the solution filtered. A sample of the filtrate gave on analysis a ratio *neo*-pentyl: Be : Cl = 1·53: 1·00: 0·42. A p.m.r. spectrum of the filtrate showed that a considerable quantity of (*neo*-pentyl)$_2$BeNMe$_3$ was present in the solution together with another species containing *neo*-pentyl groups bonded to beryllium. In contrast to the bromide, disproportionation is not complete.

10. Alkylberyllium alkoxides and their coordination complexes.

Preparation of iso-butylberyllium iso-butoxide trimer.

This compound was prepared accidentally during the preparation of di-iso-butylberyllium, in consequence of a slight leak during the final distillation at reduced pressure. It is a liquid with a boiling point at about $80^{\circ}/10^{-3}$ mm. Found: hydrolysable iso-butyl, 42·0%; Be, 6·57%; M (cryoscopically in 1·83, 1·45, 0·96 wt.% solution in benzene) 417, 429, 424. $C_{24}H_{54}Be_3O_3$ requires hydrolysable iso-butyl, 41·0%; Be, 6·49%; M, 4·17. The p.m.r. spectrum of this compound dissolved in benzene shows the following resonances:

Type	τ	Assignment	Relative Intensity
Doublet	5·97, 6·05	$\text{Be-O-C}\underline{\text{H}}_2\text{-CH-}$	2
Multiplets	Centred at 7·92 & 8·16	$\text{Be-O-CH}_2\text{-CH-}$ and $\text{Be-CH}_2\text{-C}\underline{\text{H}}\text{-}$	2
Doublets	8·69, 8·76 and 9·07, 9·14	$\text{Be-O-CH}_2\text{-CH-(CH}_3)_2$ and $\text{Be-CH}_2\text{-CH-(C}\underline{\text{H}}_3)_2$	12
Doublet	9·81, 9·89	$\text{Be-C}\underline{\text{H}}_2\text{-CH-}$	2

The spectrum in cyclopentane shows the following resonances:

Doublet	6·06, 6·13	$\text{Be-O-C}\underline{\text{H}}_2\text{-CH-}$	-
Doublet	10·13, 10·20	$\text{Be-C}\underline{\text{H}}_2\text{-CH-}$	-

The infrared spectrum of the liquid is as follows: 657 w; 792 vw; 813 vw; 869 m; 895 m; 929 s; 943 m; 973 s; 1003 s,sh; 1014 s; 1061 m; 1151 vw; 1182 m; 1276 vw; 1312 w; 1354 w; 1364 w; 1370 vw;1390 vw; 1459 m; 1463 m,sh.

Preparation of di-(iso-butylberyllium iso-butoxide), N,N,N',N'-tetramethylethylenediamine.

To 1·248 g. of Bu^iBeOBu^i (0·90 millimoles monomer) in benzene (4 ml.) was added TMED (1·2 ml.,0·95 millimoles) slowly with stirring. The solution became warm but no precipitate was produced. Removal of the solvent left a white solid which was very soluble in benzene and hexane. White needles were obtained on cooling the hexane solution to -10 - 120°, m.pt. 71-73°. Found: hydrolysable iso-butyl, 29•5%; Be, 4•60%; M (cryoscopically in 1•12, 1•67 wt.% solution in benzene) 374, 397. $C_{22}H_{52}Be_2N_2O_2$ requires hydrolysable iso-butyl, 28•9%; Be, 4•57%; M, 394. The infrared spectrum of the solid as a Nujol mull showed: 579 w; 599 w; 617 m; 670 w; 765 s; 780 s; 794 s; 849 m; 898 vw; 908 w; 942 w; 958 m; 989 w; 1001 w; 1020 m; 1069 s,br; 1106 m; 1130 m; 1153 w; 1180 m; 1210 vw; 1233 vw; 1300 w; 1335 w; 1350 w; 1360 w; 1372 w,sh; 1390 w. The p.m.r. spectrum in benzene showed resonances as follows:

Type	τ	Assignment	Relative Intensity
Singlet	7•86	$\mathrm{N{-}C\underline{H}_2{-}}$	-
Singlet	7•97	$\mathrm{N{-}C\underline{H}_3}$	-
Doublet	6•23, 6•30	$\mathrm{Be{-}O{-}C\underline{H}_2{-}}$	2
Doublets	8•53, 8•59 and 8•97, 9•03	$\mathrm{Be{-}CH_2CH(C\underline{H}_3)_2}$	12
Doublets	10•05, 10•11	$\mathrm{Be{-}C\underline{H}_2{-}}$	2
Multiplets obscured by TMED resonances.		$\mathrm{OCH_2C\underline{H}(CH_3)_2}$ $\mathrm{BeCH_2C\underline{H}(CH_3)_2}$	-

Relative intensity of TMED protons plus methine protons = 10•5.

Reaction of iso-butyleberyllium is6-butoxide with 1,2-dimethoxyethane.

a.) Bu^1BeOBu^1: DME = 2:1.

iso-Butylberyllium iso=butoxide (2•023 g., 14•6 millimoles monomer) and 1,2-dimethyoxyethane (0•76 ml., 7•3 millimoles) were mixed in benzene solution. No heat was evolved, and a clear solution was formed. A sample of this solution was taken for p.m.r. study. Comparison of the spectrum with those of 1,2-dimethoxyethane and $(i\text{-}BuBeOBu^1)_3$ in benzene showed that greater than 95% of product was in the form of the separate compounds.

b.) Bu^1BeOBe^1; DME = 1:2.

A similar solution in benzene was made up, this time containing two moles off 1,2-dimethoxyethane for every iso-butylberyllium iso-butoxide monomer. The large majority of the mixture was still in the form of the separate species but there was evidence for about 30% formation of new products, presumably coordination complexes.

Reaction of i-BuBeOBu^i with trimethylamine.

Excess trimethylamine was condensed on to a solution of i-butylberyllium i-butoxide (2·02 g., 14·5 millimoles monomer). On warming to room temperature no precipitate was seen. The excess NMe_3 was removed and then the benzene to leave a viscous liquid. A little benzene was added and a sample of the solution taken for a p.m.r. study. It was demonstrated by looking at the Be-CH_2-resonances that in addition to unreacted (i-BuBeOBu^i)$_3$ there were at least four other species containing Be-Bu^i bonds. It was estimated that in the solution the ratio i-Bu: i-BuO: NMe_3 was 1·0: 1·0: 1·6.

Reaction of Me_2Be.TMED with methanol.

To a solution of Me_2Be.TMED in benzene (0·386 g., 9·90 millimoles in 10 ml.) was added methanol (0·40ml., 9·90 millimoles) in benzene (5 ml.). The solution became warm and a gas was evolved. A precipitate was produced that would not dissolve in boiling benzene. The precipitate was filtered off and the solvent removed from the filtrate to give a white solid. This solid was recrystallised from hexane as colourless needles, which analysed correctly for Me_2Be.TMED and had a melting point of 80-81°. The p.m.r. spectrum of Me_2Be.TMED in benzene was as follows:

Type	τ	Assignment	Relative Intensity
Singlet	7·99	N-CH_3	6
Singlet	8·11	N-CH_2	2
Singlet	10·80	Ch_3-Be	3

Reaction of dimethylberyllium with tertiary butanol in a 3:4 ratio.

Preparation of $Me_2Be_3(OBu^t)_4$.

t-Butanol (1·60 ml., 17·0 millimoles) dissolved in benzene (5 ml.) was added slowly with stirring to a suspension of Me_2Be (0·496 g., 12·7 millimoles) in benzene (10 ml.). The mixture became warm and a gas was evolved. Removal of the solvent left a white solid which was crystallised from hexane as colourless plates, m.pt. 188°. Found: hydrolysable methyl, 8·65%; Be, 7·66%; M (cryoscopically in 0·33, 0·50 wt.% solution in benzene) 320, 358. (Low solubility restricted the M.Wt. determination to very dilte solution). $C_{18}H_{42}Be_3O_4$ requires hydrolysable methyl, 8·60%; Be, 7·74%; M, 349. The infrared spectrum recorded as a Nujol mull showed: 489 w; 588 w; 568 m; 774 w; 836 s; 908 w; 985 s,br; 1052 w; 1194 s; 1232 m; 1248 m; 1358 s; 1383 m; The p.m.r. spectrum in benzene showed a singlet at 8·60 and a singlet at 10·41 with an area ratio of 6 : 1. The compound could be recovered unchanged from solutions containing excess TMED.

11. Coordination complexes of alkylberyllium hydrides.

Preparation of (neo-pentylberyllium hydride)$_2$.N,N,N',N'-tetramethylethylenediamine.

To a solution in ether/benzene containing $BeBr_2$ (1·553 g., 9·20 millimoles) and (neo-pentyl)$_2$BeOEt$_2$ (2·70 g., 9·20 millimoles) was added $NaBHEt_3$ (13 ml. 1·42M solution in hexane). The precipitate of NaCl that was produced was filtered off leaving a clear, colourless solution. TMED (2·40 ml., 18·8 millimoles) was then added slowly with stirring. Evaporation of the solvent left a white solid which was recrystallised from hexane as colourless plates, m.pt. 123-125°. Found: hydrolysable hydrogen, 0·72%; hydrolysable neo-pentyl, 50·1%; Be, 6·45%; M, (cryoscopically in 0·75, 1·13 wt.% solution in benzene) 261, 267. $C_{16}H_{36}Be_2N_2$ requires hydrolysable hydrogen, 0·72%; hydrolysable neo-pentyl, 51·1%; Be, 6·48%; M, 278. The infrared spectrum recorded as a Nujol mull showed: 665 w; 683 w; 731 vw; 779 w; 803 m; 895 m; 923 s; 990 m; 998 m,sh; 1007 m; 1013 m; 1029 w;

1060 vw; 1080 w; 1093 w; 1123 m; 1149 vw; 1172 w; 1213 m; 1229 m; 1261 m,sh; 1295 s,br; 1330 sh,m; 1345 s; 1350 s,sh. The p.m.r. spectrum in benzene showed the following resonances at 30°:

Type	τ	Assignment	Relative Intensity
Multiplet	Centred at 8·07	$\mathrm{N{-}C\underline{H}_2}$ and $\mathrm{N{-}C\underline{H}_3}$	7-8
Singlet	8·40	$\mathrm{(C\underline{H}_3)_3CCH_2{-}Be}$	10
Singlet	Broad, centred at 9·64, 15 cycles wide at half height.	$\mathrm{(CH_3)_3CC\underline{H}_2{-}Be}$	2

At 60° and 80° the $\mathrm{-C\underline{H}_2-Be}$ resonances are sharper, the widths at half height being about 4 c.p.s. in each case.

Formation of <u>neo</u>-pentylberyllium hydride by the reaction between <u>neo</u>-pentylberyllium bromide and lithium hydride does not take place.

12. Reactions between dialkylberyllium complexes and alkynes.

The reaction between $\mathrm{Et_2BeTMED}$ and phenylacetylene.

The results of a series of small scale sealed tube reactions involving phenylacetylene and $\mathrm{Et_2Be,TMED}$ are summarised in the table below. Most of the reactions were carried out in benzene solution and the concentrations are those of $\mathrm{Et_2Be,TMED}$ in moles litre^{-1}. The solutions were a very pale yellow at the end of their reactions.

Reaction	Time (hrs.)	Temp. (°C)	Conc.	% Ethane produced	% Ethane formed on hydrolysis
$\mathrm{Et_2BeTMED + PhC{\equiv}CH}$	24	60	1·1	18	82
$\mathrm{Et_2BeTMED + PhC{\equiv}CH}$	96	60	1·2	31	67·5
$\mathrm{Et_2BeTMED + PhC{\equiv}CH}$	96	80	1·0	39	59
$\mathrm{Et_2BeTMED + PhC{\equiv}CH}$	24	60	No solvent	28	69·5
$\mathrm{Et_2BeTMED + 2PhC{\equiv}CH}$	96	60	1·0	40·5	58
$\mathrm{Et_2BeTMED + 2PhC{\equiv}CH}$	96	80	1·0	52	46

A large scale sealed-tube reaction was also carried out, using Et_2Be,TMED (6·14 millimoles) and PhC≡CH (12·28 millimoles) in benzene (4 ml.) for 24 days at 80°. The tube was opened in a glove box and the contents transfered to a double-limbed Schlenk tube. Removal of solvent from the yellow solution left a solid which was crystallised from benzene/hexane as colourless needles, m.pt. 168°. The i.r. spectrum was identical with that of $(PhC{\equiv}C)_2Be$,TMED. Yield 1·42 gm., 69%.

Reaction of Et_2Be,TMED with methylacetylene.

A small scale sealed-tube reaction was carried out using a 1·3M solution of Et_2Be,TMED at 60° for 96 hours, to give at the end of that time a yellow solution. Results:

Reactants, (N ccs.):	Et-Be	Be	MeC≡CH
	127	63·5	63·5

Products, (N ccs.):	Ethane	MeC≡CH	Ethane formed on hydrolysis	Be	MeC≡CH formed on hydrolysis
	3·5	13·5	103	63·0	5·0

A little pentane was used to extract any other organic products from the hydrolysis mixture. A sample of this solution was shown by g.l.c. to contain at least five compounds other than pentane and benzene.

Reaction of Et_2Be,TMED with 2-Butyne.

In sealed-tube, a 1M solution of Et_2Be,TMED (2·97 millimoles) in benzene and 2-butyne (66·5 N ccs., 2·97 millimoles) were heated for 122 hours at 70°. At the end of that time 66·2 N ccs. of 2-butyne were recovered. No reaction has taken place.

Reaction of Et_2Be,NMe_3 with phenylacetylene.

Two small scalo roactions wero conducted. Tho reaction solutions, initially colourless, went deep red during the course of the reaction.

Reaction	Time (hrs.)	Temp. (°C)	Conc.	% Ethane produced	% Ethane formed on hydrolysis
Et_2Be,NMe_3 + $PhC\equiv CH$	96	60	1·1	37	34
Et_2Be,NMe_3 + $PhC\equiv CH$	96	80	0·9	38	29

Reaction of Et_2Be,NMe_3 with 2-butyne.

A sealed-tube reaction was carried out using a 1M solution of Et_2Be,NMe_3 (2·83 millimoles) in benzene with 2-butyne (2·83 millimoles, 63·5 N ccs.) for 122 hours at 70°. At the end of that time 62·9 N ccs. of 2-butyne were recovered. No reaction has taken place.

13. Reactions of alkylberyllium hydride complexes with alkynes.

Reaction of $(EtBeH,OEt_2)_2$ with 2-butyne.

On to a solution containing $(EtBeH,OEt_2)_2$, (11·9 millimoles of monomer) in benzene (12 ml.) was condensed 2-butyne (260 N ccs., 11·6 millimoles) and the mixture was heated at 70° for 11 days. The reaction solution went pale yellow in colour. No remaining 2-butyne could be detected. A sample of the solution showed on hydrolysis a ratio Et:Be:H = 0·80: 1·00: 0·29. No further compounds having a significant vapour pressure at –40° were obtained from the hydrolysis products. Pentane was added to the hydrolysis mixture to extract any organic material. Gas-liquid chromatography showed the presence of at least four products.

Reaction of $(MeBeH,NMe_3)_2$ with 2-butyne.

The reaction was carried out on a small scale between 2-butyne and $(MeBeH,NMe_3)_2$ for 122 hours at 70°. Both 2-butyne and $MeBeH,NMe_3$ monomer were 1 molar in benzene solution. The solution was yellow at the end of the reaction. Reactants, (N ccs): $MeC\equiv CMe$ 105; Be 105; hydrolysable hydrogen 105; hydrolsable methyl 105; NMe_3 105.

Products, (N ccs): Unreacted MeC≡CMe 25; free NMe_3 22; Me_2BeNMe_3 28·5.

Products by hydrolysis, (N ccs): Methane + hydrogen 72; *trans*-2-butene 32;
unidentified gas 6; beryllium 73·5.

The ratio of methane:hydrogen was estimated from i.r. intensities to be about 50:20. The remaining mixture from hydrolysis was extracted with pentane (2 ml.) and the pentane solution analysed by g.l.c. Five major peaks and at least three minor peaks that were not pentane or benzene were observed. Some of the peaks were so long coming off the column that they must have been due to C_{10}-C_{14} hydrocarbons, which themselves were probably the result of some polymerisation during the reaction. No hexamethylbenzene was produced.

Reaction of $(EtBeH,NMe_3)_2$ with 2-butyne.

A similar reaction to that above for $(MeBeH,NMe_3)_2$ was carried out using $(EtBeH,NMe_3)_2$. The solution was pale yellow after reaction.

Reactants, (N ccs): MeC≡CMe 64·5; Be 64·5; hydrolysable hydrogen 64·5;
hydrolysable methyl 64·5; NMe_3 64·5.

Products, (N ccs.): Unreacted MeC≡CMe 14; free NMe_3 24.

Products by hydrolysis, (N ccs): hydrogen 26·5; ethane 31·5; *trans*-2-butyne
7·5; unidentified gas 3·5; Be 61·5.

Analysis as above for other organic products from the hydrolysis by g.l.c. showed a pattern similar to but by no means the same as that for the methylberyllium hydride trimethylamine reaction. In particular there were two major products which were not present in the products of the previous reaction.

Reaction of $(MeBeH,NMe_3)_2$ with PhC≡CPh and PhC≡CMe followed by n.m.r. spectroscopy.

Benzene solutions one molar in $MeBeH,NMe_3$ monomer and one molar in PhC≡CPh or PhC≡CMe were prepared and the reactions followed by changes in the p.m.r. spectra of the solutions at 30°. In both cases, the changes of NMe_3 resonances showed that the reaction was complicated, and that the reaction only involved groups attached to beryllium to a very small extent.

Discussion

Coordination complexes of diphenylethynylberyllium.

A number of these coordination complexes have been prepared and they are listed in Table I below. With monodentate ligands, complexes of both the 1:1 and the 1:2 types have been found, while the complexes with chelating ligands are all of the 1:1 type.

Preparation. The starting materials for the preparations were diphenylethynlberyllium diethyl etherate (A) or diphenylethynylberyllium bis-tetrahydrofuran (B) which were prepared by the following sequence of reactions:

$$\mathrm{PhC{\equiv}CH} + \mathrm{RLi} \longrightarrow \mathrm{PhC{\equiv}CLi} + \mathrm{RH} \qquad (\mathrm{R{=}Me,Bu^{n}})$$

$$\mathrm{2PhC{\equiv}CLi} + \mathrm{BeCl_2} \xrightarrow{\mathrm{ether}} \mathrm{(PhC{\equiv}C)_2Be,OEt_2} \quad (\mathrm{A}) \qquad (74)$$

$$\mathrm{(PhC{\equiv}C)_2Be,OEt_2} + \mathrm{THF\ (excess)} \longrightarrow \mathrm{(PhC{\equiv}C)_2Be(THF)_2} \quad (\mathrm{B})$$

Properties. All of the complexes so far examined are solids. Many of them have high melting points and many decompose at or before the melting point. They are all colourless including the bis-pyridine and bipyridyl complexes. The fact that $\mathrm{(PhC{\equiv}C)_2Be,bipy}$ is the first organoberyllium bipyridyl complex which does not have an absorption in the visible region reflects the large electron-withdrawing capacity of the phenylethynyl group. There is a much lower solubility in hydrocarbon solvents for these complexes compared with similar complexes of beryllium dialkyls. In saturated hydrocarbon solvents they are all practically insoluble and in aromatic hydrocarbons only a few are soluble to any extent.

Those soluble enough to allow cryoscopic molecular weight measurement in benzene have been found to be monomeric with the exception of $\mathrm{(PhC{\equiv}C)_2Be,OEt_2}$ which was found to have a degree of association between one and two.

Table I

Compound	M.Pt. (°C)	Solubility in benzene (25°)	Degree of association	ν C≡C (cms^{-1})
$(PhC{\equiv}C)_2Be,TMED$	168-170	Fairly soluble	1	a
$(PhC{\equiv}C)_2Be,bipy$	295-302(d)	Insoluble	-	a
$(PhC{\equiv}C)_2Be,DME$	190(d)	Insoluble	-	a
$(PhC{\equiv}C)_2Be(THF)_2$	138-140(d)	Soluble	1	a
$(PhC{\equiv}C)_2Be(py)_2$	226-230(d)	Insoluble	-	a
$(PhC{\equiv}C)_2Be(NMe_3)_2$	195-200(d)	Insoluble	-	a
$(PhC{\equiv}C)_2Be(NHMe_2)_2$	151-153	Insoluble	-	a
$(PhC{\equiv}C)_2Be(NH_2Me)_2$	86-87	Sparingly soluble	-	2100 vw
$(PhC{\equiv}C)_2Be(NH_2Ph)_2$	No m.pt.	Insoluble	-	2114 vw
$(PhC{\equiv}C)_2Be,OEt_2$	1490151(d)	Soluble	1·5-1·8[b]	2105 m
$(PhC{\equiv}C)_2Be,NMe_3$	186-188(d)	Sparingly soluble	-	2085 m
$(PhC{\equiv}C)_2Be,NEt_3$	102-106	Soluble	1	2090 m

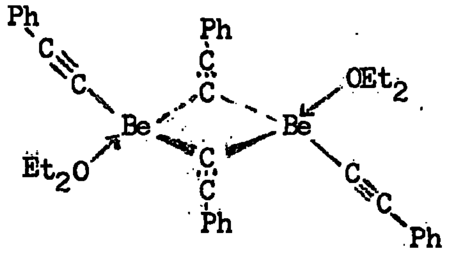
a--no absorption in region 1800-2500 cms^{-1}

b--see page 57

Table II.

Compound	M.Pt. (°C)	Solubility in benzene	Degree of association	ν C≡C (cms^{-1})
$(MeC{\equiv}C)_2Be,TMED$	198-201	Insoluble	-	2128 w
$(MeC{\equiv}C)_2Be(THF)_2$	Not recorded	Soluble	1	2137 w
$(MeC{\equiv}C)_2Be(NMe_3)_2$	No. m.pt.	Insoluble	-	2123 w

Recalling the known ability of the phenylethynyl group to act as a bridging group the complex is thought to have structure (XXVIII) but to be somewhat dissociated in solution. It is also important to realise that this compound crystallises as the 1:1 complex. In view of the known ability of diphenylberyllium to form a 1:2 complex with diethyl ether, there should be no steric difficulties to the formation of the 1:2 complex in this case also. It therefore seems very likely that the complex crystallises as the dimer and that diethyl ether is not sufficiently strong a base to break the bridge bond. This being the case it is hard to understand the observed dissociation in benzene. The triethylamine complex, $(PhC\equiv C)_2BeNEt_3$, is a monomer; this is not unexpected considering the large steric requirements of the amine. Many of the complexes showed no bands in their infrared spectra in the region expected for C≡C stretching. By far the strongest and sharpest C≡C stretching frequency absorptions were observed for the 1:1 complexes with monodentate ligands.



(XXVIII)

It can be seen from the results that replacement of alkyl groups by phenylethynyl groups has greatly increased the acceptor strength of the beryllium atom. This is exemplified by $(PhC\equiv C)_2Be(NMe_3)_2$ which, unlike its dialkylberyllium or diphenylberyllium analogues, has negligable dissociation pressure of trimethylamine at room temperature. Vigorous conditions (90-100°/10^{-3} mm Hg.) are required to remove one molecule of trimethylamine from the complex, (75). A combination of the increased electronegativity and the decreased steric

$$(PhC\equiv C)_2Be(NMe_3)_2 \longrightarrow (PhC\equiv C)_2Be,NMe_3 + NMe_3 \qquad (75)$$

requirements of the phenylethynyl group give rise to this change in acceptor strength.

The stability of the complexes towards decomposition at room temperature varies considerably. The diethyl etherate was by far the most unstable, turning yellow both in solution and in the solid state within a few days.

For the alkynyl derivatives of the most electropositive metals (Li, Na, Mg) compared with the alkyl derivatives, it is observed that despite the increased accessibility of reagents to the metal-carbon bonds and the increased polarity of the metal-carbon bonds due to the change from <u>sp</u>^{3} hybridised carbon to <u>sp</u> hybridised carbon, there is a decrease in nucleophilic reactivity. This is thought to be because the negative charge may be delocalised over at least two carbon atoms, thus reducing the bond polarity and hence, the reactivity. Recent evidence in the case of aluminium alkynyls suggests that this is not true in this case also.[226,92] The alkynyl groups of $NaAl(C{\equiv}CR)_4$ are much more reactive towards reagents such as aldehydes, alcohols and carbon dioxide, than the alkyl groups of $NaAlR_4$. Also it is found that in the reactions of $NaAlR_2(C{\equiv}CR')_2$ or $AlR_2(C{\equiv}CR')$ with these reagents, it is exclusively the alkynyl-aluminium bond which reacts. Apparently for the more covalently bonded organometallics, the effect of increased bond polarity due to the hybrisation change (<u>sp</u>^{3} carbon to <u>sp</u> carbon) is greater than the effect of delocalisation of the negative charge.

The evidence as it stands for beryllium is that there is a decreased reactivity when changing from alkyl-beryllium to alkynyl-beryllium compounds, as is demonstrated by the preference of diphenylethynylberyllium to form bis-amino adducts with methylamine and aniline rather than react by elimination of phenylacetylene. Heating at 60-80° is necessary for $(PhC{\equiv}C)_2Be(NH_2Me)_2$ to begin eliminating phenylacetylene, whereas the reaction between Me_2Be and $MeNH_2$ to give methane begins at about -90°. If it proves possible to prepare compounds of the type $M_2R_2Be(C{\equiv}CR')_2$ or $RBeC{\equiv}CR'$, as complexed or uncomplexed species, interesting comparisons with the aluminium reactions mentioned above might be carried out. As is discussed later the isolation of $RBeC{\equiv}CR'$ complexes is very likely to be prohibited by their tendency to disproportionate.

Dialkynylzinc compounds appear to act in a similar way to the beryllium compounds. Complexes of $Zn(C{\equiv}CH)_2$ and $Zn(C{\equiv}CPh)_2$ with ammonia have been isolated, whereas dialkylzinc compounds would react rapidly with ammonia. A complex of $(PhC{\equiv}C)_2Be$ with ammonia is not stable enough at room temperature to be isolated.

On addition of diphenylamine to $(PhC{\equiv}C)_2Be(THF)_2$ in benzene solution, the originally pale-yellow solution turns green. Warming causes the colour to disappear leaving a pale-yellow solution, but on cooling the colour returns. No explanation for this behavior is suggested. Only $(PhC{\equiv}C)_2Be(THF)_2$ could be isolated from the reaction mixture.

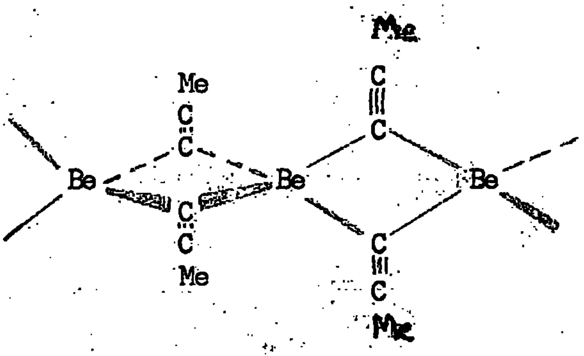
Coordination complexes of dimethylethynylberyllium.

Employing methods similar to those outlined for diphenylethynylberyllium, a few of these complexes have been prepared. Table II contains a summary of their properties. The bis-tetrahydrofuran and bis-trimethylamine complexes have very similar properties to the diphenylethynylberyllium complexes, but the complex formed with TMED is much less soluble in benzene at room temperature than $(PhC{\equiv}C)_2Be,TMED$ and crystallises from hot benzene with a molecule of benzene for each molecule of the complex. Sublimation of the complex removes the benzene.

The attempted sublimation of the complex, $(MeC{\equiv}C)_2Be(NMe_3)_2$ causes considerable decomposition. When high temperatures (110°) are employed, a small quantity of sublimate is obtained for which analysis indicates that some of the trimethylamine has been removed, but not to the extent of one molecule per beryllium.

When a solution containing dimethylethynyl beryllium in a mixed ether/

hydrocarbon solvent is concentrated, at very low volume a solid appears. If the solid is not pumped absolutely dry, it is very soluble in benzene, but insoluble in hexane. When it is filtered and pumped dry (30 mins.) then the solid is no longer completely soluble in benzene and analysis shows the compound to be $(MeC{\equiv}C)_2Be(OEt_2)_{0.37}$. After the solid has been pumped for 18 hours at 25°/10^{-3} mm. it analyses as $(MeC{\equiv}C)_2Be(OEt_2)_{0.05}$ and so it is clear that ether may be removed from dimethylethynylberyllium ether complex by pumping. This latter solid was extremely reactive towards 2-methoxyethanol at -60°, giving large quantities of carbon, and was insoluble in benzene. Its infrared spectrum recorded as a Nujol mull was very simple. From these observations it is reasonable to conclude that the compound dimethylethynylberyllium is probably a polymer with electron-deficient methylethynyl bridges similar to the polymeric structure proposed for $(PhC{\equiv}C)_2Zn$ and $(PhC{\equiv}C)_2Cd$,[65] (XXIX).



(XXIX)

Coordination complexes of phenylethynyl(methyl)beryllium.

In an attempt to prepare complexes of the type, $PhC{\equiv}CBeMe,THF$ and $PhC{\equiv}CBeMe,NEt_3$, which it was thought might contain bridging phenylethynyl groups, the following reactions were carried out,

a) addition of $(PhC{\equiv}C)_2Be(THF)_2$ in benzene solution to solid Me_2Be in a 1:1 ratio, and

b) addition of Me_2Be,NEt_3 to $(PhC{\equiv}C)_2Be,NEt_3$ in a 1:1 ratio in toluene solution.

After stirring for about an hour at room temperature the dimethylberyllium dissolved in the benzene solution of $(PhC{\equiv}C)_2Be(THF)_2$ giving a clear solution but removal of solvent only produced the starting materials. The second reaction also led to the recovery of starting materials. It was not ascertained whether the mixed species was formed in solution or not. These results indicate that the tendency to form diphenylethynylberyllium complexes is very strong and so it unlikely that alkyl(phenylethynyl)-beryllium complexes can be isolated.

Anionic complexes.

From either the 1:1 or the 2:1 reactions between $PhC{\equiv}CLi$ and $(PhC{\equiv}C)_2Be(THF)_2$, the compound $Li_2Be(C{\equiv}CPh)_4$ is produced. It has no melting point, is uncomplexed with tetrahydrofuran and is insoluble in hydrocarbon solvents. Some difficulty is observed in isolating the compound and this is probably because of the difficulty in removing the tetrahydrofuran from coordination positions about the beryllium. Most probably the structure is analogous to the ionic Li_2BeMe_4, although the relative sizes of the anion and c cations would imply a much decreased lattice energy.

Coordination complexes of phenylethynylberyllium chloride.

The following preparative routes were used in an attempt to prepare phenylethynylberyllium chloride complexes.

a) $PhC{\equiv}CLi$ + $BeCl_2$ in ether.

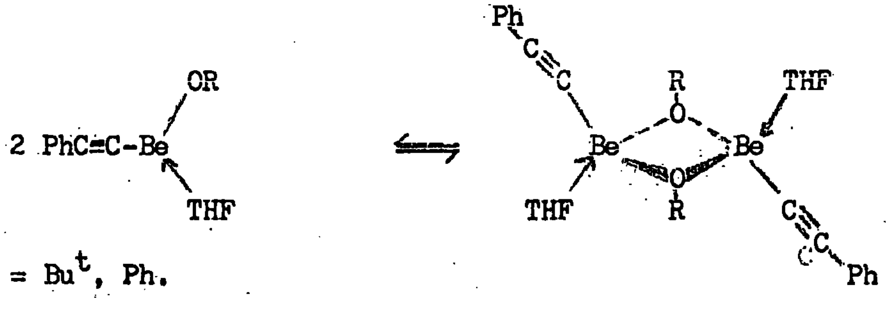
b) $(PhC{\equiv}C)_2Be(THF)_2$ + $BeCl_2$ in THF.

Method a). produced an impure solid analysing $PhC{\equiv}C$: Be : Cl = 1.12 : 1.00 : 0·65, while method b). gave a solid, m.pt. 85-87° with an analysis $PhC{\equiv}C$: Be : Cl : THF = 1·01 : 1·00 : 1·05 : 1·75 , which is thought to be a mixture of $PhC{\equiv}CBeCl,THF$ and $PhC{\equiv}CBeCl(THF)_2$. This solid could not be crystallised so excess pyridine was added to try to form a crystallisable complex. An insoluble compound was isolated which analysis indicated to be a mixture of products. Later results presented here would indicate that the use of beryllium bromide instead of beryllium chloride and the use of a chelating ligand would increase the chance of obtaining a pure product.

Reactions of diphenylethynylberyllium complexes with alcohols and thiols.

Complexes of alkylberyllium alkoxides with diethyl ether and tetrahydrfuran are known and they are monomeric or slightly associated in benzene. An equilibrium involving complexed and uncomplexed species is thought to be present in the solution (see page 25).

The reaction of $(PhC{\equiv}C)_2Be(THF)_2$ with 1 equivalent of t-butanol or phenol takes place readily at room temperature to produce the complexes $PhC{\equiv}CBeOBu^t,THF$ and $PhC{\equiv}CBeOPh,THF$. Cryoscopic molecular weight measurements in benzene indicated that the complexes had degrees of association between one and two. It therefore appears that there is a mixture of species in the solution. Uncomplexed $PhC{\equiv}CBeOBu^t$ cannot be present in solutions of $PhC{\equiv}CBeOBu^t,THF$ because this is a very insoluble compound, so it must be that there is a monomer-dimer equilibrium (76).



(76)

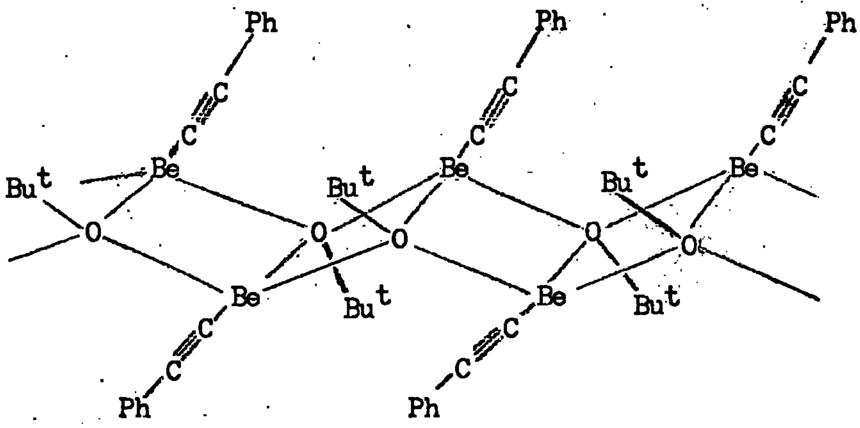
$R = Bu^t$, Ph.

The molecular weights, particularly that of $PhC{\equiv}CBeOBu^t,THF$, may not be particularly accurate owing to the limited solubility of the complexes in benzene.

The 1:1 reaction with methanol resulted in the formation of insoluble beryllium methoxide, (77).

$$(PhC{\equiv}C)_2Be(THF)_2 + MeOH \longrightarrow \tfrac{1}{2}Be(OMe)_2 + \tfrac{1}{2}(PhC{\equiv}C)_2Be(THF)_2 \quad (77)$$

Two uncomplexed phenylethynylberyllium t-butoxides have been prepared from t-butanol and diphenylethynylberyllium complexes. The first, $PhC{\equiv}CBeOBu^t$, may be obtained from the reaction in a 1:1 ratio between either $(PhC{\equiv}C)_2Be,NEt_3$ or $(PhC{\equiv}C)_2Be,OEt_2$ and t-butanol. It has a remarkable stability towards hydrolysis, being insoluble in and unaffected by 2N H_2SO_4, H_2SO_4/MeOH, NaOH/EtOH or acetic acid. However it does dissolve in warm concentrated nitric acid. The reason for this behaviour is not fully understood. A somewhat similar effect is observed for the R_2AlOR' compounds, where a greater resistance to oxygen, water and acids is observed as the size of R, and particularly the size of R', are increased. Thus $(Me_2AlOCPh_3)_2$ is insoluble in dilute hydrochloric acid, (see reference 1, page 308). A polymeric structure involving t-butoxide bridges seems the most likely of the possible structures for $PhC{\equiv}CBeOBu^t$ and it is possible that the beryllium atoms are particularly well protected from the attack of reagents such as H_3O^+ and OH^- in such a polymer, (XXX).



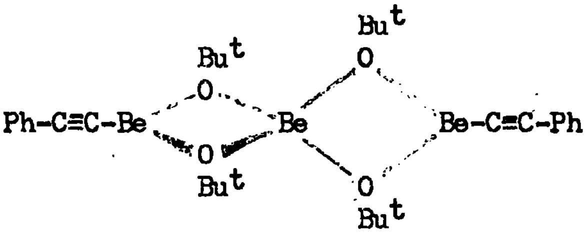
(XXX)

Another alkoxide, $(PhC{\equiv}C)_2Be_3(OBu^t)_4$, can be obtained in small yield from the reaction of $(PhC{\equiv}C)_2Be,NEt_3$ with t-butanol in a 3:4 ratio, (78).

$$3(\mathrm{PhC{=}C})_2\mathrm{Be,NEt_3} + 4\mathrm{Bu^tOH} \longrightarrow (\mathrm{PhC{\equiv}C})_2\mathrm{Be_3(OBu^t)_4} + 4\mathrm{PhC{\equiv}CH} \quad (78)$$

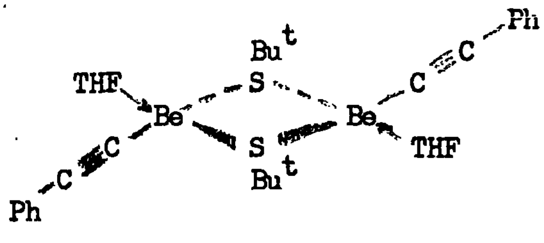
$$(\mathrm{PhC{\equiv}C})_2\mathrm{Be,OEt_2} + 2(\mathrm{Bu^tO})_2\mathrm{Be} \longrightarrow (\mathrm{PhC{\equiv}C})_2\mathrm{Be_3(OBu^t)_4} \quad (79)$$

The structure of this compound is almost certainly analogous to that of $Cl_2Be_3(OBu^t)_4$ [227,228], containing bridging oxygen atoms and terminal alkynyl groups, (XXXI). Much better yields of the compound may be obtained when it is prepared using beryllium t-butoxide, (79). It is the only phenylethynylberyllium compound so far prepared which has significant solubility in hexane.



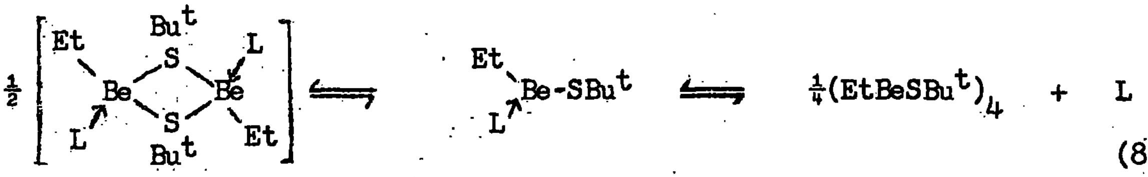
(XXXI)

When t-butanethiol is heated at 50° with $(PhC{\equiv}C)_2Be(THF)_2$ for an hour, elimination of phenylacetylene takes place to leave $PhC{\equiv}CBeSBu^t$,THF. This compound is more soluble in benzene than its oxygen counterpart and is dimeric. It is reasonable to presume that bridging through sulphur will be preferred to bridging through the alkyne and that the compound will therefore have structure (XXXII).



(XXXII)

The reactions of ethylberyllium t-butylsulphide, $(EtBeSBu^t)_4$, with tetrahydrofuran and pyridine led to the conclusion that an equilibrium (80) was present which lay predominantly to the right for tetrahydrofuran and to the left for pyridine [162].



(80)

In the present case, the comparable equilibrium lies predominantly to the left.

Thiophenol did not give a pure compound after reaction with $(PhC{\equiv}C)_2Be(THF)_2$. Table III contains a summary of the alkoxides and alkylsulphides studied.

Table III

Compound	M.Pt. (°C)	Solubility in benzene	Degree of association	ν C≡C cms^{-1}
$PhC{\equiv}CBeOBu^t,THF$	No m.pt.	Sparingly soluble	1·2-1·5[a]	b
$PhC{\equiv}CBeOPh,THF$	203-206 (dec)	Fairly Soluble	1·6-1·7[a]	b
$(PhC{\equiv}C)_2Be_3(OBu^t)_4$	212	Soluble	1	2131 w
$PhC{\equiv}CBOBu^t$	No m.pt.	Insoluble	-	2118 w
$(PhC{\equiv}CBeSBu^t,THF)_2$	150-155 (dec)	Soluble	2	2118 vw

a--see page 70

b--no absorption in region 1800-2500 cms^{-1}.

Coordination complexes of beryllium dialkyls.

A number of previously unknown coordination complexes of beryllium dialkyls have been prepared during the course of this work. Data for them is collected in Table IV. Dimethylberyllium triethylamine was prepared as part of an attempt to isolate $PhC{\equiv}C(Me)Be,NEt_3$, while the etherates of di-neo-pentylberyllium and di-benzylberyllium were prepared as part of an attempt to prepare ether-free di-neo-pentylberyllium and di-benzylberyllium. It is particularly difficult to remove the ether from these compounds. The p.m.r. spectrum of di-benzylberyllium diethyl etherate is noteworthy because of the very low field chemical shift (8·25 τ) of the $\underline{H}_2$C-Be protons.

Table IV

Compound	State	M.Pt. (°C) B.Pt. (°C/mm)	Degree of association in benzene
Me_2Be,NEt_3	liquid	$25/10^{-2}$	1
(neo-$C_5H_{11})_2Be,OEt_2$	liquid	$30/10^{-3}$	1
(neo-$C_5H_{11})_2Be,NMe_3$	liquid	$50/10^{-3}$	1
(neo-$C_5H_{11})_2Be$,TMED	solid	78-80	1
(benzyl)$_2Be,OEt_2$	solid	50-51	1
neo-C_5H_{11}BeMe,TMED	solid	41	1

Complexes of group II metal dialkyls where the alkyl groups are different have not previously been described, although a number of uncomplexed zinc and mercury mixed dialkyls are known. It was thought that using the simple n.m.r. spectra of the methyl and neo-pentyl groups information on whether such species are present or not in hydrocarbon solution might be forthcoming. In addition, while noting that the use of TMED as the complexing agent enabled the isolation of crystalline alkylberyllium bromide complexes, it was thought that this would be a good ligand to try for isolation of a mixed dialkylberyllium species.

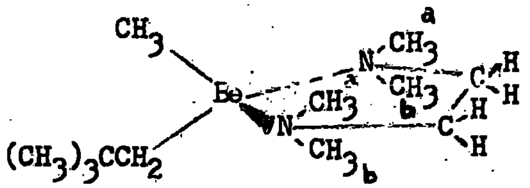
A 1:1 mixture of di-neo-pentylberyllium diethyl etherate and dimethylberyllium in reaction with 2 equivalents of TMED produces a sharp melting crystalline solid which is extremely soluble in hydrocarbon solvents. The evidence for this being a single complex, <u>neo</u>-C_5H_{11}(Me)Be,TMED rather than a mixture of Me_2Be,TMED with (<u>neo</u>-pentyl)$_2$Be,TMED comes from p.m.r. studies.

In benzene solution, the following resonances are observed at room temperature:

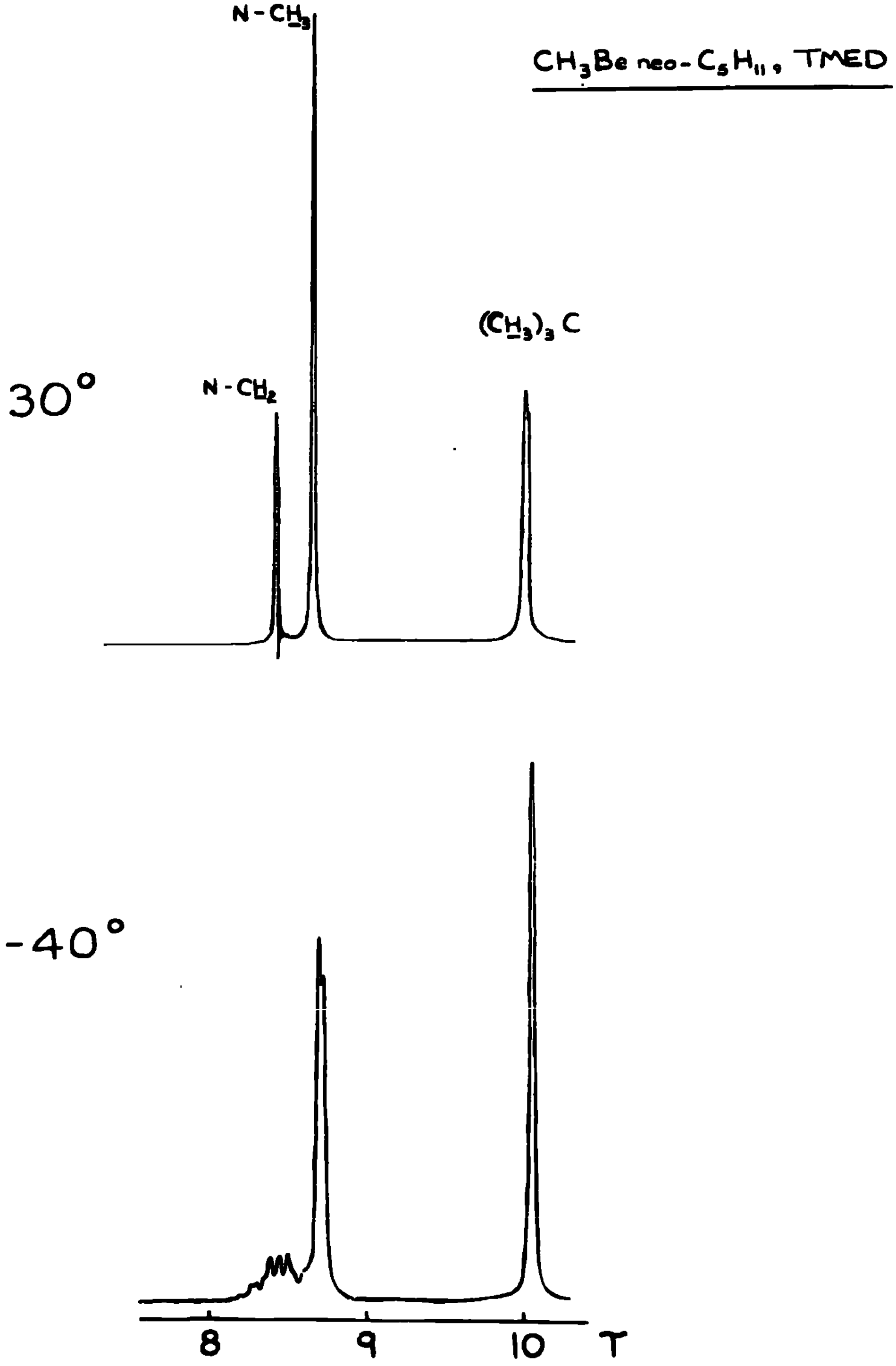
<u>Compound</u>	$C\underline{H}_3$-Be	$C\underline{H}_2$-Be	$(C\underline{H}_3)_3CC$	$C\underline{H}_3$-N	$C\underline{H}_2$-N
Me_2Be,TMED	10·80	--	--	7·99	8·11
(<u>neo</u>-Pentyl)$_2$Be,TMED	--	9·92	8·47	8·00	8·17
<u>neo</u>-PentylBeMe,TMED	10·88	10·12	8·55	7·98	8·07

The chemical shifts of the $C\underline{H}_3$Be and the $-C\underline{H}_2$Be in the mixed species are significantly different to those of the component species.

More convincing evidence comes from the low temperature studies of the mixed species in TMS. On cooling from +30° to -45° the TMED resonances change considerably. The data are given on page 79 and the spectra are shown on page 107. For a complex, <u>neo</u>-pentyl(methyl)Be,TMED, with a planar TMED group there should be two environments for N-$C\underline{H}_3$ groups and two environments for N-$C\underline{H}_2$ groups, depending on whether they are above or below the plane described by the N-C-C-N of the ligand. In the diagram (XXXII) below, N-$C\underline{H}_3$ groups labelled (a)



(XXXII)

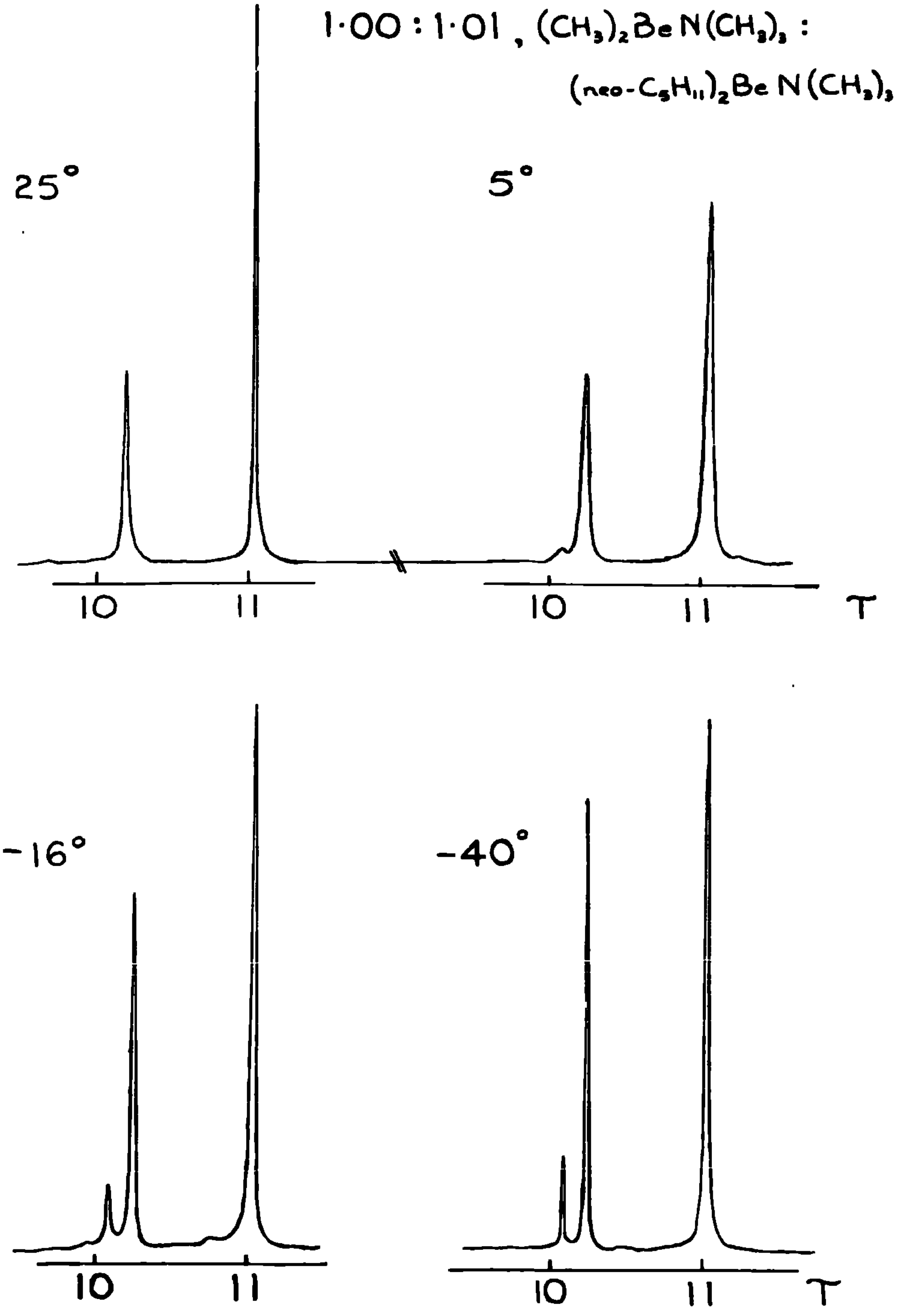

$CH_3Be\ neo\text{-}C_5H_{11} \cdot TMED$
N - CH$_3$
N - CH$_2$
$(CH_3)_3C$
30°
-40°
8
9
10
τ

are in a different environment from those labelled (b) because of the different alkyl groups bonded to beryllium. While there are single resonances for the $N\text{-}C\underline{H}_3$ and $N\text{-}C\underline{H}_2$ at room temperature, cooling to -45° produces the expected doublet for $N\text{-}C\underline{H}_3$ and a multiplet for $N\text{-}C\underline{H}_2$. Since the difference between a methyl group attached to beryllium and a methylene group attached to beryllium is not great, the chemical shift difference between the resonances of the $N\text{-}C\underline{H}_3$ doublet is not great (@ 3 cps). At room temperature a process takes place whereby the $N\text{-}C\underline{H}_3$ protons and the $N\text{-}C\underline{H}_2$ protons are no longer split. This process is most likely one involving the breaking of Be-N bonds folowed by inversion at the free nitrogen. The $(C\underline{H}_3)_3C$ group is split into a doublet (J=2 cps.) at room temperature, an observation for which no explanation is offered.

The trimethylamine complex, $(\underline{neo}\text{-pentyl})_2Be,NMe_3$ is a product of the reaction of trimethylamine with *neo*-pentylberyllium bromide. A low temperature study of cyclopentane solutions containing Me_2Be,NMe_3, $(\underline{neo}\text{-pentyl})_2Be,NMe_3$, or mixtures of the two gave the results shown on page 80. The following points need to be noted from the data:

a.) the chemical shifts of the $C\underline{H}_3\text{-}Be$ protons of Me_2Be,NMe_3 and the mixtures of Me_2Be,NMe_3 with $(\underline{neo}\text{-pentyl})_2Be,NMe_3$ are the same and do not change on lowering the temperature.

b.) the chemical shift of the $C\underline{H}_2Be$ protons of $(\underline{neo}\text{=pentyl})_2Be,NMe_3$ is not the same as of the $CH_2\text{-}Be$ protons of the mixtures. However, cooling the solution containing the 1:1 mixture causes the $C\underline{H}_2Be$ resonances to split into two peaks, one of which has the same chemical shift as that of the $C\underline{H}_2Be$ of $(\underline{neo}\text{-pentyl})_2Be,NMe_3$. This is shown on page 109. Cooling the 2·5: 1 mixture does not change the spectrum down to -16°. After that, Me_2Be,NMe_3 comes out of solution.



1·00 : 1·01, $(CH_3)_2BeN(CH_3)_3$: $(neo\text{-}C_5H_{11})_2BeN(CH_3)_3$

c.) Careful area measurement of the $C\underline{H}_3$-Be and $C\underline{H}$-Be protons of the 1:1 mixture at room temperature (30°) shows the ratio of $(CH_3)_2Be,NMe_3$ to $(\underline{neo}\text{-}C_5H_{11})_2Be,NMe_3$ = 1·00 : 1·01. At -40° the ratio remains the same but the $-C\underline{H}_2Be$ resonance is split into two peaks with a ratio 0·14 : 0·87. The smallest of the $C\underline{H}_2$-Be peaks is the one with the same chemical shift as that of the $C\underline{H}_2Be$ of $(\underline{neo}\text{-pentyl})_2Be,NMe_3$ alone and is therefore thought to represent the quantity of this compound in the solution. The other $C\underline{H}_2$-Be resonances may be assigned to the mixed species, $\underline{neo}\text{-}C_5H_{11}BeCH_3,NMe_3$. No splitting of the $C\underline{H}_3$-Be resonance of the 1:1 mixture is observed and it is believed that this is due to a degeneracy of the $C\underline{H}_3Be$ protons of $(CH_3)_2Be,NMe_3$ and $CH_3Be\underline{neo}\text{-}C_5H_{11},NMe_3$.

Using the data above, an equilibrium constant for the redistribution reaction (81) may be calculated.

$$(\text{Methyl})_2Be,NMe_3 \quad + \quad (\underline{\text{neo}}\text{-Pentyl})_2Be,NMe_3 \rightleftharpoons 2\ \text{Methyl}(\underline{\text{neo}}\text{-Pentyl})Be,NMe_3 \tag{81}$$

$$K_{eq} = \frac{(0{\cdot}87)^2}{\frac{0{\cdot}14}{2} \times \frac{1{\cdot}00-0{\cdot}87}{2}} = 170 \text{ at } -40^\circ$$

Thus, the evidence is that the equilibrium lies predominatly but not wholely in favour of the mixed species. Similar studies would enable other equilibrium constants to be calculated.

Coordination complexes of alkylberyllium halides.

The constitution of organometallic halides of group II metals in the presence of coordinating ligands, both in the crystalline state and in solution, has been the concern of chemists for many years. One of the problems has been the disproportionation equilibrium (81), which is sometimes found to the left and sometimes to the right, depending on the nature of the coordinating ligand.

$$2RMX \rightleftharpoons R_2M + MX_2 \qquad (81)$$

It now appears to be a general rule that unless insoluble metal halide complexes are formed, the equilibrium in solution lies predominantly to the left. The chart below summarizes the presently known disproportionation data of RMX compounds, where M = Be, Mg, or Zn,

Coordinating Ligand

	Et_2O	THF	1,2- dimethoxyethane.	TMED	NEt_3	NMe_3	Dioxan
RBeX	+	?	?	±	?	±	-
RMgX	+	+	-	±	+	?	-
RZnX	+	+	+	+	?	?	+

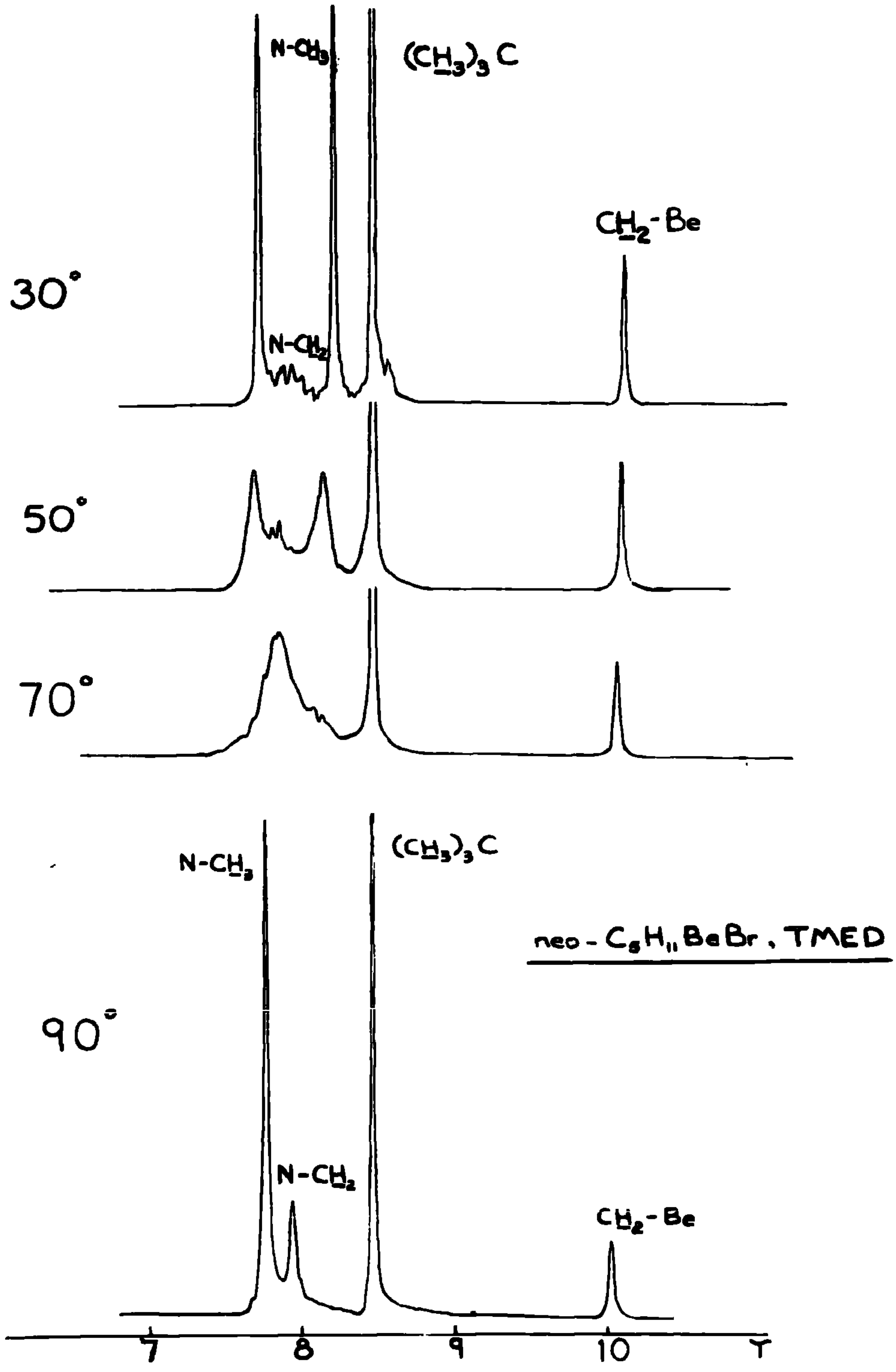
+ = disproportionation is not observed. - = disproportionation is observed. ? = effect unknown.

Changing the alkyl group R, might be expected to have little effect on the positon of the equilibrium, and this seems to be true. However, an important difference is observed between the behavior towards TMED of MeMgBr[3] on the one hand, and EtMgBr, PhMgBr and p-FC_6H_4MgBr on the other.[128] The former compound shows no tendency to disproportionate while the latter compounds do. Changing the halide might be expected to have a greater effect on the position of equilibrium since there would be changes in the solubility of the metal halide complexes. Evidence from this work suggests that the equilibrium does depend considerably on the halogen for the alkylberyllium halide complexes.

Two crystalline complexes of alkylberyllium bromides with TMED have been prepared. They are neo-pentylberyllium bromide tetramethylethylenediamine, m.pt. 104-6°, and ethylberyllium bromide tetramethylethylenediamine, m.pt. 107-9°. Both of the compounds are monomeric in benzene and show no tendency to disproportionate. . The p.m.r. spectra of these compounds in benzene show an interesting temperature dependence for the N-CH_3 and N-CH_2 resonances. At 90° they are single resonances with an area ratio of 3:1 and are of the form found for compounds such as Me_2Be,TMED. As the spectrum is cooled to 30°, the N-CH_3 resonance changes to a doublet and the N-CH_2 to a multiplet. This behavior is explained in a similar way to that for _neo_-PentylBeMe,TMED in that the two N-CH_3 groups of a dimethylamino group or the two protons of a N-CH_2 group are not equivalent at room temperature but become equivalent as the temperature is raised. Two differences from the _neo_-PentylBeMe,TMED case should be noted. First, the process whereby the N-CH_3 and N-CH_2 resonances become singlets on the n.m.r. time scale requires much higher temperatures in this case. This is as expected since alkylberyllium halides should be better acceptors than beryllium dialkyls. Secondly, for the RBeBr complexes at room temperature the chemical shift difference between the N-CH_3 resonances is much greater (30-50 cps) that the difference in the N-CH_3 resonances of _neo_-pentyl(methyl)Be,TMED at -40°. This also is to be expected. The p.m.r. spectra of _neo_-pentylBeBr,TMED at various temperatures are shown on page 113.

In the preparation of EtBeCl,TMED a crystalline solid was obtained but its analysis and p.m.r. spectrum showed it to be a mixture. One of the components was EtBeCl,TMED and the other was almost certainly a TMED complex of $BeCl_2$. This would indicate that some disproportionation had taken place.

When excess trimethylamine is condensed on to a benzene solution containing _neo_-pentylberyllium bromide and a little ether, there is quantitative disproportionation to a trimethylamine complex of beryllium bromide which is


30°
N-CH$_3$
(CH$_3$)$_3$C
CH$_2$-Be
N-CH$_2$
50°
70°
90°
N-CH$_3$
(CH$_3$)$_3$C
neo-C$_5$H$_{11}$BeBr . TMED
N-CH$_2$
CH$_2$-Be
7
8
9
10
τ

insoluble in benzene at room temperature and to di-*neo*-pentylberyllium trimethylamine, a monomeric liquid (see Table IV).

$$\textit{neo}\text{-}C_5H_{11}BeBr(Et_2O)_x + \underset{\text{excess}}{NMe_3} \longrightarrow (\textit{neo}\text{-}C_5H_{11})_2BeNMe_3 + BeBr_2(NMe_3)_y \qquad (82)$$

The reaction of excess trimethylamine with *neo*-pentylberyllium chloride in benzene containing a little ether does not result in complete disproportionation. A small quantity of insoluble material was produced. The filtrate was shown by analysis and by its p.m.r. spectrum to contain di-*neo*-pentylberyllium trimethylamine together with another species containing *neo*-pentyl groups bonded to beryllium.

Alkylberyllium alkoxides and their coordination complexes.

During an attempted preparation of di-*iso*-butylberyllium a slight leak in the course of the final distillation caused the actual preparation of *iso*-butylberyllium *iso*-butoxide, a viscous liquid, b.pt. 80°/10^{-3} mm. The compound was found to be trimeric in benzene and thus became the second known trimeric alkylberyllium alkoxide, the first being ethylberyllium triethylmethoxide.

Addition of TMED to this compound allowed the crystallisation of a complex, $(Bu^iBeOBu^i)_2$,TMED, with a melting point of 71-73°. The structure is most probably analogous to that of (EtZnOPh),TMED (see page 27, XII) with each dimethylamino group of the TMED bonded to a different beryllium. This is only the third example of this type of complex in beryllium chemistry, but more will almost certainly be found. The reaction of Me_2Be,TMED with methanol did not produce a similar complex but resulted in disproportionation (83).

$$Me_2Be,TMED + MeOH \longrightarrow \tfrac{1}{2}(MeO)_2Be + \tfrac{1}{2}Me_2Be,TMED + MeH \qquad (83)$$

It has been shown by p.m.r. studies that 1,2-dimethoxyethane does not form a complex with iso-butylberyllium iso-butoxide when present in a ratio $Bu^{i}BeOBu^{i}$: 1,2-dimethoxyethane = 2 : 1, and even when mixed in a ratio 1:2 the large majority remains in the form of the separate species. However, in the latter case there was evidence for the formation of new products, presumably coordination complexes. A similar study of the reaction with trimethylamine showed that there was indeed a reaction but that at least four new species were formed.

When t-butanol reacts with Me_2Be in a 4:3 ratio, the product is $Me_2Be_3(OBu^t)_4$, m.pt. 188°. This compound almost certainly has a structure analogous to that of $(PhC{\equiv}C)_2Be_3(OBu^t)_4$ and $Cl_2Be_3(OBu^t)_4$ (XXXI); it does not form a complex with TMED.

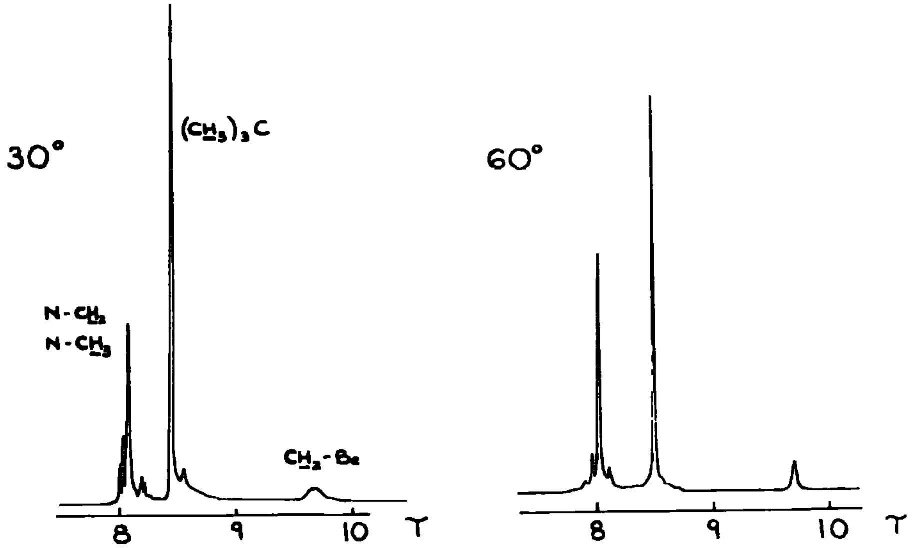
Coordination complexes of alkylberyllium hydrides.

A coordination complex, (neo-pentylBeH)$_2$TMED, m.pt. 123-125°, has been isolated. It is believed to have the same structure as the compound $(Bu^{i}BeH)_2$,TMED, for which it has been proposed that the TMED bridges the BeH_2Be unit, one dimethylamino group bonded to each beryllium (see page 31, XV). As shown on page 116, the p.m.r. spectrum of the compound has a broad resonance for the $C\underline{H}_2$-Be protons at room temperature which sharpens considerably on heating to 60°. A model shows that rotation of the neo-pentyl group about the C-Be bond is severely restricted, and this may be the cause of the broadening.

Reactions of dialkylberyllium and alkylberyllium hydride complexes with alkynes.

The results of a series of reactions between R_2Be or RBeH compounds and alkynes are found on pages 89-93. Some of the reactions produced many products,

$(\text{neo-}C_5H_{11}BeH)_2 \cdot TMED$



most of which were not identified.

A series of small scale reations between Et_2Be,TMED and phenylacetylene showed that, initially at least, the metalation reaction (83) was the only reaction taking place.

$$Et_2Be,TMED \quad + \quad 2PhC{\equiv}CH \longrightarrow (PhC{\equiv}C)_2Be,TMED \quad + \quad 2EtH \qquad (83)$$

However, when a large scale reaction was left for a comparatively long time under similar conditions to those of the small scale reactions, a yield of only 69% was obtained, suggesting that other reactions do take place.

It has been shown in many instancos that complexation of an organometallic compound can increase its metalating capability. Probably the most important example of this is the difference in metalating capabilities between organolithium compounds in the presence or absence of TMED, (reference 1, pages 19-20). Other examples include reactions (84) and (85).[61,64]

$$Et_2Zn \quad + \quad 2PhC{\equiv}CH \xrightarrow{50^{o}} (PhC{\equiv}C)_2Zn \quad + \quad 2EtH \qquad (84)$$

$$Et_2Cd \quad + \quad 2PhC{\equiv}CH \xrightarrow{20^{o}} (PhC{\equiv}C)_2Cd \quad + \quad 2EtH \qquad (85)$$

Here the rate of reaction is increased remarkably as the complexing ability of the solvent is increased. In hydrocarbon solvents the rates are extremely slow, yet reaction (84) has a half-life of 2-3 hours in THF or 1,2-dimethoxyethane, and reaction (85) a half-life of 21 hours in 1,2-dimethoxyethane or less than 5 seconds in the presence of TMED. In comparison with these reaction rates, a half-life of 96 hours at 80° for reaction (83) would indicate a much slower reaction.in this case. This may well be a further example of the influence of steric effects on the reaction rates of organoberyllium compounds.

When propyne was used instead of phenylacetylene in a small scale reaction, only a small quantity of metalated products was found. Pentane was used to extract less volatile organic products from the hydrolysis mixture and a g.l.c.

study of the extract showed the presence of at least five compounds.

From the reaction between Et_2Be,NMe_3 and phenylacetylene a deep red solution is obtained. Hydrolysis shows that metalation is not the only reaction that occurs and that beryllium-carbon bonds must have added across the triple bond.

Neither Et_2Be,TMED or Et_2Be,NMe_3 reacted with 2-butyne at an appreciable rate at 70°.

The reactions between $EtBeH,OEt_2$, $MeBeH,NMe_3$ and $EtBeH,NMe_3$ with 2-butyne have been studied briefly. They proceed in a very complicated manner giving many products, but the following conclusions may be drawn:

a.) Addition of Be-H bonds to the triple bond of 2-butyne takes place as one of, if not the most important reaction.

b.) Addition of Be-C bonds to the alkyne is possible, and is more important for the ethylberyllium hydride complexes than the methylberyllium hydride complex.

c.) For the trimethylamine complexes, free trimethylamine was found as a product of the reaction, indicating that some of the species formed during the reaction are not complexed with trimethylamine.

d.) In the case of $MeBeH,NMe_3$ plus 2-butyne a considerable quantity of Me_2Be,NMe_3 could be pumped out of the reaction tube. This probably arises from addition of the Be-H bond to the alkyne followed by disproportionation of the product.

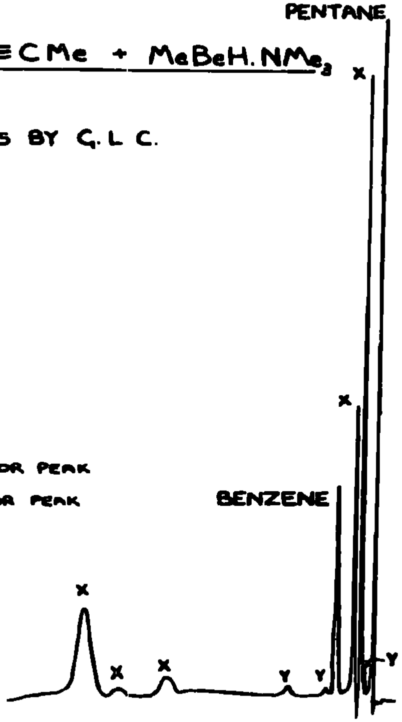
e.) Hydrolysis of the reaction products with $MeBeH,NMe_3$ or $EtBeH,NMe_3$ gave some <u>trans</u> 2-butene. No <u>cis</u> 2-butene was produced.

f.) A g.l.c. study of the less volatile organic products from the hydrolyses showed that a number of species were present. Particularly notable was the change in the g.l.c. patterns in going from the $MeBeH,NMe_3$ reaction to the

MeC≡CMe + MeBeH.NMe$_3$

PRODUCTS BY G.L.C.

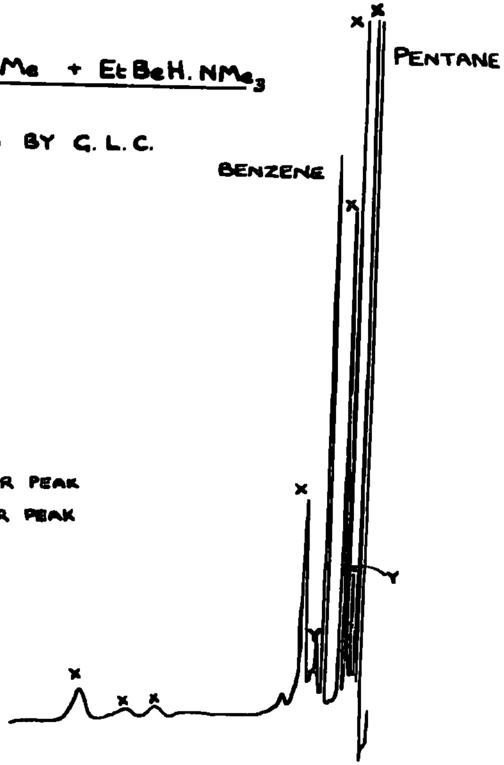
X - MAJOR PEAK
Y - MINOR PEAK



MeC≡CMe + EtBeH.NMe$_3$

PRODUCTS BY G.L.C.

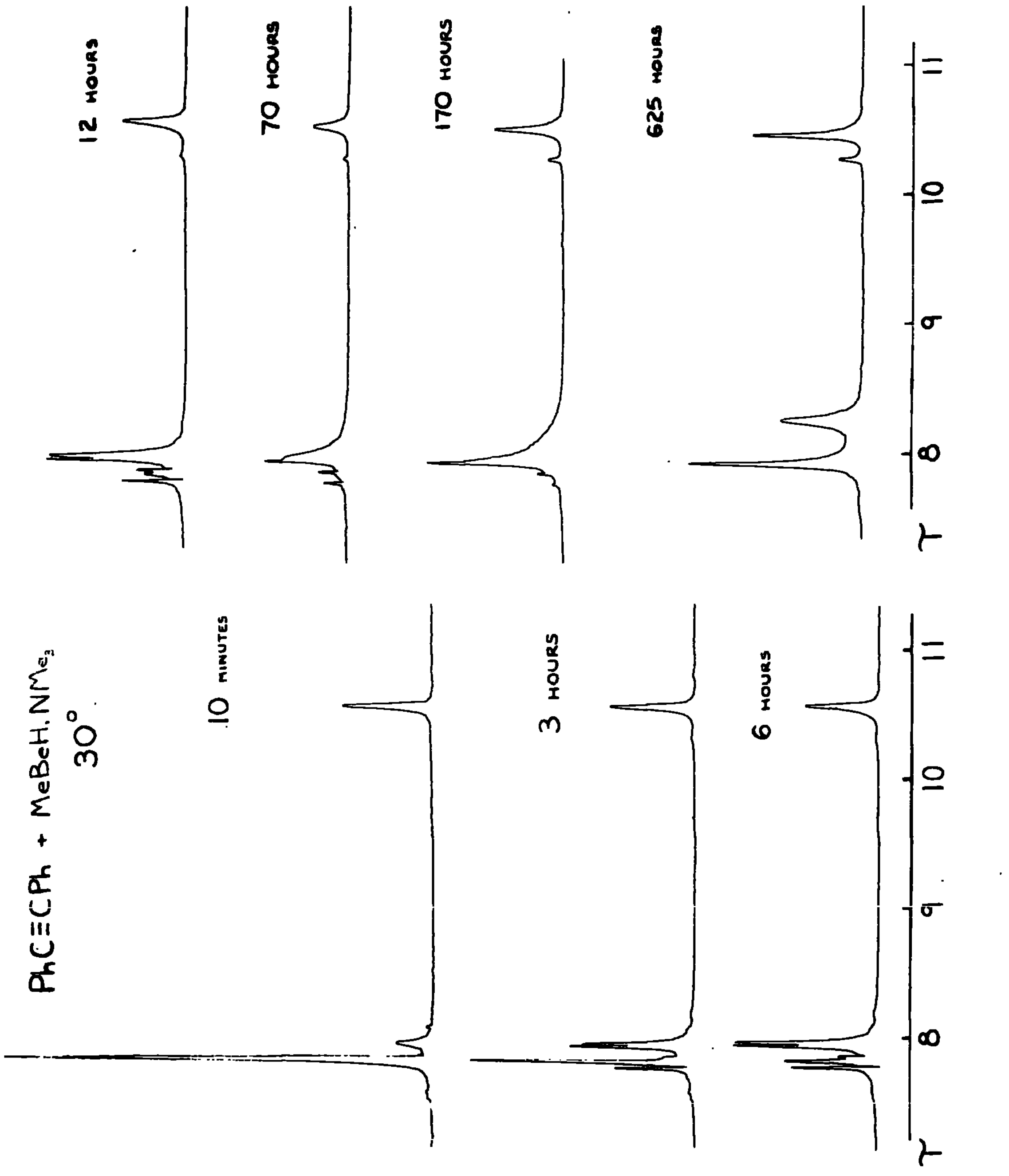
X - MAJOR PEAK
Y - MINOR PEAK



the $\mathrm{EtBeH,NMe_3}$ reaction (page 119). This showed that the reactions were far from identical. Two major hydrolysis products from the latter were not found in the former. However, all the major products from the $\mathrm{MeBeH,NMe_3}$ reaction were found in the hydrolysis products of the $\mathrm{EtBeH,NMe_3}$ reaction. Thus, it may be concluded that the Et-Be group is capable of undergoing reactions which the Me-Be group cannot. Some of the hydrolysis products had a high retention time on passing through the chromatography column and must have been the result of polymerisation reactions. No hexamethylbenzene was formed.

An n.m.r. study of the reactions between $\mathrm{MeBeH,NMe_3}$ and $\mathrm{PhC{\equiv}CPh}$ or $\mathrm{PhC{\equiv}CMe}$ was performed and this demonstrated visually the complexity of the reaction. The spectra of the $\mathrm{PhC{\equiv}CPh}$ reaction after various times at 25° are shown on page 121. It may be seen that the reaction does not involve the Me-Be bonds to a large extent. No vinyl protons upfield from $3{\cdot}3\,\tau$ were ever observed.

Finally, it is of interest that the rate of *cis*-*trans* interconversion of $\mathrm{(MeBeH,NMe_3)_2}$ appears to be slowed down in the presence of $\mathrm{PhC{\equiv}CPh}$ or $\mathrm{PhC{\equiv}CMe}$. At 30° the spectrum of the $\mathrm{(MeBeH,NMe_3)_2}$ alone shows the $\mathrm{NMe_3}$ resonances of the *cis* isomer to be a shoulder on the $\mathrm{NMe_3}$ resonance of the *trans* isomer. At a similar temperature in the presence of the acetylene the *cis* and *trans* isomers are clearly separated by 14 c.p.s. (see spectrum after 10 mins, page 121), similar to the published spectrum at 14°[170]. Is this evidence for complex formation between the acetylene and the hydride dimer? At least, it is evidence for interaction of some sort.



PhC≡CPh + MeBeH.NMe$_3$ 30°

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