Azomethine and oxyazomethine derivatives of some main group elements

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AZOMETHINE AND OXYAZOMETHINE DERIVATIVES OF SOME MAIN GROUP ELEMENTS

-by-

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MEMORANDUM

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

Parts of the work described in this thesis have been the subject of the following publications:

Azomethine Derivatives. Part I. Reactions between Diphenylketimine and Trimethylboron, Triethylboron and Triphenylboron. By I. Pattison and K. Wade. J. Chem. Soc., (A), 1967.

Azomethine Derivatives. Part III. Reactions between Diphenylketimine and Trimethylgallium, Triethylgallium and Triphenylgallium. By J.R. Jennings, I. Pattison, K. Wade and B.K. Wyatt. J. Chem. Soc., (A), 1967.

Azomethine Derivatives. Part IV. The Action of Some Organozinc Compounds on Diphenylketimine, Phenyl Cyanide and tertiary-Butyl Cyanide. By I. Pattison and K. Wade, J. Chem. Soc., (A), 1967.

Summary

The work described in this thesis can be conveniently divided into two parts: (a) Azomethine (largely diphenylketimine) derivatives of lithium, zinc and boron and (b) Oxyazomethine (largely pyridine-2-aldoxime) derivatives of Group III elements.

(a) Trimethylborane with diphenylketimine gave an adduct $Ph_2C{:}NH,BMe_3$ which at 160° eliminated methane forming $Ph_2C{:}NBMe_2$. Triethylborane with diphenylketimine at 160° gave the imine $Ph_2C{:}NCHPh_2$.

Organozinc compounds react with diphenylketimine at ca. 40° to give the dimeric derivatives $(Ph_2C{:}NZnR)_2$ which react with pyridine to form $Ph_2C{:}NZnR,2py$. In studies on reactions between organozinc compounds and nitriles, diethylzinc and phenyl cyanide at 160° were shown to give triphenyltriazine whereas diphenylzinc and phenyl cyanide at 20° form an adduct which rearranges at 100° affording bis-diphenylketiminozinc $(Ph_2C{:}N)_2Zn$.

Methyl-lithium reacts with diphenylketimine and tetramethylguanidine below room temperature yielding the derivatives $(Ph_2C{:}NLi)_n$ and $[(Me_2N)_2C{:}NLi]_2$. The former forms 1:1 complexes with pyridine and tetrahydrofuran. Phenyl cyanide and methyl-lithium give the related $(PhCMe{:}NLi)_n$.

The reactions between diphenylketimine and compounds BX_3 (where X = F, Cl, NMe_2, OMe and H) have also been studied. In two cases (X = F and H) adducts $Ph_2C:NH,BX_3$ were isolated; the borane adduct lost hydrogen at 120° to form the borazine $(Ph_2CHNBH)_3$. In two other cases (X = Cl and NMe_2), impure tris-diphenylketiminoborane was obtained. Pure tris-diphenylketiminoborane and diphenylketiminoboron dihalides were subsequently obtained from the reaction between diphenylketiminolithium and boron halides.

(b) Pyridine-2-aldoximates $C_5H_4NCH:NOMMe_2$ of boron, aluminium, gallium, indium and thallium have been prepared from the reactions between the oxime and Group II alkyls. The derivatives of aluminium, indium and thallium are dimeric in benzene solution. Spectroscopic evidence is presented in support of six-membered $(MON)_2$ ring structures with possible interaction between the metal atom and the pyridine ring nitrogen. The gallium derivative appears to dissociate in solution and the boron derivative is monomeric.

INTRODUCTION

1. Introduction.

This thesis is concerned with the preparation and co-ordination chemistry of certain, azomethine derivatives $R_2C{:}NMR'_n$ and oxyazomethine derivatives $R_2C{:}NOMR'_n$ of the elements lithium, zinc, boron, aluminium, gallium, indium and thallium. Although such derivatives of these elements were hitherto largely unknown, the chemistry of related amino derivatives $R_2NMR'_n$ and alkoxy derivatives $ROMR'_n$ has latterly been the subject of much research. The following pages are therefore devoted to a review of the methods of preparation, structures, and co-ordination chemistry of amino and alkoxy derivatives of elements of Groups I, II and III of the Periodic Table. Aspects of the co-ordination chemistry of the parent organometallic compounds are also discussed. Derivatives of Group III elements are discussed first as in some respects their chemistry is simpler than that of their Group I or Group II counterparts.

2. The preparation of amino and alkoxy derivatives of Group III.

The main preparative routes to amino derivatives of the type $R_2NMR'_2$ are as follows,

(a) by reaction between a metal alkyl or hydride and a secondary amine[1]

$$R'_3M + R_2NH \longrightarrow R_2NMR'_2 + R'H \quad (R' = \text{alkyl or H})$$

(b) by the action of an amine on a metal halide or thiol[2]

$$R'_2MCl + 2R_2NH \longrightarrow R_2NMR'_2 + R_2NHHCl$$

$$R'_2MSR'' + R_2NH \longrightarrow R_2NMR'_2 + R''SH$$

(c) by the action of a grignard reagent on a metal halide[3,4,5]

$$R_2NMX_2 + 2R'MgX \longrightarrow R_2NMR'_2 + 2MgX_2$$

(d) by the action of a metal halide on an aminolithium[6]

$$R'_2MX + R_2NLi \longrightarrow R_2NMR'_2 + LiX$$

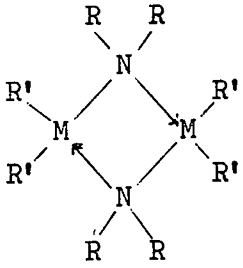
(e) by the exchange reaction between a trialkyl and a tris-amino derivative.[7]

$$2R'_3M + (R_2N)_3M \longrightarrow 3R_2NMR'_2$$

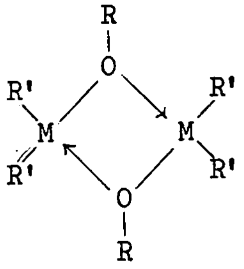
Similar preparative routes have been used to prepare the bis-amino $(R_2N)_2MR'$ and tris-amino compounds $(R_2N)_3M$. The alkoxy derivatives are prepared similarly, using alcohols instead of amines.

3. The structures of amino and alkoxy derivatives of Group III.

The amino and alkoxy derivatives of Group III metals of the type R'_2MNR_2 and R'_2MOR (where R and R' are alkyl or aryl) are either monomeric (M = B) or dimeric (M = Al, Ga, In, Tl). Where the derivative is dimeric the structure consists essentially of a four membered metal nitrogen or metal oxygen ring.



I



II

A structure of the type I enables both the metal and the nitrogen to make use of all their available tetrahedral sp^3 orbitals. All the elements of Group III have a strong tendency to expand their covalency to four and this is most marked with aluminium e.g. even trimethyl aluminium is dimeric.

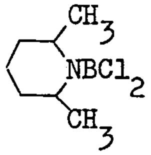
4. Factors affecting the degree of association of amino and alkoxy derivatives.

Organometallic compounds of a Group III (acceptor) atom bound to a Group V or Group VI (donor) atom have been observed as monomers, dimers, trimers, tetramers, and polymers. The factors which affect the degree of association are as follows.

(a) Electronic.

The monomeric nature of the boron compounds R'_2BNR_2 and R'_2BOR may be contrasted with the dimeric nature of the aluminium analogues $(R'_2AlNR_2)_2$ and $(R'_2AlOR)_2$. This difference is due in part to the $p_\pi - p_\pi$ bonding which can occur between the boron and the nitrogen atoms. For example Me_2BNMe_2 is monomeric and the B-N force constant[8] (from its Raman Spectrum) is consistent with a B=N multiple bond. Similarly $(Me_2N)_3B$ is monomeric the bond order being $1\frac{1}{3}$ and this is reflected in a diminution of reactivity i.e. no complex formed with trimethylamine. When relatively electronegative groups are bound to boron e.g. Cl_2BNMe_2 co-ordinative saturation is achieved by dimerisation. This compound can be obtained in two forms; the very reactive liquid monomer which slowly changes into an unreactive solid dimer.

(b) Steric.

Bulky groups R and R' in general favour low degrees of association. For example whereas dimeric Me_2NBCl_2 appears to be the more stable form at room temperature, $Pr^n_2NBCl_2$, Bu^nNBCl_2 and  exist solely in the monomeric state.[9]

(c) Entropy.

Entropy always favours low degrees of association since the number of independent molecules is then at a maximum i.e. dimers are preferred to trimers or polymers within a given phase.

(d) Valence Angle Strain.

There must necessarily be greater valence angle strain in dimers than in trimers or higher homologues. This is tolerated more readily by larger elements than those of the first period.[10]

(e) Nature of the Reaction Intermediate.

The factors outlined so far as affecting the state of association of amino or alkoxy derivatives determine which oligomer will be thermodynamically the most stable. However, a less stable product may be obtained as a result of the reaction path. Polymeric intermediates formed by an intermolecular condensation, would favour polymers, tetramers and trimers as the isolated species. Similarly a monomeric intermediate, formed by an intramolecular condensation would favour the dimer as the associated species. It is unlikely that three monomeric intermediates would associate to the trimer. Thus most of the organometallic-amino compounds are monomers, dimers or polymers whereas the dialkylphosphino compounds of dimethyl-boron,[11] aluminium,[12] gallium[13] and indium[13] are observed as trimers, tetramers and polymers.

Examples of the effect of the reaction path are observed in the preparation of H_2BNMe_2 and H_2AlNMe_2. If H_2BNMe_2 is prepared from the adduct H_3BNMe_2H[14,15] or from sodium borohydride and dimethylammonium chloride then an equilibrium mixture of monomer and dimer is obtained. However, the reaction of B_5H_9 with NMe_2H[15] gives both trimer $(Me_2NBH_2)_3$ and the equilibrium mixture of monomer and dimer. If B_5H_9 is allowed to react with the equilibrium mixture trimer is produced, but no trimer is formed when H_2BNMe_2 is heated alone. The preparation of the trimer[16] $(H_2AlNMe_2)_3$ from $LiAlH_4$ and Me_2NHHCl might involve five-co-ordinate aluminium in a polymeric intermediate. Five-co-ordinate boron must be excluded and this difference might explain the difference between the degrees of association of the borane and alane. Similarly as the compound[17] $H_3Ga(NMe_3)_2$ is unstable above -63° so H_2GaNMe_2 was predicted[13] to be dimeric if prepared from Me_3N,GaH_3 and Me_2NH on the basis of its probable reaction intermediate Me_2NH,GaH_3. This has indeed been shown to be the case.[18] When the state of association is dependent upon the nature of the reaction intermediate then the product is not necessarily in the most favoured state thermodynamically. These general principles are discussed below with reference to appropriate elements of Groups I, II and III.

B. Review of compounds of Group III elements.

1. Boron.

(a) Adducts of organoboranes.

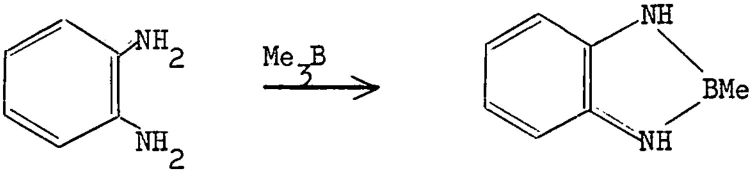
Trialkylboranes form complexes of varying strength with amines. The heat of dissociation of the complexes of trimethylborane and non sterically hindered amines are generally about 17 k.cal./mole,[19] however when the alkyl groups attached to either boron or nitrogen are large then the complex is more easily dissociated. Thus although triethylamine is a stronger base than trimethylamine with respect to proton acceptance the ΔH (k.cal./mole) values for the adducts with trimethylborane are Me_3BNMe_3 17·6 and Me_3BNEt_3 10. Similarly although α-picoline is a stronger base than pyridine, the pyridine complex with trimethylborane is much more stable than the α-picoline complex.[20] An interesting series of addition compounds between cyclic imines $(CH_2)_xNR$[21,22] ($x = 3, 4, 5$ and 6 and $R = H, Me$) and trimethylborane have shown that the stability of the complex where $R = Me$ is $x = 3 > 4 > 5 > 6$ and $R = H$, $x = 4 > 5 > 6 > 3$. The complete reversal in position of the 3-membered ring upon substituting a methyl for a proton on the nitrogen in this series is due to large steric interaction. This effect becomes more pronounced as the ring size increases, thereby leading to a systematic decrease in stability. Only in the case of the 3-membered ring does methyl substitution result in a more stable addition compound. For the ether ring compounds, methyl substitution results in decreased stability, the decrease becoming progressively larger as the ring size increases. The relative stability of adducts of trimethylborane[23] have been determined by observing the proton chemical shifts of the B-CH_3 attached protons in dichloromethane using the solvent as an internal reference standard. No shift was observed when a 1:1 mixture of diethylether and trimethylborane was observed vindicating the observation that no interaction between the components occurs.[24] The relative stabilities of the complexes were: $Me_3N \sim EtMe_2N > Et_3N > Et_2O$.

(b) Aminoboranes.

Thermal decomposition of the complex $R_2NHBR'_3$ occasionally under pressure results in the formation of a borazene $(R_2NBR'_2)_x$ and most interest has been in the value of x and the bond order of the B-N bond. The simplest borazene[25] $(H_2NBH_2)_x$ has recently been prepared by the action of sodamide on the diammonate of diborane, in liquid ammonia,

$$NaNH_2 \quad + \quad BH_2(NH_3)_2^+BH_4^- \xrightarrow{1.\ NH_3} (H_2NBH_2)_x$$

and x is mainly 5, although small yields of the dimer and trimer and minute traces of the tetramer were detected. The extent of association decreases as hydrogen is substituted by alkyl groups: thus N-methylaminoborane is trimeric[26] $(H_2BNHMe)_3$, and reversible monomer-dimer equilibria may be realized with H_2BNMe_2,[14] $MeHBNMe_2$,[27] Me_2BNHMe,[28] and Me_2BNH_2.[29] All known tetrasubstituted aminoboranes ($R_2BNR'_2$; R,R' = alkyl or aryl) appear to be monomeric.[3] Several high temperature reactions of trimethylborane have afforded a variety of heterocyclic products:[30]



The monomeric species $R_2BNR'_2$ are stabilised not only sterically but also co-ordinative saturation of both boron and nitrogen is achieved by formation of a B=N multiple bond. However the large dipole expected for the formula $R_2\overset{-}{B}=\overset{+}{N}R'_2$ is very considerably reduced by unsymmetrical electron sharing in the sense B⟶N owing to the electronegativity difference between boron and nitrogen.[31] However the fact remains that the B-N bond order is greater than one. Indeed for $Ph(Cl)BNMe_2$ it has been shown that the substantial potential barrier to rotation about the B-N bond is due to a large measure of $p_\pi - p_\pi$ bonding rather than steric reasons.[32] Where two different alkyl groups are attached to boron i.e. $R_2NBR'Ph$ two isomers have been obtained which are in equilibrium.[5] It has been suggested that the cis-trans isomers equilibrate by rotation about the B-N bond. The double bond character B=N is enhanced if the organic group attached to boron is a phenyl, in which case the B-N stretch frequency has been assigned at 1470 cm.$^{-1}$. The B-N stretching frequencies have been assigned by several workers[33,34,35] and found to vary from 1470 cm.$^{-1}$ in the above compound to 1350 cm.$^{-1}$ in Me_2BNPh_2. Azomethine derivatives of boron, which are analogous to borazenes have been prepared by the hydroboration of a cyanide.[36,37,38]

$$MeCN + Me_2BH \xrightarrow[25^{\circ}]{} \tfrac{1}{2}(MeCH{:}NBMe_2)_2$$

In all cases the derivatives were associated and in some instances cis and trans isomers were present which on occasion were separable. Alkyl migration across a cyanide was found not to occur.

Dehydrogenation or dealkylation of a borazene would give a monomeric borazine R-N-B-R' if no association occurred. However until recently all known borazines were trimeric, the simplest example borazole $(HBNH)_3$ being isoelectronic with benzene. This series of compounds has been extremely well reviewed.[39] Recently however two monomeric borazines have been prepared,[40] by refluxing a benzene solution of pentafluoroboron dichloride and a primary aromatic amine:

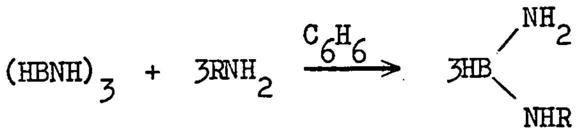
$$C_6F_5BCl_2 + ArNH_2 \longrightarrow C_6F_5B{=}NAr$$

(I) Ar = $pCH_3OC_6H_4$

(II) Ar = mesityl.

Product (I) was accompanied by 13% of the dimer, whereas (II) gave solely the monomer. The BN stretching vibration in (I) is infrared inactive but the Raman absorbtions occur at 1703 (^{11}BN) and 1710 (^{10}BN). It is thought that the B-N bond in (I) is non polar due to the electron withdrawing power of C_6F_5 which would strengthen the two possible BNπ bonds. (I) forms a crystalline 1:1 adduct with pyridine showing that a degree of unsaturation exists.

A number of bis-aminoboranes $(RR'N)_2BR''$ have been prepared[41]. All are monomeric indicating significant partial double bond character between boron and nitrogen. Recent new methods of preparation have shown that interest in this field is being maintained. Borazine reacts with primary amines:[42]



$$(HBNH)_3 + 3RNH_2 \xrightarrow{C_6H_6} 3HB(NH_2)(NHR)$$

Dimethylamino-organoboranes can be obtained by heating trisdimethylaminoalane with alkylboroximes.[43]

$$3Al(NMe_2)_3 + (RBO)_3 \xrightarrow[1\ hr.]{75^{\circ}} 3RB(NMe_2)_2 + 3/x\,[Me_2NAlO]_x$$

Bis(-alkylamino)arylboranes undergo a general transamination reaction with primary or secondary amines.[44] Thermal decomposition of the derivatives $PhB(NHR)_2$ gave the cyclic borazole[45,46] $(PhBNR)_3$. Trisaminoboranes $(R_2N)_3B$ have been prepared by numerous routes[41] as shown in Figure 1, many of which are involved in other systems. Recent methods of preparation have involved transamination[44] and the reaction between trisalkoxyboranes and trisdimethylaminoaluminium.[43] They are

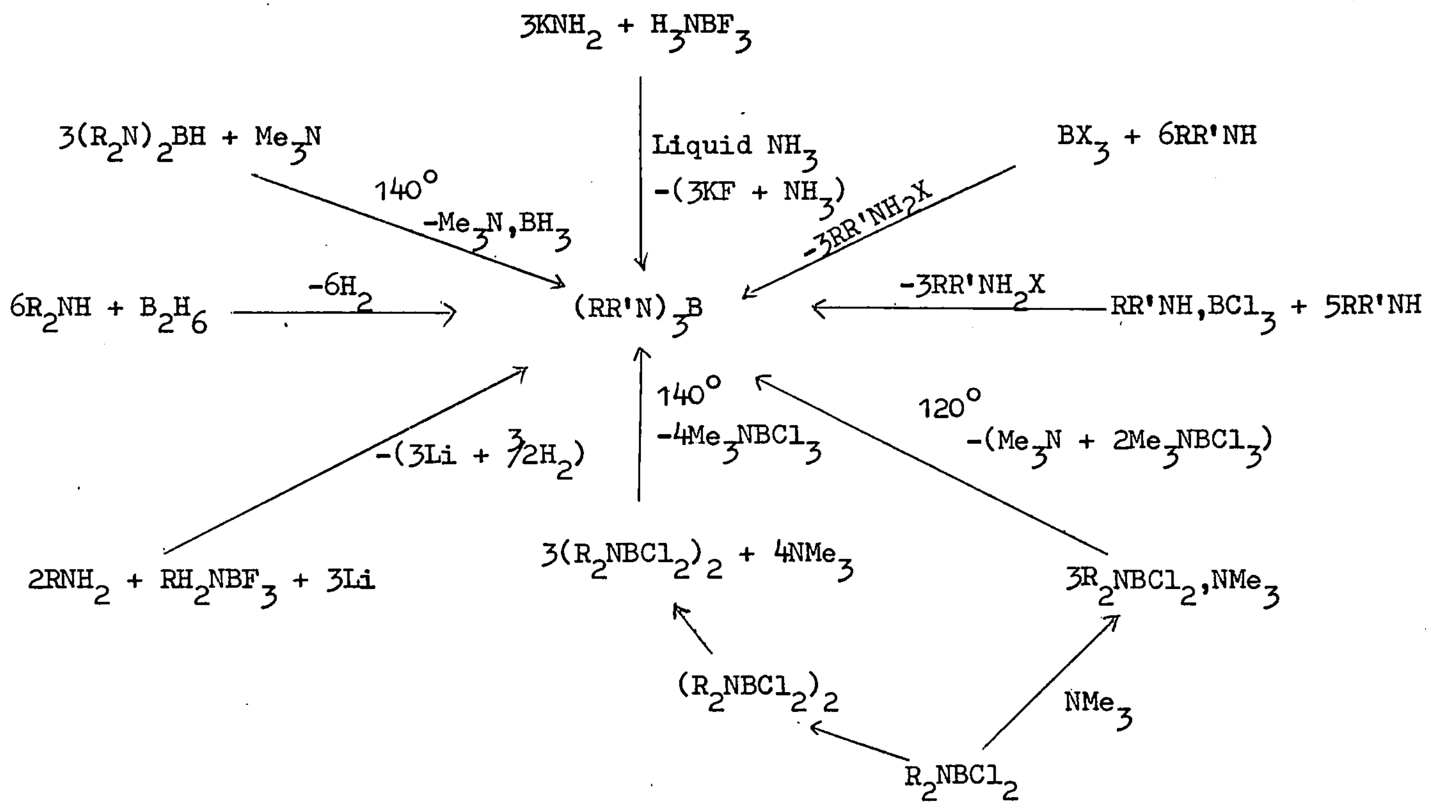

$3KNH_2 + H_3NBF_3$
Liquid NH_3
$-(3KF + NH_3)$
$3(R_2N)_2BH + Me_3N$
140°
$-Me_3N,BH_3$
$BX_3 + 6RR'NH$
$-3RR'NH_2X$
$6R_2NH + B_2H_6$
$-6H_2$
$(RR'N)_3B$
$-3RR'NH_2X$
$RR'NH,BCl_3 + 5RR'NH$
$-(3Li + 3/2H_2)$
140°
$-4Me_3NBCl_3$
120°
$-(Me_3N + 2Me_3NBCl_3)$
$2RNH_2 + RH_2NBF_3 + 3Li$
$3(R_2NBCl_2)_2 + 4NMe_3$
$3R_2NBCl_2,NMe_3$
$(R_2NBCl_2)_2$
NMe_3
R_2NBCl_2

FIGURE 1

all monomeric due to the partial double bonding between the boron and nitrogen satisfying the electron deficiency of boron. Trisdimethylaminoborane has a trigonal planar arrangement of three nitrogen atoms about the boron atom. The B-N bond length is 1·46Å and the B-N-C angles[47] are 120°.

2. Aluminium.

(a) Adducts of organoalanes.

Aluminium alkyls and hydrides form stronger co-ordination complexes with oxygen and nitrogen containing bases than do the corresponding boron derivatives. Whereas ether does not co-ordinate to trimethylborane, Me_3AlOEt_2 has a heat of co-ordination of 11·2 k.cal. mole^{-1}.

The first amine complexes of organoalanes,[48] $H_3NAl(p\text{-tolyl})_3$ and $H_3N,AlPh_3$ were described by Krause and Dittmar in 1930. The first was said to darken when heated above 120° but no decomposition products were identified. Since then many 1:1 complexes have been isolated[12,49,50,51] and some complexes are known in which the aluminium atom is five co-ordinate.[52,53,54]

(b) Aminoalanes.

Wiberg as reported by Bähr[55] has also studied amine-organoalane complexes and their thermal decomposition. His proposed reaction scheme is as follows although very little supporting evidence is produced.

$$H_3NAlMe_3 \xrightarrow[-CH_4]{70^\circ} (H_2NAlMe_2)_x \xrightarrow[-CH_4]{200^\circ} (HNAlMe)_y \rightarrow (AlN)_z$$

$$MeNH_2AlMe_3 \longrightarrow (MeNHAlMe_2)_x \longrightarrow (MeNAlMe)_y$$

Similar systems have been studied by several workers.[49,56,57] The complexes Me_3N,AlR_3 and their derivatives $(R_2NAlR_2)_x$ can also be prepared from the reaction between the aluminium hydride and organolithium or mercury compounds.[58] The amine alanes $R_2NAlR'_2$ like the aminoboranes $R_2NBR'_2$ show a decrease in the extent of their association as alkyl groups are substituted for hydrogen. Thus H_2NAlH_2[59] is polymeric, Me_2NAlH_2[16] and Me_2AlNH_2[57] are trimeric and the tetraorgano substituted derivatives are dimeric.[12,58] There is no evidence for double bonding in any of the compounds of the aluminium series or any of the similar compounds formed by the Group IIIB elements Ga, In, Tl; they all associate. They are not affected by trimethylamine nor are they significantly dissociated on vaporisation.

The rather interesting compound dimethylaluminium azide $(Me_2AlN_3)_3$ has recently been prepared and presumably contains a six membered $(AlN)_3$ ring.[60] The analogous azomethine derivatives $R_2C{:}NAlR'_2$ are however all dimeric. These have been prepared by the migration of an alkyl group or a hydrogen atom across a nitrile.[61,62,63]

$$RCN + R'_3Al \xrightarrow{110\text{-}240^\circ} (RR'C{:}NAlR'_2)_2$$

$$RCN + Me_2AlH \xrightarrow{20^\circ} (RCH{:}NAlR'_2)_2$$

The reaction of triethylaluminium with nitriles occurs in a slightly different manner to that of the other organo-aluminium compounds studied. Ethylene was evolved and hydrogen migration occurred.

$$PhCN + Et_3Al \xrightarrow{200^\circ} (PhCH{:}NAlEt_2)_2 + C_2H_4$$

Whereas the aminoalanes $(R_2NAlR'_2)_2$ reveal the effect of bond angle strain[64] in that crystal → glass → liquid change occurs when heated slowly the azomethine alanes $(R_2C{:}NAlR'_2)_2$ do not, even though the greater strain expected to be present in the alkylidene amino compounds should make a transition to a polymeric glass more likely.

Thermal decomposition of the aminoalanes $MeNHAlMe_2$,[55] $EtNHAlH_2$,[65] MeNHAlEtCl[56] and $MeNHAlPh_2$[49] have resulted in evolution of hydrocarbon or hydrogen and formation of the oligomeric derivatives $(RNAlR')_x$. When R=R' = Ph a crystalline tetramer is obtained but when ortho-substituents are present on the amine, the crystalline dimers $(Ph_2AlNHAr)_2$ are obtained.[66] The tetramers have a cubic structure having twelve essentially equal Al-N bond lengths.[67]

(c) Alkoxyalanes.

Dimethylaluminium methoxide is a cyclic trimer as is diethylaluminium methoxide, but diethylaluminium ethoxide and t-butoxide are dimeric. These compounds illustrate the steric factor governing association, there being less steric interference between bulky substituents in a dimer than in the corresponding trimer. A dimer is obtained from triethylaluminium and 2-ethoxyethanol, the ethereal oxygen atoms not being involved in co-ordination.[68] Similar alkoxides are obtained from the addition of an organoaluminium compound across a carbonyl e.g. the dimeric compound $(Ph_2C(Me)OAlMe_2)_2$ has been isolated from the reaction between benzophenone and trimethylaluminium.[69]

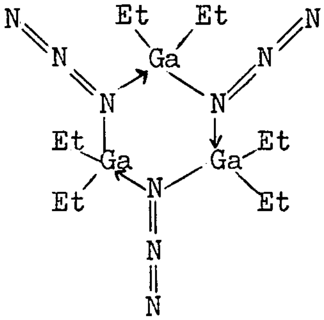
3. Gallium, Indium and Thallium.

The trimethyl derivatives of gallium, indium and thallium are rather poor acceptors. Trimethylgallium though a stronger acceptor than trimethylboron, is weaker than trimethylaluminium. The rather unstable ether complex of trimethylindium[70] may be separated into its components by fractional condensation while trimethylthallium may be separated from its very unstable ether complex Me_3Tl,OEt_2 by distillation under reduced pressure.[71] Recent proton magnetic resonance studies have related the chemical shift of the $Ga-CH_3$ attached protons to the stability of the complex.[72] Dimethylamine complexes of Me_3Ga,[73] Me_3In[74] and Me_3Tl[74] have been described, the first two eliminating methane at 120° and 140° respectively to yield the dimeric derivatives $(Me_2MNMe_2)_2$ which exist in both crystalline and glassy forms. It is believed that the latter consist of cyclic oligomers or polymers.[75] The thallium complex $Me_2NHTlMe_3$ decomposes on heating to methane, thallium and unidentified materials. It has been prepared however from the reaction between dimethylthallium bromide and dimethylaminolithium.[74] It is also dimeric.

The thermal decomposition of trimethylgallium-amine complexes RR'NHGaMe$_3$ occurs smoothly at temperatures between 70° and 130°. The loss of methane from the co-ordination compounds of trimethylboron with ammonia, methylamine and dimethylamine requires much higher temperatures than are necessary to decompose those of aluminium and gallium. The boron compounds decompose at 280-333°, whilst those of aluminium appear to be somewhat less stable than their gallium analogues, their decomposition temperatures being 57-70° (NH_3), 55-57° (NH_2Me) and 90-120° ($NHMe_2$) in contrast to 70°, 120-130° and 115-130°. The stabilities[72] of the amine complexes of trimethylgallium are predicted by p.m.r. to be $Me_2NH > NH_3 \sim MeNH_2$.

The polymeric materials $(MeGaNH)_x$ and $(MeGaNMe)_y$ are almost certainly formed when the dimeric species $(Me_2GaNH_2)_2$ and $(Me_2GaNHMe)_2$ are heated to above 140° and 180° respectively. All compounds of the type $(R'_2NMR_2)_2$ M = Al, Ga, In, Tl are dimeric; only in the case of the boron analogues are monomeric species known.

Diethylgallium azide Et_2GaN_3 has recently been prepared[76] by allowing triethylgallium to react with chloroazide. The product is trimeric its structure is presumed to be based upon a six membered Ga-N ring.



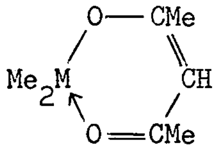
Two analogous azomethine derivatives of gallium $(PhCH{:}NGaEt_2)_2$ and $(Bu^tCH{:}NGaEt_2)_2$ have been prepared[77] by the thermal decomposition of the adducts $RCNGaEt_3$. Upon heating to 150° ethylene was evolved and hydrogen migration occurred.

$$RCN + Et_3Ga \xrightarrow{T > 150^\circ} (RCH{:}NGaEt_2)_2 + C_2H_4$$

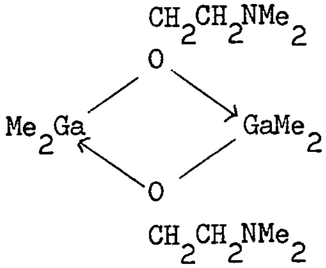
Other nitrile-alkylgallium complexes were thermally decomposed but no hydrogen or alkyl migration occurred. The complexes tended to dissociate into the components particularly under reduced pressure when heated. Methane elimination sometimes occurred with the formation of polymeric materials although trimethylgallium polymerised phenyl cyanide to 2,4,6-triphenyltriazine $(PhCN)_3$.

The alkoxides (R_2MOMe) of gallium[78] and thallium[79] are dimeric whereas dimethylindium methoxide[74] like the aluminium analogue is a cyclic trimer.

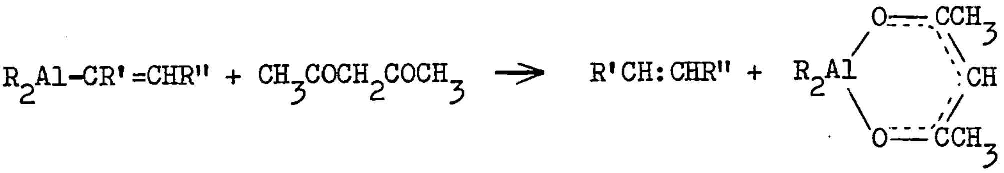
Trimethylgallium,[78] indium[74] and thallium[80] all react with acetylacetone to give methane and chelate monomers.



Trimethylgallium also reacts with salicylaldehyde with the elimination of methane and formation of a similar chelate monomer. With dimethylethanolamine however, which might be expected to form a chelate compound, a dimeric product is obtained which forms a dimethiodide with methyl iodide.[78] The complex is formulated as,



A similar dimer is obtained from triethylaluminium and 2-ethoxyethanol,[68] although the acetylacetone derivatives of dialkyl aluminium are postulated as monomers.[81]



An infrared spectroscopic study of some dimethyl-gallium and -aluminium derivatives of oxy acids[82] has shown that the dimeric acetates contain bridging acetate groups in an eight-membered cyclic structure. However on similar evidence some acetoxy boranes $R_2BOOCCH_3$ have been assigned monomeric structures. The lowered carbonyl stretching frequency indicated the presence of a chelating acetate group. The relative intensity of the band due to ν(C=O) in $Me_2BOOCCH_3$ remained constant over a large concentration range in solution suggesting the absence of an acetate bridged dimer.[83]

C. Zinc.

1. Adducts of organozinc compounds.

The first indication of the existence of co-ordination complexes of organozinc compounds was the observation of Frankland[84] in 1859, that the use of dimethyl- or diethylether as a solvent greatly facilitates the formation of dimethylzinc from zinc and methyl iodide, but that complete separation of ether from the product was impossible. The Me_2O/Me_2Zn system has recently been reinvestigated by Thiele,[85] who has demonstrated the formation of a 1:1 complex. However a complete separation was achieved by distillation of the complex through an efficient fractionating column. A series of liquid adducts with cyclic ethers was also reported which although distillable at atmospheric pressure without decomposition, dissociated in benzene solution. The strength of the bond between the dimethylzinc and the ether molecules and the possibility of co-ordination of a second ether molecule was found to increase from ethylene oxide to pentamethyleneoxide. Only 1:1

complexes were formed with ethylene oxide and trimethylene oxide, whereas with tetrahydrofuran and pentamethylene oxide 2:1 complexes are obtained. On steric grounds the reverse trend might have been expected and it was concluded that the major influencing factor was the orientation and character of the oxygen orbitals, which vary with the ring size of the ether.

Dimethylzinc yields crystalline and presumably chelate, 1:1 complexes with 1,4-dioxan and 1,4-thioxan. These cannot be distilled without decomposition. Aliphatic ethers like 1,2-dimethoxyethane yield liquid complexes containing two ether molecules to one zinc atom. The complexes can be distilled without decomposition, but they dissociate in benzene solution into a 1:1 complex and free ether.[86] Similar 1:1 complexes of diarylzinc compounds with 1,4 dioxan have been reported.[87]

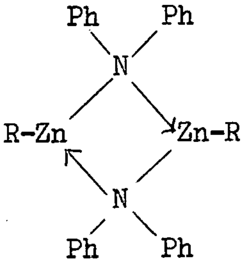
With tertiary amines, dimethylzinc yields definite co-ordination complexes. One or two molecules of trimethylamine react with one molecule of dimethylzinc to give liquid adducts, the 1:1 complex distilling without decomposition at 84° whereas the 1:2 distills at 84.5° suggesting that dissociation into the 1:1 complex and free amine takes place; such a process is observed when the 1:2 complex is dissolved in benzene. Triethylamine and pyridine afford only 1:2 complexes, which are a liquid and crystalline solid respectively; both dissociate in benzene solution yielding the respective amine and the 1:1 complex. Similar crystalline 1:1 chelate complexes of dimethylzinc with

N,N,N',N'-tetramethylethylenediamine, 2,2'-bipyridyl and 1,10-phenanthroline can be sublimed without decomposition in vacuum.[88] The rate of reaction of the co-ordination complexes with air is greatly reduced compared to that of dimethylzinc, in fact it is reported that the chelate complexes can be handled in air for a short time without noticable decomposition. Recently the 2,2'-bipyridyl, and 1,10-phenanthroline complexes of various organozinc compounds have been prepared and have been the subject of an ultra-violet and visible spectroscopic study.[89] The colour of the complexes was found to depend on the electronegativity of the alkyl group and the conclusion reached was that the spectra are due to a charge-transfer process involving donation of electrons from the ZnR_2 group into the lowest unoccupied molecular orbitals of the ligand. Unlike the similar beryllium complexes however, the intensity of the charge-transfer band increases with increasing electronegativity of R, and it is suggested that participation of the '3d' orbitals of zinc is important.

Finally a series of complexes of di-n-butylzinc, diphenylzinc and bis-pentafluorophenylzinc with a variety of donor ligands has been described.[90] It was found that the increasing electronegativity of the alkyl group attached to zinc brings about a corresponding increase in electron affinity of the vacant orbitals of the zinc atom, causing it to become a stronger electron acceptor.

2. Organozinc amides and alkoxides.

Dimethylzinc[91] reacts with dimethylamine in a 1:1 molar ratio to yield only the insoluble, involatile and evidently polymeric bis-dimethylaminozinc together with unreacted dimethylzinc. It is unknown whether the bis-amino-compound is formed by disproportionation of $(MeZnNMe_2)_n$ or by further reaction of this with dimethylamine. The latter is unlikely since the recently described ethyl(diethylamino)zinc[92] is said to be stable in the presence of excess diethylamine. The solid alkyl (diphenylamino)zinc compounds $RZnNPh_2$ (R = Me, Et, Pr^i, Bu^n, Ph) and liquid ethylzinc diethylamine are dimeric in benzene solution and presumably have the structure

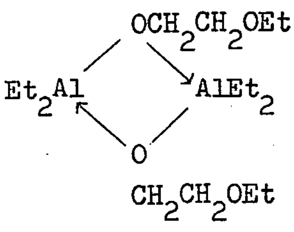


The zinc compounds show no molecular weight trend with concentration, and in the solid state they are stable crystalline solids. Consequently the zinc atoms can apparently withstand considerable valence angle strain which must be expected to exist in such a structure. The presence of co-ordinatively unsaturated zinc in these compounds is reflected in the fact that they disproportionate on heating to dimethylzinc and bisaminozinc, and that they react with pyridine in the molar ratio 1:1 to give dimethylzinc and the pale yellow complex $py_2Zn(NPh_2)_2$. Pyridine in excess yields the bright yellow $Mepy_2ZnNPh_2$.

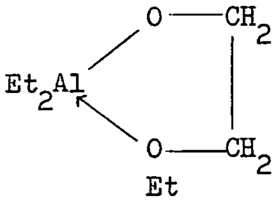
Whereas the amino derivatives of zinc are dimeric and rather unstable to disproportionation, the alkoxides[91] are tetrameric and the simpler examples e.g. MeZnOMe and $MeZnOCMe_3$ sublime unchanged. The alkylzinc alkoxides are prepared by slow addition of the alcohol to the zinc alkyl at about -80°, both being diluted with an inert solvent.

$$R_2Zn + R'OH \longrightarrow RZnOR'(I) + RH$$

The product (I) if monomeric, would contain a co-ordinatively unsaturated zinc atom bound to an oxygen atom of pronounced donor character. The replacement of an alkyl group of R_2Zn by the alkoxy group OR' results in an increase both in acceptor power of the metal and in donor character of the oxygen. This effect results in $Et_2AlOCH_2CH_2OEt$[68] having structure I rather than II despite the fact that two moles of chelate monomer would have greater entropy than one of dimer.

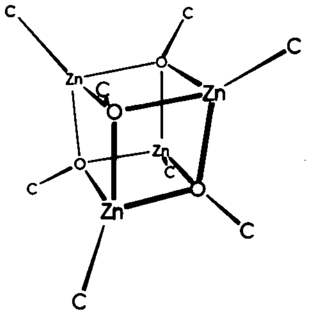


I



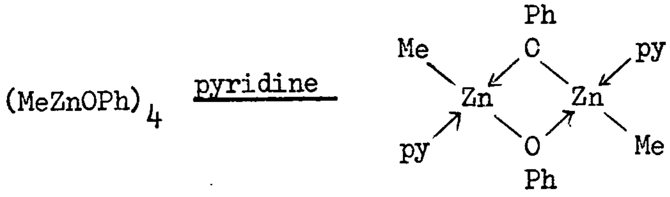
II

Dimerisation of the alkoxides RZnOR' would leave the zinc only three co-ordinate and the oxygen with a lone pair of electrons. Consequently further association occurs to give the tetrameric species shown below in which both the zinc and oxygen are 4-co-ordinate. The



$(MeZnOMe)_4$ H.M.M.Shearer & C.B.Spencer
Durham, 1965
Zn-C, 1·94; O-C, 1·46; Zn-O, 2·07 Å
Average angles in 'cube'. 96° at oxygen, 84° at zinc

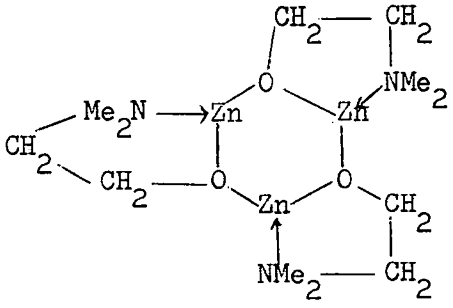
strength of these dative bonds is shown by the recovery of alkylzinc alkoxides unchanged from solutions to which pyridine has been added, although displacement does take place when the alkoxy group is replaced by the less basic phenoxy group.



The stronger Lewis base 4-dimethylamino-pyridine yields a crystalline adduct with methylzinc methoxide only on account of its relatively low solubility. In solution the adduct is dissociated very largely to free base and tetramer.

Theoretically alkylzinc alkoxides could be obtained by the addition of R-Zn across a carbonyl group. However it has been found[93] that only diphenylzinc adds across benzophenone to give the dimeric $(PhZnOCPh_3)_2$. Dimethylzinc does not react and diethylzinc gives ethylene and trimeric ethylzinc diphenylmethoxide.

The rather interesting alkylzinc derivatives of 2-dimethylamino ethanol $(RZnOC_2H_4NMe_2)_3$ are trimeric, do not form methiodides, have relatively high melting points and crystallise well. They are believed to contain 3-co-ordinate zinc.



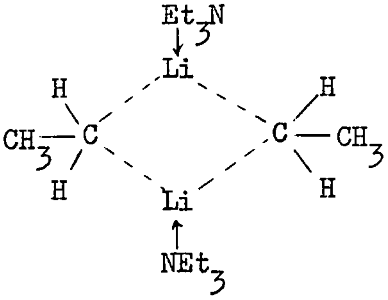
Reactions between zinc alkyls and phenyl isocyanate, giving anilides PhNH•CO•R after hydrolysis were described thirty years ago[94] but no intermediate products were isolated. Recently methyl and ethyl isocyanates were shown to be converted into their trimers in the presence of dimethyl- and diethylzinc. However phenyl isocyanate reacted with diethyl- or diphenylzinc upon heating in benzene to yield the crystalline, tetrameric products $[EtZn(NPh)COEt]_4$ and $[PhZn(NPh)COPh]_4$ the former was also obtained from the reaction between diethylzinc and propionanilide with ethane evolution. The products of addition of RZnOR' and $RZnNR'_2$ to isocyanates and similar compounds have also been described but no molecular weights were reported.[92]

D. Lithium.

Lithium alkyls, amides and alkoxides have been relatively little studied compared to the Group II and Group III derivatives, due presumably to the greater complexity and reactivity of the lithium compounds. Methyl- and ethyl-lithium are involatile solids and the crystal structures of both these compounds have been determined by X-ray analysis. Methyl-lithium[95] consists of tetramers $(MeLi)_4$ in which the lithium atoms occupy the corners of a tetrahedron and the methyl groups are located over the face centres. Ethyl-lithium[96] has a more complicated crystal structure based however on similar tetrameric units. Systems of electron deficient bonding have been discussed for both structures. In contrast n-butyl-lithium is a colourless liquid soluble in paraffin solvents. The various states of association of lithium alkyls are given in the table below.

Lithium alkyl	State of association	Solvent
t-Butyl[97]	4	C_6H_6 and C_6H_{14}
n-Butyl[98]	6	C_6H_6 and C_6H_{12}
Ethyl[99]	6	C_6H_6 and C_6H_{12}
Methyl[100]	3	$(C_2H_5)_2O$

A benzene solution of ethyl-lithium absorbs triethylamine and at low ratios of base to ethyl-lithium, co-ordination of the base to the intact ethyl-lithium hexamer occurs.[99] As the ratio base/hexamer rises, the hexamer dissociates into the co-ordinated dimer $(Et_3NLiEt)_2$ (see below), which may be further solvated at higher base concentrations.



The information in the literature on the state of association of lithium alkoxides LiOR and amides $LiNR_2$ is rather sparse. Lithium tertiary butoxide is hexameric in the vapour phase and also in benzene[100,101] and cyclohexane,[102] whereas the isopropoxide has been found to have a state of association of about eleven in cyclohexane. The lower alkoxides are insoluble in ether and apparently polymeric. The crystal structure of lithium methoxide[103] shows the lithium atoms in a plane with methoxide groups above and below that plane having four oxygen atoms co-ordinated to each lithium atom and vice versa.

No systematic study of the molecular complexity of the amino lithium compounds $LiNR_2$ has been carried out and although many have been used in the preparation of amino derivatives of other elements, few have been isolated and characterised. Dimethylaminolithium is a reagent much used in preparing dimethylamino derivatives from halides.[104]

$$(Me_2N)_2\overset{+}{C}Cl \quad Cl^- + 2LiNMe_2 \xrightarrow[R.T.]{C_6H_6} (Me_2N)_4C + 2LiCl$$

It is inferred to be polymeric due to its insolubility in hydrocarbons and very slight solubility in ethers.[105] An amino derivative of lithium which is dimeric in benzene solution has been prepared from the reaction between hexamethyldisilazane and phenyl-lithium.[106]

$$Me_3Si\text{-}NH\text{-}SiMe_3 + PhLi \longrightarrow C_6H_6 + (Me_3Si\text{-}NLi\text{-}SiMe_3)_2$$

Lithium alkoxides and amides are postulated as intermediates in the addition reactions of lithium alkyls across a carbonyl[107,108] or azomethine[109] bond.

$$RLi + R'R''C{=}NR''' \longrightarrow (RR'R''CN(R''')Li) \xrightarrow{H_2O} RR'R''CNHR''' + LiOH$$

$$RR'CO + LiC{\equiv}CH \xrightarrow[\substack{35^\circ\ 2\ hr.\\ (2)\ H_2O}]{(1)\ C_6H_6} RR'C(OH)C{\equiv}CH$$

EXPERIMENTAL

Experimental methods and apparatus.

Nitrogen Supply.

The nitrogen used was purified by passing the gas through a furnace containing 'BTS' catalyst at *ca.* 100°, then through molecular sieve (type 5A), and finally through two traps at -196°. Periodically the catalyst was regenerated with hydrogen and the molecular sieve dried by pumping at 300°.

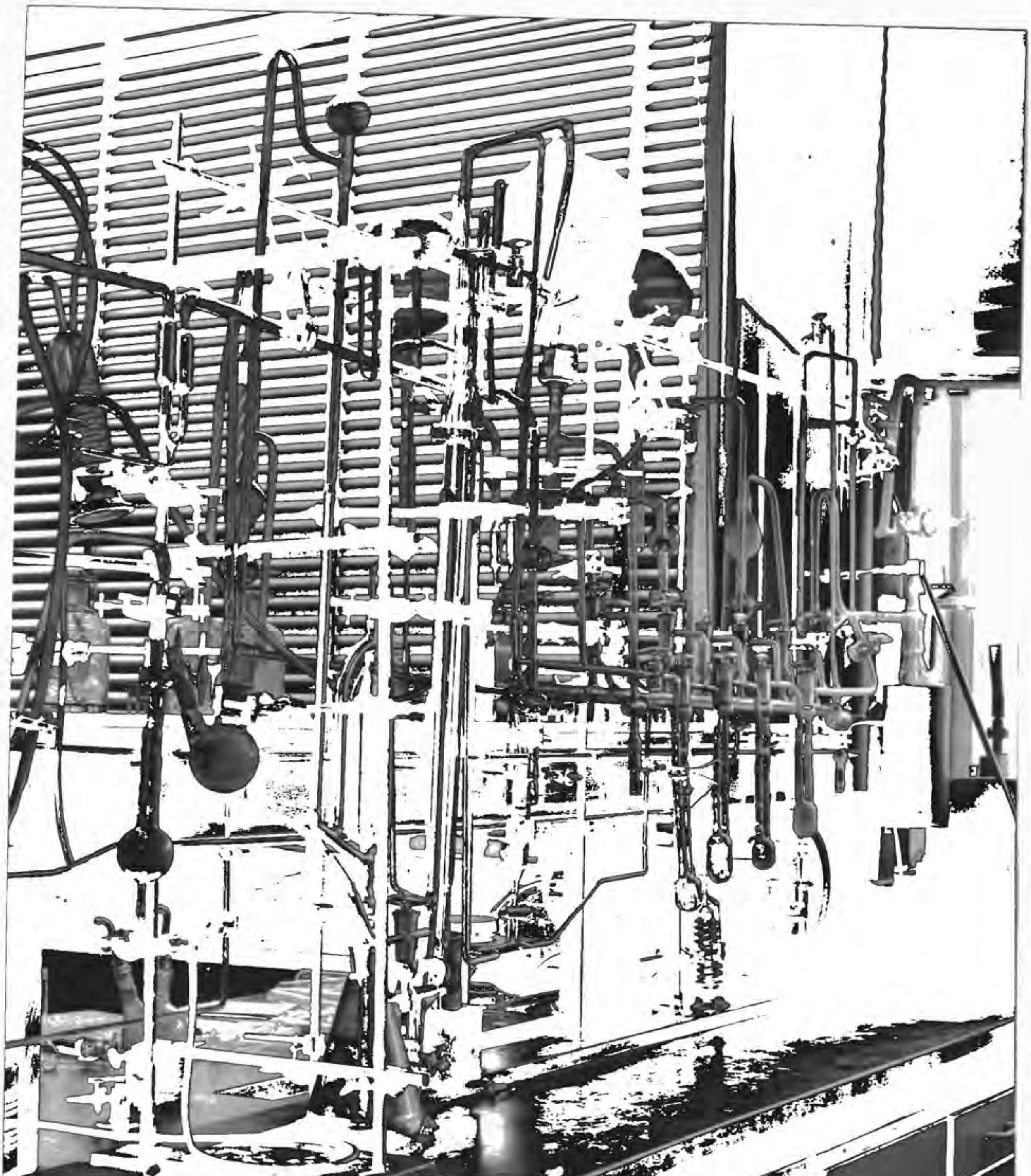
Glove Box.

Samples for analysis and infrared spectra were transferred and manipulated under a nitrogen atmosphere in a glove box of the conventional type. The nitrogen was purified as described above, and a small pump fitted inside the box provided a continuous recycling of nitrogen through the purification system when the box was not in use. Copper piping was used outside the box, to avoid the difficulty caused by the permeability of P.V.C. tubing to oxygen.

Vacuum System.[110]

A vacuum system (Photograph I) was inherited from Dr. J.E. Lloyd and used for the manipulation of many of the compounds used in the present investigation. It consisted of three sections: a, storage section; b, gas measuring section; and c, fractionation section.

a. The storage section had large (3 litre) bulbs for the storage of gases, e.g. diborane, and smaller (100 c.c.) bulbs for the storage



c. The fractionation section consisted of four U-traps connected by greased T-taps. Several inlet points were fitted using S19 and B14 sockets, and evacuation was accomplished using a rotary oil pump and a mercury diffusion pump. A rotary oil pump was also used for the secondary vacuum line controlling the mercury reservoirs.

Reactions were usually carried out in a double Schlenk tube, the compounds being purified by recrystallisation in one of the limbs. Some reactions were done in sealed tubes so that when the reaction was complete the tube was attached through a suitable adapter to the vacuum line and the volume of gas produced, measured. The tubes were then sealed under vacuum, transferred to a glove box, opened and the contents scraped into a small two-necked flask. This was removed from the glove box, and the solid compound transferred under a flow of nitrogen into a double Schlenk tube, and subsequently purified.

Infrared Spectra.

Infrared spectra (range 2 to 25 microns) were recorded either on a Grubb-Parsons GS2A prism-grating spectrophotometer or Spectromaster. Samples of involatile materials were in the form of nujol mulls or liquid films. Gases were recorded using a 10 cm. potassium bromide cell. Vapour phase spectra of only slightly volatile compounds were obtained using a Perkin-Elmer heated gas cell with potassium bromide windows.

Nuclear Magnetic Resonance Spectra.

These were recorded either on a Perkin-Elmer R10 spectrometer or on an A.E.I. R.S.2. spectrometer operating at 60 Mc./s. Samples were dissolved in deutero-benzene, with tetramethylsilane as a reference compound. The sample tubes were filled by syringing the sample solution through a constriction against a counter current of nitrogen, into the tube containing a suitable quantity of tetramethylsilane. Finally, the tubes were sealed off at the constriction under nitrogen.

Mass Spectra.

Mass spectra were recorded on an A.E.I. M.S.9 instrument at 70 eV and an accelerating potential of 8 kV, using a source temperature of 150-250° and electromagnetic scanning. Compounds were introduced using a heated inlet system or direct probe at temperatures up to 200°.

Analytical Methods.

Carbon and Hydrogen Analysis.

Analyses for these elements were carried out in this department by various members of the analytical staff. Some compounds prepared in the course of this work were too air sensitive to permit analysis by conventional combustion methods.

Hydrolyses.

Organic groups attached to aluminium and zinc were determined by hydrolysis and measurement of the hydrocarbon evolved. The compounds were either transferred in the glove box, or, on the bench, under nitrogen, to a small two-necked flask attached to the vacuum line. The compounds were hydrolysed with a few c.c. of 2-methoxyethanol followed by dilute sulphuric acid, run into the flask through a dropping funnel. The gases evolved were fractionated and measured in the gas burette using the Töepler pump.

Zinc Analysis.

The organic matter in the hydrolysate, obtained as described above, was destroyed by boiling with a mixture of nitric and sulphuric acids almost to dryness, and the resulting white solid was dissolved in a minimal amount of dilute sulphuric acid and made up to 500 mls. using distilled water. A 50 ml. aliquot was taken and the pH adjusted to 4•5 using a known volume of 0•5N sodium hydroxide solution. The zinc solutions were further buffered to a pH of 5-6 using hexamethylenetetramine, and then titrated with 0•01M "EDTA" solution using xylenol orange as indicator. The end point was given by a sharp change from red to straw yellow.

Aluminium, Gallium and Indium Analyses.

For aluminium, gallium and indium solutions it was found preferable to use a "back titration" technique. After adjusting the pH with hexamethylenetetramine an excess of 0•01M "EDTA" solution was added, followed by several drops of 0•2% xylenol orange indicator. The solution was then titrated with 0•01M zinc acetate solution until the yellow colour changed sharply to red.

Organo-gallium and indium compounds are not completely hydrolysed by dilute acids. Consequently their derivatives were boiled for several hours with concentrated hydrochloric acid to effect complete cleavage of alkyl groups.

Boron Analysis.

The sample was burned in an apparatus described and illustrated in a Ph.D. thesis in 1963 by Dr. J. Graham of this laboratory.

The compound was weighed in a small gelatine capsule filled in the glove box. The amount used was up to 0•1 gm. A 3 litre dropping funnel was purged with oxygen, and 50 c.c. water placed in it. The gelatine capsule was placed in a platinum gauge container together with a small piece of filter paper to act as a fuse. This was lit and quickly placed in the dropping funnel. After a few seconds the compound burned with a bright green flame. When the combustion was complete, the dropping funnel was shaken to dissolve the combustion products. The contents were then rinsed into a flask, made up to a standard volume and titrated against standard 0•1N caustic soda in the presence of mannitol with bromothymol blue as indicator.

Lithium Analysis.

The lithium content of a compound was determined by flame photometry. The lithium compounds prepared were hydrolysed by water and then boiled with concentrated nitric acid to destroy any organic matter. The solution was evaporated almost to dryness, and the resulting white solid dissolved in distilled water and made up to 250 ml. This solution was introduced into a non-luminous flame and the intensity of the light emitted was measured by means of a photoelectric cell attached to a suspension galvanometer. This intensity was then compared with that emitted by a series of standard lithium solutions.

Nitrogen Analysis.

Nitrogen was determined by the normal Kjeldahl method. A sample was destroyed using concentrated sulphuric acid until all the nitrogen was reduced to ammonia. This was then transferred to a small Kjeldahl flask, made alkaline with caustic soda and boiled. The ammonia was steam distilled into a flask containing a known volume of standard acid. After half the solution had been distilled the remaining acid was titrated with standard alkali.

Molecular Weights.

Molecular weights were determined where possible cryoscopically in benzene. The benzene, of analytical reagent purity, was dried over sodium wire and calibrated (in respect of its freezing point constant) using freshly sublimed biphenyl. The usual Beckmann apparatus was used, and since most of the compounds were air sensitive, a slow current of dry nitrogen was passed through the apparatus during each determination. This did not cause a significant loss of solvent by evaporation.

Preparation of Starting Materials.

Methyl-lithium.

Methyl-lithium was prepared by the reaction of methyl chloride with lithium metal, in ether as solvent. The methyl chloride was supplied under pressure in a cylinder. The apparatus consisted of a one litre three-necked flask fitted with a stirrer, a cold finger condenser maintained at -78°, and an inlet for the methyl chloride. A flow meter was used to tell approximately the rate of passage of the methyl chloride. The exact amount used was determined by weighing the cylinder before and after the experiment. The lithium was supplied in a wax which was washed off with ether before use. The apparatus was purged with pure nitrogen before starting the preparation.

Lithium (14 g.) and ether (500 c.c.) were placed in the reaction flask. Methyl chloride (50 g.) was passed into the reaction mixture over a period of 2 hours. The reaction started immediately. When the reaction was complete, the solution of methyl-lithium was filtered from lithium chloride and unreacted lithium metal, and stored as an ether solution. Analysis, by acid hydrolysis with subsequent measurement of the methane evolved, found it to be 1·2M indicating a yield of 60%.

Diphenylmercury.

Diphenylmercury was prepared in 90-95% yield by the reduction of phenyl mercuric chloride with hydrazine hydrate in boiling methanol,[111] followed by crystallisation and sublimation of the product (as colourless needles, m.p. 123° - 124°). As diphenylmercury is somewhat sensitive to light, turning yellow when exposed to light for several days, it was stored in the dark.

Diphenylzinc.

This compound was prepared by a metal-aryl exchange reaction between zinc and diphenylmercury.[112]

Diphenylmercury (15 g.) and zinc dust (12 g.) were placed in a two-necked flask with dry xylene (75 c.c.), and the flask purged with nitrogen. The flask was fitted with a nitrogen inlet, and an outlet on the top of the condenser. The xylene was refluxed for several hours then filtered hot under a nitrogen atmosphere. The colourless crystals of diphenylzinc were filtered and washed several times with hexane before being pumped dry under vacuum. The yield of diphenylzinc was 5 g. (80%), and the m.pt. 105-106° (Lit., 105-106°).

Trimethylborane.

Trimethylborane was prepared by the reaction of methylmagnesium bromide with boron trifluoride diethyl ether complex.

The apparatus consisted of a one litre three-necked flask fitted with a stirrer, a pressure-equilibrated dropping funnel and a cold finger condenser. The outlet of the condenser was connected to two traps, the first at -78°; the second at -196°. The apparatus was purged with nitrogen before the preparation began.

The Grignard reagent MeMgBr was prepared from magnesium (9·0 g.) and methyl bromide (35 g.) in ether (250 ml.). Boron trifluoride ether complex (30 g.) was added dropwise with stirring. The trimethyl borane formed, collected in the liquid air trap. The product was fractionated through a trap at -110° and collected in a trap at -135°. The yield of trimethylborane was 2·5 litres (90%).

Dimethylaluminium hydride.

This was prepared by the reaction of lithium aluminium hydride with trimethylaluminium.[113]

Lithium aluminium hydride (10 g.), dry cyclohexane (50 ml.) and trimethylaluminium (10 g.) were placed in a thick-walled Pyrex tube filled with nitrogen. The tube was sealed off and heated for 24 hours at 70°. The tube was opened and the cyclohexane and dimethylaluminium hydride distilled under vacuum, into a two-necked flask. The concentration of the solution was determined by hydrolysing a known volume of solution and measuring the mixture of hydrogen and methane evolved. The yield of dimethylaluminium hydride was 7 g. (85%).

Boron tri-iodide.

This was prepared by the reaction of lithium borohydride with iodine.[114]

In an atmosphere of nitrogen, lithium borohydride (6 g.) was added slowly to iodine (90 g.) in hexane (200 c.c.). The mixture was stirred for 24 hours, after which time a colourless solution was obtained. This solution was filtered and after some of the solvent had been removed by distillation boron tri-iodide m.p. 49° (lit. 49°) crystallised. The yield of boron tri-iodide was 18 g. (52%). As boron tri-iodide is sensitive to light, it was stored in the dark.

Diphenylketimine.[115]

Phenyl cyanide (51 g.) was added with stirring to phenyl magnesium bromide (90 g.) in ether (800 ml.). The solution was hydrolysed using methanol and vigorously stirred for eight hours. After filtration the excess methanol and ether were removed by distillation at atmospheric pressure leaving impure diphenylketimine. This was purified by vacuum distillation (b.p. 90-95° / 10^{-3} mm.). The yield was 70 g. (77%).

Acetoxime-o-methyl ether.[116]

Acetoxime (100 g.) was dissolved in a solution of sodium hydroxide (220 g.) in water (750 c.c.), and methyl sulphate (252 g.) was added with stirring during 40 minutes with occasional water cooling. Stirring was continued for a further 30 minutes after which the upper layer was separated, dried with anhydrous magnesium sulphate and finally fractionated through a 10 inch column packed with glass helices. The yield of acetoxime-o-methyl ether b.p. 72-73°/760 mm. was 40 g. (35%).

Trisdimethylaminoborane,[117] was prepared from the direct reaction between dimethylamine and boron trichloride in hexane at -78°. The solution was filtered to remove the amine hydrochloride and trisdimethylaminoborane purified by fractional distillation.

Pyridine-2-aldoxime was purified by recrystallisation from benzene whereas benzaldoxime was purified by distillation.

Dimethylzinc was prepared by Dr. D. Ridley by the reaction of zinc with dimethylmercury and was purified by fractional distillation.

The trimethylaluminium, triethylaluminium and diethylzinc were gifts from Ethyl Corporation and Borax Consolidated Ltd. They were purified by distillation and stored under nitrogen in two-necked flasks fitted with teflon sleeves.

Trimethyl and triethylgallium were prepared (by Dr. J.R. Jennings) by the reaction of gallium with the corresponding dialkyl mercury compound and purified by fractional distillation.

Trimethylindium was prepared by Dr. O.T. Beachley from the reaction of an indium-magnesium alloy with methylchloride in ether. The ether was removed by fractional distillation with benzene, and the trimethylindium was stored in ampoules.

Diborane had been prepared by the reaction of lithium aluminium hydride with boron trifluoride diethyl ether complex, and was purified by fractional distillation.

Phenyl and alkyl cyanides were purified by fractional distillation from phosphorus pentoxide.

The solvents which were used were dried and stored over sodium wire, or in the case of ethers distilled from lithium aluminium hydride and then stored over sodium. Pyridine cannot be purified by this method and was refluxed with solid caustic soda, and, after fractionating through an efficient column, stored over sodium hydroxide pellets.

Reactions of diphenylketimine with alkylzinc compounds.

Reaction of diphenylketimine with dimethylzinc.

Dimethylzinc (1·06 g., 11·1 m.moles) was condensed on to diphenylketimine (1·6 g., 9·1 m.moles) at -196° in a sealed tube, and warmed to 30°. Methane (0·16 g., 8·8 m.moles) was evolved, identified by its infrared spectrum, leaving a yellow solid which was purified by recrystallisation from a toluene-hexane mixture. The solid was methyl-(α-phenylbenzylideneamino)zinc dimer, $(Ph_2C{=}N{-}ZnMe)_2$ decomp. 80°. (Found: Zn, 24·9; hydrolysable methyl, 5·70%; M, 501. $C_{28}H_{26}Zn_2N_2$ requires Zn, 25·1; hydrolysable methyl, 5·76%; M, 520).
The infrared spectrum of the solid recorded as a nujol mull contained bands at 1311m, 1280m, 1263m, 1245m, 1190vw, 1178w, 1151m, 1074m, 1028m, 1000m, 969m, 942s, 917m, 906m, 885sh, 843w, 781s, 773sh, 725m, 697vs, 658s, 622w, 542m, 520w, 505vw, 456w and 449w $cm.^{-1}$

Reaction of diphenylketimine with diethylzinc.

Diethylzinc (1·4 g., 12 m.moles) was condensed on to diphenylketimine (2·17g. 12 m.moles) at -196° in a sealed tube and warmed to 70°. Ethane (0·29 g., 9·6 m.moles) was evolved, leaving an involatile yellow solid. After purification by recrystallisation from a toluene-hexane mixture, the pale yellow solid was identified as ethyl-(α-phenylbenzylideneamino)zinc dimer, $(Ph_2C{=}N.ZnEt)_2$, decomp. 85°, (Found: Zn, 23·4; hydrolysable ethyl 10·5%; M, 549. $C_{30}H_{30}Zn_2N_2$ requires Zn, 23·8;

hydrolysable ethyl 10·6%; M, 550).

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1611vs, 1597s, 1575m, 1493w, 1445s, 1366m, 1314m, 1284m, 1263m, 1247sh, 1193m, 1179m, 1160m, 1101m, 1062s, 1029m, 1001w, 971vw, 944m, 908w, 892m, 846vw, 787m, 778m, 758w, 700s, 674w, 663m, 622m, 604w, 521w and 505w cm.$^{-1}$

Reaction of diphenylketimine with diphenylzinc.

Diphenylketimine (0·9 g., 5 m.moles) in toluene (10 c.c.) was added to diphenylzinc (1·1 g., 5 m.moles) in toluene in one limb of a double Schlenk tube. The solution was warmed to 40°. On removal of toluene a white solid phenyl-(α-phenylbenzylideneamino)zinc dimer, $(Ph_2C{=}N.ZnPh)_2$, m.pt. 132° crystallised [Found: Zn, 20·2; C, 69·0; H, 5·06%; M, 651. $C_{38}H_{30}Zn_2N_2$ requires Zn, 20·3; C, 70·8; H, 4·66%; M, 644].

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1607vs, 1567s, 1541sh, 1451vs, 1368m, 1307vw, 1259w, 1242m, 1190m, 1176w, 1157m, 1070m, 1029m, 1000w, 9709vw, 944m, 930w, 909m, 886m, 846w, 787m, 766m, 725m, 697vs, 676m, 662m, 642m and 621m cm.$^{-1}$

Thermal decomposition of phenyl-(α-phenylbenzylidenamino)zinc.

A sample of phenyl-(α-phenylbenzylideneamino)zinc (2 g., 5 m.moles) was dissolved in toluene (30 c.c.) and heated to 80° with stirring. A white solid precipitated from the solution. The solid was found to be bisdiphenylketiminozinc, $(Ph_2C{=}N)_2Zn$, m.pt. 260° decomp. (Found:

Zn, 15•2; C, 73•1; H, 4•41%; $C_{26}H_{20}ZnN$ requires Zn, 15•4; C, 73•4; H, 4•70%).

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1600vs, 1575s, 1560sh, 1449vs, 1425m, 1368m, 1314m, 1287m, 1265m, 1248m, 1190w, 1153w, 1076m, 1071sh, 1058w, 1024m, 1001m, 999w, 972w, 947m, 926w, 919m, 886w, 850m, 789m, 776m, 725s, 704vs, 672m, 667s, 621w, 541m, 529m, 459m and 439m cm.$^{-1}$

Reaction between methyl-(α-phenylbenzylideneamino)zinc and pyridine.

(a) With an excess.

When excess dry pyridine (2•4 g., 30 m.moles) was added to methyl-(α-phenylbenzylideneamino)zinc (2•6 g., 10 m.moles) in benzene (10 c.c.) a deep yellow colour developed. Addition of hexane caused the crystallisation of methyl-(α-phenylbenzylideneamino)zinc bis-pyridine, $Mepy_2ZnNCPh_2$, m.p. 139°, which was recrystallised from a benzene-hexane mixture. [Found: Zn, 15•5; hydrolysable methyl, 3•5%; m, 428. $C_{24}H_{23}N_3Zn$ requires Zn, 15•6; hydrolysable methyl 3•6%; M, 418.]

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1613vs, 1603s, 1577m, 1466s, 1370m, 1312w, 1285m, 1258m, 1218w, 1193w, 1179w, 1157w, 1139m, 1075sh, 1071m, 1039m, 1031m, 1010w, 1007w, 943m, 908m, 888m, 787sh, 781s, 758m, 750m, 698vs, 675w, 667w, 657m, 622m, 517m, 503m and 443m cm.$^{-1}$

(b) With 1 mol. pyridine.

Repetition of the above experiment using 1 mol. of pyridine per mol. of N-methylzinc diphenylketimine in benzene gave on addition of hexane a precipitate of the adduct $Ph_2C:NZnMe,2py$, m.p. 139°, with an identical infrared spectrum to that just described.

Reaction of phenyl cyanide with diethylzinc.

A mixture of diethylzinc (1·2 g., 10 m.mole) and phenyl cyanide (1·0 g., 10 m.mole) which was liquid at 18° and which could be made from the components without any apparent evolution of heat, had $\nu_{C\equiv N}$ in the infrared spectrum at the same frequency (2229 cm.$^{-1}$) as phenyl cyanide itself. The mixture turned red when heated to 160°, and on cooling deposited crystals which after recrystallization from hot benzene were identified as 2,4,6-triphenyltriazine $(PhCN)_3$ m.p. 234° (lit., 232). (Found: C, 80·3; H, 4·6; N, 15·2%. Calc. for $C_{21}H_{15}N_3$: C, 81·6; H, 4·9; N, 13·5%).

Reaction of phenyl cyanide with diphenylzinc.

Phenyl cyanide (1·0 g., 10 m.mole) was added by syringe to a suspension of diphenylzinc (2·2 g., 10 m.mole) in toluene (20 c.c.) at -78°. The mixture was warmed to 20°, the solution was filtered and toluene was removed under vacuum. The viscous liquid residue was identified as the adduct, $PhCN,ZnPh_2$ (Found: Zn, 20·0%; $C_{19}H_{15}NZn$ requires Zn, 20·2%).

The infrared spectrum recorded as a liquid film contained bands at 3077vs, 2994s, 2967sh, 2259vs, 1600s, 1577m, 1562sh, 1493s, 1481s, 1451s, 1429vs, 1335w, 1294m, 1264sh, 1250s, 1195m, 1181m, 1167m, 1099m, 1080vs, 1053m, 1029s, 1000m, 925m, 843w, 793m, 759vs, 728vs, 706vs, 686vs, 667m, 625vw, 551vs and 443s cm.$^{-1}$

Thermal decomposition of PhCN,ZnPh$_2$. A sample of the adduct PhCN,ZnPh$_2$ when held at 100° under nitrogen gave a yellow glue which solidified on cooling. The crude material was washed several times in toluene and the residue identified by its m.p. (260° decomp.) and infrared spectrum as bis(diphenylketimino)zinc.

Mixtures of tertiary-butyl cyanide with diethylzinc, dimethylzinc and diphenylzinc.

Diethylzinc (1·2 g., 10 m.moles) and t-butyl cyanide (0·8 g., 10 m.mole) were heated together at 160°. Ethylene (0·028 g., 1 m.mole) was evolved and identified by its infrared spectrum, and most of the t-butyl cyanide (0·76 g., 9·5 m.mole) was recovered. The residue was a small quantity of brown glue. No reaction was observed when equimolar mixtures of Et_2Zn and Bu^tCN were heated in boiling toluene or tetrahydrofuran for 3 or 4 days.

No reaction occurred between Bu^tCN and either Me_2Zn or Ph_2Zn when mixtures were subjected to similar conditions to those used with Et_2Zn. The infrared spectra of the mixtures $Bu^tCN + R_2Zn$ (R = Me, Et or Ph) all had $\nu_{C\equiv N}$ at the same frequency (2235 cm.$^{-1}$) as t-butyl cyanide itself.

Reactions of ketimines with methyl-lithium

Reaction of diphenylketimine with methyl-lithium.

Diphenylketimine (0·9 g., 5 m.moles) in diethyl ether (10 c.c.) was added slowly by syringe to methyl-lithium (0·1 g., 5 m.moles) in diethyl ether (15 c.c.), in a double Schlenk tube at -78°. The solution developed a bright red colour and methane was evolved. Removal of the ether gave a yellow solid which was purified by washing with hot hexane and toluene. The yellow solid was diphenylketiminolithium, $\mathrm{Ph_2C{:}NLi}$, m.p. 260° with decomposition. [Found: Li, 3·68; C, 81·0; H, 5·01%. $\mathrm{C_{13}H_{10}NLi}$ requires Li, 3·74; C, 83·4; H, 5·35%].
The infrared spectrum of the solid recorded as a nujol mull contained bands at 1620vs, 1596s, 1578s, 1493s, 1374s, 1314m, 1287w, 1242s, 1198w, 1176m, 1157w, 1074m, 1030m, 1004w, 936m, 922w, 903s, 900sh, 848vw, 788s, 778s, 722m, 708vs, 703vs, 682m, 667m, 640vs, 623w, 603m, 518s, 472m, and 447w cm.$^{-1}$ The product was insoluble in hexane, benzene and toluene, and after isolation from ether would not redissolve.

Reaction of diphenylketiminolithium with pyridine.

A solution of pyridine (0·4 g., 5 m.moles) in diethylether (10 c.c.) was added by syringe to a solution of diphenylketiminolithium (0·93 g., 5 m.moles) in diethyl ether (25 c.c.). On removal of some of the ether, deep red crystals of diphenylketiminolithium pyridine $(\mathrm{Ph_2C{:}NLipy})_x$ m.p. 108-110° appeared. [Found: Li, 2·70; C, 81·5; H, 5·45%.

$C_{18}H_{15}N_2Li$ requires Li, 2·64; C, 81·5; H, 5·66%].
The infrared spectrum of the solid recorded as a nujol mull contained bands at 1616vs, 1600s, 1578m, 1488m, 1466s, 1304w, 1218m, 1190vw, 1174w, 1149w, 1072m, 1034m, 1027w, 1005w, 930m, 893s, 846w, 789m, 782m, 775sh, 769s, 751m, 700vs, 675sh, 667m, 633s, 621m, 592w and 467s $cm.^{-1}$

The adduct dissolved in benzene but after a short time it disproportionated to give pyridine, identified by its ultraviolet spectrum, and a yellow precipitate of α-phenylbenzylideneaminolithium identified by its infrared spectrum.

Reaction of diphenylketiminolithium with tetrahydrofuran.

Tetrahydrofuran (0·7 g., 10 m.moles) in diethyl ether (10 c.c.) was added by syringe to diphenylketiminolithium (1·9 g., 10 m.moles) in diethyl ether (20 c.c.). After removal of most of the solvent, hexane was added which caused the crystallisation of the orange adduct $(Ph_2C{=}NLi.THF)_x$, m.p. 127° [Found: C, 77·4; H, 7·35; Li, 2·65%. $C_{17}H_{18}NOLi$ requires C, 78·7; H, 6·95; Li, 2·70%].
The infrared spectrum of the solid recorded as a nujol mull contained bands at 1618vs, 1595m, 1575m, 1309w, 1284w, 1229m, 1175w, 1157w, 1073m, 1043m, 1028w, 1000w, 971vw, 978m, 901m, 855w, 786m, 769s, 720m, 700vs, 677m, 638vs, 620w, 595w, 542m and 468m $cm.^{-1}$ The adduct, like the pyridine adduct, dissolved in benzene and after a short while disproportionation occurred and the yellow solid α-phenylbenzylideneaminolithium precipitated.

The reaction of diphenylketiminolithium with 2,2'-bipyridyl in diethyl ether gave a black solution. Removal of ether gave a black tar soluble in toluene.

Reaction of tetramethylguanidine with methyl-lithium.

Tetramethylguanidine (1·2 g., 10 m.moles) was dissolved in diethyl ether (10 c.c.) and cooled to -78°. Methyl-lithium (0·22 g., 10 m.moles) in diethyl ether (30 c.c.) was added by syringe with stirring. On warming to ca. -40° methane was evolved and a white solid slowly deposited which was purified by recrystallisation from toluene. The solid was N-lithio-N',N',N",N"-tetramethylguanidine dimer $[(Me_2N)_2C:NLi]_2$, decomp. 120°. [Found: C, 47·7; H, 9·28; N, 34·5; Li, 5·9%; M, 232. $C_5H_{12}N_3Li$ requires C, 49·6; H, 9·92; N, 34·7; Li, 5·79%; M, 242]. The infrared spectrum of the solid recorded as a nujoll mull contained bands at 1632vs, 1508m, 1377m, 1285s, 1236m, 1212m, 1138m, 1096m, 1055vs, 987m, 910m, 894sh, 761s, 735w, 722w, 591s, 548s and 506m $cm.^{-1}$

Reactions of N-lithio-N',N',N",N"-tetramethylguanidine with donor molecules.

In separate experiments pyridine, tetrahydrofuran and ethylene glycol dimethyl ether (10 m.moles) were dissolved in diethyl ether (10 c.c.) and added to N-lithio-N',N',N",N"-tetramethylguanidine (10 m.moles) in diethyl ether (30 c.c.). The ether was removed by vacuum distillation and toluene (10 c.c.) added. From hot toluene colourless crystals of N-lithio-N',N',N",N"-tetramethylguanidine were obtained. No adducts were isolated under the conditions tried. With 2,2'-bipyridyl the solution first developed a red colour and after a few minutes, turned black. Removal of ether yielded a black tar soluble in toluene.

Reaction of phenylcyanide with methyl-lithium.

Methyl-lithium (0·22 g., 10 m.moles) in diethyl ether (30 c.c.) was slowly added by syringe to phenylcyanide (1·0 g., 10 m.moles) in diethyl ether (20 c.c.) cooled to -78° in one limb of a double Schlenk tube, the solutions being vigorously stirred. The solution on warming to room temperature developed a bright red colour. Removal of the ether yielded a yellow foam which after being washed with boiling hexane and toluene and stirred vigorously gave a yellow powder. The solid was α-methylbenzylideneaminolithium $(Ph(Me)C:NLi)_x$, m.p. 196°. [Found: C, 77·5; H, 5·98; Li, 5·55%. C_8H_8NLi requires C, 76·8; H, 6·40; Li, 5·60%.]

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1629m, 1592m, 1565m, 1513s, 1493s, 1351s, 1319s, 1300s, 1287s, 1235m, 1183w, 1170w, 1074m, 1029m, 1000w, 980m, 917w, 885vw, 862m, 800m, 775s, 752s, 717sh, 700 sh, 625m, 588m and 513vw cm.$^{-1}$

The product was insoluble in hexane, benzene and toluene, and after isolation from ether would not redissolve. Under the same conditions used above, it was found that methyl and ethyl lithium would not react with t-butyl cyanide.

Reactions of diphenylketiminolithium with boron halides.

Reaction of diphenylketiminolithium with boron trifluoride.

Boron trifluoride diethyl etherate (2·8 g., 20 m.moles) was slowly added by syringe to a solution of diphenylketiminolithium (3·7 g., 20 m.moles) in diethyl ether (40 c.c.) cooled to -78° in one limb of a double Schlenk tube, the solution being vigorously stirred. On warming to room temperature the deep red solution became colourless and a yellow solid precipitated. The ether was removed by vacuum distillation leaving a yellow solid insoluble in boiling toluene and which would not sublime at temperatures up to 260° at 10^{-3} m.m. pressure.

Reaction of diphenylketiminolithium with boron trichloride.

Boron trichloride (3·7 g., 20 m.mole) was condensed onto a solution of diphenylketiminolithium (3·7 g., 20 m.mole) in diethyl ether (40 c.c.) cooled to -180° in one limb of a double Schlenk tube. The solution was allowed to warm to room temperature and stirred vigorously. The deep red solution became colourless and a yellow solid precipitated. The ether was removed by vacuum distillation and toluene (60 c.c.) was added. After refluxing the toluene for five minutes the solution was filtered and allowed to cool. From the hot toluene solution colourless crystals of diphenylketiminoboron dichloride $Ph_2C:NBCl_2$, m.p. 305-309° with decomposition were obtained. [Found: C, 59·1 ; H, 3·96 ; Cl, 24·5%. $C_{13}H_{10}NBCl_2$ requires C, 59·5; H, 3·82; Cl, 27·0%].

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1608s, 1590vs, 1578s, 1449s, 1335m, 1304m, 1272m, 1195w, 1172vw, 1161vw, 1076w, 1045m, 1021s, 1000w, 935s, 898s, 870s, 862sh, 851m, 826s, 779m, 766w, 712m, 703m, 685m, 666vw, 635vw, 615vw, 561s, 532m and 488w cm.$^{-1}$

The compound was stable to air and water.

Reaction of diphenylketiminolithium with boron tribromide.

Diphenylketiminolithium (3·7 g., 20 m.moles) in diethyl ether (40 c.c.) was cooled to -180° in one limb of a double Schlenk tube. Boron tribromide (5·0 g., 20 m.moles) was added by syringe and the mixture was allowed to warm to room temperature with constant stirring. At ca. -70° the deep red solution became colourless and a yellow solid precipitated. The ether was removed by vacuum distillation and the resultant mixture was refluxed with toluene (15 c.c.) for two minutes and filtered. On cooling to room temperature the toluene solution yielded colourless crystals of diphenylketiminoboron dibromide, m.p. 173° with decomposition. [Found: C, 43·6; H, 3·7; Br, 44·9 %; M (cryoscopically in benzene) 690. $C_{26}H_{20}N_2B_2Br_4$ requires: C, 44·4; H, 2·85; Br, 45·6 %; M, 702].

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1608sh, 1586vs, 1567sh, 1560vs, 1335s, 1321s, 1299m, 1276m, 1205m, 1193m, 1163s, 1147s, 1109m, 1079w, 1050m, 1032w, 1010vs, 980w, 966sh, 926s, 894m, 820m, 794m, 780s, 756m, 730m, 712m, 699vs, 680m, 667w, 641m, 617w, 595m, 562s and 536m $cm.^{-1}$ The product was stable to air and water.

Reaction of diphenylketiminolithium with boron tri-iodide.

Diphenylketiminolithium (3·7 g., 20 m.moles) in diethyl ether (40 c.c.) was cooled to -180° in one limb of a double Schlenk tube. Boron tri-iodide (7·8 g., 20 m.mole) in toluene (10 c.c.) was added by syringe and the mixture was allowed to warm to room temperature with vigorous stirring. The deep red solution became colourless and a yellow solid precipitated. The ether was removed by vacuum distillation and then a further 10 c.c. of toluene was added. The toluene was warmed to 60° and filtered. Addition of hexane caused the precipitation of diphenylketiminoboron di-iodide, $Ph_2C{:}NBI_2$ decomp. 200°. [Found: C, 27·5 ; H, 2·31 ; I, 57·5%; M (cryoscopically in benzene), 871. $C_{26}H_{20}N_2B_2I_4$ requires C, 27·8; H, 2·25; I, 57·1%; M, 890].
The infrared spectrum of the solid recorded as a nujol mull contained bands at 1602s, 1564m, 1445vs, 1304w, 1218m, 1151m, 1112vs, 1087sh, 1078vs, 1070sh, 1037w, 1015m, 1000s, 929m, 898m, 865m, 847w, 789m, 763m, 723m, 695vs, 631s and 550 $cm.^{-1}$
The product was rapidly decomposed by water and moist air.

Reaction between diphenylketiminolithium and boron tribromide.

Boron tribromide (0·8 g., 3·2 m.moles) in toluene (10 c.c.) was added by syringe to a solution of diphenylketiminolithium

(1·9 g., 10 m.moles) in diethyl ether (40 c.c.), previously cooled to -78°, in one limb of a double Schlenk tube, the solution being vigorously stirred to promote mixing. As the solution warmed to room temperature the deep red solution turned slightly yellow and lithium bromide precipitated. The ether was removed by vacuum distillation and hexane (30 c.c.) and toluene (5 c.c.) were added. After the solution was filtered from lithium bromide and cooled to -78°, tris-diphenylketimino borane crystallised. At room temperature it is a wax.
[Found: C, 81·7; H, 6·04; N, 7·5%. $C_{39}H_{30}N_3B$ requires C, 84·9; H, 5·44; N, 7·6%].

The infrared spectrum of the material recorded as a liquid film contained bands at 3067s, 3030s, 2963m, 2955s, 2865m, 1667vs, 1604w, 1585m, 1497m, 1451s, 1358m, 1295s, 1258sh, 1241vs, 1202s, 1183s, 1149m, 1130w, 1090vs, 1047m, 1009m, 979m, 967vw, 952vw, 917s, 892s, 876m, 829w, 775s, 750m, 741m, 702s, 695s, 680vs, 658m, 647m, 638m, 612s, 606m, 600sh, 568m and 557m $cm.^{-1}$

A mass spectrum of the compound gave a strong peak at 180 i.e. $Ph_2C:N$ and peaks resulting from the fragmentation of this group.

Reaction between tris-diphenylketiminoborane and boron trifluoride.

Boron trifluoride diethyl etherate (0·95 g., 6 m.moles) was added to a solution of tris-diphenylketiminoborane (1·84 g., 3 m.moles) in toluene (20 c.c.) at room temperature in one limb of a double Schlenk tube. No reaction occurred. The solution was warmed to 70°

with vigorous stirring and a white solid of diphenylketiminoboron difluoride $Ph_2C:NBF_2$, m.p. 286° slowly precipitated. [Found: C, 66·9; H, 4·38; F, 16·8%. $C_{13}H_{10}NBF_2$ requires C, 68·1; H, 4·37; F, 16·6%].

Reactions of diphenylketimine and BX_3 compounds.

Reaction between diphenylketimine and diborane.

Diborane (0·05g., 1·8 m.moles) was condensed on to diphenylketimine (0·6 g., 3·3 m.moles) in hexane (15 c.c.) at -196° in a sealed tube and warmed to room temperature with shaking. A white solid precipitated and hydrogen (0·0008 g., 0·4 m.moles) was evolved. The solid adduct, $Ph_2C:NH,BH_3$ decomp. ca. 95°, was purified by washing with toluene. [Found: C, 81·6; H, 7·53; B, 5·5%. $C_{13}H_{14}NB$ requires C, 80·0; H, 7·2; B, 5·6%].

The infrared spectrum of the solid recorded as a nujol mull contained bands at 3257m, 2410m, 2288m, 2252m, 1620s, 1603sh, 1582m, 1499s, 1314m, 1289sh, 1280s, 1193s, 1188s, 1176s, 1148vs, 1085m, 1066w, 1047w, 1038m, 1007m, 972s, 933m, 894m, 858m, 850m, 824w, 788s, 752s, 736s, 721m, 700vs, 696sh, 667w, 630m, 617w, 602w, 561w, 546m and 448m cm.$^{-1}$

The adduct was insoluble in hexane, benzene and toluene and reacted with acetone and water.

Thermal decomposition of $Ph_2C:NH,BH_3$. A sample of the adduct (3·9 g., 20 m.moles) when heated at 120° in a sealed tube for two hours formed hydrogen (0·03 g., 15 m.moles) and N-tri-diphenylmethylborazole $(Ph_2CHNBH)_3$ m.p. 104°, isolated as colourless crystals after recrystallisation from a toluene-hexane mixture. [Found: C, 81·6; H, 6·83; N, 7·04%. $C_{13}H_{12}NB$ requires C, 80·8; H, 6·22; N, 7·2%].

Parent peak in mass spectrum at 579•3201, calculated 579•3188.

The infrared spectrum of the solid recorded as a nujol mull contained bands at 2525m, 2433m, 2404m, 1495s, 1355vs, 1335s, 1312m, 1263m, 1176s, 1170s, 1149s, 1142sh, 1081m, 1063s, 1032s, 1003w, 975w, 962w, 952w, 923w, 909m, 900s, 826w, 760m, 735s, 698vs, 667w, 663w, 638vw, 617vw, 611m and 585s cm.$^{-1}$

The borazine when heated to 130° for 48 hours formed diphenylmethane b.p. 80° at 10^{-3} mm. identified by its infrared and proton magnetic resonance spectrum.

Reaction of diphenylketimine with trimethylborane.

Trimethylborane (0•62 g., 11 m.mole) was condensed on to diphenylketimine (2•06 g., 11 m.mole) in 20 ml. pentane at -196°. The mixture was allowed to warm to room temperature when the adduct $Ph_2C{=}NH.BMe_3$ precipitated as a white solid which was characterised by its infrared spectrum.

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1604vs, 1564s, 1543ms, 1319m, 1297s, 1276s, 1284s, 1203m, 1193m, 1157m, 1111w, 1081s, 1055s, 1031m, 1026m, 1000m, 998m, 986m, 960w, 951m, 922w, 897s, 855vw, 849vw, 791w, 782s, 769m, 757m, 733w, 727w, 694vs, 662vw, 623m, 607vw, 570 vw and 535 cm.$^{-1}$

Trimethylborane could be pumped readily from the adduct at room temperature, the dissociation pressure at 23•5° was 28 m.m. Vapour pressures in the temperature range 0 —— 44° can be represented to within 1 mm. by the equation $\log_{10}p(\text{mm.}) = 4{\cdot}220 - \frac{802{\cdot}1}{T}$.

Thermal decomposition of $Ph_2C{=}NH.BMe_3$. Trimethylborane (0·56 g., 10 m.mole) was condensed on to diphenylketimine (1·81 g., 10 m.mole) at -196° in an evacuated tube, and the mixture was then held at 160° for 24 hr. Methane (0·019 g., 1·16 m.mole) was recovered from the tube and identified by its infrared spectrum, together with some unchanged trimethylborane (0·32 g., 5·7 m.mole). The residue, a brown solid, was dissolved in hot benzene to give colourless crystals of dimethyl-(α-phenylbenzylideneamino)borane, $Ph_2C{=}NBMe_2$, m.p. 173° on cooling. [Found: B, 4·8; N, 6·3%. $C_{15}H_{16}BN$ requires B, 4·9; N, 6·3%]. The infrared spectrum of the solid recorded as a nujol mull contained bands at 1662s, 1597w, 1580w, 1488m, 1439m, 1337m, 1295m, 1280s, 1166m, 1152w, 1124w, 1110w, 1087m, 1074m, 1054s, 1024s, 1014s, 952m, 932w, 910w, 897vw, 848w, 839w, 800m, 756m, 741m, 734m, 717sh, 706s, 696m, 592m, and 537m cm.^{-1}

Reaction of diphenylketimine with triethylborane.

Triethylborane (0·98 g., 10·0 m.mole) was condensed on to diphenylketimine (1·81 g., 10·0 m.mole) at -196° in an evacuated tube, which was sealed and held at 155° for one week. The volatile contents of the tube were then transferred to a vacuum line and identified by their infrared spectra as ethylene (0·16 g., 5·8 m.mole) and triethylborane (0·62 g., 6·3 m.mole). The residual involatile yellow solid was dissolved in hexane from which crystals, m.p. 152-153·5°, separated on cooling which were identified as the ketimine $Ph_2C:NCHPh_2$. [Found: C, 89·4; H, 5·3; N, 4·5%. $C_{26}H_{21}N$ requires C, 89·8; H, 6·0; N, 4·0%].

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1628vs, 1592s, 1570m, 1488s, 1116m, 1290sh, 1280s, 1250m, 1178m, 1152m, 1073m, 1036m, 1028s, 1021sh, 667w, 658m, 640m, 619m, 606m and 594s cm.$^{-1}$

Reaction of diphenylketimine with triphenylborane.

Triphenylborane and diphenylketimine were recovered unchanged after being heated together to 160° for several hours. No evidence of adduct formation was found, but after several days' heating at 160° a trace of benzene was detected in the reaction mixture, which still, however, consisted essentially of the starting materials.

Reaction of diphenylketimine with trimethoxyborane.

Diphenylketimine (5·4 g., 30 m.moles) was placed in a two-necked flask fitted with a reflux condenser and dropping funnel, and warmed to 70°. Trimethoxyborane (1·0 g., 10 m.moles) was added dropwise and the resulting mixture was refluxed for 4 hours. On removal of unreacted trimethoxyborane a brown liquid remained; on heating at 100° at 10^{-3} mm. diphenylketimine (5 g., 27·6 m.moles) distilled and left a small amount of an involatile brown solid which contained boron.

Reaction of diphenylketimine with tris-dimethylaminoborane.

Tris-dimethylaminoborane (1·4 g., 10 m.moles) was placed in a two-necked flask fitted with a reflux condenser and diphenylketimine (5·4 g., 30 m.moles) added. The mixture was stirred and heated to 150° for 36 hours. Dimethylamine was given off identified by its infrared spectrum and the solution turned dark brown. On distillation the solution yielded tris-dimethylaminoborane (0·085 g., 0·57 m.moles) and diphenylketimine. The remaining dark brown viscous liquid was dissolved in a toluene/hexane mixture, filtered and pumped dry. The infrared spectrum of the liquid showed a strong C:N stretching vibration at 1667 cm.$^{-1}$, however another was observed at 1603 cm.$^{-1}$ i.e. $Ph_2C:NH$. [Found: C, 78·5; H, 4·87; B, 2·29%. $C_{39}H_{30}N_3B$ requires C, 84·9; H, 5·44; B, 2·0%].

Reaction of diphenylketimine with boron trichloride.

Diphenylketimine (14 g., 77 m.moles) was dissolved in hexane (200 c.c.) and cooled to -78°. Boron trichloride (1·4 g., 13 m.moles) was passed through the hexane solution with vigorous stirring. A white solid, diphenylketimine hydrochloride, precipitated. The hexane was removed by distillation. The residual mixture was stirred with benzene (20 c.c.) and filtered. Removal of the benzene by pumping left a viscous liquid from which diphenylketimine distilled out at 100° at 10^{-3} mm. pressure. The involatile material which remained contained boron and its infrared spectrum showed two C:N stretching vibrations at 1667 and

and 1603 $cm.^{-1}$ The material was presumed to be tris-diphenylketiminoborane contaminated with diphenylketimine.

Reaction of diphenylketimine with boron trifluoride.

Diphenylketimine (1·8 g., 10 m.moles) in diethyl ether (20 c.c.) was added to boron trifluoride diethyl ether complex (1·4 g., 10 m.moles) in diethyl ether (20 c.c.) in one limb of a double Schlenk tube, the solution being vigorously stirred to promote mixing. A white solid, diphenylketimine boron trifluoride $Ph_2C:NH,BF_3$ precipitated immediately. The solid, purified by washing with ether, began to decompose at ca. 180° and finally liquefied at 207°. [Found: C, 62·8; H, 4·13; F, 24·3; N, 5·6%. $C_{13}H_{11}NBF_3$ requires C, 62·6; H, 4·41; F, 22·9; N, 5·6%].

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1628vs, 1592s, 1572m, 1504m, 1330m, 1319m, 1282s, 1190m, 1182m, 1170s, 1143s, 1121s, 1087s, 1070s, 1031m, 1001m, 978sh, 963s, 935s, 915s, 899m, 851m, 794s, 769vw, 750m, 724m, 704s, 694m, 667w, 655w, 611vw, 592s, 565vw and 551m $cm.^{-1}$

Reaction of diphenylketimine with trimethylgallium.

Trimethylgallium (0·6 g., 5 m.moles) was condensed on to a solution of diphenylketimine (0·9 g., 5 m.moles) in hexane (20 c.c.) at -196°. The mixture was allowed to warm to room temperature when the adduct $Ph_2C:NH,GaMe_3$ precipitated as a white solid. [Found: hydrolysable methyl 5·03%; M (cryoscopic in benzene), 301. $C_{16}H_{20}NGa$ requires hydrolysable methyl, 5·07%; M, 296.]

The infrared spectrum of the solid recorded as a nujol mull contained bands at 3279m, 1604s, 1576s, 1466sh, 1451s, 1393s, 1379sh, 1326w, 1295w, 1236m, 1186m, 1176m, 1161w, 1089sh, 1079w, 1032w, 1002w, 975w, 935m, 914m, 875s, 792s, 763s, 737sh, 730s, 720sh, 698vs, 672vw, 635m, 583vw, 541vs and 510m, $cm.^{-1}$

Reaction of diphenylketimine with triethylgallium.

Triethylgallium (0·8 g., 5 m.mole) was condensed on to diphenylketimine (0·9 g., 5 m.mole) in hexane (20 c.c.) at -196° in one limb of a double Schlenk tube. The mixture was allowed to warm to room temperature. The hexane was removed by vacuum distillation yielding the adduct $Ph_2C:NH,GaEt_3$.

The infrared spectrum recorded as a liquid film contained bands at 3268m, 1603s, 1574s, 1495m, 1451s, 1420sh, 1393s, 1374sh, 1325w, 1290w, 1236s, 1183m, 1161m, 1076m, 1031m, 1001m, 990m, 952m, 932m, 906m, 875s, 843w, 787s, 764s, 738w, 725m, 697vs, 641s, 614sh and 526s $cm.^{-1}$

Reaction of diphenylketiminolithium and gallium trichloride.

α-Phenylbenzylideneaminolithium (3·7 g., 20 m.moles) in ether (40 c.c.) was cooled to -180° in one limb of a double Schlenk tube.

Gallium trichloride (3·5 g., 20 m.moles) in hexane (20 c.c.) and ether (3 c.c.) was added by syringe and the mixture was allowed to warm to room temperature with constant stirring. At ca. -80° the red colour disappeared and a yellow solid precipitated. At room temperature the ether was removed by vacuum distillation and toluene (15 c.c.) was added. After boiling the toluene for two minutes the mixture was filtered and on cooling colourless crystals of α-phenylbenzylideneaminogallium dichloride, m.p. 272° were formed. [Found: C, 49·5; H, 3·42; Cl, 22·4%; M, cryoscopically in benzene 601. $C_{26}H_{20}N_2Ga_2Cl_4$ requires C, 48·6; H, 3·20; Cl, 21·8%; M, 642].

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1605sh, 1591vs, 1577sh, 1566vs, 1326m, 1295m, 1271m, 1250sh, 1181vw, 1163w, 1076w, 1029w, 1001w, 975sh, 958m, 925sh, 919w, 886vw, 925w, 790sh, 786s, 767m, 730sh, 708vs, 698vs, 680m, 667w, 621vw, 553w and 463w cm.$^{-1}$

Reactions of aldoximes with Group III alkyls.

Reaction of pyridine-2-aldoxime with trimethylborane.

Trimethylborane (0·43 g., 7·6 m.moles) was condensed on to pyridine-2-aldoxime (0·8 g., 6·6 m.moles) and toluene (20 c.c.) at -196° in a sealed tube. Upon warming to 90° the pyridine-2-aldoxime dissolved to give a clear yellow solution and this solution was left at 90° for several days. Methane (0·10 g., 6·3 m.moles) identified by its infrared spectrum was evolved and after concentration of the solution by removal of half the solvent by vacuum distillation small crystals of o-dimethylboron pyridine-2-aldoxime $C_5H_4NCH{:}NOBMe_2$, m.p. 132° formed. [Found: B, 6·6; N, 17·0%; M (cryoscopic in benzene), 169. $C_8H_{11}N_2BO$ requires B, 6·7; N, 17·3%; M, 162].

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1615s, 1567w, 1534m, 1481s, 1330m, 1304vs, 1287vs, 1267m, 1253m, 1232w, 1189vw, 1161m, 1134m, 1111s, 1094vs, 1081s, 1062vs, 1044s, 1026s, 985vs, 971s, 934s, 909m, 899vs, 868s, 820w, 791m, 774s, 767vs, 750m, 699s, 664vw, 570s, 546w, 489m and 447w $cm.^{-1}$

Reaction of pyridine-2-aldoxime with trimethylaluminium.

Trimethylaluminium (0·75 g., 10·4 m.moles) was added dropwise by syringe to a suspension of pyridine-2-aldoxime (1·2 g., 10 m.moles) in toluene (20 c.c.) at -78° in one limb of a double Schlenk tube.

On warming and stirring the aldoxime dissolved to give a yellow solution which became colourless as methane was evolved. After concentration of the solution by removal of some of the solvent by vacuum distillation, small crystals of dimeric o-dimethylaluminium pyridine-2-aldoxime $(C_5H_4NCH{:}NOAlMe_2)_2$ were formed. The product decomposes on heating until it melts at 115° with frothing. [Found: Al, 15·1; hydrolysable methyl, 17·2%; M (cryoscopic in benzene), 348. $C_{16}H_{22}N_4Al_2O_2$ requires Al, 15·2; hydrolysable methyl, 16·9%; M, 356]. The infrared spectrum of the solid recorded as a nujol mull contained bands at 1605s, 1582w, 1553m, 1353m, 1302w, 1267w, 1224m, 1186m, 1152w, 1115s, 1093vs, 1052w, 1028w, 1017m, 987w, 927m, 898m, 789m, 770s, 746m, 725sh, 703vs, 671vs, 666vs, 639s, 562w, 539w, 516m and 485m $cm.^{-1}$ The product did not form a methiodide.

Reaction of pyridine-2-aldoxime with triethylaluminium.

Triethylaluminium (1·1 g., 10 m.moles) was added dropwise by syringe to a suspension of pyridine-2-aldoxime (1·2 g., 10 m.moles) in toluene (20 c.c.) at -78° in one limb of a double Schlenk tube. On warming and stirring the aldoxime dissolved to give a yellow solution which became colourless as ethane was evolved. The toluene was removed by vacuum distillation to give the viscous liquid o-diethylaluminium pyridine-2-aldoxime $(C_5H_4NCH{:}NOAlEt_2)_x$. The ratio of aluminium to hydrolysable ethyl was 1:1·98.

The infrared spectrum recorded as a liquid film contained bands at: 1603s, 1572w, 1545m, 1351m, 1303w, 1251w, 1231m, 1187m, 1154w, 1111s, 1092vs, 1048w, 1027w, 1015s, 987w, 970s, 920m, 899m, 789m, 772s, 748m, 720s, 700vs, 668vs, 665vs, 632m, 568m, 540m, 510m, 490m, and 452w cm.$^{-1}$

Reaction of syn-benzaldoxime with trimethylaluminium.

Trimethylaluminium (0·75 g., 10·4 m.moles) was added dropwise by syringe to a solution of syn-benzaldoxime (1·2 g., 10 m.moles) in ether (20 c.c.) at -78° in one limb of a double Schlenk tube. On warming methane was evolved. Removal of the solvent by vacuum distillation yielded the viscous liquid o-dimethylaluminium benzaldoxime ($C_6H_5CH:NOAlMe_2)_x$ which was purified by recrystallisation from hexane at -78°. The product gave a ratio of aluminium to hydrolysable methyl of 1:1·97. The infrared spectrum recorded as a liquid film contained bands at 3021m, 2924s, 2890sh, 2825m, 1605m, 1577m, 1493m, 1453s, 1376w, 1316m, 1300sh, 1203s, 1164w, 1099w, 1076m, 1029s, 972m, 940vw, 921w, 897m, 870sh, 850s, 816m, 781m, 758s, 692vs, 668s, 568w, 548w, 505m, and 444w cm.$^{-1}$

Reaction of pyridine-2-aldoxime with trimethylgallium.

Trimethylgallium (0·99 g., 8·7 m.moles) was condensed at -196° on to a frozen suspension of pyridine-2-aldoxime (1·06 g., 8·7 m.moles) in toluene (20 c.c.). On warming and stirring the aldoxime dissolved to give a yellow solution which on evolution of methane became colourless. The solvent was removed by vacuum distillation leaving a viscous liquid which after repeated washings with boiling hexane gave a white powder. The solid was o-dimethylgallium pyridine-2-aldoxime $(C_5H_4NCH:NOGaMe_2)_{1\cdot5}$ m.p. 35°. [Found: C, 44·9; H, 5·23; Ga, 31·1%; M (cryoscopic in benzene), 335. $C_{16}H_{22}N_4Ga_2O_2$ requires C, 43·5; H, 5·0; Ga, 31·6%; M, 441].

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1603vs, 1579vs, 1566sh, 1547s, 1495m, 1480s, 1471sh, 1436s, 1379w, 1350m, 1327w, 1303m, 1326w, 1224s, 1200s, 1149m, 1110vs, 1087vs, 1050s, 1030m, 995s, 979s, 907s, 882m, 772vs, 743vs, 731vs, 695vs, 686sh, 667s, 635s, 629sh, 619m, 588s, 535m, 516m and 463m $cm.^{-1}$

Reaction of pyridine-2-aldoxime with trimethylindium.

Trimethylindium (1·17 g., 7·3 m.moles) in toluene (20 c.c.) was added by syringe to a suspension of pyridine-2-aldoxime (0·89 g., 7·3 m.moles) in toluene (20 c.c.) at -78°. On warming and stirring the aldoxime dissolved to form a yellow solution which on evolution of methane became colourless. After concentrating the solution by removal of some of the solvent by vacuum distillation, small crystals of o-dimethylindium pyridine-2-aldoxime $(C_5H_4NCH:NOInMe_2)_2$ separated. The product had m.p. 164°. [Found: N, 10·3; In, 42·4%; M (cryoscopic in benzene), 539. $C_{16}H_{22}N_4In_2O_2$ requires N, 10·5; In, 43·2%; M, 532].

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1601s, 1581sh, 1535m, 1526m, 1478s, 1339m, 1340m, 1302w, 1236w, 1247s, 1145m, 1112sh, 1110s, 1088vs, 1037w, 1012m, 1000w, 900s, 887m, 787m, 771m, 751w, 703m, 685s, 667m, 634s, 524s, 516m and 481w cm.$^{-1}$

Reaction of pyridine-2-aldoxime with trimethylthallium.

Trimethylthallium (1·7 g., 6·9 m.moles) in ether (10 c.c.) was added dropwise by syringe to a suspension of pyridine-2-aldoxime (0·83 g., 6·8 m.moles) in ether (20 c.c.) at room temperature in one limb of a double Schlenk tube. A white solid immediately precipitated which evolved methane and deposited a yellow solid. The solid o-dimethylthallium pyridine-2-aldoxime $(C_5H_4NCH:NOTlMe_2)_2$ m.p. 139° was recrystallised from a tetrahydrofuran-diethyl ether mixture.

[Found: C, 27·2; H, 3·32; N, 7·7%; M (cryoscopic in benzene), 696. $C_{16}H_{22}N_4Tl_2O_2$ requires C, 27·0; H, 3·1; N, 7·9%, M, 710].

The infrared spectrum of the solid recorded as a nujol mull contained bands at 1590s, 1570sh, 1505s, 1424w, 1323m, 1239vw, 1217w, 1147m, 1098m, 1053vs, 1000vs, 995w, 987vw, 897m, 867w, 788m, 776s, 741m, 718vw, 679s, 666w, 624m, 544m and 524w cm.$^{-1}$

Reaction of acetoxime-o-methyl ether with trimethylaluminium.

Trimethylaluminium (0·7 g., 10 m.moles) was added by syringe to a solution of acetoxime-o-methyl ether (0·9 g., 10 m.moles) in hexane (20 c.c.) in one limb of a double Schlenk tube. The solution was stirred for five minutes, filtered and cooled to -78° when a white solid crystallised. On warming to room temperature the crystals melted to form the viscous liquid adduct $Me_2C:NOMe,AlMe_3$. [Found: Al, 16•8; hydrolysable methyl 27•8%; M, 164. $C_7H_{18}NAlO$ requires Al, 17•0; hydrolysable methyl 28•3%; M, 159.]

The infrared spectrum recorded as a liquid film contained bands at 3003sh, 2933vs, 2890s, 2825s, 1639s, 1466m, 1439s, 1379s, 1279m, 1190s, 1083m, 1025s, 986m, 917m, 893w, 840w, 806w, 702vs, 632s, 526m and 435w $cm.^{-1}$

<u>Thermal decomposition of $Me_2C:NOMe,AlMe_3$.</u> A sample of the adduct $Me_2C:NOMe,AlMe_3$ (1•6 g., 10 m.moles) when heated to 120° under vacuum formed methane (0•14 g., 8•7 m.moles) identified by its infrared spectrum, and an involatile brown-black glass. Heating the glass under vacuum to 240° only resulted in further decomposition of the glass.

DISCUSSION

Discussion

As indicated in the introduction, few azomethine derivatives of the main group elements have been prepared, and little is known of their properties. Previously, azomethine derivatives $(RR'C{:}NMR''_2)_2$ of Group III elements M have been prepared by addition reactions of nitriles. For example the hydroboration of nitriles RCN by organoboron hydrides $(R''_2BH)_2$ leads to aldimine derivatives $(RCH{:}NBR''_2)_2$.[36,37] Both aldimine $(RCH{:}NAlR''_2)_2$ and ketimine $(RR''C{:}NAlR''_2)_2$ derivatives of aluminium can be prepared from the nitrile RCN and an appropriate organoaluminium compound (R''_2AlH or R_3Al),[62,63] while aldimine derivatives of gallium are accessible by such reactions as the following:[77]

$$2PhCN + 2GaEt_3 \longrightarrow (PhCH{:}NGaEt_2)_2 + 2C_2H_4$$

However, the lower reactivity of organo-boron and -gallium compounds as opposed to organoaluminium compounds towards insertion of an unsaturated functional group like a nitrile causes ketimine derivatives $(RR'C{:}NMR''_2)_2$ of boron and gallium to be inaccessible by this general route. Furthermore even in the case of Al a different type of reaction occurs if the nitrile has hydrogen atoms attached to the α carbon atom, as in acetonitrile CH_3CN. This acts as a weak protic acid and cleaves alkyl groups from aluminium when adducts CH_3CN,AlR_3 are heated e.g.

$$nCH_3CN,AlMe_3 \longrightarrow nCH_4 + (CH_2CNAlMe_2)_n$$

The object of this investigation was to determine the most suitable methods of preparing ketimine derivatives of boron, zinc and lithium. Initially the possibility of preparing ketimine derivatives of zinc by reaction of a ketimine with organozinc compounds was explored:

$$R_2C{:}NH \quad + \quad R'_2Zn \longrightarrow \tfrac{1}{2}(R_2C{:}NZnR')_2 \quad + \quad R'H$$

This reaction would be analogous to the well-established method of attaching amino groups to zinc using secondary amines:[91]

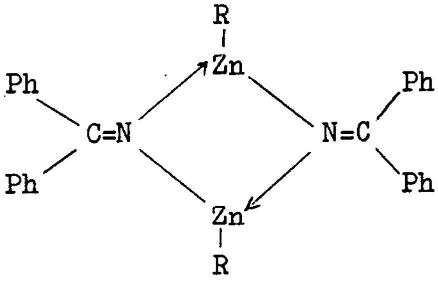
$$R_2NH \quad + \quad R'_2Zn \longrightarrow \tfrac{1}{2}(R_2NZnR')_2 \quad + \quad R'H$$

The ketimine chosen was diphenylketimine, which is readily prepared from benzonitrile by the Grignard route, and is relatively resistant to hydrolysis and to polymerisation or rearrangement reactions. Dialkylketimines with small alkyl groups appear to be highly susceptible to polymerisation or rearrangement reactions, so much so that the dimethyl compound $Me_2C{:}NH$ has apparently never been isolated during attempts at its preparation using methyl cyanide and grignard or lithium reagents.[118] Unsuccessful attempts have been made in these laboratories[119] to prepare diethylketimine by methanolysis of the products of reactions between EtCN and EtLi and EtMgX,[115] and by acetylacetone cleavage at -78° of products of EtCN/Et_3Al reactions.[63,120] It is likely that the instability of dialkylketimines is in part associated with the presence of hydrogen attached to the carbon α to the azomethine group [as in $(\gt CH)_2C{=}NH$], a disadvantage avoided by the use of diphenylketimine.

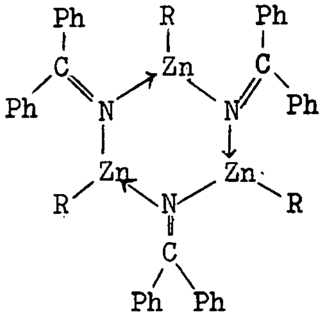
Equimolar mixtures of diphenylketimine and dimethyl- or diethylzinc react slowly at room temperature in the absence of solvent and rapidly at about 40°, eliminating methane or ethane respectively:-

$$Ph_2C{:}NH \;+\; R_2Zn \longrightarrow \tfrac{1}{2}(Ph_2C{:}NZnR)_2 \;+\; RH$$

Diphenylketimine and diphenylzinc undergo a similar reaction in toluene solution to form $(Ph_2C{:}NZnPh)_2$. The azomethine derivatives produced are air- and moisture-sensitive crystalline solids, which dissolve in benzene as dimeric species $(Ph_2C{:}NZnR)_2$, which are presumed to have a planar skeleton based on a $(ZnN)_2$ four-membered ring (I) such as has been shown by an X-ray crystallographic study to occur in the amino compound $(MeZnNPh_2)_2$.[121]



I

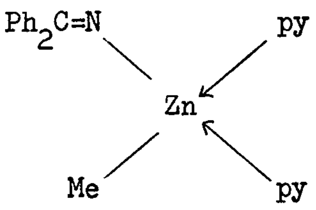


II

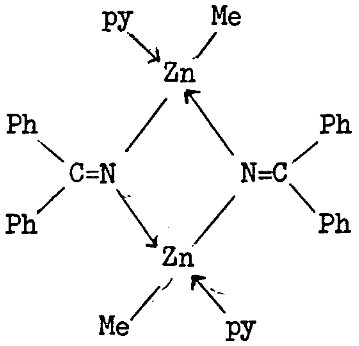
In this respect they resemble their Group III analogues $(RR'C{:}NMR''_2)_2$.[62,63,77] Although a trimeric structure II based on a planar six-membered $(ZnN)_3$ ring would have allowed the zinc and nitrogen atoms to adopt a strain-free configuration, it is likely that in such a structure there would be serious crowding of the substituent groups. Six-membered $(ZnN)_3$ rings are nevertheless believed to occur in urea and carbamate derivatives $(RZn.NPh.CO.NR'_2)_3$ and $(RZn.NPh.CO.OR)_3$ which are trimeric in benzene,[122] although the aminozinc alkyls $(Ph_2NZnMe)_2$ and $(Ph_2NZnEt)_2$ are dimeric, and four-membered rings (often cross linked in the form of cubes) are a common feature of compounds RZnX in which zinc is bound to a donor atom such as oxygen,[91,93,123] sulphur[91,124] chlorine[125] or bromine.[125]

The azomethine derivatives $(Ph_2C:NZnR)_2$ decompose at or above 80°. For example, a solution of the phenyl compound in toluene at 80° slowly deposited bis(diphenylketimino)zinc, $[(Ph_2C:N)_2Zn]_n$, an involatile, insoluble and presumably polymeric solid. Diphenylaminozinc alkyls also decompose when heated, presumably with disproportionation and tend also to disproportionate in the presence of donor molecules.[91] Dimethylaminozinc alkyls may well be even less thermally stable to disproportionation in that an attempt to prepare Me_2NZnMe from equimolar proportions of dimethylamine and dimethylzinc at about 70° led to bisdimethylaminozinc and unchanged alkyl.[91]

The zinc-nitrogen ring of our azomethine derivatives can be cleaved by donor molecules. For example, addition of an excess of pyridine to a benzene solution of the methyl compound $(Ph_2C:NZnMe)_2$ gave a yellow solution from which the yellow crystalline adduct $Ph_2C:NZnMe,2py$ was precipitated by hexane. The monomeric nature of this adduct in benzene is consistent with a structure III, with four-co-ordinate zinc and a terminal diphenylketimine group. The same product was obtained even



III



IV

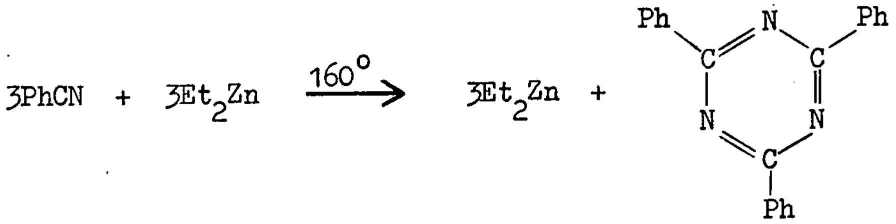
when the proportion of pyridine was limited to 2 mol. per mol. of dimer $(Ph_2C{:}NZnMe)_2$, when an adduct IV was expected, analogous to the alkoxide adduct $(MeZnOPh)_2$,2py.[91] The compound $(MeZnNPh_2)_2$ in contrast disproportionates in the presence of a limited amount of pyridine, giving $py_2Zn(NPh_2)_2$.[91]

An azomethine derivative of zinc was obtained from only one of the reactions between nitriles and organozinc compounds that we studied. Equimolar quantities of phenyl cyanide and diphenylzinc gave an involatile viscous liquid adduct PhCN,$ZnPh_2$ readily identified as such by the nitrile stretching frequency $\nu C{\vdots}N$ in its infrared spectrum which was located at 2259 $cm.^{-1}$, some 30 $cm.^{-1}$ higher in frequency than $\nu C{\vdots}N$ for phenyl cyanide itself. This adduct decomposed at 100° to give a yellow mass from which solid bisdiphenylketiminozinc $(Ph_2C{:}N)_2Zn$ was obtained by washing with toluene. The product was identical to that obtained from the disproportionation of $(Ph_2C{:}NZnPh)_2$ at 80°, and indeed its formation in the nitrile reaction probably involved $(Ph_2C{:}NZnPh)_2$

as an intermediate which disproportionated as it was formed:-

$$PhCN,ZnPh_2 \xrightarrow{100^\circ} [Ph_2C{:}NZnPh] \xrightarrow{80^\circ} (Ph_2C{:}N)_2Zn + Ph_2Zn$$

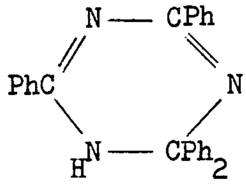
Our study of the system PhCN/$ZnEt_2$ gave no evidence of adduct formation, $\nu C{\equiv}N$ being the same as for phenyl cyanide itself, and confirmed the observations of Frankland and Evans[126] that at elevated temperatures diethylzinc catalyses the trimerisation of phenyl cyanide to 2,4,6-triphenyltriazine. Dimethylzinc has a similar effect on phenyl cyanide.[93]



Among other substances which catalyse the trimerisation of phenyl cyanide are trimethylaluminium,[127] trimethylgallium,[77] sodium,[128,129] organolithium and organomagnesium compounds,[130] concentrated sulphuric acid,[131] chlorosulphuric acid[129] and Raney nickel.[132] Although a common mechanism appears unlikely, the reactions involving organometallic compounds may well occur by initial insertion of one nitrile unit into a metal-alkyl bond, followed by successive insertions of further nitriles into the resulting metal nitrogen bond:-

$$R\text{-}Zn \xrightarrow{PhCN} R\text{-}C(Ph){:}NZn \xrightarrow{PhCN} RC(Ph){:}N{\cdot}C(Ph){:}NZn \quad \text{etc.}$$

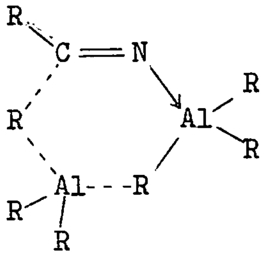
Cyclisation and elimination of the triazine could occur after the uptake of further moles of nitrile. Evidence for such a mechanism in the reaction catalysed by sodium has been obtained by the isolation of sodium cyanide (thought to be formed in an initial reaction $PhCN + 2Na \longrightarrow PhNa + NaCN$) and the compound V.[130]



V

This mechanism requires a metal-nitrogen link to be more reactive to insertion of unsaturated substances than a metal-carbon link, and Noltes has already shown Zn-O and Zn-N links to be more reactive than Zn-C links to insertion of isocyanates and similar compounds.[92] Alternatively but less likely, if a trimeric derivative $(PhC(R):NZnR)_3$ were formed it might act as a template in the manner suggested by Noltes and Boersma[122] to explain the trimerisation of isocyanates by trimeric urea or carbamate derivatives $(RZnNPhCOX)_3$ where $X = NPh_2$ or OR.

Studies of the systems Bu^tCN/R_2Zn (R = Me, Et or Ph) surprisingly afforded neither adducts Bu^tCN,ZnR_2 nor azomethine derivatives $(Bu^tCR:NZnR)_n$. The nitrile stretching frequency of t-butyl cyanide was unaffected by the presence of R_2Zn, and the components were recovered unchanged after mixtures Bu^tCN/Me_2Zn or Bu^tCN/Ph_2Zn had been heated to 160°. t-Butyl cyanide was likewise unaffected by diethylzinc, even at temperatures at which the latter decomposed by loss of ethylene (contrast Bu^tCN,MEt_3, where M = Al[62,63] or Ga,[77] which gave derivatives $(Bu^tCH:NMEt_2)_2$ under similar conditions) or at lower temperatures in toluene or tetrahydrofuran. It has been postulated[133] that addition of organoaluminium compounds across nitriles involves the intermediate VI.



VI

Three factors seem likely to operate against a reaction involving such an intermediate in the present zinc systems, all of which stem from the greater electronegativity of zinc than of aluminium; the Allred-Rochow values for the electronegativities of aluminium and zinc are Al, 1·47; Zn, 1·66.[134] Firstly with the exception of $PhCN,ZnPh_2$ adducts of the type RCN,ZnR_2 do not exist at 25° and are presumably less likely at about 150°, even under pressure in a sealed tube. Secondly organozinc compounds unlike organoaluminium compounds do not form strong alkyl bridges. Thirdly, nucleophilic attack on the carbon of the co-ordinated nitrile will presumably occur less readily if the migrating alkyl group is attached to a more electronegative metal and so carries a lower negative charge.

Nitriles $>$CHCN with α hydrogen were avoided in the present work as they afford poor routes to azomethine derivatives for reasons given above.

Infrared spectra.

Frequencies of some characteristic bands in the spectra of the diphenylketimino-zinc compounds are listed in Table 1.

TABLE 1

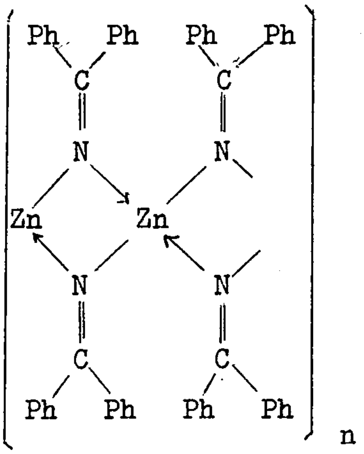
Infrared spectroscopic data for diphenylketimine derivatives of zinc

Compound	ν(C=N)cm^{-1}	ρ(Zn-Me)cm^{-1}rock	ν(Zn-Me)cm^{-1}
$(Ph_2C:N\cdot ZnMe)_2$	1624	673	538
$(Ph_2C:N\cdot ZnEt)_2$	1611	622*	520*
$(Ph_2C:N\cdot ZnPh)_2$	1607	-	-
$[(Ph_2C:N)_2Zn]_n$	1600	-	-
$Ph_2C:NZnMe,2py$	1613	622	503

All figures relate to Nujol mulls.

* Zn - CH$_2$ modes

The variation of νC:N with R in compounds $(Ph_2C:NZnR)_2$ may well reflect the changing mass and electronegativity of R, in that νC:N decreases in the sequence R = Me $>$ Et $>$ Ph. This will be discussed in greater detail with the Group III derivatives. The low value of νC:N for bisdiphenylketiminozinc is consistent with its formulation as a co-ordination polymer VII in which all the



VII

azomethine groups are bridging groups. In the monomeric adduct $Ph_2C{:}NZnMe,2py$, however, the diphenylketimino group is terminal, not bridging, and νC:N is accordingly higher, although surprisingly not as high as νC:N for $(Ph_2C{:}NZnMe)_2$. On electronic grounds νC:N for co-ordinated (bridging) azomethine groups would be expected to be appreciably lower than νC:N for terminal $Ph_2C{:}N-$.

Other figures in Table 1 relate to vibrations of the zinc-attached alkyl groups. Coates and Ridley[91] have shown that ν(Zn-Me) tends to fall as the co-ordination number of the zinc increases, from 615 $cm.^{-1}$ for Me_2Zn to 506-514 $cm.^{-1}$ when the metal is 4 co-ordinate. The figures obtained for $(Ph_2C{:}NZnMe)_2$ and $(Ph_2C{:}NZnEt)_2$ with three co-ordinate zinc and for $Ph_2C:NZnMe,2py$, with four co-ordinate zinc, are consistent with this generalization.

Proton magnetic resonance (p.m.r.) spectra. Chemical shifts and assignments of peaks in the p.m.r. spectra of the soluble azomethine derivatives, recorded in hexadeuterobenzene solutions, are listed in Table 2. The peak due to the protons of the diphenylketimine residue in all cases appeared as a sharp singlet at τ = 2·70 - 2·80 p.p.m. (as listed) with a slight shoulder on the downfield side possibly attributable to the ortho and meta/para sets of protons which would be expected to be magnetically different in these derivatives. In the spectra of $(Ph_2C:NZnMe)_2$ and $Ph_2C:NZnMe,2py$ the marked difference between the τ values for the methyl groups probably reflects the difference between the

TABLE 2

Proton magnetic resonance spectra

	τ values of peaks (p.p.m.; C_6D_6 solvent)	
Compound	$=CPh_2$	ZnR
$(Ph_2C:N\cdot ZnMe)_2$	$2\cdot7_7$s	$10\cdot6_3$s
$(Ph_2C:N\cdot ZnEt)_2$	$2\cdot7_9$s	$8\cdot7_7$q, $9\cdot5_4$t
$(Ph_2C:N\cdot ZnPh)_2$	$2\cdot8_0$s	$2\cdot9_1$s
$Ph_2C:N\cdot ZnMe,2py$	2·7br	$10\cdot0_1$s

s = singlet, t = triplet, q = quartet, br = broad.

co-ordination numbers of zinc in these compounds (3 and 4 respectively). Sensitivity of τ (Be-CH_3) to the co-ordination number of beryllium has been noticed recently for methylberyllium alkoxides $(MeBeOR)_{2 \text{ or } 4}$,[135] and a similar correlation is seen in the marked concentration dependence of τ (Zn-CH_3) for solutions of $(MeZnOBu^t)_n$, for which n varies from 2 for dilute solutions to 4 for concentrated solutions.[136]

Azomethine derivatives of lithium.

Only one azomethine derivative $R_2C:NM$ of the Group I elements has been prepared. That is diphenylketimino sodium, obtained from the reaction between sodium in liquid ammonia and diphenylketimine. It was found to be impossible to separate the product from excess ammonia and sodium. A similar reaction using potassium (2 mol.) gave N,N'-dipotassium benzhydrylamine $Ph_2C(NHK)_2$.[137]

Consequently methods involving strong donors are to be avoided if pure azomethine derivatives of Group I elements are to be obtained.

An equimolar mixture of diphenylketimine and methyl-lithium in ether at ca. -50° eliminated methane to give a deep red solution.

$$Ph_2C:NH + MeLi \longrightarrow {}^1/n\,(Ph_2C:NLi)_n + CH_4$$

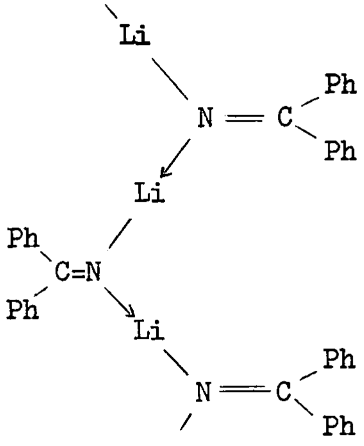
Removal of the solvent gave a yellow froth demonstrating the tenacity with which ether is held by the lithium derivative. After washing with hot toluene a yellow powder was obtained, insoluble in hexane, toluene and diethyl ether, and extremely air and moisture sensitive, so much so that a sample placed on a watch glass and exposed to air caused the glass to become extremely hot.

A related compound $(PhMeC:NLi)_n$ was prepared by the addition of methyl-lithium across benzonitrile below 0°

$$MeLi + PhCN \longrightarrow {}^1/n\,(PhMeC:NLi)_n$$

in diethyl ether solution. Again a deep red solution formed and the product, which frothed on removal of ether was purified by washing with hot toluene.

Diphenylketiminolithium $Ph_2C:NLi$ and α-methylbenzylideneaminolithium PhMeC:NLi are both presumed to be polymeric, having a structure VIII on the basis of their insolubility and stability to heat.



VIII

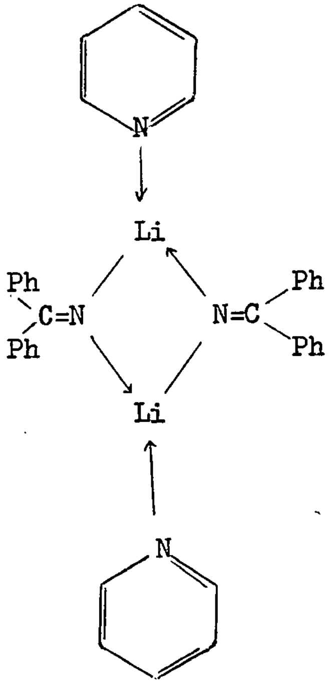
This type of structure VIII allows the lithium and nitrogen atoms to adopt a strain free configuration. Dimethylaminolithium is also polymeric (insoluble in ethers etc.) and presumably has a similar structure.

The lithium atoms being bivalent are co-ordinatively unsaturated and consequently react with donor molecules such as pyridine and tetrahydrofuran. The 1:1 pyridine complex obtained from cooling an ether solution of the reactants was bright red in colour whereas the tetrahydrofuran complex was a bright orange.

It is thought that the colours of the complexes are due to the transfer of an electron from the donor molecule into the lowest unoccupied π^* orbital of the delocalised ketimine system or vice versa.

The bright red pyridine adduct was found to dissolve in benzene to give initially a bright red solution. However, after a very short time a yellow solid precipitated, which was identified as diphenylketiminolithium. Pyridine was isolated from the benzene solution by extraction into acid solution, separation of the acid solution from the benzene, neutralisation of the acid and finally distillation of the pyridine and identification by its ultraviolet spectrum.

It is thought that the pyridine adduct of diphenylketiminolithium is a low molecular weight species possibly having a structure IX similar to that of $(Et_3NLiEt)_2$ and which disproportionates in benzene.

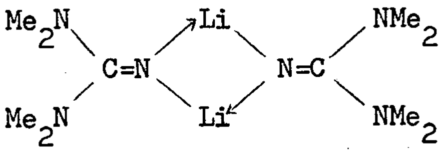


IX

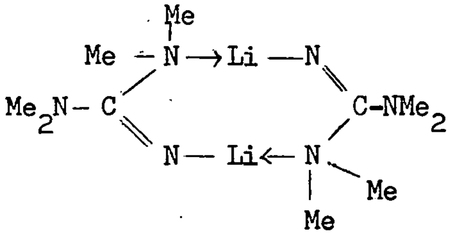
The proton magnetic resonance spectrum of $Ph_2C{:}NLi$ as a dilute solution in tetrahydrofuran was recorded, with tetramethylsilane ($\tau = 10{\cdot}0_0$) as internal reference and found to consist of two multiplets at $\tau = 2{\cdot}5_3$ p.p.m. and $\tau = 2{\cdot}6_0$ p.p.m., attributable to the ortho and meta/para sets of protons respectively which would be expected to be magnetically different in these derivatives.

In complete contrast was N-lithio-N',N',N",N"-tetramethylguanidine $[(Me_2N)_2C{:}NLi]_2$ prepared from tetramethylguanidine and methyllithium at ca. -50°. It was soluble in hot ether, benzene and toluene giving a colourless solution and crystallised readily from hot toluene as large plates.

It is dimeric in benzene and thought to have a skeleton based on either a $(LiN)_2$ four membered ring X such as is presumed to exist in the compound $[(Me_3Si)_2NLi]_2$[106] or an eight membered ring XI.



X



XI

Structure X is unlikely as the N-Li-N angle would be 90° compared to a strain free 180° obtained in structure XI. An attempted preparation of the analogous $Me_2NC(Me){=}NLi$ from methyl-lithium and dimethyl cyanamide

Me_2NCN resulted in the evolution of almost 1 mol. methane and the precipitation of a white solid which exploded when oxygen was passed over it.

$$Me_2NCN + MeLi \longrightarrow CH_4 + {}^1/n\,(LiCH_2NCH_3CN)_n$$

Further light has been cast upon this type of reaction recently[119] from a study of the reactions between methyl and ethyl cyanide and methyl- and ethyl-lithium. In all cases alkane was evolved (60%) and a white precipitate obtained which had a Li/N ratio of 1:1•2. This is consistent with the following scheme:

$$MeCN + MeLi \longrightarrow MeH + {}^1/n\,(LiCH_2CN)_n$$

$${}^1/n\,(LiCH_2CN)_n + MeCN \longrightarrow {}^1/n\,(Li\text{-}N{=}C(Me)\text{-}CH_2CN)_n$$

In contrast to diphenylketiminolithium, N-lithio-N',N',N",N"-tetramethylguanidine did not react with pyridine, tetrahydrofuran or ethylene glycol dimethyl ether, which would seem to indicate that the dimeric molecule is in the eight membered ring form as the formation of a 1:1 complex with pyridine would require a N-Li-N angle of 120° and the strain involved would be greater for the eight membered ring than for the four membered one.

Both $Ph_2C{:}NLi$ and $(Me_2N)_2C{:}NLi$ react with 2,2'-bipyridyl to give a black tar, possibly due to addition across the C=N bond of the bipyridyl.

The proton magnetic resonance spectrum of N-lithio-N',N',N",N"-tetramethylguanidine as a dilute solution in benzene was recorded with tetramethyl silane as internal reference, and consisted of a sharp singlet at $7{\cdot}38\,\tau$ originating from $N\text{-}CH_3$ attached protons. The p.m.r. spectrum of $(Me_2N)_2C{:}NH$ shows the $N\text{-}CH_3$ attached protons at $7{\cdot}36\,\tau$. If the compound has structure XI then one would expect two $N\text{-}CH_3$ resonances due to the different environments in which they are to be found unless there is rapid exchange between the dimeric molecules. A mass spectrum of the compound showed merely the breakdown pattern of $(Me_2N)_2C{:}NH$.

The infrared azomethine stretching vibrations are given in Table 3. In general the results are similar to those obtained for the zinc derivatives i.e. the νC=N of the metal derivatives are higher than those of the free imines, and complexes of the metal derivatives show a νC=N between the two. The compounds $Ph_2C{:}NLi$ and PhMeC:NLi demonstrate

Table 3

Infrared spectroscopic results for ketiminolithium compounds.

Compound	νC=N cm^{-1}	Compound	νC=N cm^{-1}
$Ph_2C{:}NH$	1603	$Ph_2C{:}NLi$,T.H.F.	1618
$Ph_2C{:}NLi$	1620	$(Me_2N)_2C{:}NH$	1601
PhMeC:NLi	1629	$(Me_2N)_2C{:}NLi$	1632
$Ph_2C{:}NLi$,py	1616		

All figures, except $Ph_2C{:}NH$ and $(Me_2N)_2C{:}NH$ which were recorded as liquid films, relate to Nujol mulls.

the effect of different electron withdrawing groups attached to the azomethine carbon atom upon the C=N stretching vibration. Two phenyl groups have a greater electron withdrawing power than a phenyl and a methyl group and consequently the νC=N is lower by 9 $cm.^{-1}$

Azomethine derivatives of Group III.

Whereas reactions between ketimines and alkyls of zinc and lithium eliminate alkane at room temperature and below diphenylketimine forms adducts with the alkyls of the Group III elements R_3M (M = B, Al and Ga).

Trimethylborane formed an unstable solid adduct $Ph_2C:NH,BMe_3$ over which the dissociation pressure of trimethylborane was 28 mm. at $23{\cdot}5^o$. The change of dissociation pressure of this adduct with temperature over the range $0-44^o$ corresponded to a heat of dissociation for the solid adduct into liquid diphenylketimine and gaseous trimethylborane of the order of 4 $kcal.mole^{-1}$. Vapour pressure measurements on diphenylketimine itself over the temperature range 110^o to 185^o corresponded to a heat of vaporisation of $16{\cdot}6$ $kcal.mole^{-1}$. Accordingly an upper limit of $20{\cdot}6$ $kcal.mole^{-1}$ can be set on the value of the heat of dissociation of gaseous $Ph_2C:NH,BMe_3$ into gaseous $Ph_2C:NH$ and gaseous Me_3B. The actual value will differ from this by an amount equal to the heat of sublimation of crystalline $Ph_2C:NH,BMe_3$, which cannot be measured directly but is likely to be about 16 $kcal.mole^{-1}$ by analogy with structurally similar organic compounds.[138]

The approximate value of 4 $kcal.mole^{-1}$ for the heat of dissociation of $Ph_2C:NH,BMe_3$ in the gas phase may be compared with the gas phase heats of dissociation of the secondary amine adducts Me_2NH,BMe_3 ($19{\cdot}3$ $kcal.mole^{-1}$),[139] Et_2NH,BMe_3 ($16{\cdot}3$ $kcal.mole^{-1}$)[140] and $(CH_2)_3NH,BMe_3$

(22·5 kcal.mole).[21] No evidence has previously been found of adduct formation in the systems RCN/BMe_3 and thus towards trimethylborane as the reference acid, diphenylketimine is intermediate in donor power between amines and nitriles. In view of the weak donor power of diphenylketimine towards trimethylborane, it was not surprising that no complex formation in the systems of diphenylketimine with the weaker Lewis acids Et_3B and Ph_3B was detected.

The infrared spectrum of a nujol mull of the adduct $Ph_2C{:}NH,BMe_3$ contained a band at 1604 $cm.^{-1}$ attributable to νC:N. The frequency of this band was essentially the same as that of the corresponding band in the spectrum of the free ketimine, whether in the liquid phase or in chloroform solution. The absence of any appreciable change in νC:N on formation of the adduct is consistent with the very weak co-ordinate link in this compound.

The proton magnetic resonance spectrum of $Ph_2C{:}NH,BMe_3$ was recorded using perdeuterio-benzene as solvent with tetramethylsilane as internal standard (τ = 10·00 p.p.m.). The spectrum consisted of a singlet of low intensity at τ = 0·0 p.p.m. attributable to the nitrogen attached proton, a strong multiplet centred on τ = 2·63 p.p.m., arising from the aromatic protons and a singlet at τ = 9·80 p.p.m. due to the methyl groups. The chemical shift of the last peak may be compared with the value τ = 9·25 p.p.m. for trimethylborane itself in the same solvent. The change in chemical shift, $\Delta\tau$, on co-ordination is in the direction expected on electronic grounds, as the co-ordinate link supplies electronic charge to the boron with consequent electron drift to the boron-attached methyl groups. Moreover, the magnitude of $\Delta\tau$ is significantly lower than $\Delta\tau$ for the change $Me_3B \longrightarrow Me_3N,BMe_3$ (1·08 p.p.m.)[141] affording further evidence of the relative donor properties of diphenylketimine and trimethylamine.

Similar crystalline solid complexes $Ph_2C:NH,MR_3$ (R = Me, M = Al, Ga) and liquid complexes (R = Et, Ph, M = Al, Ga) have been isolated. The methyl compounds $Ph_2C:NHAlMe_3$ and $Ph_2C:NHGaMe_3$ are crystalline solids readily obtained from equimolar mixtures of the components in hexane, dissolving in cold benzene without dissociation as shown by cryoscopic measurements. The triethyl and triphenyl adducts $Ph_2C:NH,AlEt_3$, $Ph_2C:NH,GaEt_3$, $Ph_2C:NH,AlPh_3$ and $Ph_2C:NH,GaPh_3$ were obtained as viscous liquids after removal of solvent under vacuum from hexane or toluene solutions of equimolar mixtures of the components. Cryoscopic studies on these four adducts were not attempted because of the possibility that solvent remained trapped in the samples, but the extent of interaction between the components was revealed by a study of their proton magnetic resonance (p.m.r.) spectra. Chemical shift values and relative intensities of peaks in their p.m.r. spectra in hexadeuterobenzene solutions are listed in table 4. In the spectrum of diphenylketimine itself in C_6D_6 the broad absorption centred on τ = 2·4 p.p.m. (intensity 4) probably arose from the ortho protons of the phenyl

Table 4

Proton magnetic resonance spectroscopic results for adducts

$Ph_2C{:}NH{,}MR_3$

Compound	values = N-H	(Me_4Si = 10·00 p.p.m.) = CPh_2	MR_3
$Ph_2C{:}NH$ [a]	$0{\cdot}0_4$s(1)	$2{\cdot}4$br(4), $2{\cdot}7_3$m(6)	-
$Ph_2C{:}NH{,}GaMe_3$ [a]	$0{\cdot}8_8$s(1)	$2{\cdot}7_8$m(4), $3{\cdot}0_2$m(6)	$10{\cdot}1_3$s(9)
Me_3Ga [a]	-	-	$9{\cdot}8_9$s
$Ph_2C{:}NH{,}GaEt_3$ [a]	$0{\cdot}9_7$s(1)	$2{\cdot}7_0$m(4), $2{\cdot}8_2$m(6)	$8{\cdot}7_1$t(9), $9{\cdot}5_9$q(6)
Et_3Ga [a]	-	-	$8{\cdot}8_6$t(3), $9{\cdot}3_9$q(2)
$Ph_2C{:}NH{,}GaPh_3$ [a]	$0{\cdot}5_8$s(1)	$2{\cdot}3$br, $2{\cdot}7$-$3{\cdot}1$m(25)	
Ph_3Ga [b]	-	-	$2{\cdot}2_7$br(2), $2{\cdot}7_2$m(3)
$Ph_2C{:}NH{,}BMe_3$ [a]	$0{\cdot}0_0$s(1)	$2{\cdot}6_3$m(10)	$9{\cdot}8_0$s(9)
$Ph_2C{:}NH{,}AlMe_3$ [a]	$1{\cdot}2_0$s(1)	$2{\cdot}8_0$m(4), $3{\cdot}0_5$m(6)	$10{\cdot}4_5$s(9)
$(Me_3Al)_2$ [c]	-	-	$10{\cdot}3_6$s
$Ph_2C{:}NH{,}AlEt_3$ [a]	$0{\cdot}4_0$s(1)	$2{\cdot}7$br(4), $2{\cdot}9_5$m(6)	$8{\cdot}8_7$t(9), $10{\cdot}1_2$q(6)
$(Et_3Al)_2$ [c]	-	-	$8{\cdot}8_9$t(3), $9{\cdot}7_0$q(2)
$Ph_2C{:}NH{,}AlPh_3$ [b]	$0{\cdot}4_5$s(1)	$2{\cdot}1$br, $2{\cdot}6$-$3{\cdot}0$m(25)	
$(Ph_3Al)_2$ [b]	-	-	$2{\cdot}7_2$m(3), $2{\cdot}8_7$br(2)

a, C_6D_6 solvent; b, $C_6D_5CD_3$ solvent; c, C_6H_6 solvent.

s = singlet, m = multiplet, t = triplet, q = quartet, br = broad.

Relative intensities in parentheses, all concentrations ~ 30 wt. %.

groups, and the sharper multiplet centred on τ = 2·73 p.p.m. (intensity 6) could be attributed to the meta and para protons, which would differ from the ortho protons as a result of the electron withdrawing properties of the azomethine group.[142]

The figures in Table 4 show that all the peaks in the spectrum of $Ph_2C{:}NH$ including, surprisingly the peaks due to the aromatic protons are shifted to higher fields on co-ordination. The shift is most marked in the case of the N-H peak and is moreover in the direction opposite to that expected on electronic grounds, in that co-ordination through nitrogen should reduce electron density in the N-H bond. Likewise, electron-withdrawing substituents on benzene normally cause the aromatic protons to absorb at lower fields than in benzene itself. Values of τ N-H for adducts $Ph_2C{:}NH,MMe_3$ (M = B, Al, Ga) are consistent with decreasing Lewis acidity in the sequence $Me_3Al > Me_3Ga > Me_3B$ a sequence established by thermodynamic data[19] and supported by infrared spectroscopic studies on nitrile adducts. However by the same criterion Et_3Ga is a stronger Lewis acid than Et_3Al and Ph_3Ga is a stronger Lewis acid than Ph_3Al conclusions inconsistent with those deduced from infrared spectroscopic studies on nitrile adducts.[63,77]

It is therefore concluded that the change in τ N-H on complexing by $Ph_2C{:}NH$ is a poor criterion of adduct stability. A similar poor correlation between changes in τ CH_3 and τ CH_2 values and adduct stabilities has been noted for gallium halide adducts of Et_2O and Et_2S.[143]

Changes in that part of the p.m.r. spectrum arising from the protons of R_3Ga are also caused by interaction with $Ph_2C:NH$. Thus, the peak arising from the gallium-attached methyl groups of $Ph_2C:NH,GaMe_3$ is located at higher field than the corresponding peak for Me_3Ga itself i.e. the change on co-ordination is in the direction expected on electronic grounds. The magnitude of the change, 0·24 p.p.m. is appreciably less than that resulting from co-ordination of Me_3N to Me_3Ga (0·76 p.p.m.),[72] and again reflects the weak donor strength of $Ph_2C:NH$ compared with Me_3N. Similarly, the quartet arising from the gallium-attached methylene groups of $Ph_2C:NH,GaEt_3$ is located at higher field than the corresponding peak for Et_3Ga itself, while the triplet arising from the methyl section of the gallium-attached ethyls which would be little affected by co-ordination, in fact moves to lower field on addition of $Ph_2C:NH$. Changes in the spectrum of Ph_3Ga brought about by co-ordination to $Ph_2C:NH$ cannot be interpreted in any detail because of overlap of the signals from the two types of phenyl group in the adduct. Similar changes were observed for the aluminium complexes $Ph_2C:NHAlEt_3$ and $Ph_2C:NHAlPh_3$.[119]

The infrared spectra of the adducts $Ph_2C:NH,AlR_3$[119] and $Ph_2C:NHGaR_3$ were recorded and the frequencies of the key bands are listed in Tables 5 and 6 respectively.

TABLE 5

Infrared spectroscopic results for adducts $Ph_2C:NH,AlR_3$

Compound	Phase	$\nu_{N-H}cm^{-1}$	$\nu_{C=N}cm^{-1}$
$Ph_2C:NH$	$CHCl_3$ soln.	3256	1603
$Ph_2C:NH,AlMe_3$	Nujol mull	3290	1605
$Ph_2C:NH,AlEt_3$	liquid	3268	1594
$Ph_2C:NH,AlPh_3$	liquid	3257	1603

TABLE 6

Infrared spectroscopic results for adducts $Ph_2C:NH,GaR_3$

Compound	Phase	$\nu_{N-H}cm^{-1}$	$\nu_{C=N}cm^{-1}$
$Ph_2C:NH$	$CHCl_3$ soln.	3256m	1603s
$Ph_2C:NH,GaMe_3$	nujol mull	3279m	1604s
$Ph_2C:NH,GaEt_3$	liquid	3268m	1603s
$Ph_2C:NH,GaPh_3$	liquid	3268m	1595vs

$\delta_{sym\ Ga-Me}$, 1186 cm.$^{-1}$; ρ_{Ga-Me}, 730s cm.$^{-1}$; $\nu_{asym\ GaMe_3}$, 583vw cm.$^{-1}$ $\nu_{sym\ GaMe_3}$, 541vs cm.$^{-1}$

There is surprisingly little change in the frequencies of these bands from one system to another. However νN-H for the adducts is slightly higher than νN-H for diphenylketimine itself while νC=N decreases perceptibly on co-ordination in two cases, viz: $Ph_2C{:}NHAlEt_3$ and $Ph_2C{:}NHGaPh_3$, and increases in two cases, viz: $Ph_2C{:}NHAlMe_3$ and $Ph_2C{:}NHGaMe_3$. Among other characteristic bands readily identified in the spectrum of $Ph_2C{:}NH,GaMe_3$, it may be noted that there are two bands attributable to gallium-carbon stretching vibrations, as expected for the pyramidal co-ordinated $\rightarrow GaMe_3$ but not for planar unco-ordinated Me_3Ga.[144]

The diphenylketimine-trimethylborane adduct underwent the expected reaction with elimination of methane when heated in a tube at 160-200° for 24 hours, but the azomethine derivative $Ph_2C{:}NBMe_2$ was isolated in only very poor yield (~ 15%) from the mixture, a high proportion of the reactants remaining unchanged. Subsequent experiments, involving heating at 180° for two weeks gave yields in excess of 50%. Clearly, the elimination of methane occurs only slowly even under such forcing conditions and in this respect the system is similar to the dimethylamine-trimethylborane system, in which the adduct Me_2NH,BMe_3, itself readily prepared below room temperature, but tending to dissociate at room temperature, eliminates methane to form Me_2NBMe_2 only when heated to 300°. The somewhat readier elimination of methane from the diphenylketimine adduct than from the dimethylamine adduct may well reflect the greater acid character of the nitrogen-attached hydrogen of diphenylketimine.

The thermal decomposition of the related aluminium[119] ($Ph_2C{:}NH,AlR_3$ and gallium[127] ($Ph_2C{:}NH,GaR_3$) adducts also led to the analogous azomethine derivatives $Ph_2C{:}NMR_2$ (M = Al, Ga, R = Me, Et and Ph) but in high (> 90%) yield. The products were all crystalline solids and the reactivity with air decreased in the order $Ph_2C{:}NAlMe_2 > Ph_2C{:}NGaMe_2 > Ph_2C{:}NBMe_2$. The last was stable in air for several days. The temperatures needed for decomposition of the organogallium adducts were higher than those needed for corresponding organoaluminium adducts of diphenylketimine, but lower than that at which $Ph_2C{:}NH,BMe_3$ loses methane. Significantly, cleavage of alkane from $Ph_2C{:}NH,MR_3$ occurs less readily and dissociation of the adduct into its components more readily as M becomes less electropositive (the Allred-Rochow electronegativities of B, Al and Ga are 2·01, 1·47 and 1·82 respectively) and so the group R becomes less negative. Increasingly forcing conditions are also needed for the comparable thermal decomposition of the dimethylamine adducts Me_2NH,MMe_3 (M = Al, Ga and B).

A further point of similarity between $Ph_2C{:}NMR_2$ and Me_2NMR_2 is their states of association. The aminoborane is monomeric in the gas phase at room temperature, although apparently associated in the liquid phase.[145] Molecular weight data on solutions of the azomethine derivative $Ph_2C:NBMe_2$ in benzene in which its solubility is low proved to be unreliable but the mass spectrum of the compound was recorded. Mass and intensity values for the main peaks are listed in Table 7, together with suggested assignments. Significantly there are no peaks at

TABLE 7

Mass spectroscopic results for $Ph_2C:N.BMe_2$

$^m/_e$	Relative intensity	Assignment
221,220	17,4	Ph_2CNBMe_2
206,205	100,25	Ph_2CNBMe
191,190	2,0·5	Ph_2CNB
180	51	Ph_2CN
166	2	Ph_2C
165,164	7,2	Ph_2B
144,143	5,1	$PhCNBMe_2$
103	97	$PhCN, Ph^{11}BMe$
102	19	$Ph^{10}BMe$
77	42	Ph
41,40	35,9	Me_2B
15	4	Me

higher m/e values than 221, the molecular weight of monomeric $Ph_2C:NBMe_2$ and no sets of peaks were observed with the characteristic relative intensities associated with the presence of two boron atoms in a fragment. Peaks attributable to fragments containing boron occurred in pairs, differing by one mass unit and with the higher mass peak some four times as intense as the lower as expected from the natural abundances of ^{11}B (80%) and ^{10}B (20%). The mass spectra of several known dimeric azomethine derivatives of boron have been shown to contain several intense peaks corresponding to fragments with the $(BN)_2$ ring intact. It is therefore concluded that the mass spectrum of $Ph_2C:NBMe_2$ provides evidence either that this compound exists in the gas phase solely in the form of monomeric molecules or that, if associated species are present, these dissociate unexpectedly readily. The remaining major peaks in the mass spectrum, listed in Table 7, show that the main features of the breakdown pattern involve the loss of the terminal methyl groups from boron or (less readily) phenyl groups from carbon or fission of the molecular skeleton at the B-N bond. Fission at the C=N bond is of relatively minor importance. A particularly interesting feature of the spectrum of $Ph_2C:NBMe_2$ is that one of the most intense peaks can be assigned to the ion $Ph^{11}BMe^+$ the presence of which must result from the transfer of a phenyl group from carbon to boron. Similar rearrangements or recombinations must also account for the presence of Ph_2B^+. These observations suggest that, although the formula of the monomer $Ph_2C:N \rightleftharpoons BMe_2$ can be written with a multiple $N \rightleftharpoons B$ link to give a molecule isoelectronic with an allene $Ph_2C:C:CMe_2$ the present evidence does not indicate a high bond order for the B-N link. The compound, even if monomeric in the gas phase, is probably dimeric in the condensed phase as deduced by its non reactivity with atmospheric moisture.

The azomethine derivatives of aluminium $(Ph_2C:NAlR_2)_2$ and gallium $(Ph_2C:NGaR_2)_2$ have been found to be dimeric in benzene solution and in the gas phase (mass spectroscopy R = Me, Ph). In the mass spectrum peaks assignable to the parent dimeric ion have been found. However peaks corresponding to monomeric $Ph_2C:NMR_2^+$ have been found as intense as those assignable to the dimeric ion $(Ph_2C:NMR_2)_2^+$. A typical mass spectroscopic result which reveals the presence of dimeric species in the gas phase of $(Ph_2C:NGaMe_2)_2$ is given in Table 8. As in the spectrum of $Ph_2C:NBMe_2$ transfer of a phenyl group from carbon to metal atom occurs and peaks assignable to $Ph^{69}GaMe^+$, Ph_2Ga^+ and $PhGa^+$ are observed.

Despite the insensitivity of νC:N to the state of co-ordination of $Ph_2C:NH$ noted above, νC:N in the infrared spectra of the derivatives $(Ph_2C:NMR_2)_2$ varies according to R for a constant M in the same manner as was found for the corresponding zinc compounds as shown in Table 9. Thus the more electron withdrawing the group R the lower the νC:N. This is especially noticeable with $[Ph_2C:NGaCl_2]_2$ where νC:N is 1591 $cm.^{-1}$ In most cases moreover, νC:N for the azomethine derivative is higher than

TABLE 8

Mass spectroscopic results for $(Ph_2C{:}N{\cdot}GaMe_2)_2$

$^m/_e$	Relative intensity	Assignment
562, 560, 558	1, 2, 1	$Ph_4(CN)_2Ga_2Me_4$
547, 545, 543	25, 62, 37	$Ph_4(CN)_2Ga_2Me_3$
532, 530, 528	1, 2, 1	$Ph_4(CN)_2Ga_2Me_2$
382, 380, 378	8, 21, 13	$Ph_2CNGa_2Me_4$
367, 365, 363	8, 19, 11	$Ph_2CNGa_2Me_3$
352, 350, 348	1, 3, 2	$Ph_2CNGa_2Me_2$
337, 335, 333	2, 5, 3	Ph_2CNGa_2Me
281, 279	3, 4	$Ph_2CNGaMe_2$
266, 264	17, 25	$Ph_2CNGaMe$
225, 223	4,5	Ph_2Ga
181	19	Ph_2CNH
180	37	Ph_2CN
174, 172	5, 8	PhCNGa
163, 161	67, 100	PhGaMe
148, 146	4, 5	PhGa
103	8	PhCN
101, 99	35, 52	$GaMe_2$
86, 84	2, 3	GaMe
78	11	PhH
77	22	Ph
71, 69	56, 84	Ga

TABLE 9

Infrared spectroscopic results for azomethine derivatives $(Ph_2C:N\cdot MR_2)_n$

Compound	$\nu_{C:N}$ cm.$^{-1}$	Compound	$\nu_{C:N}$ cm.$^{-1}$
$Ph_2C:NBMe_2$	1662	$(Ph_2C=NAlBr_2)_2$	1587
$(Ph_2C:N\cdot AlMe_2)_2$	1616	$(Ph_2C:N\cdot GaMe_2)_2$	1626
$(Ph_2C:N\cdot AlEt_2)_2$	1609	$(Ph_2C:N\cdot GaEt_2)_2$	1613
$(Ph_2C:N\cdot AlPh_2)_2$	1604	$(Ph_2C:N\cdot GaPh_2)_2$	1612
$(Ph_2C=NAlCl_2)_2$	1593	$(Ph_2C\cdot N\cdot GaCl_2)_2$	1591

All figures relate to Nujol mulls.

νC:N for diphenylketimine itself. Co-ordination through the azomethine group such as occurs in the association of the azomethine derivatives would be expected to reduce the electron desntiy in the azomethine link, causing a corresponding reduction in νC:N, but the mechanical constraint imposed on the vibration of the azomethine group by incorporation of the nitrogen in the $(MN)_2$ ring is likely to be more than sufficient to offset this electronic effect when comparison is made between $Ph_2C:NH$ and $(Ph_2C:NMR_2)_2$. Furthermore it has been shown[146] that methiodides of aromatic imines i.e. $[Ar_2C:NMeAr]^+ I^-$ have a higher νC:N than the parent imine. It was thought that the presence of a positive charge on the nitrogen atom would counter the electron withdrawing effects of groups attached to the carbon and nitrogen atoms, thus preventing a lowering of the νC:N. This effect could also operate in the metal azomethine derivatives above and consequently the νC:N would be expected to rise. From tables 1 and 9 it can be seen that the νC:N is dependent not only on R but also to a greater extent on M, i.e. the more electronegative the metal the higher the νC:N.

The p.m.r. spectra of the azomethine derivatives $Ph_2C:NMR_2$ recorded as dilute solutions in perdeuterobenzene, were found to be very similar. For example $Ph_2C:NBMe_2$ consisted of two multiplets in the region $\tau = 2{\cdot}7 - 2{\cdot}9$ p.p.m. (τ Me_4Si = 10 p.p.m.) clearly originating from the aromatic protons, and a singlet at $\tau = 9{\cdot}70$ p.p.m. originating from the methyl protons. The absorptions due to aromatic protons, a multiplet at $\tau = 2{\cdot}77$ p.p.m. (relative intensity 2) and a multiplet at $\tau = 2{\cdot}84$ p.p.m. (relative intensity 3) probably arose from the ortho and meta-para protons respectively, which would become differentiated on substitution of an electron withdrawing group in the benzene nucleus.

Of the other organoboranes treated with diphenylketimine, triphenylborane did not react with diphenylketimine at temperatures up to 200° over periods of up to one week. In all cases both reactants were recovered essentially unchanged, although traces of benzene were detected in experiments carried out under the more extreme conditions.

Triethylborane reacted with diphenylketimine on heating to 160° for a week, but in a manner different from trimethylborane. Ethylene, not ethane, was the volatile reaction product, being formed in roughly twice the molar quantities that triethylborane was consumed, as if the consumption of triethylborane involved essentially the reaction $Et_3B \rightarrow [EtBH_2] + 2C_2H_4$. The only involatile reaction product identified was the N-substituted ketimine $Ph_2C:NCHPh_2$ which was formed in some 30% yield from the diphenylketimine taken.

The identification of this unexpected reaction product was effected as follows. Full elemental analysis revealed the appropriate proportions of carbon, hydrogen and nitrogen, and the absence of boron. The proton magnetic resonance spectrum (C_6D_6 solution) contained absorptions which could be assigned to aromatic protons (τ = 2·66 p.p.m., intensity 20) and to an aliphatic proton (τ = 4·39 p.p.m., intensity 1). No absorptions were observed which could be assigned to an ethyl group, nor to a nitrogen-attached proton. The infrared spectrum contained no absorption attributable to ν_{N-H}, but a peak at 1628 $cm.^{-1}$ could readily be assigned to $\nu_{C=N}$. A further infrared spectrum recorded as a KBr disc contained three absorptions attributable to νC-H, two assignable to aromatic protons at 3049 and 3012 $cm.^{-1}$ and a singlet assignable to an aliphatic proton at 2857 $cm.^{-1}$

The strongest peak in the mass spectrum of the material occurred at $^m/_e$ = 347 mass units/unit charge, and the accurate mass of this fragment was found to be within 1 p.p.m. of that calculated for $C_{26}H_{21}N$. Mass and intensity data for the main peaks in the mass spectrum are listed in Table 10, together with suggested assignments. It will be seen that all the major peaks may be assigned to fragments arising from a molecule $Ph_2C{:}NCHPh_2$. The only peak at a mass higher than 347 was a feeble peak (relative intensity 1) at $^m/_e$ = 375, which could be attributed to trace quantities of a contaminant, probably $Ph_2C{:}NCEtPh_2$.

The manner in which $Ph_2C{:}NCHPh_2$ comes to be formed in this reaction deserves comment. It is well known[118] that amines $R'NH_2$ displace ammonia from imines $R_2C{:}NH$ to form N-substituted imines $R_2C{:}NR'$, and it seems likely that in the present reaction some diphenylketimine is reduced to the amine stage Ph_2CHN by interaction with Et-B groups, which in the process lose ethylene. A subsequent condensation reaction between the amine and an unreduced diphenylketimine molecule would afford $Ph_2C{:}NCHPh_2$, the nitrogen eliminated probably ending up bound to boron in the final reaction mixture in oligomeric or polymeric materials such as $(EtBNH)_n$ which would have been undetected because of the method used to work up the reaction mixture.

This formation of $Ph_2C{:}NCHPh_2$ from diphenylketimine and triethylborane is clearly analogous to the formation of $Bu^tCH{:}NCH_2Bu^t$ (in 30% yield) from Bu^tCN and Bu^tMgCl at 150°,[147] and to the formation of $PhCH{:}NCH_2Ph$ in the reduction of PhCN by R_2AlH at 45°.[148] Other examples involving boron-nitrogen systems are also known, e.g. the formation of $Et_2NB_2H_5$ in the reaction between diborane and methyl cyanide,[127] while the formation of a compound $C_8H_{17}N$ (either $Me_2CHCH{:}NBu^i$ or $Me_2C{:}CHNHBu^i$) in the pyrolysis of $(Bu^iNH)_2BPh$ may well occur by a similar mechanism.[46]

TABLE 10

Mass spectroscopic results for $Ph_2C{:}NCHPh_2$

$^m/_e$	Relative intensity	Assignment
347	100	$Ph_2CNCHPh_2$
270	10	$Ph_2CNCHPh$ or $PhCNCHPh_2$
193	2	$Ph_{2,1\text{ or }0}CNCHPh_{0,1\text{ or }2}$
192	2	193 minus H
180	17	Ph_2CN
167	53	Ph_2CH
166	43	Ph_2C
116	2	CNCHPh
115	10	CNCPh
103	6	PhCN
89	7	PhC
77	59	Ph

The reactions between diphenylketimine and BX_3 (where X = H, NMe_2, OMe, F or Cl).

The purpose of a study of the systems $Ph_2C:NH/BX_3$ (where X = H, NMe_2, OMe, F or Cl) was to investigate the possibility of isolating adducts $Ph_2C:NH,BX_3$ and to determine whether the elimination of HX from such systems would allow the preparation of derivatives $(Ph_2C:N)_nBX_{3-n}$, particularly $(Ph_2C:N)_3B$, trisdiphenylketiminoborane.

Diborane and diphenylketimine were found to interact in hexane to precipitate an adduct $Ph_2C:NH,BH_3$ which even at 20° eliminated hydrogen slowly. Its identity was revealed both by analytical data and also by its infrared spectrum, which significantly had a medium intensity band at 3257 $cm.^{-1}$ (attributable to νN-H), a set of medium intensity absorptions in the B-H stretching region (at 2410, 2288 and 2252 $cm.^{-1}$) and a strong absorption at 1620 $cm.^{-1}$ (νC=N). Previous νC=N of complexes $Ph_2C:NH,MR_3$ have been in the region of νC=N for Ph_2C=NH itself. Co-ordination to boron trifluoride (see below) also raises νC=N of diphenylketimine (from 1603 to 1628 $cm.^{-1}$) and diphenylketimine hydrochloride $Ph_2C:NH_2^+Cl^-$, which may be regarded as the adduct of diphenylketimine with a proton has νC=N at 1653 $cm.^{-1}$ Goulden's argument that νC=N should rise upon co-ordination implies that the stronger the acceptor the higher the νC:N. Thus from the change in νC=N, the following order of acceptor strength is obtained:

$$H^+ > BF_3 > BH_3 > BMe_3$$

However all the adducts $Ph_2C{:}NH,MR_3$ (M = Al, Ga, R = Me, Et, and Ph) have approximately the same νC=N and therefore change in νC=N is considered to be a poor criterion of adduct stability.

The thermal decomposition of diphenylketimine-borane at 120° did not afford a diphenylketiminoborane. Although hydrogen was eliminated as expected, simultaneous migration of a hydrogen atom from boron to the azomethine carbon reduced the C=N double bond to a single bond and the product isolated was the borazine $(Ph_2CNNBH)_3$.

$$Ph_2C{:}NH,BH_3 \longrightarrow \frac{1}{3}\,(Ph_2CHNBH)_3 + H_2$$

The identity of the product was established as follows. Elemental analyses confirmed the empirical formula, and the infrared spectrum which contained no absorptions in the N-H or C=N stretching regions had three bands in the B-H stretching region (at 2525m, 2433m and 2404m $cm.^{-1}$) and a very strong absorption at 1355 $cm.^{-1}$ in the region typical of borazines.[149]

The proton magnetic resonance spectrum of the borazine as a dilute solution in hexadeuterobenzene was recorded with cyclohexane as internal reference, and found to consist of two multiplets in the region $\tau = 2{\cdot}8 - 3{\cdot}0$ p.p.m. ($\tau\ Me_4Si = 10{\cdot}0_0$ p.p.m.) clearly originating from the aromatic protons, and a singlet at $\tau = 3{\cdot}96$ originating from the aliphatic proton. The absorptions due to the aromatic protons, a multiplet at $\tau = 2{\cdot}89$ p.p.m. (relative intensity 3) and a multiplet at $\tau = 3{\cdot}0_0$ p.p.m. (relative intensity 2) are the reverse of what has previously been obtained for the azomethine derivatives $Ph_2C:NMR_n$ (M = B, Al, Ga, Zn, R = Me, Et and Ph) and also at higher field than these derivatives. However if these absorptions arose from the meta-para and ortho protons respectively, differentiated by substitution of an electron donating group in the benzene nucleus, it is difficult to explain the low τ value of the aliphatic proton.

As borazines $(RNBX)_n$ are frequently tetrameric[150] in cases where the substituents R and X are too bulky to be accommodated about the planar six-membered ring of a trimeric borazine, the molecular complexity of the present compound was investigated by mass spectroscopy.

The mass spectrum of $(Ph_2CHNBH)_3$ confirmed its identity. Masses, relative intensities and assignments of the main peaks having $m/e > 225$ are listed in Table 11. Peaks generally occurred in sets, the masses quoted relate to fragments in which all the borons are ^{11}B, however in all cases attendant ^{10}B satellites were observed at 1, 2 and 3 mass units below these and fragments having 1 or 2 fewer hydrogen atoms than the fragments quoted caused the set of peaks to extend in most cases over 6 mass units. No peak corresponding to a tetramer $(Ph_2CHNBH)_4$ was observed, and the measured mass of the parent molecular ion, 579·3201, was within 2·3 p.p.m. of that calculated for $(Ph_2CHN^{11}BH)_3$. The only peaks at higher mass than this could be attributed to a trace of impurity in which one boron of the borazine had a Ph_2CN substituent. The main feature of the breakdown pattern,

TABLE 11

Mass spectrum of $(Ph_2CHNBH)_3$

$^m/_e$	Relative Intensity	Assignment
758	0·2	$(Ph_2CH)_3N_3B_3H_2NCPh_2$
579	50	$(Ph_2CH)_3N_3B_3H_3$
502	100	$(Ph_2CH)_3N_3B_3H_3$ minus Ph
425	10	$(Ph_2CH)_3N_3B_3H_3$ minus 2Ph
412	1	$(Ph_2CH)_2N_3B_3H_3$
348	4	$(Ph_2CH)_3N_3B_3H_3$ minus 3Ph
335	3	$(Ph_2CH)_2N_3B_3H_3$ minus Ph
258	2	$(Ph_2CH)_2N_3B_3H_3$ minus 2Ph

apart from loss of individual hydrogen atoms (probably from boron), involved the successive loss of phenyl or diphenylmethyl groups leaving the ring intact. The peaks at $^m/_e$ = 166, 167 and 168 corresponding to Ph_2C^+, Ph_2CH^+ and $Ph_2CH_2^+$ were very intense (diphenyl methane was found to be a major product of the thermal decomposition of $(Ph_2CHNBH)_3$, and a further interesting feature of the spectrum at $^m/_e < 255$ was the appearance of sets of peaks at half integer intervals ranging from masses 251, 212·5 and 174 and of relative intensities 1, 8 and 2 respectively, which clearly corresponded to the doubly charged ions resulting from loss of 1,2 or 3 phenyl groups from the parent. Naturally a peak at m/e = 180 corresponding to $Ph_2C{:}N$ which was always a major fragment in the mass spectra of azomethine derivatives $(Ph_2C{:}NMR_2)_{1 \text{ or } 2}$ was absent.

Trisdimethylaminoborane and diphenylketimine reacted at 150° and 1 atmos. nitrogen pressure under a reflux condenser with evolution of dimethylamine:-

$$(Me_2N)_3B + nPh_2C{:}NH \longrightarrow (Ph_2C{:}N)_nB(NMe_2)_{3-n} + nMe_2NH$$

This reaction is analogous to the transamination reaction of aminoboranes in which a relatively involatile secondary amine displaces a more volatile amine (such as dimethylamine) from an aminoborane, e.g.

$$(Me_2N)_3B + 3R_2NH \longrightarrow (R_2N)_3B + 3Me_2NH$$

Even when an excess of diphenylketimine was used however, the infrared spectrum of the viscous liquid produced contained bands at 2933 and 2865 $cm.^{-1}$ indicative of aliphatic C-H, showing that not all the dimethylamino groups had been replaced by diphenylketimino groups. This was confirmed by the detection (by infrared spectroscopy) of small quantities of dimethylamine in the ammonia evolved when samples of the material were heated with concentrated aqueous sodium hydroxide. Moreover, the analytical results were consistent with contamination of the trisdiphenylketiminoborane $(Ph_2C{:}N)_3B$ by some aminobisketiminoborane $(Ph_2C{:}N)_2BNMe_2$. The proportion of this impurity could not be determined precisely from the analytical data (carbon analyses may give low results on boron-containing samples), but the reaction between trisdimethylaminoborane and an excess of diphenylketimine is clearly a poor preparative route to trisdiphenylketiminoborane. A further experimental difficulty was presented by the need to remove unchanged diphenylketimine which was soluble in the same solvents as the boron derivative. Vacuum distillation was also complicated as the diphenylketimine could be distilled out of the mixture only slowly at temperatures low enough to prevent decomposition of the ketimino-borane.

Trimethoxyborane and diphenylketimine were recovered essentially unchanged after being held at 70^{o} and 1 atmos. dry nitrogen pressure under a reflux condenser for four hours. The lack of reaction in this system was not unexpected in view of the tendency for boron-nitrogen links in aminoboranes to be cleaved by reaction with water or alcohols.

Boron trifluoride and diphenylketimine gave an adduct $Ph_2C{:}NH,BF_3$ in which the co-ordinate link was strong enough to allow vacuum sublimation at $100\text{-}120^{o}$. Although this compound decomposed above about 180^{o}, no evidence was obtained that the decomposition, by elimination of hydrogen fluoride, led to diphenylketiminoboranes $Ph_2C{:}NBX_2$. The related amine adduct Me_2NH,BF_3 unlike Me_2NH,BCl_3, does not thermally decompose until 250^{o}.[151]

$$2Me_2NH,BF_3 \xrightarrow{240\text{-}295^{o}} \tfrac{1}{2}(Me_2NBF_2)_2 + Me_2NH_2BF_4$$

Boron trichloride and diphenylketimine however eliminated hydrogen halide so readily that even at -78° diphenylketimine hydrochloride was deposited from a hexane solution of the mixture and no adduct $Ph_2C:NH,BCl_3$ could be isolated. Treatment of boron trichloride (1 mol.) with diphenylketimine (6 mol.) was therefore investigated as a preparative route to trisdiphenylketiminoborane although it was borne in mind that excess diphenylamine reacted with boron trichloride to give Ph_2NBCl_2 and even using forcing conditions, i.e. triethylamine and higher temperatures only one more halide group was exchanged[152] i.e.

$$Ph_2NBCl_2 \ + \ xs\ Ph_2NH \xrightarrow{Et_3N} (Ph_2N)_2BCl$$

After the reaction between 6 mol. of diphenylketimine and 1 mol. of boron trichloride was completed, the diphenylketimine hydrochloride was separated by filtration, and solvent was removed under vacuum leaving a residual syrup which had an infrared spectrum similar to that of the impure trisdiphenylketiminoborane obtained from diphenylketimine and trisdimethylaminoborane, but having no bands characteristic of aliphatic C-H vibrations. The material was contaminated by traces of chloride, however, and some diphenylketimine distilled out of a sample which was held at 100° under vacuum. It appears that, although an excess of diphenylketimine reacts with either trisdimethylaminoborane or boron trichloride to give trisdiphenylketiminoborane, the physical properties of the product (an involatile viscous, apparently thermally unstable, liquid) are such as to cause practical difficulties of separation from unchanged diphenylketimine and other reaction products.

The reactions of diphenylketiminolithium with BX_3 (where X = F, Cl, Br, I) compounds

As described above, the attempted preparation of trisdiphenylketiminoborane from diphenylketimine and BX_3 (X = NMe_2 and Cl) yielded impure trisdiphenylketiminoborane which was impossible to purify. A much purer sample was obtained from the reaction:

$$3Ph_2C{:}NLi + BBr_3 \longrightarrow (Ph_2C{:}N)_3B + 3LiBr$$

The reaction was carried out in ether below 0° using a slight excess of diphenylketiminolithium, in order that

(a) the reaction went to completion.

(b) no side reactions occurred.

Consequently only three compounds $(Ph_2C{:}N)_3B$, LiBr and $Ph_2C{:}NLi$ remained in the mixture and of these only trisdiphenylketiminoborane was soluble in toluene. Thus after the ether had been removed, the mixture heated with toluene, filtered and cooled the trisdiphenylketiminoborane crystallised out at -78°. The product at room temperature was a viscous liquid from which it was difficult to remove the last traces of toluene. The product was presumed to be monomeric as molecular weight studies in benzene were unreliable due to unremoved toluene. An attempted mass spectroscopic study of the compound gave an intense peak at 180 ($Ph_2C{:}N^+$) and a breakdown pattern of this unit.

The infrared of $(Ph_2C{:}N)_3B$ gave a characteristic absorption in the

C=N stretching region at 1667 cm.$^{-1}$ This high frequency is due to the terminal $Ph_2C:N$ unit although some drift of electrons into the B-N bond would be expected and consequently the frequency is lower than the terminal C=N of $[(Ph_2C:N)_3Al]_2$ which shows two types of C=N stretching vibrations, one terminal and one bridging.

The proton magnetic resonance spectrum of the trisdiphenylketiminoborane as a dilute solution in hexadeuterobenzene was recorded with tetramethylsilane (τ $Me_4Si = 10{\cdot}0_0$ p.p.m.) as internal reference, and found to consist of two multiplets at $\tau = 2{\cdot}47$ p.p.m. (relative intensity 2) and $\tau = 2{\cdot}83$ p.p.m. (relative intensity 3), attributable to the ortho and meta/para sets of protons which would again be expected to be magnetically different in these derivatives.

The reaction used to prepare trisdiphenylketiminoborane was used to prepare the monosubstituted derivatives

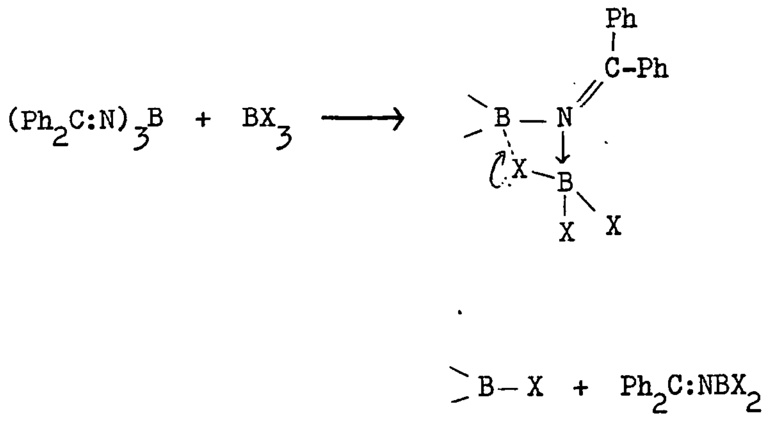
$Ph_2C:NBX_2$ (where X = F, Cl, Br and I)

$$Ph_2C:NLi + BX_3 \longrightarrow Ph_2C:NBX_2 + LiX$$

In all cases the reaction proceeded smoothly in ether at temperatures less than 0°. When the reaction had reached completion the solution was colourless and a copious yellow precipitate of $Ph_2C:NBX_2$ mixed with lithium halide was obtained. After removal of the ether solvent, toluene was added, refluxed, filtered and allowed to cool. The dibromo derivative crystallised as plates, the dichloro as needles, the diiodo was too soluble to crystallise from toluene and the difluoride was insoluble. Pure diphenylketiminoboron difluoride $Ph_2C:NBF_2$ proved to be inaccessible by this method especially since the compound did not sublime at temperatures as high as 240°. Consequently another route was tried. The exchange reaction between boron trifluoride and trisdiphenylketiminoborane proved successful:

$$(Ph_2C:N)_3B \; + \; 2BF_3 \longrightarrow 2Ph_2C:NBF_2$$

The reaction proceeded in ether at ca. 60° and the difluoride $Ph_2C:NBF_2$ precipitated. A mechanism for this type of reaction has been proposed.[153] It is suggested that initially an addition product is formed which then rearranges by an intermolecular process to give $(Ph_2C:N)_2BX$ and $Ph_2C:NBX_2$. Then $(Ph_2C:N)_2BX$ can similarly react with another molecule of BX_3 to give two molecules of $Ph_2C:NBX_2$



The molecular complexity of the derivatives $Ph_2C:NBX_2$ has been investigated by mass spectroscopic studies, Tables 12, 13 and 14 and where possible cryoscopic molecular weights have been obtained in benzene.

The dichloride, dibromide and di-iodide are apparently dimeric in the gas phase or benzene solution. The mass spectra of the dichloride and the dibromide show peaks corresponding to fragments with the $(BN)_2$ ring intact. Neither spectrum contained a peak corresponding to the parent ion, the highest being due to loss of halide ion or phenyl group. In both cases the peak corresponding to the monomer was intense as were the peaks corresponding to monomer less halide and phenyl group. Another interesting feature of both spectra was that intense peaks could be assigned to the ions $PhBBr^+$, $PhBCl^+$ and Ph_2B^+, which must result from the transfer of a phenyl group from carbon to boron. The dibromide and di-iodide were dimeric in benzene but the dichloride was too insoluble for reliable measurements to be obtained.

The mass spectrum of diphenylketiminoboron difluoride was quite different to those of the dichloride and dibromide. No peaks assignable to a dimeric molecule or dimer less fluorine or phenyl groups were obtained. Peaks corresponding to the monomer and breakdown units thereof were obtained as well as masses containing the unit $(Ph_2C{:}N)_2B$. Since $(Ph_2C{:}N)BF_2$ is involatile it is unlikely to be monomeric and its behaviour on heating i.e. shrinking over the temperature range 255-286° would appear to be consistent with a polymer breaking up into smaller units.

Peaks resulting from a transfer of a phenyl group from carbon to boron were again obtained although of a greater variety and intensity

Table 12

Mass spectroscopic results for $Ph_2C:NBCl_2$

m/e	Relative intensity	Assignment
487	42	$(Ph_2C:N)_2B_2Cl_3$
452	6	$(Ph_2C:N)_2B_2Cl_2$
406	11	$(Ph_2C:N)_2BCl$
371	8	$(Ph_2C:N)_2B$
342	12	$Ph_2C:NB_2Cl_4$
307	8	$Ph_2C:NB_2Cl_3$
261	42	$Ph_2C:NBCl_2$
226	46	$Ph_2C:NBCl$
184	44	$PhCNBCl_2$
180	100	$Ph_2C:N$
165	21	Ph_2B
123	51	PhBCl
77	64	Ph

All masses quoted relate to fragments in which all the borons are ^{11}B and chlorines are ^{35}Cl.

Table 13

Mass spectroscopic results for $Ph_2C:NBBr_2$

$^m/_e$	Relative intensity	Assignment
621	0·2	$(Ph_2C:N)_2B_2Br_4$ minus Ph
619	0·1	$(Ph_2C:N)_2B_2Br_3$
450	5	$(Ph_2C:N)_2BBr$
371	32	$(Ph_2C:N)_2B$
349	18	$Ph_2C:NBBr_2$
272	100	$PhCNBBr_2$
270	92	$Ph_2C:NBBr$
180	19	Ph_2CN
169	38	BBr_2
167	41	PhBBr
114	16	PhCNB
88	8	PhB
77	43	Ph

All masses quoted relate to fragments in which the borons are ^{11}B and the bromines are ^{79}Br.

Table 14

Mass spectroscopic results for $Ph_2C:NBF_2$

$^m/_e$	Relative intensity	Assignment
551	18	$(Ph_2C:N)_3B$
448	17	$(Ph_2C:N)_2BPh$
390	21	$(Ph_2C:N)_2BF$
371	100	$(Ph_2C:N)_2B$
313	13	$(Ph_2C:N)_2BF$ minus Ph
287	5	$PhB(F)NCPh_2$
268	13	$PhBNCPh_2$
229	43	$Ph_2C:NBF_2$
210	31	$Ph_2C:NBF$
180	80	$Ph_2C:N$
165	58	Ph_2B
152	65	$PhCNBF_2$
126	12	$PhBF_2$
107	31	PhBF
77	50	Ph
68	3	BF_3
49	21	BF_2

Masses quoted relate to fragments in which all the borons are ^{11}B.

than previously observed, of particular interest is a peak assignable to $(Ph_2C{:}N)_3B$ which was not observed in the mass spectrum of $(Ph_2C{:}N)_3B$.

The C=N stretching vibrations are given in Table 15 and it can be seen that there is a general trend in that νC=N decreases in the sequence Me > F > Cl > Br. This type of trend has previously been discussed in terms of changing mass and electronegativity of the group attached to the metal atom.

Table 15

Infrared spectroscopic data for diphenylketimino derivatives of boron.

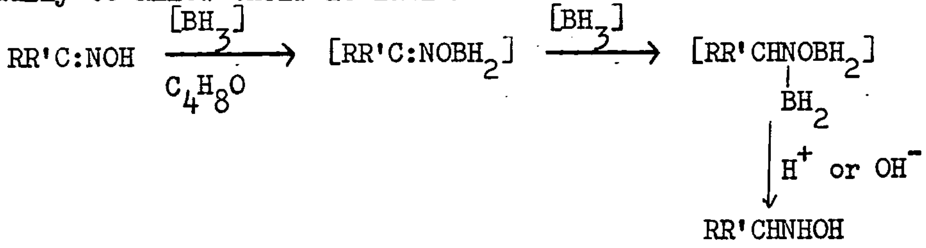
Compound	νC=N cm.$^{-1}$	Compound	νC:N cm.$^{-1}$
$Ph_2C{:}NBMe_2$	1662	$Ph_2C{:}NBCl_2$	1590
$Ph_2C{:}NBF_2$	1620	$Ph_2C{:}NBBr_2$	1586

All figures relate to Nujol mulls.

Reactions between oximes and organo derivatives of Group III elements.

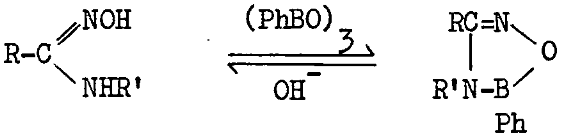
Oximes RR'C:NOH have long been known to cleave alkyl groups from reactive organometallic compounds RMX_n, presumably forming oximates $RR'C{:}NOMX_n$. For example, Grignard reagents[154] generally give materials RR'C:NOMgX which may subsequently rearrange or undergo further reaction to give ultimately on hydrolysis such widely differing products as ethylene imines[155] RCHCHR'NH or acid amides RCONHR.[154] The oxyazomethine derivatives RR'C:NOMgX initially formed in these reactions have however received little attention. More is known about oxime derivatives of zinc. Zinc dialkyls with acetoxime in ether give successively $(Me_2C{:}NOZnR)_n$ and $[(Me_2C{:}NO)_2Zn]_m$.[93,156] The derivative $(Me_2C{:}NOZnMe)_4$ is tetrameric in benzene solution and is thought to have a cage structure composed of two cross-linked $(ZnON)_2$ six-membered rings.[93]

In group III, boron halides like many other Lewis acids catalyse the Beckmann rearrangement of oximes to amides.[157] Diborane reduces oximes to hydroxylamine derivatives in a reaction which may well involve intermediates $(RR'C{:}NOBH_2)_n$ which however apparently undergo hydroboration too readily to allow their isolation:-[158]



$$RR'C{:}NOH \xrightarrow[C_4H_8O]{[BH_3]} [RR'C{:}NOBH_2] \xrightarrow{[BH_3]} [RR'CH\underset{\underset{BH_2}{|}}{N}OBH_2] \xrightarrow{H^+ \text{ or } OH^-} RR'CHNHOH$$

Compounds retaining an oxyazomethine grouping attached to boron have been isolated from reactions between amidoximes and boronic acids or anhydrides, which afford 1,3,5,2-oxadiazaboroles:-[159]



Recently acetoxime derivatives $(Me_2C{:}NOMMe_2)_n$ of boron, aluminium, gallium and thallium and the related lithium derivative $(Me_2C{:}NOLi)_n$ have been prepared by the cleavage of methane from the methyl derivative of the appropriate element using acetoxime:-[127]

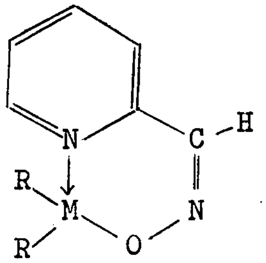
$$Me_2C{:}NOH + Me_3M \longrightarrow CH_4 + {}^1/_n\,(Me_2C{:}NOMMe_2)_n$$

The related siliconated ketoxime derivatives have been prepared by the following reactions:-[160]

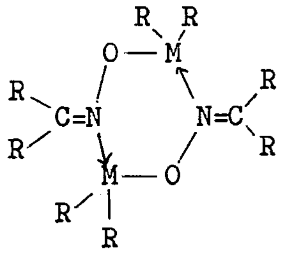
$$RR'C{:}NOH \xrightarrow{H_2NSiR''_3} RR'C{:}NOSiR''_3 + NH_3$$

$$RR'C{:}NOH + HSiR''_3 \xrightarrow{ZnCl_2} RR'C{:}NOSiR''_3 + H_2$$

The purpose of a study of the products of the reactions between pyridine-2-aldoxime and Group III alkyls, was to examine the possibility of obtaining monomeric derivatives XII rather than the previously obtained six membered MONMON ring XIII.

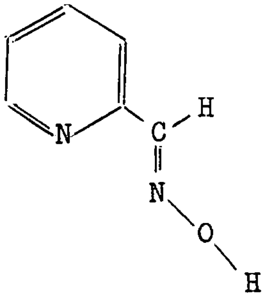


XII



XIII

Pyridine-2-aldoxime XIV is obtainable only in the syn form.



XIV

Since both isomers of pyridine-2-aldoxime methiode[161] are known and one form can be converted to the other upon warming under conditions slightly less vigorous than those required for a Beckmann rearrangement i.e. reaction with a weak acid, rearrangement of the syn to the anti form could easily occur and thence formation of XII.

Pyridine-2-aldoxime reacted with Me_3M (M = Al, Ga, In) at -78° in toluene giving a deep yellow solution possibly due to the formation of a complex $C_5H_4NCH:NOH,MMe_3$ which on warming eliminated methane. With trimethylthallium a white solid precipitated which eliminated methane at ca. 15°. By contrast trimethylborane showed no sign of reaction with pyridine-2-aldoxime at room temperature and reaction occurred to give the desired product $C_5H_4NCH{:}NOBMe_2$ only after a toluene solution of pyridine-2-aldoxime with trimethylborane was heated to 95° in a sealed tube. The conditions for this reaction were rather important, as heating to temperatures greater than 95° produced a red viscous material from which it was impossible to isolate $C_5H_4NCH{:}NOBMe_2$.

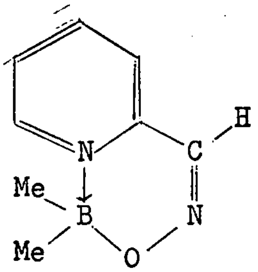
The Group III derivatives described above were all moisture sensitive crystalline materials which afforded pyridine-2-aldoxime on mild hydrolysis. It is clear therefore that their preparation does not involve simultaneous Beckmann rearrangement of the oxime, and that they should be formulated $(C_5H_4CH{:}NOMR_2)_n$ not $[HC(OMR_2){:}NC_5H_4N]_n$.

The boron compound $C_5H_4NCH{:}NOBMe_2$ was found to be monomeric in benzene solution. Derivatives having $(MON)_2$ six-membered rings are already well known in the case of boron. First isolated from among the products of reactions between nitric oxide and trialkylboranes,[162] they are readily prepared from hydroxylamines and borinic acids:-[163]

$$R_2NOH + R'_2BOH \longrightarrow (R_2NOBR'_2)_n + H_2O$$

It is interesting that these derivatives are normally dimeric (n = 2) unless the bulk of the groups R and R' prevents association. Cryoscopic studies on benzene solutions of $(Me_2C{:}NOBMe_2)_n$ indicated an average value of n = 1·3 — 1·4 for these solutions, although it was thought to be dimeric in the solid phase.[127] Here it was thought that the difference between alkylaminoxy and alkylideneaminoxy derivatives was related to the relative donor strengths of amines R_3N and azomethines $R_2C:NR$ ($R_3N > R_2C:NR$).

Since the shape of $C_5H_4NCH:NOBMe_2$ is such that steric interference of the organic groups does not hinder association but nevertheless the molecule was found to be monomeric, the increased stability in the monomeric nature of the pyridine-2-aldoxime derivative may be due to its existence in the form:-



XV

Cryoscopic studies on benzene solutions of the aluminium indium and thallium compounds confirmed their dimeric state of association in solution. The gallium compound $(C_5H_4NCH:NOGaMe_2)_n$ however was found to have an average value of n = 1·5 and here it is thought that a monomer-dimer equilibrium is operating in solution.

Nuclear Magnetic Resonance Spectra.- It has previously been reported that syn-anti isomers of aldoximes can be distinguished by the position of the aldehydic hydrogen resonances.[164] The syn isomer shows a C-H resonance at τ = 1·3 —— 1·9 p.p.m. and the anti isomer at τ = 2·2 —— 2·8 p.p.m. relative to tetramethylsilane (τ = $10{\cdot}0_0$ p.p.m.). Pyridine-2-aldoxime itself has one aldehydic proton resonance at τ = 1·69 p.p.m. which is consistent with it being solely the syn isomer. The results for the metal derivatives $C_5H_4NCH{:}NOMR_2$ are listed in Table 16 together with assignments for the peaks. Owing to the low solubility of the dimethyl metal derivatives of pyridine-2-aldoxime the position of the aldehydic proton resonance could not be determined with any certainty, except for gallium which showed this derivative to be in the syn form. The diethylaluminium derivative of pyridine-2-aldoxime $C_5H_4NCH{:}NOAlEt_2$ prepared in the same manner as the dimethyl compound, was much more soluble and a strong aldehydic proton resonance indicated the syn form. Furthermore syn benzaldoxime was found to react with trimethylaluminium to give methane and O-dimethylaluminium syn benzaldoxime and so it would appear likely that the derivatives $(C_5H_4NCH{:}NOMMe_2)_2$ (where M = Al, In and Tl) are syn isomers.

The absorption attributable to the metal-attached methyl groups appeared as the expected singlet in all spectra except in the case of the thallium compound in carbon tetrachloride solution for which $^{205}Tl - {}^{1}H$ spin-spin coupling gave rise to a characteristically widely spaced doublet. The magnitude of J $^{205}Tl - {}^{1}H$ (392 c/sec.) for this compound is of the order typical of organo-thallium compounds.[165]

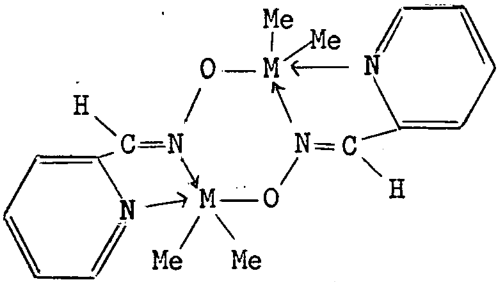
Table 16

Proton magnetic resonance spectroscopic data.

Compound	Solvent	C-H	M-R_2
$C_5H_4NCH{:}NOH$	Acetone	1·69	
$C_5H_4NCH{:}NOBMe_2$	d.Benzene		9·39
$C_5H_4NCH{:}NOAlMe_2$	d.Benzene		10·13
$C_5H_4NCH{:}NOAlEt_2$	d.Benzene	1·51	9·05(t), 9·98(q)
$C_5H_4NCH{:}NOGaMe_2$	d.Benzene	1·44	9·68
$C_5H_4NCH{:}NOInMe_2$	d.Benzene		9·87
$C_5H_4NCH{:}NOTlMe_2$	CCl_4		9·06(d) (J = 392c.sec^{-1})
syn.$C_6H_5CH{:}NOH$	d.Benzene	1·69	
syn.$C_6H_5CH{:}NOAlMe_2$	d.Benzene	1·49	10·74
$Me_2C{:}NOBMe_2$	d.Benzene		9·64
$Me_2C{:}NOAlMe_2$	d.Benzene		10·50
$Me_2C{:}NOGaMe_2$	d.Benzene		10·10
$Me_2C{:}NOInMe_2$	d.Benzene		10·16
$Me_2C{:}NOTlMe_2$	d.Benzene		9·00(d) (J = 378c.sec^{-1})

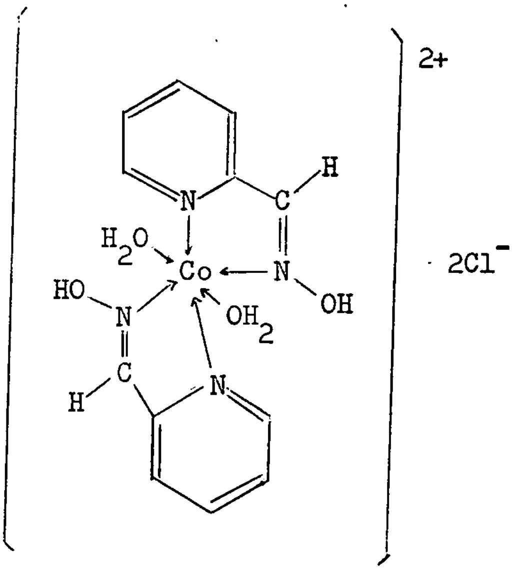
d, doublet, t, triplet, q, quartet - all other peaks singlets.

It has previously been observed that an increase in co-ordination number of a compound of the type $(Ph_2C:NZnMe)_2$ resulted in a decrease in the frequency of the $Zn-CH_3$ attached proton resonances. Table 16 shows that the $M-CH_3$ attached protons of $(C_5H_4NCH:NOMMe_2)_n$ are further downfield than would be expected when compared with related derivatives. This could be due to a change in co-ordination number of the metal by interaction with the pyridine ring nitrogen. This evidence is interpreted as indicating that the most probable structure of the derivatives $(C_5H_4NCH:NOMMe_2)_n$ (M = Al, Ga, In and Tl) is:-



XVI

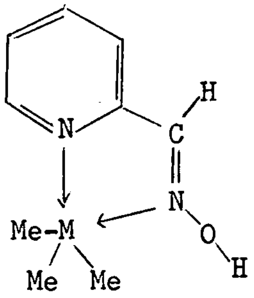
This structure (XVI) incorporates two types of heterocyclic ring as well as the pyridine rings. One is the MONMON ring which is thought to exist in all associated metal derivatives of oximes and the other is a five membered ring which is thought to be very common among transition metal derivatives of pyridine-2-aldoxime.[166] For example, the structure of the complex of pyridine-2-aldoxime with metal chloride is given below.[167]



Thus the dimer structure XVI can be thought of as being formed, either by:-

a. elimination of alkane, formation of MONMON ring and finally co-ordination of pyridine ring nitrogen.

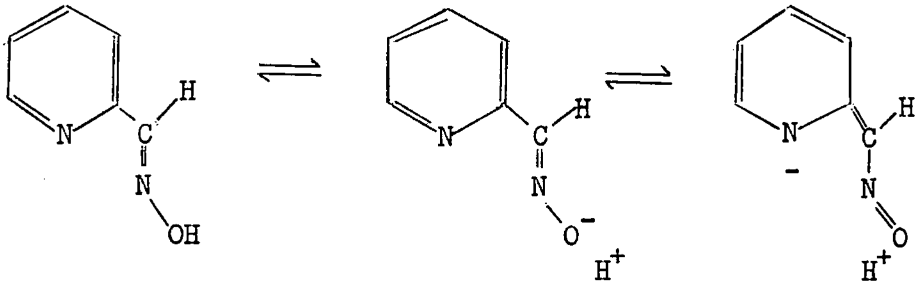
b. formation of complex XVII, elimination of alkane and finally formation of MONMON ring.



XVII

O-Dimethylaluminium pyridine-2-aldoxime was found not to react with methyl iodide which suggests that the pyridine ring nitrogen is co-ordinatively saturated. Furthermore a scale model of this compound having structure XVIhas virtually no strain and the pyridine ring nitrogen atoms are in close proximity to the metal atoms.

Infrared Spectra.- Several bands in the spectrum of pyridine-2-aldoxime have been assigned[168] including the acyclic C=N stretching vibration at 1520 cm.$^{-1}$ This low value is thought to be the result of ionisation of the pyridine-2-aldoxime (HPOX) .



For confirmation the potassium salt of pyridine-2-aldoxime was found to have an acyclic C=N stretching vibration at 1517 cm.$^{-1}$ The infrared spectra of the pyridine-2-aldoxime derivatives contain a band in the region 1554 - 1505 cm.$^{-1}$ which may be assigned to the acyclic C=N stretching vibration which decreases progressively as the atomic weight of the metal increases. The frequencies of these bands νC:N are listed in Table 17 together with the pyridine ring vibrations

Table 17

Infrared spectroscopic data for compounds $(C_5H_4NCH{:}NOMMe_2)_n$.

Compound	νC:N(cm.$^{-1}$)acyclic	Pyridine ring bands			
HPOX	1520	1597	1568	1472	1440
Me_2BPOX	1554	1615	1583	1492	1441
Me_2AlPOX	1552	1605	1582	1483	1449
Me_2GaPOX	1545	1604	1579	1480	1436
Me_2InPOX	1537	1600	1581	1476	1436
Me_2TlPOX	1505	1590	1570	1472	1439

identified by making use of the data that 2-substituted pyridine ring bands are expected at 1615-1585, 1576-1568, 1477-1465 and 1438-1428 cm.$^{-1}$ and 2-substituted pyridine N-oxide ring bands are expected at 1640-1600, 1577-1557, 1540-1480 and 1445-1425 cm.$^{-1}$ [168] The most intense peak in pyridine-2-aldoxime and its derivatives can be assigned to the N-O stretching vibration and the frequencies of these bands are listed in Table 18 together with bands arising from vibrations of groups attached to the Group III elements. The bands attributable to the M-CH_3 symmetric stretching vibration are in all cases rather weak or non-existent and are therefore further indication of interaction between the pyridine

Table 18

Infrared spectroscopic data for compounds $(C_5H_4NCH:NOMMe_2)_n$

Compound	N-O st.	M-CH_3 (sym.)	M-CH_3 rock	M$(CH_3)_2$ stretch(asym.)	M$(CH_3)_2$ stretch(sym.)
HPOX	982				
Me_2BPOX	1099	1290vs	939m	1163m	793m
Me_2AlPOX	1093	1186m	724sh	694vs	563vw
Me_2GaPOX	1085	1198m	731vs	589s	535m
Me_2InPOX	1089	1160m	703s	516s	
Me_2TlPOX	1055	1151w	791m	543m	

ring nitrogen and metal atom. The broad band at 822 cm.$^{-1}$ in the spectrum of pyridine-2-aldoxime which has been assigned to an out of plane wag of O-H is naturally missing from the spectra of the metal derivatives.

It is concluded that the aluminium, indium and thallium derivatives $(C_5H_4NCH:NOMMe_2)_2$ exist as dimeric species probably having structure XVI in solution and crystal phases; that the boron compound $C_5H_4NCH:NOBMe_2$ is monomeric in solution and possibly in the crystal phase, having structure XV and that the gallium compound is probably dimeric in the crystal phase but partly dissociates in solution.

REFERENCES

1. A.B. Burg and C.L. Randolph, J. Amer. Chem. Soc., 1949, 71, 3451.
2. B.M. Mikhoulov and N.S. Fedotov, Zh. Obsch. Khim., 1962, 32, 93.
3. K. Niedenzu and J.W. Dawson, J. Amer. Chem. Soc., 1959, 81, 5553.
4. C.E. Erickson and F.C. Gunderloy, J. Org. Chem., 1959, 24, 1161.
5. K. Niedenzu and J.W. Dawson, J. Amer. Chem. Soc., 1960, 82, 4223.
6. G.E. Coates and R.A. Whitcombe, J. Chem. Soc., 1956, 3351.
7. A.J. Banister, N.N. Greenwood, B.P. Straughan and J. Walker, J. Chem. Soc., 1964, 995.
8. H.J. Becher and J. Goubeau, Z. anorg. Chem., 1952, 268, 133.
9. O.C. Musgrave, J. Chem. Soc., 1956, 4305.
10. R.J. Gillespie, J. Amer. Chem. Soc., 1960, 82, 5978.
11. A.B. Burg and R.I. Wagner, J. Amer. Chem. Soc., 1953, 75, 3872.
12. N. Davidson and H.C. Brown, J. Amer. Chem. Soc., 1942, 64, 316.
13. O.T. Beachley and G.E. Coates, J. Chem. Soc., 1965, 3241.
14. E. Wiberg, A. Bolz, and K. Buchheit, Z. anorg. Chem., 1948, 256, 285.
15. L.M. Trefonas and W.N. Lipscomb, J. Amer. Chem. Soc., 1959, 81, 4435; A.B. Burg, ibid., 1957, 79, 2129.
16. J.K. Ruff and M.F. Hawthorne, J. Amer. Chem. Soc., 1960, 82, 2141.
17. N.N. Greenwood, A. Storr and M.G.H. Wallbridge, Inorg. Chem., 1963, 2, 1036.
18. N.N. Greenwood, E.J.F. Ross and A. Storr, J. Chem. Soc., (A), 1966, 707.

19. F.G.A. Stone, Chem. Rev., 1958, 58, 101.

20. H.C. Brown and G.K. Barbaras, J. Amer. Chem. Soc., 1947, 69, 1137.

21. H.C. Brown and M. Gernstein, J. Amer. Chem. Soc., 1950, 72, 2926.

22. D.E. McLaughlin, T. Tamres, S. Searles, Jr. and F. Block, J. Inorg. Nuc. Chem., 1961, 18, 118.

23. T.D. Coyle and F.G.A. Stone, J. Amer. Chem. Soc., 1961, 83, 4138.

24. W.A.G. Graham and F.G.A. Stone, J. Inorg. Nuc. Chem., 1956, 3, 164.

25. K.W. Bodder, S.G. Shore and R.K. Bunting, J. Amer. Chem. Soc., 1966, 88, 4396.

26. T.C. Bissot and R.W. Parry, J. Amer. Chem. Soc., 1955, 77, 3481.

27. A.B. Burg and J.L. Boone, J. Amer. Chem. Soc., 1956, 78, 1521.

28. E. Wiberg and K. Hertwig, Z. anorg. Chem., 1947, 255, 141.

29. E. Wiberg and K. Buchheit, F.I.A.T. Review of German Science, 1948, Inorganic Chemistry, Vol. 1, p.218.

30. D. Ulmschneider and J. Goubeau, Chem. Ber., 1957, 90, 170.

31. G.E. Coates and J.G. Livingstone, J. Chem. Soc., 1961, 1000.

32. P.A. Barfield, M.F. Lappert and J. Lee, Proc. Chem. Soc., 1961, 421.

33. L.J. Bellamy, W. Gerrard, M.F. Lappert and R.L. Williams, J. Chem. Soc., 1958, 2412.

34. H.J. Becher and H. Diehl, Chem. Ber., 1965, 98, 527.

35. R.E. Hester and C.W.J. Scaife, Spectro. chim. Acta., 1966, 22, 755.

36. M.F. Hawthorne, Tetrahedron, 1962, 17, 117.

37. J.E. Lloyd and K. Wade, J. Chem. Soc., 1964, 325, 1649.

38. A.J. Leffler, J. Inorg. Chem., 1964, 3, 145.

39. J.C. Sheldon and B.C. Smith, Quart. Rev., 1960, 14, 200.

40. P.I. Paetjold and W.M. Simson, Ang. Chem., 1966, 5, 842.

41. W. Gerrard, "The Organic Chemistry of Boron", Academic Press, 1961.

42. A. Kreutzberger and F.C. Ferris, J. Org. Chem., 1965, 30, 360.

43. J.K. Ruff, J. Org. Chem., 1962, 27, 1020.

44. W.D. English, A.L. McClosky and H. Steinberg, J. Amer. Chem. Soc., 1961, 83, 2122.

45. J.E. Burch, W. Gerrard and E.F. Mooney, J. Chem. Soc., 1962, 2200.

46. J.A. Semlyen and P.S. Flory, J. Chem. Soc., (A), 1966, 191.

47. H.J. Becher, Z. anorg. Chem., 1956, 287, 235 and 285.

48. E. Krause and P. Dittmar, Chem. Ber., 1930, 63, 240.

49. A.W. Laubengayer, K. Wade and G. Lengnick, Inorg. Chem., 1962, 1, 632.

50. W.P. Neuman, Annalen., 1963, 667, 1.

51. T. Mole, Aust. J. Chem., 1963, 16, 801.

52. R. Ehrlich, A.R. Young II, B.M. Lichstein and D.D. Perry, Inorg. Chem., 1963, 2, 650.

53. N.R. Fetter and D.W. Moore, Canad. J. Chem., 1964, 42, 885.

54. A.R. Young II and R. Ehrlich, Inorg. Chem., 1965, 4, 1358.

55. G. Bahr, F.I.A.T. Review of German Science, 1948, Inorganic Chemistry, Vol. 1, p. 155.

56. A.W. Laubengayer, J.D. Smith and G.G. Ehrlich, J. Amer. Chem. Soc., 1961, 83, 542.

57. A. Cohen, J. Gilbert and D. Smith, J. Chem. Soc., 1965, 1093.

58. J.K. Ruff, J. Amer. Chem. Soc., 1961, 83, 1798.

59. E. Wiberg and A. May, Z. Naturforschg., 1955, 10b, 229.

60. K. Dehnicke, J. Strahle, D. Seybold and J. Muller, J. Organometal. Chem., 1966, 6, 298.

61. G.K.J. Gibson and D.W. Hughes, Chem. and Ind., 1964, 544.

62. J.E. Lloyd and K. Wade, J. Chem. Soc., 1965, 2662.

63. J.R. Jennings, J.E. Lloyd and K. Wade, J. Chem. Soc., 1965, 5083.

64. O.T. Beachley, G.E. Coates and G. Kohnstam, J. Chem. Soc., 1965, 3248.

65. R. Ehrlich, A.R. Young II, B.M. Lichstein and D.D. Perry, Inorg. Chem., 1964, 3, 628.

66. J.I. Jones and W.S. McDonald, Proc. Chem. Soc., 1962, 366.

67. T.R.R. McDonald and W.S. McDonald, Proc. Chem. Soc., 1963, 382.

68. E.G. Hoffman, Annalen., 1960, 629, 104.

69. T. Mole and R. Surtees, Austral. J. Chem., 1964, 17, 961.

70. F. Runge, W. Zimmermann, H. Pfeiffer and I. Pfeiffer, Z. anorg. Chem., 1951, 267, 39.

71. H. Gilman and R.G. Jones, J. Amer. Chem. Soc., 1946, 68, 517.

72. A. Lieb, M.T. Emerson and J.P. Oliver, Inorg. Chem., 1965, 4, 1825.

73. G.E. Coates, J. Chem. Soc., 1951, 2003.

74. G.E. Coates and R.A. Whitcombe, J. Chem. Soc., 1956, 3351.

75. O.T. Beachley, G.E. Coates and G. Kohnstam, J. Chem. Soc., 1965, 3248.

76. J. Muller and K. Dehnicke, J. Organometall. Chem., 1967, 7, 1.

77. J.R. Jennings and K. Wade, J. Chem. Soc. (A), 1967, in press.

78. G.E. Coates and R.G. Hayter, J. Chem. Soc., 1953, 2519.

79. R.C. Menzies and A.R.P. Walker, J. Chem. Soc., 1934, 1131.

80. R.C. Menzies, J. Chem. Soc., 1928, 1288.

81. B. Bogdanovic, Angew Chem., 1965, 4, 954.

82. G.E. Coates and R.N. Mukherjee, J. Chem. Soc., 1964, 1295.

83. A. Duncanson, W. Gerrard, M.F. Lappert, H. Pyszora and R. Shafferman, J. Chem. Soc., 1958, 3652.

84. E. Frankland, Annalen, 1859, 111, 62.

85. K.H. Thiele, Z. anorg. Chem., 1962, 319, 183.

86. Idem., Ibid., 1963, 322, 71.

87. N.I. Sheverdina, L.V. Abramova and K.A. Kocheskov, Doklady Akad. Nauk U.S.S.R., 1959, 128, 320.

88. K.H. Thiele, Z. anorg. Chem., 1963, 325, 156.

89. J.G. Noltes and J.W.G. van den Hurk., J. Organometall. Chem., 1965, 3, 222.

90. J.G. Noltes and J.W.G. van den Hurk., J. Organometall. Chem., 1964, 1, 377.

91. G.E. Coates and D. Ridley, J. Chem. Soc., 1965, 1870.

92. J.G. Noltes, Rec. Trav. chim., 1965, 84, 126.

93. G.E. Coates and D. Ridley, J. Chem. Soc. (A), 1966, 1064.

94. H. Gilman and K.E. Marple, Rec. Trav. chim., 1936, 55, 133.

95. E. Weiss and E.A.C. Lucken, J. Organometal. Chem., 1964, 2, 197.

96. H. Dietrich, Acta. Cryst., 1963, 16, 681.

97. M. Weiner, G. Vogel and R. West, Inorg. Chem., 1962, 1, 654.

98. D. Margerison and J.P. Newport, Trans. Farad. Soc., 1963, 59, 2058.

99. T.L. Brown, R.L. Gerteis, D.A. Bafus and J.A. Ladd, J. Amer. Chem. Soc., 1964, 86, 2135.

100. M. Weiner, G. Vogel and R. West, Inorg. Chem., 1962, 1, 654.

101. G. Hartwell and T.L. Brown, Inorg. Chem., 1966, 5, 1257.

102. M.S. Bains, Canad. J. Chem., 1964, 42, 945.

103. P.J. Wheatley, J. Chem. Soc., 1960, 4270.

104. H. Weingarte and W.A. White, J. Amer. Chem. Soc., 1966, 88, 2885.

105. Lithium Corporation of U.S.A., Bulletin 207-563, May 1963.

106. U. Wannagat and H. Niedergrum, Chem. Ber., 1961, 94, 1540.

107. O.F. Beumel Jr., and R.F. Harris, J. Org. Chem., 1964, 29, 1872.

108. H.D. Rausch, F.E. Tibbetts and H.B. Gordon, J. Organometal. Chem., 1966, 5, 493.

109. J. Huet, Bull. Soc. Chim. France, 1964, 952.

110. R.T. Sanderson, "Vacuum Manipulation of Volatile Compounds", John Wiley and Sons Inc., N.Y., 1948.

111. H. Gilman and M.M. Barnett, Rec. Trav. Chim., 1936, 55, 563.

112. K.A. Kozeschkow, A.N. Nesmeyanov and W.I. Potrosov, Chem. Ber., 1934, 67, 1138.

113. T. Wartick and H.I. Schlesinger, J. Amer. Chem. Soc., 1952, 75, 835.

114. T. Renner, Angew. Chem., 1957, 69, 478.

115. P.L. Pickard and T.L. Tolbert, J. Org. Chem., 1961, 26, 4887.

116. A.I. Vogel, W.T. Cresswell, G.H. Jeffrey and J. Leicester, J. Chem. Soc., 1952, 514.

117. E. Wiberg and K. Schuster, Z. anorg. Chem., 1933, 77, 213.

118. R.W. Layer, Chem. Rev., 1963, 63, 489.

119. K. Wade and B.K. Wyatt, unpublished observations.

120. B. Bogdanovic, Angew.Chem. Internat. Edn., 1965, 4, 954.

121. H.M.M. Shearer and C.B. Spencer, personal communication.

122. J.G. Noltes and J. Boersma, J. Organometal. Chem., 1967, 7, 6.

123. F. Schindler, H. Schmidbaur and U. Kruger, Angew. Chem. Internat. Edn., 1965, 4, 876; H.M.M. Shearer and C.B. Spencer, Chem. Comm., 1966, 194.

124. G.W. Adamson and H.M.M. Shearer, personal communication.

125. J. Boersma and J.G. Noltes, Tetrahedron Letters, 1966, 14, 1521.

126. E. Frankland and J. Evans, J. Chem. Soc., 1880, 37, 563.

127. J.R. Jennings and K. Wade, unpublished observations.

128. J. Hofmann, Chem. Ber., 1868, 1, 198.

129. A.H. Cook and D.G. Jones, J. Chem. Soc., 1941, 278.

130. R.M. Anker and A.H. Cook, J. Chem. Soc., 1941, 323.

131. S. Pinner and F. Klein, Chem. Ber., 1878, 11, 764.

132. W.Z. Heldt, J. Organometal. Chem., 1966, 6, 292.

133. S. Pasynkiewicz and W. Kuran, Roczniki Chem., 1965, 39, 1199.

134. A.L. Allred and E.G. Rochow, J. Inorg. Nucl. Chem., 1958, 5, 264.

135. G.E. Coates and A.H. Fishwick, personal communication.

136. J.M. Bruce, B.C. Cutsforth, D.W. Farren, F.G. Hutchinson, F.M. Rabagliati and D.R. Reed, J. Chem. Soc. (B), 1966, 1020.

137. G.E.P. Smith, Jr. and F.W. Bergstrom, J. Amer. Chem. Soc., 1934, 56, 2095.

138. T.E. Jordan, "Vapour Pressure of Organic Compounds", Interscience, New York, 1954.

139. H.C. Brown, H. Bartholemay and M.D. Taylor, J. Amer. Chem. Soc., 1944, 66, 435.

140. H.C. Brown and M.D. Taylor, J. Amer. Chem. Soc., 1947, 69, 1332.

141. T.D. Coyle and F.G.A. Stone, J. Amer. Chem. Soc., 1961, 83, 4138.

142. P.L. Corio and B.P. Dailey, J. Amer. Chem. Soc., 1956, 78, 3034; H. Spiesecke and W.G. Schneider, J. Chem. Phys., 1961, 35, 731.

143. N.N. Greenwood and T.S. Srivastava, J. Chem. Soc. (A), 1966, 703.

144. G.E. Coates and A.J. Downs, J. Chem. Soc., 1964, 3353; J.R. Hall, L.A. Woodward and E.A.V. Ebsworth, Spectrochim. Acta., 1964, 20, 1249.

145. E. Wiberg and K. Buchheit, unpublished work quoted by J. Goubean in the F.I.A.T. Review of German Science, 1939-46, Inorg. Chem., 1949, 1, 228.

146. J.D.S. Goulden, J. Chem. Soc., 1953, 997.

147. E.J. Blanz and H.S. Mosher, J. Org. Chem., 1958, 23, 492.

148. A.E.G. Miller, J.W. Biss and L.H. Schwartzman, J. Org. Chem., 1959, 24, 627.

149. M.F. Lappert, Proc. Chem. Soc., 1959, 59.

150. H.S. Turner and R.J. Warne, J. Chem. Soc., 1965, 6421.

151. J.F. Brown, Jr., J. Amer. Chem. Soc., 1952, 74, 1219.

152. D.W. Aubrey, M.F. Lappert and M.K. Majumdar, J. Chem. Soc., 1962, 4088.

153. N.N. Greenwood, K.A. Hooton and J. Walker, J.C.S. (A), 1966, 21.

154. M.S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice-Hall Inc., New York, 1954.

155. K.N. Campbell, B.K. Campbell, L.G. Hess and I.J. Schaffner, J. Org. Chem., 1944, 9, 184; D.R. Smith, M. Maienthal and J. Tipton, ibid., 1952, 17, 294.

156. D.F. Menard and J.G. Aston, J. Amer. Chem. Soc., 1934, 56, 1601.

157. C.R. Hauser and D.S. Hoffenberg, J. Org. Chem., 1955, 20, 1482, 1496; W. Gerrard, M.F. Lappert and J.W. Wallis, J. Chem. Soc., 1960, 2141, 2144.

158. H. Fener, B.F. Vincent and R.S. Bartlett, J. Org. Chem., 1965, 30, 2877.

159. E.J. Pribyl, H.L. Yale and J. Bernstein, U.S.P. 3,137,723, June 16, 1964. A. Dernow and K. Fischer, Chem. Ber., 1966, 99, 68.

160. E. Frainnet and F. Duboudin, Compt. rend., 1966, 262C, 1693.

161. S. Ginsberg and I.B. Wilson, J. Amer. Chem. Soc., 1957, 79, 481.

162. M. Inatome and L.P. Kuhn, Boron-Nitrogen Chemistry, Advan. in Chem. Series, 1964, 42, 183; S. Brois, Tetrahedron Letters, 1964, 345.

163. L.P. Kuhn and M. Inatome, J. Amer. Chem. Soc., 1963, 85, 1206; H.J. Roth and B. Miller, Archiv. der. Pharmzie, 1964, 297, 744.

164. R.J. Crawford and C. Woo, Canad. J. Chem., 1965, 43, 3178.

165. J.P. Maher and D.F. Evans, J. Chem. Soc., 1965, 637.

166. R. Breslow and D. Chipman, J. Amer. Chem. Soc., 1965, 87, 4195; S. Bolton and A. Beckett, J. Pharm. Sciences, 1964, 53, 55.

167. M.W. Blackmore and R.J. Magee, Austral. J. Chem., 1967, 20, 427.

168. R.A. Krause, N.B. Colthup and D.H. Busch, J. Phys. Chem., 1961, 65, 2216.