Studies on some azomethine derivatives

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STUDIES ON SOME AZOMETHINE DERIVATIVES

by

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C O N T E N T S

EXPERIMENTAL

EXPERIMENTAL RESULTS

Reactions of diphenylketiminolithium with chlorosilanes

Reactions of diphenylketimine with chlorosilanes

Reactions of 1,1,3,3-tetramethylguanidyl-lithium with chlorosilanes

DISCUSSION

A C K N O W L E D G E M E N T S

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

M E M O R A N D U M

The work described in this thesis was carried out in the University of Durham between September 1966 and June 1969. 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:

Monomeric Diphenylketiminodiphenylborane, a Boron-Nitrogen Analogue of an Allene.

By J.R. Jennings, I.Pattison, C.Summerford, K.Wade and B.K.Wyatt. Chem.Comm., 1968, 250.

Infrared Spectroscopic Evidence of Dative Beryllium-Nitrogen π-Bonding in Bis(ketimino) Derivatives of Beryllium.

By C. Summerford, K.Wade and B.K. Wyatt. Chem.Comm., 1969, 61.

Azomethine Derivatives. Part VIII. The Preparation of Some Diphenylketimino-silanes, and the Use of Diphenylketiminotrimethylsilane to prepare Diphenylketiminoboranes.

By C. Summerford and K. Wade. J.Chem.Soc. (A), 1969.

SUMMARY

This thesis describes the preparation of some azomethine derivatives of silicon, boron and beryllium. The structural implications of their infrared, and in some cases, proton magnetic resonance and mass spectra are discussed. As a background to this work the literature on azomethine derivatives of the more electropositive elements is surveyed.

Diphenylketiminolithium reacts with chlorosilanes giving the diphenylketiminosilanes, $Ph_2C{:}NSiR_3$ (R=Me, Et or Ph) and $(Ph_2C{:}N)_4Si$. 1,1,3,3-tetramethylguanidyl-lithium reacts with chlorosilanes in a similar fashion giving the 1,1,3,3-tetramethylguanidylsilanes, $(Me_2N)_2C{:}NSiR_3$ (R=Me, Et or Ph).

Reactions between diphenylketiminotrimethylsilane and boron trihalides or organoboron halides in toluene provide convenient routes to diphenylketiminoboranes; one, two or three ketimino groups being transferred to boron under mild conditions. Bis(diphenylketimino)boron halides could not be isolated, apparently disproportionating into diphenylketiminoboron dihalides and tris(diphenylketimino)borane.

Iminoboranes, $R^1R^2C{:}NBR^3R^4$, have also been obtained by reaction of organoboron halides with ketiminolithium compounds and with two moles of imine. Reaction of diphenylketimine hydrochloride with sodium tetraphenylborate at 109° gives the ketiminoborane, $Ph_2C{:}NBPh_2$; di-p-tolylketimine hydrochloride gives the adduct, $p\text{-tolyl}_2C{:}NH,BPh_3$, under the same conditions.

Some of the iminoboranes prepared were monomeric, a state of

association previously unknown for this type of compound. The evidence available supports a linear, pseudo-allenic structure involving significant $p\pi$-$p\pi$ interaction between nitrogen and boron. The factors affecting the degree of association of the iminoboranes are discussed.

Reactions of beryllium chloride with one or two moles of ketiminolithium compounds give dimeric ketiminoberyllium chlorides or bis(ketimino)beryllium derivatives respectively. Infrared spectroscopic evidence suggests significant $p\pi$-$p\pi$ interaction between nitrogen and beryllium in the latter compounds.

Features of the infrared spectra of boron trifluoride adducts and hydrochloride salts of a series of imines, $R^1R^2C{:}NR^3$, are discussed in an appendix.

INTRODUCTION

The reaction between a nitrile and a Grignard reagent followed by hydrolysis of the reaction mixture has been used for many years as a route to ketones[1] and ketimines.[2] Subsequent work showed that this reaction could be extended to organolithium[3] and organoaluminium compounds.[4] For example, Gilman and Marple[4] obtained phenyl p-tolyl ketone in 17% yield on hydrolysis of the product from the reaction of phenyl cyanide and tri-p-tolylaluminium at about 130-140°.

$$PhC{:}N + (p\text{-tolyl})_3Al \longrightarrow [p\text{-tolyl}C(Ph){:}NAl(p\text{-tolyl})_2] \xrightarrow{H_2O} p\text{-tolyl}C(Ph)=O$$

Similarly the reduction of nitriles to amines by excess lithium aluminium hydride[5,6] can be stopped at the C=N stage by limiting the amount of lithium aluminium hydride.[7]

However until recently very little effort has been made to isolate and characterise the metal-containing azomethine derivatives, $RR^1C{:}NMX_n$, of the type which must constitute the intermediates in these reactions.

Thus in 1934 Smith and Bergstrom isolated apparently impure diphenylketiminosodium, $Ph_2C{:}NNa$, from the reaction between diphenylketimine and sodamide in liquid ammonia,[8] but not until 1957 was the first pure azomethine metal derivative of this type reported.[9] This was butyraldiminodi-i-butylaluminium, $(PrCH{:}NAlBu^i_2)_n$, b.p. 160-161°/1 mm., obtained from the reaction of propyl cyanide and di-i-butylaluminium

hydride.

$$PrC{:}N + Bu^{i}_{2}AlH \longrightarrow \frac{1}{n}(PrCH{:}NAlBu^{i}_{2})_{n}$$

Since then however activity in this area has been gathering momentum, with the realisation that these compounds offered vast scope, greater in many respects than amino-derivatives, for the study of important aspects of metal-nitrogen chemistry, including co-ordination chemistry, reactivity of the metal-nitrogen bond and especially metal-nitrogen partial double bonding. A brief survey of this field is therefore presented in the following pages.

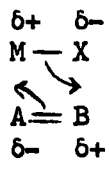
General Preparative Aspects.

Two main routes to azomethine derivatives of metals and metalloids have been used.

The first route, of which the preparation of $(PrCH{:}NAlBu^{i}_{2})_{n}$ is an example, is by an insertion reaction. This type of reaction involves the insertion of a multiple bond (in this case -C≡N) into a bond between a metal (or metalloid) and a relatively electronegative atom, i.e.

$$\overset{\delta+\ \delta-}{M-X} + \overset{\delta-\ \delta+}{A=B} \longrightarrow M\text{-}A\text{-}B\text{-}X$$

The reaction may be pictured as involving a cyclic transition state.



This type of reaction has been applied to many systems involving unsaturated substrates other than nitriles and has been reviewed fairly recently.[10]

The second route, which is that used in this work, involves a metathetical reaction using a preformed imine, $R^1R^2C{=}NH$,[11,12] or derivative thereof, $R^1R^2C{=}NY$ (Y = Li,[11,13] $SiMe_3$,[14] SCl,[15] etc.).

$$Q_nM\text{-}X + R^1R^2C{=}NY \longrightarrow R^1R^2C{=}NMQ_n + YX$$

In surveying the literature on azomethine derivatives of the more electropositive elements it will be simplest to deal with each Group in turn.

Group I.

As mentioned above, the reaction of diphenylketimine with sodamide in liquid ammonia was used in an attempt to prepare diphenylketiminosodium, $Ph_2C{:}NNa$.[8] The reaction was reported to give a dark red solution which after standing for several days was decanted from excess sodamide and on evaporation of the ammonia gave a dark red solid. However last traces of ammonia could not be removed, even in vacuo, and the authors were unable to properly characterise the product.

Diphenylketiminolithium, $Ph_2C{:}NLi$, has been obtained by two routes.[11]

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

off the solvent diphenylketiminolithium was obtained as an air-sensitive yellow solid.

$$Ph_2C{:}NH + MeLi \longrightarrow Ph_2C{:}NLi + MeH$$

The same product resulted when an equimolar mixture of phenyl-lithium and phenyl cyanide in ether was allowed to warm up from -196° to room temperature and the ether then pumped away.

$$PhC{:}N + PhLi \longrightarrow Ph_2C{:}NLi$$

Solid diphenylketiminolithium is insoluble in hydrocarbons and diethyl ether but dissolves in tetrahydrofuran and pyridine with which it forms 1:1 adducts which can be isolated as orange crystalline solids.

Its infrared spectrum shows a strong absorption at 1620 $cm.^{-1}$, assignable to the C=N stretching frequency.

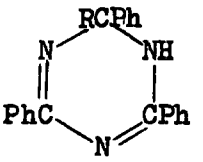
It is thought that diphenylketiminolithium when first formed in ether solution remains dissolved, probably as monomeric or oligomeric species stabilised by co-ordination to the solvent, but that the unsolvated solid exists as a co-ordination polymer which dissolved only in solvents which are strong enough donors to break up the polymer.

The reaction between phenyl cyanide and methyl-lithium in ether gives a red solution from which the ketimine derivative PhCMe:NLi can be obtained as an orange, apparently polymeric, solid.[11] However the yield from this reaction is very low. This is thought to be a consequence of a competing side reaction in which the phenyl cyanide is

polymerised. This type of reaction is known to occur when organolithium compounds are treated with an excess of phenyl cyanide.[3] It is thought to proceed by successive insertions of phenyl cyanide into azomethine derivatives of lithium,

$$RLi \xrightarrow{PhCN} RPhC{:}NLi \xrightarrow{PhCN} R(PhCN)_2Li \xrightarrow{PhCN} R(PhCN)_3Li \text{ etc.}$$

and has been used to prepare heterocycles of the type[3]:



where R = Me, Et, Pr, Pr^i, Bu and Ph

Alkyl cyanides, RCH_2CN, having hydrogen atoms attached to the α-carbon atom do not afford azomethine derivatives with organolithium compounds.[11] Instead alkane is eliminated by acid reaction of these hydrogen atoms and insoluble, involatile and seemingly polymeric materials are obtained.

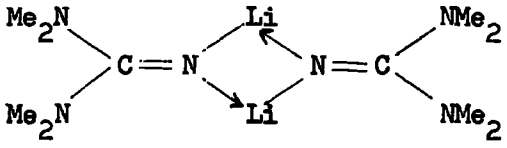
$$R^1CH_2CN + R^2Li \longrightarrow (R^1CHCNLi)_n + R^2H$$

(R^1 = H or Me, R^2 = Me or Et)

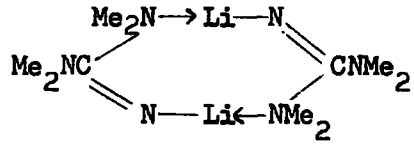
t-Butyl cyanide, which has no hydrogen atoms attached to the α-carbon atom, has been reported not to react at all with methyl- or

ethyl-lithium in ether at or below room temperature.[11]

In contrast to the polymeric ketiminolithium compounds, tetramethylguanidyl-lithium, $(Me_2N)_2C{:}NLi$, which results from the reaction of tetramethylguanidine and methyl-lithium in ether, is a colourless solid which dissolves in benzene as a dimer.[11] On the basis of its proton magnetic resonance (p.m.r.) spectrum the molecule is thought to have structure I, with terminal dimethylamino groups, rather than structure II.



I



II

Surprisingly, in spite of the apparent co-ordinative unsaturation of the lithium atom, it does not appear to form isolable adducts with donors such as pyridine or tetrahydrofuran.

Group II.

The only known azomethine derivatives of beryllium were prepared as part of this work, in conjunction with Dr. B.K. Wyatt, and will be dealt with in the Discussion.

In spite of their use in the preparation of ketones and ketimines no azomethine derivatives of the type $(R^1R^2C{:}NMgX)_n$, where X = halogen,

have been isolated to date. In fact only one fully characterised example of an azomethine derivative of magnesium has been reported. That is $(PhCEt{:}NMgEt)_n$, prepared by the reaction of phenyl cyanide with diethylmagnesium in ether.[16]

$$PhC{:}N + Et_2Mg \longrightarrow \frac{1}{n}(PhCEt{:}NMgEt)_n$$

The product is obtained as a yellow syrup from which ether can be slowly removed by pumping at room temperature; the resulting solid being purified by washing with hexane. It is soluble in benzene in which it is extensively associated, its apparent degree of association being 13 at 1·1 and 21 at 4·3 wt.-% concentration. The infrared spectrum of the solid contains a strong band at 1626 $cm.^{-1}$, assignable to the C=N stretching frequency.

Reaction of diethylmagnesium with t-butyl cyanide in diethyl ether gives a colourless syrup from which residual ether can not be removed.[16] However the product forms a crystalline complex with tetrahydrofuran $(Bu^tCEt{:}NMgEt)_x(THF)_y$ which melts at ca. -20°. An infrared spectrum of the liquid product contained no absorption that could be assigned to cyanide groups, but the strongest absorption was at 1631 $cm.^{-1}$

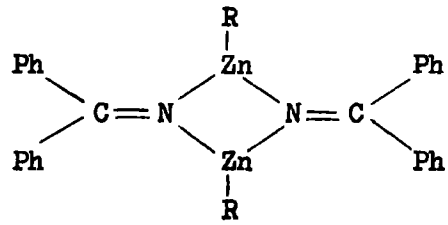
Reaction of di-i-propylmagnesium with t-butyl cyanide in diethyl ether gives only the crystalline co-ordination complex $Bu^tCN,MgPr^i_2$.[16]

Zinc.

Equimolar mixtures of diphenylketimine and dimethyl- or diethylzinc react rapidly at about 40° in the absence of solvent, with elimination of alkane, and diphenylketimine reacts similarly with diphenylzinc in toluene giving dimeric azomethine derivatives,[17] $(Ph_2C{:}NZnR)_2$, (R = Me, Et or Ph).

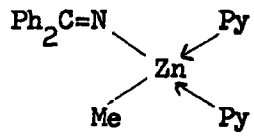
$$Ph_2C{:}NH + R_2Zn \longrightarrow \tfrac{1}{2}(Ph_2C{:}NZnR)_2 + RH$$

The compounds are air and moisture sensitive colourless crystalline solids. The dimeric molecules are believed to have a planar skeleton based on a $(ZnN)_2$ four-membered ring (I) such as has been shown by X-ray crystallography to occur in the amino-compound $(Ph_2NZnMe)_2$.[18]



I

This ring is easily cleaved by donor molecules. For example, addition of excess pyridine to a benzene solution of $(Ph_2C{:}NZnMe)_2$ gives the yellow crystalline adduct $Ph_2C{:}NZnMe,2py$ whose monomeric nature is consistent with structure II.



II

The same product is obtained even when the proportion of pyridine is limited to 2 mol. per mol. of dimer, $(Ph_2C{:}NZnMe)_2$.

$(Ph_2C{:}NZnPh)_2$ disproportionates when a solution of it in toluene is held at 80°, bis(diphenylketimino)zinc, $[(Ph_2C{:}N)_2Zn]_n$, an involatile, insoluble and presumably polymeric solid being slowly deposited.

$$(Ph_2C{:}NZnPh)_2 \longrightarrow \tfrac{1}{n}[(Ph_2C{:}N)_2Zn]_n + Ph_2Zn$$

In contrast to the magnesium case mixtures of t-butyl cyanide and dimethyl-, diethyl- or diphenylzinc show no sign of interaction, even when solutions of them in toluene or tetrahydrofuran are boiled for 3 to 4 days.[17] However heating similar mixtures of dimethyl- or diethylzinc and phenyl cyanide between 100 and 150° in sealed tubes results in the trimerisation of the phenyl cyanide;[17,19,20] the dialkylzinc being recovered quantitatively.[19] This trimerisation, which was first observed by Frankland in 1880, may well involve successive insertions of phenyl cyanide into initially zinc-carbon and subsequently zinc-nitrogen links in a similar fashion to that previously discussed in connection with the system PhCN-RLi.

Diphenylzinc, on the other hand, forms a viscous liquid adduct $PhCN,ZnPh_2$ with phenyl cyanide.[17] This, when heated to 100°, gives bis(diphenylketimino)zinc,[17] presumably via the disproportionation of initially formed diphenylketiminophenylzinc.

$$PhCN,ZnPh_2 \longrightarrow (Ph_2C{:}NZnPh)_2 \longrightarrow \tfrac{1}{n}[(Ph_2C{:}N)_2Zn)_n + Ph_2Zn$$

Group III.

Boron.

In 1960 spectroscopic evidence was reported for the intermediate formation of a compound $(MeCH:NBH_2)_n$[21] in the pyrolysis of the adduct between acetonitrile and diborane, $MeC:N,BH_3$. This compound, a volatile liquid, was thought to have arisen in the stepwise transfer of hydrogen atoms from boron to carbon which leads to the formation of N'N''N'''-triethylborazine, $Et_3N_3B_3H_3$, in this reaction.

$$MeC:N,BH_3 \longrightarrow (MeCH:NBH_2)_n \longrightarrow (MeCH_2NBH)_3$$

Its infrared spectrum showed a strong band at 1635 $cm.^{-1}$ which was tentatively assigned to a C=N vibration, but the compound was not obtained in large enough quantities for purification and full characterisation.

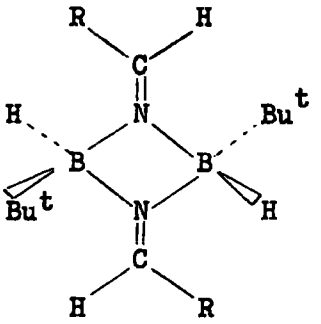
Subsequent work by one of the authors showed that this compound was not an azomethine derivative but was in fact μ-diethylaminodiborane, $Et_2NB_2H_5$.[22] The report nevertheless stimulated the preparation and study of azomethine derivatives of boron.

The first preparative route to be studied involved insertion of a nitrile into a B-H bond. Thus reaction of trimethylamine t-butyl borane with a series of nitriles in diglyme at 100° gave a series of dimeric crystalline aldiminoboranes.[23]

$$RC{:}N + Bu^tBH_2,NMe_3 \longrightarrow \tfrac{1}{2}(RCH{:}NBHBu^t)_2 + NMe_3$$

R = Me, Et, Pr^n, Pr^i, Ph, p-$MeOC_6H_4$, p-ClC_6H_4, p-FC_6H_4, p-MeC_6H_4, m-MeC_6H_4.

The compounds derived from aliphatic nitriles each showed a band in their infrared spectra attributable to C=N stretching at ca. 1660 $cm.^{-1}$; those derived from aromatic nitriles showed a similar band at ca. 1640 $cm.^{-1}$ Their ^{11}B n.m.r. spectra indicated that the boron atoms were four-co-ordinate and a structure based on a four-membered $(BN)_2$ ring was proposed.



In each case where R = aryl a small amount of relatively insoluble material was isolated along with the dimeric compounds. This material had in each case the same empirical formula as the dimeric compounds and indeed could also be obtained by fusion of them. In the absence of any evidence to the contrary it was suggested that this material consisted of more highly associated oligomers of the iminoboranes, possibly cyclic trimers.

Using a similar preparative approach the dimeric aldiminoboranes, $(MeCH{:}NBMe_2)_2$ and $(MeCH{:}NBEt_2)_2$, were obtained by the gas phase reaction of acetonitrile and the tetra-alkyldiborane at room temperature.[24]

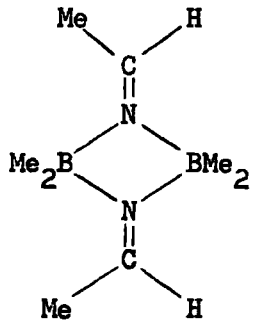
$$2MeC{:}N + (R_2BH)_2 \longrightarrow (MeCH{:}NBR_2)_2$$

The same products were also isolated together with N'N''N'''-triethylborazine from the reaction of the unsym-dialkyldiboranes, $Me_2BH{\cdot}BH_3$ and $Et_2BH{\cdot}BH_3$, with acetonitrile.[24]

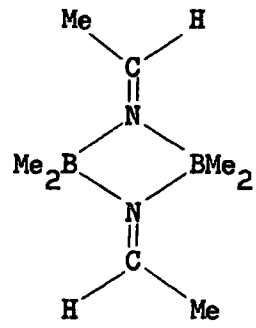
$$2MeC{:}N + R_2BH{\cdot}BH_3 \longrightarrow \tfrac{1}{2}(MeCH{:}NBR_2)_2 + \tfrac{1}{3}(MeCH_2NBH)_3$$

It was found possible to separate acetaldiminodimethylborane, $(MeCH{:}NBMe_2)_2$, into two isomers by repeated vacuum distillation. These were a crystalline solid, v.p. 0·6 mm./20°, m.p. 76°, and a liquid, v.p. 1·8 mm./20°, m.p. ca. -5°. Both isomers were dimeric in the gas phase at 100-150° and in benzene solution, and their infrared spectra were very similar. Their p.m.r. spectra in CCl_4 were identical except that the liquid isomer gave two peaks arising from boron-attached methyls whereas the solid isomer gave only a singlet.

On the basis of this evidence a cis structure was assigned to the liquid isomer and a trans structure to the solid isomer.



cis



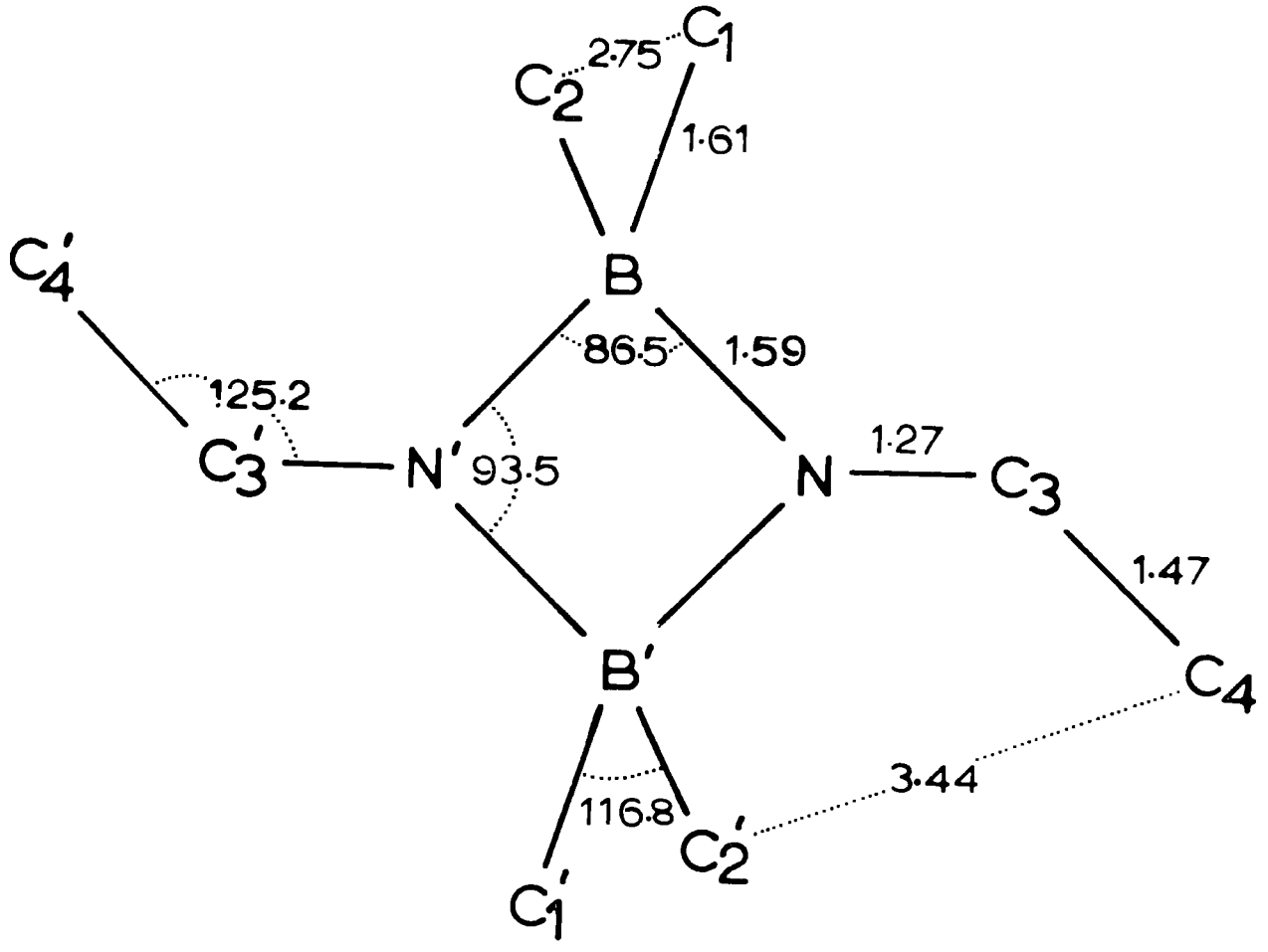
trans

This study provided further support for the structure, based on a $(BN)_2$ ring, previously suggested.

That this was indeed a true interpretation of the evidence was later proved by an X-ray crystallographic study of the crystalline isomer.[25] The results of this study are shown in fig. 1.

The average B-N distance of 1·59Å is the same as that in $(Me_2NBCl_2)_2$[26] which also contains a four-membered boron-nitrogen ring. This close agreement arises in spite of the nitrogen atoms being formally sp^2 hybridised in $(MeCH{:}NBMe_2)_2$ and sp^3 hybridised in $(Me_2NBCl_2)_2$. The BNB angle is greater than 90° as might be expected from the formal sp^2 hybrid nature of the nitrogen atom and its greater electronegativity than boron. That in $(Me_2NBCl_2)_2$ by contrast is 86·9°. The C=N length is 1·27Å. This value is also found for dimethylglyoxime.[27] The B-C distance of 1·61Å is the same as that in tetramethyldiborane.[28]

The dimeric, acetaldiminodiethylborane, $(MeCH{:}NBEt_2)_2$, defied attempts to separate it into isomers by vacuum distillation or vapour-



$(Me_2BNCHMe)_2$

FIGURE 1.

phase chromatography,[24] although the melting range of the compound indicates that it was probably a mixture of isomers.

Attempts to prepare monomeric acetaldiminodiethylborane, $MeCH{:}NBEt_2$, by thermal dissociation of the dimer were unsuccessful.[24] Interestingly no evidence of conversion of one isomer of acetaldiminodimethylborane into the other via thermal dissociation into the monomeric form, $MeCH{:}NBMe_2$, could be obtained on heating either isomer to 150°.

Although reaction of diborane with acetonitrile does not afford an isolable azomethine derivative of boron,[21] the reaction of trichloroacetonitrile and diborane in 1,2-dimethoxyethane at room temperature yields the iminoborane, $(CCl_3CH{:}NBH_2)_n$,[29] as a sublimable white solid, m.p. 116°.

$$2CCl_3C{:}N + B_2H_6 \longrightarrow \frac{2}{n}(CCl_3CH{:}NBH_2)_n$$

The degree of association of the compound was not determined.

On heating the dry solid explosions occur, but when heated in mineral oil for 2 hours at 140° N'N''N'''-tris(β,β,β-trichloroethyl)borazine results.[29]

$$(CCl_3CH{:}NBH_2)_n \longrightarrow \frac{n}{3}(CCl_3CH_2NBH)_3$$

This compound also results from the vapour-phase reaction of trichloroacetonitrile and diborane at 85°.[29]

Trifluoroacetonitrile and diborane in 1,2-dimethoxyethane yield

N'N''N'''-tris(β,β,β-trifluoroethyl)borazine, $(CF_3CH_2NBH)_3$, direct.[29] In ether or neat no reaction occurs,[30] apparently because trifluoroacetonitrile is too weak a donor to cleave the B···H···B bonds.

Several iminoboranes have been prepared by thioboration of nitriles,[31] a reaction analogous to the hydroborations discussed above. Thus reaction of acetonitrile with a series of esters of dialkylthioboronic acids in CCl_4 at room temperature gave a series of crystalline dimeric iminoboranes.[31]

$$2MeC{:}N + 2R_2BSR^1 \longrightarrow (MeC(SR^1){:}NBR_2)_2$$

where R = Pr, R^1 = Bu; R = Bu, R^1 = Bu; R = Pr, R^1 = Et; R = Ph, R^1 = Bu. On heating the compounds in vacuo the reverse reaction occurs.

Their infrared spectra in CCl_4 solution show a strong band assigned to C=N stretching at ca. 1629 $cm.^{-1}$ When the solutions are heated this band decreases in intensity and a new band appears at ca. 1820 $cm.^{-1}$ This band is assigned to a mode of the $>B{=}N{=}C<$ unit in a transiently stable monomeric iminoborane and its appearance provided the first evidence for the existence of such a species.

Similar behaviour has recently been reported for the aldiminoborane, $(Bu^tCH{:}NBBu_2)_2$.[32,33] This compound was prepared by two routes both of which are believed to proceed through di-n-butylborane, (Bu_2BH), as an intermediate, with subsequent insertion into the B-H bond.

$$Bu^tC{:}N + Bu_3B \xrightarrow{150\text{-}260^\circ} \frac{1}{n}(Bu^tCH{:}NBBu_2)_n + C_4H_8$$

$$3Bu^tC{:}N + BH_3,NEt_3 + 2Bu_3B \xrightarrow{110\text{-}130^\circ} \tfrac{3}{n}(Bu^tCH{:}NBBu_2)_2 + NEt_3$$

The compound is a crystalline solid, m.p. 74-76°, which boils/sublimes at 75°/0·3 mm. It is dimeric in cold benzene solution and probably in the solid but vapour density measurements show it to be monomeric in the vapour-phase at ca. 110°. Mass spectra run with inlet temperatures of 25° and 160° and variable-temperature ^{11}B n.m.r. studies in benzene support the conclusion that in the vapour-phase and in solution a monomer-dimer equilibrium exists which is displaced to the right at elevated temperatures.

$$(Bu^tCH{:}NBBu_2)_2 \rightleftharpoons 2Bu^tCH{:}NBBu_2$$

Like the iminoboranes $(MeC(SR^1){:}NBR_2)_2$, this compound shows a strong infrared absorption at 1674 $cm.^{-1}$ at room temperature which is replaced by a strong absorption at 1850 $cm.^{-1}$ at 120° (vapour). This behaviour is in strking contrast to that of acetaldiminodimethylborane.

$Bu^tCH{:}NBBu_2$ reacts with BCl_3 and BBr_3 at ca. 100° giving the dimeric aldiminoboron dihalides,[33] $(Bu^tCH{:}NBX_2)_2$.

$$2Bu^tCH{:}NBBu_2 + 2BX_3 \longrightarrow (Bu^tCH{:}NBX_2)_2 + 2BuBCl_2$$

X = Cl, Br

These two compounds showed no sign of dissociation into monomers at elevated temperatures.

Ketiminoboranes $(RR^1C{:}NBX_2)_n$ are in principle preparable by the insertion of a nitrile into a B–C bond.

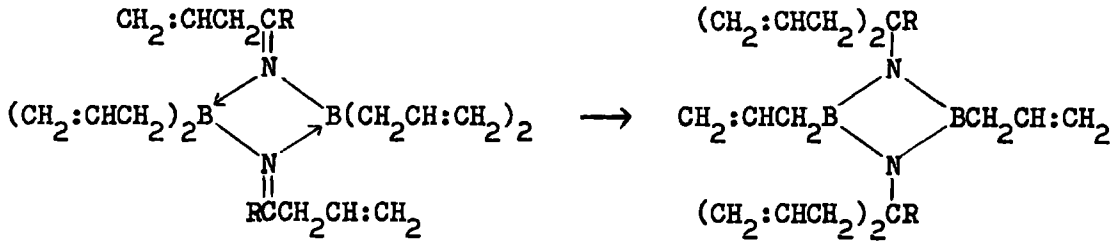
$$RC{:}N + R^1BX_2 \longrightarrow \frac{1}{n}(RR^1C{:}NBX_2)_n$$

However this reaction has so far been realised only using triallylborane, $(CH_2{:}CHCH_2)_3B$, which reacts with nitriles in isopentane at -30° giving dimeric ketiminoboranes[34] in over 90% yield.

$$RCN + (CH_2{:}CHCH_2)_3B \longrightarrow [CH_2{:}CHCH_2CR{:}NB(CH_2CH{:}CH_2)_2]_2$$

$$R = Me,\ Ph,\ CH_2{:}CH-$$

When these compounds are heated to 100° the dimers do not apparently dissociate but surprisingly a second allyl group is transferred from boron to carbon giving substituted 1,3-diaza-2,4-diborines.[34]



By contrast no sign of interaction was observed when mixtures of gaseous trimethyl- or triethylborane and gaseous or liquid acetonitrile had been left for two weeks at room temperature.[24]

In general B-C bonds exhibit a rather low susceptibility towards insertion of unsaturated groups compared with Li-C, Mg-C or Al-C bonds. Also nitriles are not in general found to be particularly reactive substrates in this type of reaction compared, for example, with ketones, $R_2C{:}O$, or isocyanates, RNCO.

An alternative approach to the preparation of ketiminoboranes was therefore required.

The first method investigated was the reaction between a ketimine, $RR^1C{:}NH$, and a tri-organoborane. This reaction is analogous to the well established method of attaching amino-groups to boron by use of secondary amines.[35]

$$R_2NH + R^1{}_3B \longrightarrow R_2NBR^1{}_2 + R^1H$$

Diphenylketimine, $Ph_2C{:}NH$, reacts with trimethylborane forming a 1:1 adduct, $Ph_2C{:}NH,BMe_3$.[36] On heating in a sealed tube at 160-200° for 24 hours methane is evolved and diphenylketiminodimethylborane is produced but was isolated only in 15% yield.[36]

$$Ph_2C{:}NH,BMe_3 \longrightarrow \tfrac{1}{2}(Ph_2C{:}NBMe_2)_2 + CH_4$$

The colourless crystalline compound, m.p. 173°, appears to be dimeric in solution and in the solid but a mass spectrum obtained using an inlet temperature of ca. 200° showed peaks arising only from the monomer, indicating that at 200° the compound is completely dissociated.

Diphenylketimine and triphenylborane were recovered unchanged after being heated together at 160° for several hours.[36] There was no evidence of adduct formation or of reaction to give an iminoborane.

Diphenylketimine and triethylborane reacted in a sealed tube kept at 155° for a week to give the N-substituted ketimine $Ph_2C{:}NCHPh_2$[36] rather than an iminoborane.

Attempts to prepare tris(diphenylketimino)borane, $(Ph_2C{:}N)_3B$, from trisdimethylaminoborane and diphenylketimine[37] or from boron trichloride and a two-fold excess of diphenylketimine[37] were unsuccessful due to incompleteness of the reaction and difficulties in separating the product. However this compound was isolated as a hydrolytically sensitive, apparently monomeric wax from the reaction of boron tribromide with 3 mol. of diphenylketiminolithium.[11]

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

Diphenylketiminolithium has also been used to prepare a series of diphenylketiminoborondihalides.[13]

$$Ph_2C{:}NLi + BX_3 \longrightarrow \frac{1}{n}(Ph_2C{:}NBX_2)_n + LiX$$

where X = F, Cl, Br, I

The dichloride, dibromide and di-iodide are crystalline dimeric solids. The difluoride is completely insoluble in all solvents tried and is believed to be polymeric. This property made it inseparable from the lithium fluoride produced and a pure sample was therefore obtained from the reaction of tris(diphenylketimino)borane with boron trifluoride etherate.[13]

$$(Ph_2C{:}N)_3B + 2BF_3 \longrightarrow \frac{2}{n}(Ph_2C{:}NBF_2)_n$$

It has recently been discovered that boron-halogen bonds will undergo insertion reactions with nitriles in which the C≡N group is attached to a relatively electron-withdrawing atom or group.[30] Using this reaction a series of highly-halogenated iminoboranes has been prepared.

Thus chloro- and bromocyanide react quantitatively at 0° in CCl_4 with BCl_3, BBr_3 or $PhBCl_2$ giving sublimable, crystalline, dimeric iminoboranes.[38]

$$2XC{:}N + 2BYZ_2 \longrightarrow (XZC{:}NBYZ)_2$$

where X=Y=Z=Cl; X=Y=Z=Br; X=Cl, Y=Z=Br; X=Br, Y=Z=Cl; X=Br, Y=Ph, Z=Cl; X=Cl, Y=Ph, Z=Cl.

Dimethylboronbromide reacts similarly with halocyanides giving low melting, dimeric products, $(XBrC{:}NBMe_2)_2$,[39] where X = Cl, Br.

These two compounds can be converted by distillation to monomers which slowly revert to the dimeric form.

The compounds $(Cl_2C{:}NBX_2)_2$, where X = Cl, Br, have also been prepared by a metathetical reaction in CCl_4 at -20° using $Cl_2C{:}NSCl$.[15]

$$2Cl_2C{:}NSCl + 2BX_3 \longrightarrow (Cl_2C{:}NBX_2)_2 + 2SClX$$

where X = Cl, Br

Perhalo-organic cyanides also insert into boron-halogen bonds. Thus trifluoro-[15] and trichloroacetonitrile[39] react with BCl_3 and BBr_3 giving sublimable, crystalline dimers.

$$2CX_3C{:}N + 2BX^1_3 \longrightarrow (CX_3CX^1{:}NBX^1_2)_2$$

where X=F, X^1=Cl; X=F, X^1=Br; X=Cl, X^1=Cl; X=Cl, X^1=Br

These compounds are dimeric in benzene solution but those derived from trichloroacetonitrile appear to be at least partly dissociated into monomers in CCl_4,[39] as shown by infrared absorptions at ca. 1840 $cm.^{-1}$, and also possibly in the vapour-phase.

Trichloroacetonitrile has been found to react in the same way with certain organoboron bromides.[39]

$$CCl_3CN + BrBXY \longrightarrow CCl_3CBr{:}NBXY$$

where X=Y=Ph; X=Y=Me; X=Br, Y=Ph; X=Br, Y=Me

The products are however extremely moisture sensitive liquids which, judging from their infrared spectra, exist mainly in the monomeric form in equilibrium with a small amount of dimeric form.

Pentafluorobenzonitrile, C_6F_5CN, reacts with BBr_3, $PhBBr_2$ and $MeBBr_2$ in boiling CCl_4 giving crystalline dimeric iminoboranes.[39]

$$2C_6F_5CN + 2Br_2BX \longrightarrow (C_6F_5CBr{:}NBBrX)_2$$

where X = Br, Ph or Me

Unlike the trichloroacetonitrile derivatives, the monomeric form of these compounds does not result from vacuum sublimation; the cyanide adducts, C_6F_5CN,Br_2BX, are instead obtained.[15,39]

Aluminium.

Following the previously mentioned isolation of the aldiminoaluminium derivative, $(PrCH{:}NAlBu^i_2)_n$,[9] from the reaction of propyl cyanide and di-i-butylaluminium hydride, several other similar derivatives have been prepared and characterised.

Thus dimethylaluminium hydride reacts below room temperature with nitriles giving colourless dimeric aldiminoaluminium derivatives, $(RCH{:}NAlMe_2)_2$, in 90% yield.[40,41]

$$2RCN + 2Me_2AlH \longrightarrow (RCH{:}NAlMe_2)_2$$

R = Me, Bu^t, Ph

Aldimino derivatives have also been obtained by pyrolysis of the adducts between triethylaluminium and t-butyl cyanide[41] and phenyl cyanide[40] at temperatures above 155°. The triethylaluminium in these reactions acts effectively as a source of diethylaluminium hydride by loss of a molecule of ethylene.

$$RCN + Et_3Al \longrightarrow RCN,AlEt_3 \longrightarrow [RCN,AlEt_2H] + C_2H_4$$

$$R = Bu^t, Ph \qquad \downarrow$$

$$\tfrac{1}{2}(RCH{:}NAlEt_2)_2$$

Aluminium-carbon bonds are relatively much more labile towards insertion of nitriles than are boron-carbon bonds. Thus adducts between nitriles and organoaluminium compounds rearrange at elevated temperatures (100-200°) giving dimeric ketiminoaluminium derivatives.[40,41,42,43,44]

$$RCN + AlR^1_3 \longrightarrow RCN,AlR^1_3 \longrightarrow \tfrac{1}{2}(RR^1C{:}NAlR^1_2)_2$$

where, for example, R=R¹=Ph; R=Bu^t, R¹=Me; R=Me, R¹=Ph; R=Et, R¹=Me

Good yields are obtained using t-butyl or phenyl cyanide but with methyl or ethyl cyanide yields are much lower. This is explained by the presence of hydrogen atoms on the α-carbon atoms of methyl and ethyl cyanide which allow the possibility of acidic reaction. As a consequence the main reaction involved in the pyrolysis of their adducts with organoaluminium compounds is cleavage of organic groups from aluminium giving rise to polymers,[41] e.g.

$$nCH_3CN,AlR_3 \longrightarrow (R_2AlCH_2CN)_n + nRH$$

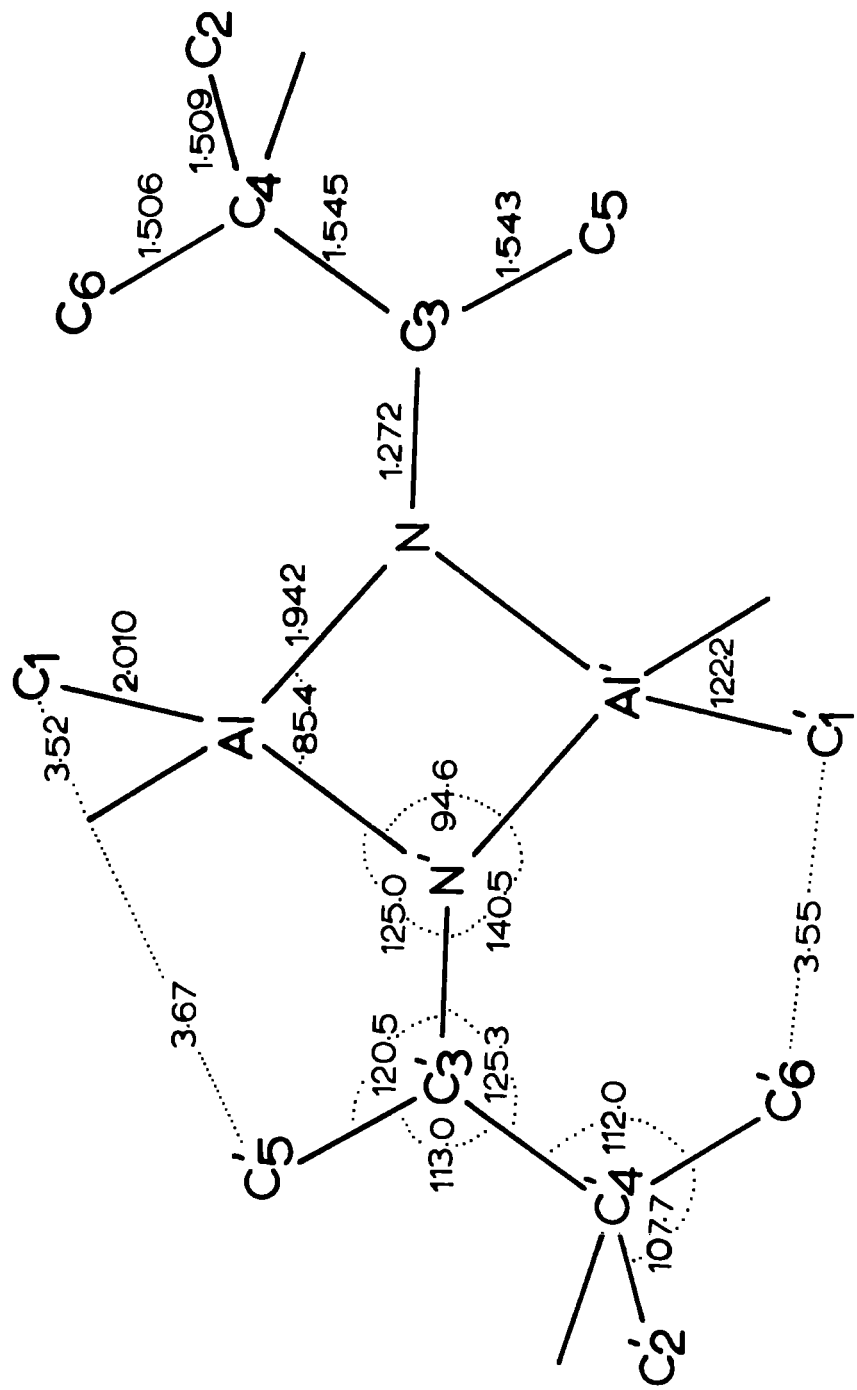
This reaction is analogous to that between methyl and ethyl cyanides and organolithium compounds.[11]

The reaction between diphenylketimine and organoaluminium compounds has also been studied as a route to ketiminoaluminium compounds.[12] In contrast to the analogous reactions involving tri-organoboranes,[36] alkane (or benzene) was in each case eliminated below 100° giving the crystalline ketiminoaluminium derivatives.

$$Ph_2C:NH + R_3Al \longrightarrow \tfrac{1}{2}(Ph_2C:NAlR_2)_2 + RH$$

$$R = Me, Et, Ph$$

In all cases where reliable molecular weight measurements have been made, azomethine derivatives of aluminium have proved to be dimeric. The structure of <u>trans</u>-$(Bu^tCMe:NAlMe_2)_2$ has been determined X-ray crystallographically[25] and is based on a four-membered aluminium-nitrogen ring, apparently the configuration adopted by all known azomethine derivatives, $(R^1R^2C:NAlR^3R^4)_2$, of aluminium. The results of the X-ray structure determination are shown in fig. 2.



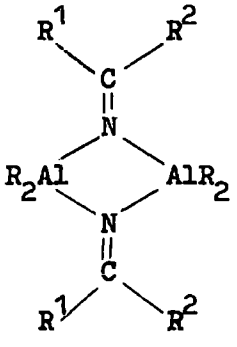
$(Bu^tMeCNAlMe_2)_2$

FIGURE 2.

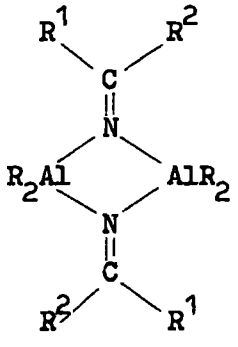
Apart from the greater Al-N bond length as compared with the B-N bond length in $(MeCH:NBMe_2)_2$, the main difference between the two structures is the distortion of the AlNC bond angles. This occurs presumably to accommodate the bulky Bu^t groups. The C=N bond length is again the same as that in dimethylglyoxime and the Al-C bond length of 2·01Å is in good agreement with the value of 1·99Å found for the terminal Al-C bonds in trimethylaluminium.[45]

The structures of $(Bu^tCMe:NAlMe_2)_2$ and $(MeCH:NBMe_2)_2$ are interesting in that considerable bond-angle strain at the tri-co-ordinate nitrogen might have been expected to be a consequence of the four-membered rings. A trimeric structure based on a six-membered $(MN)_3$ ring could accommodate a larger angle at nitrogen. Presumably entropy factors, which would favour dimers, outweigh such considerations.

As for the boron analogues, derivatives with unlike substituents on the azomethine carbon atom can in principle exist in two isomeric forms.



Cis



Trans

P.m.r. spectroscopic evidence for the existence of both cis and trans isomers has been published for $(MeCH{:}AlMe_2)_2$[41] and $(PhCMe{:}NAlMe_2)_2$,[40] but in the majority of cases only one isomer appears to be formed.

Gallium.

Unlike nitrile adducts of trimethylaluminium those of trimethylgallium do not afford ketimino derivatives of the metal on pyrolysis.[46] Thus when the adduct between acetonitrile and trimethylgallium is held at 145° for 6 hours the acetonitrile acts as a protic acid.[46] This reaction is the same as the cleavage reaction previously noted for the analogous aluminium adduct[41] except that in this case it is almost quantitative.

$$nCH_3CN,GaMe_3 \longrightarrow (Me_3GaCH_2CN)_n + nCH_4$$

When the adduct $Bu^tCN,GaMe_3$[46] was similarly treated no reaction occurred at all, while heating the adduct $PhCN,GaMe_3$[46] in a sealed tube for 5 hours at 118° resulted in trimerisation of the phenyl cyanide.

$$PhCN,GaMe_3 \longrightarrow (PhCN)_3 + GaMe_3$$

The thermal decomposition of the triethylgallium adducts, $PhCN,GaEt_3$[46] and $Bu^tCN,GaEt_3$,[46] follows a similar course to that of their aluminium counterparts.[40,41] Both lose ethylene at about 160° giving the dimeric aldimino derivatives $(PhCH{:}NGaEt_2)_2$ and $(Bu^tCH{:}NGaEt_2)_2$ respectively.

The only reported ketimino derivatives of gallium were obtained using a preformed ketimine.[47]

Diphenylketimine reacts with organogallium compounds in the same way as with organoaluminium compounds except that slightly higher temperatures (110–120°) are required to effect the elimination of alkane (or benzene).[47] The diphenylketimine derivatives obtained are again colourless, dimeric, crystalline compounds.

$$PhC{:}NH + GaR_3 \longrightarrow \tfrac{1}{2}(Ph_2C{:}NGaR_2)_2 + RH$$

R = Me, Et, Ph

Group IV.

Silicon.

The first azomethine derivative of silicon to be reported was benzaldiminotriethylsilane, $PhCH{:}NSiEt_3$[48] prepared by the reaction of phenyl cyanide and excess triethylsilane in the presence of zinc chloride at 200° in an autoclave.

$$PhCN + nEt_3SiH \longrightarrow PhCH{:}NSiEt_3 + (n-1)Et_3SiH$$

The product, obtained in 54% yield, is a liquid, b.p. 143°/17 mm.

The reaction of excess triethylsilane with aliphatic cyanides RCH_2CN, having hydrogen atoms attached to the α-carbon atom, is more complex.[48] After heating the reactants (in 2:1 molar proportions) to 140° for several days two liquid fractions were isolated, the aminosilane, $RCH_2CH_2NHSiEt_3$ and the iminosilane, $RCH(CN)C(CH_2R){:}NSiEt_3$.

Other higher boiling fractions remained in the distillation pot.

The aminosilane is possibly produced by hydrogenation of an intermediate iminosilane.

$$RCH_2CN + Et_3SiH \longrightarrow [RCH_2CH{:}NSiEt_3] \xrightarrow{2H} RCH_2CH_2NHSiEt_3$$

R = Me, Et

The reactions involved in the formation of $RCH(CN)C(CH_2R){:}NSiEt_3$ are less obvious. Treatment of $MeCH(CN)CEt{:}NSiEt_3$ with methanol yielded the iminonitrile, MeCH(CN)CEt:NH which when heated with triethylsilane for 40 hours in the presence of zinc chloride reacted with elimination of hydrogen regenerating the iminosilane.[48]

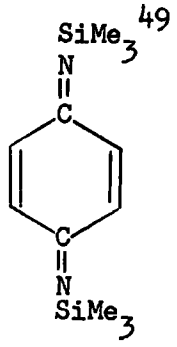
$$\begin{array}{l} MeCH\text{-}C\text{-}Et \\ \quad\;\; |\;\; \| \\ \quad CN\; N \\ \quad\quad\; H \end{array} + Et_3SiH \longrightarrow \begin{array}{l} MeCH\text{-}C\text{-}CEt \\ \quad\;\; |\;\; \| \\ \quad CN\; N \\ \quad\quad\; SiEt_3 \end{array} + H_2$$

During an investigation of the chemistry of sodium bis(trimethylsilyl)amide, $NaN(SiMe_3)_2$, it was found that non-enolisable aldehydes and ketones afforded N-trimethylsilyl azomethine derivatives with this reagent.[49]

$$NaN(SiMe_3)_2 + R^1R^2C{=}O \longrightarrow R^1R^2C{=}NSiMe_3 + NaOSiMe_3$$

where $R^1{=}R^2{=}Ph$; $R^1{=}Ph$, $R^2{=}H$

This route has since been used to prepare several other imino-silanes viz.



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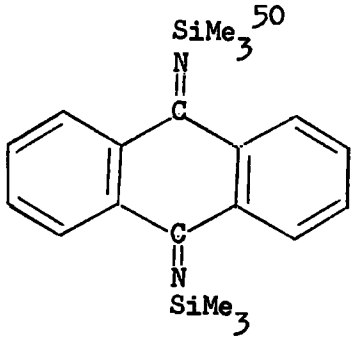

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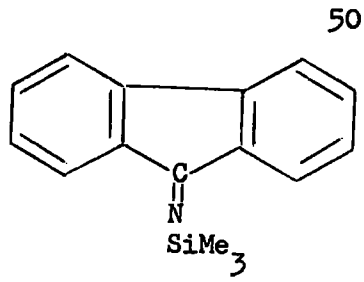

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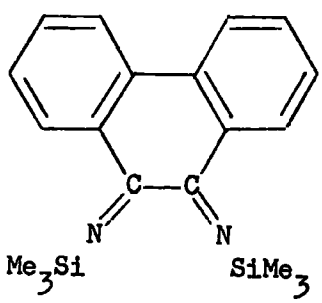

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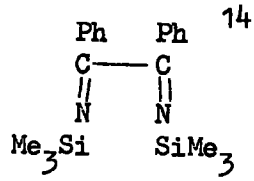

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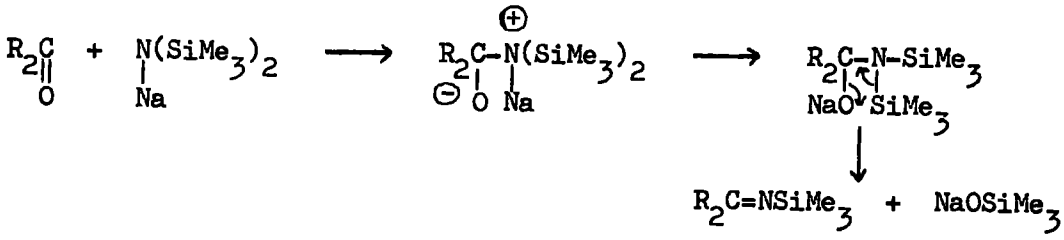
$(CF_3)_2C{:}NSiMe_3$ [50] $(CF_2Cl)_2C{:}NSiMe_3$ [50]

The reaction is thought to proceed thus:



It is unsuitable as a route to N-trimethylsilyl derivatives of aliphatic ketimines or aldimines since carbonyl compounds having hydrogen atoms attached to the α-carbon atom react in the enol form giving hexamethyldisilazane and the sodium enolate only.[51]

$$-\underset{H}{\overset{|}{C}}H-\underset{O}{\overset{||}{C}}- \;+\; NaN(SiMe_3)_2 \longrightarrow -CH=\underset{ONa}{\overset{|}{C}}- \;+\; HN(SiMe_3)_2$$

After the work on silicon described in this thesis was completed, the preparation of a series of ketiminosilanes by a route very similar to that used in the present work, i.e. reaction of a ketiminolithium compound with a silicon halide, was reported.[50]

$$nR^1R^2C{:}NLi \;+\; R^3_{4-n}SiX_n \longrightarrow (R^1R^2C{:}N)_nSiR^3_{4-n} \;+\; nLiX$$

where, for example, n=1, R^1=R^2=Ph, R^3=Me; n=1, R^1=p-tolyl, R^2=Ph, R^3=Me; n=3, R^1=R^2=Ph, R^3=Ph

All the ketiminosilanes which have been prepared by these two routes are moisture sensitive, yellow oils or crystalline solids, miscible with most organic solvents. Compounds containing amino, chlorine or alkoxy groups on silicon are less thermally stable than the others, apparently disproportionating on heating.[50]

$$2Ph_2C{:}NSiMe_2X \longrightarrow (Ph_2C{:}N)_2SiMe_2 \;+\; X_2SiMe_2$$

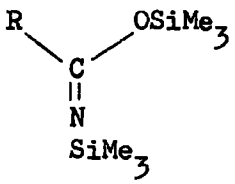
X = NEt_2, Cl

Diphenylketiminotriethoxysilane, $Ph_2C{:}NSi(OEt)_3$, gave tetraethoxysilane on attempted distillation.[50]

With the exception of the two fluorinated compounds, all the iminosilanes showed a strong absorption in their infrared spectra, due to the C=N stretching vibration between 1630 and 1690 $cm.^{-1}$

As a result of a study of their ultraviolet spectra it was concluded that pπ-dπ interaction between nitrogen and silicon is not strong in these compounds.[50]

Bis(trimethylsilyl)carboxylic acid amide derivatives, $RCON(SiMe_3)_2$, have been prepared by several methods[52,53,54] and are believed, on the basis of infrared and p.m.r. evidence, to exist at room temperature in form I rather than form II.[54]



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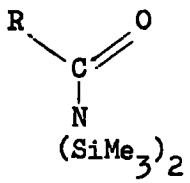


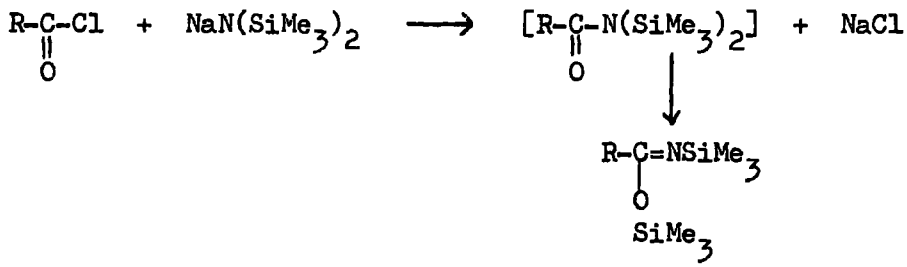
II

Bis(trimethylsilyl)acetamide, $MeC(OSiMe_3){:}NSiMe_3$, obtained by the reaction of acetamide with trimethylchlorsilane in the presence of triethylamine, was the first compound of this class to be prepared.[52]

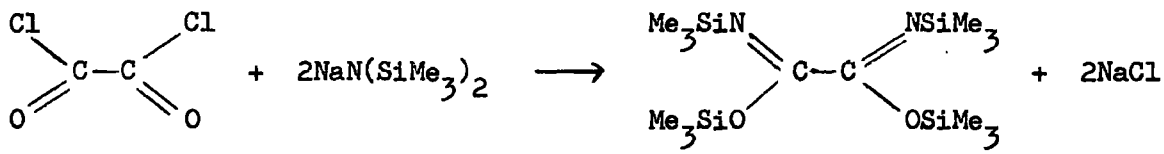
$$MeCONH_2 + 2Me_3SiCl + 2Et_3N \longrightarrow MeC(OSiMe_3){:}NSiMe_3 + 2Et_3N,HCl$$

It is a colourless, hydrolytically sensitive liquid, b.p. 67·5°/30 mm. It has been found particularly useful in preparing trimethylsiloxy derivatives, suitable for vapour-phase chromatography, of various organic compounds.[55] The compound $CH_2{:}CHC(OSiMe_3){:}NSiMe_3$, b.p. 73·5°/22 mm. was prepared similarly.[52]

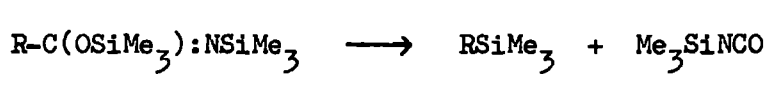
Reaction of carboxylic acid chlorides with sodium bis(trimethylsilyl)amide also gives compounds of this type.[54]



R = Ph, ^{t}Bu, 2-pyridyl, MeO, EtO



The compounds are hydrolytically sensitive liquids which can be distilled in vacuo. The methoxy and ethoxy derivatives are extremely thermally unstable and on briefly refluxing at atmospheric pressure are quantitatively decomposed.[54]



R = MeO, EtO

The t-butyl and phenyl derivatives are much more thermally stable being incompletely decomposed after refluxing for many hours.[54]

$$R\text{-}C(OSiMe_3):NSiMe_3 \longrightarrow RCN + (Me_3Si)_2O$$

$$R = {}^tBu,\ Ph$$

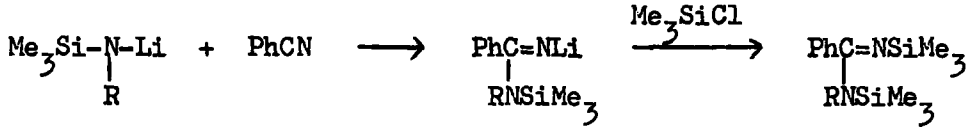
Besides the above preparation, bis(trimethylsilyl)benzamide, $PhC(OSiMe_3):NSiMe_3$, has been obtained by reaction of sodium bis(trimethylsilyl)amide with a variety of other derivatives of benzoic acid viz. $PhCOOMe$, $PhCOOSiMe_3$, $(PhCO)_2O$ and $PhCONHSiMe_3$.[53] In the last case the analogous amidine derivative, $PhC(NHSiMe_3):NSiMe_3$, is also obtained in 25% yield.

$$\begin{matrix} PhC{=}O \\ | \\ HNSiMe_3 \end{matrix} + NaN(SiMe_3)_2 \longrightarrow \begin{matrix} PhC{=}NSiMe_3 \\ | \\ HNSiMe_3 \end{matrix} + NaOSiMe_3$$

N,N'-bis(trimethylsilyl)benzamidine is a colourless, crystalline solid, m.p. 73-75°. It is less thermally stable than bis(trimethylsilyl)-benzamide, decomposing in an analogous manner on heating.[53]

$$PhC(NHSiMe_3):NSiMe_3 \longrightarrow PhCN + (Me_3Si)_2NH$$

The N-methyl and -ethyl analogues of this compound have been prepared from the appropriate amidino-lithium compound (prepared in situ) and trimethylchlorsilane.[56]



R = Me, Et

The p.m.r. spectra of these amidine derivatives in CCl_4 show evidence of intramolecular exchange of Me_3Si groups at room temperature;[56] the Me_3Si protons appearing as a broad singlet at 35° which is split into two sharp singlets at -30°.

The amidino-silanes, $PhC(NHMe):NSiMe_3$, $PhC(NMe_2):NSiMe_3$, $PhC(NMe_2):NSiMe_2Cl$ and $[PhC(NMe_2):N]_2SiMe_2$ were similarly obtained as low melting, hydrolytically sensitive solids from the appropriate amidino-lithium compound (prepared in situ) and the appropriate chlorosilane.[56]

The compound $PhC(NHMe):NSiMe_3$ shows evidence of Me_3Si exchange similar to that discussed above for the bis(trimethylsilyl)amidines.[56] The dimethylamino derivatives however show no evidence of exchange processes in their p.m.r. spectra.[56]

Organic cyanates react quantitatively at room temperature with trimethylsilyl derivatives of secondary amines giving compounds of the

type $ROC(NR^1_2):NSiMe_3$.[57]

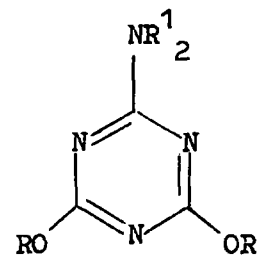
$$ROCN + R^1_2NSiMe_3 \longrightarrow ROC(NR^1_2)=NSiMe_3$$

where, for example, R = Ph, $NR^1_2 = NEt_2$; R = p-tolyl, NR^1_2 = 

The compounds are colourless, high boiling liquids, which can be distilled in vacuo. Above 150° they decompose into the silylether and diorganocyanamide.[57]

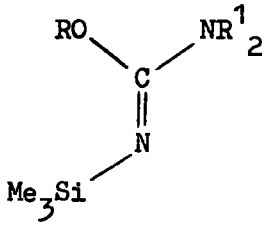
$$ROC(NR^1_2)=NSiMe_3 \longrightarrow ROSiMe_3 + R^1_2N\text{-}CN$$

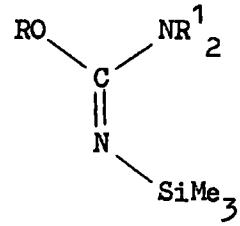
With 2 mol. of arylcyanate substituted 2-amino-4,6-diaryoxy-1,3,5-triazines are produced in an exothermic reaction.[57]

$$ROC(NR^1_2)=NSiMe_3 + 2ROCN \longrightarrow \text{  } + ROSiMe_3$$

In each case two strong absorptions assignable to C=N stretching occur between 1755 and 1685 $cm.^{-1}$ in the infrared spectra of these iminosilanes, $ROC(NR^1_2):NSiMe_3$. This was taken as evidence of syn-anti

isomerism in these compounds.[57]

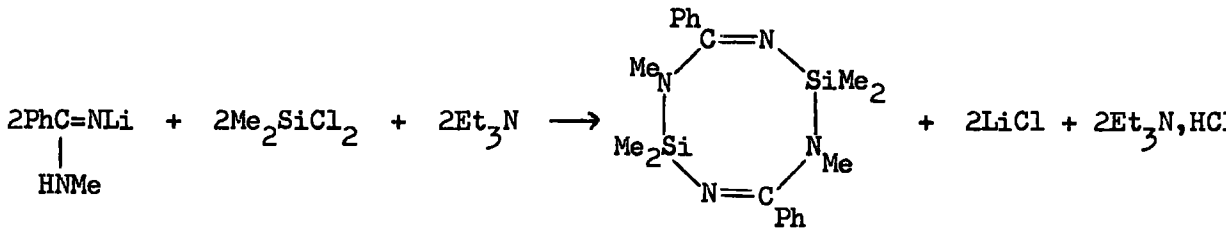




However no evidence for the existence of two isomers could be obtained from the p.m.r. spectrum of $PhOC(NEt_2):NSiMe_3$ in CS_2 even at -97°.[57]

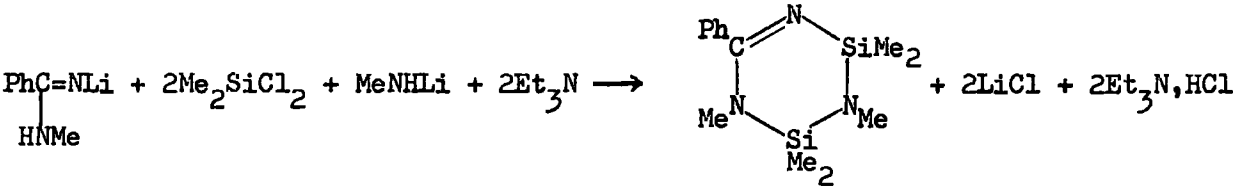
Cyclic iminosilanes.

Reaction of the amidino-lithium compound, PhC(NHMe):NLi, with an equimolar amount of dichlorodimethylsilane in the presence of triethylamine gives an eight-membered heterocycle.[58]



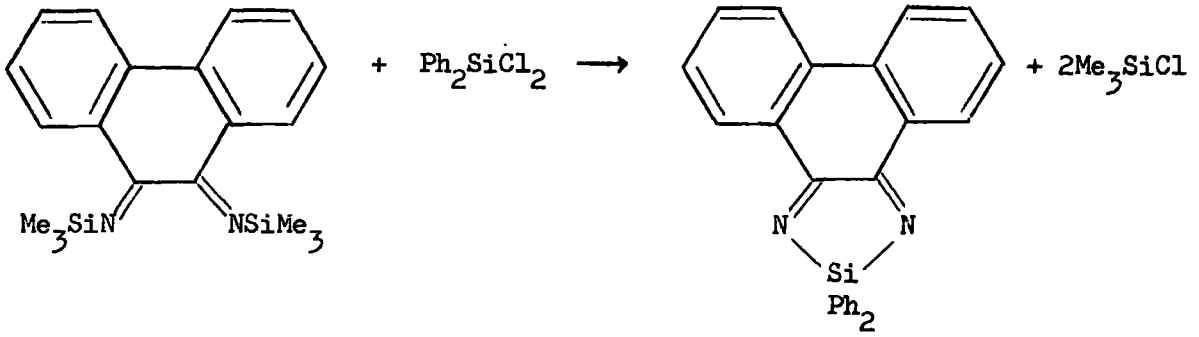
The product is a hydrolytically sensitive, colourless solid, m.p. 77-79°. The p.m.r. spectrum of this compound in CCl_4 recorded between 0 and 50° indicates the presence of several conformational isomers.[58]

If lithium methylamide, MeNHLi, is also present during the reaction, a six-membered heterocycle is formed containing only one C=N bond.[58]

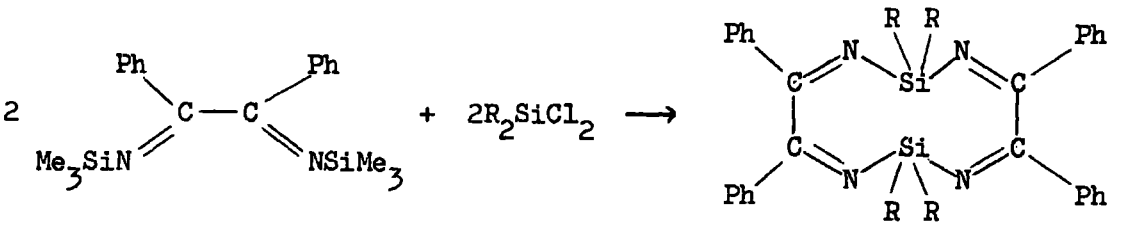


The product is a hydrolytically sensitive, colourless solid, m.p. 62-64°. However the p.m.r. spectrum of this compound at room temperature contains five sharp signals only, arising from the phenyl group and the four magnetically non-equivalent methyl groups.[58]

The 1,2-bis(trimethylsilyl)imino derivative of phenanthraquinone reacts with dichlorodiphenylsilane to give a five-membered heterocycle.[14]



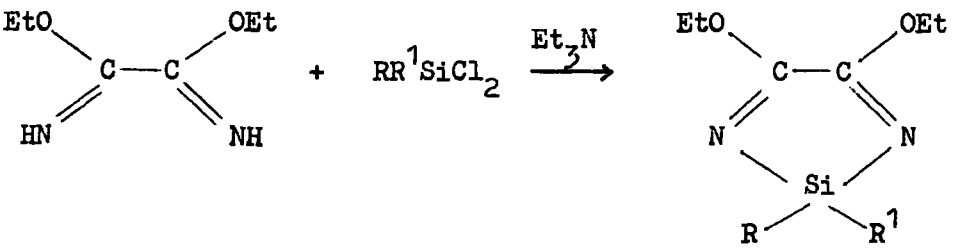
By contrast the 1,2-bis(trimethylsilyl)imino derivative of benzil gives ten-membered heterocycles with dichlorodiphenylsilane and with dichlorodiethylsilane.[14]



R = Et, Ph

+ $4Me_3SiCl$

Similar ring systems have also been obtained from the reaction of diethyloxalimidate with dichlorodiorganosilanes.[59]



$R=R^1=Me$; $R=Me$, $R^1=Ph$; $R=R^1=OEt$

When $R=R^1=OMe$ the ten-membered ring is obtained.

Germanium, Tin and Lead.

No aldimino derivatives of these compounds have been reported. However diphenylketimino derivatives of germanium and tin have been prepared by the reaction of diphenylketiminolithium with triorganometal halides.[50]

$$R_3MX + Ph_2C{:}NLi \longrightarrow Ph_2C{:}NMR_3 + LiX$$

R = Me, Ph; M = Ge, Sn

The ketimino derivatives are bright yellow hydrolytically sensitive solids (except for $Ph_2C{:}NGeMe_3$, a liquid b.p. 109-110°/0·17 mm.). The C=N stretching frequency is found ca. 1630 $cm.^{-1}$ for the germanium compounds and at 1613 $cm.^{-1}$ for the tin compounds.[50]

N-trimethylgermyl and stannyl derivatives of N'N'-dimethylbenzamidine are obtained in the same way as their silicon analogues.[56]

$$PhC(NMe_2){:}NLi + Me_3MCl \longrightarrow PhC(NMe_2){:}NMMe_3 + LiCl$$

M = Ge, Sn

The tin compound has also been obtained by an insertion reaction between phenyl cyanide and Me_2NSnMe_3 which goes in good yield under very mild conditions.[60,61]

$$PhC{:}N + Me_2NSnMe_3 \longrightarrow PhC(NMe_2){:}NSnMe_3$$

Diethylaminotributyl-lead, Et_2NPbBu_3, is reported to react with phenyl cyanide in the same way.[62]

$$PhC{:}N + Et_2NPbBu_3 \longrightarrow PhC(NMe_2){:}NPbBu_3$$

Organic cyanides, RCH_2CN, containing α-hydrogen atoms do not afford amidine derivatives on reaction with Me_2NSnMe_3[61] but instead act, as has been noted in other systems, as protic acids. Thus with methyl cyanide dimethylamine is quantitatively evolved.[61]

The compounds $PhC(NMeSiMe_3):NMMe_3$ where M = Ge, Sn and Pb, have been obtained as colourless oils in the same way as their silicon analogues.[56]

$$PhC(NMeSiMe_3):NLi + Me_3MCl \longrightarrow PhC(NMeSiMe_3):NMMe_3$$

M = Ge, Sn, Pb

An attempt to prepare the tin compound by reaction of $Me_3SiN(Me)SnMe_3$ with phenyl cyanide was not successful. The reactants were recovered unchanged after 3 hours at 150°.[56]

These three compounds show no evidence of exchange processes in their p.m.r. spectra.[56]

Trichloroacetonitrile has been found to insert under very mild conditions into Sn-O[63] and Pb-O[64] bonds affording N-substituted azomethine derivatives.

$$CCl_3C{:}N + MeOSnBu_3 \longrightarrow CCl_3C(OMe):NSnBu_3$$

$$CCl_3C{:}N + MeOPbPh_3 \longrightarrow CCl_3C(OMe):NPbPh_3$$

$$CCl_3C{:}N + Ph_3PbOPbPh_3 \longrightarrow CCl_3C(OPbPh_3):NPbPh_3$$

N-metal substituted ketenimines and carbodiimides.

The only carbodiimide or ketenimine-metal derivatives which have been fully characterised involve Group IV metals.

Ketenimine derivatives.

(a) Silicon

Nitriles, $RCH_2C{:}N$, having hydrogen atoms attached to the α-carbon atom react with bases such as sodium or $NaN(SiMe_3)_2$ giving sodium salts which with trimethylchlorosilane afford keteniminotrimethylsilanes,[51,65] e.g.[51]

$$CH_3C{:}N + 3NaN(SiMe_3)_2 \longrightarrow (C{=}C{=}N)^{3-},3Na^+ \xrightarrow{3Me_3SiCl} (Me_3Si)_2C{:}C{:}NSiMe_3$$

Similarly obtained are $Ph_2C{:}C{:}NSiMe_3$[51] and $Ph(Me_3Si)C{:}C{:}NSiMe_3$.[51] Using sodium or sodamide as the base, $Me_3SiCH{:}C{:}NSiMe_3$[65] and $PhCH{:}C{:}NSiMe_3$[65] were obtained but were thought to be contaminated with the isomeric cyanides, $(Me_3Si)_2CHC{:}N$ and $Ph(Me_3Si)CHC{:}N$.

Keteniminotrimethylsilanes are described as yellow, high boiling liquids which exhibit much greater thermal stability than their organic counterparts. Their infrared spectra all show a strong absorption ca. 2020 $cm.^{-1}$ due to C:C:N stretching.[51,65]

Surprisingly $Me_3SiCH{:}C{:}NSiMe_3$[65] is not hydrolysed when stirred overnight with water. It rearranges instead into bis(trimethylsilyl)-

acetonitrile, $(Me_3Si)_2CHCN$. The same rearrangement also occurs when the compound is heated at 100° for 6 hours with aniline.[65]

(b) Tin and Lead.

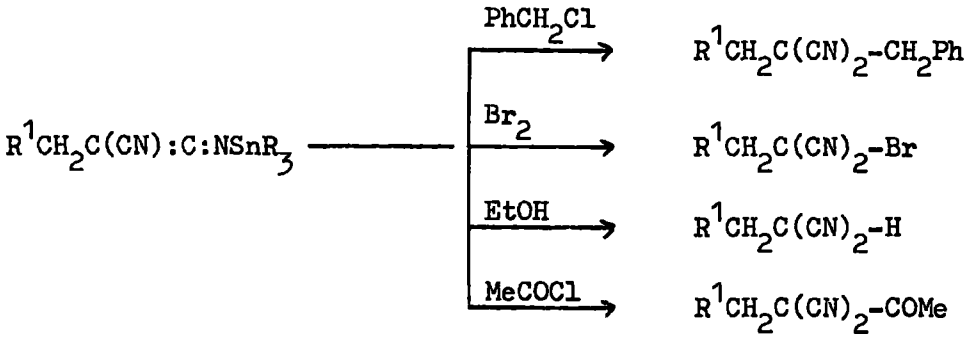
In contrast to their lack of reaction with simple nitriles,[66] organotin hydrides, R_3SnH, react exothermically at 20° with alkylidene malononitriles, $R^1CH{:}C(CN)_2$, giving as 1,4-addition products N-stannylketenimines, $R^1CH_2C(CN){:}C{:}NSnR_3$.[67]

$$R^1CH{:}C(CN)_2 + HSnR_3 \longrightarrow R^1CH_2{-}C(CN){:}C{:}NSnR_3$$

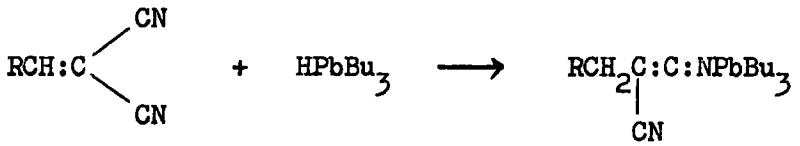
where, for example, R^1 = Me, EtO, Ph, $p\text{-}NO_2C_6H_4$; R = Et, Bu.

They are bright yellow, hydrolytically and thermally sensitive, viscous, undistillable oils. Their average molecular weight in benzene increases rapidly with concentration, possibly by association through penta-co-ordinate tin. All show a very intense band due to C:C:N stretching between 2060 and 2110 $cm.^{-1}$ in their infrared spectra.[67]

N-stannylketenimines are very reactive and give substituted malononitrile derivatives with a variety of reagents under mild conditions,[68] e.g.



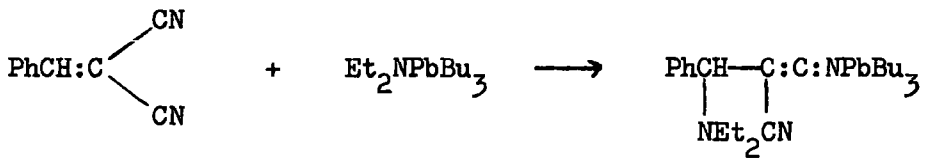
The analogous lead derivatives have been prepared in exactly the same way as the tin compounds.[69]



R = Ph, Me

Their physical and chemical properties appear almost identical to those of their tin analogues.[69]

Diethylaminotributyl-lead, Et_2NPbBu_3, reacts with benzylidene malononitrile, $PhCH:C(CN)_2$, in the same way as tributyl-lead hydride giving the ketenimine derivative, $PhCH(NEt_2)C(CN):C:NPbBu_3$.[62]



Carbodiimide derivatives.

Carbodiimide derivatives of the Group IV metals have been prepared by a great variety of methods, e.g.

$$Ag_2CN_2 + 2H_3SiI \longrightarrow H_3SiN{:}C{:}NSiH_3 + 2AgI \quad [70]$$

$$2NaN(SiMe_3)_2 + COCl_2 \longrightarrow Me_3SiN{:}C{:}NSiMe_3 + (Me_3Si)_2O + 2NaCl \quad [71]$$

$$Me_3SiN{:}C{:}NSiMe_3 + 2H_3GeF \longrightarrow H_3GeN{:}C{:}NGeH_3 + 2Me_3SiF \quad [73]$$

$$2Ph_3SnCl + NaNHCN \longrightarrow Ph_3SnN{:}C{:}NSnPh_3 + HCl + NaCl \quad [74]$$

The preparation of silyl-substituted carbodiimides has been surveyed in a review on carbodiimides.[72]

With the exception of a series of polymeric silicon derivatives,[75] $(-SiRR^1-N{:}C{:}N-)_n$ where $R=R^1=Me$; $R=Me$, $R^1=Ph$ etc., bis-organosilyl-carbodiimides are generally colourless, hydrolytically sensitive, mobile liquids which distil undecomposed at atmospheric pressure up to 240°. Disilyl-[70] and digermylcarbodiimide,[73] $H_3MN{:}C{:}NMH_3$, M = Si, Ge, are however much less stable, decomposing after a few hours at room temperature.

$H_3SiN{:}C{:}NSiH_3$, the first compound of this class to be prepared,[70] was shown to have a carbodiimide structure rather than a cyanamide structure, $(H_3Si)_2N{\cdot}C{:}N$, by its ^{14}N n.m.r. spectrum[76] and also its vibrational spectra.[77] However it was not found possible to distinguish between a completely linear structure, I, which would allow

maximum pπ-dπ interaction between nitrogen and silicon, and one involving

I II

angular SiNC units, II; although it is thought that the SiNC bond angles must be at least of the order of 150°.[77]

Similar studies on $H_3GeN{:}C{:}NGeH_3$ indicate that it has a carbodiimide structure with angular GeNC units.[73]

A carbodiimide structure was also assigned to $(Me_3Si)_2CN_2$ on the basis of the synthetic routes by which it was obtained and its infrared spectrum.[71] A dipole moment of 1·31 Debye units has been determined for this compound.[50]

Tabular survey of azomethine derivatives of the electropositive elements.

Group I $(R^1R^2C{:}NM,D)_n$

M	R^1	R^2	D	n	$\nu_{C=N}$, $cm.^{-1}$	ref.
Li	Ph	Ph	-	polymer	1620	11
Li	Ph	Me	-	polymer	1629	11
Li	Me_2N	Me_2N	-	2	1632	11
Li	Ph	Ph	T.H.F.	?	1618	11
Li	Ph	Ph	py	?	1616	11

Group II $(R^1R^2C{:}NMR^3)_n,D$

M	R^1	R^2	R^3	D	n	$\nu_{C=N}$, $cm.^{-1}$	ref.
Mg	Ph	Et	Et	-	13-21	1626	16
Mg	Bu^t	Et	Et	xT.H.F.	?	1631	16
Zn	Ph	Ph	Me	-	2	1624	17
Zn	Ph	Ph	Et	-	2	1611	17
Zn	Ph	Ph	Ph	-	2	1607	17
Zn	Ph	Ph	Me	2py	1	1613	17
Zn	Ph	Ph	Ph_2CN	-	polymer	1600	17

Group III

Boron $(R^1R^2C{:}NBR^3R^4)_n$

R^1	R^2	R^3	R^4	n	$\nu_{C=N}$ or $\nu_{C=N\cdots B}$ cm.$^{-1}$	ref.
Me	H	H	Bu^t	2	1660	23
Et	H	H	Bu^t	2	1660	23
Pr	H	H	Bu^t	2	1660	23
Pr^i	H	H	Bu^t	2	1660	23
Ph	H	H	Bu^t	2	1640	23
p-$MeOC_6H_4$	H	H	Bu^t	2	1640	23
p-ClC_6H_4	H	H	Bu^t	2	1640	23
p-FC_6H_4	H	H	Bu^t	2	1640	23
p-MeC_6H_4	H	H	Bu^t	2	1640	23
m-MeC_6H_4	H	H	Bu^t	2	1640	23
Me	H	Me	Me	2	1698	24
Me	H	Et	Et	2	1692	24
Bu^t	H	Bu	Bu	2	1674	33
				1[a]	1850	
Bu^t	H	Cl	Cl	2	1684	33
Bu^t	H	Br	Br	2	1662	33
CCl_3	H	H	H	?	?	29
Me	C_3H_5	C_3H_5	C_3H_5	2	?	34

Boron (continued)

R^1	R^2	R^3	R^4	n	$\nu_{C=N}$ or $\nu_{C=N\cdots B}$ cm.$^{-1}$	ref.
Ph	C_3H_5	C_3H_5	C_3H_5	2	?	34
CH_2:CH	C_3H_5	C_3H_5	C_3H_5	2	?	34
BuS	Me	Pr	Pr	2	1629	31
				1[b]	1820	
BuS	Me	Bu	Bu	2	1629	31
				1[b]	1820	
EtS	Me	Pr	Pr	2	1629	31
				1[b]	1820	
BuS	Me	Ph	Ph	2	1629	31
				1[b]	1820	
Ph	Ph	Me	Me	2	1662	36
Ph	Ph	F	F	polymer	1620	13
Ph	Ph	Cl	Cl	2	1590	13
Ph	Ph	Br	Br	2	1586	13
Ph	Ph	I	I	2	1602	13
Ph	Ph	Ph_2CN	Ph_2CN	1	1667	11
Cl	Cl	Cl	Cl	2	1648, 1602	15, 38
Cl	Cl	Br	Br	2	1655, 1605	15
Br	Cl	Cl	Cl	2	1615	38

Boron (continued)

R^1	R^2	R^3	R^4	n	$\nu_{C=N}$ or $\nu_{C=N\cdots B}$ $cm.^{-1}$	ref.
Br	Cl	Br	Br	2	1603	38
Br	Br	Br	Br	2	1600	38
Cl	Cl	Cl	Ph	2	1635	38
Br	Cl	Cl	Ph	2	1630	38
Br	Cl	Me	Me	2	1650	39
				1[a]	1810	
Br	Br	Me	Me	2	1640	39
				1[a]	1840	
CF_3	Cl	Cl	Cl	2	1663	30
CF_3	Br	Br	Br	2	1645	30
CCl_3	Cl	Cl	Cl	2	1640	39
				1[c]	1825	
CCl_3	Br	Br	Br	2	1610	39
				1[c]	1840	
CCl_3	Br	Br	Ph	1	1842	39
CCl_3	Br	Br	Me	1	1835	39
				2[d]	1680	
CCl_3	Br	Ph	Ph	1	1840	39

Boron (continued)

R^1	R^2	R^3	R^4	n	$\nu_{C=N}$ or $\nu_{C=N\cdots B}$ $cm.^{-1}$	ref.
CCl_3	Br	Ph	Ph	1	1840	39
				2[d]	1597	
C_6F_5	Br	Br	Ph	2	1650	39
C_6F_5	Br	Br	Me	2	1655	39
C_6F_5	Br	Br	Br	2	1645	39

a - obtained on heating dimer.

b - obtained on heating CCl_4 solution of dimer.

c - equilibrium constituent in CCl_4 solution.

d - minor equilibrium constituent.

Aluminium $(R^1R^2C{:}NAlR^3R^4)_2$

R^1	R^2	R^3	R^4	$\nu_{C=N}$, $cm.^{-1}$	ref.
Me	H	Me	Me	1675	41
Bu^t	H	Me	Me	1661	41
Ph	H	Me	Me	1630	40
Bu^t	H	Et	Et	1656	41
Ph	H	Et	Et	1633	40
Pr	H	Bu^i	Bu^i	?	9
Me	Me	Me	Me	1658	41
Et	Me	Me	Me	1653	41
Bu^t	Me	Me	Me	1630	41
Ph	Me	Me	Me	1634	40
Me	Et	Et	Et	1650	41
Me	Ph	Ph	Ph	1621	41
Bu^t	Ph	Ph	Ph	1616	41
Ph	Ph	Ph	Ph	1604	40,12,42
Me	Me	Cl	Me	1650	41
Bu^t	Me	Cl	Me	1625	41
Ph	Me	Cl	Me	1619	40
Ph	Me	Cl	Cl	?	43,44
Ph	Ph	Me	Me	1616	12
Ph	Ph	Et	Et	1609	12

Gallium $(R^1R^2C{:}NGaR^3R^4)_2$

R^1	R^2	R^3	R^4	$\nu_{C=N}$, $cm.^{-1}$	ref.
Bu^t	H	Et	Et	1658	46
Ph	H	Et	Et	1633	46
Ph	Ph	Me	Me	1626	47
Ph	Ph	Et	Et	1613	47
Ph	Ph	Ph	Ph	1612	47

Group IV

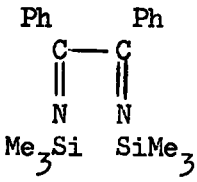
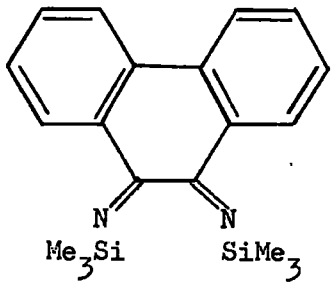
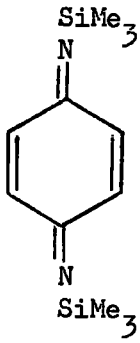
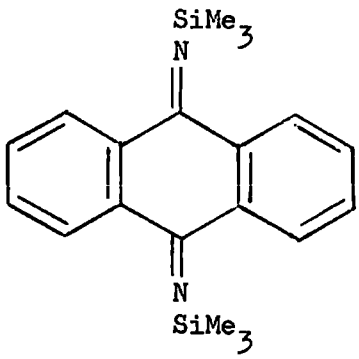
Silicon $R^1R^2C{:}NSiR^3R^4R^5$

R^1	R^2	R^3	R^4	R^5	$\nu_{C=N}$, $cm.^{-1}$	ref.
Ph	H	Et	Et	Et	?	48
MeCH(CN)	Et	Et	Et	Et	?	48
EtCH(CN)	Pr	Et	Et	Et	?	48
Ph	H	Me	Me	Me	1700,1652	49
Ph	Ph	Me	Me	Me	1653	49,50
Ph	Ph	Et	Et	Et	1657	50
Ph	Ph	Pr^i	Pr^i	Pr^i	1670	50
Ph	Ph	Bu	Bu	Bu	1655	50
Ph	Ph	Ph	Ph	Ph	1662	50

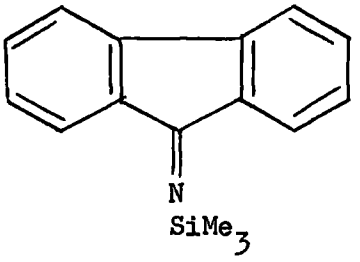
Silicon (continued)

R^1	R^2	R^3	R^4	R^5	$\nu_{C=N}$, $cm.^{-1}$	ref.
Ph	Ph	CH_2Ph	CH_2Ph	CH_2Ph	1658	50
Ph	Ph	Me	Me	$CHCl_2$	1645	50
Ph	Ph	Me	Me	$CH:CH_2$	1640	50
Ph	Ph	Me	Me	$CH_2CH:CH_2$	1647	50
Ph	Ph	Me	Me	NEt_2	1653	50
Ph	Ph	Me	Me	OBu	1650	50
p-ClC_6H_4	Ph	Me	Me	Me	1645	50
m-ClC_6H_4	Ph	Me	Me	Me	1652	50
o-ClC_6H_4	Ph	Me	Me	Me	1658	50
p-MeC_6H_4	Ph	Me	Me	Me	1643	50
m-MeC_6H_4	Ph	Me	Me	Me	1650	50
o-MeC_6H_4	Ph	Me	Me	Me	1641	50
p-$MeOC_6H_4$	Ph	Me	Me	Me	1645	50
p-MeC_6H_4	p-MeC_6H_4	Me	Me	Me	1643	50
o-MeC_6H_4	o-MeC_6H_4	Me	Me	Me	1647	50
CF_3	CF_3	Me	Me	Me	1780	50
CF_2Cl	CF_2Cl	Me	Me	Me	1780	50
Ph	Me	Me	Me	Me	1690	50

Silicon (continued)

	$\nu_{C=N}$, $cm.^{-1}$	ref.
	?	14
	?	14
	?	49
	1678	50

Silicon (continued)

	$\nu_{C=N}$, cm.$^{-1}$	ref.
	1670	50
$(Ph_2C{:}N)_2SiMe_2$	1630	50
$(Ph_2C{:}N)_3SiMe$	1643	50
$(Ph_2C{:}N)_2SiPh_2$	1669	50
$(Ph_2C{:}N)_3SiPh$	1670	50

$R^1R^2C{:}NSiMe_3$

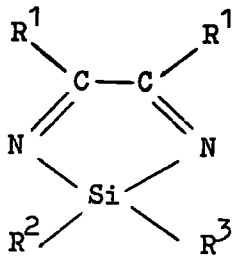
R^1	R^2	$\nu_{C=N}$, cm.$^{-1}$	ref.
Me	Me_3SiO	?	52
Ph	Me_3SiO	1695	53,54
Bu^t	Me_3SiO	1725	54
1-pyridyl	Me_3SiO	?	54
MeO	Me_3SiO	1697	54
EtO	Me_3SiO	?	54
$(Me_3SiO{-}C{=}NSiMe_3)_2$		1720, 1685	54

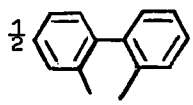
Silicon (continued)

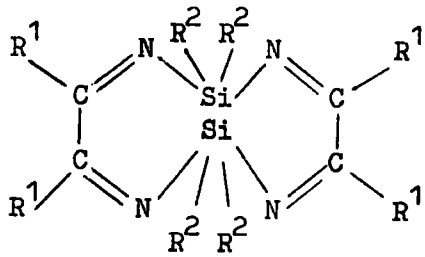
R^1	R^2	$\nu_{C=N}$, $cm.^{-1}$	ref.
Ph	Me_3SiNH	?	53
Ph	Me_3SiNMe	1630	56
Ph	Me_3SiNEt	1630	56
Ph	MeNH	1645	56
Ph	Me_2N	1630	56
$PhC(NMe_2):NSiMe_2Cl$		1600, 1590	56
$(PhC(NMe_2):N)_2SiMe_2$		1620	56
PhO	Et_2N	1748, 1698	57
PhO		1745, 1695, 1685	57
PhO		1755, 1692	57
$p\text{-}MeC_6H_4O$		1748, 1685	57
$p\text{-}ClC_6H_4O$		?	57
$o\text{-}MeOC_6H_4O$	Et_2N	1755, 1695	57
EtO	Et_2N	?	57

Silicon (continued)

	$\nu_{C=N}$, $cm.^{-1}$	ref.
$Me_2SiN{=}CPhNMeSiMe_2N{=}CPhNMe$	1620	58
$Me_2SiN{=}CPhNMeSiMe_2NMe$	1620	58



R^1	R^2	R^3	
EtO	Me	Me	59
EtO	Me	Ph	59
EtO	EtO	EtO	59
Ph	Ph	Ph	15
Ph	Et	Et	15
	Ph	Ph	15



R^1	R^2	
EtO	MeO	59
Ph	Ph	15
Ph	Et	15

Germanium $R^1R^2C{:}NGeR^3R^4R^5$

R^1	R^2	R^3	R^4	R^5	$\nu_{C=N}$, $cm.^{-1}$	ref.
Ph	Ph	Me	Me	Me	1630	50
Ph	Ph	Ph	Ph	Ph	1633	50
Ph	Me_2N	Me	Me	Me	1590	56
Ph	Me_3SiNMe	Me	Me	Me	1615	56

Tin $R^1R^2C{:}NSnR^3R^4R^5$

R^1	R^2	R^3	R^4	R^5	$\nu_{C=N}$, $cm.^{-1}$	ref.
Ph	Ph	Me	Me	Me	1613	50
Ph	Ph	Ph	Ph	Ph	1613	50
Ph	Me_2N	Me	Me	Me	1585	56,61
Ph	Me_3SiNMe	Me	Me	Me	1555	56
CCl_3	MeO	Bu	Bu	Bu	?	63

Lead $R^1R^2C{:}NPbR^3R^4R^5$

R^1	R^2	R^3	R^4	R^5	$\nu_{C=N}$, $cm.^{-1}$	ref.
Ph	Et_2N	Bu	Bu	Bu	?	62
CCl_3	MeO	Ph	Ph	Ph	?	64
CCl_3	Ph_3PbO	Ph	Ph	Ph	?	64

Keteniminosilanes $R^1R^2C{:}C{:}NSiR^3_3$

R^1	R^2	R^3	$\nu_{C:C:N}$, $cm.^{-1}$	ref.
Me_3Si	Me_3Si	Me	2020	51
Me_3Si	Ph	Me	?	51
Me_3Si	H	Me	2028	65
Ph	Ph	Me	?	51
Ph	H	Me	?	65

Keteniminostannanes $R^1C(CN){:}C{:}NSnR^2_3$

R^1 = Et, Pr^i, $EtOCH_2$, $PhCH_2$, Ph_2CH, $p\text{-}Me_2NC_6H_4CH_2$, $p\text{-}MeOC_6H_4CH_2$, $p\text{-}ClC_6H_4$, $p\text{-}NO_2C_6H_4$,  .

R^2 = Et or Bu. $\nu_{C:C:N}$ = 2060–2110 $cm.^{-1}$ ref. 67

Keteniminoplumbanes $R^1C(CN){:}C{:}NPbR^2_3$

R^1	R^2	$\nu_{C:C:N}$, $cm.^{-1}$	ref.
Me	Bu	2070	69
Ph	Bu	2070	69
	Bu	2070	69
$PhCHNEt_2$	Bu	2060	62

Carbodiimides $R^1_3MN{=}C{=}NMR^2_3$

M	R^1_3	R^2_3	$\nu_{N=C=N}$, $cm.^{-1}$	ref.
Si	H_3	H_3	2255	77
Si	D_3	D_3	2237	77
Si	Me_3	Me_3	2190	71
Si	Et_3	Et_3	2200	78
Si	Pr_3	Pr_3	2190	78
Si	$nHex_3$	$nHex_3$	2190	78
Si	Ph_3	Ph_3	2180	78
Si	EtO_3	EtO_3	2230	78
Si	Me_3	Ph_3	2190	78
Si	Me_3	F_3	?	79
Si	Me_2Ph	Me_2Ph	2200	78
Si	$MePh_2$	$MePh_2$	2190	78
Si	$(CH_2{:}CH)Ph_2$	$(CH_2{:}CH)Ph_2$	2200	78
Ge	H_3	H_3	2168	73
Ge	Bu_3	Bu_3	2100	80
Sn	Ph_3	Ph_3	?	74

$(-SiR^1R^2-N=C=N-)_n$

R^1	R^2	n	$\nu_{C:C:N}$, $cm.^{-1}$	ref.
Me	Me	8·3	2160	75
Ph	Ph	8·0	2150	75
Me	Ph	7·8	2200	75
Me	CH_2:CH	-	2220	75
EtO	EtO	6·7	2180	75

EXPERIMENTAL

General Techniques.

Most of the reactions described below involved handling compounds sensitive to hydrolysis by atmospheric moisture.

Unless otherwise stated, reactions were carried out in an atmosphere of pure dry nitrogen in one limb of a double Schlenk tube. Purification of the product by fractional crystallisation was normally effected in the second limb of the Schlenk tube.

A system consisting of a rotary oil pump backing a mercury diffusion pump was used in conjunction with conventional apparatus for distillations and sublimations at reduced pressure and for pumping off solvents.

Nitrogen Supply.

'White Spot' nitrogen, taken directly from a cylinder, was dried by passing through two traps maintained at -196°, and delivered to a 'pig', providing multiple outlets. A constant pressure of nitrogen was maintained in the system by connecting one of the outlets to an oil bubbler.

Glove Box.

Samples for analysis and infrared spectra were transferred and manipulated under a nitrogen atmosphere in a glove box of conventional design. When the box was not in use, the atmosphere was continuously pumped through a trap at -196°, through two furnaces at 400° containing copper wire (to remove traces of oxygen), and back to the box via a second trap at -196°. Where possible, external tubing was of copper or

glass, to reduce diffusion of oxygen or moisture into the system. The furnaces were regenerated when necessary by passing hydrogen over the oxidised copper.

Spectra.

Infrared Spectra.

Infrared spectra were recorded in the range 2·5 - 25 microns using either a Grubb-Parsons GS2A prism-grating spectrophotometer or Spectromaster. 'Fingerprint' spectra for identification purposes were recorded on a Perkin-Elmer 137 or 157.

Samples were in the form of nujol mulls, thin films or solutions in a suitable solvent, as appropriate. Potassium bromide cells were used in each case.

Nuclear Magnetic Resonance Spectra.

Proton magnetic resonance spectra were recorded at 60 Mc./sec. on a Perkin-Elmer R10 spectrometer. Samples were either pure liquids or solutions in carbon tetrachloride, deutero-benzene, cyclohexane or chloroform. Tetramethylsilane was commonly used as the internal reference standard, but on occasion benzene or cyclohexane was used. The sample tubes were filled by syringe against a counter-current of nitrogen, and were sealed under nitrogen.

Mass Spectra.

Mass spectra were recorded on an A.E.I. M.S.9 mass spectrometer at 70eV and an accelerating potential of 8 kv, with a source temperature of 150-250° and electromagnetic scanning. Compounds were introduced by direct insertion into the ion source.

Ultraviolet Spectra.

Ultraviolet spectra were recorded in the region 200-450mμ on a Unicam S.P.800 ultraviolet spectrophotometer using samples in cyclohexane solution, contained in 1 cm. quartz silica cells fitted with ground glass stoppers.

Analyses.

Analyses for carbon, hydrogen, nitrogen and halogens were carried out either in this department by various members of the analytical staff or by external analysts (Dr. Weiler and Dr. Strauss, Oxford).

Molecular Weights.

Molecular weights were determined, where solubility limitations permitted, cryoscopically in benzene. The benzene, of analytical reagent purity, was dried over extruded sodium and calibrated (in respect of its freezing point constant) using freshly sublimed biphenyl. A conventional Beckmann apparatus was flushed out with nitrogen before each determination, and during the determination air was excluded by

passing a current of nitrogen through the apparatus slowly enough to cause negligible loss of solvent by evaporation.

Solvents.

Pentane, hexane, cyclohexane, 80-100° petroleum ether, benzene, toluene and diethyl ether were dried and stored over extruded sodium.

Carbon tetrachloride was dried and stored over phosphorus pentoxide.

Preparation of starting materials.

Diphenylketimine.

Diphenylketimine was prepared by the method of Pickard and Tolbert,[81] from benzonitrile and phenylmagnesium bromide.

Bromobenzene (78·5g., 0·5 mole) was added slowly to magnesium turnings (12·5g., 0·51g.atom) in diethyl ether (300 ml.). When the reaction was complete, the solution was cooled to room temperature, and benzonitrile (46·5g., 0·45 mole) was slowly added. The resultant slurry was stirred at reflux temperature for eight hours, and then allowed to cool to room temperature. Anhydrous methanol (96g., 3 moles) was added and the solid was removed by filtration. The ether and excess methanol were distilled off, and the residual liquid distilled under vacuum, discarding the first 5 ml. B.p. $92^{\circ}/10^{-3}$ mm. Yield, 80%.

Di-p-tolylketimine,[82] b.p. 138-140°/2 mm., di-(p-chlorophenyl)-ketimine,[83] b.p. 138-141°/0·5 mm., and (p-bromophenyl)phenylketimine,[84] b.p. 125-127°/1 mm., were prepared in good yield by exactly analogous methods.

The preparation of (p-tolyl)t-butylketimine[85] required more forcing conditions. Thus after the preparation of t-butyl magnesium chloride, from t-butyl chloride (0·75 mole) and magnesium turnings (0·76g.atom) in 300 ml. of ether, 150 ml. of ether was distilled out of the reaction vessel and an equal volume of toluene added. The mixture was then fractionally distilled until the distillate temperature reached 100°; the distillate was replaced by an equal volume of toluene. p-Tolyl cyanide was added dropwise and the mixture stirred at reflux temperature for two days. Following this reaction period the product was worked up by methanolysis as described above and distilled at 107-108°/1 mm.

1,1,3,3-Tetramethylguanidine.

1,1,3,3-Tetramethylguanidine was available commercially. It was purified by distillation from sodium hydroxide pellets and stored over sodium hydroxide.

Triphenylchlorsilane.

Triphenylchlorsilane was prepared from silicon tetrachloride and phenylmagnesium bromide by the method of Wannagat, Buerger and Ringel.[86]

Silicon tetrachloride (34·0g., 0·2 mole) and magnesium turnings (14·6g., 0·61g.atom) in ether (35 ml.) were treated with bromobenzene (94·0g., 0·6 mole) in ether (75 ml.) at a rate causing vigorous reflux. The mixture was refluxed for three hours after which the ether was distilled off and replaced by toluene. The mixture was refluxed a further five hours, cooled and filtered. The solvent was distilled off the filtrate and on standing triphenylchlorsilane crystallised. This was filtered from the remaining liquid and recrystallised four times from 80-100° petroleum ether. Yield 40%, m.p. 95° (Lit.[86] 96°).

Phenylboron dichloride.

Phenylboron dichloride was prepared from boron trichloride and tetraphenyltin.[87]

Boron trichloride (30·6g., 0·26 mole) was added to tetraphenyltin (25·3g., 0·06 mole) at -78°. As the mixture was allowed to warm up a vigorous reaction set in. After this had died down the mixture was heated to 170° for four hours. Distillation through a short column gave stannic chloride, b.p. 113-115°, and phenylboron dichloride, b.p. 170-174°/760 mm., which was then redistilled. Yield 70%.

Diphenylboron chloride.

Diphenylboron chloride was prepared from crude phenylboron dichloride and tetraphenyltin.[88]

The above synthesis was repeated and stannic chloride removed by distillation. Tetraphenyltin (21·3g., 0·05 mole) was added to the crude phenylboron dichloride and the mixture held at 170° for four hours. Stannic chlorides were removed by distillation at atmospheric pressure, and vacuum distillation of the residue gave diphenylboron chloride which was then redistilled, b.p. 93-96°/0·1 mm. Yield 60%.

Dimesitylboron fluoride.

Dimesitylboron fluoride was prepared from mesitylmagnesium bromide and boron trifluoride etherate.[89]

Mesitylmagnesium bromide was prepared from bromomesitylene (47·8g., 0·24 mole) and magnesium turnings (7·0g., 0·29g.atom) in diethyl ether (300 ml.). Freshly distilled boron trifluoride diethyl etherate (10·0g., 0·07 mole) was added dropwise and the mixture refluxed for two hours. On standing for eighteen hours the solution separated into two layers. The upper layer was decanted off under nitrogen and the ether distilled from it leaving a liquid residue. Distillation of the residue at 127-129°/0·5 mm. afforded dimesitylboron fluoride.

2,2'-Biphenylylboron fluoride.

2,2'-Biphenylylboron fluoride was prepared from 2,2'-dilithiobiphenyl and boron trifluoride etherate.

n-Butyl-lithium (0·1 mole in hexane) was added to a solution of 2,2'-dibromobiphenyl (15·6g., 0·05 mole) in hexane (70 ml.), cooled to -78°. The mixture was allowed to warm to room temperature and stirred for two hours, after which it was cooled to -78°. Boron trifluoride diethyl etherate (7·1g., 0·05 mole) was added and the mixture allowed to warm up and then refluxed for two hours. Lithium fluoride was filtered off and the solvent distilled off the filtrate leaving a yellow liquid residue. Distillation of this liquid at 128-131°/1 mm. afforded 2,2'-biphenylylboron fluoride. (Found: F, 10·4%. $C_{12}H_8BF$ requires F, 10·4%).

2-Chloro-1,3,2-benzodioxaborole.

2-Chloro-1,3,2-benzodioxaborole was prepared from catechol and boron trichloride.[90]

A suspension of freshly sublimed catechol (8·0g., 0·072 mole), in 80-100° petroleum ether (50 ml.) was added dropwise to a solution of boron trichloride (10g., 0·085 mole) in 80-100° petroleum ether at -78°. The mixture was allowed to warm to room temperature and stirred for 30 min. Liberated hydrogen chloride, excess boron trichloride and the solvent were pumped off and the product was distilled at 64°/10 mm. It was then sublimed in vacuo at 30°. Yield 90%.

Beryllium chloride.

A sample of beryllium chloride, provided by Mr. T. Caygill of these laboratories, was prepared by the reaction of chlorine gas with beryllium metal.

Diphenylketiminolithium.

Diphenylketiminolithium was prepared by the action of n-butyl-lithium on diphenylketimine in diethyl ether.[11] Since the product crystallised very readily, forming insoluble polymeric species, it was prepared in sufficient quantity for reaction in situ, and no attempt was made to store it.

n-Butyl-lithium (10 mmole in hexane) was added by syringe to a frozen (-196°) solution of diphenylketimine (1·81g., 10 mmole) in ether (20 ml.). On allowing the mixture to warm a bright red colour developed at about -50°. The clear red solution was stirred at 20° for 40 min., to ensure complete reaction, and used immediately.

Di-p-tolylketiminolithium and (p-tolyl)t-butylketiminolithium were prepared in exactly the same way, from the ketimine and n-butyl-lithium in ether.

1,1,3,3-Tetramethylguanidyl-lithium.

1,1,3,3-tetramethylguanidyl-lithium was prepared from the guanidine and n-butyl-lithium in hexane.[11] Although the compound will redissolve in toluene after it has been isolated in a crystalline form, it is very

air-sensitive and it was generally more convenient to prepare it in situ just prior to use.

n-Butyl-lithium (10 mmole in hexane) was added by syringe to a frozen (-196°) solution of 1,1,3,3-tetramethylguanidine (1·15g., 10 mmole) in hexane (20 ml.). On allowing the mixture to warm colourless solid tetramethylguanidyl-lithium crystallised out of the solution. After stirring at 20° for 30 min. the solvent was pumped off leaving the dry solid which was redissolved in toluene (50 ml.) and used immediately.

Benzaldiminotrimethylsilane.

Benzaldiminotrimethylsilane was prepared by the reaction of benzaldehyde with lithium bis(trimethylsilyl)amide, a modification of the method of Kruger, Rochow and Wannagat.[49]

n-Butyl-lithium (0·1 mole of hexane solution) was added to a frozen (-196°) solution of hexamethyldisilazane (16·1g., 0·1 mole) in toluene (100 ml.). The mixture was allowed to warm and the clear solution stirred for two hours at 20°. Freshly distilled benzaldehyde (9·5g., 0·09 mole) was added dropwise when a gelatinous white precipitate appeared and heat was evolved. The mixture was refluxed for six hours after which it was cooled and trimethylchlorsilane (10·8g., 0·1 mole) was added. After refluxing the mixture for a further two hours a granular white precipitate of lithium chloride was produced, which was removed from the cooled mixture by filtration. The solvent and

hexamethyldisiloxane were distilled off the filtrate at atmospheric pressure leaving a pale yellow liquid residue. Distillation of the residue at 96-98°/18 mm. afforded benzaldiminotrimethylsilane.

Fluorenoneiminotrimethylsilane, b.p. 127-129°/1 mm. was prepared in exactly the same way from fluorenone and lithium bis(trimethylsilyl)-amide.

Reactions of diphenylketiminolithium with chlorosilanes.

Reaction of diphenylketiminolithium with trimethylchlorsilane.

Trimethylchlorsilane (10·8g., 100 mmoles) was added by syringe to a frozen (-196°) solution of diphenylketiminolithium (18·7g., 100 mmoles) in ether. The red colour of the solution changed to yellow as the mixture warmed to 0°, and lithium chloride was precipitated. The solution was stirred for 30 min. and then filtered to remove lithium chloride. The ether was pumped off, leaving a yellow liquid which after distillation at 92-94°/10^{-2} mm. was identified as diphenylketimino-trimethylsilane, $Ph_2C{:}NSiMe_3$. Yield 24·1g., 95%. (Found: C, 75·8; H, 7·3%. Calculated for $C_{16}H_{19}NSi$: C, 75·9; H, 7·6%).

Its i.r. spectrum was identical to that reported by Krüger, Rochow and Wannagat.[49]

Reaction of diphenylketiminolithium with triethylchlorsilane.

Triethylchlorsilane (1·51g., 10 mmoles) was added by syringe to a frozen (-196°) solution of diphenylketiminolithium (1·87g., 10 mmoles) in ether. On allowing the mixture to warm to room temperature there was no visible reaction, but on heating to 35° the red colour changed to yellow and lithium chloride was precipitated. The solution was refluxed for 30 min. and then filtered to remove lithium chloride. The ether was pumped off, leaving a yellow liquid which after distillation at 117-118°/10^{-2} mm. was identified as diphenylketiminotriethylsilane,

$Ph_2C{:}NSiEt_3$. Yield 2·5g., 85%. (Found: C, 77·1; H, 8·4%. $C_{19}H_{25}NSi$ requires C, 77·3; H, 8·5%). ν_{max} (Thin film) 1666vs, 1605m, 1575m, 1493w, 1453s, 1422m, 1270s, 1316m, 1271s, 1245s, 1199m, 1183m, 1153w, 1076m, 1032m, 1016s, 1004s, 976m, 937s, 908s, 892m, 826vs, 790s, 761m, 737vs, 725vs, 699vs, 678sh, 630m, 624s, 591w, 578w and 526w $cm.^{-1}$

Reaction of diphenylketiminolithium with triphenylchlorsilane.

Triphenylchlorsilane (1·48g., 5 mmoles) in ether (60 ml.) was added by syringe to a frozen (-196°) solution of diphenylketiminolithium (0·94g., 5 mmoles) in ether. The mixture was allowed to warm up to room temperature and then boiled but there was no reaction. All but 10 ml. of the ether was pumped off and toluene (40 ml.) added. On boiling the solution a copious white precipitate was formed and the solution turned yellow. The solution was refluxed for 30 min. and then filtered to remove lithium chloride. The solvent was pumped off leaving a yellow semi-solid. This was dissolved in a minimum amount of boiling 80-100° petroleum ether and on cooling yellow crystals of diphenylketimino-triphenylsilane, $Ph_2C{:}NSiPh_3$, m.p. 124-125°, were deposited. Yield 1·7g., 77%. (Found: C, 84·3; H, 5·5%. $C_{31}H_{25}NSi$ requires C, 84·7; H, 5·7%). ν_{max} (Nujol mull) 1667s, 1650s, 1700w, 1580w, 1434s, 1314m, 1267s, 1188w, 1178w, 1153w, 1114s, 1105m, 1075w, 1029m, 1002w, 937m, 906m, 837s, 780m, 753m, 741m, 720m, 712vs, 690vs, 633m, 547m, 513s, 510vs, 478m and 453w $cm.^{-1}$

Reaction of diphenylketiminolithium with silicon tetrachloride.

Silicon tetrachloride (0·85g., 5 mmoles) was added by syringe to a frozen (-196°) solution of diphenylketiminolithium (3·74g., 20 mmoles) in ether. The red colour changed to yellow as the mixture warmed to 0°, and lithium chloride was precipitated. The mixture was stirred for one hour at room temperature and then filtered to remove lithium chloride. The ether was pumped off leaving a yellow semi-solid. This was dissolved in boiling hexane and on cooling large yellow crystals of tetrakis(diphenylketimino)silane, $(Ph_2C{:}N)_4Si$, m.p. 132-133°, were deposited. (Found: C, 83·0; H, 5·3; N, 7·2%; M, 723. $C_{52}H_{40}N_4Si$ requires C, 83·4; H, 5·4; N, 7·3%; M, 748). ν_{max} (Nujol mull) 1646vs, 1600m, 1580m, 1488w, 1450s, 1316m, 1271s, 1181m, 1163m, 1075m, 1031m, 1003w, 990w, 939s, 930m, 913s, 866s, 848s, 835s, 790s, 761m, 754m, 699vs, 681m, 635s, 623w, 615w, 557sh, 551m, 540m and 459w $cm.^{-1}$

Reactions of diphenylketimine with chlorosilanes.

Reaction of trimethylchlorsilane and diphenylketimine (1:2).

Trimethylchlorsilane (1·1g., 10 mmoles) in ether (10 ml.) was added by syringe to a solution of diphenylketimine (3·6g., 20 mmoles) in ether (20 ml.). The mixture was refluxed overnight when a small amount of white solid appeared. This was filtered off and identified by its i.r. spectrum as diphenylketimine hydrochloride. On pumping off the ether from the filtrate a yellow liquid remained which, after distillation at

90-94° in vacuo, was shown by its i.r. spectrum to consist essentially of unchanged diphenylketimine.

Reaction of triphenylchlorsilane and diphenylketimine (1:2).

Triphenylchlorsilane (2·95g., 10 mmoles) in ether (100 ml.) was added to a solution of diphenylketimine (3·6g., 20 mmoles) in ether (20 ml.). The mixture was refluxed for two hours after which no precipitate had appeared. The ether was therefore pumped off and replaced by toluene (60 ml.) and the mixture refluxed. A white solid was slowly precipitated. After refluxing for twelve hours the mixture was cooled and the white solid filtered off and identified by its i.r. spectrum as diphenylketimine hydrochloride. The toluene was pumped off the filtrate leaving a yellow semi-solid. This was crystallised from 80-100° petroleum ether and identified by its m.p. and i.r. spectrum as diphenylketiminotriphenylsilane. (Yield 1·91g., 42%).

Reactions of 1,1,3,3-tetramethylguanidyllithium with chlorosilanes.

Reaction of 1,1,3,3-tetramethylguanidyllithium with trimethylchlorsilane.

Trimethylchlorsilane (1·62g., 15 mmoles) was added by syringe to a frozen (-196°) solution of tetramethylguanidyllithium (1·82g., 15 mmoles) in toluene (50 ml.). Lithium chloride precipitated as the mixture warmed up to room temperature. The solution was stirred for two hours and then filtered to remove lithium chloride. The toluene was pumped

off leaving a colourless liquid which after distillation at 185-188° was identified as 1,1,3,3-tetramethylguanidyltrimethylsilane, $(Me_2N)_2C{:}NSiMe_3$. (Found: C, 51·5; H, 11·4; N, 22·7%. $C_8H_{21}N_3Si$ requires C, 51·4; H, 11·3; N, 22·5%). ν_{max} (Thin film) 1680vs, 1612s, 1500s, 1468s, 1433m, 1416m, 1389s, 1361wsh, 1264s, 1205w, 1149w, 1120m, 1081s, 1063s, 1014m, 897s, 849s, 833s, 784w, 759m, 736w, 690w, 638w, 622w and 563w $cm.^{-1}$

Reaction of 1,1,3,3-tetramethylguanidyllithium with triethylchlorsilane.

Triethylchlorsilane (1·5g., 10 mmoles) was added by syringe to a frozen (-196°) solution of tetramethylguanidyllithium (1·21g., 10 mmoles) in toluene. Lithium chloride precipitated as the mixture warmed up to room temperature. The solution was stirred for three hours and then filtered to remove lithium chloride. The toluene was pumped off leaving a colourless liquid which after distillation at 57-59°/10^{-3} mm. was identified as 1,1,3,3-tetramethylguanidyltriethylsilane, $(Me_2N)_2C{:}NSiEt_3$. (Found: C, 57·4; H, 12·0; N, 18·1%. $C_{11}H_{27}N_3Si$ requires C, 57·7; H, 11·9; N, 18·3%). ν_{max} (Thin film) 1681vs, 1610sh, 1490m, 1464s, 1429m, 1351s, 1239m, 1147w, 1115s, 1063s, 1019s, 971w, 911w, 887s, 731s, 719sh, 695m, 614w and 560w $cm.^{-1}$

Reaction of 1,1,3,3-tetramethylguanidyllithium with triphenylchlorsilane.

Triphenylchlorsilane (2·94g., 10 mmoles) in toluene (20 ml.) was added by syringe to a frozen (-196°) solution of tetramethylguanidyllithium

(1·21g., 10 mmoles) in toluene. The mixture was allowed to warm up to room temperature and then stirred for 15 min. but there was no reaction. The mixture was then stirred at 50° for one hour when lithium chloride precipitated. The toluene was pumped off and 80–100° petroleum ether was added and the mixture boiled. The solution was filtered hot to remove lithium chloride and on cooling colourless crystals of 1,1,3,3-tetramethylguanidyltriphenylsilane, $(Me_2N)_2C{:}NSiPh_3$, m.p. 97–98°, were deposited. (Found: C, 73·7; H, 6·9; N, 11·1%. $C_{23}H_{27}N_3Si$ requires C, 74·0; H, 7·3; N, 11·3%). ν_{max} (Nujol mull) 1647s, 1612s, 1597s, 1572m, 1429s, 1359m, 1307w, 1266w, 1190w, 1163w, 1124vs, 1099s, 1075wsh, 1056m, 1031m, 1000m, 917w, 909wsh, 896m, 856w, 743msh, 740s, 714vs, 702vs, 680w, 624w, 613w, 562w, 513vs, 505s and 484s $cm.^{-1}$

Reactions of diphenylketiminotrimethylsilane with boron halides.

Reaction of diphenylketiminotrimethylsilane with boron trifluoride etherate (1:1)

Diphenylketiminotrimethylsilane (1·27g., 5 mmoles) in toluene (5 ml.) was added by syringe to a solution of freshly distilled boron trifluoride etherate (0·71g., 5 mmoles) in toluene (10 ml.), cooled to -78°. On allowing to warm up a white solid was deposited at 0°. The mixture was boiled for 10 min. but no further reaction appeared to occur. The insoluble white solid was filtered off, washed with pentane and pumped dry. It was identified as diphenylketiminoboron difluoride, $(Ph_2C{:}NBF_2)_n$, by comparison of its m.p. and i.r. spectrum with those of an authentic sample. (Yield 0·88g., 77%).

Reaction of diphenylketiminotrimethylsilane with boron trichloride (1:1)

Diphenylketiminotrimethylsilane (1·27g., 5 mmoles) in toluene (5 ml.) was added by syringe to a solution of boron trichloride (0·59g., 5 mmoles) in toluene (10 ml.), cooled to -78°. On allowing to warm up a white solid was deposited below 0°. The mixture was stirred for 50 min. at room temperature but no further reaction appeared to occur. The white solid was filtered off, washed with a further 10 ml. of toluene and pumped dry. Fractionation of the mother liquor and washings gave trimethylchlorsilane (identified by b.p. and i.r. spectrum), 0·34g., 62%. A sample of the white solid, yield 0·94g., 70·5%, was recrystallised from

toluene and identified as diphenylketiminoboron dichloride, $(Ph_2C:NBCl_2)_2$, by comparison of its m.p. and i.r. spectrum with those of an authentic sample.

Reaction of diphenylketiminotrimethylsilane with boron tribromide (1:1)

Diphenylketiminotrimethylsilane (1·33g., 5·3 mmoles) in toluene (5 ml.) was added by syringe to a solution of boron tribromide (1·33g., 5·3 mmoles) in toluene (10 ml.), cooled to -78°. A red gelatinous precipitate was immediately formed but on allowing the mixture to warm up this redissolved giving a yellow solution and a pale yellow solid was deposited below 0°. After stirring for 30 min. at room temperature the pale cream solid was filtered off, washed with pentane and pumped dry. A sample was recrystallised from toluene and identified as diphenylketiminoboron dibromide, $(Ph_2C:NBBr_2)_2$, by comparison of its m.p. and i.r. spectrum with those of an authentic sample. (Total yield 1·52g., 82%).

Reaction of diphenylketiminotrimethylsilane with 2-chloro-1,3,2-benzodioxaborole.

Diphenylketiminotrimethylsilane (1·32g., 5·2 mmoles) in toluene (5 ml.) was added by syringe to a solution of freshly sublimed 2-chloro-1,3,2-benzodioxaborole (0·8g., 5·2 mmoles) in toluene (20 ml.), cooled to -78°. A gelatinous red precipitate was immediately formed. This redissolved and a yellow solid was deposited almost immediately the reaction vessel was removed from the acetone/CO_2 bath. Reaction

appeared complete below 0° but the mixture was stirred a further 30 min. before pumping off toluene and trimethylchlorsilane. The product was obtained as well formed golden needles by recrystallisation from toluene, and was identified as 2-(diphenylketimino)-1,3,2-benzodioxaborole, $(Ph_2C:NBO_2C_6H_4)_n$, m.p. 210-212°. (Found: C, 75·5; H, 5·1; N, 4·8%. $C_{19}H_{14}BNO_2$ requires C, 76·3; H, 4·7; N, 4·7%). ν_{max} (Nujol mull) 1624s, 1600m, 1570w, 1490vs, 1328m, 1299w, 1266w, 1235s, 1209w, 1174w, 1134w, 1099s, 1087s, 1071s, 1029m, 1004m, 971w, 943s, 923m, 909sh, 867w, 828w, 783w, 735s, 714s, 698sh, 620w and 576m $cm.^{-1}$

Reaction of diphenylketiminotrimethylsilane with phenylboron dichloride (1:1)

Diphenylketiminotrimethylsilane (1·27g., 5·0 mmoles) in toluene (5 ml.) was added by syringe to a solution of phenylboron dichloride (0·80g., 5·0 mmoles) in toluene (10 ml.), cooled to -78°. On allowing to warm up a white solid was deposited below 0° and on reaching room temperature the solution had turned colourless. After boiling the mixture for 15 min. the toluene and trimethylchlorsilane were pumped off. The product was obtained as colourless needles by recrystallisation from toluene, and was identified as diphenylketiminophenylboron chloride, $(Ph_2C:NBPhCl)_n$, m.p. 237-238°. (Found: C, 75·2; H, 5·2; N, 4·7; Cl, 12·0%. $C_{19}H_{15}BClN$ requires C, 75·3; H, 5·0; N, 4·6; Cl, 11·7%). ν_{max} (Nujol mull) 1612m, 1587s, 1565m, 1333m, 1316sh, 1271m, 1200w, 1186s, 1172w, 1111w, 1075w, 1042w, 1028wsh, 1013s, 930s, 917w, 885s, 848m, 833sh, 830m, 789m, 763m, 746w, 706s, 698s, 680m, 672w, 568s, 502w and 479w $cm.^{-1}$

Reaction of diphenylketiminotrimethylsilane with diphenylboron chloride

Diphenylketiminotrimethylsilane (2·16g., 8·5 mmoles) in toluene (10 ml.) was added by syringe to a solution of diphenylboron chloride (1·71g., 8·5 mmoles) in toluene (20 ml.), cooled to -78°. On allowing to warm up the yellow colour of the solution became somewhat paler between 0° and room temperature. The mixture was boiled for two hours after which the toluene and trimethylchlorsilane (identified by its i.r. spectrum) were pumped off leaving a white solid. This was dissolved in hot 80-100° petroleum ether and, after filtration, the solution on cooling afforded colourless crystals of monomeric diphenylketimino-diphenylborane, $Ph_2C{:}N{\cdot}BPh_2$, m.p. 143-144°. (Found: C, 86·8; H, 5·9; N, 4·2%; M, 331. $C_{25}H_{20}BN$ requires C, 87·0; H, 5·8; N, 4·1%; M, 345). ν_{max} (Nujol mull) 1786vs, 1595m, 1328w, 1316w, 1269s, 1250s, 1235vs, 1179w, 1149m, 1092m, 1074m, 1064m, 1031m, 990w, 970w, 930m, 909m, 894w, 885s, 799br sh, 787s, 766m, 752m, 726vs, 695vs, 633vs, 606s and 579vs $cm.^{-1}$

Reaction of diphenylketiminotrimethylsilane with dimesitylboron fluoride

Diphenylketiminotrimethylsilane (1·47g., 5·83 mmoles) in toluene (5 ml.) was added by syringe to a stirred toluene solution of dimesitylboron fluoride (1·56g., 5·83 mmoles) at room temperature. The mixture was boiled for 30 min. after which the solvent was pumped off. An i.r. spectrum of the remaining viscous liquid showed it to be a mixture of the starting materials. The mixture was heated at 150° for two hours after which an i.r. spectrum showed a small peak at 1792 $cm.^{-1}$ After a

further 14 hours at 150° this peak had grown considerably in intensity. After allowing to cool to room temperature the mixture was dissolved in warm pentane and on standing the solution slowly deposited colourless crystals of monomeric diphenylketiminodimesitylborane, $Ph_2C{:}N{\cdot}B(C_6H_2Me_3)_2$, m.p. 174–175° (after recrystallisation from 80–100° petroleum ether). (Found: C, 86·2; H, 7·8; N, 3·2%; M, 443 [cryoscopically]; M, 429·2645 [mass spectroscopy]. $C_{31}H_{32}BN$ requires C, 86·7; H, 7·5; N, 3·3%; M, 429·2628). ν_{max} (Nujol mull) 1792vs, 1610s, 1546w, 1449vs, 1429sh, 1376s, 1316m, 1289sh, 1282s, 1256m, 1241w, 1221sh, 1212m, 1182w, 1149m, 1133m, 1085w, 1075w, 1058w, 1030m, 1018sh, 1001w, 980w, 962w, 935s, 914m, 904sh, 882w, 853vs, 840vs, 788vs, 770m, 742m, 708s, 698vs, 667w, 657w, 641s, 633m, 625s, 615m, 583m, 563w and 560w $cm.^{-1}$

Reaction of diphenylketiminotrimethylsilane with 2,2'-biphenylylboron fluoride

Diphenylketiminotrimethylsilane (2·99g., 11·8 mmoles) in toluene (10 ml.) was added by syringe to a solution of 2,2'-biphenylylboron fluoride (2·15 g., 11·8 mmoles) in toluene (30 ml.), cooled to -78°. The mixture was allowed to warm up to room temperature and then boiled for three hours. The mixture was then pumped down leaving a white solid and a little yellow liquid. Pentane was added, the solid was filtered off and after recrystallisation from toluene was identified as diphenylketimino 2,2'-biphenylylborane, $[Ph_2C{:}NB(C_6H_4)_2]_n$, m.p. 295–295·5°. (Found: C, 87·5; H, 5·5; N, 4·4%. $C_{25}H_{18}BN$ requires C, 87·5; H, 5·3; N, 4·1%), ν_{max} (Nujol mull) 1616m, 1597s, 1575m, 1328m, 1273s,

1193w, 1170w, 1149s, 1088w, 1031w, 1010s, 943w, 917m, 897s, 886s, 861m, 840w, 783m, 769w, 760m, 752m, 743m, 734vs, 708s, 699s, 691s, 622w, 581s, 520w and 482w $cm.^{-1}$

Reaction of diphenylketiminotrimethylsilane with boron trifluoride etherate (2:1)

Diphenylketiminotrimethylsilane (4·03g., 16 mmoles) in toluene (10 ml.) was added by syringe to a solution of boron trifluoride etherate (1·13g., 8 mmoles) in toluene (10 ml.), cooled to -78°. On allowing to warm up there was no visible reaction until room temperature was reached when a white solid was deposited over a period of 40 min. This was filtered off, washed with pentane and after pumping dry was identified as diphenylketiminoborondifluoride, $(Ph_2C{:}NBF_2)_n$, by comparison of its m.p. and i.r. spectrum with those of an authentic sample. On pumping the volatiles off the filtrate a yellow viscous liquid remained which was identified as tris(diphenylketimino)borane, $(Ph_2C{:}N)_3B$, by comparison of its i.r. spectrum with that of an authentic sample.

Reaction of diphenylketiminotrimethylsilane with boron trichloride (2:1)

Diphenylketiminotrimethylsilane (2·22g., 8·8 mmoles) in toluene (10 ml.) was added by syringe to a solution of boron trichloride (0·51g., 4·4 mmoles) in toluene (20 ml.), cooled to -78°. On allowing to warm up to room temperature the yellow colour of the solution became much paler. After boiling for 30 min. the volatiles were pumped off leaving a white

solid suspended in a very viscous liquid. These were separated by adding 20 ml. of 80-100° petroleum ether, warming and filtering off the insoluble solid and pumping down the filtrate to give the viscous liquid. The solid and liquid were identified by their i.r. spectra as diphenylketiminoborondichloride, $(Ph_2C{:}NBCl_2)_2$ and tris(diphenylketimino)borane, $(Ph_2C{:}N)_3B$, respectively.

Reaction of diphenylketiminotrimethylsilane with boron tribromide (2:1)

Diphenylketiminotrimethylsilane (2·65g., 10·6 mmoles) in toluene (10 ml.) was added by syringe to a solution of boron tribromide (1·33g., 5·3 mmoles) in toluene (10 ml.), cooled to -78°. A red gelatinous precipitate was immediately formed which redissolved giving a yellow solution on allowing the mixture to warm up. At about 0° a pale yellow solid was deposited; this dissolved on boiling the mixture. On pumping off the volatiles a yellow semi-solid remained. This was dissolved in boiling toluene and on cooling crystals of diphenylketiminoboron dibromide, $(Ph_2C{:}NBBr_2)_2$, identified by its i.r. spectrum and m.p., were deposited. On pumping down the mother liquor a viscous liquid remained which was identified as tris(diphenylketimino)borane by its i.r. spectrum.

In a separate experiment the pale yellow solid deposited at 0° was filtered off at room temperature without boiling the mixture and was identified by its i.r. spectrum as diphenylketiminoborondibromide.

Reaction of diphenylketiminotrimethylsilane with phenylboron dichloride (2:1)

Diphenylketiminotrimethylsilane (2·81g., 11·1 mmoles) in toluene (5 ml.) was added by syringe to a solution of phenylboron dichloride (0·93g., 5·6 mmoles) in toluene (20 ml.). On allowing to warm to room temperature the solution remained clear but the yellow colour became much paler. The solution was boiled for 20 min. after which the volatiles were pumped off leaving a white semi-solid. This was dissolved in boiling 80–100° petroleum ether and on cooling colourless needles of monomeric bis(diphenylketimino)phenylborane, $(Ph_2C{:}N)_2BPh$, m.p. 127–128°, were deposited. (Found: C, 85·1; H, 5·6; N, 6·0%, M, 441. $C_{32}H_{25}BN_2$ requires C, 85·7; H, 5·6; N, 6·3%; M, 448). ν_{max} (Nujol mull) 1672vs, 1598m, 1577w, 1311m, 1266sh, 1250s, 1217s, 1176w, 1159w, 1122s, 1072w, 1058m, 1027w, 1009s, 999m, 990w, 927m, 926m, 908m, 848w, 788m, 767m, 749s, 719w, 699vs, 679sh, 642s, 586sh and 578m $cm.^{-1}$

Reaction of diphenylketiminotrimethylsilane with boron trichloride (3:1)

Diphenylketiminotrimethylsilane (3·94g., 15·6 mmoles) in toluene (10 ml.) was added by syringe to a solution of boron trichloride (0·61g., 5·2 mmoles) in toluene (10 ml.), cooled to -78°. The clear solution was allowed to warm to room temperature and then boiled for 30 min., after which the volatiles were pumped off leaving a viscous liquid which was identified as tris(diphenylketimino)borane by its i.r. spectrum.

Reaction of fluorenoneiminotrimethylsilane with diphenylboron chloride.

Fluorenoneiminotrimethylsilane (1·70g., 9·6 mmoles) in toluene (10 ml.) was added by syringe to a solution of diphenylboron chloride (1·92g., 9·6 mmoles) in toluene (30 ml.), cooled to -78°. The solution was allowed to warm up to room temperature and then boiled for two hours, its yellow colour remaining unchanged. On pumping off the toluene a viscous orange liquid remained. Addition of pentane gave a yellow solid which after recrystallisation from 80-100° petroleum ether was identified as monomeric fluorenoneiminodiphenylborane, $(C_6H_4)_2C{:}NBPh_2$, m.p. 128-130°. (Found: C, 86·8; H, 5·3; N, 4·4%; M, 335. $C_{25}H_{18}BN$ requires C, 87·5; H, 5·3; N, 4·1%; M, 343). ν_{max} (Nujol mull) 1827w, 1766s, 1646w, 1613m, 1597m, 1437s, 1333w, 1299m, 1263s, 1238s, 1185w, 1163msh, 1155m, 1101m, 1061m, 1028m, 1000m, 970w, 950w, 936w, 911s, 885m, 877m, 792s, 767m, 747m, 742m, 729vs, 699vs, 652s, 645m, 631m, 613m, 606m, 591w and 580m $cm.^{-1}$

Reaction of benzaldiminotrimethylsilane with phenylboron dichloride (1:1)

Benzaldiminotrimethylsilane (0·89g., 5·0 mmoles) in toluene (5 ml.) was added by syringe to a solution of phenylboron dichloride (0·79g., 5·0 mmoles) in toluene (25 ml.). Heat was evolved but the solution remained clear. The solution was boiled for 15 min. and then toluene and trimethylchlorsilane were pumped off leaving a white solid. This was recrystallised from a 1:1 mixture of benzene and 80-100° petroleum

ether and identified as dimeric benzaldiminophenylboron chloride, $(PhCH:NBPhCl)_2$, m.p. 222-223°. (Found: C, 67·9; H, 4·6; Cl, 15·5%; M, 438. $C_{26}H_{22}B_2Cl_2N_2$ requires C, 68·6; H, 4·9; Cl, 15·6%; M, 454). ν_{max} (Nujol mull) 1639vs, 1603s, 1582m, 1435s, 1418w, 1312m, 1304w, 1220w, 1186s, 1110w, 1075w, 1031w, 1006s, 996s, 984s, 930s, 901vs, 877s, 868vs, 826m, 800w, 769w, 750s, 717vs, 703s, 682s, 657m, 617w, 546w, 505w, 496m, 476m and 472m $cm.^{-1}$

Reaction of benzaldiminotrimethylsilane with diphenylboron chloride.

Benzaldiminotrimethylsilane (1·15g., 6·5 mmoles) in toluene (5 ml.) was added by syringe to a solution of diphenylboron chloride (1·31g., 6·5 mmoles) in toluene (25 ml.), cooled to -78°. On allowing the mixture to warm up a white solid was precipitated at 0°. After stirring for 10 min. the solution was boiled, when the solid dissolved, to ensure complete reaction. The toluene and trimethylchlorsilane were then pumped off leaving a white solid which was recrystallised from toluene and identified as dimeric benzaldiminodiphenylborane, $(PhCH:NBPh_2)_2$, m.p. 122-124°. (Found: C, 83·9; H, 6·2; N, 4·8%; M, 580. $C_{38}H_{32}B_2N_2$ requires C, 84·7; H, 6·0; N, 5·2%; M, 538). ν_{max} (Nujol mull) 1643s, 1609m, 1587w, 1435s, 1319w, 1299w, 1261w, 1205msh, 1179s, 1160wsh, 1131m, 1075w, 1029w, 1018w, 1001w, 975m, 952s, 925m, 905m, 896s, 870s, 857s, 816m, 753vs, 745vs, 725m, 705vs, 689s, 645s, 629w, 620w, 615w, 524m and 498m $cm.^{-1}$

Reaction of benzaldiminotrimethylsilane with dimesitylboron fluoride.

Benzaldiminotrimethylsilane (3·89g., 22 mmoles) and dimesitylboron fluoride (5·89g., 22 mmoles) were mixed together in the absence of solvent at room temperature; there was no apparent reaction. The mixture was then stirred at 135° for three days. An i.r. spectrum of the resulting yellow liquid showed bands arising from the starting materials as well as additional bands including a strong one at ~1820 $cm.^{-1}$ Unreacted benzaldiminotrimethylsilane and dimesitylboron fluoride were distilled out of the reaction vessel in vacuo, leaving an extremely viscous yellowish liquid. This was dissolved in warm pentane (10 ml.) and, on standing, the solution slowly deposited colourless, cubic crystals of monomeric benzaldiminodimesitylborane, $PhCH{:}NB(C_6H_2Me_3)_2$, m.p. 97-98°. (Found: C, 84·2; H, 8·1; N, 3·7%; M, 332. $C_{25}H_{28}BN$ requires C, 85·0; H, 8·0; N, 4·0%; M, 353). ν_{max} (Nujol mull) 1818vs, 1733vw, 1608s, 1553w, 1424s, 1316w, 1280w, 1245s, 1220s, 1195m, 1160s, 1080vw, 1056m, 1031m, 1020wsh, 1005w, 973w, 963w, 951m, 972vw, 909vw, 885vw, 862wsh, 854vs, 839vs, 822m, 752vs, 735s, 725wsh, 694vs, 654wsh, 649s, 637s, 617vw, 595m, 578m, 572m, 562m, 538vw, 526w, 515m, 505w, 488m, 467vw and 453m $cm.^{-1}$

Reactions of diphenylketiminolithium with boron halides.

Reaction of diphenylketiminolithium with diphenylboron chloride.

Diphenylboron chloride (2·0g., 10 mmoles) in toluene (10 ml.) was added by syringe to a frozen (-173°) solution of diphenylketiminolithium (1·87g., 10 mmoles) in ether. The red colour changed to yellow as the mixture warmed to 0°, and lithium chloride was precipitated. After stirring at room temperature for 30 min., the solvent was pumped off and 80–100° petroleum ether was added. The solution was boiled, filtered to remove lithium chloride, and on cooling deposited colourless crystalline diphenylketiminodiphenylborane, $Ph_2C{:}NBPh_2$, which was identified by comparison of its m.p. and i.r. spectrum with those of an authentic sample.

Reaction of diphenylketiminolithium with dimesitylboron fluoride.

Dimesitylboron fluoride (1·24g., 4·6 mmoles) in toluene (10 ml.) was added by syringe to a frozen (-173°) solution of diphenylketiminolithium (0·86g., 4·6 mmoles) in ether. The mixture was allowed to warm to room temperature and then stirred for 15 min., after which no reaction appeared to have occurred. The ether was distilled off and replaced by toluene and the mixture stirred at 100° for three hours after which the solvent was pumped off leaving a viscous red-brown liquid. Pentane was added and on stirring a pale cream solid precipitated out. This

was pumped dry and dissolved in boiling 80-100° petroleum ether. The solution was filtered hot and on cooling afforded colourless crystals which after a further recrystallisation were identified by m.p. and i.r. spectrum as diphenylketiminodimesitylborane, $Ph_2C{:}NB(C_6H_2Me_3)_2$.

Reaction of diphenylketiminolithium with 2-chloro-1,3,2-benzodioxaborole.

2-Chloro-1,3,2-benzodioxaborole (1·61g., 10·4 mmoles) in toluene (15 ml.) was added by syringe to a frozen (-173°) solution of diphenylketiminolithium (1·95g., 10·4 mmoles) in ether. Reaction set in at ~ -85°, a yellow solid being produced. The mixture was allowed to warm to room temperature and stirred for 30 min. before pumping off the solvent. Toluene (40 ml.) was added and on boiling a small amount of the yellow solid dissolved. The solution was filtered hot and on cooling deposited bright yellow needles which were identified by their m.p. and i.r. spectrum as 2-(diphenylketimino)-1,3,2-benzodioxaborole, $Ph_2C{:}NBO_2C_6H_4$.

Reaction of diphenylketiminolithium with phenylboron dichloride (2:1)

Phenylboron dichloride (1·99g., 12·6 mmoles) in toluene (10 ml.) was added by syringe to a frozen (-173°) solution of diphenylketiminolithium (4·71g., 25·2 mmoles) in ether. As the solution warmed up its red colour changed successively yellow then brown and finally became green at room temperature. After stirring for 15 min. the solvent was pumped off and 80-100° petroleum ether added. The solution was boiled when it became colourless, filtered hot, and on cooling afforded colourless

crystals identified by their m.p. and i.r. spectrum as bis(diphenylketimino)phenylborane, $(Ph_2C{:}N)_2BPh$.

Reaction of diphenylketiminolithium with boron trichloride (2:1)

Boron trichloride (1·07g., 9·2 mmoles) was condensed on to a frozen (-173°) solution of diphenylketiminolithium (3·44g., 18·4 mmoles) in ether. The mixture turned light brown as it warmed up. After stirring at room temperature for one hour the solvent was pumped off and toluene was added when the mixture consisted of a pale solid suspended in a brown solution. The solution was filtered and the toluene pumped off leaving a brown viscous mass which could not be crystallised. (Found: Cl, 11·5%. $C_{26}H_{20}BClN_2$ requires Cl, 8·7%).

Infrared spectra of this material were of insufficient quality to be of value.

Reaction of di-p-tolylketiminolithium with diphenylboron chloride.

Diphenylboron chloride (1·22g., 6·1 mmoles) in toluene (10 ml.) was added by syringe to a frozen (-173°) solution of di-p-tolylketiminolithium (1·31g., 6·1 mmoles) in ether. The red colour changed to yellow as the mixture warmed to 0°, and lithium chloride was precipitated. After stirring at room temperature for 30 min., the solvent was pumped off and 80-100° petroleum ether was added. The solution was boiled and filtered to remove lithium chloride. On pumping off the solvent a light brown viscous liquid remained. This was very soluble even in pentane and could

not be crystallised. It was therefore distilled in vacuo into a 'bucket' attached to a cold finger (bath temperature 140°). The viscous, colourless liquid thus obtained was identified as monomeric di-p-tolylketiminodiphenylborane, $(p\text{-}MeC_6H_4)_2C{:}NBPh_2$. (Found: C, 86·2; H, 6·4; N, 3·6%; M, 363. $C_{27}H_{24}BN$ requires C, 86·9; H, 6·4; N, 3·8%; M, 373). ν_{max} (Thin film) 1957vw, 1916vw, 1840wsh, 1792vs, 1610s, 1595s, 1570msh, 1508m, 1453msh, 1435s, 1412m, 1383m, 1326m, 1316s, 1290s, 1269vs, 1235vs, 1183s, 1153s, 1120m, 1088vw, 1068m, 1033m, 1024m, 1000m, 971w, 952w, 920s, 903m, 888s, 831s, 823s, 805m, 783m, 763s, 751m, 733s, 724s, 699vs, 667m, 652w, 634s, 625m, 606s, 574s, 562s, 479msh, 471m and 446w $cm.^{-1}$

Reactions of diphenylboron chloride with ketimines.

Reaction of diphenylboron chloride with diphenylketimine (1:1)

Diphenylketimine (0·83g., 4·6 mmoles) in 80-100° petroleum ether (10 ml.) was added by syringe to a stirred solution of diphenylboron chloride (0·92g., 4·6 mmoles) in 80-100° petroleum ether (10 ml.). A gelatinous white precipitate appeared immediately but on stirring for 30 min. this became much more granular. The precipitate was filtered off, washed with more solvent and pumped dry. It was identified by its i.r. spectrum as diphenylketimine hydrochloride. After pumping off the solvent from the filtrate a liquid residue remained whose i.r. spectrum indicated that it consisted largely of starting materials.

Reaction of diphenylboron chloride with diphenylketimine (1:2)

Diphenylketimine (1·5g., 8·3 mmoles) was added by syringe to a stirred solution of diphenylboron chloride (0·83g., 4·15 mmoles) in toluene (30 ml.). Heat was evolved and a white solid immediately precipitated. The mixture was refluxed for three hours, allowed to cool, and then filtered. The white solid was identified by its i.r. spectrum as diphenylketimine hydrochloride. Yield 0·74g., 83%. The toluene was pumped off the filtrate leaving a light brown semi-solid. This was crystallised from 80-100° petroleum ether and after sublimation at 140°/ 0·1 mm. was identified by its i.r. spectrum and m.p. as diphenylketimino-diphenylborane.

Reaction of diphenylboron chloride with di(p-chlorophenyl)ketimine (1:2)

Di(p-chlorophenyl)ketimine (4·10g., 16·4 mmoles) in 80–100° petroleum ether (50 ml.) was added by syringe to a stirred solution of diphenylboron chloride (1·64g., 8·2 mmoles) in 80–100° petroleum ether (10 ml.). Heat was evolved and a white solid precipitated. The mixture was refluxed for three hours, allowed to cool, and then filtered to remove ketimine hydrochloride. On pumping down the filtrate a viscous oil remained. Pentane (10 ml.) was added and the oil dissolved but on boiling a white solid precipitated out. This was recrystallised from a 1:4 mixture of pentane and 80–100° petroleum ether and identifed as monomeric di(p-chlorophenyl)ketiminodiphenylborane, $(p\text{-}ClC_6H_4)_2C{:}NBPh_2$, m.p. 119–120°C. (Found: C, 71·7; H, 4·4; N, 3·5; Cl, 17·8%; M, 395. $C_{25}H_{18}BCl_2N$ requires C, 72·6; H, 4·4; N, 3·4; Cl, 17·2%; M, 414). ν_{max} (Nujol mull) 1826w, 1775s, 1587s, 1560msh, 1435s, 1314w, 1294m, 1255s, 1235s, 1205wsh, 1171m, 1156w, 1145m, 1088s, 1063m, 1030m, 1014s, 998m, 988w, 971w, 957w, 943w, 909s, 893m, 883s, 866wsh, 840s, 833s, 820m, 762s, 741s, 735s, 717m, 694vs, 651m, 635w, 624m, 595s and 503m $cm.^{-1}$

Reaction of diphenylboron chloride with di-p-tolylketimine (1:2)

Di-p-tolylketimine (5·44g., 26·0 mmoles) in toluene (15 ml.) was added by syringe to a stirred solution of diphenylboron chloride (2·60g., 13·0 mmoles) in toluene (15 ml.). Heat was evolved and a white solid immediately precipitated. The mixture was refluxed for two hours, allowed

to cool, and then filtered. The white solid was identified by its i.r. spectrum as di-p-tolylketimine hydrochloride. Yield 2·91g., 91%. The toluene was pumped off the filtrate leaving a light brown viscous liquid. This was distilled in vacuo into a 'bucket' and identified by its i.r. spectrum as di-p-tolylketiminodiphenylborane.

Reaction of diphenylboron chloride with (p-bromophenyl)phenylketimine (1:2)

(p-Bromophenyl)phenylketimine (3·19g., 12·3 mmoles) in toluene (15 ml.) was added by syringe to a stirred solution of diphenylboron chloride (1·23g., 6·15 mmoles) in toluene (10 ml.). A white solid precipitated immediately. The mixture was refluxed for three hours, allowed to cool and then filtered. The toluene was pumped off the filtrate leaving a light brown viscous liquid. This was distilled in vacuo into a 'bucket' attached to a cold finger (bath temperature 140°) and the colourless, viscous liquid thus obtained was identified as monomeric (p-bromophenyl)phenylketiminodiphenylborane, $(p\text{-}BrC_6H_4)PhC{:}NBPh_2$. (Found: C, 69·7; H, 4·4; N, 3·6; Br, 20·1%; M, 398. $C_{25}H_{19}BBrN$ requires C, 70·7; H, 4·5; N, 3·3; Br, 18·9%; M, 424). ν_{max} (Thin film) 1792vs, 1600s, 1493m, 1445s, 1404s, 1366s, 1271s, 1239s, 1200m, 1182m, 1155m, 1110w, 1075s, 1031w, 1015s, 1005w, 966w, 931w, 916w, 890s, 831s, 775m, 740m, 722s, 699vs, 645m, 625w, 606w, 583w, 575w and 465m $cm.^{-1}$

Reaction of diphenylketiminoboron dibromide with phenyllithium.

Freshly distilled phenyl iodide (1·73g., 8·5 mmoles) in 80–100° petroleum ether (10 ml.) was cooled to -173° and n-butyllithium (8·5 mmoles of hexane solution) was added by syringe. On allowing to warm up the solution became clear and then a white solid was precipitated. After stirring the solution for one hour at room temperature the volatiles were pumped off leaving a white powder which was dissolved in ether (10 ml.). This solution was added by syringe to a frozen (-173°) solution of diphenylketiminoboron dibromide (1·49g., 4·25 mmoles) in toluene (60 ml.). On allowing to warm up the solution turned green and then brown. After stirring for 1 hour at 20° the mixture was boiled for 15 min. and then the solvent was pumped off leaving a brown paste. 80–100° petroleum ether was added and the mixture was boiled and then filtered to remove lithium bromide. On cooling no solid appeared in the filtrate. The solvent was therefore pumped off leaving a brown tar. An i.r. spectrum of this tar contained a strong absorption at 1786 $cm.^{-1}$, indicating the presence of diphenylketiminodiphenylborane but attempts to isolate the pure compound were unsuccessful.

Reaction of diphenylketimine hydrochloride with sodium tetraphenylborate.

Diphenylketimine hydrochloride (1·79g., 8·25 mmoles) and sodium tetraphenylborate (2·82g., 8·25 mmoles) were suspended together in toluene and the mixture refluxed overnight. After allowing the brown solution to cool, the remaining white solid was filtered off and the toluene

pumped off the filtrate, leaving a pale brown semi-solid. This was dissolved in boiling 80-100° petroleum ether and the solution filtered. On allowing to cool, colourless crystals were deposited and identified by their m.p. and i.r. spectrum as diphenylketiminodiphenylborane.

Reaction of di-p-tolylketimine hydrochloride with sodium tetraphenylborate.

Di-p-tolylketimine hydrochloride (2·16g., 8·45 mmoles) and sodium tetraphenylborate (2·89g., 8·45 mmoles) were suspended together in toluene and the mixture refluxed overnight. The toluene was then pumped off leaving a buff coloured solid. Benzene was added and the mixture boiled and then filtered. On cooling colourless well-formed crystals of the adduct, p-tolyl$_2$C:NH,BPh$_3$, m.p. 171-172°, separated. (Found: C, 86·8; H, 6·4; N, 3·4; M, 430. $C_{33}H_{30}BN$ requires C, 87·7; H, 6·5; N, 3·2; M, 451). ν_{max} (Nujol mull) 3322m, 1613m, 1594s, 1562s, 1515w, 1490w, 1429s, 1321w, 1284w, 1267s, 1198m, 1190m, 1170w, 1163m, 1143w, 1122w, 1075w, 1035w, 1019w, 1000w, 960m, 943w, 917w, 888s, 867w, 842w, 825s, 803m, 782m, 752s, 741s, 735s, 731s, 714wsh, 703vs, 689w, 675m, 660w, 629s, 619m, 614w, 588w, 565m, 505m and 473m cm.$^{-1}$

Thermal decomposition of p-tolyl$_2$C:NH,BPh$_3$.

On heating a sample of the adduct at 230° for 15 min. a brown viscous liquid was produced. After distillation in vacuo into a 'bucket' attached to a cold finger, this liquid was identified by its i.r. spectrum as di-p-tolylketiminodiphenylborane.

Reaction of 1,1,3,3-tetramethylguanidyl-lithium with diphenylboron chloride.

Diphenylboron chloride (1·75g., 8·8 mmole) in toluene (10 ml.) was added by syringe to a frozen (-173°) solution of 1,1,3,3-tetramethylguanidyl-lithium (1·07g., 8·8 mmole) in toluene (40 ml.). On warming to room temperature the mixture took on an opaque grey appearance but after stirring at 60° for one hour it consisted of a white solid suspended in a colourless solution. The solution was filtered and the toluene pumped off the filtrate leaving a colourless viscous liquid which could not be crystallised. This liquid was identified as 1,1,3,3-tetramethylguanidyl-diphenylborane, $(Me_2N)_2C{:}NBPh_2$. (Found: N, 14·9%. $C_{17}H_{22}BN_3$ requires N, 15·1%). ν_{max} (Thin film) 1770s, 1600m, 1569m, 1550s, 1515s, 1490m, 1456s, 1435s, 1408s, 1361msh, 1300w, 1271m, 1242s, 1190m, 1143w, 1131m, 1096m, 1066w, 1056m, 1031m, 1000w, 988m, 917w, 891m, 875m, 845w, 810vw, 749s, 735m, 704vs, 676vw, 661m, 649m, 628w, 617m, 614m, 602m and 526w $cm.^{-1}$

During attempts to crystallise this compound, an insoluble brown oil was deposited from boiling solutions of it in 80-100° petroleum ether.

Infrared spectra of this oil indicated that it contained -C≡N groups.

Attempts to distill $(Me_2N)_2C{:}NBPh_2$ in vacuo into a 'bucket' attached to a cold finger cooled to -78° (bath temperature 50°), resulted in the isolation of a colourless oil from the bucket. This oil was identifed as dimethylaminodiphenylborane,[91] Me_2NBPh_2, by comparison of its i.r. spectrum with that of an authentic sample.

Reactions of ketiminolithiums with beryllium chloride.

Reaction of di-p-tolylketiminolithium with beryllium chloride (1:1)

Beryllium chloride (0·67g., 8·4 mmoles) in ether (25 ml.) was added by syringe to a frozen (-173°) solution of di-p-tolylketiminolithium (1·81g., 8·4 mmoles) in ether. The mixture was allowed to warm and was stirred at 20° for four hours when the red colour disappeared leaving a white solid in a colourless solution. The ether was pumped off, leaving a white solid, and toluene (20 ml.) was added. This was boiled for several minutes and then the toluene pumped off. Benzene was added and the mixture boiled and then filtered hot to remove lithium chloride. On cooling colourless crystals of dimeric di-p-tolylketiminoberyllium chloride, $(p\text{-tolyl}_2C{:}NBeCl)_2$, m.p. 168-170°, separated. (Found: C, 68·9; H, 5·2; N, 5·2%; M, 529. $C_{30}H_{28}Be_2Cl_2N_2$ requires C, 71·2; H, 5·6; N, 5·5%; M, 505). ν_{max} (Nujol mull) 1610s, 1600msh, 1566m, 1510w, 1316w, 1295m, 1258m, 1212w, 1185m, 1159w, 1115w, 1036w, 1020w, 962s, 941s, 926m, 877m, 844msh, 824s, 807msh, 769m, 742m, 734m, 720m, 692w, 671w, 647w, 633m, 614w, 593w, 550m and 474m $cm.^{-1}$

Reaction of (p-tolyl)t-butylketiminolithium with beryllium chloride (1:1)

Beryllium chloride (1·50g., 19·0 mmoles) in ether (40 ml.) was added by syringe to a frozen (-173°) solution of (p-tolyl)t-butylketiminolithium (3·44g., 19·0 mmoles) in ether. The mixture was allowed to warm and was stirred at 20° for four hours when the red colour disappeared leaving a

white solid in a colourless solution. The ether was pumped off leaving a white semi-solid. Toluene was added and the mixture boiled for 20 min. before pumping the solvent off and adding hexane. This was boiled and the mixture filtered hot to remove lithium chloride. On pumping off the hexane a colourless syrup remained which frothed and then solidified. The colourless solid was identified as dimer (p-tolyl)t-butylketimino-beryllium chloride, $(p\text{-tolylC}(Bu^t):NBeCl)_2$, m.p. 160-165° decomp. (Found: C, 67·1; H, 7·6; N, 5·8%; M, 402. $C_{24}H_{32}Be_2Cl_2N_2$ requires C, 65·9; H, 7·4; N, 6·4%; M, 436). ν_{max} (Nujol mull) 1614s, 1570msh, 1506w, 1408m, 1258m, 1220m, 1195m, 1185m, 1114m, 1101w, 1067w, 1035m, 1018w, 985s, 979s, 938m, 885msh, 975s, 839s, 823s, 790s, 769w, 749m, 732m, 718s, 687w, 654w, 637w, 611s, 555m, 545s and 531m $cm.^{-1}$

Reaction of (p-tolyl)t-butylketiminolithium with beryllium chloride (2:1)

Beryllium chloride (1·74g., 18·35 mmoles) in ether (35 ml.) was added by syringe to a frozen (-173°) solution of (p-tolyl)t-butylketimino-lithium (6·64g., 36·7 mmoles) in ether. The mixture was allowed to warm and stirred at 20° overnight. The ether was pumped off leaving a yellow semi-solid. Toluene was added and the mixture boiled and filtered hot to remove lithium chloride. After pumping off the toluene, hexane was added and the mixture boiled. On pumping down a yellow syrup remained which frothed and then solidified. This process of washing with hexane was repeated twice giving a yellow solid which was identified as dimeric

bis[(p-tolyl)t-butylketimino]beryllium, $[(p\text{-tolylC}(Bu^t):N)_2Be]_2$. The solid softened at 73° and decomposed at *ca.* 280°, without becoming liquid. (Found: C, 80·0; H, 8·6; N, 8·5%; *M*, 698. $C_{48}H_{64}Be_2N_4$ requires C, 80·7; H, 9·0; N, 7·8%; *M*, 714). ν_{max} (Nujol mull) 1739s, 1637s, 1515m, 1282w, 1264m, 1218m, 1195msh, 1188s, 1111m, 1062s, 1042s, 1020s, 974s, 950m, 926s, 899m, 847s, 823vs, 781s, 733msh, 722m, 649w, 636w, 614m, 562m, 546m and 522w $cm.^{-1}$

DISCUSSION

When this work was commenced only one example of a ketiminosilane had been prepared. This was diphenylketiminotrimethylsilane, prepared by the reaction of benzophenone with sodium bis(trimethylsilyl)amide.[49] It was of interest to study further examples of this type of compound in that they might shed more light on the question of $p\pi$-$d\pi$ partial multiple bonding between nitrogen and silicon and also they might prove to be convenient intermediates in the synthesis of ketimino derivatives of other elements.

The route originally used to prepare diphenylketiminotrimethylsilane, while useful for the preparation of trimethylsilyl derivatives, is of less value for the preparation of ketiminosilanes, $R_2C{:}NSiR^1_3$, where R^1 is other than a methyl group since hexa-organodisilazanes, $(R_3Si)_2NH$, where $R \neq Me$, (from which sodium bis(triorganosilyl)amides are obtained) are less readily available than hexamethyldisilazane, $(Me_3Si)_2NH$. Also only a single ketimino group can be attached to the silicon atom using this route. Two alternative routes suggested themselves:

a. The reaction of a ketiminolithium compound, $R^1_2C{:}NLi$, with a silicon halide.

$$R_{4-n}SiX_n + nR^1_2C{:}NLi \longrightarrow (R^1_2C{:}N)_nSiR_{4-n} + nLiX$$

b. The reaction of a silicon halide with two moles of a ketimine.

$$R_3SiX + 2R^1_2C{:}NH \longrightarrow R^1_2C{:}NSiR_3 + R^1_2C{:}NH^+_2Cl^-$$

The ketimine chosen was diphenylketimine, which is readily prepared by methanolysis of the product from the reaction of benzonitrile and phenyl magnesium bromide,[81] 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. Unsuccessful attempts have been made in these laboratories[93] to repeat the preparation of diethylketimine by methanolysis of the products of reactions between EtCN and EtLi or EtMgX,[81] or by acetylacetone cleavage at -78° of the product of the reaction between EtCN and Et_3Al.[94] It is likely that the instability of dialkylketimines is in part associated with the presence of hydrogen atoms attached to the carbon atom α to the azomethine group [as in $(>CH)_2C{=}NH$], a disadvantage avoided by the use of diphenylketimine.

Equimolar mixtures of diphenylketiminolithium and triorganochlorsilanes reacted to give the ketiminosilanes in high yield.

$$Ph_2C{:}NLi + R_3SiCl \longrightarrow Ph_2C{:}NSiR_3 + LiCl$$

$$R = Me, Et, Ph$$

The temperature needed to effect complete reaction between $Ph_2C{:}NLi$ and R_3SiCl increased in the sequence R = Me < Et < Ph. Thus for R = Me

reaction was essentially complete below 0°C, for R = Et it was necessary to boil the ether solution while for R = Ph most of the ether had to be pumped off and replaced by toluene, which was then heated to boiling. The increasingly forcing reaction conditions required probably reflect the degree of steric crowding at the silicon atom.

Silicon tetrachloride reacted below room temperature with four molar equivalents of diphenylketiminolithium giving tetrakis(diphenylketimino)-silane, $(Ph_2C{:}N)_4Si$, which crystallised as large yellow cubes from hexane.

This route to ketiminosilanes is essentially the same as that reported subsequently by Chan and Rochow[50] who used it to prepare a large number of ketiminosilanes. However, whereas Chan and Rochow prepared diphenylketiminolithium in situ from phenyl cyanide and phenyl-lithium and then added the silicon halide, the procedure used in the present work was to prepare $Ph_2C{:}NLi$ from diphenylketimine and butyl-lithium. This allowed more precise control over the relative proportions of $Ph_2C{:}NLi$ and $R_{4-n}SiX_n$ and yields of ketiminosilanes based on the chlorosilane were accordingly significantly higher than those quoted by Chan and Rochow. Also it allowed the preparation of tetrakis(diphenylketimino)-silane, a compound which Chan and Rochow were unable to prepare.

The reaction between Ph_3SiCl and an excess of diphenylketimine in boiling toluene was found to be an alternative route to $Ph_2C{:}NSiPh_3$, although much slower than that between $Ph_2C{:}NLi$ and Ph_3SiCl.

$$2Ph_2C{:}NH + Ph_3SiCl \longrightarrow Ph_2C{:}NSiPh_3 + Ph_2C{:}NH_2Cl$$

An attempt to prepare $Ph_2C{:}NSiMe_3$ by a similar reaction between $2Ph_2C{:}NH$ and Me_3SiCl failed, apparently because Me_3SiCl distilled out of the solution at the temperature needed for reaction. It appears likely that $Ph_2C{:}NSiMe_3$ could be prepared, albeit rather inconveniently, from $2Ph_2C{:}NH + Me_3SiCl$ in a sealed vessel at ca. 100°.

Diphenylketiminosilanes are bright yellow liquids, R = Me, Et, or solids, R = Ph and $(Ph_2C{:}N)_4Si$. They are hydrolysed on exposure to atmospheric moisture, $(Ph_2C{:}N)_4Si$ very rapidly, $Ph_2C{:}NSiPh_3$ only slowly.

The infrared spectra of the compounds were recorded and the frequencies of some characteristic bands are shown in Table 1.

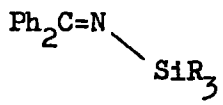
Table 1.

Infrared spectroscopic data for diphenylketiminosilanes.

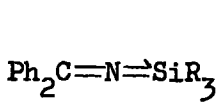
Compound	Phase	$\nu_{C=N}$, $cm.^{-1}$	ν_{Si-N}, $cm.^{-1}$
$Ph_2C{:}NH$	liquid	1603	-
$Ph_2C{:}NSiMe_3$	liquid	1653	908
$Ph_2C{:}NSiEt_3$	liquid	1666	908
$Ph_2C{:}NSiPh_3$	nujol mull	1667	906
$(Ph_2C{:}N)_4Si$	nujol mull	1646	913

The spectra all show a strong absorption characteristic of the azomethine stretching frequency, $\nu(C=N)$, in the region 1645-1670 $cm.^{-1}$ Also a band at ca. 900 $cm.^{-1}$ appears in all the spectra and has been assigned by Chan and Rochow to the Si-N stretching vibration (cf. 900-1000 $cm.^{-1}$ for silazanes[95] and 899 $cm.^{-1}$ for N-(trimethylsilyl)aniline[96]).

These features are consistent with a 'bent' structure for the molecule I rather than a linear structure II, which would allow maximum $p\pi$-$d\pi$ interaction between the nitrogen lone pair and vacant 3d orbitals on silicon, since a structure of type II would be expected to give rise to a strong absorption, due to the asymmetric stretching vibration of the linear C=N=Si unit, at a much higher frequency than that at which C=N groups normally absorb (1600-1670 $cm.^{-1}$ [97]).



I



II

However a 'bent' structure does not necessarily eliminate the possibility of $p\pi$-$d\pi$ interaction since Ebsworth[98] has calculated that substantial $p\pi$-$d\pi$ overlap is possible in a non-linear silicon-nitrogen system of this type.

The variation of $\nu_{C=N}$ with the groups, R, attached to silicon does not appear to follow any easily identifiable trend. However it is interesting to note that $\nu_{C=N}$ increases in the series Sn[50] < Ge[50] < Si,

for analogous azomethine derivatives.

There appear to be three major factors affecting $\nu_{C=N}$ in these compounds.

a. The electronegativity of the metal.

The less electronegative the metal, the greater should be the electron density in the azomethine link and the higher the C=N stretching frequency. The uncertainty regarding the relative electronegativities of Si, Ge and Sn make it difficult to assess the importance of this effect. However the observed trend in $\nu_{C=N}$ does not appear to parallel the trend shown in any of the common sets of electronegativity values.

b. Nitrogen to metal partial double bonding.

It might be thought that involvement of the nitrogen lone pair in $p\pi-d\pi$ interaction would reduce the electron density in the azomethine link. However it has been found that adducts $R_2C{:}NR^1,MX_n$ of ketimines $R_2C{:}NR^1$ with Lewis acids MX_n exhibit <u>higher</u> C=N stretching frequencies than the free ketimines.[37] It would therefore seem not unreasonable to expect $\nu_{C=N}$ in metal-substituted ketimine derivatives to increase with increasing $p\pi$-$d\pi$ interaction. Increasing $p\pi$-$d\pi$ overlap would also be likely to result in an increase in the s character of the nitrogen orbitals (as $C{:}\hat{N}$ M approaches 180°) and a consequent shortening of the C=N bond resulting in an increase in $\nu_{C=N}$. On this basis the observed increase in $\nu_{C=N}$ going from tin to silicon agrees with the expected increase in $p\pi$-$d\pi$ interaction.

c. Kinetic effects.

If the force constant of the metal-nitrogen (M-N) bond were very large compared with that of the C=N bond it could be argued that $\nu_{C=N}$ should decrease as the mass of the metal increases, i.e. regarding NM as a point mass. However this picture seems unlikely to be a true representation of the situation. It seems more likely that the mechanical constraint put on the C:N vibration by the M-N bond will be a more significant factor. This mechanical constraint, which will have the effect of increasing $\nu_{C=N}$, will increase as the force constant of the M-N bond increases going from tin to silicon; the observed increase in $\nu_{C=N}$ is consistent with this interpretation.

An interesting comparison may be drawn between $(Ph_2C{:}N)_4Si$, which appears to have angular SiNC units, and the pseudohalide derivatives $Si(NCS)_4$ and $Si(NCO)_4$. These two latter compounds have been shown by infrared and Raman spectroscopy to possess tetrahedral symmetry and hence linear Si-N-C-X, X = S, O, units.[99,100] It is not easy to see why pπ-dπ interaction should be stronger in the pseudohalide compounds than in the ketimino compound. The difference may lie in a significant contribution from the mechanical form,

$$Si-\overset{\oplus}{N}\equiv C-\overset{\ominus}{\ddot{X}}:$$

to the bonding of the pseudohalides.[101] However the theory that dative π bonding also plays a part is supported by the fact that $Ge(NCO)_4$

appears to have angular GeNC units.[100] It is worth noting that even in the field of pseudohalide compounds the situation is not entirely clear since Me_3SiNCO and Me_3SiNCS have angular structures[102] while H_3SiNCS is linear.[103]

The mass spectrum of $(Ph_2C{:}N)_4Si$ was recorded and mass and intensity values for the main peaks are shown in Table 2, together with suggested assignments.

Peaks due to fragments containing silicon were readily identified by their characteristic isotope pattern arising from the natural abundances of ^{28}Si (92·3%), ^{29}Si (4·7%) and ^{30}Si (3·0%). The monomeric state of association of $(Ph_2C{:}N)_4Si$, found by cryoscopy on benzene solutions, was supported by the absence of peaks of m/e greater than those appropriate for $(Ph_2C{:}N)_4Si^+$. The breakdown apparently involves sequential cleavage of $Ph_2C{:}N$ groups, occasional loss or aquisition of hydrogen atoms and some migration of phenyl groups to silicon. A particularly interesting feature is the number and in two cases the relative intensity of peaks arising from doubly charged fragments. For example, the peak at m/e = 194 apparently arises from the doubly charged ion $(Ph_2C{:}N)_2Si^{2+}$ for which a cumulene-type structure $[Ph_2C{:}N{:}Si{:}N{:}CPh_2]^{2+}$ appears possible (cf. the relative abundance of $(Ph_2C{:}N)_2B^+$, which could be written $Ph_2C{:}N{:}B{:}N{:}CPh_2^+$, in the mass spectrum of $(Ph_2C{:}NBF_2)_n$[13]). The relative abundance of $Ph_2CNSiPh^{2+}$ (m/e 142·5) is less readily understood.

Table 2.

Mass spectroscopic results for $(Ph_2C{:}N)_4Si$

m/e	Relative intensity	Assignment
748	12	$(Ph_2CN)_4Si$
645	1	$(Ph_2CN)_3SiPh$
568	30	$(Ph_2CN)_3Si$
465	4	$(Ph_2CN)_2SiPh$
388	2	$(Ph_2CN)_2Si$
387	4	388 minus H
374	0·1	$(Ph_2CN)_4Si$ ≠
285	4	$Ph_2CNSiPh$
284	13	$Ph_2CNSiPh$ minus H
259	10	Ph_3Si
245·5	0·1	$(Ph_2CN)_3Si$ minus Ph ≠
232·5	0·1	$(Ph_2CN)_2SiPh$ ≠
208	1	Ph_2CNSi
194	6	$(Ph_2CN)_2Si$ ≠
182	7	Ph_2Si
181	60	Ph_2CNH
180	100	Ph_2CN
142·5	8	$Ph_2CNSiPh$ ≠
105	9	PhSi
104	50	PhCNH
90	5	PhCH
78	27	PhH
77	38	Ph

≠ doubly charged ions

Reactions of 1,1,3,3-tetramethylguanidyl-lithium with chlorosilanes.

1,1,3,3-Tetramethylguanidyl-lithium reacted with trimethyl-, triethyl-, and triphenylchlorsilane in toluene in the same way as did diphenylketiminolithium.

In this case however slightly milder conditions were required e.g. triethylchlorsilane reacted below room temperature although the reaction mixture involving triphenylchlorsilane required heating to 50°.

$$(Me_2N)_2C{:}NLi + R_3SiCl \longrightarrow (Me_2N)_2C{:}NSiR_3 + LiCl$$

$$R = Me, Et, Ph$$

The products are colourless, hydrolytically sensitive liquids, R = Me, Et, or solids, R = Ph. They appear to possess greater thermal stability than the related compounds, $ROC(NR^1_2){:}NSiMe_3$, which are reported to decompose above 150° thus.[57]

$$ROC(NR^1_2){:}NSiMe_3 \longrightarrow ROSiMe_3 + R^1_2N{-}CN$$

When $(Me_2N)_2C{:}NSiMe_3$ was refluxed at 186° for two hours and then distilled through a fractionation column no forerun, containing Me_2NSiMe_3 or $Me_2N{-}CN$, arising from an analogous decomposition was obtained.

$$(Me_2N)_2C{:}NSiMe_3 \not\longrightarrow Me_2NSiMe_3 + Me_2N{-}CN$$

The infrared spectra of the guanidylsilanes were recorded and the frequencies of some characteristic bands are shown in Table 3.

Table 3.

Infrared spectroscopic data for 1,1,3,3-tetramethylguanidylsilanes.

Compound	Phase	$\nu_{C=N}$, $cm.^{-1}$	ν_{Si-N}, $cm.^{-1}$
$(Me_2N)_2C:NH$	liquid	1596	-
$(Me_2N)_2C:NSiMe_3$	liquid	1680	?
$(Me_2N)_2C:NSiEt_3$	liquid	1681	911
$(Me_2N)_2C:NSiPh_3$	nujol mull	1647	907

The spectra all show a strong absorption assignable to the C:N stretching vibration. This band appears at a significantly lower frequency for the triphenylsilyl compound than for the trimethyl- or triethylsilyl compounds. However the significance of this is dubious due to the different physical state of the sample in this case. An absorption at ca. 910 $cm.^{-1}$ is tentatively assigned to the Si-N stretching frequency in the spectra of $(Me_2N)_2C:NSiEt_3$ and $(Me_2N)_2C:NSiPh_3$, by analogy with the assignment made for the ketiminosilanes. This band appears to be obscured by others in the same region in the spectrum of $(Me_2N)_2C:NSiMe_3$. The appearance of these absorptions is again regarded as indicative of a structure involving angular SiNC units, for the reasons previously discussed in connection with the ketiminosilanes.

The p.m.r. spectra of the guanidylsilanes were recorded and the results are summarised in Table 4. These show the apparent insensitivity

Table 4.

Proton magnetic resonance results for $(Me_2N)_2C{:}NSiR_3$

Compound	τ values (p.p.m.)	
	Me_2N-	SiR_3
$(Me_2N)_2C{:}NSiMe_3$ [a]	$7{\cdot}4_0$s(4)	$9{\cdot}6_6$s(3)
$(Me_2N)_2C{:}NSiEt_3$ [a]	$7{\cdot}3_7$s(4)	$9{\cdot}1_0$m(5)
$(Me_2N)_2C{:}NSiPh_3$ [b]	$7{\cdot}3_4$s(4)	$2{\cdot}4_6$br(2), $2{\cdot}7_3$m(3)

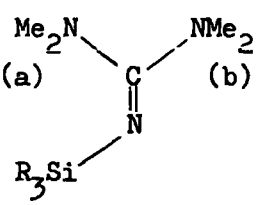
a, neat liquid, reference C_6H_6 ($\tau_{C_6H_6}$ = 2·73)

b, CCl_4 solution, reference T.M.S. ($\tau_{T.M.S.}$ = 10·00)

s = singlet, br = broad, m = multiplet. Intensities in parentheses.

of the N-Me protons to the substituent attached to the azomethine nitrogen atom cf. τ values for N-Me protons in $(Me_2N)_2C{:}NH$ and $[(Me_2N)_2C{:}NLi]_2$ are $7{\cdot}3_6$ and $7{\cdot}3_8$ respectively.[11]

The fact that the N-Me protons give rise to a singlet provides strong evidence that these compounds do not have a fixed angular structure.



If this were the case two peaks of equal intensity would be expected arising from the N-Me protons close to (a) and remote from (b) the R_3Si group. That this is not observed does not necessarily prove that the SiNC unit is linear but more likely that the R_3Si group is 'flipping' rapidly from one side of the C=N bond to the other. In this connection it is interesting to note that Martin et al. were unable to 'freeze out' geometrical isomers of $PhOC(NEt_2):NSiMe_3$ even at -97°,[57] indicating a very low activation energy for this process.

Reaction of diphenylketiminotrimethylsilane with boron halides.

During investigations of azomethine derivatives of boron, ketimino and aldimino boranes have been prepared by methods which are exemplified by the following equations.

$$Ph_2C{:}NLi + BX_3 \longrightarrow LiX + \tfrac{1}{n}(Ph_2C{:}NBX_2)_n \quad ^{11,13} \qquad (1)$$

$$Ph_2C{:}NH + Me_3B \longrightarrow MeH + \tfrac{1}{2}(Ph_2C{:}NBMe_2)_2 \quad ^{36} \qquad (2)$$

$$6Ph_2C{:}NH + BCl_3 \longrightarrow 3Ph_2C{:}NH_2Cl + (Ph_2C{:}N)_3B \quad ^{37} \qquad (3)$$

$$2MeC{:}N + Me_4B_2H_2 \longrightarrow (MeCH{:}NBMe_2)_2 \quad ^{24} \qquad (4)$$

Even when such reactions proceed essentially to completion, however, they do not necessarily provide convenient routes to particular iminoboranes, as the reaction conditions may require careful control[36] or difficulty may be experienced in separating the products of reactions of type (1)[13] or (3)[37]. It appeared that the reaction between a diphenylketiminosilane and a boron halide $R_{3-n}BX_n$ might provide a useful alternative route to diphenylketiminoboranes.

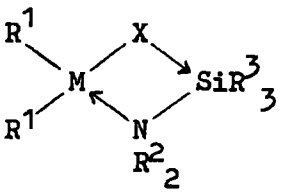
$$nPh_2C{:}NSiMe_3 + R_{3-n}BX_n \longrightarrow nMe_3SiX + (Ph_2C{:}N)_nBR_{3-n}$$

Diphenylketiminotrimethylsilane was chosen because it is easily prepared from readily available starting materials (as previously described) and in order that the volatility of the by-product, Me_3SiX, should allow its easy separation from the ketiminoborane.

This route is analogous to the established route to aminoboranes using aminosilanes.[104]

$$nR^1_2NSiMe_3 + R^2_{3-n}BX_n \longrightarrow nMe_3SiX + (R^1_2N)_nBR^2_{3-n}$$

The reaction between aminosilanes and metal (or metalloid) halides is thought to proceed via initial formation of 1:1 adducts such as $(SiH_3)_3N,BCl_3$,[105] $Me(SiH_3)_2N,BF_3$,[106] $Me_3SiNHEt,Me_3SnBr$[107] which subsequently eliminate silyl halide, usually below room temperature, via an intermediate of the type:



The use of aminosilanes in this type of reaction has recently been reviewed.[104]

Diphenylketiminotrimethylsilane reacted in the expected manner with boron trihalides, taken in equimolar proportions.

$$Ph_2C{:}NSiMe_3 + BX_3 \longrightarrow Me_3SiX + \frac{1}{n}(Ph_2C{:}NBX_2)_n$$

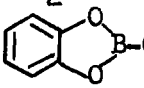
$$X = F, Cl, Br$$

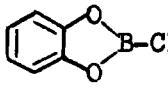
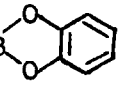
Reaction apparently occurred as the mixture warmed to about 0^o, as shown by the deposition of solid $(Ph_2C{:}NBX_2)_n$ although stirring was normally

continued for half to one hour at 20° to ensure completion of the reaction. The product, obtained in each case in high yield, was readily separated from Me_3SiX and toluene by filtration, and identified by comparison of its m.p. and infrared spectrum with samples prepared from $(Ph_2C{:}N)_3B + BF_3$,[13] or from $Ph_2C{:}NLi + BX_3$.[13]

It is notable that diphenylketiminotrimethylsilane reacted rapidly with boron trifluoride diethyl etherate at a temperature well below that at which BF_3,Et_2O is appreciably dissociated.

Reaction of diphenylketiminotrimethylsilane with boron trihalides affords probably the best route to $(Ph_2C{:}NBF_2)_n$, and a more convenient route to the other dihalides than does the ketiminolithium route,[37] which involves tedious separations from lithium halide of the slightly toluene soluble chloride $(Ph_2C{:}NBCl_2)_2$ and bromide $(Ph_2C{:}NBBr_2)_2$.

When 2-chloro-1,3,2-benzodioxaborole,  , was treated with an equimolar quantity of diphenylketiminotrimethylsilane in toluene at -78° a red gelatinous precipitate (possibly an intermediate complex) was formed which rapidly dissolved on warming. At about -50° a yellow precipitate formed. This after recrystallisation was identified as the sparingly soluble 2-diphenylketimino-1,3,2-benzodioxaborole.

$$Ph_2C{:}NSiMe_3 + \text{  } \longrightarrow Me_3SiCl + \frac{1}{n}(Ph_2C{:}N\text{  })_n$$

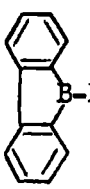
This compound along with other new iminoboranes which were prepared during this work will be discussed later.

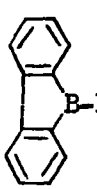
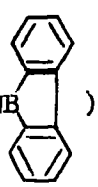
Phenylboron dichloride reacted with an equimolar amount of diphenylketiminotrimethylsilane in toluene in the same way as the boron trihalides giving the colourless, very sparingly soluble diphenylketiminophenylboron chloride.

$$Ph_2C{:}NSiMe_3 + PhBCl_2 \longrightarrow Me_3SiCl + \frac{1}{n}(Ph_2C{:}NBPhCl)_n$$

In reactions involving diarylboron halides, diphenylboron chloride and diphenylketiminotrimethylsilane reacted to form monomeric $Ph_2C{:}NBPh_2$ and trimethylchlorsilane apparently at about 0-20° in toluene, when the colour due to the silane faded, though the solution was boiled for two hours to ensure completion of the reaction.

$$Ph_2C{:}NSiMe_3 + Ph_2BCl \longrightarrow Me_3SiCl + Ph_2C{:}NBPh_2$$

The reaction between diphenylketiminotrimethylsilane and 2,2'-biphenylboron fluoride,  , required slightly more forcing conditions. Thus after an equimolar mixture of the two components in toluene had been boiled for three hours only a relatively low yield of the sparingly soluble, colourless product, $[Ph_2C{:}NB(C_6H_4)_2]_n$, was obtained.

$$Ph_2C{:}NSiMe_3 + \text{  } \longrightarrow Me_3SiF + \frac{1}{n}(Ph_2C{:}NB\text{  })_n$$

The very sterically hindered dimesitylboron fluoride, $(Me_3C_6H_2)_2BF$, did not appear to react at all with diphenylketiminotrimethylsilane during 30 min. in boiling toluene, and the reaction was incomplete even after the mixture had been held at 150° in the absence of solvent for two hours. However, fourteen hours at 150° sufficed to ensure a reasonable extent of reaction and monomeric diphenylketiminodimesitylborane, $Ph_2C{:}NB(C_6H_2Me_3)_2$, was obtained on recrystallisation of the residue.

$$Ph_2C{:}NSiMe_3 + (Me_3C_6H_2)_2BF \longrightarrow Me_3SiF + Ph_2C{:}NB(C_6H_2Me_3)_2$$

When the boron trihalides were treated with two mol. of diphenylketiminotrimethylsilane in toluene at -78°, and the solutions were allowed to warm up slowly, in attempts at the preparation of bis(diphenylketimino)-boron halides,

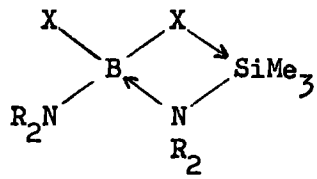
$$BX_3 + 2Ph_2C{:}NSiMe_3 \longrightarrow 2Me_3SiX + (Ph_2C{:}N)_2BX$$

the products obtained in each case were $(Ph_2C{:}NBX_2)_n$ (as a precipitate, which separated at about 0°) and $(Ph_2C{:}N)_3B$ (recovered as a wax on evaporation of the solvent).

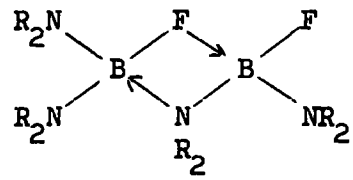
It appears that bis(diphenylketimino)boron halides are unstable with respect to disproportionation into $Ph_2C{:}NBX_2$ and $(Ph_2C{:}N)_3B$, and that the products isolated from these reactions reflect the low solubility of the dihalides $(Ph_2C{:}NBX_2)_n$ which are precipitated from solution, thereby displacing to the right the following equilibrium.

$$2(Ph_2C{:}N)_2BX \rightleftharpoons \tfrac{1}{n}(Ph_2C{:}NBX_2)_n + (Ph_2C{:}N)_3B$$

As the low solubility of the dihalides and the co-ordinative saturation of the boron atoms makes them slow to react further with $Ph_2C{:}NSiMe_3$ in toluene, it appears that formation of $(Ph_2C{:}N)_2BX$, and its disproportionation into $(Ph_2C{:}NBX_2)_n$ and $(Ph_2C{:}N)_3B$, proceeds in solution at the low temperature (ca. 0°) at which $(Ph_2C{:}NBX_2)_n$ slowly separates as a precipitate, rather than that solid $(Ph_2C{:}NBX_2)_n$ is first formed and then reacts further with $Ph_2C{:}NSiMe_3$. In this respect an interesting comparison may be drawn with the behaviour of aminoboranes. The formation of bisaminoboranes from aminosilanes,[108] and redistribution reactions of bisaminoboranes,[109,110] are believed to involve intermediate complexes of types I and II respectively.

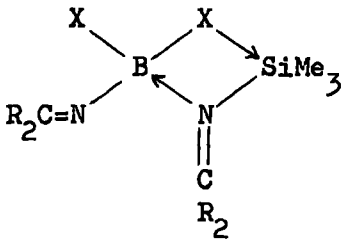


(I)

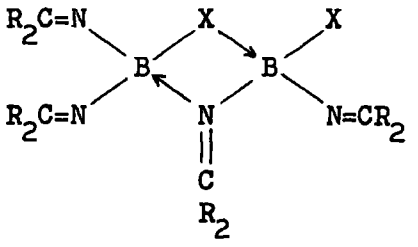


(II)

When the amino groups R_2N are bulky, these intermediates can form less readily, and the bisaminoboranes are more difficult to prepare by this route, though less liable to disproportionate once formed.[109,111] In the case of the iminoboranes, the shape of the imino group $Ph_2C{:}N$ possibly allows readier access to the nitrogen atom for the formation of analogous intermediates III and IV.



(III)



(IV)

A further indication that two mol. of diphenylketiminotrimethylsilane will rapidly replace two halogen atoms attached to boron below 0° in toluene was provided by a study of the system $PhBCl_2/2Ph_2C{:}NSiMe_3$. When the reactants were mixed at -78° in toluene and the mixture then allowed to warm up to 20° no solid $(Ph_2C{:}NBPhCl)_2$ was precipitated, and when the mixture was heated to 96° and then the solvent was pumped off the only solid product obtained was bis(diphenylketimino)phenylborane, $(Ph_2C{:}N)_2BPh$. This compound was stable with respect to disproportionation into $(Ph_2C{:}N)_3B$ and $Ph_2C{:}NBPh_2$, despite its monomeric state of association. The greater stability to disproportion of $(Ph_2C{:}N)_2BPh$ than of $(Ph_2C{:}N)_2BX$ (X = F, Cl, Br) may result from the greater bulk and weaker bridging properties of phenyl groups compared with halogens, both of which factors would inhibit formation of an intermediate IV (X=R=Ph).

Rapid transfer of diphenylketimino groups from silicon to boron was also observed in a study of the system $BCl_3/3Ph_2C{:}NSiMe_3$ in toluene. The components were mixed at -78°, the solution warmed to 20° with stirring, and ultimately heated to boiling for 30 min. At no time did a

precipitate separate and the only boron-containing product obtained was $(Ph_2C{:}N)_3B$.

Fluorenoneiminotrimethylsilane,  , reacted with diphenylboron chloride in an entirely analogous manner to diphenylketiminotrimethylsilane giving the bright yellow monomeric iminoborane,  . Similarly benzaldiminotrimethylsilane, $PhCH{:}NSiMe_3$, reacted with $PhBCl_2$ and Ph_2BCl taken in 1:1 molar proportions giving the dimeric benzaldiminoboranes, $(PhCH{:}NBPhCl)_2$ and $(PhCH{:}NBPh_2)_2$. Like the preparation of its diphenylketimino analogue, the preparation of monomeric benzaldiminodimesitylborane, $PhCH{:}NB(C_6H_2Me_3)_2$, required very forcing conditions. Thus the product was obtained only in <u>ca.</u> 30% yield after heating the reactants at 135° for three days and could not be crystallised from the reaction mixture without prior removal of the large quantity of unchanged reactants.

Iminotrimethylsilanes have thus been shown to rapidly replace one, two or three halogen atoms attached to boron and to provide a useful general route to iminoboranes, especially the sparingly soluble examples and those derived from free imines which are not isolable or cannot be obtained from RCN + R^1Li or R^1MgX.

Alternative routes to iminoboranes.

It was of interest to study alternative routes to iminoboranes both as a check on the identity of the novel monomeric iminoboranes and also since alternative routes might prove especially convenient for the preparation of particular examples.

Reaction of diphenylketiminolithium with boron halides.

Diphenylketiminolithium reacted in the expected manner with both Ph_2BCl and $PhBCl_2$, below room temperature in ether, producing the monomeric iminoboranes $Ph_2C{:}NBPh_2$ and $(Ph_2C{:}N)_2BPh$. These were easily separated from lithium chloride, produced in the reaction, by dissolving them in hot 80-100° petroleum ether and filtration of the solution.

The reaction with dimesitylboron fluoride required the ether to be replaced by toluene and the mixture stirred at 100° for three hours. However under these conditions the reaction appeared to proceed essentially to completion and the product $Ph_2C{:}NB(C_6H_2Me_3)_2$ was easily worked up in the same way as above.

Diphenylketiminolithium reacted at very low temperature with the catechol derivative, $C_6H_4O_2BCl$, with apparently exclusive cleavage of the B-Cl bond, giving the yellow compound $(Ph_2C{:}NBO_2C_6H_4)_n$. Toluene was added and boiled and the hot solution filtered. On cooling the compound crystallised. However it was only sparingly soluble and several extractions of this kind were necessary to isolate a reasonable amount of material.

In all the foregoing cases the iminoboranes prepared by this route were identical to those prepared via diphenylketiminotrimethylsilane.

Reaction of two mol. of diphenylketiminolithium with boron trichloride did not yield an isolable sample of $(Ph_2C:N)_2BCl$. A toluene-soluble brown viscous mass was obtained from which a pure compound could not be isolated.

The reaction of di-p-tolylketiminolithium and diphenylboron chloride yielded the monomeric iminoborane, $(p\text{-}MeC_6H_4)_2C:NBPh_2$, as an extremely viscous liquid. This compound is extremely soluble in hydrocarbon solvents and could not be crystallised. It was therefore purified by vacuum distillation into a 'bucket' attached to a cold finger.

Reactions of ketimines with diphenylboron chloride.

Although the reaction of boron trichloride with six mol. of diphenylketimine had previously been found to be an unsatisfactory method of preparing $(Ph_2C:N)_3B$,[37] the reaction of two mol. of a ketimine with diphenylboron chloride appeared to present a route to iminoboranes which avoided the use of the intermediate lithio- or trimethylsilylketimine derivatives.

$$2Ar_2C:NH + Ph_2BCl \longrightarrow Ar_2C:NH_2Cl + Ar_2C:NBPh_2$$

It is thought that reactions of this type proceed through an intermediate complex $Ar_2C:NH,Ph_2BCl$. Accordingly an attempt was made to isolate $Ph_2C:NH,Ph_2BCl$.

When diphenylketimine and diphenylboron chloride were mixed in equimolar proportions in 80-100° petroleum ether, a gelatinous white precipitate appeared immediately. However on stirring for 30 min. the precipitate became more granular and when filtered off proved to consist essentially of diphenylketimine hydrochloride. When the reaction was carried out in toluene no gelatinous precipitate appeared but after a few minutes insoluble diphenylketimine hydrochloride was deposited. It seems likely that the gelatinous precipitate was in fact $Ph_2C{:}NH,Ph_2BCl$ and that it is soluble in toluene; however, attempts to isolate it were not successful.

When Ph_2BCl was treated with two mol. of $Ph_2C{:}NH$ and of p-$tolyl_2C{:}NH$ in toluene (in separate experiments) a white solid immediately precipitated and heat was evolved. The mixtures were refluxed for two hours, cooled and the white solid filtered off. This was identified in each case as the ketimine hydrochloride. On evaporation of the filtrate the known iminoboranes, $Ph_2C{:}NBPh_2$ and p-$tolyl_2C{:}NBPh_2$, remained and were identified after purification.

Under similar conditions Ph_2BCl reacted with two mol. of $(p\text{-}ClC_6H_4)_2C{:}NH$ and of $(p\text{-}BrC_6H_4)PhC{:}NH$, giving the monomeric iminoboranes $(p\text{-}ClC_6H_4)_2C{:}NBPh_2$ and $(p\text{-}BrC_6H_4)PhC{:}NBPh_2$. The former could be crystallised with difficulty, the latter could not be crystallised and was distilled into a 'bucket'.

This route is useful for the preparation of freely soluble iminoboranes derived from ketimines carrying substituents which may cause side

reactions to occur with organo-lithium reagents e.g. $(p\text{-}ClC_6H_4)_2C{:}NH$. For non-crystalline iminoboranes contamination of the product with unchanged ketimine is more likely than when a ketiminolithium compound is used.

Reaction of diphenylketiminoboron dibromide with phenyl-lithium.

Reaction of a ketiminoboron dihalide with an organolithium or Grignard reagent appeared to offer a route to a series of iminoboranes by which the groups attached to boron could be conveniently varied.

$$(R^1_2C{:}NBX_2)_2 + 4R^2Li \longrightarrow \frac{2}{n}(R^1_2C{:}NBR^2_2)_n + 4LiX$$

Accordingly the reaction of diphenylketiminoboron dibromide with phenyl-lithium was investigated. After stirring the reactants in ether and toluene for one hour and then briefly boiling the mixture lithium bromide was filtered off. However on pumping the solvent off the filtrate a brown tar remained. An infrared spectrum of this material indicated that diphenylketiminodiphenylborane was present but attempts to isolate it in a pure form were unsuccessful.

The failure of this reaction to give clean products was possibly due to simultaneous side reactions involving attack of the organolithium compound on the azomethine bond.

Reaction of ketimine hydrochlorides with sodium tetraphenylborate.

In an attempt to find a route to monomeric iminoboranes from easily available, air-stable starting materials the reaction between certain ketimine hydrochlorides and sodium tetraphenylborate was investigated.

Equimolar amounts of diphenylketimine hydrochloride (obtained by passing hydrogen chloride through an ether solution of the ketimine) and sodium tetraphenylborate were suspended in toluene and the mixture refluxed overnight. After cooling, filtering and pumping off the solvent from the filtrate a discoloured semi-solid remained which, after recrystallisation from 80-100° petroleum ether, was identifed as diphenylketiminodiphenylborane. The formation of this compound is believed to proceed via the following stages.

$$Ph_2C{:}NH_2Cl + NaBPh_4 \longrightarrow Ph_2C{:}NH^+{}_2BPh^-{}_4 \xrightarrow{-C_6H_6} Ph_2C{:}NH,BPh_3 \xrightarrow{-C_6H_6} Ph_2C{:}NBPh_2$$

Elimination of benzene from ammonium tetraphenylborates has been observed before, e.g.[112]

$$Me_3NHBPh_4 \xrightarrow{200^\circ} Ph_3B + C_6H_6 + Me_3N$$

However the elimination of a second mole of benzene was somewhat unexpected, especially under such mild conditions, since diphenylketimine and triphenylborane have been previously reported not to interact on heating for several hours at 160°.[36]

Further evidence of a stepwise elimination of benzene as opposed to simultaneous elimination of two molecules of benzene was furnished by a study of the system p-tolyl$_2$C:NH$_2$Cl/NaBPh$_4$.

The reaction was performed under exactly the same conditions as that between Ph$_2$C:NH$_2$Cl and NaBPh$_4$ and the product was worked up in the same way except that it was crystallised from benzene from which it was obtained as colourless cubic crystals, m.p. 171-172°. This compound was identified as the adduct p-tolyl$_2$C:NH,BPh$_3$ as follows. Elemental analysis revealed the appropriate proportions of carbon, hydrogen and nitrogen, and the presence of boron, but did not eliminate the possibility of the compound being p-tolyl$_2$C:NH$^+_2$BPh$^-_4$ or (p-tolyl$_2$C:NBPh$_2$)$_n$.

The infrared spectrum, recorded as a nujol mull, did not correspond to a superimposition of the spectra of NaBPh$_4$ and p-tolyl$_2$C:NH$^+_2$Cl$^-$ as might have been expected for p-tolyl$_2$C:NH$^+_2$BPh$^-_4$. In particular the C=N stretching frequency was 1613 cm.$^{-1}$ cf. 1645 cm^{-1} for p-tolyl$_2$C:NH$^+_2$Cl.[84] No peak appeared at 1792 cm.$^{-1}$ showing that the compound was not monomeric p-tolyl$_2$C:NBPh$_2$ but a medium intensity peak appeared at 3322 cm.$^{-1}$ characteristic of =N-H stretching.

A p.m.r. spectrum recorded in CDCl$_3$ with tetramethylsilane as internal standard consisted of a multiplet between 2·6$_2$ and 3·1$_7$ τ, arising from aromatic protons, and a singlet at 7·7$_0$ τ, arising from CH$_3$ protons. The relative intensities were 23:6 as required for p-tolyl$_2$C:NH,BPh$_3$, as opposed to 28:6 and 18:6 required for p-tolyl$_2$C:NH$^+_2$BPh$^-_4$ and (p-tolyl$_2$C:NBPh$_2$)$_n$ respectively.

A mass spectrum of the compound run with a source temperature of 180° showed peaks due to p-tolyl$_2$C:NH and BPh$_3$ and their fragmentation products only.

A molecular weight determination by cryoscopy in benzene solution gave a value of 430 which is in good agreement with 451 required for undissociated p-tolyl$_2$C:NH,BPh$_3$ [(p-tolyl$_2$C:NBPh$_2$)$_2$ requires 746] and the adduct sublimed, apparently unchanged, in vacuo at 140°.

The isolation of this adduct and its apparent stability are presumably due to the presence of methyl groups on the benzene rings of the ketimine which increase the basic character of the nitrogen atom and reduce the acidity of the N-attached proton via an inductive effect. Its stability to dissociation may also be due in part to a high crystal lattice energy and the relative involatility of both donor and acceptor moieties.

When the adduct was heated to 230° for 15 min. a dark brown viscous liquid was obtained which on vacuum distillation afforded colourless di-p-tolyl$_2$C:NBPh$_2$.

$$(p\text{-}MeC_6H_4)_2C{:}NH,BPh_3 \longrightarrow (p\text{-}MeC_6H_4)_2C{:}NBPh_2 + C_6H_6$$

Monomeric iminoboranes.

Previous to this work all known iminoboranes $(R^1R^2C{:}NBR^3R^4)_n$ whose states of association had been measured had proved to be dimeric. Some evidence for the existence of monomeric species which were transiently stable at elevated temperatures had been obtained for the compounds $R^1C(SR^2){:}NBR^3_2$ [31] and $Ph_2C{:}NBMe_2$ [36] but the only example of an iminoborane which was apparently monomeric in the condensed phase was $(Ph_2C{:}N)_3B$.[11]

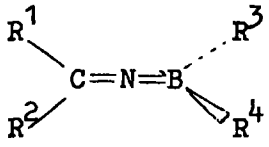
This situation was in contrast to that observed for the aminoboranes, $R^1R^2NBR^3R^4$, where monomeric species as well as dimers or higher oligomers are very common.[113]

Co-ordinative saturation of both boron and nitrogen in monomeric aminoboranes is achieved by pπ-pπ bonding which gives rise to a partial multiple bond between boron and nitrogen. Thus in monomeric Me_2NBMe_2 the B-N force constant (from its Raman spectrum) indicates a double $\overset{-}{B}{=}\overset{+}{N}$ bond.[114] Similarly in monomeric $(Me_2N)_3B$ the bond order is thought to be greater than unity on the basis of its failure to form complexes with amines and its relatively high resistance to hydrolysis.[110] However the large dipole expected for the formula $R_2\overset{+}{N}{=}\overset{-}{B}R^1_2$ is very considerably reduced by unsymmetrical electron sharing in the sense B→N owing to the electronegativity difference between boron and nitrogen, and in fact dipole moment measurements on monomeric aminodiarylboranes indicate that N-methyl compounds have polarities of different sign from those of N-aryl compounds:[115]

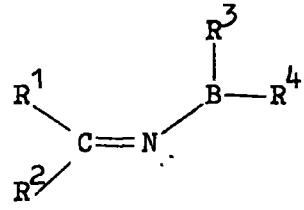
$Me_2\overset{+\rightarrow}{N}\text{-}BPh_2$ and $Ph_2\overset{\leftarrow+}{N}\text{-}BPh_2$

A consequence of the multiplicity of the B⇐N bond in monomeric aminoboranes is that rotation about this bond is hindered. Thus for $Me_2NBClPh$ it has been shown that the potential barrier to rotation about the B–N bond of 18 ± 2 kcal. $mole^{-1}$ is due to a large measure of pπ–pπ bonding rather than steric reasons.[116]

A consequence of strong multiple BN bonding in a monomeric iminoborane, $R^1R^2C{:}N{\cdot}BR^3R^4$, is that a structure involving a linear C:NB unit would be expected (I) rather than a 'bent' structure (II).



I



II

Of the iminoboranes of the type $R^1R^2C{:}NBR^3R^4$, whose preparation was described in the previous section, seven proved to be monomeric in benzene solution. The compounds are crystalline solids or, in two cases, extremely viscous liquids, which are freely soluble in non-polar solvents. All are colourless, with the exception of the yellow fluorenoneiminodiphenylborane, $(C_6H_4)_2C{:}NBPh_2$, which is derived from a yellow coloured ketimine. Except for $Ph_2C{:}NB(C_6H_4Me_3)_2$, which was apparently unaffected by moisture, all the monomeric iminoboranes are extremely rapidly hydrolysed, to the

ketimine and presumably the diarylborinic acid, on exposure to the atmosphere. Dimeric iminoboranes, by contrast, are reported to be relatively resistant to hydrolysis.[13,23,24]

The infrared spectra of the monomeric iminoboranes were recorded as nujol mulls or thin films. The spectra are characterised by the absence of a band in the normal azomethine stretching region (1590-1660 $cm.^{-1}$) and the appearance of an intense absorption in the region 1765-1820 $cm.^{-1}$ The frequency of this band for each compound is shown in Table 5.

Table 5.

Infrared spectroscopic data for monomeric iminoboranes.

Compound	$\nu_{C=N\cdots B}$, $cm.^{-1}$
$Ph_2C{:}NBPh_2$	1786
$Ph_2C{:}NB(C_6H_2Me_3)_2$	1792
$PhCH{:}NB(C_6H_2Me_3)_2$	1818
$(C_6H_4)_2C{:}NBPh_2$	1766
$(p\text{-}MeC_6H_4)_2C{:}NBPh_2$ [a]	1792
$(P\text{-}ClC_6H_4)_2C{:}NBPh_2$	1775
$(p\text{-}BrC_6H_4)PhC{:}NBPh_2$ [a]	1792

[a] sample as thin liquid film; all other figures refer to nujol mulls.

This absorption is believed to arise from the asymmetric stretching vibration of a linear C-N-B unit in these compounds.

$$\overrightarrow{C}—\overleftarrow{N}—\overleftarrow{B}$$

Its position may be compared with that of the asymmetric stretching mode of the isoelectronic allenes 1900-1970 $cm.^{-1}$ [97]

The appearance of this band is thus regarded as strong evidence in favour of a linear B-N-C structure and hence strong pπ-pπ multiple bonding between two-co-ordinate nitrogen and three-co-ordinate boron, giving a pseudoallenic structure as in I in which the groups attached to the boron atom are in a plane at right angles to the plane containing the groups attached to carbon. That this bonding is unaffected by the presence of donors was shown by infrared spectra of $Ph_2C{:}NBPh_2$ recorded in pyridine and tetrahydrofuran solutions. In both cases $\nu_{C=N\cdots B}$ increased slightly to 1799 $cm.^{-1}$ and 1797 $cm.^{-1}$ respectively in the same way as it did in carbon tetrachloride solution (1798 $cm.^{-1}$).

The variation in $\nu_{C=N\cdots B}$ from one compound to another is belived to reflect the variation of the force constant of the C=N bond due to different carbon-attached substituents rather than a variation in the degree of pπ-pπ bonding, since it parallels the variation in $\nu_{C=N}$ of the parent ketimines.

Another monomeric iminoborane prepared during this study bis(diphenyl-ketimino)borane, $(Ph_2C{:}N)_2BPh$, is similar to the above compounds in that

it is a very hydrolytically sensitive, colourless crystalline solid, freely soluble in hydrocarbons. However its infrared spectrum, unlike that of $Ph_2C{:}NBPh_2$, shows no intense absorption at ca. 1790 $cm.^{-1}$ but instead a strong band at 1672 $cm.^{-1}$ (nujol mull), (cf. $\nu_{C=N}$ for $(Ph_2C{:}N)_3B$ at 1667 $cm.^{-1}$ [11]). These results indicate that the C:NB units in $(Ph_2C{:}N)_2BPh$ and $(Ph_2C{:}N)_3B$ are probably bent and that the observed absorptions arise from C:N stretching rather than from the asymmetric stretching of the linear C:NB units. Thus it appears that a greater degree of $p\pi$-$p\pi$ overlap between nitrogen and boron than is possible in $(Ph_2C{:}N)_2BPh$ and $(Ph_2C{:}N)_3B$, where respectively two and three nitrogen lone pairs are competing for one vacant p orbital on boron, is required to produce linear C:NB units.

It is interesting to note that these monomeric iminoboranes appear to be hydrolysed in the atmosphere much more readily than the analogous monomeric secondary amino derivatives of boron.[115] This phenomenon might be taken to indicate that the boron atom is less co-ordinatively saturated in the iminoboranes than in the aminoboranes. However in view of their apparent lack of Lewis acidity a more likely explanation is that nucleophilic attack by water molecules is less sterically hindered for iminoboranes with the notable exception of $Ph_2C{:}NB(C_6H_2Me_3)$, than for aminoboranes.

In an effort to obtain further information about the degree of co-ordinative saturation of the boron atoms in the monomeric iminoboranes

an attempt was made to record the ^{11}B n.m.r. spectra of $Ph_2C{:}NBPh_2$, $(p\text{-}MeC_6H_4)_2C{:}NBPh_2$, $(Ph_2C{:}N)_2BPh$ and $(Ph_2C{:}N)_3B$ using concentrated solutions of the compounds in toluene. However in each case only the resonance due to the external standard, BF_3,EtO, was observed. This failure was probably due to the low percentage of boron in the compounds and also because of the broadening of the ^{11}B resonance which is often found for compounds in which phenyl groups are attached to the boron atom.[117]

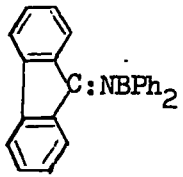
Similarly the ultraviolet spectra of several of the iminoboranes (monomeric and dimeric) were recorded in cyclohexane solution in the hope of studying the effect on the $n\rightarrow\pi^*$ transition of $p\pi\text{-}p\pi$ bonding, as was done by Chan and Rochow for the ketiminosilanes.[50] However a number of bands were observed in the spectra of both monomers and dimers and it was found impossible to assign any of them with certainty to the required transition.

All the monomeric iminoboranes prepared carried aryl groups attached to both boron and carbon rendering proton magnetic resonance studies of limited value. However the p.m.r. spectra of several of the compounds were recorded and the results are summarised in Table 6.

The spectrum of $(C_6H_4)_2C{:}NBPh_2$ in CCl_4 consists of two closely spaced low field multiplets centred on $\tau = 2{\cdot}4_0$ and $2{\cdot}7_5$ respectively. The relative intensities are 4:5 suggesting that they may possibly arise from the carbon-attached aryl groups and the boron-attached phenyl groups respectively. However this is by no means certain since the spectrum of

Table 6.

Proton magnetic resonance spectroscopic results for iminoboranes.

Compound	τ values ($\tau_{T.M.S.}$ = 10·00 p.p.m.)		
	Aromatic protons	CH_3	N=C-H
	$2{\cdot}4_0$m(4), $2{\cdot}7_5$m(5)	-	-
$(p\text{-}MeC_6H_4)C{:}NBPh_2$ [b]	$2{\cdot}4_5$m(3), $2{\cdot}8_7$m(6)	$7{\cdot}7_1$s(3)	-
$Ph_2C{:}NB(mesityl)_2$	$2{\cdot}5_8$m(2), $2{\cdot}6_8$m(3), $3{\cdot}4_0$s(2)	$7{\cdot}8_0$s(3), $8{\cdot}0_0$s(6)	-
$Ph_2C{:}NB(mesityl)_2$ [a]	$2{\cdot}6_7$m(2), $2{\cdot}9_9$m(3), $3{\cdot}2_8$s(2)	$7{\cdot}8_2$s(6), $7{\cdot}9_6$s(3)	-
$PhCH{:}NB(mesityl)_2$	$2{\cdot}4_5$m(10), $3{\cdot}2_7$s(4)	$7{\cdot}7_9$s(18)	$1{\cdot}6_4$s(1)
$PhCH{:}NB(mesityl)_2$ [a]	$2{\cdot}7_2$m(10), $3{\cdot}1_3$s(4)	$7{\cdot}5_5$s(12), $7{\cdot}7_8$s(6)	$2{\cdot}0_5$s(1)

[a] C_6D_6 solvent; all other figures refer to samples in CCl_4 as solvent.

[b] internal reference C_6H_{12} ($\tau_{C_6H_{12}}$ = 8·56)

s = singlet, m = multiplet.

Relative intensities in parentheses.

$(p\text{-}MeC_6H_4)_2C{:}NBPh_2$ in CCl_4 also shows two similar low field multiplets centred on $\tau = 2{\cdot}4_5$ and $2{\cdot}8_7$, but in this case the relative intensities are 1:2. The CH_3 protons in this latter compound appear as a sharp singlet at $\tau = 7{\cdot}7_1$. This is at slightly lower field than is found for the CH_3 protons in the spectrum of the free ketimine in CCl_4 which appear at $\tau = 7{\cdot}9_8$ [118] and may reflect the involvement of the nitrogen lone pair in $p\pi\text{-}p\pi$ multiple bonding in the iminoborane rather than in the conjugated aromatic system in the free ketimine. In any event the relative intensities of the aryl and methyl proton resonances (3:1) provide useful confirmation of the formulation of the compound.

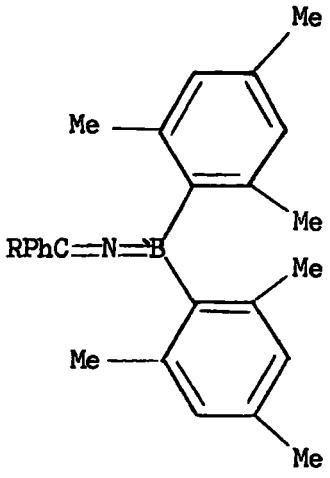
In the p.m.r. spectrum of $Ph_2C{:}NB(C_6H_2Me_3)_2$ run in CCl_4 the singlets at $\tau = 8{\cdot}0_0$ and $\tau = 7{\cdot}8_0$ (relative intensity 6:3) are readily assigned to the ortho and para CH_3 protons respectively. The ring protons meta to the boron atom appear as a singlet at $\tau = 3{\cdot}4_0$ (relative intensity 2), while the ring protons of the ketimine group appear as two multiplets centred on $\tau = 2{\cdot}5_8$ (relative intensity 2) and $\tau = 2{\cdot}6_8$ (relative intensity 3). These two multiplets are belived to arise from the ortho and meta/para sets of protons as has previously been noted for diphenylketimino derivatives e.g. $(Ph_2C{:}N)_3B$,[11] $(Ph_2C{:}NAlMe_2)_2$ [12] etc.

An interesting solvent dependence was noted when the spectrum was recorded in deutero benzene, C_6D_6. Slight shifts occurred in the positions of the aromatic proton resonances but the most striking difference in the spectra was that the resonance due to the ortho CH_3 groups (relative intensity 6) now appeared at lower field than that due to the

para CH_3 group (relative intensity 3), the reverse of what was observed in the spectrum run in CCl_4. A similar solvent dependence was also found in the p.m.r. spectra of the monomeric aldiminoborane, $PhCH{:}NB(C_6H_2Me_3)_2$. In C_6D_6 the ortho CH_3 protons appeared as a singlet at $\tau = 7{\cdot}7_5$ (relative intensity 12) and the para CH_3 protons as a singlet at $\tau = 7{\cdot}7_8$ (relative intensity 6) while in CCl_4 the ortho and para CH_3 protons appear as a lone singlet (relative intensity 18) at $\tau = 7{\cdot}7_9$.

The mesityl ring protons appear in the spectra of $PhCH{:}NB(C_6H_2Me_3)_2$ as a sharp singlet (relative intensity 4) found at $\tau = 3{\cdot}1_3$ in C_6D_6 and at $\tau = 3{\cdot}2_7$ in CCl_4 while the ring protons of the aldimine group appear as low field multiplets which in this case cannot easily be resolved into contributions from ortho and meta/para protons. The methine proton was observed in the spectra run in both C_6D_6 and CCl_4 as a sharp singlet (relative intensity 1) at $\tau = 2{\cdot}0_5$ and $\tau = 1{\cdot}6_4$ respectively.

The appearance of the methyl resonances in the mesityl compounds as two singlets of relative intensity 2:1 effectively rules out a fixed planar structure for the $B(mesityl)_2$ unit (I) since ideally three singlets of relative intensity 1:1:1 would be expected to arise from such a configuration. This structure is in any case unlikely on purely steric considerations.



R = Ph, H

I

However it cannot be automatically assumed that the rings are twisted through 90° about the B-C bonds from the position shown. Free rotation about the B-C bonds seems unlikely in such a sterically crowded system; however it is possible that rapid 'flip' between equivalent intermediate positions may occur and that an 'average' situation is observed.

The mass spectra of $Ph_2C{:}NBPh_2$ and of $(C_6H_4)_2C{:}NBPh_2$ were recorded and significantly there were no peaks at higher m/e values than 345 and 343 respectively, the molecular weights of the monomeric units. Also no sets of peaks were observed with the characteristic relative intensities associated with the presence of two boron atoms in a fragment. Unfortunately both spectra contained peaks due to products of partial hydrolysis which could not be avoided during sampling. However the parent peaks were reasonably intense and easily identifiable and peaks due to loss of one phenyl group were of greater relative intensity than the parent peaks.

The mass spectra of the less hydrolytically sensitive dimesityl derivatives, $Ph_2C{:}NB(C_6H_2Me_3)_2$ and $PhCH{:}NB(C_6H_2Me_3)_2$ were also recorded and

mass and intensity values for the main peaks are listed in Tables 7 and 8, together with suggested assignments. Again no peaks were observed at higher m/e values than 429 and 353, the molecular weights of the monomeric units, and only peaks arising from fragments of the monomers were observed. An accurate mass measurement on the parent peak of $Ph_2C{:}NB(C_6H_2Me_3)_2$ gave a value of 429·2645 which is correct to within 4 p.p.m. for this compound. The low resolution spectra both show fairly intense peaks due to the parent ions and in both cases the base peak arises from direct elimination of mesitylene, $C_6H_3Me_3$, from the parent ion. Other intense peaks arise from loss of one methyl group from both the base and parent peaks in both cases. Cleavage of the boron-nitrogen link does not appear to be a very important feature of the breakdown pattern as evidenced by the relatively low abundances of $B(C_6H_2Me_3)_2^+$ and $PhRCN^+$ (R = Ph, H). This is in contrast to what has previously been observed for $Ph_2C{:}NBMe_2$,[36] which was apparently monomeric in the vapour phase, and may reflect a higher B-N bond order in these iminodimesitylboranes. Other interesting features of the spectra are the high abundance of the doubly charged parent ions and also the occurrence in the spectrum of $Ph_2C{:}NB(C_6H_2Me_3)_2$ of Ph_2B^+ which must result from the transfer of phenyl groups from carbon to boron.

1,1,3,3-tetramethylguanidyldiphenylborane.

Tetramethylguanidyl-lithium reacted with diphenylboron chloride giving $(Me_2N)_2C{:}NBPh_2$ as a colourless, viscous liquid. The compound

Table 7.

Mass spectroscopic results for $Ph_2C{:}NB(C_6H_2Me_3)_2$

m/e	Relative intensity	Assignment
429	33	$Ph_2C{:}NB(C_6H_2Me_3)_2$
414	85	$Ph_2C{:}NB(C_6H_2Me_3)(C_6H_2Me_2)$
352	51	$PhCNB(C_6H_2Me_3)_2$
309	100	$Ph_2C{:}NBC_6HMe_3$
294	40	$Ph_2C{:}NBC_6HMe_2$
249	9	$B(C_6H_2Me_3)_2$
232	8	$PhCNBC_6HMe_3$
214.5	9	$Ph_2C{:}NB(C_6H_2Me_3)_2$ ⁄
205	10	$PhCNBHC_6H_3Me_2$
180	3	Ph_2CN
168.5	8	$PhCNB(C_6H_2Me_3)(C_6H_2Me_2)$ ⁄
165	7	BPh_2
144	5	$NBC_6H_2Me_3$
129	8	BC_6HMe_3
119	9	$C_6H_2Me_3$
105	5	$C_6H_3Me_2$
103	6	PhCN
91	5	$C_6H_5CH_2$
89	7	PhBH
77	5	Ph

All masses quoted relate to fragments in which the borons are ^{11}B

⁄ doubly charged.

Table 8.

Mass spectroscopic results for $PhCH{:}NB(C_6H_2Me_3)_2$

m/e	Relative intensity	Assignment
353	62	$PhCHNB(C_6H_2Me_3)_2$
338	65	$PhCHNB(C_6H_2Me_3)(C_6H_2Me_2)$
276	12	$CHNB(C_6H_2Me_3)_2$
260	10	$CHNB(C_6H_2Me_3)(C_6H_2Me_2)$
249	7	$B(C_6H_2Me_3)_2$
233	100	$PhCHNBC_6HMe_3$
218	60	$PhCHNBC_6HMe_2$
176•5	8	$PhCHNB(C_6H_2Me_3)_2$ ≠
168•5	5	$PhCHNB(C_6H_2Me_3)(C_6HMe_2)$ ≠
161•5	8	$PhCHNB(C_6H_2Me_2)_2$ ≠
156	6	$CNBC_6H_2Me_3$
129	15	BC_6HMe_3
119	14	$C_6H_2Me_3$
105	13	$C_6H_3Me_2$
104	12	PhCHN
103	20	PhCN
91	10	$C_6H_5CH_2$
89	9	PhBH
77	9	Ph

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

≠ doubly charged.

could not be crystallised or distilled so molecular weight determinations were not attempted. However its rapid hydrolysis in the atmosphere and the presence of a straong band at 1770 $cm.^{-1}$ in its infrared spectrum suggest that it is monomeric with a linear C:NB unit like the iminoboranes discussed above.

Interestingly an attempt to distil the compound in vacuo yielded Me_2NBPh_2, apparently by elimination of dimethylcyanamide.

$$(Me_2N)_2C{:}NBPh_2 \longrightarrow Me_2NBPh_2 + Me_2N{\cdot}CN$$

This reaction is analogous to the thermal decomposition of the compounds $MeC(SR^1){:}NBR_2$.[31]

$$MeC(SR^1){:}NBR_2 \longrightarrow R^1SBR_2 + MeCN$$

Associated iminoboranes.

During this investigation of iminoboranes a number of relatively insoluble, high melting examples were prepared. These were unaffected by several days' exposure to the atmosphere, indicating that they contained four-co-ordinate boron atoms. Only two of the compounds, $PhCH{:}NBPh_2$ and PhCH:NBClPh, were sufficiently soluble in benzene to allow determination of their molecular complexity by cryoscopy in that solvent. In both cases they proved to be dimeric. An attempt was therefore made to determine the molecular complexity of $Ph_2C{:}NBClPh$,

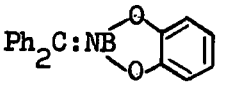
$Ph_2C{:}NBO_2C_6H_4$ and  by mass spectroscopy. The last compound proved too involatile to allow its mass spectrum to be recorded. However a spectrum of $Ph_2C{:}NBO_2C_6H_4$ was obtained and the mass and intensity values for the main peaks are listed in Table 9, together with suggested assignments.

These results indicate that the compound exists in the vapour phase at ca. 200° largely as the monomer. However weak peaks arising from associated species were also observed. As for the iminodimesitylboranes loss of a phenyl group from the imino residue is relatively important but in contrast to the spectra of those compounds a large peak is observed at m/e = 180 due to Ph_2CN^+ although no peak due to $C_6H_4O_2B^+$ could be detected. This phenomenon has previously been observed in the mass spectrum of $(Ph_2C{:}NBCl_2)_2$ in which no peak due to BCl_2^+ was detected.[13]

The mass spectrum of $Ph_2C{:}NBClPh$, summarised in Table 10, shows no peaks at all at higher m/e than 303, the molecular weight of the monomer. Again a large peak due to Ph_2CN^+ is observed, while losses of a chlorine atom or a phenyl group from the parent monomer are important. A peak due to Ph_2B^+ arising from migration of a phenyl group from carbon to boron is also observed.

These observations are by no means conclusive in determining the molecular complexity of these iminoboranes. However further information was obtained from their infrared spectra, recorded as nujol mulls.

Table 9.

Mass spectroscopic results for $Ph_2C{:}NB$ 

m/e	Relative intensity	Assignment
402	very weak	$(Ph_2CN)_2BO_2C_6H_4$ minus Ph
387	very weak	$(Ph_2CN)_2BO$
328	1	$Ph_2CNB_2O_3PhH$
313	1	$Ph_2CNBO_2C_6H_4N$
299	11	$Ph_2CNBO_2C_6H_4$
254	30	$Ph_2CNBC_5H_3$
222	33	$PhCNBO_2C_6H_4$
196	2	$PhBO_2C_6H_4$
180	59	Ph_2CN
149·5	1	$Ph_2CNBO_2C_6H_4$ ⁄
136	14	$PhCNBO_2$
104	44	PhCNH
92	17	C_6H_4O
77	100	Ph

All masses quoted relate to fragments in which the borons are ^{11}B

⁄ doubly charged

Table 10.

Mass spectroscopic results for $Ph_2C{:}NBClPh$

m/e	Relative intensity	Assignment
303	11	$Ph_2CNBClPh$
268	5	Ph_2CNBPh
226	15	Ph_2CNBCl
180	100	Ph_2CN
165	8	Ph_2B
154	8	Ph_2
123	10	PhBCl
104	46	PhCHN
78	20	PhH
77	33	Ph

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

The C=N stretching frequencies are listed in Table 11.

Table 11.

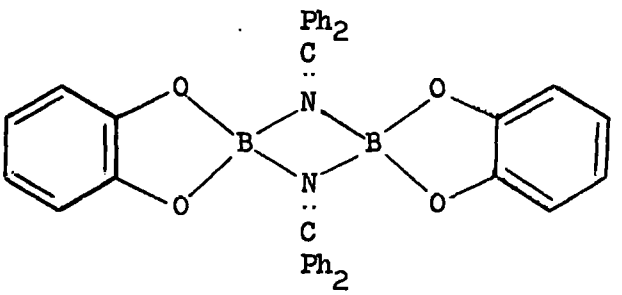
Infrared spectroscopic data for iminoboranes

Compound	$\nu_{C=N}$, $cm.^{-1}$
$(Ph_2C:NBO_2C_6H_4)_n$	1623
$(Ph_2C:NB(C_6H_4)_2)_n$	1616
$(Ph_2C:NBClPh)_n$	1612
$(Ph_2C:NBCl_2)_2$ [13]	1590
$(PhCH:NBPh_2)_2$	1643
$(PhCH:NBClPh)_2$	1639

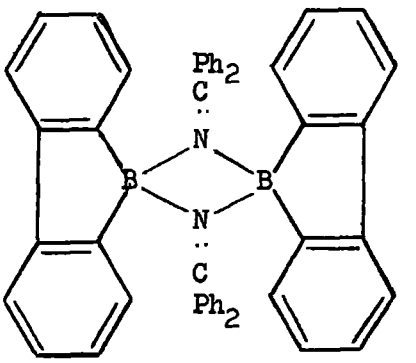
All figures relate to nujol mulls

The frequencies for the diphenylketiminoboranes are in good agreement with the values found for bridging ketimino groups in dimeric diphenylketimino derivatives, $(Ph_2C:NMX_2)_2$, of boron[13] (X = Cl, Br, I), aluminium (X = Cl, Br,[118] Me, Et, Ph[12]) and gallium (X = Cl,[118] Me, Et, Ph[47]). The C=N stretching frequencies for the benzaldiminoboranes are slightly higher, as is to be expected by analogy with dimeric benzaldimino derivatives of aluminium.[40] Thus, while higher degrees of association

are not completely eliminated, it is probable that these diphenylketiminoboranes are dimeric in the solid phase, $Ph_2C{:}NBO_2C_6H_4$ and $Ph_2C{:}NB(C_6H_4)_2$ having structures I and II respectively.



I



II

Factors affecting the degree of association of iminoboranes.

One of the reasons for preparing the iminoboranes described above was to study the factors which determine their degree of association. In general compounds in which an acceptor atom (e.g. boron) is attached to a donor atom (e.g. nitrogen) associate in order to make maximum use of their available orbitals for bonding. Thus, for example, alkoxy and amino derivatives of aluminium $ROAlR^1_2$ and $R_2NAlR^1_2$ generally dimerise forming donor-acceptor bridges between oxygen (or nitrogen) and aluminium.[113] Aminoboranes can behave in the same way or can make use of 'internal-co-ordination' or $p\pi$-$p\pi$ bonding, described previously, to achieve co-ordinative saturation of the boron atom. This factor may

therefore reduce the tendency of aminoboranes to associate. However they are normally only monomeric when bulky substituents are attached to boron and/or nitrogen. Aminoboranes with small substituents are normally dimeric (especially if the boron-attached substituents are strongly electron withdrawing e.g. Cl) or, occasionally, trimeric.[119]

Entropy considerations always favour low degrees of association since the number of independent molecules is then a maximum i.e. monomers are preferred to dimers or trimers with a given phase.

Monomers are also favoured by valence angle strain since this will be negligible for monomers while being more important for dimers than for trimers.

There appear to be two obvious major factors which could determine the state of association of the iminoboranes prepared in this study viz. (a) steric factors, (b) stabilisation due to pπ-pπ overlap.

If the over-riding factor were (b) it is difficult to understand why pπ-pπ overlap should be weaker in $Ph_2C{:}NB(C_6H_4)_2$ than in $Ph_2C{:}NBPh_2$ or in $PhCH{:}NBPh_2$ than in $PhCH{:}NB(mesityl)_2$. However it is significant that the bulk of the groups attached to boron and carbon is in each case greater in the monomers than in the dimers. It is also worth noting that, as might be expected, the bulk of the groups attached to boron appears more important than those attached to carbon; $Ph_2C{:}NBPh_2$ being monomeric while $PhCHC{:}NBPh_2$ is dimeric. Thus the steric factor appears to be dominant.

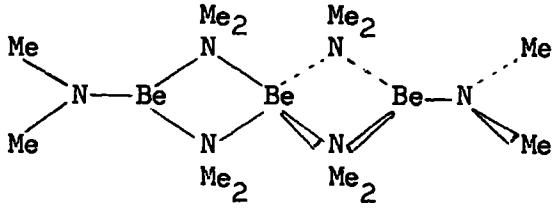
This conclusion appears to be supported by the previous studies on aldimino and ketiminoboranes, outlined in the Introduction, where the degree of steric crowding caused by the substituents carried on boron and carbon was not sufficiently large to prevent formation of dimers, although in two cases, $Bu^tCH{:}NBBu_2$ [32,33] and $Ph_2C{:}NBMe_2$,[36] the dimers dissociated in the vapour phase, as apparently occurred with $Ph_2C{:}NBClPh$.

The apparently monomeric nature of the highly halogenated iminoboranes $CCl_3CBr{:}NBXY$ (X = Ph, Me or Br; Y = Ph or Me), recently reported by Meller and Maringgele,[39] also appears explicable on largely steric grounds, it being significant that similar compounds containing less bulky substituents e.g. $Cl_2C{:}NBCl_2$ [15] are dimeric. The compound which Meller formulated as monomeric $BrCH{:}NBBr_2$ [39] appears anomalous but significantly it was only poorly characterised, having been obtained in less than 1% yield from the reaction between HCN and BBr_3.

Ketimino derivatives of beryllium.

Having found that pπ-pπ partial multiple bonding can easily be detected in monomeric iminoboranes, $R^1_2C{:}NBR^2_2$, by infrared spectroscopy, it was of interest to use the same technique to examine possible pπ-pπ interaction between nitrogen and beryllium.

An X-ray crystallographic study by Atwood and Stucky showed that bis(dimethylamino)beryllium, $[(Me_2N)_2Be]_3$, has structure I.[120]

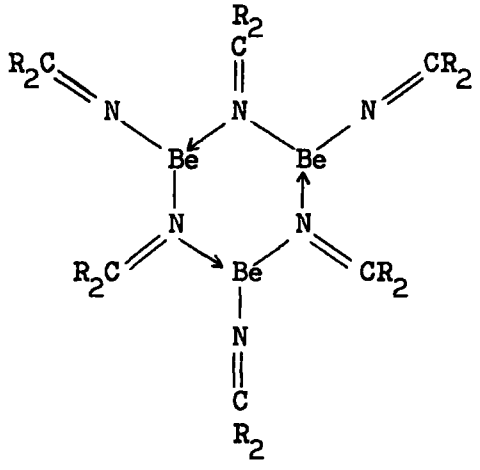


I

It was found that the co-ordination about the terminal nitrogen atoms was trigonal planar with the terminal—N$\begin{smallmatrix} C \\ \diagdown \\ \diagup \\ C \end{smallmatrix}$ units in the same plane as the adjacent $(BeN)_2$ ring. On the basis of this and measurements of the ^{13}C-H coupling constants it was suggested[120] that a significant degree of pπ-pπ bonding between nitrogen and beryllium exists in this compound.

In order to investigate the possibility of pπ-pπ interaction between nitrogen and beryllium in ketimino derivatives of beryllium, Dr. B.K. Wyatt of this department prepared $(Ph_2C{:}N)_2Be$ and $(p\text{-tolyl}_2C{:}N)_2Be$ from $BeCl_2$ and 2 mol. of the appropriate ketiminolithium in ether, and also $Ph_2C{:}NBeCl$

from $Ph_2C{:}NSiMe_3$ + $BeCl_2$. $Ph_2C{:}NBeCl$ is a colourless crystalline solid which dissolves in benzene as the dimer. The bis-ketimino derivatives are yellow solids which were found to be insufficiently soluble in benzene to allow reliable cryoscopic molecular weight determinations, although a determination by the author on $[(p\text{-tolyl}_2C{:}N)_2Be]_n$ gave a value for n of 2·7. A value for n of 3 was supported by the p.m.r. spectrum of $(p\text{-tolyl}_2C{:}N)_2Be$, recorded in C_6D_6, in which the aromatic protons gave rise to multiplets at τ = 3·0 p.p.m. (intensity 2) and τ = 2·1 p.p.m. (intensity 1). These are believed to arise from the four bridging and two terminal ketimino groups respectively of a linear trimer similar to $[(Me_2N)_2Be]_3$ and appear to rule out the possibility of a cyclic structure (II), for this compound, which has an equal number of bridging and terminal ketimino groups.



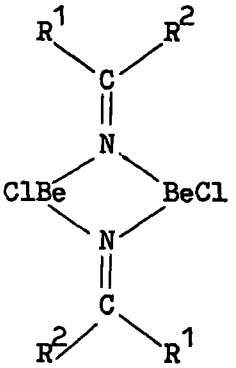
II

Unfortunately the p-CH_3 protons were not split into two singlets, arising from bridging and terminal ketimino groups, as had been hoped,

possibly due to their remoteness from the beryllium-nitrogen skeleton of the molecule.

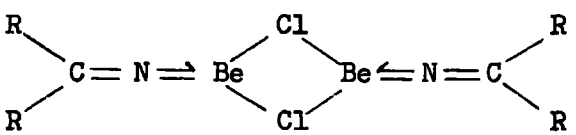
In an attempt to obtain a more soluble bis-ketimino derivative, $(p\text{-tolyl}C(Bu^t):N)_2Be$ was prepared from 2 $p\text{-tolyl}C(Bu^t):NLi + BeCl_2$. The product was obtained as a yellow powder, freely soluble in hydrocarbon solvents, and was dimeric in benzene solution. The p.m.r. spectrum of this compound, recorded in C_6D_6, consisted of a broad multiplet at $\tau = 2{\cdot}8_7$ (intensity 4), arising from the aryl protons, two overlapping singlets at $\tau = 7{\cdot}7_7$ and $\tau = 7{\cdot}8_3$ (combined intensity 3), evidently arising from the protons of the $p\text{-}CH_3$ groups, and a somewhat broadened singlet at $\tau = 8{\cdot}7_9$ (intensity 9) arising from the protons of the t-butyl groups. That the $p\text{-}CH_3$ resonance is split into two singlets of apparently equal intensity is somewhat surprising in view of their appearance as a lone singlet in $[(p\text{-tolyl}_2C:N)_2Be]_3$. However several geometrical isomers of $[(p\text{-tolyl}C(Bu^t):N)_2Be]_2$ can in principle exist.

The ketiminoberyllium chlorides, $p\text{-tolyl}_2C:NBeCl$ and $p\text{-tolyl}C(Bu^t):NBeCl$ were also obtained from the appropriate ketiminolithium and $BeCl_2$ as colourless solids. These, like $Ph_2C:NBeCl$, dissolve in benzene as the dimers and a structure (III), involving bridging nitrogen atoms, appears possible as is the case in the related dimeric ketiminoaluminium and boron dihalides, $(Ph_2C:NAlX_2)_2$ (X = Cl, Br) and $(Ph_2C:NBX_2)_2$ (X = Cl, Br, I).



III

However an alternative structure (IV) involving chlorine bridges, as occur for example in beryllium chloride itself, must be considered for the ketiminoberyllium chlorides, especially if nitrogen to beryllium pπ-pπ partial multiple bonding has a significant stabilising influence



IV

In this context it would be useful to know the mode of association of aminoberyllium chlorides, R_2NBeCl. However this field does not appear to have been investigated.

The infrared spectra of all the ketiminoberyllium derivatives were recorded as nujol mulls and the frequencies of some characteristic bands are listed in Table 12.

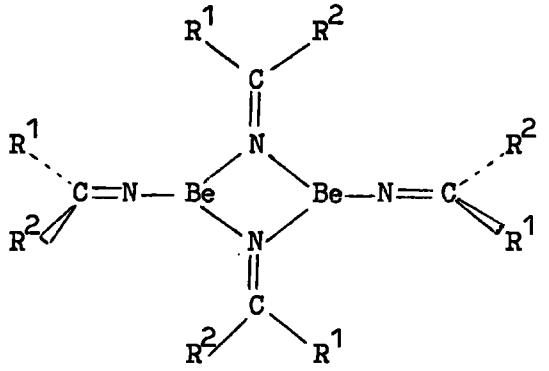
Table 12.

Compound	$\nu_{C=N}$ (bridging) $cm.^{-1}$	$\nu_{C=N\rightarrow Be}$ (terminal) $cm.^{-1}$
$(Ph_2C:NBeCl)_2$	1608	-
$(p\text{-tolyl}_2C:NBeCl)_2$	1610	-
$(p\text{-tolylC}(Bu^t):NBeCl)_2$	1614	-
$[(Ph_2C:N)_2Be]_n$	1627	1732
$[(p\text{-tolyl}_2C:N)_2Be]_3$	1626	1731
$[(p\text{-tolylC}(Bu^t):N)_2Be]_2$	1637	1739

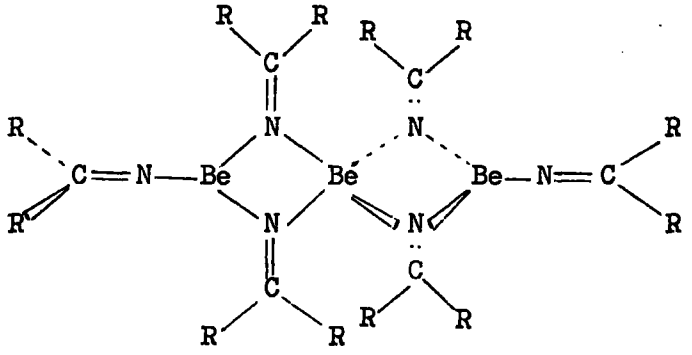
The spectra of the ketiminoberyllium chlorides $(R^1R^2C:NBeCl)_2$ show a strong band at ca. 1610 $cm.^{-1}$ This is in the region typical of $\nu_{C=N}$ for bridging ketimine groups and thus supports the nitrogen bridged structure (III). That nitrogen acts as a stronger donor to beryllium than does chlorine is not unexpected and it is possible that $p\pi$-$p\pi$ interaction occurs between chlorine and beryllium since covalent radii of beryllium, nitrogen and chlorine indicate that $p\pi$-$p\pi$ interaction between beryllium and chlorine is as likely as between beryllium and nitrogen.

The infrared spectra of the bis-ketimino derivatives $[(R^1R^2C:N)_2Be]_n$ contain two strong bands, near 1630 $cm.^{-1}$ and near 1735 $cm.^{-1}$ The lower

frequency band is again assignable to $\nu_{C=N}$ for bridging ketimine groups. The higher frequency band is believed to arise from asymmetric stretching of linear C=N–Be units involving terminal ketimine groups. The structures of $[(p\text{-tolyl}C(Bu^t):N)_2Be]_2$ and $[(p\text{-tolyl}_2C:N)_2Be]_3$ are thus thought to be as shown in V and VI respectively.



V



VI

The frequency of the bands due to C=N–Be is ca. 50 $cm.^{-1}$ lower than the frequency of corresponding absorptions due to C=N–B asymmetric stretching in the monomeric ketiminoboranes. This difference is believed to reflect

the difference in the N⋯M bond orders although differences in the substituents attached to B and Be may also contribute. These frequencies can moreover be compared with $\nu_{C:N:C}$ at 1845 $cm.^{-1}$ for the dialkylidene-ammonium cation, $[Ph_2C:N:CPh_2]^+$, which is isoelectronic with the bis-ketimino derivatives of beryllium and the monomeric ketiminoboranes and has been obtained in salts of the type $[Ph_2C:N:CPh_2]^+SbCl_6^-$.[121] The decreasing frequency of $\nu_{C=N\cdots M}$ in the sequence M = C > B > Be is believed to reflect the decreasing N⋯M bond order in the same sequence.

APPENDIX

The infrared spectra of imine adducts, $R^1R^2C{:}NR^3,MX_n$, and salts, $[R^1R^2C{:}NR^3H]^+X^-$.

During attempts to prepare iminoboranes the adduct $Ph_2C{:}NH,BF_3$ and the salt $[Ph_2C{:}NH_2]^+Cl^-$ were obtained and their infrared spectra recorded.[36] The spectra revealed an unexpected <u>increase</u> in $\nu_{C=N}$ over the value for the free imine ($\nu_{C=N}$, 1603 cm^{-1}) on formation of the adduct ($\nu_{C=N}$, 1628 cm^{-1}) and of the salt ($\nu_{C=N}$, 1653 cm^{-1}). If donation of the nitrogen lone pair to BF_3 and H^+ involves a drain of electron density from the azomethine linkage then a <u>decrease</u> in $\nu_{C=N}$ for the adducts might have been expected. Since this effect is likely to have a bearing on the position of $\nu_{C=N}$ in metal-substituted azomethine derivates, especially those involving bridging imino groups, e.g. $(Ph_2C{:}NZnMe)_2$,[17] $(Ph_2C{:}NBCl_2)_2$[13] etc., it was of interest to investigate this effect further. Accordingly a series of adducts between imines and boron trifluoride, $R^1R^2C{:}NR^3,BF_3$, and of imine hydrochlorides, $[R^1R^2C{:}NR^3H]^+Cl^-$, were prepared and their infrared spectra recorded as nujol mulls.

Experimental

PhCH:NPh was prepared by heating benzaldehyde with aniline and recrystallised from ethanol and from hexane, m.p. 52-53°. $Ph_2C{:}NPh$ was prepared by refluxing benzophenone with aniline together with a little concentrated hydrochloric acid and was recrystallised from hexane, m.p. 112-113°. PhCH:NMe was prepared by the reaction of benzaldehyde with 40% aqueous methylamine.[122] and the product distilled through a fractionation column, b.p. 182-184°.

$Ph_2C:NMe$ was prepared by the reaction of benzophenone with gaseous methylamine at 180°[123] and then distilled, b.p. 80-82°/0·03 mm.

Preparation of the adducts, $R^1R^2C:NR^3,BF_3$

Freshly distilled boron trifluoride etherate was added by syringe to an equimolar quantity of the imine in ether. The solid adduct was immediately precipitated, filtered off, washed with more ether and then pumped dry. The following adducts were prepared in this way:

Compound	Appearance	m.p., °C.
$Ph_2C:NPh,BF_3$	Yellow solid	232-235
$Ph_2C:NMe,BF_3$	Colourless solid	111-112
$PhCH:NPh,BF_3$	Yellow solid	154-156
$PhCH:NMe,BF_3$	Colourless solid	126-129

Preparation of the hydrochlorides, $R^1R^2C:NR^3,HCl$.

Dry hydrogen chloride was bubbled through a solution of the imine in ether until precipitation was complete. The solid was filtered off, washed with more ether and pumped dry. The following hydrochlorides were prepared in this way:

$Ph_2C:NPh,HCl$, m.p. 154-156°, yellow solid. (Found: C, 77·3; H, 5·1; Cl, 12·4%. $C_{19}H_{16}ClN$ requires C, 77·4; H, 5·5; Cl, 12·4%).

$Ph_2C;NMe,HCl$, m.p. 152°, colourless solid. (Found: C, 72·1; H, 5·7; Cl, 15·3%. $C_{14}H_{14}ClN$ requires C, 72·6; H, 6·1; Cl, 15·3%).

$PhCH:NPh,HCl$, m.p. 186-188°, yellow solid. (Found: C, 71·5; H, 5·3; Cl, 16·0%. $C_{13}H_{12}ClN$ requires C, 71·7; H, 5·6; Cl, 16·3%).

PhCH:NMe,HCl, m.p. 172-174°, colourless solid. (Found: C, 61·3; H, 6·0; Cl, 22·7%. $C_8H_{10}ClN$ requires C, 61·7; H, 6·5; Cl, 22·8%).

The values of $\nu_{C=N}$ found in the infrared spectra of the adducts are shown in Table 1.

TABLE

Infrared spectroscopic results for imine adducts and hydrochlorides

Imine	$\nu_{C=N}$ cm^{-1}.	$\nu_{C=N,HCl}$[b], cm^{-1}.	$\Delta\nu_{HCl}$, cm^{-1}.	$\nu_{C=N,BF_3}$[c] cm^{-1}.	$\Delta\nu_{BF_3}$, cm^{-1}.
$Ph_2C:NPh$	1616	1623	7	1621	5
$Ph_2C:NMe$	1631[a]	1669	38	1661	30
PhCH:NPh	1634	1672	38	1673	39
PhCH:NMe	1645[a]	1695	50	1712	67

a, sample as liquid film; all other figures refer to nujol mulls.

b, $\nu_{C=N}$ for imine hydrochlorides, $[R^1R^2C:NR^3H]^+Cl^-$.

c, $\nu_{C=N}$ for imine adducts, $R^1R^2C:NR^3,BF_3$.

It can be seen that, in each case, $\nu_{C=N}$ rises on co-ordination to BF_3 or H^+. A similar effect was noted by Goulden for 3,4,1-$(CH_2O_2)C_6H_3CH$:NCH_2CH_2Ph and its methiodide[124] which was rationalised by assuming that the positive charge on nitrogen in the salt would counter the electron withdrawing effects of the groups attached to the carbon and nitrogen atoms, thus preventing a lowering of $\nu_{C=N}$. This effect could also operate in the present

compounds in which the nitrogen is considered to carry at least a partial positive charge.

The observed increase in $\nu_{C=N}$ is in marked contrast to the decrease in $\nu_{C=O}$ found in the isoelectronic complexes of ketones with BF_3, $AlCl_3$[125] etc. which has been attributed to a weakening of the C=O linkage on complex formation. It is thus obvious that other, as yet unknown, factors are involved in determining $\nu_{C=N}$ in the imine adducts and hydrochlorides.

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