Alkylideneamino derivatives of some main group elements

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ALKYLIDENEAMINO DERIVATIVES OF SOME MAIN GROUP ELEMENTS

by

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A thesis submitted for the degree of Doctor of Philosophy
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To My Mother and Father

CONTENTS

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R. Snaith.
Durham 1971.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between September 1968 and September 1971. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

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

Azomethine Derivatives. Part XIII. Azomethine Stretching Frequencies of some Di- and Tri-Substituted Methyleneamines, their Hydrochlorides, and their Boron Trifluoride Adducts, by B. Samuel, R. Snaith, C. Summerford and K. Wade, J. Chem. Soc.(A), 1970, 2019. (Reference 2).

Azomethine Derivatives. Part XIV. Dimeric Alkylideneaminoaluminium Dihalides and Monomeric Trialkylideneamino-derivatives of Aluminium, by R. Snaith, C. Summerford, K. Wade and B.K. Wyatt, J. Chem. Soc.(A), 1970, 2635. (Reference 26).

Dative $N \rightleftharpoons M$ π-Bonding in Monomeric Iminoboron Aryls and Related Compounds, by R. Snaith, C. Summerford and K. Wade, Proc. IVth Internat. Conf. on Organometallic Chem., Bristol, 1969, R6. (Reference 28).

Di-t-butylmethyleneamino Derivatives of Group III Elements by J.B. Farmer, R. Snaith and K. Wade, Autumn Meeting of the Chemical Society, Imperial College, London, 1970, B.14. (Reference 29).

I.R. and ^{1}H n.m.r. Spectroscopic Evidence of Dative Aluminium-Nitrogen π-Bonding in Tris(diphenylketimino) and Tris(di-t-butylketimino)aluminium, by R. Snaith, K. Wade and B.K. Wyatt, Inorganic Nucl. Chem. Letters, 1970, 6, 311. (Reference 30).

Azomethine Derivatives. Part X. 1,1,3,3-Tetramethylguanidine Adducts of Trimethylaluminium, Triethylaluminium and Aluminium Trichloride: Dimethyl-, Diethyl- and Dichloro-bis(dimethylamino)methyleneamino-aluminium, by R. Snaith, K. Wade and B.K. Wyatt, J. Chem. Soc.(A), 1970, 380. (Reference 33).

Lithium Tetrakis(di-t-butylmethyleneamino)aluminate by H.M.M. Shearer, R. Snaith, J.D. Sowerby and K. Wade, J. Chem. Soc.(D), 1971, 1275. (Reference 47b).

Azomethine Derivatives. Part XV. Di-t-butylmethyleneaminoboranes by M.R. Collier, M.F. Lappert, R. Snaith and K. Wade, J. Chem. Soc.(A), 1972, in press, (Paper 1/1663). (Reference 158).

ABSTRACT

This thesis describes the preparation of some alkylideneamino derivatives containing groups $\mathrm{R_2C{:}N}$-attached to lithium, boron, aluminium, gallium, silicon and phosphorus, compounds which were prepared with the object of finding model systems for the study of dative $\mathrm{N}\,\underline{\rightarrow}\,\mathrm{M}$ π-bonding between nitrogen and these elements. Systems in which $\mathrm{R} = {}^{t}\mathrm{Bu}$ proved particularly apt for this purpose.

The new compounds di-t-butylmethyleneamine, ${}^{t}\mathrm{Bu_2C{:}NH}$, and its N-lithio and N-trimethylsilyl derivatives, ${}^{t}\mathrm{Bu_2C{:}NLi}$ and ${}^{t}\mathrm{Bu_2C{:}NSiMe_3}$, were prepared (Chapter I) and used to synthesise di-t-butylmethyleneamino-boranes (Chapter III), -alanes (Chapter IV) and -silanes (Chapter VI). The infrared and ^{1}H n.m.r. spectra of the boranes $({}^{t}\mathrm{Bu_2C{:}N})_x\mathrm{BX}_{3-x}$ were consistent with allene-like geometries for these compounds, with the linear $\mathrm{C{=}N}\,\underline{\rightarrow}\,\mathrm{B}$ skeletons appropriate for significant ($p \longrightarrow p$) π-interaction between nitrogen and boron. Similar ($p \longrightarrow p$) and also ($p \longrightarrow d$) $\mathrm{N}\,\underline{\rightarrow}\,\mathrm{Al}$ π-interactions were detected spectroscopically in 3- and 4-co-ordinate aluminium derivatives, and ($p \longrightarrow d$) $\mathrm{N}\,\underline{\rightarrow}\,\mathrm{Si}$ π-bonding was apparently indicated by the spectra of some di-t-butylmethyleneaminosilanes, ${}^{t}\mathrm{Bu_2C{:}NSiR_nCl_{3-n}}$. Such interactions have subsequently been confirmed by X-ray crystallographic work on one boron and one aluminium compound.

Studies on tetramethylguanidine adducts, $\mathrm{(Me_2N)_2C{:}NH{,}AlX_3}$ and on derivatives $\mathrm{[(Me_2N)_2C{:}NAlX_2]_2}$ (X = Et, Cl) (Chapter V) showed them to contain only single Al-N bonds, and apparently four-co-ordinate aluminium in each case. The spectroscopic effects of co-ordination of either a proton or boron trifluoride to various alkylideneamines $\mathrm{R^1R^2C{:}NH}$, needed as reference systems for interpreting the spectra of derivatives $\mathrm{R^1R^2C{:}NMX_n}$, are described in Chapter II.

The experimental techniques used in this research are described in Appendix I; exploratory studies on gallium and phosphorus derivatives of di-t-butylmethyleneamine are described in Appendices II and III.

NOTE ON NOMENCLATURE

The Chemical Society have requested the name "methyleneamine" be used for the (unknown) compound CH_2:NH and that derivatives be named accordingly. Thus CH_2NMX_n is a methyleneamino derivative of the metal M, RCH:NMX_n (R = Alkyl) is an alkylmethyleneamino derivative (or "aldimino" derivative) and RR'C:NMX_n (R,R' = Alkyl) is a dialkylmethyleneamino derivative (or "ketimino" derivative). These are all alkylideneamino derivatives. Similarly, 1,1,3,3-Tetramethylguanidine, $(Me_2N)_2C$:NH, named systematically becomes bis(dimethylamino)methyleneamine.

This nomenclature has been used in chapter headings and in the naming of compounds in the Experimental Sections. In the Discussions, however, the terms "aldimino" and "ketimino" have often been used, partly for the sake of brevity and partly because such terminology clearly distinguishes "imino" from "amino" derivatives.

CHAPTER I

This chapter describes the preparation of di-t-butylmethyleneamine, (^{t}Bu$_2$C:NH), and its N-lithio-, (^{t}Bu$_2$C:NLi) and N-trimethylsilyl-, (^{t}Bu$_2$C:NSiMe$_3$) derivatives. These compounds have been used as starting materials in the preparation of di-t-butylmethyleneamino derivatives of some Main Group elements, ^{t}Bu$_2$C:NMX$_n$ (M = B, Al, Ga, Si, P) which will be discussed in later chapters of this thesis. The structural significance of the i.r. and ^{1}H n.m.r. spectra of the above three compounds is discussed after the presentation of the experimental results.

EXPERIMENTAL SECTION

Starting Materials

t-Butylcyanide was purified by distillation from phosphorus pentoxide under dry nitrogen. t-Butyl-lithium (ca.2M in hexane or pentane), available commercially, was standardised by diluting a measured amount of the solution with dry pentane and titrating this solution with a 1M solution of sec-butanol in dry xylene, using 1,10-phenanthroline as indicator.[1]

Preparation of Di-t-butylmethyleneaminolithium

t-Butyl-lithium (10.0 ml. of a 2.1M solution in hexane, 21 mmole) was added by syringe to a frozen (-196°) solution of t-butyl cyanide (1.74 gm., 21 mmole) in hexane (20 ml.). The mixture was allowed to warm up to room temperature with stirring when a pale yellowish-green solution was formed. After a few minutes stirring at room temperature, a white solid began to precipitate out of solution. Removal of solvent left an off-white powder which was washed with hot hexane and identified as di-t-butylmethyleneaminolithium, ^{t}Bu$_2$C:NLi, m.p. 191-193°. (Found: C,73.8; H,11.7; Li,4.7; N,9.7%; M (by cryoscopy in benzene), 255. $C_9H_{18}LiN$ requires C,73.4; H,12.3; Li,4.8; N,9.5%; M (monomer), 147). ν_{max} (Nujol mull), 3175w, 2941sh, 2910vs, 2849vs, 2721w, 1608vs, 1567sh, 1481sh, 1460vs, 1381vs, 1362vs, 1323m, 1264m, 1220sh, 1205ms, 1099w, 1081m, 1033s, 1022ms, 972m, 927vs, 922vs, 876m, 802m, 722w, 639ms, 556vs and 488vs cm^{-1}.

The ketimino-lithium, $^{t}\mathrm{Bu}_2\mathrm{C{:}NLi}$, could be prepared in a variety of solvents such as hexane, pentane, petroleum ether, diethyl ether, toluene or benzene. After complete removal of solvent, the white solid could be redissolved on warming in such solvents; pale yellow, moisture-sensitive crystals were obtained on allowing the resulting solutions to cool. The off-white powder could also be sublimed (188°/0.01 mm) to give small, pale yellow needles.

In another experiment, the reaction between t-butylcyanide and t-butyllithium was followed by mixing the reagents in an infra-red solution cell at ca. -50° and slowly allowing the mixture to warm up. At ca. -40°, a slight decrease in the size of the $\mathrm{C}\vdots\mathrm{N}$ stretching frequency, $\nu(\mathrm{C}\vdots\mathrm{N})$, of the nitrile (2220 cm^{-1}) was observed, with the appearance of the $\mathrm{C{:}N}$ stretching frequency, $\nu(\mathrm{C{:}N})$, of the ketimino-lithium (1608 cm^{-1}). At ca. -20°, the band corresponding to $\nu(\mathrm{C}\vdots\mathrm{N})$ had disappeared, indicating that the insertion reaction had gone to completion.

$^{t}\mathrm{Bu}_2\mathrm{C{:}NLi}$ was also prepared by reaction of equimolar amounts of di-t-butylmethyleneamine and n-butyl-lithium.

Reactions of Di-t-butylmethyleneaminolithium with Nitrogen and Oxygen Donors

Tetramethylethylenediamine, T.M.E.D., (2.44 gm., 21 mmole) was added to a freshly prepared solution of di-t-butylmethyleneaminolithium (3.09 gm., 21 mmole) in hexane, and the mixture refluxed at 80° for two days. Removal of solvent from the orange solution left an orange-brown oil whose i.r. spectrum has a strong band at 1618 cm^{-1}. (The i.r. spectrum of a mull of $^{t}\mathrm{Bu}_2\mathrm{C{:}NLi}$ with T.M.E.D. has a band at 1608 cm^{-1}). Addition of pentane to the oil precipitates a white solid which was identified as the ketimino-lithium.

Attempts were made to prepare adducts of di-t-butylmethyleneaminolithium with pyridine and tetrahydrofuran by addition of equimolar amounts of these donor molecules to freshly prepared solutions of the ketimino-lithium. In each case, removal of solvent left a white powder, identified as the ketimino-lithium by its i.r. spectrum. No signs of co-ordination were found after heating the donor/ketimino-lithium mixtures or on addition of the donors to freshly prepared ketimino-lithium solid.

Preparation of Di-t-butylmethyleneamine[2]

Di-t-butylmethyleneamine, $^{t}Bu_2C{:}NH$, which had previously been prepared by the action of sodium on t-butylcyanide,[3] was prepared by methanolysis of di-t-butylmethyleneaminolithium.[2]

t-Butylcyanide (3.48 gm., 42 mmole) in pentane (20 ml.) was added to a frozen (-196°) solution of t-butyl-lithium (20 ml. of a 2.1M solution in hexane, 42 mmole). The mixture was warmed to 20°, stirred for several minutes and methanol (ca. 5 ml.) added. The solution was then heated under reflux for one day, lithium methoxide was filtered off, and the solvents removed by distillation at normal pressure. The product was then distilled at 164-166°/755 mm. (lit.,[3] 164-166°) and identified as di-t-butylmethyleneamine, $^{t}Bu_2C{:}NH$. Yield, 5.0 gm., ca. 85%. (Found: C,76.1; H,12.0; N,9.8%; M,140. $C_9H_{19}N$ requires C,76.6; H,13.5; N,9.9%; M,141). ν_{max} (Liquid film) 3378w, 2994sh, 2959vs, 2920sh, 2874s, 1689w, 1610vs, 1488s, 1468sh, 1397ms, 1370s, 1326ms, 1218s, 1195s, 1054m, 1031m, 1026sh, 977w, 952ms, 930m, 877s, 842w, 783m, 719m and 544m cm^{-1}.

The ketimine is very slowly oxidised to di-t-butyl ketone on exposure to the air. The preparations of the hydrogen chloride and boron trifluoride adducts of di-t-butylmethyleneamine are described in the experimental section of Chapter II.

Preparation of Di-t-butylmethyleneaminotrimethylsilane

Trimethylchlorosilane (4.34 gm., 40 mmole) was added by syringe to a frozen (-196°) solution of di-t-butylmethyleneaminolithium (5.88 gm., 40 mmole) in hexane (40 ml.). After warming to room temperature, the reaction mixture was refluxed at 70° for two days. A yellow colour gradually developed and lithium chloride was precipitated. After filtration and removal of solvent by pumping, the residual liquid was distilled at 58-60°/0.2 mm. to give a yellowish-green liquid, identified as <u>di-t-butylmethyleneaminotrimethylsilane</u>, $^{t}Bu_2C{:}NSiMe_3$. Yield <u>ca</u>. 60%. (Found: C,67.6; H,11.1; N,6.5%; M,215. $C_{12}H_{27}NSi$ requires C,67.6; H,12.7; N,6.6%; M,213). ν_{max} (Liquid film) 2994sh, 2963s, 2915sh, 2874sh, 1735vs, 1704sh, 1610w, 1486m, 1479sh, 1468sh, 1393m, 1368m, 1321w, 1261sh, 1252ms, 1230w, 1205w, 1042m, 959m, 930w, 899s, 834vs, 761w, 745w, 732w, 687w, 667w and 624w cm^{-1}.

The preparations of several other di-t-butylmethyleneaminosilanes are described in the experimental section of Chapter VI.

DISCUSSION

Di-t-butylmethyleneamine, $^{t}Bu_2C:NH$

Di-t-butylmethyleneamine, $^{t}Bu_2C:NH$, was prepared by the methanolysis, under forcing conditions, of di-t-butylmethyleneaminolithium,[2] the yield of ca.85% being a substantial improvement on that obtained in the previous synthesis of $^{t}Bu_2C:NH$, by the action of sodium on t-butylcyanide, (yield ca.25%).[3] The conditions needed to methanolyse the ketimino-lithium, which appears to be only slowly affected by atmospheric moisture (cf. diphenylmethyleneaminolithium, $Ph_2C:NLi$, which is extremely moisture-sensitive and is converted rapidly to $Ph_2C:NH$ on addition of methanol at room temperature[4]), emphasise the comparative unreactivity of this species, a characteristic noted later in this thesis when its reactions with various organohalides of some Main Group Elements are discussed.

A great many ketimines (RR'C:NH), aldimines (R'CH:NH) and N-substituted derivatives thereof ($RR'C:NR^2$ and $R'CH:NR^2$) have been prepared, the methods of their synthesis having been thoroughly reviewed in a recent book[5] and in a review article.[6] Two routes are of particular importance, namely, insertion reactions of Main Group organometallic compounds (especially Grignard reagents[7a] and organo-lithium[7b] and -aluminium compounds[7c,d]) into the C⋮N bond of nitriles, followed by hydrolysis of the ketimino- or aldimino-element intermediate (Equation I.1), and condensation reactions between primary amines and carbonyl compounds[8a,b] ("Schiff's reaction", Equation I.2).

$$RC{\vdots}N + R'X \longrightarrow (RR'C{:}NX) \xrightarrow{MeOH} RR'C{:}NH \qquad (I.1)$$

where $X = Li, MgBr, AlR_2$

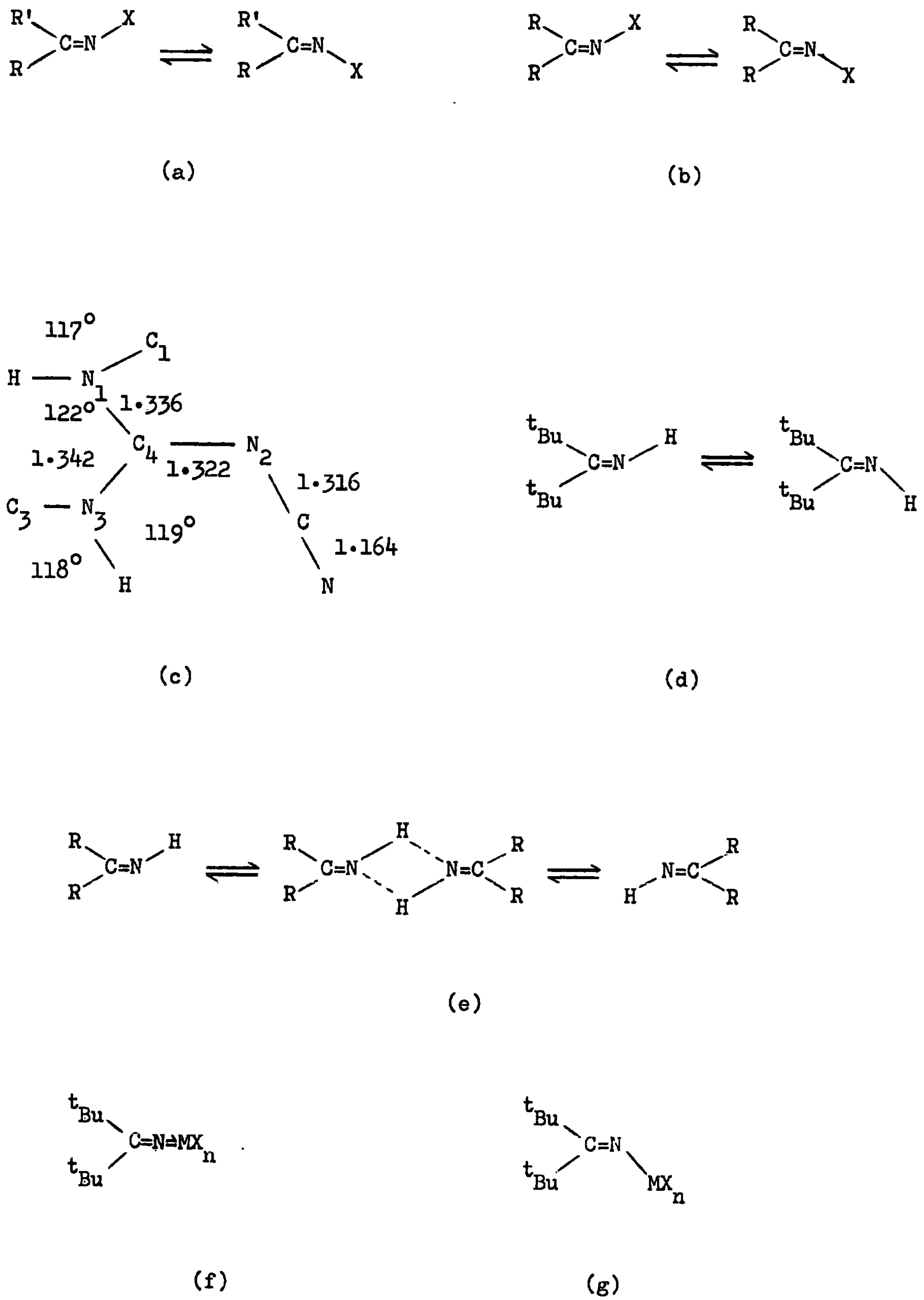
$$RR'C{:}O + R^2NH_2 \longrightarrow RR'C{:}NR^2 + H_2O \qquad (I.2)$$

Other synthetic routes include the reaction of primary amines with activated olefins or acetylenes,[9] reaction of iminophosphoranes with carbonyl compounds[10] and the partial reduction of nitriles with lithium aluminium hydride[11a,b] or hydrogen.[12] References relating to the preparation of some specific ketimines and aldimines are given in the experimental section of Chapter II.

Di-t-butylmethyleneamine, ${}^{t}Bu_2C{:}NH$, is a colourless, fairly volatile (b.p. 164-166°) liquid which is slowly hydrolysed to ${}^{t}Bu_2C{:}O$ on exposure to the atmosphere. Its infra-red spectrum shows a strong band at 1610 cm^{-1} which is assigned as the azomethine stretching frequency, $\nu(C{:}N)$. The position of this absorption in ketimines and aldimines, and in their hydrogen chloride and boron trifluoride adducts is discussed in Chapter II.

Syn-anti isomerisation at the C=N bond has been extensively investigated over the past few years and the topic has recently been reviewed.[13] Many compounds of type $RR'C{:}NX$ (R,R' = alkyl, aryl, hydrogen, halogen) have been synthesised and studied, mainly by n.m.r. techniques. When $R \neq R'$, and the angle $C{=}N{-}X \neq 180^{\circ}$, then clearly two isomers can arise (Figure I.1.a). Usually, however, crystalline derivatives are obtained as single stereoisomers - a recent exception being the isolation of the *cis* and *trans* isomers of $Cl(CN)C{:}NF$[14] - although the evidence available suggests that such species are present in solution as rapidly equilibrating mixtures of *syn*- and *anti*-isomers. For example, oximes, shown by several X-ray structural determinations to possess angular C=N-O- groups (angle CNO 113 ± 2°)[15-18] giving rise to isomerism, have been studied by ^{1}H n.m.r. spectroscopy. Thus the ^{1}H n.m.r. spectra of aldoximes, $RCH{:}NOH$[19a,b] show two multiplets, separated by *ca.*0·6 p.p.m., due to the aldehydic protons, and this is ascribed to the simultaneous existence of *syn*- and *anti*-isomers in solution. Similar isomerisation has been detected from the ^{1}H n.m.r. spectra of N-arylketimines such as $Ph(p\text{-}MeOC_6H_4)C{:}NC_6H_4Me$,[20a,b] where the methoxy protons appear as a well-defined doublet with a separation of 0·06 p.p.m. at room temperature. When $R = R'$

FIGURE I.1.



(a) (b) (c) (d) (e) (f) (g)

(i.e. in compounds $R_2C{:}NX$) and the angle $C{=}N{-}X \neq 180^\circ$, then again solution isomerisation can result from inversion of the group X about the nitrogen atom (Figure I.1.b). The groups R will here be magnetically inequivalent only if the energy of activation of inversion of X about N is large enough, at a given temperature, for the isomerisation to be slow on the n.m.r. time scale, in which case the resonances of the protons on the groups R will appear in the ^1H n.m.r. spectrum twice, with equal intensity. Thus the ^1H n.m.r. spectra of various N-cyanoketimines, $X_2C{:}N{\cdot}C!N$[21] ($X = SMe, OMe, NMe_2$) show single resonances for the methyl protons at room temperature, cooling causing the resonances to split into doublets; when X = Me, two singlets are apparent even at room temperature, coalescing only at 85°. The activation energies for these inversions are in the range 10-19 $kcal.mole^{-1}$. It has been suggested that syn/anti isomerisation in such N-cyanoketimines proceeds via an intermediate of type $X_2C{=}\overset{+}{N}{=}C{=}\overset{-}{N}$ having a linear CNCN skeleton; this seems unlikely in view of the recent report of the molecular conformation of 2-cyano-1,3-dimethylguanidine, $(MeNH)_2C{:}N{\cdot}C!N$[22] which is almost planar with four near-equal carbon-nitrogen bond lengths, implying considerable delocalisation over the N_2CNC skeleton (Figure I.1.c). Presumably the increase of the C_4N_2 bond order, as implied in the proposed intermediate, would diminish the C_4N_1 and C_4N_3 bond orders and cause rehybridisation at N_1 and N_3 (which, judging from the bond angles and the positions of the N-attached hydrogen atoms, are sp^2 hybridised in $(MeNH)_2C{:}N{\cdot}C!N$) and thus loss of planarity in the molecule. The ^1H n.m.r. spectra of various N-substituted dimethylketimines, $Me_2C{:}NR$, all show two resonances of equal area for the protons of the C-attached methyl groups; when R = Ph,[23] the two signals (separation 0·37 p.p.m.) coalesce only at 126°, ΔG for the inversion being calculated as 20·3 $kcal.mole^{-1}$; when $R = PhCH_2-$,[24] the two signals (separation 0·16 p.p.m.) remain separated even at 170° ($\Delta G > 23$ $kcal.mole^{-1}$). The ^{19}F n.m.r. spectrum of the fluoroketimine, $(CF_3)_2C{:}N{-}CF(CF_3)_2$,[25] also exhibits similar temperature dependence, the signals due to the two $=C-CF_3$ groups being separated by > 5 p.p.m. at temperatures below their coalescence temperature of 32°; the energy of activation for this isomerisation has been calculated as 13 ± 3 kcal.mole^{-1}. Clearly, the ^1H n.m.r. spectrum of di-t-butylmethyleneamine (Table I.1) should similarly show two distinct absorptions due to the presence in solution of thetwo possible isomeric species (Figure I.1.d). At +33°, the spectrum has only a single absorption attributable to the t-butyl groups, presumably due to very rapid isomerisation.[26] The reversible changes with temperature in the ^1H n.m.r. spectra of ^{15}N-labelled ketimines[27] have been interpreted in terms of intermolecular proton exchange between monomer and monomer (Figure I.1.e); the activation energies for such exchange processes were calculated as 13·8 ± 2 kcal.mole^{-1} and 6·5 kcal.mole^{-1} for Ph_2C:NH and Ph(sec-Bu)C:NH respectively and it was inferred that, in derivatives R_2C:NH where R = alkyl, this energy would be less than 5-7 kcal.mole^{-1} i.e. that inversion would be very rapid. However, on cooling a solution of $^tBu_2C$:NH to -60°, two peaks of equal intensity (at 8·73 and 8·90τ, a separation of 0·17 p.p.m.) are observed in the ^1H n.m.r. spectrum, indicating that at this temperature inversion at nitrogen is indeed slow enough for the t-butyl groups to be seen to be magnetically inequivalent. This result indicated that, in principle, the ^1H n.m.r. spectra of di-t-butylmethyleneamino-derivatives of Main Group Elements, $^tBu_2C:NMX_n$ (those studied including M = B,[28,29] Al,[26,29,30] Si,[31] Ga,[31,32] Be[28,32]) would be of value in the elucidation of their structures; in particular, the t-butyl groups of compounds containing linear C=N-M units (Figure I.1.f) will be magnetically equivalent and hence indistinguishable in their ^1H n.m.r. spectra, whereas the t-butyl groups of compounds having bent C=N-M skeletons (Figure I.1.g) should, in the absnece of any rapid exchange process, give rise to two distinct absorptions because of their different environments, syn and anti, with respect to the group

MX_n. The ^1H n.m.r. spectra of the derivatives $^tBu_2C{:}NMX_n$ (M = B,Al,Si) will be discussed in detail in later chapters.

Table I.2 shows the masses, relative intensities and assignments of peaks in the mass spectrum of di-t-butylmethyleneamine. The same fragments are observed in the mass spectra of all the derivatives $^tBu_2C{:}NMX_n$ (M = B,Al,Si).

TABLE I.1

^{1}H n.m.r. spectroscopic results for ^{t}Bu$_2$C:NH, ^{t}Bu$_2$C:NLi and ^{t}Bu$_2$C:NSiMe$_3$

Compound	Temperature	τ(=N-H)	τ(-^{t}Bu$_2$)	τ(-SiMe$_3$)
^{t}Bu$_2$C:NH	+33°	6·66(1)	8·83$_s$(18)	
	-30°	6·61(1)	8·74$_s$(9); 8·88$_s$(9)	
	-60°	6·58(1)	8·73$_s$(9); 8·90$_s$(9)	
(^{t}Bu$_2$C:NLi)$_n$	+33°		9·15$_s$	
	-50°		9·21$_s$	
^{t}Bu$_2$C:NSiMe$_3$	+33°		8·88$_s$(18)	9·79$_s$(9)
	-60°		8·89$_s$(18)	9·75$_s$(9)
	-80°		8·92$_s$(18)	9·76$_s$(9)

Spectra were recorded for *ca.* 10 wt.% solutions in toluene using T.M.S. as internal reference. τ(Me$_4$Si) = 10·00 p.p.m.

s = singlet; relative intensities in parentheses.

TABLE I.2

Mass spectroscopic results for $^{t}Bu_2C{:}NH$

m/e	Relative Intensity	Assignment
142	0·1	$Bu_2C{:}NH_2$
141	1	$Bu_2C{:}NH$
126	2·5	$Bu(Me_2C)CNH)$
84	46	BuCNH
68	26	$Me_2C{\cdot}CN$
59	28	BuH_2
58	4	BuH
57	84	Bu
56	15	C_4H_8
43	10	MeCHNH
42	53	MeCNH
41	100	MeCN
39	37	HCCN
29	18	H_2CNH
27	21	HCN
16	2	MeH
15	12	Me

Di-t-butylmethyleneaminolithium, $^{t}Bu_2C{:}NLi$

Despite their important uses in organometallic syntheses, rather few amino-lithium, RR'NLi, or ketimino-lithium, RR'C:NLi, compounds have been isolated and studied. Two general routes have been employed to prepare ketimino-lithium compounds. The first, as shown in Equation I.3, involves reaction of the appropriate ketimine with an alkyl-lithium (usually MeLi or $^{n}BuLi$) in ether.

$$RR'C{:}NH + R^2Li \xrightarrow{ether} RR'C{:}NLi + R^2H \qquad (I.3)$$

Compounds RR'C:NLi with R = R' = Ph,[4] Me_2N[4,33] and CF_3[34] have previously been prepared by this method.

The second route, as shown in Equation I.4, involves the addition of the appropriate organo-lithium reagent to the C≡N group of the appropriate nitrile.

$$RC{\vdots}N + R'Li \longrightarrow RR'C{:}NLi \qquad (I.4)$$

Compounds RR'C:NLi with R = R' = Ph[4] and R = Ph, R' = Me[35] and R = NR'_2, R' = Ph[36] have been prepared by this method. The yield of the ketimino-lithium compound PhMeC:NLi is, however, only <u>ca.</u>10% probably because of the competing polymerisation of phenyl cyanide which is known to occur in the presence of organo-lithium reagents.[76] However, when R and R' are alkyl groups, simple ketimino-derivatives RR'C:NLi are not normally obtained. The products of the reactions between methyl or ethyl cyanide and methyl- or ethyl-lithium in ether (all four possible combinations) were insoluble, involatile and seemingly polymeric materials believed to contain $>C=C=N-$ groups, alkane being eliminated by acid reaction of the hydrogen atoms attached to the α-carbon atom of the alkyl cyanide.[4] t-Butyl-lithium, in excess, polylithiates methyl cyanide at -78° to give Li_2C_2HN and two equivalents of isobutane.[37]

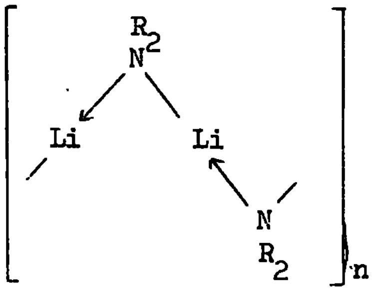
Although t-butyl cyanide, which has no hydrogen atoms attached to the α-carbon atom, has been reported not to react at all with methyl- or ethyl-lithium in ether at or below 20°,[4] it has been found to react with t-butyl-lithium in a variety of solvents, low temperature i.r. spectroscopic experiments indicating that insertion is apparently complete at as low a temperature as -20°. The product of this insertion reaction, di-t-butylmethyleneaminolithium, $^{t}Bu_2C{:}NLi$, was isolated as an off-white powder on removal of solvent from the pale yellowish-green solution; it could be re-dissolved in a variety of hot solvents, pale yellow crystals being formed on cooling the solution, and sublimed under a moderate vacuum to give small needle-shaped crystals. Some attention has recently been paid to the mechanism of organo-lithium/nitrile reaction (Equation I.4). The kinetics of the n-BuLi/PhCN reaction[38] in ether have been found to be first order in PhCN and 0·33 order with respect to n-BuLi. These observations indicate a dissociative mechanism, the reactive species being monomeric n-butyl-lithium. As t-BuLi, like n-BuLi, is probably tetrameric in hydrocarbon solvents, both having cubic structures with substantial C-Li covalent bonding,[39-42] it seems likely that a similar mechanism operates in the $^{t}BuCN/^{t}BuLi$ reaction.

Amino-lithium and ketimino-lithium compounds pose several interesting structural and valence problems in that, if unsolvated, the lithium they contain has a maximum possible co-ordination number of two. Thus diphenylmethyleneaminolithium solid, $Ph_2C{:}NLi$, and lower alkylamino-derivatives such as Me_2NLi are thought to exist as co-ordination polymers (Figure I.2.a). $Ph_2C{:}NLi$ will dissolve only in solvents which are strong enough donors to break up the polymer, probably forming in solution dimeric species stabilised by co-ordination of solvent molecules to the lithium atoms (Figure I.2.b). Solid adducts of $Ph_2C{:}NLi$ with pyridine and tetrahydrofuran have been isolated.[4]

The state of association of the silyl derivative, $(Me_3Si)_2NLi$, in various solvents has been investigated recently.[43,44] The concentration- and

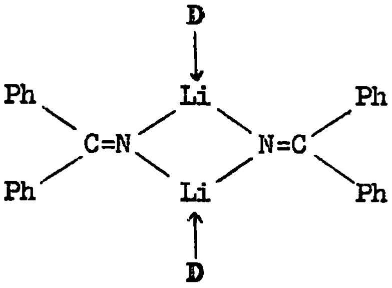
FIGURE I.2

Proposed structures of some Amino- and Ketimino-lithium derivatives



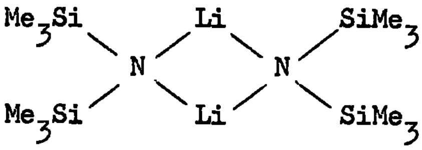
(R_2 = Me_2, $Ph_2C:N$)

(a)

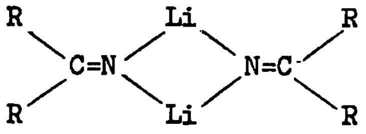


(D = donor molecules such as pyridine, T.H.F.)

(b)



(c)

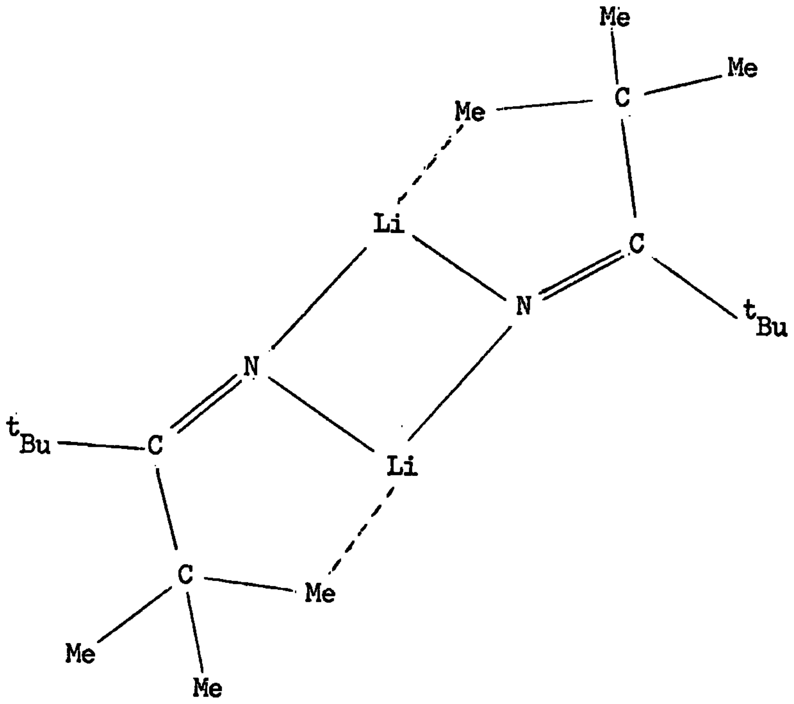


(R = Me_2N, ^tBu)

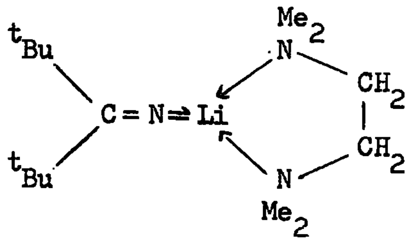
(d)

contd./

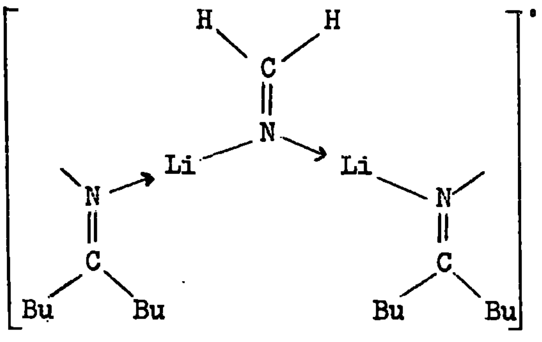
FIGURE I.2 contd.



(e)



(f)



(g)

temperature-dependent ^{1}H and ^{7}Li n.m.r. spectra have been interpreted in terms of a monomer-dimer equilibrium in T.H.F. and a dimer-tetramer equilibrium in hydrocarbons.[43] $(Me_3Si)_2NLi$ had already been found to be dimeric in benzene and a structure involving NLiN bridges has been proposed[44] (Figure I.2.c.). The low degree of association of these solution species (cf. LiO^tBu and $LiOSiMe_3$ which are hexameric in benzene) may be explained by removal of charge from bridging nitrogen by interaction of a nitrogen pπ orbital with a vacant dπ orbital of silicon. It has been indicated that formation of strong bridge bonds involving carbon is associated with localisation of charge on the bridging atoms[45] i.e. organic groups which facilitate delocalisation of negative charge on the lithium-bearing carbon have a lower tendency towards higher aggregate formation (cf. benzyl-lithium is monomeric in basic solvents whereas alkyl lithiums are usually tetrameric[42]); presumably similar considerations apply to nitrogen- and oxygen-bridged systems. A recent X-ray crystallographic study has shown that solid $(Me_3Si)_2NLi$ exists as a trimer having a planar six-membered ring with alternating nitrogen and lithium atoms.[46]

Bis(dimethylamino)methyleneaminolithium, $(Me_2N)_2C{:}NLi$, was prepared as a crystalline solid which dissolved in benzene as a dimer.[4] The dimeric species is thought, on the basis of its ^{1}H n.m.r. spectrum, to contain terminal dimethylamino-groups (Figure I.2.d). Similarly di-t-butylmethyleneaminolithium, $^tBu_2C{:}NLi$, is found to dissolve in weakly interacting solvents such as common hydrocarbons, toluene and benzene; in the latter, the molecule is dimeric (by cryoscopy) presumably having a structure as shown in Figure I.2.d. Unlike diphenylmethyleneaminolithium, both $(Me_2N)_2C{:}NLi$ and $^tBu_2C{:}NLi$ fail to form solid adducts with donors such as pyridine and tetrahydrofuran, despite the apparent co-ordinative unsaturation of their lithium atoms. In the case of $(Me_2N)_2C{:}NLi$, it has been suggested[4] that this surprising lack of reactivity may be due to interaction of dimers in the crystal serving to raise the co-ordination number of the lithium to three or four. A similar argument could be applied to ${}^{t}Bu_2C{:}NLi$, although an attractive alternative explanation would be that there is a bonding interaction between one methyl group of each of the bridging $(Me_3C)_2C{=}N$- groups with each lithium. A scale model of the "symmetrical" bridged dimer structure (Figure I.2.d) indicates that, although there is some sterically-induced "shielding" of the lithium atoms by the bulky t-butyl groups, the methyl carbon-lithium distances are well outside the sum of the covalent radii of these two atoms. For such a bonding interaction as envisaged above, therefore, the Li_2N_2 four-membered ring would have to be distorted so that, although two methyl carbons might be close enough to the lithium atoms as to be considered as bonding to them, the two t-butyl groups whose methyl groups are not involved are moved much further away so that each lithium atom is left open on one side (Figure I.2.e). Thus, although such distortion might well serve to increase the co-ordination numbers of the lithium atoms from two to three, any steric shielding of the lithium atoms by the bulky t-butyl groups would be largely dissipated. Such carbon-lithium interactions have been observed between two methyl groups of the bridging ketimino-units and the lithium atom in lithium tetrakis(di-t-butylmethyleneamino)aluminate, $LiAl(N{:}C{}^{t}Bu_2)_4$,[47a,b] whose crystal structure has recently been carried out,[47a] and serve to impart an effective co-ordination number of four on the lithium atom (see Chapter IV, p. 89). The ${}^{1}H$ n.m.r. spectrum of ${}^{t}Bu_2C{:}NLi$ in toluene (Table I.1) shows only a single resonance due to the t-butyl groups, positioned at 9·21τ at -50°; perhaps significantly, the ${}^{1}H$ n.m.r. spectrum of $LiAl(N{:}C{}^{t}Bu_2)_4$ at -50° consists of a series of complex resonances, plus a singlet at 9·24τ. The similar positions of these two resonances (t-butyl groups of other derivatives ${}^{t}Bu_2C{:}NMX_n$ usually appear in the range 8·7-8·9τ in the ${}^{1}H$ n.m.r. spectra) may well indicate that a similar methyl group-lithium interaction to that found in $LiAl(N{:}C{}^{t}Bu_2)_4$ also operates in di-t-butylmethyleneaminolithium oligomer.

The i.r. spectrum of di-t-butylmethyleneaminolithium, ${}^{t}Bu_2C{:}NLi$, has a strong band at 1608 cm^{-1}, assigned to the azomethine stretching vibration, ν(C:N). Although pyridine and T.H.F., did not appear to form adducts with ${}^{t}Bu_2C{:}NLi$, reaction with tetramethylethylenediamine (T.M.E.D.) produced an orange oil whose i.r. spectrum showed a strong band at 1618 cm^{-1}, assigned to the azomethine stretching vibration, ν(C:N). This small increase (10 cm^{-1}) in ν(C:N), plus the fact that the oil decomposed on addition of pentane to give ${}^{t}Bu_2C{:}NLi$, indicates that the product is a weak adduct formed by co-ordination of one of the nitrogen atoms of T.M.E.D. to each lithium atom in the ketimino-lithium oligomer. A monomeric species (Figure I.2.f) having both nitrogen atoms of the T.M.E.D. co-ordinated to the lithium atom, thus producing a linear $C{=}N\overset{\cdot\cdot\cdot}{-}Li$ unit, would be expected to show a skeletal asymmetric stretching vibration, $\nu(C{=}N\overset{\cdot\cdot\cdot}{-}Li)$, at a much higher frequency (ca.1700 cm^{-1}) in its i.r. spectrum, by comparison with other cumulatively π-bonded systems (Table I.3).[26,30,48-55] Thus, it is believed, a high value for the azomethine stretching frequency in compounds ${}^{t}Bu_2C{:}NMX_n$ is indicative of considerable $N{\doteq}M$ dative π-bonding and hence of linear $C{:}N{\doteq}M$ units in such molecules. The azomethine stretching frequencies for a number of compounds of type ${}^{t}Bu_2C{:}NMX_n$ (M = B,Al,Si) believed to have linear $C{:}N{\doteq}M$ units will be given in the relevant chapters.

The mass spectrum of di-t-butylmethyleneaminolithium was recorded and Table I.4 shows the masses, relative intensities and assignments of some of the peaks obtained. It seems clear that the ketimino-lithium is associated in the vapour phase and the spectrum would seem to indicate a structure as shown in Figure I.2.a. Cleavage of two N-Li bonds in the polymer followed by loss of butene presumably gives rise to the peak of highest m/e value (Figure (I.2.g), and subsequent breakdown from this species involves cleavage of two of the remaining N-Li bonds.

TABLE I.3

Skeletal Stretching frequencies, ν(X=Y=Z) of some cumulatively π-bonded systems

Compound	ν(X=Y=Z) (cm^{-1})	(X=Y=Z)	Reference
RN:C:NR	ca.2140	N=C=N	48
$Ph_2C:C:NMe$	1998	C=C=N	49
$R_2C:C:CR_2$	ca.1950	C=C=C	50
$Ph_2C:N:CPh_2^+(MX_n^-)$	ca.1845	C≠N=C	51
$Ph_2C:NBPh_2$	1786	C=N≐B	52,53
$[(Ph_2C:N)_2Be]_n$	1732	C=N≐Be	54,55
$(Ph_2C:N)_3Al$	1686	C=N≐Al	26,30

TABLE I.4

Mass spectroscopic results for $({}^{t}Bu_2C{:}NLi)_n$

m/e	Relative Intensity	Assignment
322	1	$(Bu_2C{:}NLi)(H_2C{:}N)(LiN{:}CBu_2)$ (Fig.I.2.g)
182	1·5	$(Bu_2C{:}NLi)(H_2C{:}N)Li$
127	1·5	$(Me_2CH{\cdot}CHMe{:}NLi)(H_2C{:}N)Li$
105	1·5	$(Me_2CH{\cdot}CH{:}NLi)(H_2C{:}N)$
85	25	BuCHNH
70	98	Me_2CHCNH
58	59	BuH
57	100	Bu
56	18	C_4H_8
49	76	MeCH:NLi
48	20	MeCNLi
41	98	MeCN
29	71	$H_2C{:}NH$
28	34	HCNH
27	22	HCN
15	10	Me

Di-t-butylmethyleneaminotrimethylsilane, $^{t}Bu_2C{:}NSiMe_3$

Di-t-butylmethyleneaminotrimethylsilane, $^{t}Bu_2C{:}NSiMe_3$, was prepared from the reaction between di-t-butylmethyleneaminolithium, and trimethylchlorosilane (Equation I.5).

$$^{t}BuC{:}N + {}^{t}BuLi \xrightarrow{hexane} \frac{1}{n}(^{t}Bu_2C{:}NLi)_n \xrightarrow{Me_3SiCl} {}^{t}Bu_2C{:}NSiMe_3 + LiCl \qquad (I.5)$$

For an optimum yield (ca.60%) the reaction mixture has to be refluxed at 70° for several days, again emphasising the comparative unreactivity of $^{t}Bu_2C{:}NLi$ (cf. the reaction between $Ph_2C{:}NLi$ and Me_3SiCl which gives a near-quantitative yield of $Ph_2C{:}NSiMe_3$ after merely stirring at room temperature for 30 minutes[12,35]).

Di-t-butylmethyleneaminotrimethylsilane, $^{t}Bu_2C{:}NSiMe_3$, is a yellowish-green liquid, b.p. 58-60°/0·2 mm, which appears to be moisture-stable. Its infra-red spectrum shows a strong band at 1735 cm^{-1}, assigned to the asymmetric stretching vibration, $\nu(C{=}N{\rightleftharpoons}Si)$, of the apparently linear $C{=}N{\rightleftharpoons}Si$ unit in the molecule. Such an arrangement is also indicated by the ^{1}H n.m.r. spectrum of $^{t}Bu_2C{:}NSiMe_3$ in toluene (Table I.1), where the sharp singlet due to the t-butyl groups shows no significant change either in shape or chemical shift on cooling the solution down as far as -80°. As discussed earlier in this chapter, this result implies either that the molecule contains a linear $C{=}N{\rightleftharpoons}Si$ skeletal backbone (Figure I.1.f) or that, if bent (Figure I.1.g), inversion of the Me_3Si-group about the nitrogen is so rapid even at -80° as to make the magnetically unequivalent t-butyl groups indistinguishable. The preparation and spectral and structural properties of this and several other di-t-butylmethyleneaminosilanes are more fully discussed in Chapter VI.

CHAPTER II

This chapter describes the preparation and i.r. spectra of a number of ketimines RR'C:NH, N-substituted ketimines $RR'C:NR^2$ and N-substituted aldimines $R'CH:NR^2$, and of their hydrogen chloride salts and boron trifluoride adducts. Invariably an increase in the azomethine stretching frequency, ν(C:N), is observed in the i.r. spectra of the imines on co-ordination. Possible reasons for such an increase are discussed after the initial presentation of the experimental results.

EXPERIMENTAL SECTION

Preparation of the methyleneamine derivatives, $RR'C:NR^2$

α-(p-Bromophenyl)-benzylideneamine,[2] $(p\text{-}BrC_6H_4)PhC:NH$, was prepared from the reaction between phenyl cyanide and p-bromophenylmagnesium bromide in ether followed by methanolysis of the resultant imino-magnesium halide. After filtration and removal of solvent, the residual yellow oil was distilled at low pressure from a bath at 180°. Re-distillation at 115-120°/0.1 mm. gave the new benzylideneamine, $p\text{-}BrC_6H_4(Ph)C:NH$. (Found: C,60.8; H,3.9; Br,30.6%. $C_{13}H_{10}BrN$ requires C,60.0; H,3.9; Br,30.8%).

α-Phenylbenzylideneamine,[56] $Ph_2C:NH$, α-(p-chlorophenyl)-p-chlorobenzylideneamine,[57] $(p\text{-}ClC_6H_4)_2C:NH$, and α-(p-tolyl)-p-methylbenzylideneamine,[57,58] $(p\text{-}MeC_6H_4)_2C:NH$, were prepared similarly from the appropriate arylmagnesium bromide and arylcyanide followed by methanolysis and identified by elemental analysis and m.p. or b.p. The preparation of α-(t-butyl)-p-methylbenzylideneamine,[59] $({}^tBu)(p\text{-}MeC_6H_4)C:NH$, (from t-butylmagnesium chloride and p-tolyl cyanide) required more vigorous conditions; the ether used for the preparation of t-butylmagnesium chloride was replaced by toluene, p-tolyl cyanide was added, and the solution was heated under reflux for 2 days to ensure reaction.

Di-t-butylmethyleneamine, ${}^tBu_2C:NH$,[2] which had previously been prepared by the action of sodium on t-butylcyanide,[3] was prepared by methanolysis of di-t-butylmethyleneaminolithium (see Chapter I of this thesis).

N-Methyl-α-phenylbenzylideneamine,[60] $Ph_2C:NMe$, was prepared by the reaction of benzophenone with gaseous methylamine at 180° and was then distilled. N-Phenyl-α-phenylbenzylideneamine,[61] $Ph_2C:NPh$, was prepared by refluxing aniline with benzophenone in the presence of a little concentrated hydrochloric acid, and recrystallised from hexane. N-Methylbenzylideneamine,[62] PhCH:NMe, was prepared by the reaction of benzaldehyde with 40% aqueous methylamine, and distilled through a fractionation column. N-Phenylbenzylideneamine,[63] PhCH:NPh, was prepared by heating benzaldehyde with aniline and recrystallised from ethanol-hexane.

N-t-butylmethyleneamine,[64] $CH_2:N^tBu$, was prepared by addition of formaldehyde to t-butylamine. After stirring at room temperature for 30 min., potassium hydroxide pellets were added and the organic layer separated by distillation through a short column. A further column distillation gave N-t-butylmethyleneamine, $CH_2:N^tBu$, b.p. 62-65° (lit.[64] 63-65°). (Found: C,69.9; H,12.6; N,16.1%; M,87. $C_5H_{11}N$ requires C,70.4; H,12.9; N,16.4%; M,85). ν_{max} (Liquid film) 2959vs, 2915sh, 2874sh, 2793m, 2667m, 1655w, 1471m, 1410m, 1391m, 1364s, 1272ms, 1250ms, 1220s, 1205vs, 1178ms, 1153ms, 1075m, 1028ms, 1003m, 987m, 909ms, 899ms, 835m and 613w cm^{-1}.

N-t-butylethylideneamine,[64] $MeCH:N^tBu$, was similarly prepared from the reaction between acetaledehyde and t-butylamine. Distillation at 72-78° from potassium hydroxide pellets gave the ethylideneamine $MeCH:N^tBu$. (Found: C,72.2; H,13.5; N,14.0%; M,107. $C_6H_{13}N$ requires C,72.6; H,13.1; N,14.3%; M,99). ν_{max} (Liquid film) 2950s, 2907sh, 2878sh, 1718w, 1672ms, 1658sh, 1608sh, 1466sh, 1458m, 1439sh, 1433m, 1420sh, 1377sh, 1361s, 1258sh, 1235sh, 1215s, 1124m, 1099w, 1036w, 976w, 862m, 750w, 744w and 667vw cm^{-1}.

Attempts to prepare benzylideneamine, PhCH:NH,[65] by the reduction of benzonitrile with an ethereal solution of stannous chloride saturated with hydrogen chloride, failed. The intermediate complex, $(PhCHNH_2)_2SnCl_6$, was isolated and characterised by its i.r. spectrum and elemental analysis, but the attempted decomposition with triethylamine gave highly coloured, gummy resins rather than the aldimine.

Preparation of the adducts, $RR'C{:}NR^2.BF_3$

Freshly distilled boron trifluoride - diethyl ether was added by syringe to an equimolar quantity of the methyleneamine derivative in ether. The adduct was precipitated immediately, and was filtered off, washed with ether, and pumped dry.

The following adducts were prepared (by the author) in this way:

$^{t}Bu_2C{:}NH.BF_3$,[2] white solid, m.p.88°. (Found: H,9.0; B,5.2; F,28.4; N,6.5%. $C_9H_{19}BF_3N$ requires H,9.1; B,5.4; F,27.2; N,6.7%).

$(p\text{-}ClC_6H_4)_2C{:}NH.BF_3$,[2] white solid, m.p.76°. (Found: H,3.2; B,3.7; Cl,22.0; F,18.5; N,4.1%. $C_{13}H_9BCl_2F_3N$ requires H,2.8; B,3.5; Cl,22.2; F,17.9; N,4.4%).

$(^{t}Bu)(p\text{-}MeC_6H_4)C{:}NH.BF_3$,[2] white solid, m.p.118°. (Found: C,60.1; H,7.2; B,4.3; F,23.7%. $C_{12}H_{17}BF_3N$ requires C,59.3; H,7.0; B,4.5; F,23.4%).

$CH_2{:}N^{t}Bu.BF_3$, white solid, m.p.43°. (Found: C,38.2; H,6.8; B,7.3; F,36.6; N,8.9%. $C_5H_{11}BF_3N$ requires C,39.1; H,7.2; B,7.2; F,37.2; N,9.1%).

The reaction between $MeCH{:}N^{t}Bu$ and $BF_3.OEt_2$ gave a brown viscous oil.

Preparation of the hydrochlorides, $RR'C{:}NR^2H^+Cl^-$

Dry hydrogen chloride was bubbled through a solution of the methyleneamine derivative in ether until precipitation was complete. The solid was filtered off, washed with ether, pumped dry and stored under dry nitrogen. The following hydrochlorides, all of which deliquesced in moist air, were prepared (by the author) in this way:

$^{t}Bu_2C{:}NH_2{}^+Cl^-$,[2] white solid, m.p. 203°. (Found: C,60.0; H,11.7; Cl,20.3; N,7.6%. $C_9H_{20}ClN$ requires C,60.9; H,11.3; Cl,19.8; N,7.9%).

$(p\text{-}ClC_6H_4)_2C{:}NH_2{}^+Cl^-$,[2] pale yellow solid, decomposes at 80°. (Found: C,54.0; H,3.8; Cl,36.3; N,5.3%. $C_{13}H_{10}Cl_3N$ requires C,54.5; H,3.5; Cl,36.9; N,4.9%).

$({}^tBu)(p\text{-}MeC_6H_4)C{:}NH_2{}^+Cl^-$,[2] white solid, decomposes at 221°. (Found: C,67.6; H,7.8; Cl,16.7; N,6.6%. $C_{12}H_{18}ClN$ requires C,68.1; H,8.5; Cl,16.8; N,6.6%).

$CH_2{:}N{}^tBu.HCl$, white solid, decomposes at 212°. (Found: H,10.3; Cl,28.9; N,11.3%. $C_5H_{12}ClN$ requires H,9.9; Cl,28.9; N,11.6%).

$MeCH{:}N{}^tBu.HCl$, white solid, decomposes at 270°. (Found: H,10.5; Cl,26.6; N,11.2%. $C_6H_{14}ClN$ requires H,10.3; Cl,25.9; N,10.3%).

Satisfactory analytical data were obtained for all the other boron trifluoride and hydrogen chloride adducts described in this chapter (prepared by B. Samuel and C. Summerford, see reference 2). The infra-red spectra of the adducts were recorded. Finally the i.r. spectra of the ketimines, of their N-substituted derivatives, and of the N-substituted aldimines were recorded both in Nujol and carbon tetrachloride solutions. These spectroscopic results are presented and analysed in the discussion which now follows this experimental section.

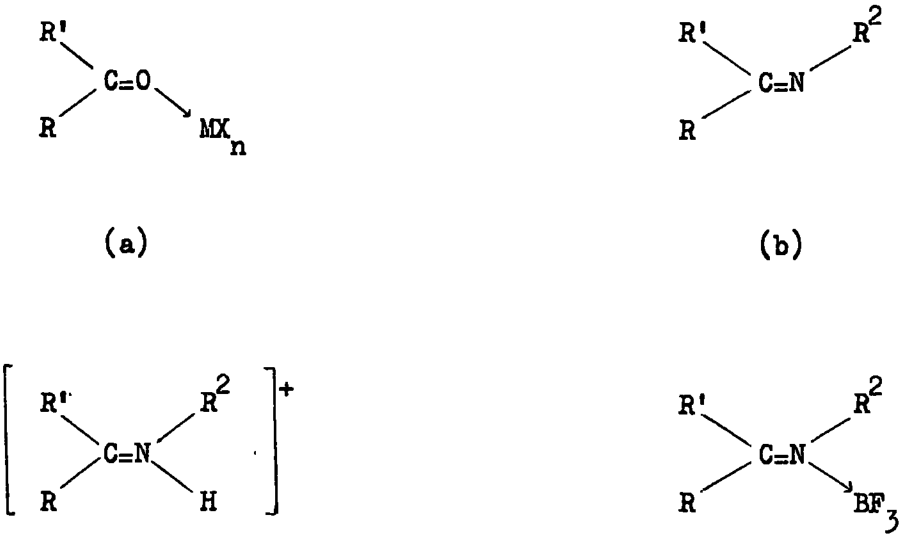
DISCUSSION

The co-ordination of ketones RR'C:O,[66-73] or other carbonyl compounds RCOX[70,71,74,75] to Lewis acids MX_n (especially Group III and IV halides) through the carbonyl oxygen (Figure II.1.a) has been extensively studied by i.r. spectroscopic methods. Such co-ordination is invariably accompanied by a marked decrease in the carbonyl stretching frequency, ν(C:O). The generality of this decrease allows its use to identify the co-ordination site in compounds having more than one potential donor atom.[70,76] Further, its magnitude has been used as a guide to the relative acidities of a series of Lewis acids[74] and to the donor strength of the particular carbonyl compound,[77] since the strength of the $\rangle C{=}O \rightarrow M$ bond should be reflected in the extent of polarisation of the C:O bond which in turn produces a change in the C:O bond stretching force constant; proton resonance shifts and, for BX_3 complexes, ^{11}B chemical shifts have similarly been used as guides to acid and base strengths.[72,75] Recently, however, it has been concluded from a study of some thirty ketone-boron trifluoride complexes[73] that, while ^{19}F n.m.r. chemical shifts and B-O stretching frequencies can provide a quantitative measure of relative donor strength, changes in ν(C:O) and ^{1}H n.m.r. chemical shifts, being essentially properties of the ketone itself, are of little significant value in this respect.

The decrease in the carbonyl stretching frequency has been attributed to a weakening of the C=O bond through electron-flow to the co-ordinate link and possibly also through repulsion between the electrons forming the CO link and the group X in the Lewis acid.[78]

Both the isoelectronic relationship between ketones RR'C:O and imines $RR'C{:}NR^2$ (Figure II.1.b) and the fact that in this thesis and elsewhere the position of the azomethine stretching frequency, ν(C:N), in ketimino derivatives of Main Group elements, $RR'C{:}NMX_n$, is argued to be indicative of the linearity or otherwise of the C=N-Metal link, prompted the investigation of the effect of

FIGURE II.1



(a) (b)

(c) (d)

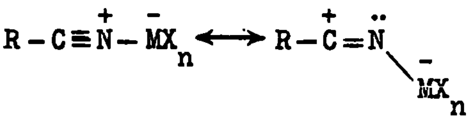
FIGURE II.2

$R-C\equiv N\rightarrow MX_n$

(a)

$R-C\equiv\ddot{N}\longleftrightarrow R-\overset{+}{C}=\overset{-}{N}:$

(b)



$R-C\equiv\overset{+}{N}-\overset{-}{M}X_n\longleftrightarrow R-\overset{+}{C}=\ddot{N}\diagdown\overset{-}{M}X_n$

(c)

co-ordination on $\nu(C:N)$ for a series of imines with protonated imine (Fig.II.1.c) and boron trifluoride adduct (Fig.II.1.d) as reference species. No systematic study of imine complexes had previously been made, although an increase in $\nu(C:N)$ on formation of salts $(RR'C:NR^2R^3)^+X^-$ had been noted in specific cases.[79-86] Co-ordination to the proton (in $Ph_2C:NH_2{}^+Cl^-$), to borane or to boron trifluoride was known to cause an increase in $\nu(C:N)$ of $Ph_2C:NH$[86] (by 50, 17 and 25 cm^{-1} respectively), although co-ordination of this imine to boron-,[87] aluminium-[88] or gallium-[89] alkyls, and of $^tBu_2C:NH$[90] and $(Me_2N)_2C:NH$[33] to aluminium-alkyls, hardly affected $\nu(C:N)$. Increases in $\nu(C:N)$ of various Schiff bases of type $R'CH:NR^2$ (R',R^2 = substituted aryl groups) on co-ordination with niobium pentachloride[91] ($\Delta\nu$ 15-22 cm^{-1}) and niobium trioxychloride[92] ($\Delta\nu$ 20-30 cm^{-1}) have also been found.

This chapter describes a study of the methyleneamino-derivative $Ph_2C:NH$[56] and its derivatives $p\text{-}BrC_6H_4(Ph)C:NH$,[2] $(p\text{-}ClC_6H_4)_2C:NH$,[57] and $(p\text{-tolyl})_2C:NH$;[57,58] the t-butyl compounds $p\text{-tolyl}(^tBu)C:NH$[59] and $Bu^t{}_2C:NH$;[2,3] the N-substituted ketimines $Ph_2C:NMe$,[60] $Ph_2C:NPh$[61] and aldimines $PhCH:NMe$,[62] $PhCH:NPh$;[63] and the N-t-butyl substituted derivatives $CH_2:N^tBu$[64] and $MeCH:N^tBu$.[64] The first ten compounds $RR'C:NR^2$ were chosen so that the substituents R, R' and R^2 were either hydrogen or organic groups (aryl or t-butyl) with no hydrogen on the α-carbon atom. This avoids complications arising from imine-enamine tautomerisations[93-96] (Equation II.1) or aldol-type condensations (Equation II.2).[6,65]

$$R_2CH\cdot CR':NR^2 \rightleftharpoons R_2C:CR'\cdot NHR^2 \tag{II.1}$$

$$nRCH_2\cdot CH:NR^2 \longrightarrow RCH_2\cdot CH[:CRCH]_{n-2}:CR\cdot CH:NR^2 + (n-1)R^2NH_2 \tag{II.2}$$

Boron trifluoride was used as reference acid to avoid elimination reactions such as that shown in Equation II.3 that tend to occur with chloride Lewis acids.[86]

$$2R_2C{:}NH + BCl_3 \longrightarrow R_2C{:}NH_2^+Cl^- + R_2C{:}N{\cdot}BCl_2 \qquad \text{II.3}$$

The last two compounds, $CH_2{:}N^tBu$ and $MeCH{:}N^tBu$, were initially prepared in the course of studying another independent topic and as they, and their supposed hydrochlorides and boron trifluoride adducts, exhibited some seemingly ambiguous properties, they will be discussed now.

The product from the reaction of formaldehyde and t-butylamine[64] was a colourless liquid, b.p.62-65°C, which analysed correctly for $C_5H_{11}N(CH_2{:}N^tBu)$. A freshly prepared sample was found to have a molecular weight of 87 (by cryoscopy in benzene, $C_5H_{11}N$ requires M 85); a sample a few hours old had a molecular weight of 174. Thus it appears that dimerisation occurs very quickly at room temperature. The infra-red spectra of both samples showed only an extremely weak band at 1655 cm^{-1} in the 2000-1500 cm^{-1} range; no appreciable increase in the intensity of this band was observed in the spectrum of a freshly prepared sample run at 0°C. The mass spectra of both samples indicate the presence of only a monomeric species in the vapour phase. Addition of hydrogen chloride and boron trifluoride to a solution of a freshly prepared sample gave seemingly stable white solids which analysed correctly for compounds of empirical formula $C_5H_{12}NCl$ and $C_5H_{11}NBF_3$ respectively. Their i.r. spectra showed bands at 1608 and 1577 cm^{-1}, and at 1608 and 1572 cm^{-1} respectively in the range 2000-1500 cm^{-1}; the spectrum of the supposed hydrochloride also had a band at 3236 cm^{-1}, assigned to ν(N-H).

The product from the reaction between acetaldehyde and t-butylamine was a colourless liquid, b.p. 72-78°, which analysed correctly for $C_6H_{13}N(MeCH{:}N^tBu)$. The molecular weight of the product was found to be 107 (by cryoscopy in benzene; $C_6H_{13}N$ requires M 99); there was no sign of polymerisation after allowing the liquid to stand at room temperature for several days. The infra-red spectrum of the product shows a medium-intensity band at 1672 cm^{-1} in the range 2000-1500 cm^{-1}. The addition of hydrogen chloride to the supposed N-substituted aldimine gave a white solid which analysed correctly for a compound of empirical formula $C_6H_{14}NCl$ and whose i.r. spectrum had bands at 1718, 1613 and 1508 cm^{-1} in the range 2000-1500 cm^{-1}, plus a band at 3356 cm^{-1} assigned to ν(N-H). The product of boron trifluoride addition, on the other hand, gave only a brown oil whose i.r. spectrum contained bands at 1698, 1653 and 1587 cm^{-1} in the range 2000-1500 cm^{-1}.

The absence of any band assignable to ν(C:N) in the i.r. spectrum of the supposed product of condensation between t-butylamine and formaldehyde (CH_2:N^tBu) indicates that dimerisation occurs rapidly even at room temperature while the multiplicity of the bands in the expected region in the i.r. spectra of the hydrogen chloride and boron trifluoride adducts of MeCH:N^tBu makes any assignment of ν(C:N) in these compounds untenable.

Turning to the remaining ten ketimines and aldimines named above, Table II.1 lists the melting, boiling or decomposition points; azomethine stretching frequencies, few of which have been reported before,[84-86,97-101] are shown in Table II.2, together with the carbonyl stretching frequencies ν(C:O) of the related ketones[102-104] and benzaldehyde.[105] The figures agree well with those of earlier workers, except in the case of ν(C:N) for $(p\text{-}ClC_6H_4)_2C{:}NH$ (Table II.2); the high frequency reported by Pickard and Polly[97] appears to relate to hydrochloride impurity. The data in Table II.2 reveal certain interesting differences between the C=X stretching frequencies of ketones and imines, both in the manner in which ν(C=X) varies with R and R', and also in the manner in which ν(C=X) changes upon co-ordination.

The carbonyl stretching frequencies of many benzophenone derivatives $(XC_6H_4)_2C{:}O$ have been recorded and related to the electronic affect of the substituents X.[102] In particular, ν(C:O) <u>decreases</u> in the sequence $(p\text{-}ClC_6H_4)_2C{:}O > Ph_2C{:}O > (p\text{-}tolyl)_2C{:}O$. The opposite effect on ν(C:N) is apparent for the related imines; ν(C:N) <u>increases</u> in the sequence $(p\text{-}ClC_6H_4)_2C{:}NH < Ph_2C{:}NH) < (p\text{-}tolyl)_2C{:}NH$.

TABLE II.1

Melting or boiling points or decomposition temperatures of the imines, their hydrochlorides, and their boron trifluoride adducts

	Imine	Imine, HCl	Imine, BF_3
$Ph_2C{:}NH$	b.p. 90-95°/0.1 mm.[a]	m.p. 137-139°[b]	m.p. 205-207°[c]
$p\text{-}BrC_6H_4(Ph)C{:}NH$	b.p.115-120/1 mm.	decomp.*ca.* 180°	m.p. 185-187°
$(p\text{-}ClC_6H_4)_2C{:}NH$	b.p.138-141/0.5 mm.[d]	decomp.*ca.* 80°	m.p. 76-77°
$(p\text{-}Tolyl)_2C{:}NH$	b.p.138-140/2 mm.[e]	m.p. 210-214°[f]	decomp.*ca.*200°
$p\text{-}Tolyl({}^tBu)C{:}NH$	b.p.107-109/1 mm.[g]	m.p. 221°[h]	m.p. 118°
${}^tBu_2C{:}NH$	b.p.164-166/755 mm.[i]	m.p. 203°	m.p. 88°
$Ph_2C{:}NMe$	b.p. 80-82/0.3 mm.[j]	m.p. 152°	m.p.111-112°
$Ph_2C{:}NPh$	m.p.112-113°[h]	m.p. 190°[l]	m.p.232-235°
$PhCH{:}NMe$	b.p.182-184/760 mm.[m]	m.p. 172-174°	m.p.126-129°
$PhCH{:}NPh$	m.p. 52-53°[n]	m.p. 186-188°[o]	m.p.154-156°[p]

a. Lit.,[56] 127°/3.5 mm.

b. Lit.,[56] 137-139°

c. Reference 86.

d. Lit.,[57] m.p.59.5-60.5°, b.p.138-144°/0.5 mm.

e. Lit.,[57] m.p.67-69°; lit.,[58] b.p.150-152°/2 mm.

f. Lit.,[57,58] m.p.211-215°

g. Lit.,[3] 93-95°/5 mm.

h. Lit.,[59] 229°

i. Lit.,[3] 165-166°/760 mm.

j. Lit.,[60] 93°/0.4 mm.

k. Lit.,[61] m.p.211-215°

l. Lit.,[109] m.p.191-194°

m. Lit.,[62] 183-185°/760 mm.

n. Lit.,[63] m.p. 52°

o. Lit.,[110] m.p. 176°

p. Lit.,[111] m.p. 158-163°

TABLE II.2

Azomethine stretching frequencies, $\nu(C{:}N)$, of the imines, their hydrochlorides and their boron trifluoride adducts

$RR'C{:}NR^2$	$\nu(C{:}N)$ (cm^{-1})			$\Delta\nu^{\neq}$ (cm^{-1})		$\nu(C{:}O)$ (cm^{-1})
	Imine	Imine,HCl	Imine, BF_3	Imine, HCl	Imine, BF_3	$RR'C{:}O$
$Ph_2C{:}NH$	1607[a]	1653	1628	46	21	1664[f]
$p\text{-}BrC_6H_4(Ph)C{:}NH$	1607	1652	1629	45	22	1665[g]
$(p\text{-}ClC_6H_4)_2C{:}NH$	1590[b]	1654	1633	64	43	1670[h]
$(p\text{-}Tolyl)_2C{:}NH$	1610	1643	1626	33	16	1659[i]
$p\text{-}Tolyl(^tBu)C{:}NH$	1617	1656	1666	39	49	-
$^tBu_2C{:}NH$	1610	1670	1672	60	62	1687[j]
$Ph_2C{:}NMe$	1634	1669	1661	35	27	1664[f]
$Ph_2C{:}NPh$	1616[c]	1623	1621	7	5	1664[f]
$PhCH{:}NMe$	1658[d]	1695	1712	37	54	1708[k]
$PhCH{:}NPh$	1634[e]	1672	1673	38	39	1708[k]

Except where otherwise stated, figures for solid compounds are for Nujol mulls, and figures for liquid compounds are for Nujol solution.

$\neq$ $\nu(C{:}N)_{\text{adduct}} - \nu(C{:}N)_{\text{parent imine}}$

a. Lit.,[97] 1603 cm^{-1} (liquid film).

b. Lit.,[97] 1653 cm^{-1} (liquid film)

c. Lit.,[98] 1614 cm^{-1} (CCl_4 soln.)

d. Lit., [99,100] 1654 cm^{-1} ($CHCl_3$ soln.)

e. Lit., [99,100] 1630 cm^{-1} (CCl_4 soln.); 1628 cm^{-1} ($CHCl_3$ soln.); Lit.,[101] 1631 cm^{-1} (CCl_4 soln.)

f. CCl_4 soln.;[102] ref. 103 gives 1663 cm^{-1}

g. CCl_4 soln.;[102] ref. 103 gives 1662 cm^{-1}

h. CCl_4 soln.[102]

i. CCl_4 soln.;[102] ref. 103 gives 1650 cm^{-1}

j. C_2Cl_4 soln.[104]

k. CCl_4 soln.[105]

The effect of R^2 on ν(C:N) of $RR'C:NR^2$ is illustrated by comparing the values for $Ph_2C:NMe$ and $Ph_2C:NPh$, or for PhCH:NMe and PhCH:NPh. The greater π-electronic delocalisation, and consequently lower C:N bond order, may well contribute to the lower value of ν(C:N) when R^2 = Ph. A similar effect presumably causes ν(C:N) of organometallic derivatives of α -phenylbenzylideneamine, $(Ph_2C:N.MR_n)_2$ where M = Al,[88] Ga,[89] Zn,[106] to vary consistently with R, decreasing in the sequence Me > Et > Ph. Detailed studies have also been made of the variation of ν(C:N) with R' and R^2 in compounds $R'CH:NR^2$.[107,108]

The infra-red spectra of the imines were recorded as contact films and as Nujol and carbon tetrachloride solutions (for liquids) and as Nujol mulls and carbon tetrachloride solutions (for solids); the figures in Table II.2 refer to ca. 10 wt.% solutions or mulls in Nujol. For some liquid imines for which R^2 = H, ν(C:N) decreased slightly with increasing concentration of the imine solution, apparently as the degree of hydrogen bonding increased. For example, $Ph_2C:NH$ and $p-BrC_6H_4(Ph)C:NH$ as neat liquids absorbed at 1603 cm^{-1}; di-t-butylmethyleneamine, however, absorbed at 1610 cm^{-1} as the neat liquid or in solution in Nujol or carbon tetrachloride.

Table II.1 also shows the melting or decomposition points of the hydrochlorides and boron trifluoride adducts. Table II.2 lists the azomethine stretching frequencies of the imine hydrochlorides and boron trifluoride adducts. Although several of the imine hydrochlorides were known,[84-86,56-59,109,110] only two of the boron trifluoride adducts ($Ph_2C:NH,BF_3$[86] and $PhCH:NPh,BF_3$[111]) have been previously described.

As can be seen from Table II.2, co-ordination of the imines studied, whether to the proton or to boron trifluoride, although causing little change in the relative intensity of the azomethine stretching band, invariably caused an increase (Δν) in ν(C:N). The magnitude of Δν varied considerably, from ca.5 cm^{-1} in the case of $Ph_2C:NPh$ (the imine with the most extensive delocalised π-electronic system) to ca.60 cm^{-1} in such cases as $(p\text{-}ClC_6H_4)_2C{:}NH$, $^tBu_2C{:}NH$ and PhCH:NMe, i.e. apparently significantly including the imine with no aryl substituents conjugated with the azomethine group. The decrease in ν(C:O) of ketones is usually in the range 70-130 cm^{-1}. Some trends have been observed in the shift of ν(C:O) on complex formation of some 30 ketones with boron trifluoride;[73] for dialkyl ketones Δν(C:O) is in the range 73 ± 6 cm^{-1}, for alkylaryl ketones Δν = 125 ± 9 cm^{-1} and for $Ph_2C{:}O$ and Me(naphthyl)C:O Δν = 107 ± 2 cm^{-1}. Such results are taken as demonstrating that the donor strengths of the ketones decrease in the order alkylaryl > $Ph_2C{:}O$ and Me(naphthyl)C:O > dialkyl ketones. For the ketimine, boron trifluoride adducts studied here, the order would seem to be dialkyl (Δν 62 cm^{-1}) > alkylaryl (Δν 49 cm^{-1}) > diaryl (Δν 16-43 cm^{-1}), although it must be said that this sequence is statistically rather meaningless as only six such adducts have been studied. Co-ordination of Lewis acids to the C:N group would, based on the argument used to explain the decrease in ν(C:O) on similar co-ordination of Lewis acids to carbonyl compounds i.e. a weakening of the C=X bond by electron-flow to the co-ordinate link, have been expected to cause a decrease in ν(C:N). Goulden's[79] argument that such co-ordination of diarylketimines causes an increase in the C:N bond order by offsetting the electron-withdrawing effect of the aryl groups obviously should, but does not, apply equally to diarylketone adducts. It has further been argued that imine-enamine tautomerism of the type illustrated in Equation II.1 could be inferred from the increase in ν(C=X) that occurred on immonium salt formation, as it appeared that the frequency shift reflected the change from C:C to C:N.[93-96] These results cited here, for systems where such tautomerism is impossible, show such arguments to be spurious.

The general increase in ν(C:N) of imines on co-ordination may be compared with the increase that invariably occurs in ν(C⋮N) of nitriles when they act as σ-electron donors[112] (Fig.II.2.a). Such an increase has been found in nitrile adducts of aluminium-[113-116] and gallium-[117] trialkyls, of boron trihalides,[118-121] of Group IV halides[119,121,122] and of nitrilium salts of type $PhCNR^+BCl_4^-$[123] (R = Ph,Et,Me), $MeCNMe^+SbCl_6^-$,[124] and $PhCNPh^+AlCl_4^-$.[125] The nitrile stretching frequencies for some of these adducts and nitrilium salts are presented in Table II.3. For a series of adducts of a particular nitrile, such $\Delta\nu$(C:N) values have been taken as a guide to the Lewis acidities of the acceptor moieties in cases where the acceptor moieties have comparable masses.[78] Lowering of ν(C:N) has only been found for complexes in which the nitrile group co-ordinates to a metal through its C:N π-system, for example in various nickel-cyanamide complexes,[126,127] in chelation complexes such as $Et_2N{\cdot}CH_2C{:}N,MCl_4$ (M = Sn, Ti, Zr)[120] and in compounds such as $M(CO)_3(NCRCN)X$ where M = Mn and Re.[128]

Although this <u>increase</u> in ν(C:N) on co-ordination through the lone pair of the nitrogen, is believed to arise in part from the mechanical constraint applied to the nitrogen of the co-ordinated nitrile,[119,129,130] there is much evidence that co-ordination is accompanied by a fractional <u>increase</u> in the bond order of the C:N bond. It was originally argued that, whereas in the free nitrile the CN link is approximately intermediate between a double and a triple bond (Fig.II.2.b), such mesomerism (as shown in Fig.II.2.c) would not be possible in the adduct because of the very different geometry of the two structures.[118] The structure involving a linear C:N→B co-ordinate link (sp hybridised nitrogen) was regarded as substantially representing the structure of the compound; and, if true, would indicate a shorter C:N bond length and an increase in the C:N bond order in the adduct as compared to that in the free nitrile. Following this, normal co-ordinate analyses[78,131,132] and M.O. calculations[131,132] on some acetonitrile adducts indicated that the force constant of the CN bond increased to some extent upon co-ordination and that this increase was brought about by stronger binding within the CN σ system due essentially to a greater dominant contribution from the donor atom s orbital.

TABLE II.3

Nitrile stretching frequencies for some nitrile adducts and nitrilium salts

Nitrilium salt	$\nu(C\equiv N)$ (cm^{-1})	$\Delta\nu$ (cm^{-1})	Ref.	Nitrile Adduct	$\nu(C\equiv N)$ (cm^{-1})	$\Delta\nu$ (cm^{-1})	Ref.
$PhCNPh^{+}BCl_4^{-}$	2318	88	123	$PhCN,BCl_3$	2304	74	118
$PhCNEt^{+}BCl_4^{-}$	2365	135	123	$PhCN,BF_3$	2336	106	119
$PhCNMe^{+}BCl_4^{-}$	2380	150	123				
$PhCNPh^{+}AlCl_4^{-}$	2310	80	125	$PhCN,AlMe_3$	2272	42	114 115
				$PhCN,AlEt_3$	2270	40	114
				$PhCN,GaMe_3$	2260	30	117
				$PhCN,GaEt_3$	2258	28	117
$MeCNMe^{+}SbCl_6^{-}$	2416	163	124	$MeCN,BF_3$	2359	106	119
				$MeCN,AlMe_3$	2296	43	115
				$MeCN,AlEt_3$	2290	37	115
				$MeCN,GaMe_3$	2285	32	117
				$MeCN,GaEt_3$	2279	26	117

$\nu(C\equiv N)$ Values: PhCN, 2230 cm^{-1}; MeCN, 2253 cm^{-1}

X-ray crystallographic evidence that co-ordination of a nitrile does result in a strengthening, and hence shortening, of the C⋮N bond comes from the study of the complex MeCN,BF_3[133] in which the CN bond length is found to be 1.122Å (cf. CN bond length in MeCN,[134] 1.157Å). It seems possible that there is a comparable fractional increase in the C:N bond order of imines on co-ordination.

Although changes in ν(C:N) were the most noticeable effect of co-ordination in the i.r. spectra of the imines, other effects were noted. For those imines with R^2 = H, the band assignable to the N-H stretching vibration, ν(N-H), was broad and ill-defined. Co-ordination to boron trifluoride caused this band to sharpen and shift to lower frequency, e.g. $(p\text{-tolyl})_2C{:}NH$ has ν(N-H) at ca. 3400 cm^{-1}, whereas $(p\text{-tolyl})_2C{:}NH,BF_3$ absorbs at ca. 3280 cm^{-1}. Although ν(N-H) would be expected to decrease in this way as electronic charge is drained from the nitrogen, an increase in ν(N-H) in diphenylmethyleneamine adducts $Ph_2C{:}NH,MR_3$ (M = Al,[88] Ga,[89]) and in bis(dimethylamino)methyleneamine adducts $(Me_2N)_2C{:}NH,AlR_3$[33] (R = Me, Et, Cl) has been noted. The broadness of these bands in the spectra of the parent imines prevent precise measurement of these frequency changes, however. A second feature of the spectra of each of the boron trifluoride adducts was a band of medium intensity, at 615 ± 10 cm^{-1}, absent from the spectra of the parent imines, and assignable to $\nu(B \rightarrow N)$ by analogy with the assignments of related bands in the spectra of boron halide-amine adducts.[135,136]

CHAPTER III

This chapter describes the preparation and spectroscopic properties of a series of monomeric di-t-butylmethyleneaminoboranes, $^{t}Bu_2C{:}NBXY$. On the basis of their i.r. and ^{1}H n.m.r. spectra, they are proposed as having allene-type structures, containing linear C:NB skeletons, the shape appropriate for maximum $N \rightarrow B(p \rightarrow p)\,\pi$ multiple bonding.

EXPERIMENTAL SECTION

Starting Materials

t-Butylcyanide was purified by distillation from phosphorus pentoxide under dry nitrogen, t- and n-butyl-lithium solutions were standardised by titration with sec-butanol.[1] Di-t-butylmethyleneamine[2] and its N-trimethylsilyl derivative were prepared as described earlier (see Chapter I). Triethylboron and boron trichloride were vacuum distilled before use. Phenylborondichloride[137] and diphenylboron chloride[138] were prepared from boron trichloride and tetraphenyl tin. Dimesitylboronfluoride[139] was prepared from boron trifluoride etherate and mesitylmagnesium bromide. Materials throughout were handled under dry nitrogen or in vacuo.

Preparation of Di-t-butylmethyleneaminodichloroborane, $^{t}Bu_2C{:}NBCl_2$

A solution of di-t-butylmethyleneaminolithium was prepared by adding $^{t}BuLi$ (20.0 ml. of 1.9M solution, 38 mmole) to $^{t}BuCN$ (3.16 gm., 38 mmole) in 20 ml. pentane. Boron trichloride (4.48 gm., 38 mmole) was added by condensation at -196°. The mixture was allowed to warm to 15° with stirring, when lithium chloride was precipitated. The solution was filtered hot, pentane was removed at low pressure, and the pale yellow-green liquid was distilled from a greaseless apparatus at ca. 79-81° at 2 mm. to form a colourless distillate which was identified as monomeric di-t-butylmethyleneaminodichloroborane, $^{t}Bu_2C{:}NBCl_2$ (Found: C,49.6; H,8.3; B,4.5; Cl,32.0; N,6.1%; M,224. $C_9H_{18}BCl_2N$ requires C,48.7; H,8.1; B,5.0; Cl,31.9; N,6.3%; M,222). ν_{max} (Liquid film)

2976s, 2941ms, 2924ms,sh, 2878m, 1951w, 1843s, 1773m,sh, 1653w, 1515w,sh, 1481s, 1460s, 1395s, 1370s, 1307s, 1287s, 1199ms, 1048s, 1029m, 976ms, 935m, 909ms,br, 871s,br, 833ms, 730w, 694w, 649s, 552ms,br, 475w,br and 461 ms,br cm^{-1}. This compound was readily hydrolysed and fumed strongly in moist air.

Preparation of Di-t-butylmethyleneaminodiphenylborane, tBu$_2$C:NBPh$_2$

Equimolar proportions of di-t-butylmethyleneaminolithium (2·79 gm., 19 mmole) and diphenylboron chloride (3·80 gm., 19 mmole) were allowed to react in pentane on warming from -196° to 18°. Solvent was removed at reduced pressure, leaving a semi-solid residue from which a pale yellow liquid could be extracted using pentane. This liquid, which darkened on exposure to air and decomposed during an attempt at its vacuum distillation, was identified as monomeric *di-t-butylmethyleneaminodiphenylborane*, ^{t}Bu$_2$C:NBPh$_2$. (Found: C,84·0; H,9·4; N,4·3%; M,324. $C_{21}H_{28}BN$ requires C,82·7; H,9·1; N,4·6%; M,305). ν_{max} (Liquid film) 3058m, 3012ms,sh, 2967vs, 2941vs,sh, 2878s, 1953w, 1825vs, 1736w, 1595m, 1488ms, 1466ms, 1437s, 1395m, 1370s, 1316ms, 1304m,sh, 1250s,sh, 1233vs, 1198m,sh, 1189m,sh, 1160w, 1046ms, 1036m,sh, 1024m, 999m, 972s, 934w, 901m, 884s, 836m, 787m, 762ms, 749m, 730s, 699vs, 625ms, 609s,sh, 605vs, and 546m,br cm^{-1}.

^{t}Bu$_2$C:NBPh$_2$ was also obtained from the reaction between diphenylboron chloride (4·00 gm., 20 mmole) and di-t-butylmethyleneaminotrimethylsilane (4·16 gm., 20 mmole). The reactants were heated together in toluene solvent at 100° for 5 hours, and the product isolated as described above.

Reaction of Dimesitylboron fluoride with di-t-butylmethyleneaminolithium and with di-t-butylmethyleneaminotrimethylsilane

Dimesitylboron fluoride (1·88 gm., 7 mmole) and di-t-butylmethyleneaminolithium (1·03 gm., 7 mmole) were heated together in toluene at 110° for several hours. Removal of solvent left a viscous liquid whose i.r. spectrum showed a band at 1610 cm^{-1}. When the reagents were held at 150° for three days in the absence of solvent, a similar oil was obtained. Distillation effected separation into two components and these were shown (by their i.r. spectra) to be the original starting materials.

There appeared similarly to be no reaction between equimolar proportions of dimesitylboron fluoride (2·68 gm., 10 mmole) and di-t-butylmethyleneamino-trimethylsilane (2·13 gm., 10 mmole) when they were heated together at 120° for three days; distillation of the mixture afforded near-quantitative recovery of the two reagents.

Preparation of Di-t-butylmethyleneaminochlorophenylborane, ${}^{t}Bu_2C:NBClPh$

This compound was prepared from equimolar proportions of phenylboron dichloride (1·59 gm., 10 mmole) and di-t-butylmethyleneaminolithium (1·47 gm., 10 mmole) during 2 hr. at 18° in hexane. The hexane was removed at reduced pressure, and the residue was extracted with hot toluene. Removal of toluene and subsequent distillation from a greaseless apparatus afforded the colourless liquid, monomeric di-t-butylmethyleneaminochlorophenylborane, ${}^{t}Bu_2C:NBPhCl$, b.p. 100-101° at 0·03 mm. (Found: C,68·2; H,8·3; Cl,13·1; N,5·3%; M,286. $C_{15}H_{23}BClN$ requires C,68·5; H,8·7; Cl,13·5; N,5·3%; M,263·5). ν_{max} (Liquid film) 3058m,sh, 3044m, 2959s, 2915ms,sh, 2861m, 1942vw, 1838vs, 1773vw, 1603w, 1481ms, 1460m, 1437ms, 1393ms, 1368ms, 1333m, 1314s, 1277w, 1222m, 1183w, 1161m,sh, 1147ms, 1070w, 1048m, 1027m, 1000w, 976ms, 935w, 899ms, 876vs, 834ms, 754s, 697vs, 679s, 619m, 610m, 576m, 565s and 539m,br cm^{-1}.

Preparation of Bis(di-t-butylmethyleneamino)phenylborane, $({}^{t}Bu_2C:N)_2BPh$

A solution of phenylboron dichloride (1·59 gm., 10 mmole) in toluene (20 ml.) was added by syringe to a frozen (-196°) solution of di-t-butylmethyleneaminolithium in hexane, prepared from t-butyl cyanide (1·66 gm., 20 mmole) and t-butyl-lithium (10 ml. of a 2·0M solution, 20 mmole). The solution was held under reflux at 95° for 3 hr., during which time a pale yellow solid was deposited. Solvent was removed at low pressure and the residue was extracted with hot petroleum ether, from which colourless needles, m.p. 134-135°, were obtained and identified as the monomeric bis(di-t-butylmethyleneamino)phenyl borane, $(^{t}Bu_2C{:}N)_2BPh$. (Found: C,78·6; H,10·8; N.7·5%; M,352. $C_{24}H_{41}BN_2$ requires C,78·3; H,11·1; N,7·6%; M,368). ν_{max} (Nujol mull) 1936w, 1774s, 1753s, 1592w, 1570w, 1475s,sh, 1456s, 1437s, 1362s, 1318ms, 1309ms, 1295ms, 1263s, 1245s,sh, 1214s, 1182ms, 1101w, 1067m, 1044s, 1026m, 1002m, 990m, 965s, 931m, 833s, 793w, 752ms, 742m, 724w, 698s, 667w, 624ms,br, 619ms, 597m,br, 581ms,br, 537m,br and 435m,br cm^{-1}. This compound was unaffected by several days exposure to moist air.

Preparation of Bis(di-t-butylmethyleneamino)chloroborane, $(^{t}Bu_2C{:}N)_2BCl$

Di-t-butylmethyleneaminodichloroborane, $^{t}Bu_2C{:}NBCl_2$ (2·22 gm., 10 mmole) and di-t-butylmethyleneaminolithium (1·47 gm., 10 mmole) were heated together in boiling toluene for 6 hr. Lithium chloride was removed by filtration. Distillation of the resulting solution from a greaseless apparatus gave a colourless liquid, b.p. 110-112° at 0·01 mm. which, on cooling, crystallised as white needles, m.p. 56-58°, which were identified as monomeric bis(di-t-butylmethyleneamino)chloroborane, $(^{t}Bu_2C{:}N)_2BCl$. (Found: C,67·9; H,11·5; B,3·1; Cl,9·2; N,8·6%; M,368. $C_{18}H_{36}BClN_2$ requires C,66·5; H,11·0; B,3·4; Cl,10·7; N,8·6%; M,326·5). ν_{max} (Liquid film), 1936vw, 1777vs, 1754s,sh, 1479vs, 1458ms,sh 1389s, 1362vs, 1328m,sh, 1304s, 1271m, 1233m, 1202ms, 1120w, 1103m, 1079ms,sh, 1064s, 1045s, 1003s, 966vs, 932m, 906w, 858w, 848w, 833s, 794w, 752w, 731m, 702ms,sh, 694vs, 623m, 578w, 549m, 529w and 490m cm^{-1}. (An i.r. spectrum of the solid, as a Nujol mull, was identical to the above).

This bis(ketimino)borane is, in contrast to $(^{t}Bu_2C{:}N)_2BPh$, moisture sensitive. On exposing the liquid to moist air for several minutes, a white powder is deposited which analyses correctly for the bis(ketimino)boronic acid,

$(^tBu_2C{:}N)_2BOH$. Its i.r. spectrum shows bands at ca.3300 and 1755 cm^{-1}.

Reactions of two and three molar proportions of di-t-butylmethyleneamino-lithium with di-t-butylmethyleneaminodichloroborane, $^tBu_2CNBCl_2$, and boron trichloride, respectively, produced only bis(di-t-butylmethyleneamino)chloroborane, $(^tBu_2CN)_2BCl$; tris(di-t-butylmethyleneamino)borane, $(^tBu_2C{:}N)_3B$, was not formed.

Preparation of Di-t-butylmethyleneaminodiethylborane, $^tBu_2C{:}NBEt_2$

Triethylborane (1·03 gm., 10·5 mmole) was added by syringe to a frozen (-196°) solution of di-t-butylmethyleneamine, $^tBu_2C{:}NH$, (1·48 gm., 10·5 mmole) in pentane (10 ml.). No indication of reaction was noted when the solution was warmed to 18°. Toluene (20 ml.) was added and the solution boiled for 17 hr. Solvent and unchanged reactants were removed under low pressure, leaving a clear, colourless liquid which was identified as monomeric di-t-butylmethyleneaminodiethylborane, $^tBu_2C{:}NBEt_2$, which decomposed during attempts at its vacuum distillation. (Found: H,13·5; B,4·8; N,6·5%; M,215. $C_{13}H_{28}BN$ requires H,13·4; B,5·2; N,6·7%; M,209). ν_{max} (Liquid film) 3597vw, 2959s,sh, 2933s, 2875ms,sh, 2870s, 2801m,sh, 2717w, 1944w, 1818s, 1770w, 1616vw, 1608m, 1481s, 1458s, 1408ms,sh, 1389s, 1364s, 1312s,sh, 1292s, 1259s, 1205ms, 1087s,br, 1044s, 1020s,br, 971s, 926ms, 873m, 836ms, 803s,br, 759m, 727m,br, 699m,br and 552m,br cm^{-1}.

Preparation of Di-t-butylmethyleneamino(di-n-butyl)borane, $^tBu_2C{:}NB^nBu_2$

n-Butyl-lithium (10·0 ml. of a 1·4M solution in hexane, 14 mmole) was added by syringe to a frozen (-196°) solution of di-t-butylmethyleneaminodichloroborane, $^tBu_2C{:}NBCl_2$, (1·44 gm., 6·6 mmole) in hexane (20 ml.). A strongly exothermic reaction occurred as the mixture was allowed to warm to 15°, and lithium chloride was precipitated. The mixture was stirred at 15° for 2 days, solvent was removed under vacuum, and the residue was extracted with warm toluene, from which the liquid di-t-butylmethyleneamino(di-n-butyl)borane, $^{t}Bu_2C{:}NB^{n}Bu_2$, b.p. 85-88°/0·1 mm., was recovered by distillation. (Found: C,76·6; H,13·3; N,5·6%; M,277. $C_{17}H_{36}BN$ requires C,77·0; H,13·6; N,5·3%; M,265). ν_{max} (Liquid film) 2963vs, 2924vs, 2871s, 1821s, 1774vw,sh, 1486ms, 1464ms, 1408m,sh, 1393ms, 1368ms, 1342ms, 1325ms, 1309ms,sh, 1266m, 1235m, 1205m, 1106m, 1047s, 1028m, 975ms, 935w, 901w, 877vw, 838w, 800w,br and 552w,br cm^{-1}.

Preparation of Di-t-butylmethyleneaminochloroborane, $^{t}Bu_2C{:}NBHCl$

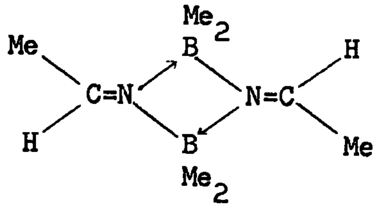
t-Butyl-lithium (10 ml. of a 1·9M solution, 19 mmole) was added to di-t-butylmethyleneaminodichloroborane, $^{t}Bu_2CNBCl_2$ (4·22 gm., 19 mmole) in pentane (40 ml.) at -196°. On warming to 18°, lithium chloride was precipitated. Filtration and removal of solvent left a colourless liquid which was identified as di-t-butylmethyleneaminochloroborane, $^{t}Bu_2C{:}NBHCl$ (Found: C,57·3; H,10·3; B,5·2; Cl,18·8; hydrolysable H,0·50%; M,203. $C_9H_{19}BClN$ requires C,57·6; H,10·1; B,5·9; Cl,18·8; hydrolysable H,0·54%; M,187·5). ν_{max} (Liquid film) 2941vs, 2865s, 2433m, 1845vs, 1786m,sh, 1770m,sh, 1667m, 1481ms,sh, 1468ms, 1390ms,sh, 1370s, 1344ms,sh, 1305ms,sh, 1294ms, 1202m, 1161w, 1120w, 1075w, 1048m, 1030w, 1005w, 977m, 943w,sh, 932w,sh, 917ms, 880s, 834m, 797w, 699w, 652m, and 552m,br cm^{-1}.

DISCUSSION

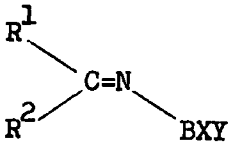
Alkylideneaminoboranes $(R^1R^2C{:}NBXY)_{\underline{n}}$ are normally associated, usually existing as dimeric species ($\underline{n}$ = 2) in the vapour, solution and solid phases.[12,52,53,140-150] Their structures are typified by that of $(MeCH{:}NBMe_2)_2$[151] (Figure III.1.a), determined by X-ray crystallography. Monomers (Figure III.1.b. or III.1.c) are apparently observed only when the substituents R^1, R^2, X and Y are so bulky as to prevent association,[12,52,53,150/2 although monomers have also been noted in the vapour phases of some of the associated species,[52,87,141] on heating solutions of the dimers[153,154] and occasionally, as minor constituents of monomer-dimer equilibria in solutions of the dimers.[154-156]

The structures of the monomeric species are of particular interest since the alkylideneamino group $R^1R^2C{:}N$-, when terminally attached to co-ordinatively unsaturated metals or metalloids (M) in derivatives of type $R^1R^2C{:}NMX_n$, should provide a convenient probe for the study of dative $N \rightleftharpoons M$ π-bonding. The C:NM skeleton in such molecules may be expected to be bent, (CNM angle *ca.*120°) where there is little or no π-bonding. In cases where there is considerable $N \rightarrow M$ π-bonding, however, a linear structure (CNM angle *ca.*180°) having an allene-type skeleton, is likely. Prior to the commencement of this work the only structural information available for monomeric alkylideneaminoboranes has been the high (*ca.*1760-1850 cm^{-1}; see Table III.1) azomethine stretching frequency observed in their i.r. spectra, appropriate [Assigned $\nu(C\dot{=}N\rightleftharpoons B)$] for an allene-type structure containing a linear $C{=}N\rightleftharpoons B$ skeleton (Figure III.1.d); the isoelectronic allenes $R_2C{:}C{:}CR_2$ have their ν(C:C:C) absorption at 1920-2000 cm^{-1} [50] (see Table I.3, p.20). Such a high value for the azomethine stretching frequency is difficult to reconcile with a bent structure (Figure III.1.b) for which a frequency nearer that of the dimers (*ca.*1580-1680 cm^{-1}; see Table III.1) and of azomethines in general (1590-1690 cm^{-1}; see Table II.2)[84-86,97-101,107,108,157] might have been expected.

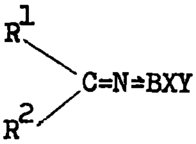
FIGURE III.1



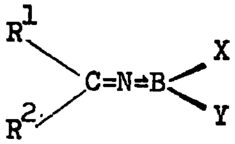
(a)



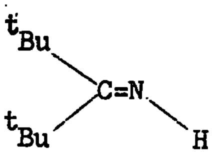
(b)



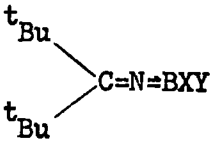
(c)



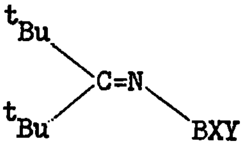
(d)



(e)



(f)



(g)

TABLE III.1

Skeletal Stretching frequencies [ν(C=N=B) and ν(C:N)] of the eight new monomeric di-t-butylmethyleneaminoboranes and of their diphenylmethyleneamino - analogues (where known)

[^{t}Bu$_2$C:NBXY]$_n$			[Ph$_2$C:NBXY]$_n$				
Compound	ν(C=N=B) (cm^{-1})	n	Compound	ν(C=N=B) (cm^{-1})	ν(C=N) (cm^{-1})	n	Ref.
^{t}Bu$_2$C:NBHCl	1845*	1					
^{t}Bu$_2$C:NBCl$_2$	1843*	1	Ph$_2$C:NBCl$_2$		1590	2	12 52 140
^{t}Bu$_2$C:NBPhCl	1838*	1	Ph$_2$C:NBPhCl		1612	2	12 52 53
^{t}Bu$_2$C:NBPh$_2$	1825*	1	Ph$_2$C:NBPh$_2$	1786		1	12 52 53
^{t}Bu$_2$C:NB^{n}Bu$_2$	1821*	1					
^{t}Bu$_2$C:NBEt$_2$	1818*	1	Ph$_2$C:NBEt$_2$	1793		1	52
(^{t}Bu$_2$C:N)$_2$BCl	1777(1754sh)	1					
(^{t}Bu$_2$C:N)$_2$BPh	1774(1753sh)	1	(Ph$_2$C:N)$_2$BPh		1672	1	12 52

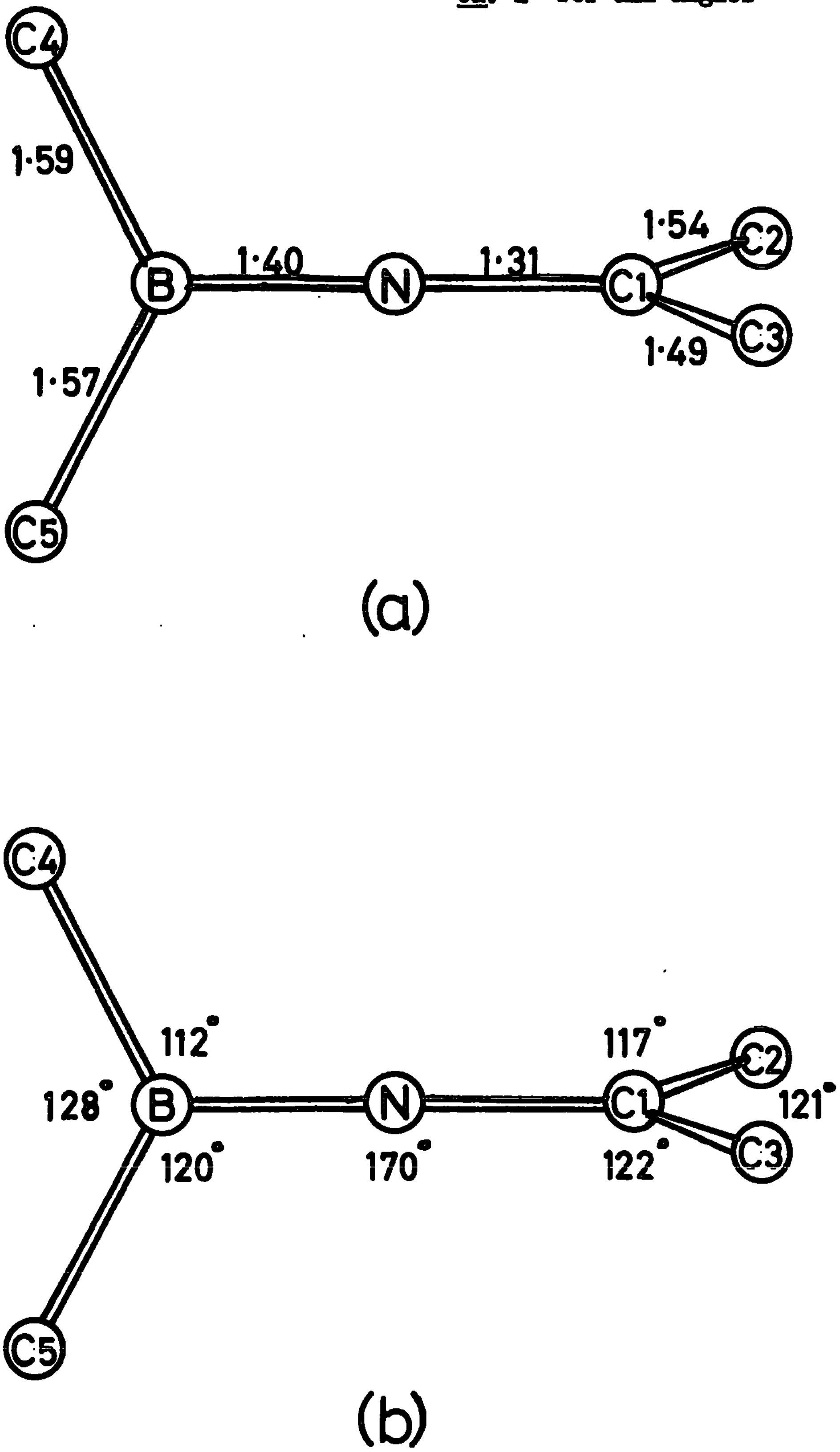
* liquid film; all other Figures relate to Nujol mulls.

To obtain further structural information, a new series of alkylideneaminoboranes have been prepared, containing the di-t-butylmethyleneamino group, $^tBu_2C$:N-, chosen so that the bulk of the t-butyl groups should be sufficient to prevent association and so that their ^1H n.m.r. could be studied for evidence of linearity of the C:NB skeleton. As described earlier in this thesis (see Chapter I, p.9), di-t-butylmethyleneamine itself, $^tBu_2C$:NH, which has a bent C:NH skeleton with magnetically non-equivalent t-butyl groups (Figure III.1.e), gives separate resonances attributable to these.[26] A di-t-butylmethyleneaminoborane, $^tBu_2C$:NBXY, with a linear skeleton (Figure III.1.f) should give only one signal. Three of this series of new compounds $^tBu_2C$:NBXY (X = Y = Cl,Ph, ^nBu) have been independently prepared and studied by Professor Lappert and Dr. Collier, and form the basis of a joint paper which has been submitted for publication.[158] Finally, the preliminary results of an X-ray structural investigation[159] on monomeric Ph_2C:NB(mesityl)$_2$ (Figure III.2.a,b), which has established a linear geometry at nitrogen, will be discussed.

FIGURE III.2

The Crystal and Molecular Structure of $Ph_2C{:}NB(mesityl)_2$

Bond lengths in Å: E.s.d.'s are: N–C 0·02Å
remainder 0·03Å
ca. 2° for all angles



Preparation of Di-t-butylmethyleneaminoboranes

The eight new di-t-butylmethyleneaminoboranes prepared are listed in Table III.1, together with their azomethine stretching frequencies. The compounds, except for $^{t}Bu_2C{:}NBPh_2$ and $(^{t}Bu_2C{:}N)_2BPh$, are readily hydrolysed in the atmosphere. The compounds $^{t}Bu_2C{:}NBCl_2$,[158] $^{t}Bu_2C{:}NBPh_2$,[158] and $^{t}Bu_2C{:}NBPhCl$ were prepared from equimolar proportions of $^{t}Bu_2C{:}NLi$ (prepared in situ from $^{t}BuCN$ and $^{t}BuLi$) and BCl_3, Ph_2BCl and $PhBCl_2$ respectively (Equation III.1).

$$^{t}BuCN \xrightarrow{^{t}BuLi} {}^{t}Bu_2C{:}NLi \xrightarrow{R_{\underline{n}}BCl_{3-\underline{n}}} {}^{t}Bu_2C{:}NBR_{\underline{n}}Cl_{2-\underline{n}} + LiCl \qquad \text{(III.1)}$$

In the procedure found most convenient (see Experimental section for details), the reagents in the form of hydrocarbon solutions were mixed at -196°. Lithium chloride normally separated as the mixture warmed up to room temperature, and reaction was found to be complete after a few hours stirring at room temperature. A similar route, though here preparing the ketimino-lithium reagent by lithiation of the parent ketimine with $^{n}BuLi$, had previously been used to prepare the monomeric alkylideneaminoboranes $Ph_2C{:}NBPh_2$,[52,53] $Ph_2C{:}NB(mesityl)_2$,[52,53] $(p\text{-}MeC_6H_4)_2C{:}NBPh_2$[53] and $(Me_2N)_2C{:}NBPh_2$,[160] and the associated ketiminoboranes $(Ph_2C{:}NBO_2C_6H_4)_{\underline{n}}$[53] ($\underline{n}$ probably equals 2) and $(Ph_2C{:}NBX_2)_{\underline{n}}$[52,140] ($\underline{n}$ = 2 for X = Cl,Br,I; the fluoride is polymeric). It was not possible, however, to prepare the derivative $^{t}Bu_2C{:}NB(mesityl)_2$ by the reaction between $^{t}Bu_2C{:}NLi$ and $mesityl_2BF$, despite the use of such forcing conditions as heating the reagents in boiling toluene or holding them at 150° for several days in the absence of solvent; in contrast, $Ph_2C{:}NB(mesityl)_2$ has been prepared from $Ph_2C{:}NLi$ and $mesityl_2BF$, albeit under unusually forcing conditions (3 hrs. heating at 100°).[52,53] Presumably the failure to prepare $^{t}Bu_2C{:}NB(mesityl)_2$ reflects the greater steric crowding of the nitrogen atom in di-t-butylmethyleneaminolithium as compared to that in the diphenyl analogue, and this, together with the bulk of the mesityl groups on the boron atom in mesityl$_2$BF, prevents the nitrogen and boron atoms from coming close enough together to form a suitable reaction intermediate.

The two bis(di-t-butylmethyleneamino)boranes, $(^t\text{Bu}_2\text{C:N})_2\text{BCl}$ and $(^t\text{Bu}_2\text{C:N})_2\text{BPh}$ were prepared from the reactions of two equivalents of $^t\text{Bu}_2\text{C:NLi}$ with BCl_3 and with PhBCl_2 respectively (Equation III.2) and from the reactions of $^t\text{Bu}_2\text{C:NLi}$ with equimolar proportions of the alkylideneamino derivatives $^t\text{Bu}_2\text{C:NBCl}_2$ and $^t\text{Bu}_2\text{C:NBPhCl}$ (Equation III.3).

$$2\,^t\text{Bu}_2\text{C:NLi} + \text{RBCl}_2 \longrightarrow (^t\text{Bu}_2\text{C:N})_2\text{BR} + 2\text{LiCl} \qquad \text{III.2}$$

$$(\text{R} = \text{Ph, Cl})$$

$$^t\text{Bu}_2\text{C:NLi} + {}^t\text{Bu}_2\text{C:NBRCl} \longrightarrow (^t\text{Bu}_2\text{C:N})_2\text{BR} + \text{LiCl} \qquad \text{III.3}$$

Attachment of the second alkylideneamino group to boron required the reagents to be held together for several hours in toluene at 95°. Treatment of $(^t\text{Bu}_2\text{C:N})_2\text{BCl}$, $^t\text{Bu}_2\text{C:NBCl}_2$ and BCl_3 with, respectively, one, two and three molar proportions of $^t\text{Bu}_2\text{C:NLi}$ failed to afford the tri(alkylideneamino) borane, $(^t\text{Bu}_2\text{C:N})_3\text{B}$.Bis(diphenylmethyleneamino)phenylborane, $(\text{Ph}_2\text{C:N})_2\text{BPh}$,[12,52,53] and tris(diphenylmethyleneamino)borane, $(\text{Ph}_2\text{C:N})_3\text{B}$,[4,12,52,53] have previously been prepared from analogous reactions of PhBCl_2 and BCl_3 with, respectively, two and three equivalents of $\text{Ph}_2\text{C:NLi}$ (or $\text{Ph}_2\text{C:NSiMe}_3$). However, the successful preparation of $(^t\text{Bu}_2\text{C:N})_2\text{BCl}$ may be contrasted with the earlier failure to prepare $(\text{Ph}_2\text{C:N})_2\text{BCl}$,[12,53] which was apparently unstable with respect to disproportionation into $\text{Ph}_2\text{C:NBCl}_2$ and $(\text{Ph}_2\text{C:N})_3\text{B}$. (Equation III.4; R = Ph, n = 2).

$$2(\text{R}_2\text{C:N})_2\text{BCl} \longrightarrow \frac{1}{n}(\text{R}_2\text{C:NBCl}_2)_n + (\text{R}_2\text{C:N})_3\text{B} \qquad \text{III.4}$$

The stability of $(^t\text{Bu}_2\text{C:N})_2\text{BCl}$ to a comparable disproportionation

(Equation III.4; $R = {}^{t}Bu$, $n = 1$) is readily understood. Firstly, the dichloride ${}^{t}Bu_2C{:}NBCl_2$ is a liquid, whereas $(Ph_2C{:}NBCl_2)_2$ is a crystalline solid whose lattice energy provides a driving force for the disproportionation. Secondly, even if $({}^{t}Bu_2C{:}N)_3B$ were capable of existence without excessive crowding of the substituents, the unsuccessful attempts at its preparation and experiments with scale models, suggest that there will be severe crowding of substituents in the four co-ordinate boron intermediate likely to be involved in its formation.

A further general route, namely that between an alkylideneaminosilane and an arylboron halide (Equation III.5) was employed as an alternative preparation of ${}^{t}Bu_2C{:}NBPh_2$.

$$R^1R^2C{:}NSiMe_3 + Ar_2BX \longrightarrow R^1R^2C{:}NBAr_2 + Me_3SiX \qquad \text{III.5}$$

This route, analogous to that used to prepare aminoboranes (Equation III.6)[161,162] has previously been employed to prepare monomeric and dimeric arylmethyleneaminoboranes and diarylmethyleneaminoboranes,[12,52,53] and, although requiring more forceful conditions (generally, a brief period of heating in toluene to ensure complete reaction) often has advantages over the route from alkylideneamino-lithium reagents (Equation III.1); in particular, associated species such as the dihalides $(R^1R^2C{:}NBX_2)_n$[12,52,140] ($X = F,Cl,Br,I$; $R^1 = H$, R^2 = aryl and $R^1 = R^2$ = aryl) are sparingly soluble in all common solvents and hence difficult to separate from the lithium chloride formed during the latter route.

$$nMe_3SiNR^1_2 + R^2_{3-n}BX_n \longrightarrow nMe_3SiX + (R^1_2N)_nBR^2_{3-n} \qquad \text{III.6}$$

A third general route, alkylation of an alkylideneaminoboron dihalide, was used to prepare ${}^{t}Bu_2C{:}NB{}^{n}Bu_2$ (Equation III.7)

$${}^{t}Bu_2C{:}NBCl_2 + 2{}^{n}BuLi \longrightarrow {}^{t}Bu_2C{:}NB{}^{n}Bu_2 + 2LiCl \qquad \text{III.7}$$

Collier and Lappert[158] have also prepared this compound from the reaction between $^{t}Bu_2C{:}NLi$ and $^{n}Bu_2BCl$ (Equation III.1; $R = {}^{n}Bu$, $n = 2$). Similar reactions employing organo-lithium reagents or organomagnesium halides have been used to prepare monomeric $Ph_2C{:}NBPh_2$[53] (from dimeric $Ph_2C{:}NBBr_2$ + 2PhLi), dimeric $Cl_2C{:}NB^{n}Bu_2$[149] (from dimeric $Cl_2C{:}NBCl_2$ + $2{}^{n}BuLi$) and dimeric $Cl_2C{:}NB^{n}BuCl$[149] (from dimeric $Cl_2C{:}NBCl_2$ + $^{n}BuMgCl$); aminoboranes of type $R^1{}_2NBR^2{}_2$ have also been prepared from reaction of $R^1{}_2NBX_2$ (X = halogen) with similar reagents.[162,163] Reaction (III.7) reveals the low susceptibility to reduction of the di-t-butylmethyleneamino group, in that, in reaction with $^{n}BuLi$, the chlorines of $^{t}Bu_2C{:}NBCl_2$ are replaced by n-butyl groups while the azomethine group remains unaffected.

In marked contrast, the reaction between $^{t}Bu_2C{:}NBCl_2$ and one molar equivalent of $^{t}BuLi$ did not give the expected product, di-t-butylmethyleneamino(t-butyl)chloroborane, $^{t}Bu_2C{:}NB^{t}BuCl$, but rather, di-t-butylmethyleneaminochloroborane, $^{t}Bu_2C{:}NBHCl$. (Equation III.8).

$$^{t}Bu_2C{:}NBCl_2 + {}^{t}BuLi \longrightarrow {}^{t}Bu_2C{:}NBHCl + LiCl + C_4H_8 \qquad \text{III.8}$$

This unexpected product was fully characterised by elemental analysis, including estimation of hydrolysable hydrogen content; its i.r. spectrum had a band at 2433 cm^{-1}, the region appropriate for a terminal B-H stretching frequency, ν(B-H). Elimination of butene <u>after</u> initial formation of $^{t}Bu_2C{:}NB^{t}BuCl$ seems unlikely as the reactants were not warmed above 18°, and a more likely mechanism may involve initial production of radicals (Equation III.9) such as those detected in reactions between alkyl halides and alkyllithiums.[164]

$$\begin{aligned} {}^{t}BuLi + {}^{t}Bu_2C{:}NBCl_2 &\longrightarrow {}^{t}Bu^{\bullet} + {}^{t}Bu_2C{:}NBCl^{\bullet} + LiCl \\ {}^{t}Bu\cdot &\longrightarrow H\cdot + C_4H_8 \qquad \text{III.9} \\ H\cdot + {}^{t}Bu_2C{:}NBCl\cdot &\longrightarrow {}^{t}Bu_2C{:}NBHCl \end{aligned}$$

Whatever the mechanism, it seem reasonable to assume that steric factors control the course of their reaction and to this effect it is interesting to note that t-butyl groups could not be introduced onto the boron atoms in $(Cl_2C{:}NBCl_2)_2$ by reaction with ^tBuLi or ^tBuMgCl (whereas one or both of the B-attached chlorine atoms could be replaced by n-butyl groups).[149] The reaction between $^tBu_2C{:}NBCl_2$ and two equivalents of ^tBuLi gave a complex mixture which could not be separated, extensive decomposition occurring on attempted distillation. The i.r. spectrum of the mixture showed two bands appropriate for $\nu(B\text{-}H)_{terminal}$ (at 2439 and 2326 cm^{-1}) and one appropriate for $\nu(C{=}N{\doteq}B)$ (at 1828 cm^{-1}). The mixture did not contain chlorine and it is possible that one of the products of this reaction was di-t-butylmethyleneaminoborane itself, $^tBu_2C{:}NBH_2$.

The fourth route used to prepare this series of di-t-butylmethyleneaminoboranes has its parallel in the preparation of dialkylaminoboranes Alk_2NBR_2 from dialkylamines, Alk_2NH, and trialkylboranes, R_3B.[162,165] Reaction between $^tBu_2C{:}NH$ and Et_3B at 96° gave the monomeric alkylideneaminoborane, $^tBu_2C{:}NBEt_2$ (Equation III.10).

$$^tBu_2C{:}NH + Et_3B \xrightarrow{96^\circ} {}^tBu_2C{:}NBEt_2 + EtH \qquad III.10$$

This represents the first successful use of such a route to an alkylideneamino<u>diethyl</u>borane; in an earlier study it was found that Et_3B reduced $Ph_2C{:}NH$ to $Ph_2C{:}NCHPh_2$, ethylene being the by-product.[87] The yield of $^tBu_2C{:}NBEt_2$ was almost quantitative after 17 hrs. heating in toluene, whereas $Ph_2C{:}NBMe_2$[87] is formed in only ca.15% yield on heating the adduct $Ph_2C{:}NH,BMe_3$ for a day at 160-200°.

State of Association and Probable Structures of the Di-t-butylmethyleneaminoboranes

All eight of the di-t-butylmethyleneaminoboranes, listed in Table III.1 together with their azomethine stretching frequencies, were monomeric (by cryoscopy) in benzene solution and (by mass spectroscopy) in the vapour. Of the known related diphenylmethyleneaminoboranes, $Ph_2C{:}NBXY$, also shown in Table III.1, together with their azomethine stretching frequencies, the compounds $(Ph_2C{:}NBCl_2)_2$[12,52,140] and $(Ph_2C{:}NBPhCl)_{\underline{n}}$[12,52,53] had been found to be associated, and $Ph_2C{:}NBPh_2$,[12,52,53] $Ph_2C{:}NBEt_2$[52] and $(Ph_2C{:}N)_2BPh$[12,52] monomeric. Earlier studies on a series of monomeric and dimeric arylmethyleneaminoboranes $R^1HC{:}NBXY$ and diarylmethyleneaminoboranes $R^1R^2C{:}NBXY$, indicated that the state of association depends on the bulk of the substituents R^1, R^2 and, especially, X and Y.[53] For example, $(PhCH{:}NBPh_2)_{\underline{n}}$ is dimeric, while $Ph_2C{:}NBPh_2$, $(p\text{-tolyl})_2C{:}NBPh_2$, $(p\text{-}ClC_6H_4)_2C{:}NBPh_2$ and $p\text{-}BrC_6H_4(Ph)C{:}NBPh_2$ are all monomeric; $(Ph_2C{:}NBPhCl)_{\underline{n}}$ is associated (probably $\underline{n} = 2$) while $Ph_2C{:}NBPh_2$ and $Ph_2C{:}NB(mesityl)_2$ are both monomeric; the fluorenylideneamino derivative $C_{12}H_8C{:}NBPh_2$ is monomeric, as is $Ph_2C{:}NBPh_2$, whereas when the phenyl substituents on boron are linked together, as in $(Ph_2C{:}NBC_{12}H_8)_{\underline{n}}$, this association ($\underline{n} = 2$) is apparently allowed. Previous to the preparation of such compounds, the only example of an imino-borane which was apparently monomeric in the condensed phase was $(Ph_2C{:}N)_3B$,[4,12,52,86] although some evidence for the existence of monomeric species at elevated temperatures had been obtained for the compounds $R^1C(SR^2){:}NBR^3_2$ [153] [apparently monomeric in hot CCl_4 solution, ν(C=N=B) at 1820 cm^{-1}], $Ph_2C{:}NBMe_2$[52,87] (apparently monomeric in the gas phase at ca.200°, by mass spectrometry) and $^tBuCH{:}NB^nBu_2$[141] [apparently monomeric in the vapour at ca.110°, ν(C=N=B) at ca.1840 cm^{-1}]. This situation was in contrast to that observed for the aminoboranes, $R^1R^2NBR^3R^4$,[166-168] where monomeric species (as well as dimers and higher oligomers) are very common. More recently, a series of highly halogenated alkylideneaminoboranes, prepared by the 1,2 addition of haloboranes to nitrile groups,[169] have been reported, and here also the degree of association seems explicable largely on steric grounds. Thus, while compounds $XYC{:}NBR^1R^2$[147-149] (X,Y = halogen; R^1,R^2 = halogen, Ph, ^nBu) are dimeric [ν(C:N) 1600-1655 cm^{-1}], compounds $Cl_3C{\cdot}(X)C{:}NBR^1R^2$[152,154] ($X,R^1$ = halogen; R^2 = halogen, Ph,Me) are essentially monomeric, the dimeric forms being minor equilibrium constituents in solution; significantly, the C-perfluoromethyl- and C-monohalomethyl-substituted derivatives, $F_3C{\cdot}(X)C{:}NBR^1R^2$[146] ($X,R^1,R^2$ = halogen) and $YH_2C{\cdot}(X)C{:}NBR^1R^2$[155] ($X,Y$ = halogen; R^1,R^2 = halogen, Me), are purely dimeric. A series of carbon sulphur-substituted alkylideneaminoboranes, $X{\cdot}(RS)C{:}NB(SR)_2$ have also been prepared, either by thioboration of nitriles and of thiocyanates[150,156] or by reaction of C-halogenated alkylideneaminoboranes with alkylthiols,[156,170] and here again the bulk of the substituent X seems to determine the degree of association; thus when X = FCH_2,[150,156] the compounds are dimeric, when X = Cl_3C, MeS or ^iPrS,[150,170] they are monomeric.

Clearly, the t-butyl groups in the derivatives $^tBu_2C{:}NBXY$ are extremely good at preventing association and do so irrespective of the sizes of the groups X and Y on boron. Experiments with scale models suggest that there would be extreme steric interference between the methyl groups of the t-butyl groups with the groups X and Y on the bridging boron atoms in a dimeric structure typified by that found for $(MeCH{:}NBMe_2)_2$.[151] (Figure III.1.a).

The di-t-butylmethyleneaminoboranes were also apparently monomeric in their condensed phase. The high values of the azomethine stretching frequencies of the six mono(alkylideneamino)boranes with ν(C:N) 1818-1845 cm^{-1} (Table III.1) (cf. ν(C:N) in parent $^tBu_2C{:}NH$ at 1610 cm^{-1}) are consistent with these absorptions being attributable to the unsymmetrical stretching vibrations, $\nu(C{=}N{\doteq}B)$, of a linear $C{=}N{\doteq}B$ skeleton (Figure III.1.f) by comparison with the values of bands in other apparently monomeric alkylideneaminoboranes [$\nu(C{=}N{\doteq}B)$ at 1760-1850 cm^{-1}, see Table III.1][12,52,53,87,141,150-154,170] and in other cumulative π-systems [ν(X=Y=Z) at ca.1845-2140 cm^{-1}, see Table I.3, p.20]. Such a linear skeleton would imply considerable N ⟶ B (p ⟶ p) π-bonding within the molecule. The slightly lower frequencies of the corresponding absorptions of the crystalline bis(alkylideneamino)boranes (ca.1775 cm^{-1}, see Table III.1) are also appropriate for linear C=N≐B groups, but with, understandably, somewhat lower N≐B bond order as the two dative π-bonds use the same boron acceptor p-orbital. The much lower azomethine stretching frequency observed for $(Ph_2C{:}N)_2BPh$[12,52] (at 1672 cm^{-1}) has been interpreted in terms of a bent C:NB unit in this molecule.

The first X-ray crystallographic study of a monomeric alkylideneaminoborane has recently been carried out.[159] Diphenylmethyleneaminodimesitylborane, $Ph_2C{:}NB(mesityl)_2$,[12,52,53] prepared from $Ph_2C{:}NLi$ and $mesityl_2BF$, was recrystallised from a hexane-toluene mixture.

The geometry of central part of the molecule, shown in Figures III.2.a and III.2.b., closely resembles that of an allene (see also Figure III.1.d) in the following respects:

(i) the B-N-C link is very nearly linear (BNC = 170°)

(ii) the B-N (1·40Å) and N-C (1·31Å) distances are both short, and

(iii) the C(1)-C(2)-C(3) and B-C(4)-C(5) planes are almost perpendicular (angle between planes 87°)

Although the e.s.d.'s of the bond lengths and angles are at present fairly large, and further refinement of the structure is continuing, several important conclusions may still be drawn. These features clearly confirm that there is π-bonding between the boron and nitrogen atoms producing a linear C=N≐B system, and, at the same time, provide ample justification for the view that a high value of the azomethine stretching frequency in the i.r. spectra of monomeric alkylideneaminoboranes is indicative of such a linear framework and hence of appreciable N ⟶ B (p ⟶ p) π-bonding. [ν(C=N≐B) in $Ph_2C{:}NB(mesityl)_2$ was assigned at 1792 cm^{-1}].[12,52,53] The slight deviation of the B-N-C angle from

180° results from atom C(1) lying 0·23Å out of the plane N-B-C(4)-C(5). The benzene rings are not coplanar with the neighbouring C(1)-C(2)-C(3) or B-C(4)-C(5) planes, but are rotated through angles ranging from 29° to 64°. By this means, steric interference between methyl groups or hydrogen atoms attached to the rings is avoided.

The CN bond length (1·31Å) is fairly typical for a double bond, predicted by Pauling[171] to have a length of 1·29-1·31Å (cf. single CN bond length of ca. 1·47Å), and can be compared with CN bond lengths in a series of oximes[15-18] (1·25-1·29Å), in $(MeCH{:}NBMe_2)_2$[151] (1·27Å), in $(^tBuMeC{:}NAlMe_2)_2$[151] (1·27Å) and $[C_6H_4Br.(Ph)C{:}NAlPh_2]_2$[172] (1·28Å), and in $(Me_2C{:}NMe_2)^+$ [173] (1·30Å).

The numerous structural determinations over the past few years, employing both X-ray and electron diffraction techniques, on Boron-Nitrogen compounds have recently been reviewed by Hess.[174] Compounds containing tetravalent boron and nitrogen, such as borazanes, cycloborazanes and amine-boronium salts, usually exhibit only slight variation in BN bond lengths, the mean value being 1·58Å[175-187] (cf. the sum of the B and N covalent radii is 1·58Å, whereas a BN double bond is expected to have a length of ca. 1·35Å),[171] exceptions only occurring when the BN bond is seriously weakened by steric or electronic effects. Some typical BN bond lengths for such compounds are given in Table III.2. When both boron and nitrogen are in trigonal co-ordination, as in monomeric aminoboranes and borazines, much larger variations in BN bond lengths are found, in agreement with the predicted varying π-bonding component in such bonds. The extent of N → B (p → p) π-bonding in aminoboranes has been extensively studied by, for example, force constant calculations (from vibrational spectra), estimation of rotation barriers about the multiple BN bond (from ^1H and ^{11}B n.m.r. spectra), ionisation potentials and fragmentation patterns (from mass spectra) and numerous S.C.F. and L.C.A.O.-M.O. calculations.[188] Such results have been verified by structural studies;[189-200] thus the BN bonds are found to be shortest in monoaminoboranes and somewhat longer in compounds where two

TABLE III.2

Boron-Nitrogen bond lengths in some compounds containing four co-ordinate boron and nitrogen

Compound	B-N bond length (Å)	Reference
Borazanes		
Me_3N,BF_3	1·636* 1·585	175 176
Me_3N,BCl_3	1·610 1·575	175 177
Me_3N,BH_3	1·65*	178
Me_3N,BBr_3	1·603	179
Me_3N,BI_3	1·584	179
MeH_2,BF_3	1·58	180
H_3N,BF_3	1·60	181
Aziridine Borane, $(CH_2)_2NH,BH_3$	1·558	182
Hexamethylenetetramine-Borine	1·661	183
Cycloborazanes		
$(Me_2NBCl_2)_2$	1·591	184
$(Me_2NBF_2)_2$	1·601	185
$(Et_2NBF_2)_2$	1·638	186
Amine-Boronium Salts		
(4-methylpyridine)$(Me_3N)BBrH^+PF_6^-$	1·579 av.	187
Alkylideneaminoboranes		
$(MeCH{:}NBMe_2)_2$	1·59	151

* from Microwave spectrum; other structures by X-ray crystallographic methods.

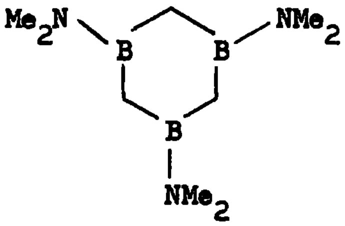
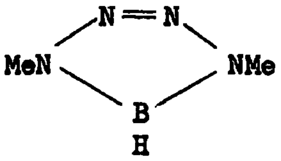
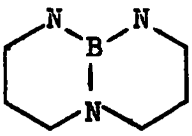
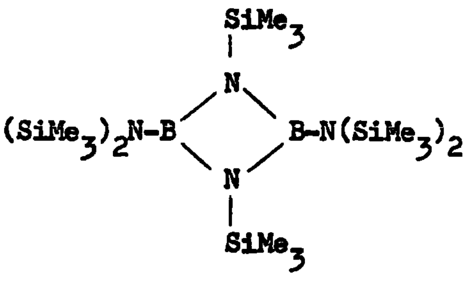
or three nitrogens are bonded to one boron atom, and vice-versa (Table III.3). Clearly the BN bond length in $Ph_2C{:}NB(mesityl)_2$ (1·40Å) indicates a π-BN bond order comparable to that found in aminoboranes and borazines, but, although π-multiple bonding in these latter compounds has long been known to lead to a trigonal planar environment for the nitrogen atoms, the structure of $Ph_2C{:}NB(mesityl)_2$ provides the first demonstration of a linear environment analogous to allene. The di-t-butylmethyleneaminoboranes, having their azomethine stretching frequencies some 170-240 cm^{-1} higher than ν(C:N) in the parent di-t-butylmethyleneamine, are thought to have analogous structures (Figure III.1.f).

The use of ^{11}B n.m.r. to establish the state of aggregation of organic boron compounds is well-established[201] and has been employed to distinguish the monomeric form of $^tBuCH{:}NB^nBu_2$[141] (chemical shift -38.8 ± 0.5 p.p.m. relative to $BF_3.OEt_2$) from its dimer (chemical shift -7.4 ± 0.4 p.p.m. on the same scale). The dimer, with four co-ordinate boron, has the boron atoms more magnetically shielded and hence the signal is at higher field. Collier and Lappert[158] have recorded the ^{11}B n.m.r. spectra of three of the derivatives $^tBu_2C{:}NBXY$ (X = Y = Ph, ^nBu, Cl) and found these data (chemical shifts in the range ca. -28 to -36 p.p.m. relative to $BF_3.OEt_2$) to be consistent with the formulation of the di-t-butylmethyleneaminoboranes as monomers. Clearly, in these three compounds the boron atom is more shielded than in the monomeric $^tBuCH{:}NB^nBu_2$ or in the related amido compounds Me_2NBXY[201] (X = Y = Ph, ^nBu, Cl; chemical shifts in the range ca. -31 to -46). These observations reflect the decreasing electron release in the series $^tBu_2C{:}N- > {}^tBuCH{:}N- > Me_2N-$, when these ligands are attached to boron.

The ^1H n.m.r. spectra of the di-t-butylmethyleneaminoboranes were all consistent with linearity of the C:NB skeletons.[28,29] Spectra were recorded using ca.20 wt.% toluene solutions at +33° and at temperatures down to -80°. Details of the +33° spectra are given in Table III.4. In all cases, the

TABLE III.3

Boron-nitrogen bond lengths in some compounds containing three-co-ordinate boron and nitrogen

Compound	B-N bond length (Å)	Ref.
$Me_2N.BMe_2$	1·42	189
$Me_2N.BCl_2$	1·38*	190
	1·40	191
$(SiH_3)_2NBF_2$	$1{\cdot}49_6$*	192
	$1{\cdot}41_3$*	193
$B_3H_3N_3H_3$	$1{\cdot}43_5$*	194
$(Me_2N)_3B$	$1{\cdot}43_1$*	195
	$1{\cdot}42_1$	196
$(o\text{-}C_6H_4O_2B)_3N$	$1{\cdot}43_8$	197
	$1{\cdot}44_1$ (exocyclic) $1{\cdot}45_4$ (ring)	198

contd./

TABLE III.3 contd.

Compound	B-N bond length (Å)	Ref.
$(H_2N)B_3H_2N_3H_3$	$1{\cdot}49_8$ (exocyclic)* $1{\cdot}41_8$ (ring)	199
$(Me_2N)_3B_3N_3H_3$	$1{\cdot}42_9$ (exocyclic) $1{\cdot}43_1$ (ring)	200

* by electron diffraction; other structures by X-ray crystallographic methods.

TABLE III.4

^{1}H n.m.r. spectroscopic results for the di-t-butylmethyleneaminoboranes (ca. 20 wt.% solutions in toluene at +33°)

Compound	τ Values	
$^{t}\mathrm{Bu_2C{:}NBHCl}^{*}$		8·95s
$^{t}\mathrm{Bu_2C{:}NBCl_2}$		8·92s
$^{t}\mathrm{Bu_2C{:}NBPhCl}$	2·24c(2), 2·74c(3)	8·89s(18)
$^{t}\mathrm{Bu_2C{:}NBPh_2}$	2·31c(4), 2·75c(6)	8·86s(18)
$^{t}\mathrm{Bu_2C{:}NB}^{n}\mathrm{Bu_2}$	8·4–9·2c	8·85s
$^{t}\mathrm{Bu_2C{:}NBEt_2}$	9·78c(4), 9·04c(6)	8·89s(18)
$(^{t}\mathrm{Bu_2C{:}N})_2\mathrm{BCl}$		8·80s
$(^{t}\mathrm{Bu_2C{:}N})_2\mathrm{BPh}$	2·69c(1)	8·73s(7)

* Boron-attached proton not observed

$\tau(\mathrm{Me_4Si})$ = 10·00 p.p.m.; s = single, c = complex; relative intensities in parentheses t-butyl absorption was a sharp singlet which did not change significantly in shape or chemical shift when the solutions were cooled. In contrast, the spectrum of di-t-butylmethyleneamine, ${}^{t}Bu_2C{:}NH$ (Figure III.1.e) in toluene, whilst having only a single absorption attributable to the t-butyl groups at $+33^\circ$ (presumably due to rapid exchange of positions between the N-attached hydrogen and the lone pair on nitrogen) has two peaks of equal intensity at -60° at 8.73 and 8.90τ (see Table I.1, p.11) as inversion at nitrogen is then sufficiently slow for the t-butyl groups to be seen to be magnetically inequivalent.[26] The chemical shift difference of 0.17 p.p.m. between the types of proton, which are four bonds distant from the azomethine nitrogen, may be compared with a separation of 0.16-0.37 p.p.m. for the two types of methyl proton in isopropylideneamines, $Me_2C{:}NR$[23,24] and of 0.42 p.p.m. for the methylene protons of $H_2C{:}NMe$,[202] at temperatures well above room temperature in the case of the N-alkylated or -arylated compounds. The sensitivity of the hydrogen resonance to syn-anti isomerism (see Chapter I, p.6) decreases progressively as the number of bonds separating the hydrogens from the azomethine nitrogen increases, but is still large enough for compounds ${}^{t}Bu_2C{:}NBXY$ to be expected, if bent at nitrogen (Figure III.1.g), to give rise to two readily distinguishable resonances at temperatures low enough for inversion at nitrogen to be slow. The ${}^{1}H$ n.m.r. spectra of the di-t-butylmethyleneaminoboranes thus indicate either that their structures involve linear C:NB units (Figure III.1f) or that bent C:NB skeletons invert at nitrogen with a rapidity at -60° implying a very low activation energy for this process.

The mass spectra of all eight alkylideneaminoboranes were recorded. Except for the peaks of m/e 142 and 141 (assigned as ${}^{t}Bu_2C{:}NH_2$ and ${}^{t}Bu_2CNH$, respectively), the same fragments as were found in the mass spectrum of ${}^{t}Bu_2C{:}NH$ (see Table I.2, p.12) were present in all the spectra; there were certain other common features. In all cases a feeble monomeric parent peak was observed as the fragment with the highest m/e value. Initial fragmentation invariably involved loss of a butyl group as the source of the most abundant high mass ions, and butyl cations were invariably the most abundant fragments. Alkyl groups on boron tended to lose alkene to form B-H residues, but the t-butyls of the alkylideneamino group much less readily eliminated butene to leave C-H residues. Some of these common features are illustrated in the Tables III.5-8, relating to the mass spectra of the compounds $^{t}Bu_2C{:}NBCl_2$ (Table III.5), $^{t}Bu_2C{:}NBEt_2$ (Table III.6), $^{t}Bu_2C{:}NBPh_2$ (Table III.7) and $(^{t}Bu_2C{:}N)_2BCl$ (Table III.8).

TABLE III.5

Boron-containing fragments in the mass spectrum of $^{t}Bu_2C:NBCl_2$

m/e	Relative Intensity	Assignment
221	0.3	Bu_2CNBCl_2
186	0.7	Bu_2CNBCl
164	62	$BuCNBCl_2$
149	0.6	$Me_2C.CNBCl_2$
79	14	Me_2CCNB

TABLE III.6

Boron-containing fragments in the mass spectrum of $^{t}Bu_2C:NBEt_2$

m/e	Relative Intensity	Assignment
209	0.1	Bu_2CNBEt_2
194	0.3	$Bu_2CNBEt(CH_2)$
180	2	Bu_2CNBEt
152	42	$BuCNBEt_2$
124	40	$BuCNBHEt$
96	32	$BuCNBH_2$
69	32	Et_2B

TABLE III.7

Boron-containing fragments in the mass spectrum of $^{t}Bu_2C:NBPh_2$

m/e	Relative Intensity	Assignment
305	0·5	Bu_2CNBPh_2
248	24	$BuCNBPh_2$
228	5·4	Bu_2CNBPh
172	5·4	BuCHNBPh
165	8	Ph_2B
115	8	HCNBPh
95	6·7	BuCNBH

TABLE III.8

Boron-containing fragments in the mass spectrum of $(^{t}Bu_2C:N)_2BCl$

m/e	Relative Intensity	Assignment
328	0·1	$(Bu_2CN)_2BCl$
291	4	$(Bu_2CN)_2B$
269	24	$Bu_2CN(BuCN)B$
186	2	Bu_2CNBCl
152	2	Bu_2CNBH
130	12	BuCHNBCl

For all four spectra

m/e values for fragments containing chlorine relate to ^{35}Cl isotopes, and for fragments containing boron to ^{11}B isotopes.

CHAPTER IV

This chapter describes the preparation of dimeric di-t-butylmethyleneamino-aluminium dichloride, $(^{t}Bu_2C{:}NAlCl_2)_2$, monomeric tris(di-t-butylmethylamino)-aluminium, $(^{t}Bu_2C{:}N)_3Al$, and lithium tetrakis(di-t-butylmethyleneamino)aluminate, $LiAl(N{:}C^{t}Bu_2)_4$. Aspects of their i.r. and ^1H n.m.r. spectra are discussed, together with the results of a recent X-ray crystallographic study on one of the compounds, $LiAl(N{:}C^{t}Bu_2)_4$.

EXPERIMENTAL SECTION

Starting Materials

t-Butyl cyanide was distilled from phosphorus pentoxide under dry nitrogen before use. t-Butyl-lithium solution was standardised by titration with sec-butanol.[1] Di-t-butylmethyleneaminolithium was usually prepared in situ as required by adding t-butyl-lithium in pentane to t-butylcyanide in a variety of solvents (see p.1). Aluminium chloride was purified by sublimation at low pressure.

Manipulations were generally carried out under dry nitrogen.

Reaction of Aluminium Trichloride with Di-t-butylmethyleneaminolithium.[26]

A slurry of aluminium trichloride (1.34 gm., 10 mmole) in ether was added by syringe to a solution of di-t-butylmethyleneaminolithium (1.47 gm., 10 mmole) in diethyl ether (25 ml.) at -196°. When the solution was warmed, it remained clear until ca.0° when a copious white precipitate separated. This was collected, extracted with a toluene-petroleum ether solvent mixture, and after crystallisation identified as di-t-butylmethyleneaminoaluminium dichloride dimer, $(^{t}Bu_2C{:}NAlCl_2)_2$, m.p. 124-126°. (Found: C,44.7; H,7.8; Al, 11.4; Cl, 30.3; N,5.8%; M,493. $C_{18}H_{36}Al_2Cl_4N_2$ requires C,45.2; H,7.5; Al,11.3; Cl,29.8; N,5.9%; M,476), ν_{max} (Nujol mull) 1664ms, 1546s,sh, 1538s, Nujol, 1372s, 1348ms,sh, 1259w, 1215ms, 1200m,sh, 1163w,sh, 1157m, 1055ms,sh, 1049s, 1034ms,sh 975s, 971s, 936m, 932m, 909m, 876m, 840m, 813m,br, 798ms, 762m, 707vs,br, 667ms, 641vs,br, 617ms, 575s, 546vs and 516s cm^{-1}.

Reaction of Aluminium Trichloride with Di-t-butylmethyleneaminolithium (3 molar equivalents)[26,30]

A solution of di-t-butylmethyleneaminolithium (4.41 gm., 30 mmole) in ether (20 ml.) was added to a solution of aluminium trichloride (1.34 gm., 10 mmole) in ether (15 ml.) at -196°. On warming to room temperature, a white solid deposited, leaving a clear yellow solution which left a yellow solid on evaporation of the solvent. Extraction of the residue with warm pentane afforded deep yellow crystals of tris(di-t-butylmethyleneamino)aluminium, $(^{t}Bu_2C{:}N)_3Al$, m.p. 194-195°. (Found: C,71.6; H,11.2; Al,5.9; N,9.1%; M,469. $C_{27}H_{54}AlN_3$ requires C,72.4; H,12.1; Al,6.1; N,9.4%; M,447); ν_{max} (Nujol mull) 1704s,sh, 1690vs, 1642m,sh, Nujol, 1361s, 1325w,sh, 1212ms,br, 1035ms, 996m,sh, 943m,sh, 941m, 930m,sh, 885m, 877m,sh, 853w, 790w,sh, 774ms, 754m, 725w,br, 764w, 595w, 573w, 540w, 476m, 408m and 357m cm^{-1}.

The crystals were extremely moisture-sensitive, giving a white powder immediately on exposure to the atmosphere. Qualitative analysis for lithium and chloride proved negative.

Reaction of Aluminium Trichloride with Di-t-butylmethyleneaminolithium (2 molar equivalents)[26]

A solution of aluminium trichloride (1.52 gm., 11.4 mmole) in ether (20 ml.) was treated with a cooled (-196°) solution of di-t-butylmethyleneaminolithium (3.35 gm., 22.8 mmole) in ether (20 ml.). On warming to room temperature, a white precipitate formed, leaving a pale yellow solution. The ether was pumped off and the residue was extracted with pentane at 35-40°. Some off-white solid separated when the pentane cooled, or upon addition of light-petroleum ether. The i.r. spectrum of this solid showed it to be the dimer, di-t-butylmethyleneaminoaluminium dichloride, $(^{t}Bu_2C{:}NAlCl_2)_2$. A yellow compound remained which, after removal of solvent and recrystallisation from pentane, was identified by its i.r. spectrum and its melting point as tris(di-t-butylmethyleneamino)aluminium, $(^{t}Bu_2C{:}N)_3Al$.

Reaction of Aluminium Trichloride with Di-t-butylmethyleneaminolithium (4 or more molar equivalents)[47b]

An ethereal solution of aluminium trichloride (1.29 gm., 9.6 mmole) was added by syringe to a cold (-196°) solution of di-t-butylmethyleneaminolithium (5.73 gm., 39 mmole) in hexane (40 ml.). On warming, a white precipitate formed, leaving a pale yellow solution. After removal of solvent by pumping, the yellow residue was extracted with hot toluene and the resulting solution filtered. Cooling of the solution afforded pale-yellow transluscent crystals of lithium tetrakis(di-t-butylmethyleneamino)aluminate, $LiAl(N:C^{t}Bu_2)_4$, decomposition temperature 294-298°. (Found: C,71.3; H,11.9; Al,4.7; Li,1.1; N,9.7%; M,588. $C_{36}H_{72}AlLiN_4$ requires C,72.8; H,12.1; Al,4.5; Li,1.2; N,9.4%; M,594); ν_{max} (Nujol mull), 1870vw, 1700vs, 1642vs, 1602m, 1380vs, 1367vs,sh, 1358vs, 1338m, 1260m, 1219ms, 1203ms, 1036ms, 1019ms, 954ms, 936ms, 925ms,sh 886w, 847m, 792m, 768ms, 762m, 703ms, 600m, 570ms, 540w, 477ms, 454ms and 415ms cm^{-1}.

The crystals were moderately moisture-sensitive, giving a white powder after a few seconds exposure to the atmosphere.

DISCUSSION

Alkylideneamino derivatives of aluminium, $(R^1R^2C{:}NAlR^3R^4)_n$, (R^1 = alkyl, aryl, R_2N; R^2 = alkyl, aryl, H, R_2N; R^3,R^4 = alkyl, aryl, halogen) have previously been prepared by two general methods, the most important of which is the insertion reaction between cyanides R^1CN and organoaluminium compounds, $R^2R^3R^4Al$ (Equation IV.1).

$$\begin{tikzcd}
R^1C{:}N + R^2R^3R^4Al \arrow[r] & R^1C{:}N{,}AlR^2R^3R^4 \arrow[d, "\text{heat}"] \\
& \frac{1}{n}(R^1R^2C{:}NAlR^3R^4)_n
\end{tikzcd}$$

IV.1

The products of such reactions depend critically on the type of nitrile and organoaluminium reagent used. When R^2 = H[7c,114-116] or Et[114-116,203,204] aldimino derivatives, $(R^1CH{:}NAlR^3R^4)_n$ are formed, $EtAlR^3R^4$ acting as a source of $HAlR^3R^4$; aluminium hydride itself has been found to give polymeric species on reaction with acetonitrile.[205] When R^2 is an aryl group or an alkyl group (other than ethyl) or an amino group, then insertion occurs smoothly to produce alkylideneamino derivatives, $(R^1R^2C{:}NAlR^3R^4)_n$ (R^1 = Ph, ^{t}Bu; R^2 = Me, Ph[114,115] and R_2N)[206,207] except when R^1 of R^1CN has α-carbon-attached hydrogens. In such cases (R^1 = Me,Et),[114,115,203,204,208-210] the main products are polymeric materials formed by cleavage of organic groups from aluminium (Equation IV.2).

$$\begin{tikzcd}
RCH_2C{:}N + AlR^2R^3R^4 \arrow[r] & RCH_2CN{,}AlR^2R^3R^4 \arrow[dl] \arrow[dr] & \\
\frac{1}{n}(RCH{:}C{:}NAlR^3R^4)_n + R^2H & & \frac{1}{n}[RCH(AlR^3R^4)CN]_n + R^2H
\end{tikzcd}$$

IV.2

The reaction leading to formation of C-Al bonds is analogous to the reaction between nitriles of type $RCH_2C{:}N$ (R = H,Me) and alkyl-lithium reagents, R'Li (R' = Me, Et,[4] ^{t}Bu[37]) (Equations IV.3 and IV.4).

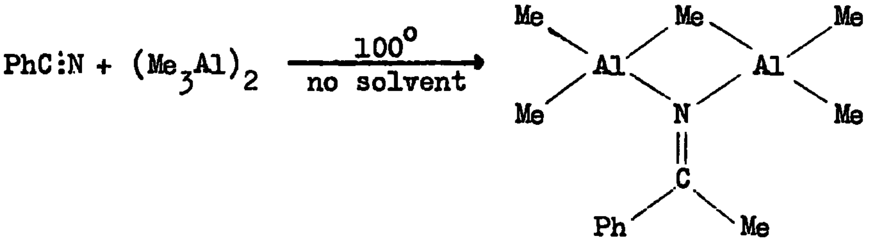
$$RCH_2C{:}N + R'Li \longrightarrow \frac{1}{n}[RCH(Li)CN]_n + R'H \qquad \text{IV.3}$$

$$R = H,Me$$

$$R' = Me,Et$$

$$CH_3C{:}N + 2\,{}^{t}BuLi \xrightarrow[-78^{\circ}]{ether} \frac{1}{n}[HC(Li)_2CN]_n + 2\,{}^{i}BuH \qquad \text{IV.4}$$

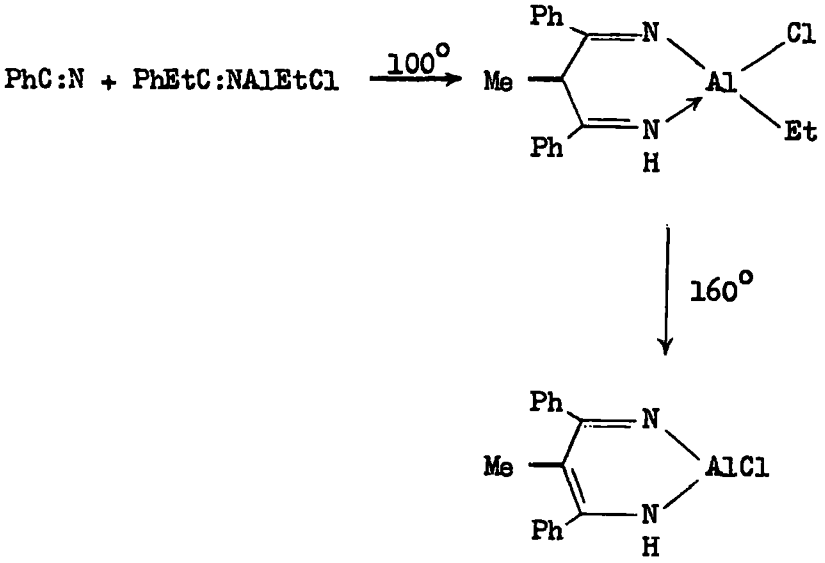
As well as the nature of the reactants, reaction conditions and the stoichiometric proportions used can also determine the reaction products. Thus, when benzonitrile and two equivalents of trimethylaluminium are heated together at 100° in the absence of solvent, the product is not $(PhMeC{:}NAlMe_2)_n$ but rather $Me_2Al.N{:}CPhMe.Me.AlMe_2$[211] (Equation IV.5); such a reaction is analogous to that between trialkyl-aluminium and aldehydes or ketones, giving "hemialkoxides".[211-213]



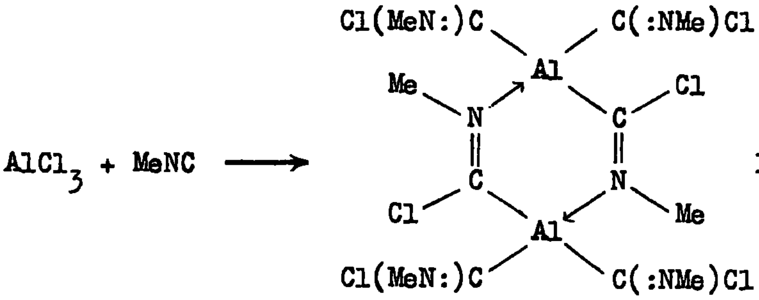
IV.5

Further, derivatives $(R^1R^2C{:}NAlR^3R^4)_n$, prepared from R^1CN and $R^2R^3R^4Al$ (where R^2 contains α-C-attached hydrogens; R^3,R^4 = Et,Cl), react with a further equivalent of cyanide to give cyclic derivatives[214,215] (Equation IV.6).

Finally, isocyanides react with aluminium compounds to give cyclic products with $(AlCN)_2$ ring structures[216] (Equation IV.7).



IV.6



IV.7

The second route to alkylideneamino-aluminium derivatives is the reaction between alkylideneamines and trialkyl- or triaryl-aluminiums[33,88,90] (Equation IV.8).

$$\begin{tikzcd} R_2C{:}NH + \tfrac{1}{2}(R'_3Al)_2 \arrow[r] & R_2C{:}NH,AlR'_3 \arrow[d, "\text{heat}"] \\ & \tfrac{1}{n}(R_2C{:}NAlR'_2)_n + R'H \end{tikzcd}$$

IV.8

$R = Ph,^{88}\ Me_2N,^{33}\ {}^tBu^{90}$

$R' = Me,^{33,88,90}\ Et,^{33,88}\ Ph,^{33}\ {}^iBu^{90}$

$Ph_2C{:}NH$ reacts with R'_3Al (R' = Me,Et,Ph), alkane or benzene being eliminated below 100°, giving crystalline derivatives, $(Ph_2C{:}NAlR'_2)_n$,[88] in marked contrast to its reaction with the corresponding boranes.[87] Similarly, $(Me_2N)_2C{:}NH$ adducts of R'_3Al (R' = Me,Et) lose alkane when heated to give the $[(Me_2N)_2C{:}NAlR'_2]_n$ derivatives[33] (see Chapter V). Recent work has shown that thermal decomposition of the adducts $^tBu_2C{:}NH,AlR'_3$ (R' = Me, ^iBu) similarly gives compounds $(^tBu_2C{:}NAlR'_2)_n$.[90] Such elimination reactions are analogous to those used to prepare aminoalanes from secondary amines and aluminium hydride[217,218] (Equation IV.9), and from amines or ammonia and compounds of type R_nAlX_{3-n}[219,220] (e.g. Equations IV.10 and IV.11).

$$AlH_3,NR_2H \xrightarrow{-H_2} (H_2AlNR_2)_n \xrightarrow[R_2NH]{-H_2} HAl(NR_2)_2 \xrightarrow[R_2NH]{-H_2} Al(NR_2)_3 \qquad IV.9$$

$$EtAlCl_2,NH_3 \xrightarrow{-EtH} (Cl_2AlNH_2)_n \qquad IV.10$$

$$Ph_3Al,NPhH_2 \xrightarrow{-PhH} (Ph_2AlNHPh)_2 \xrightarrow{-PhH} (PhAlNPh)_4 \qquad IV.11$$

All the alkylideneaminoälanes $(R^1R^2C{:}NAlR^3R^4)_n$, previously prepared as described above, are thought to be dimeric (n = 2) in solution (by cryoscopy, where solubility permits), in the vapour (by mass spectrometry) and in the condensed phase (by i.r. spectroscopy). Four-membered $(AlN)_2$ ring structures (Figure IV.1.a) have been proposed for these dimeric species and, indeed, have been confirmed by X-ray crystallography for the compounds $[^tBuC(Me){:}NAlMe_2]_2$[151] (Figure IV.1.b) and $[p\text{-}BrC_6H_4.C(Ph){:}NAlPh_2]_2$[172] (Figure IV.1.c).

This chapter describes a further route to alkylideneaminoalanes, from aluminium chloride and di-t-butylmethyleneaminolithium, $^tBu_2C{:}NLi$, which has been used to prepare the dimeric di-t-butylmethyleneaminoaluminium dichloride,

$(^{t}Bu_2C{:}NAlCl_2)_2$,[26,29,30] (Equation IV.12), monomeric tris(di-t-butylmethyleneamino)aluminium, $(^{t}Bu_2C{:}N)_3Al$,[26,29,30] (Equation IV.13), and lithium tetrakis-(di-t-butylmethyleneamino)aluminate, $LiAl(N{:}C^{t}Bu_2)_4$,[47b] (Equation IV.14). The crystal structure[47a,b] of this last compound shows some very unusual features which will be discussed later in this chapter.

$$AlCl_3 + {}^{t}Bu_2C{:}NLi \longrightarrow \tfrac{1}{2}(^{t}Bu_2C{:}NAlCl_2)_2 + LiCl \qquad \text{IV.12}$$

$$AlCl_3 + 3\,{}^{t}Bu_2C{:}NLi \longrightarrow (^{t}Bu_2C{:}N)_3Al + 3LiCl \qquad \text{IV.13}$$

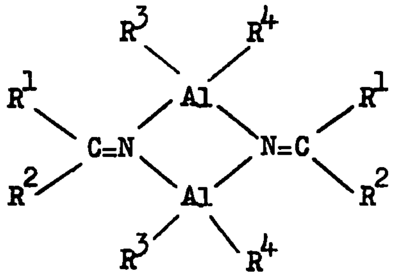
$$AlCl_3 + 4\,{}^{t}Bu_2C{:}NLi \longrightarrow LiAl(N{:}C^{t}Bu_2)_4 + 3LiCl \qquad \text{IV.14}$$

A similar route, the reaction between aluminium halides and $Ph_2C{:}NLi$, had previously been employed to prepare the diphenylmethyleneaminoaluminium compounds $(Ph_2C{:}NAlCl_2)_2$,[26] $(Ph_2C{:}NAlBr_2)_n$,[26] and $(Ph_2C{:}N)_3Al$;[26,30] the dihalides were also prepared from aluminium halides and the alkylideneaminosilane, $Ph_2C{:}NSiMe_3$ (Equation IV.15).

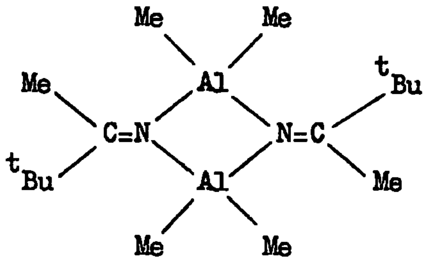
$$AlX_3 + Ph_2C{:}NSiMe_3 \longrightarrow \tfrac{1}{n}(Ph_2C{:}NAlX_2)_n + Me_3SiX \qquad \text{IV.15}$$

The preparation of $[(Me_2N)_2C{:}NAlCl_2]_n$[33] from bis(dimethylamino)methyleneaminolithium, $(Me_2N)_2C{:}NLi$, and aluminium chloride is described in Chapter V of this thesis.

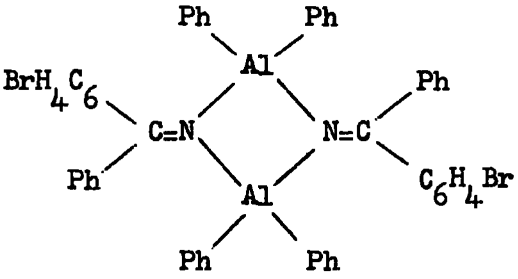
FIGURE IV.1



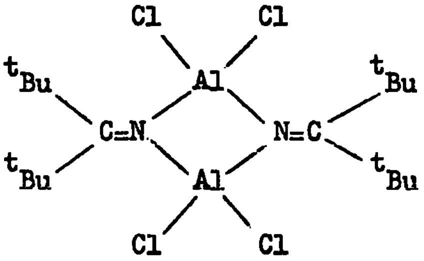
(a)



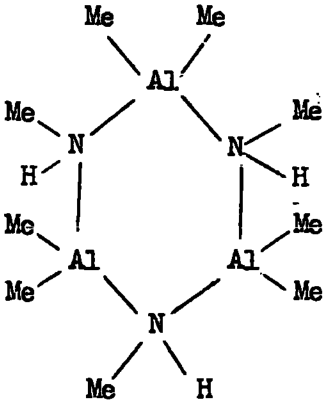
(b)



(c)



(d)



(e)

Di-t-butylmethyleneaminoaluminium dichloride, $(^tBu_2C{:}NAlCl_2)_2$

An equimolar mixture of aluminium trichloride and di-t-butylmethyleneaminolithium reacted in ethereal solution below 0° to precipitate a mixture of LiCl and $(^tBu_2C{:}NAlCl_2)_2$[26] (Equation IV.12), from which the latter could readily be extracted as an off-white crystalline solid with a hot toluene-petroleum ether mixture. The compound was found to be dimeric in benzene (by cryoscopy), although its mass spectrum contained only organic fragments arising from its thermal decomposition. Its i.r. spectrum had a strong, readily identified band at 1664 cm^{-1} (see Table IV.1), assigned as the azomethine stretching frequency, $\nu(C{:}N)$ of a bridging azomethine group; the azomethine stretching frequencies for monomeric derivatives $^tBu_2C{:}NBXY$ (see Chapter III) and $^tBu_2C{:}NSiR_nCl_{3-n}$ (see Chapter VI), which clearly contain terminal $^tBu_2C{:}N$-groups, are in the region 1820-1845 cm^{-1} and 1730-1740 cm^{-1}, respectively, some 130-230 cm^{-1} higher than $\nu(C{:}N)$ in the parent ketimine, $^tBu_2C{:}NH$ [$\nu(C{:}N)$ at 1608 cm^{-1}, see Chapter I]. All other derivatives $[R^1R^2C{:}NAlR^3R^4]_2$ hitherto prepared have $\nu(C{:}N)$ in the range 1590-1675 cm^{-1}; for example $(Ph_2C{:}NAlCl_2)_2$ has $\nu(C{:}N)$ at 1593 cm^{-1} [26] while $(^tBuCMe{:}NAlMe_2)_2$, for which crystallographic studies have confirmed a $(AlN)_2$ ring structure[151] (Figure IV.1.b), has $\nu(C{:}N)$ at 1630 cm^{-1}.[115] On this basis, an analogous structure (Figure IV.1.d) is proposed for $(^tBu_2C{:}NAlCl_2)_2$. Similar $(AlN)_2$ ring structures have also been proposed for the dimeric aminoalanes $(^iPr_2NAlH_2)_2$, $(Me_2NAlCl_2)_2$, $[(Me_2N)_2AlH]_2$, $[(Me_2N)_2AlCl]_2$ and $[(Me_2N)_3Al]_2$[217,218] (although increasing the size of the group on nitrogen results in monomeric species) and in numerous aminogallanes.[221,222] A trimeric structure for $(^tBu_2C{:}NAlCl_2)_n$ $(n = 3)$, as found in related azide systems $(R_2AlN_3)_3$[223] and in some aminoalanes such as certain $(R_2NAlH_2)_3$[218] species and in $(Me_2AlNHMe)_3$[224] (Figure IV.1.e), would allow a greater Al-N-Al angle and hence less strain at the three co-ordinated nitrogen atom. However, kinetic results on the nitrile/R_3Al reactions have indicated that the dimeric state of association of alkylideneaminoalanes is thermodynamically the most stable.[225] The i.r. spectrum of $(^tBu_2C{:}NAlCl_2)_2$ also contains a strong band at 516 cm^{-1}, assigned as the ν(Al-N) bridge mode by analogy with published assignments of ν(Al-N) in compounds containing $(AlN)_2$ rings[226,227] [cf. $(Me_2AlNMe_2)_2$[227] with ν(Al-N) at 509 cm^{-1}]. Details of the ^1H n.m.r. spectrum of $(^tBu_2C{:}NAlCl_2)_2$ are given in Table IV.2.

TABLE IV.1

Azomethine stretching frequencies [ν(C=N) and ν(C=N⇌Al)] of the di-t-butylmethyleneamino-aluminium derivatives

Compound	ν(C=N⇌Al)	ν(C=N)
$(^tBu_2C{:}NAlCl_2)_2$		1664ms
$(^tBu_2C{:}N)_3Al$	1690s	
$LiAl(N{:}C^tBu_2)_4$	1700vs	1642vs, 1602m

TABLE IV.2

^1H n.m.r. spectra of the di-t-butylmethyleneamino-aluminium derivatives

Compound	Temperature	τ
$(^tBu_2C{:}NAlCl_2)_2$	+33°	8.68s
$(^tBu_2C{:}N)_3Al$	+33°	8.71s
	-60°	8.74s
$LiAl(N{:}C^tBu_2)_4$	+33°	8.69c; 9.02c
	-50°	8.55c; 8.77c; 8.92c; 9.12c; 9.24s

Spectra were recorded for saturated solutions in toluene using T.M.S. an internal reference.

$\tau(Me_4Si)$ = 10.00 p.p.m.

s = singlet; c = complex.

Tris(di-t-butylmethyleneamino)aluminium, $(^{t}Bu_2C{:}N)_3Al$

The reaction between di-t-butylmethyleneaminolithium and aluminium trichloride in 3:1 molar proportions (Equation IV.13) afforded deep yellow crystals of $(^{t}Bu_2C{:}N)_3Al$[26,29,30] which was found to be monomeric (by mass spectrometry, Table IV.3) in the vapour, (by cryoscopy)in benzene, and apparently (by i.r. spectroscopy) in the solid. The i.r. spectrum of the compound (Table IV.1), recorded both as a Nujol mull and in benzene solution, shows a strong band at 1690 cm^{-1} in the azomethine stretching region, some 80 cm^{-1} higher than $\nu(C{:}N)$ in the parent ketimine. Further, the extreme moisture-sensitivity of $(^{t}Bu_2C{:}N)_3Al$ indicated the presence of three- (as found in a monomeric structure, Figure IV.2.a) rather than four-co-ordinate aluminium (as in a dimeric structure, Figure IV.2.b). The compound $(Ph_2C{:}N)_3Al$[26,30] was also monomeric in benzene (by cryoscopy) and, apparently, in the crystal, as shown by the similarity of its solution and mull i.r. spectra [$\nu(C{:}N)$ at 1686 and 1690 cm^{-1} respectively]. These two compounds thus constitute the first examples of monomeric alkylideneaminoalanes. Certain sterically crowded tris(amino)alanes, such as $(^{i}Pr_2N)_3Al$[217,218] and $[(Me_3Si)_2N]_3Al$,[228,229] are also monomeric, although association occurs when less bulky substituents are attached to the nitrogen atoms, as in $[(Me_2N)_3Al]2$.[217,218] Scale models of the hypothetical dimers of $(^{t}Bu_2C{:}N)_3Al$ and $(Ph_2C{:}N)_3Al$ indicate that the molecules would be quite strained and the orientation of the t-butyl and phenyl groups severely limited, so it appears that lack of association of these tris(alkylideneamino)aluminiums is due to the bulk of these groups.

Dative (2p → 3p) N → Al π-bonding may, in principle, occur in monomeric tris(amino)alanes, $(R_2N)_3Al$, for which the optimum orientation for such π-bonding, with the trigonal planar hybridisation of the amino-nitrogens, requires the substituents R to be coplanar with the AlN_3 skeleton (Figure IV.2.c). However, the very bulk of the groups R, necessary to prevent association, also prevents such coplanar orientations; thus, for example,

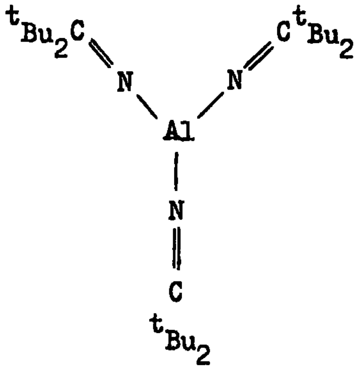
TABLE IV.3

Mass spectroscopic results for $(^{t}Bu_2C{:}N)_3Al$

m/e	Relative Intensity	Assignment
390	2	$^{t}Bu_5(CN)_3Al^+$
375	1	$^{t}Bu_5(CN)_3Al^+$-Me
360	2	$^{t}Bu_5(CN)_3Al^+$-2Me
195	7	$^{t}Bu_2H_2(CN)_2Al$
141	1	$^{t}Bu_2CNH^+$
126	30	$^{t}Bu_2CNH^+$-Me
85	30	$^{t}Bu_2CNH^+$-isobutene
84	100	$^{t}BuCNH^+$
83.5	2	$^{t}Bu_2CNAl^{2+}$
70	14	Me_2CCHNH^+
69	7	Me_2CCNH^+
68	7	Me_2CCN^+
58	30	$^{t}BuH^+$
57	100	$^{t}Bu^+$
56	17	$C_4H_8^+$
55.5	4	$^{t}BuCHNAl^{++}$
41	86	$MeCN^+$

Peaks with m/e $<$ 41 omitted

FIGURE IV.2



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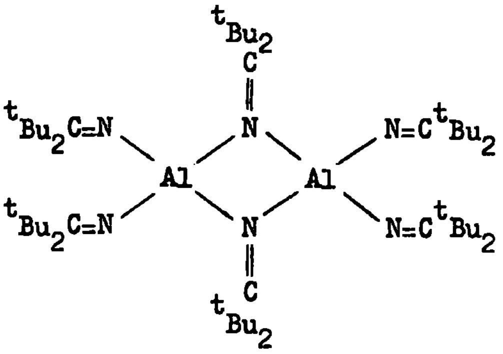

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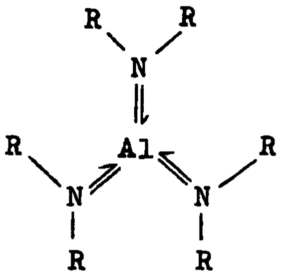

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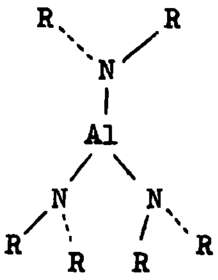
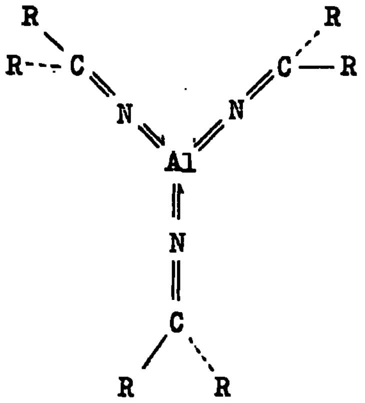
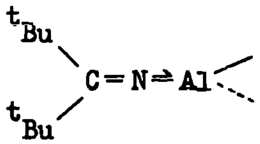


(d)

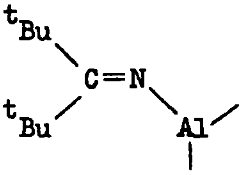
(R = Me_3Si)



(e)



(f)



(g)

$[(Me_3Si)_2N]_3Al$[229] is propeller shaped (Figure IV.2.d), with a dihedral angle of 50° between the AlN_3 and $AlNSi_2$ planes. An interesting contrast is provided by the compounds $(R_2C{:}N)_3Al$, ($R = Ph, {}^tBu$), in which the Al-N bond energy will be maximised if the C:NAl units are linear, as this condition allows greater overlap of the N 2p and Al 3p orbitals available for $N \rightarrow Al$ π-bonding. Such linearity would also cause the C-attached substituents to adopt a "paddle-wheel" orientation (Figure IV.2.e) normal to the AlN_3 plane; this orientation would allow most room for the substituents. The i.r. spectrum of $({}^tBu_2C{:}N)_3Al$ (Table IV.1) indicates that the C:NAl groups may indeed be linear. The strong peak in the azomethine stretching frequency region at 1690 cm^{-1} [assigned $\nu(C{=}N{\doteq}Al)$] is appropriate for a linear $C{=}N{\doteq}Al$ system by comparison with $\nu(C{:}N)$ in other monomeric species which are believed to contain linear C;NM skeletons; for example, $({}^tBu_2C{:}N)_2BPh$ has $\nu(C{=}N{\doteq}B)$ at 1774 cm^{-1} (see Table III.1, p.48), while $Ph_2C{:}NB(mesityl)_2$, shown by X-ray crystallography to contain a linear C:NB system[159] (see Figure III.2, p.50), has $\nu(C{=}N{\doteq}B)$ at 1792 cm^{-1}. The dimeric alkylideneamino/aluminium derivatives of type $(R^1R^2C{:}NAlR^3R^4)_2$ have $\nu(C{:}N)$ at much lower frequencies (in the range 1593-1660 cm^{-1}).[26,33,88,114-116,207]

Further evidence for linear C:NAl units (Figure IV.2.f) in $({}^tBu_2C{:}N)_3Al$ comes from its ^1H n.m.r. spectrum (Table IV.2) which, at +33°, consisted of a single sharp absorption at 8.71τ which did not change significantly in shape or chemical shift when the solution was cooled to -60°. The magnetically inequivalent <u>syn</u>- and <u>anti</u>-t-butyl groups of a molecule with bent C:NAl units (Figure IV.2.g) would have been expected to give rise to two absorptions, as in the spectrum of ${}^tBu_2C{:}NH$ itself at -60°[26] (see Table I.1, p.11). It seems unlikely, considering the steric hindrance in $({}^tBu_2C{:}N)_3Al$, that bent C:NAl units would invert at nitrogen at -60° with such a rapidity that the magnetically inequivalent t-butyl groups would be indistinguishable.

Thus, on the basis of i.r. and ^1H n.m.r. spectroscopy, the compounds

$(^tBu_2C{:}N)_3Al$ and $(Ph_2C{:}N)_3Al$ are believed to be the first crystalline aluminium-nitrogen compounds to have three co-ordinate aluminium bound to organo-nitrogen ligands with orientations appropriate for maximum dative $N \rightarrow Al$ π-bonding and, as such, they clearly afford a unique opportunity for the study of such bonding, uncomplicated by inappropriate molecular shape or by competing π-bonding to the substituents, as in $[(Me_3Si)_2N]_3Al$.[229]

Attempted preparation of Bis(di-t-butylmethyleneamino)aluminium chloride, $(^{t}Bu_2C{:}N)_2AlCl$

The reaction between aluminium trichloride and two molar equivalents of di-t-butylmethyleneaminolithium gave, not $(^{t}Bu_2C{:}N)_2AlCl$ (Equation IV.16.), but rather a mixture of $(^{t}Bu_2C{:}NAlCl_2)_2$ and $(^{t}Bu_2C{:}N)_3Al$,[26] which were separated by fractional crystallisation and identified by their i.r. spectra and melting points; the reaction system $AlCl_3 + 2Ph_2C{:}NLi$ behaved similarly.[26] Thus it appears that the bis(alkylideneamino) derivatives, which presumably must be involved in the formation of the tris(alkylideneamino)alanes described above, are unstable with respect to disproportionation (Equation IV.17).

$$AlCl_3 + 2\,^{t}Bu_2C{:}NLi \longrightarrow (^{t}Bu_2C{:}N)_2AlCl + 2LiCl \qquad \text{IV.16}$$

$$2(^{t}Bu_2C{:}N)_2AlCl \longrightarrow \tfrac{1}{2}(^{t}Bu_2C{:}NAlCl_2)_2 + (^{t}Bu_2C{:}N)_3Al \qquad \text{IV.17}$$

Thus $(Ph_2C{:}N)_2AlCl$ resembles its boron analogue, $(Ph_2C{:}N)_2BCl$, which disproportionates into $(Ph_2C{:}NBCl_2)_2$ and $(Ph_2C{:}N)_3B$,[12,53] while, for the $^{t}Bu_2C{:}N$- systems, there is a marked contrast between the behaviour of the boron and aluminium derivatives. As already noted (see Chapter III, p.52), $(^{t}Bu_2C{:}N)_2BCl$ is stable with respect to disproportionation into $^{t}Bu_2C{:}NBCl_2$ and $(^{t}Bu_2C{:}N)_3B$, presumably because the dihalide is a liquid so that there is no lattice energy "driving force", and also because, even if $(^{t}Bu_2C{:}N)_3B$ were capable of resistance, (attempts at its preparation having failed) there would be strong steric crowding of substituents in the four co-ordinate boron intermediate likely to be involved in its formation. However, in the aluminium systems, both $(^{t}Bu_2C{:}NAlCl_2)_2$ and $(^{t}Bu_2C{:}N)_3Al$ are crystalline solids and further, the increased size of the aluminium atom over a boron atom presumably can allow a four co-ordinate aluminium intermediate as indicated by the fact that $^{t}Bu_2C{:}NAlCl_2$ is dimeric while $^{t}Bu_2C{:}NBCl_2$ is monomeric and that the aluminium atom in $LiAl(N{:}C^{t}Bu_2)_4$ is tetrahedrally surrounded by four $^{t}Bu_2C{:}N$- groups.[47a,b]

Lithium Tetrakis(di-t-butylmethyleneamino)aluminate, $LiAl(N:C^tBu_2)_4$

Reaction between aluminium trichloride and four or more molar equivalents of di-t-butylmethyleneaminolithium (Equation IV.14), followed by removal of solvent and extraction of the residue with hot toluene, afforded pale yellow crystals which analysed correctly as $LiAl(N:C^tBu_2)_4$.[47b] The moisture-sensitive compound was monomeric in benzene solution (by cryoscopy) and in the vapour (by mass spectrometry). Its i.r. spectrum (Table IV.1) shows bands at 1700, 1642 and 1602 cm^{-1}, the band at highest frequency being assigned as the unsymmetrical skeletal stretching absorption, $\nu(C{=}N\overset{\rightarrow}{-}Al)$, of ketimino groups, $^tBu_2C:N-$, terminally attached to the aluminium by linear C:NAl units, the shape appropriate for optimum N $\longrightarrow$ Al dative π-bonding. The bands at lower frequency (1642 and 1602 cm^{-1}) may be due to bridging ketimino groups or they may be a consequence of loss of symmetry in going from the planar environment of nitrogen around aluminium in $(^tBu_2C:N)_3Al$[26,30] to the tetrahedral arrangement present in $LiAl(N:C^tBu_2)_4$; in this respect, the benzonitrile adduct of $(^tBu_2C:N)_3Al$ has bands at 1695, 1636 and 1605 cm^{-1} in its i.r. spectrum,[31] as well as a band at 2256 cm^{-1} reflecting the expected increase in $\nu(C{\vdots}N)$ of a nitrile on co-ordination [*cf.* $PhC{\vdots}N$ has $\nu(C{\vdots}N)$ at 2232 cm^{-1}] whereas $(^tBu_2C:N)_3Al$[26,30] itself has only a band at 1690 cm^{-1} in the same region.

The ^1H n.m.r. spectrum of $LiAl(N:C^tBu_2)_4$, (Table IV.2), was extremely complex, this in itself indicating the presence of more than one type of $^tBu_2C:N-$ group in the molecule. At room temperature, two complex resonances of unequal intensity were observed, centred at *ca.*8.7 and 9.0τ. On cooling down to -50^o, these peaks split further into five distinct resonances in the range 8.55 to 9.24τ, four of the bands being complex, the fifth (at 9.24τ) being a singlet. Integration of the peak areas failed to lead to any rationalisation of the spectrum, although it was noted that the resonance at 9.24τ was at an appreciably higher field than previously observed for derivatives $^tBu_2C:NMX_n$ with the sole exception of the t-butyl signal in the ^1H n.m.r. spectrum of

$^tBu_2C:NLi$ (at 9.21τ at -50°, see Table I.1, p.11).

The monomeric nature of $LiAl(N:C^tBu_2)_4$ in the crystal has been confirmed by a determination of its crystal structure by X-ray diffraction.[47a,b] The structure of the molecule is shown in Figure IV.3 together with some of the more important bond lengths and bond angles.

The molecule has a two-fold symmetry axis through the metal atoms, which are bridged by two of the ketimino groups, the remaining two ketimino groups being terminally attached to the aluminium atom by short Al-N bonds and a large Al-N(1)-C(1) bond angle, as appropriate for considerable $N \rightleftharpoons Al$ (p → d) dative π-bonding. The terminal $Al \leftrightharpoons N$ bond length of 1.78Å may be compared with the terminal $Al \leftrightharpoons N$ bond lengths of 1.78Å in $[(Me_3Si)_2N]_3Al$[229] and 1.79Å in $Al_4Cl_4(NMe_2)_4(NMe)_2$[230] (contrast ca.1.94Å for Al-N single bonds[151,224,230-236]). In addition, the Al-N(1)-C(1) unit is very nearly linear (angle AlN_1C_1 = 167°). Clearly, this crystal structure, together with that of $Ph_2C:NB(mesityl)_2$[159] described earlier (Figure III.2, p.50, angle CNB = 170°), provides ample substantiation for the postulated correlation between a high azomethine stretching frequency and linearity of the C:NM skeleton in monomeric alkylideneamino derivatives of co-ordinatively unsaturated metals and metalloids; it also provides the first example of a near-linear C:NM unit in which (p → d) rather than (p → p) π-bonding is indicated.

The slight deviation of the AlN(1)C(1) unit from linearity is not due to interference with other molecules in the unit cell. However, one methyl carbon of each of the terminally attached $(Me_3C)_2C:N-$ units is only 1.8Å away from the two-fold axis, so that the distance between these two carbons (across the axis) is 3.6Å. It is clear from an accurately scaled model of the structure that pushing the AlN(1)C(1) and AlN(1')C(1') units nearer to linearity would cause these two methyl carbons to approach even closer to the two-fold axis (Figure IV.4.a), so that when the angle reaches 180°, it is estimated that the carbon-carbon distance (across the axis) would be less than 3Å. As the Van

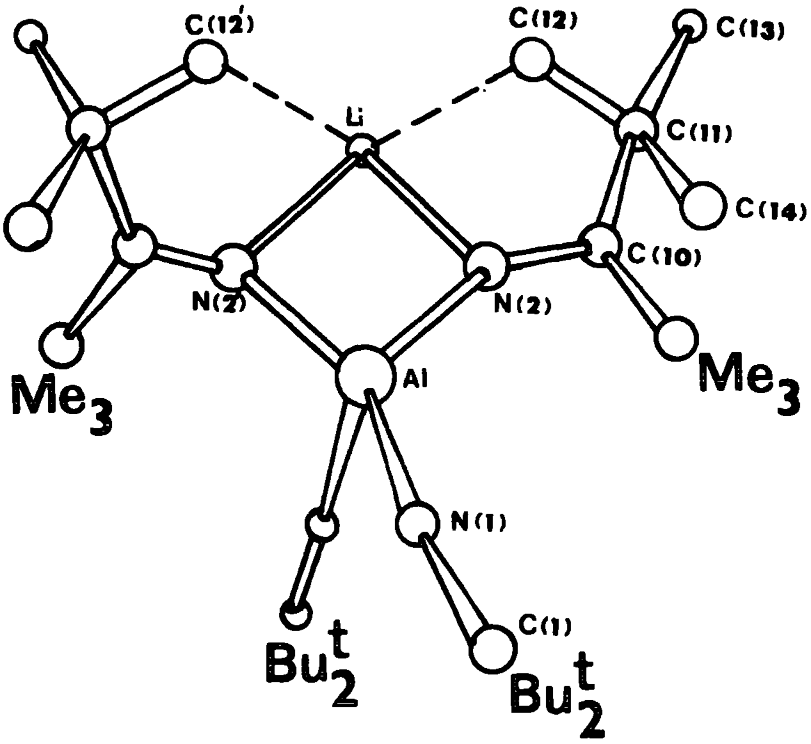


FIGURE IV.3

Crystal and Molecular Structure of Lithium Tetrakis(di-t-butylmethyleneamino)aluminate, $LiAl(N:C^tBu_2)_4$

Bond Lengths

C(1)-N(1)	1.26	C(10)-N(2)	1.27
Al-N(1)	1.78	Al-N(2)	1.85
Al.....Li	2.55	Li-N(2)	1.95*
		Li-C(12)	2.37*
		C(10)-C(11)	1.56
		C(11)-C(12)	1.54*

Bond Angles

C(1)-N(1)-Al	167°	C(10)-N(2)-Li	127.3°
C(10)-N(2)-Al	148.6°	N(2)-Li-N(2')	93.7°
N(2)-Al-N(2')	98.5°	N(2)-Li...(C(12)	77°
Al-N(2)-Li	83.9°	N(2)-C(10)-C(11)	118°
		C(10)-C(11)-C(12)	110°
		C(11)-C(12)-Li	107°
		C(12)...Li...C(12')	112°

Interatomic distances in Å

E.s.d.'s: 0.02Å for distances marked with an asterisk
0.01Å for the remainder
1° for all angles

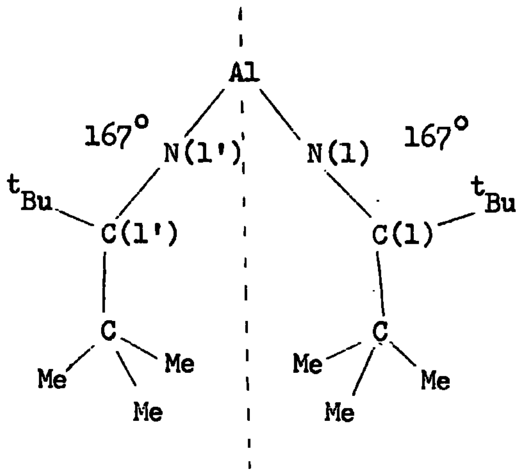
der Waal's radius of a methyl group is *ca.* 2Å,[171] the result of full linearity would be considerable steric interference between these two methyl groups. However it is also obvious from study of the scale model that decreasing the AlN(1)C(1) angle from 167° would not cause any appreciable steric hindrance between the methyl groups of the terminal, and those of the bridging, ketimino groups $(Me_3C)_2C{:}N-$, at least until that angle approached 120° i.e. although not quite linear, there are no stereochemical reasons why the terminal AlNC angles should not be much less than they are, say even as low as 120°.

A lesser though still apparently significant degree of $N \rightleftharpoons Al$ $(p \longrightarrow d)$ dative π-bonding is unexpectedly indicated by the comparative shortness of the *bridging* Al-N(2) bonds (1.87Å) and by the large angle Al-N(2)-C(10) (148.6°). Bridging Al-N bond distances are usually in the range 1.92-1.96Å;[231] for example 1.92Å in $(C_6H_4Br.PhC{:}NAlPh_2)_2$[172] and $Al_4Cl_4(NMe_2)_4(NMe)_2$,[230] 1.93Å in $(PhNAlPh)_4$[232] and $[Me_2AlN(CH_2)_2]_3$,[233] 1.94Å in $(^tBuMeC{:}NAlMe_2)_2$,[151] 1.95Å in $(Me_2AlNHMe)_3$,[224] and 1.96Å in $(PhCO.PhN.AlMe_2)_2$,[234] $(Me.CO.PhN.AlMe_2)_3$[235] and $[Me_2Al(NMe_2)]_2$;[236] the sum of the Al and N covalent radii is 1.96Å.[171] The AlN_2Li ring geometry is also unusual in its short Li....Al distance [2.55(4)Å] and small Li-N(2)-Al angle (84°). A particularly acute angle at the bridging nonmetal atom and a short metal...metal distance are normally found in systems with electron deficient bridges,[237] as in $LiAlEt_4$,[238] for which the Li-Al distance is 2.71Å and the angle Li-C-Al is 77°. The Li-N(2) bridging bonds are of a length (1.95Å) appropriate for essentially single bonds [*cf.* 1.94Å for the Li-N bonds in $Li(NH_3)_4$[239]]. The C-N bond lengths of both the terminal (1.26Å) and bridging (1.27Å) ketimino groups are similar to those found in other alkylideneamino systems [*cf.* 1.25-1.29Å in a series of oximes,[15-18] 1.27Å in $(MeCH{:}NBMe_2)_2$[151] and $(^tBuMeC{:}NAlMe_2)_2$,[151] and 1.28A in $(C_6H_4Br.PhC{:}NAlPh_2)_2$[172]].

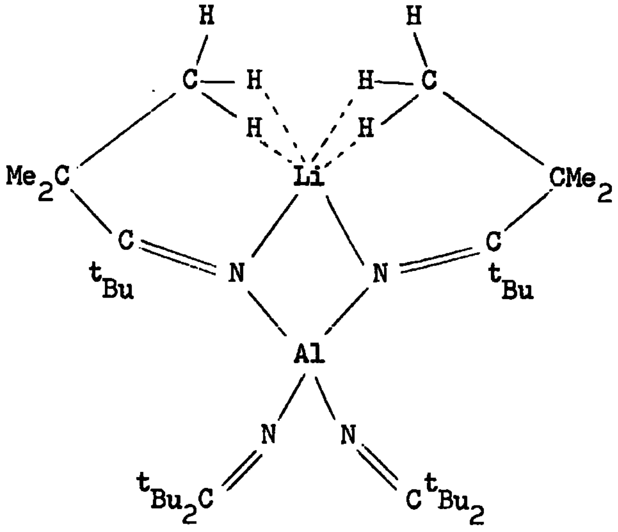
The larger bridging Al-N(2)-C(10) angle means that one t-butyl group of each bridging $^tBu_2C{:}N-$ unit leans towards the lithium atom. Although in principle free rotation about the ^tBu-C bond can occur and there would be room for the butyl group to be so orientated that its methyl groups did not point towards the lithium, nevertheless one methyl carbon, C(12), adopts a position as close as possible to the lithium, bearing in mind that carbon, C(12) is at a normal single bond distance from C(11). The Li-C(12) distance of 2.37Å is little longer than the Li-C distances in $LiAlEt_4$[238] (2.30Å) and $(MeLi)_4$[240] (2.31Å). Although the positions of the hydrogen atoms could not be found, the position of carbon C(12) is such that the most probable orientation of its three hydrogen atoms will place two of them effectively in bridging positions between the carbon and the lithium (Figure IV.4.b). Calculations show that such an orientation would lead to a Li...H distance of *ca.* 2.1(2)Å [*cf.* Li-H bond distance of 2.08 in lithium hydride[171]]. The compound $LiAl(N:C^tBu_2)_4$ thus apparently shows a novel type of Li...H-C interaction.

Significantly, the ^1H n.m.r. spectrum, which has been discussed above (Table IV.2) consists of several complex resonances rather than the set of three peaks, of relative intensity 2:1:1, that would be expected if there were no Li-C interactions and so free rotation about the C(10)-C(11) bond. Similar ^1H n.m.r. and i.r. spectroscopic features for $LiGa(N:C^tBu_2)_4$[32] imply that this compound is isostructural with $LiAl(N:C^tBu_2)_4$.

FIGURE IV.4



(a)



(b)

CHAPTER V

This chapter describes the preparation of the 1,1,3,3-tetramethylguanidine adducts $(Me_2N)_2C:NH,AlX_3$ (X = Et,Cl) and of the 1,1,3,3-tetramethylguanidino- [or bis(dimethylamino)methyleneamino-] derivatives $[(Me_2N)_2C:NAlX_2]_2$ (X = Et,Cl). I.r. spectroscopic details are given for all these new compounds. Also discussed are the ^1H n.m.r. spectra of the alkylaluminium compounds and the mass spectra of $(Me_2N)_2C:NH$, $(Me_2N)_2C:NH,AlCl_3$ and $[(Me_2N)_2C:NAlEt_2]_2$.

EXPERIMENTAL SECTION

Starting Materials

Triethylaluminium was distilled, and aluminium chloride sublimed, under reduced pressure before use. Bis(dimethylamino)methyleneamine (or tetramethylguanidine) was purified by distillation from sodium hydroxide. Manipulations were with a conventional vacuum line, nitrogen-filled glove box, or nitrogen-filled apparatus as appropriate.

Reactions of Triethylaluminium with Bis(dimethylamino)methyleneamine[33]

Triethylaluminium (0·84 gm., 7·36 mmole) was added slowly by syringe to a solution of bis(dimethylamino)methyleneamine (0·85 gm., 7·36 mmole) in 20 ml. hexane at -196°. The solution was warmed to 16° and the solvent was removed at low pressure, leaving the colourless liquid adduct, $(Me_2N)_2C:NH,AlEt_3$. (Found: Al,11·4; hydrolysable Et 36·8%; M,245. $C_{11}H_{28}AlN_3$ requires Al,11·8; hydrolysable Et 38·0%; M,229); ν_{max} (Liquid film) 3350w; 2994sh, 2924s, 2882s, 2841s, 2786w, 1603m,sh, 1572s, 1548s, 1490w, 1460m, 1425m, 1406ms, 1381ms, 1330m, 1256m, 1229m, 1195sh, 1176w, 1133ms, 1074ms, 1062ms, 1037m, 1010m, 980m, 943m, 910sh, 901ms, 890sh, 817ms, 800ms, 779m, 750m, 733w, 692ms, 679m, 638wm, 624wm, 598w, 578wm and 558wm cm^{-1}.

Thermal Description of $(Me_2N)_2C:NH,AlEt_3$[33]

A sample of the adduct held at 115° for 30 min. evolved ethane (1·03 mol. per mol. of adduct) leaving the colourless liquid diethylbis(dimethylamino)-

methyleneaminoaluminium, $[(Me_2N)_2C:NAlEt_2]_2$ (Found: Al,13·5; hydrolysable Et, 29·9%; M,440. $C_{18}H_{44}Al_2N_6$ requires Al,13·6; hydrolysable Et, 29·2%; M,398); ν_{max} (Liquid film) 2924ms, 2882ms, 2875ms, 1610m, 1572ms, 1548s, 1431w, 1385ms, 1258w, 1232w, 1179ms, 1142ms, 1112ms, 1075ms, 1052ms, 990m, 946m, 915ms, 877w, 796s, 755m, 732m, 680s,br and 637m,br cm^{-1}.

Reaction of Aluminium Chloride with Bis(dimethylamino)methyleneamine[33]

A solution of bis(dimethylamino)methyleneamine (0·97 gm., 8·44 mmole) in diethyl ether (10 ml.) was added by syringe to a solution of aluminium chloride (1·127 gm., 8·44 mmole) in diethyl ether (20 ml.) at -196°. Small white crystals of the adduct, $(Me_2N)_2C:NH,AlCl_3$, m.p. 108-110°, separated on concentration of the solution by evaporation. (Found: C,24·4; H,5·6; Al,10·5; Cl,41·8%. $C_5H_{13}AlCl_3N_3$ requires C,24·1; H,5·2; Al,10·9; Cl,42·8%). ν_{max} (Nujol mull) 3413sh, 3311m, 3145m, 1653ms, 1605ms, 1560ms, 1410m, 1340sh, 1312w, 1259m, 1235sh, 1190w, 1139w, 1107sh, 1085m, 1060m, 1037m, 1018sh, 969w, 872m, 820sh, 800m,br and 719m cm^{-1}.

Reaction of Aluminium Chloride with Bis(dimethylamino)methyleneaminolithium[33]

A solution of $(Me_2N)_2C:NLi$ (11·65 mmole) was prepared from $(Me_2N)_2C:NH$ (1·34 gm., 11·65 mmole) in diethyl ether (20 ml.) and ^nBuLi (0·75 gm., 11·65 mmole) in hexane (5 ml.) at -196° with subsequent warming to 16°. This solution was filtered onto a solution of $AlCl_3$ (1·556 gm., 11·65 mmole) in ether (20 ml.) at -196°, and the mixture was warmed to 16°, whereupon a cream-coloured precipitate separated. This was filtered off and discarded, as it consisted mainly of lithium chloride. Concentrationof the filtrate by evaporation gave off-white crystals of the dimeric compound, dichlorobis(dimethylamino)methyleneaminoaluminium, $[(Me_2N)_2C:NAlCl_2]_2$, decomp. 75-80°. (Found: C,29.0; H,5·4; Al,12·5; Cl,33·6%; M,444. $C_{10}H_{24}Al_2Cl_4N_6$ requires C,28·3; H,5·7; Al,12·7; Cl, 33·5%; M,424). ν_{max} (Nujol mull) 3300w, 1658m, 1647ms, 1597ms, 1550s, Nujol, 1323sh, 1259m, 1229m, 1182sh, 1163sh, 1147ms, 1111sh, 1087w, 1060ms, 1034ms, 1019sh, 969w, 901w, 873w, 820sh, 800w, 774w, 749w and 719ms cm^{-1}. This compound was only very slightly soluble in the common organic solvents, and in some experiments was difficult to separate from lithium chloride during its preparation. Attempts at its recrystallisation from boiling toluene gave a dark brown insoluble mass. It was just soluble enough in cold benzene, however, for determination of M; evaporation of its benzene solutions gave dark brown viscous residues.

DISCUSSION

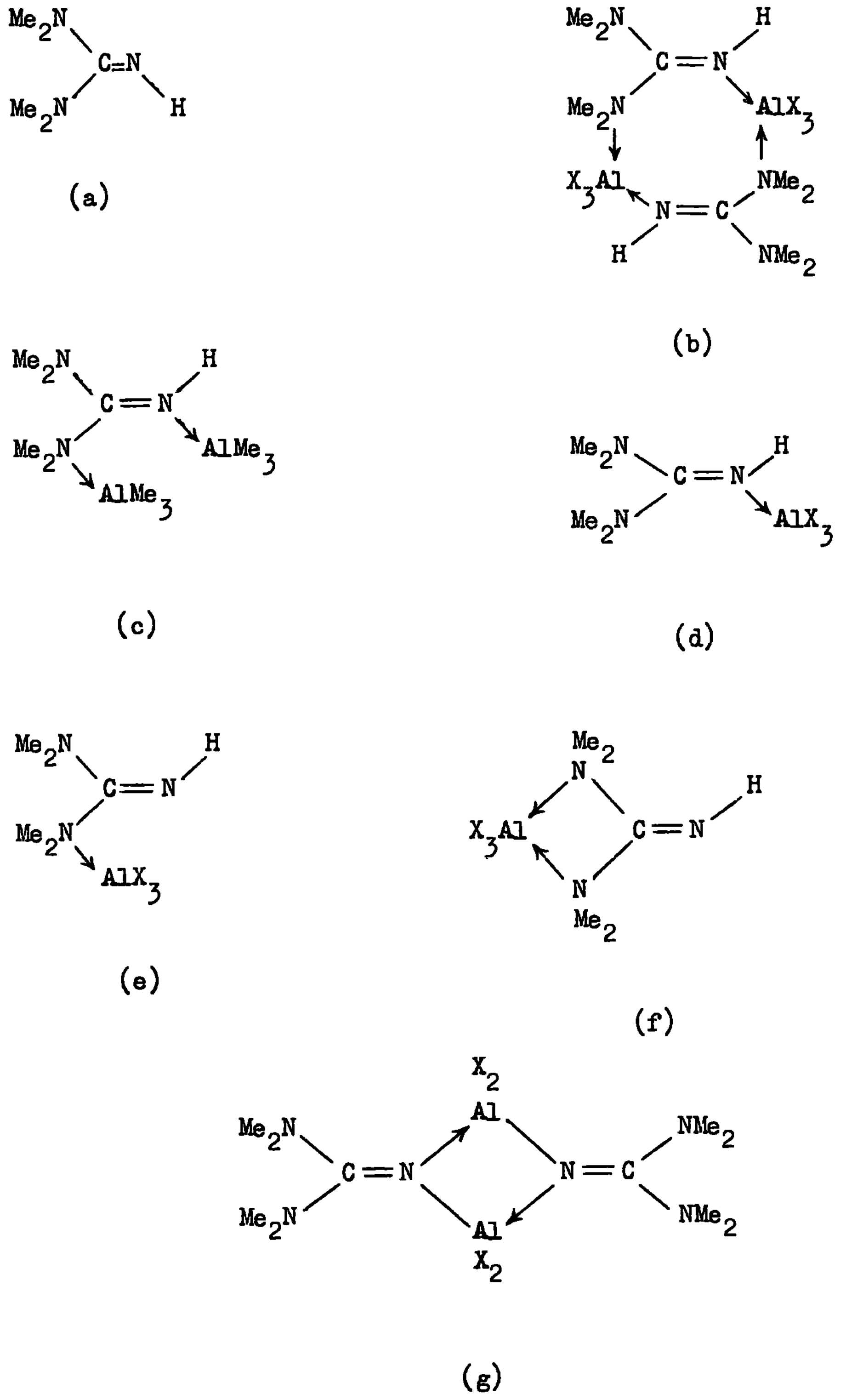
Bis(dimethylamino)methyleneamine, or (trivially) 1,1,3,3-tetramethylguanidine, $(Me_2N)_2C{:}NH$, (Figure V.1.a) has three potential donor sites, viz. the two dimethylamino-nitrogens and one imino-nitrogen. This chapter[33] reports a study of its interaction with some aluminium compounds in an attempt to investigate whether incorporation of other potential donor sites in a molecule containing the imino group $\rangle C{=}NH$ affected the manner of its interaction with aluminium Lewis acids. In earlier studies, diphenylmethyleneamine adducts $Ph_2C{:}NH,AlR_3$[88] (R = Me,Et,Ph) were found to lose RH when heated, forming alkylideneamino-aluminium derivatives $(Ph_2C{:}NAlR_2)_2$ for which four-membered ring structures (Figure IV.1.a) were suggested; the adducts ${}^tBu_2C{:}NH,AlR_3$[90] (R = Me, ${}^iBu$) behave similarly. Similar methods have been used to prepare aminoalanes, many of which are dimeric,[217,218] by elimination of RH (R = H, alkyl, aryl) from adducts of amines and organoaluminium hydrides.[217-220] Dimeric alkylideneamino-alanes, $(R^1R^2C{:}NAlR^3R^4)_2$ ($R^1 = R^2$ = Ph or ${}^tBu$; $R^3 = R^4$ = halogen) (Figure IV.1.a,d) have also been prepared from alkylideneamino-lithium reaegnts and aluminium halides,[26] and from reactions between nitriles and organoaluminium compounds.[7c,114-116,203-215] These three preparative routes have been discussed fully in Chapter IV of this thesis (pp.72 to76). X-ray crystallographic studies on $({}^tBuCMe{:}NAlMe_2)_2$[151] (Figure IV.1.b) and $(p\text{-}BrC_6H_4.PhC{:}NAlPh_2)_2$[172] (Figure IV.1.c) have confirmed as $(AlN)_2$ ring structure for these compounds. A similar cyclic structure (Figure I.1.d) has been suggested for $[(Me_2N)_2C{:}NLi]_2$,[4] prepared from $(Me_2N)_2C{:}NH$ and RLi (R = ${}^nBu$,Me), even though this left the Me_2N groups unco-ordinated in the presence of two co-ordinate lithium. $(Me_2N)_2C{:}NH$ is believed to co-ordinate to transition metals through the imino-nitrogen.[241]

1,1,3,3-Tetramethylguanidine Adducts, $(Me_2N)_2C{:}NH,AlX_3$

The adducts were prepared from equimolar proportions of the components in hexane (X = Me,Et) or in diethyl ether (X = Cl). The solids $(Me_2N)_2C{:}NH,AlMe_3$ and $(Me_2N)_2C{:}NH,AlCl_3$ crystallised from solution; the liquid $(Me_2N)_2C{:}NH,AlEt_3$ was left after evaporation of the solvent. All were stable to dissociation at 15°, and did not lose $(Me_2N)_2C{:}NH$ or AlX_3 when subjected to prolonged pumping. Although $(Me_2N)_2C{:}NH,AlCl_3$ was too insoluble in benzene for cryoscopic or spectroscopic study, the other adducts were readily soluble. They were monomeric (by cryoscopy) in dilute (1% w/w) solution, but apparently partially associated in more concentrated solution. Apparent degrees of association in the range 1.2-1.4 were obtained in cryoscopic studies in benzene solutions in the concentration range 5-10% (w/w). Association to dimers, $[(Me_2N)_2C{:}NH,AlX_3]_2$, or higher oligomers could in principle occur either through alkyl bridges or by use of more than one of the nitrogen atoms of the guanidine, as in Figure V.1.b. Both forms of co-ordination would involve five co-ordinate aluminium. No tendency for $(Me_2N)_2C{:}NH$ to co-ordinate simultaneously through two separate nitrogens to two separate acceptor molecules was found, however, in experiments in which $(Me_2N)_2C{:}NH$ was treated with an excess of $(Me_3Al)_2$. Attempts at the preparation of a 1:2 adduct $(Me_2N)_2C{:}NH,2AlMe_3$ (Figure V.1.c) afforded only $(Me_2N)_2C{:}NH,AlMe_3$ and unco-ordinated $(Me_3Al)_2$.[33]

A structure (V.1.d) for the monomeric 1:1 adducts appears more likely on steric grounds than structures (V.1.e) or (V.1.f), co-ordinated through one or both amino-nitrogens. Co-ordination through the imino-nitrogen might have been expected to be accompanied by marked changes in the C=N and N-H i.r. stretching frequencies. The observed marked decrease in ν(C:O)[66-78] and increase in ν(C⋮N),[113-121] (except when the C≡N group co-ordinates through its π-system),[120,126-128] on co-ordination of compounds containing the carbonyl and nitrile groups respectively, to Group III alkyls and halides have already been noted in Chapter II of this thesis, as has the shift of ν(C:N) to higher,

FIGURE V.1


(a) (b) (c) (d) (e) (f) (g)

and of ν(N-H) to lower, frequencies on co-ordination of substituted alkylideneamines to boron trifluoride.[2] In contrast, ν(C:N) of $Ph_2C:NH$ and $^tBu_2C:NH$ seem little affected by co-ordination to boron-,[87] aluminium-[88,90] and gallium-[89] alkyls, although there is a small increase in ν(N-H). In transition metal complexes of $(Me_2N)_2C:NH$,[241] where co-ordination is believed to occur through the imino-nitrogen, ν(C:N) is shifted by 40-60 cm^{-1} to lower wave numbers. However, the spectra of the adducts $(Me_2N)_2C:NH,AlX_3$ (X = Me,Et,Cl) gave a less clear indication of their structures, as all contained three bands in the region 1540-1660 cm^{-1}; $(Me_2N)_2C:NH$ itself has only one band in this region, at 1592 cm^{-1}. The N-H stretching absorption was more easily identified at a slightly higher frequency in the i.r. spectra of the adducts (X = Me, at 3356[33] cm^{-1}; X = Et, at 3350 cm^{-1}; X = Cl, at 3413 cm^{-1}) than that (3322 cm^{-1}) characteristic of free $(Me_2N)_2C:NH$.

The ^1H n.m.r. spectra of the two soluble adducts, $(Me_2N)_2CNH,AlX_3$ (X = Me,Et) were recorded (Table V.1). That of $(Me_2N)_2C:NH,AlMe_3$[33] appears to indicate a structure (V.1.d), in that τ(N-H) is affected much more than τ(NMe_2) by co-ordination, whereas the spectrum of $(Me_2N)_2C:NH,AlEt_3$ has both ligand peaks shifted slightly upfield with respect to those of free $(Me_2N)_2C:NH$. That this result was not caused by dissociation of the adduct into its components was shown by the molecular weight measurements already referred to, by the insensitivity of the peak positions to the concentration of the solution, and by the fact that the triplet and quartet arising from the Lewis acid had an internal chemical shift and τ values appropriate for co-ordinated Et_3Al, rather than free $(Et_3Al)_2$. A further notable feature of the ^1H n.m.r. spectra of these two adducts is the singlet nature of the dimethylamino-resonance. Structures (Figure V.1.d → f) might be expected to give rise to two distinct Me_2N resonances arising from the magnetically distinct amino-groups in these adducts unless rapid exchange occurred, or unless the orientation of the amino-groups in Figure V.1.d was such as to minimise their magnetic difference. The spectrum of unco-ordinated $(Me_2N)_2C:NH$ at +33° likewise contains a singlet attributable to the Me_2N-protons.

The mass spectra of $(Me_2N)_2C:NH$ and $(Me_2N)_2C:NH,AlCl_3$ were recorded. Relative intensities and suggested assignments for the high-mass peaks, and for the more intense low-mass peaks, are in Table V.2. Peaks attributable to fragments containing aluminium and/or chlorine atoms were readily detected by comparison of the two spectra, and the isotope patterns characteristic of chlorine containing fragments provided further guides to assignments. No peak was obtained which was indicative of associated molecules $[(Me_2N)_2C:NH,AlCl_3]_n$ (where $n > 1$). Breakdown involved sequential loss of chlorine atoms, dimethylamino-groups, methyl groups or hydrogen atoms. The persistence of the AlNC skeleton is consistent with a structure (V.1.d) for the adduct, with the aluminium attached to the imino-nitrogen, though it cannot be taken as strong structural evidence because of the possibility of rearrangement accompanying breakdown.

TABLE V.1

^1H n.m.r. spectroscopic results for $(Me_2N)_2C{:}NH$, $(Me_2N)_2C{:}NH,AlR_3$ and $[(Me_2N)_2C{:}NAlR_2]_2$. (R = Me, Et)

Compound	τ(NH)	$\tau(NMe_2)$	$\tau(AlR_{2\text{ or }3})$
$(Me_2N)_2C{:}NH$	4.73s(1)	7.36s(12)	-
$(Me_2N)_2C{:}NH,AlMe_3$	5.58s(1)	7.69s(12)	10.44s(9)
$[(Me_2N)_2C{:}NAlMe_2]_2$	-	7.37s(2)	10.34s(1)
$(Me_2N)_2C{:}NH,AlEt_3$	4.82s(1)	7.50s(12)	8.59t(9); 9.88q(6) J = 7.8c/sec.
$[(Me_2N)_2C{:}NAlEt_2]_2$	-	7.54s(6)	8.48t(3); 9.65q(2) J = 7.8c/sec.

Samples were in the form of ca. 20 wt.% solutions in benzene

$\tau(Me_4Si)$ = 10.00 p.p.m.

s = singlet, t = triplet, q = quartet; relative intensities in parentheses.

TABLE V.2

Mass spectroscopic results for $(Me_2N)_2C{:}NH$ and $(Me_2N)_2C{:}NH.AlCl_3$

m/e	Relative intensity (a)	(b)	Assignment
212	3		$(Me_2N)_2CNHAlCl_2$
211	5		$(Me_2N)_2CNAlCl_2$
196	0.4		211 minus Me
176	0.2		$(Me_2N)_2CNAlCl$
167	2		$Me_2NCNAlCl_2$
153	1		$MeNHCNAlCl_2$
140	3		$(Me_2N)_2CNAl$
116	2	7	$(Me_2N)_2CNH_2$
115	14	32	$(Me_2N)_2CNH$
100	5	3	115 minus Me
97	2		Me_2NCNAl
96	9		97 minus H
86	4	5	$Me_2NC(NH)_2$
82	5		MeNCNAl
71	32	73	Me_2NCNH
70	38	30	Me_2NCN
69	70	52	70 minus H
55	5	7	MeNCN
53	9		CNAl
44	100	100	Me_2N
42	30	46	$C_2H_4N, C(NH)_2$
40	6	5	C_2H_2N, CN_2
36	50		HCl
35	8		Cl

(a) in spectrum of $(Me_2N)_2CNH,AlCl_3$

(b) in spectrum of $(Me_2N)_2CNH$

Chlorine containing fragments relate only to ^{35}Cl isotopes.

1,1,3,3-Tetramethylguanidino-derivatives, $[(Me_2N)_2C:NAlX_2]_2$

Th~~y~~e thermal decomposition of the adducts $(Me_2N)_2C:NH,AlR_3$ (R = Me,Et) followed a similar course to that of similar diphenylmethyleneamine,[88] $Ph_2C:NH$, and di-t-butylmethyleneamine,[90] $^tBu_2C:NH$, adducts; alkane was evolved leaving the dialkyl(diaminomethyleneamino)aluminium (Equation V.1).

$$2(Me_2N)_2C:NH,AlR_3 \xrightarrow{heat} [(Me_2N)_2C:NAlR_2]_2 + 2RH \qquad V.1$$

$$R = Me,Et$$

As the thermal decomposition of $(Me_2N)_2C:NH,AlCl_3$, was not an equally satisfactory route to $[(Me_2N)_2C:NAlCl_2]_2$, but afforded an intractable mixture {the decomposition temperature of $(Me_2N)_2C:NH,AlCl_3$ apparently exceeds that of $[(Me_2N)_2C:NAlCl_2]_2$}, the diaminomethyleneaminoaluminium dichloride was prepared instead from $(Me_2N)_2C:NLi$[3] and $AlCl_3$ in ether (Equation V.2), a route analogous to that used to prepare $(Ph_2C:NAlCl_2)_2$ and $(^tBu_2C:NAlCl_2)_2$.[26] (See Chapter IV).

$$2(Me_2N)_2C:NLi + 2AlCl_3 \longrightarrow [(Me_2N)_2C:NAlCl_2]_2 + 2LiCl \qquad V.2$$

All three guanidino-aluminium derivatives $[(Me_2N)_2C:NAlX_2]_2$ were dimeric (by cryoscopy) in benzene, in which they are presumed to have structures as shown in Figure V.1.g. I.r. spectroscopic details (see Experimental Section and reference 33) indicate a similar structure in the condensed phase; the compounds $[(Me_2N)_2C:NAlX_2]_2$ have bands in the usual azomethine stretching absorption region (X = Me, at 1618 cm^{-1};[33] Et, at 1610 cm^{-1}; Cl, at 1647 cm^{-1}), found for all other previously prepared derivatives, $(R^1R^2C:NAlR^3R^4)_2$ [26,88,90,114,116,203-210] [ν(C:N) in range 1593-1675; see Chapter IV] which are thought to have a $(AlN)_2$ four-membered ring structure, confirmed by X-ray crystallography for $(^tBuCMe:NAlMe_2)_2$[151] (Figure IV.1.b) and $(p\text{-}BrC_6H_4.PhC:NAlPh_2)_2$[172] (Figure IV.1.c).

The ^1H n.m.r. spectroscopic details for the soluble dialkyls are shown in Table V.1. For both dialkyls, the dimethylamino-resonances were sharp singlets at τ values little different from that appropriate for unco-ordinated $(Me_2N)_2C:NH$, and the signals due to the aluminium-attached alkyl groups were at chemical shifts appropriate for structure (V.1.g). The resonances due to the ethyl groups of diethylaluminium compounds $(Et_2AlX)_n$ have been shown to be particularly sensitive to the nature of X, in that the internal chemical shift Δ between the methyl triplet and the methylene quartet varies markedly with X.[242] The value of Δ (-1.17 p.p.m.) for $[(Me_2N)_2C:NAlEt_2]_2$ is in line with the values for other dimeric diethylaluminium-nitrogen compounds, which fall in the range -1.10 ± 0.07 p.p.m.[88,115,116,243] A higher value of Δ characterises triethylaluminium adducts of nitrogen donors (-1.25 → -1.29 p.p.m.; *cf.* free Al_2Et_6 for which Δ = -0.81 p.p.m.).[88,243]

The mass spectra of $[(Me_2N)_2C:NAlCl_2]_2$ and $[(Me_2N)_2C:NAlEt_2]_2$ were recorded. Although the former was apparently dimeric (by cryoscopy) in benzene, its mass spectrum had no peak of higher mass than those corresponding to the various isomers of $(Me_2N)_2C:NAlCl_2^+$ and $(Me_2N)_2CNHAlCl_2^+$, and the breakdown fragments were essentially the same as those found for the adduct $(Me_2N)_2C:NH,AlCl_3$. The mass spectrum of $[(Me_2N)_2C:NAlEt_2]_2$ by contrast (Table V.3) gave a clear indication of its dimeric nature in the vapour phase. The molecular ion $[(Me_2N)_2C:NAlEt_2]_2^+$ was relatively abundant, and the fragment derived from this by the loss of ethylene was the most abundant fragment. The major features of the breakdown were the loss of ethylene from aluminium-attached ethyl groups, and the loss of Me_2N groups, or of molecular Me_2NCN, from the guanidino-section of the molecule. The presence of Me_2NAl units in the later stages of breakdown is not necessarily indicative of direct dimethylamino-aluminium links in the starting material; it has previously been found that related amidino-derivatives $(Me_2N.CR:NAlR_2)_2$ may lose RCN to form dimethylamino-aluminium alkyls $(Me_2NAlR_2)_2$.[116]

In conclusion, the guanidine adducts and guanidino-derivatives prepared in this work probably have structures as shown in Figures V.d and V.g, respectively, with the imino-nitrogen, but not the amino-nitrogens, of the guanidine residue attached to aluminium, though these structures are not unambiguously supported by all the spectroscopic data obtained.

TABLE V.3

Mass spectroscopic results for $[(Me_2N)_2C{:}NAlEt_2]_2$

m/e	Relative Intensity	Assignment
398	20	$(Me_2N)_4(CN)_2Al_2Et_4$
370	100	$(Me_2N)_4(CN)_2Al_2Et_3H$
300	9	$(Me_2N)_3CNAl_2Et_3H$
241	16	$(Me_2N)_2CNAl_2Et_2CH_3$
231	9	$(Me_2N)_2Al_2Et_3H$ plus H
203	12	$(Me_2N)_2Al_2Et_2H_2$ plus H
198	9	$(Me_2N)_2CNAlEt_2$ minus H
170	25	$(Me_2N)_2CNAlEt$
101	9	$Me_2NAlEtH$
100	13	Me_2NAlEt
86	5	$Me_2NAlEtH$ minus Me
70	20	Me_2NCN

CHAPTER VI

This chapter describes the preparation of a series of di-t-butylmethyleneaminosilanes, $^{t}Bu_2C:NSiR_nCl_{3-n}$ (R = Me, n = 0 to 3; R = vinyl, n = 1). On the basis of their i.r. and ^{1}H n.m.r. spectra, these compounds are thought to contain linear C=N≐Si units, the stereochemical requisite for appreciable N ⟶ Si (p ⟶ d) multiple π-bonding.

EXPERIMENTAL SECTION

Starting Materials

Trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, vinyltrichlorosilane and silicon tetrachloride were distilled before use. Di-t-butylmethyleneaminolithium was prepared in situ as required by mixing equimolar amounts of t-butyl-lithium and t-butyl cyanide.

Manipulations were carried out using a nitrogen-filled glove box or nitrogen-filled apparatus as appropriate.

The reaction between trimethylchlorosilane, Me_3SiCl, and di-t-butylmethyleneaminolithium, $^{t}Bu_2C:NLi$, to give di-t-butylmethyleneaminotrimethylsilane, $^{t}Bu_2C:NSiMe_3$, has already been described in the Experimental Section of Chapter I.

Reaction of Dimethyldichlorosilane with di-t-butylmethyleneaminolithium

Dimethyldichlorosilane (2·58 gm., 20 mmole) was added to a solution of di-t-butylmethyleneaminolithium (2·94 gm., 20 mmole) in hexane (30 ml.) at -196°. As no precipitate was evident on warming the mixture to room temperature, the mixture was refluxed at 80° for several hours, whereupon a white solid was formed. After filtration and removal of solvent, the pale yellow residual liquid was identified as di-t-butylmethyleneaminodimethylchlorosilane, $^{t}Bu_2C:NSiMe_2Cl$. (Found: C,56·7; H,9·6; Cl,15·6; N,5·7%; M,214. $C_{11}H_{24}ClNSi$ requires C,56·7; H,10·1; Cl,15·2; N,6·0%; M,233). ν_{max} (Liquid film) 2959vs, 2933s,sh, 2874ms, 1736vs, 1610vw, 1486ms, 1468m,sh, 1395m, 1370m, 1325vw, 1297vw, 1258s, 1233m, 1205w, 1172w, 1045ms,br, 965ms, 940m, 910s, 831vs, 820vs, 794vs, 664m, 578w,br, 542w,br and 480ms,br cm^{-1}.

Reaction of Dimethyldichlorosilane with di-t-butylmethyleneaminolithium (2 molar equivalents)

In two different experiments, mixtures of dimethyldichlorosilane (1·29 gm., 10 mmole) and di-t-butylmethyleneaminolithium (2·94 gm., 20 mmole) were heated together for 20 hours at 80° in hexane, and for several days at 120° in toluene. After filtration and removal of solvent, the final product in each preparation was identified (by i.r. and mass spectra) as di-t-butylmethyleneaminodimethylchlorosilane, $^{t}Bu_2C{:}NSiMe_2Cl$.

Reaction of Methyltrichlorosilane with di-t-butylmethyleneaminolithium

A mixture of methyltrichlorosilane (2·99 gm., 20 mmole) and di-t-butylmethyleneaminolithium (2·94 gm., 20 mmole) in petroleum ether (30 ml.) was heated at 70° for several hours. Filtration and vacuum removal of solvent left a pale yellow liquid which, after distillation from a greaseless apparatus at 79-80°/0·8 mm, was identified as di-t-butylmethyleneaminomethyldichlorosilane, $^{t}Bu_2C{:}NSiMeCl_2$. (Found: C,47·9; H,8·9; Cl,27·3; N,5·3%; M,241. $C_{10}H_{21}Cl_2NSi$ requires C,47·2; H,8·3; Cl,28·0; N,5·5%; M,254). ν_{max} (Liquid film) 2950s, 2915s, 2857s, 1762ms,sh, 1736vs, 1672m, 1531w, 1484ms, 1468ms,sh, 1404w,sh, 1393m, 1368ms, 1292w, 1263ms, 1232w, 1202w, 1149m, 1078ms,br, 1044s, 1005m, 966ms, 942w, 914ms, 815s, 797s,br, 741w, 733w, 642w, 614w,br, 581w,br, 541m,br, 525m,br and 500m,br cm^{-1}.

Reaction of Methyltrichlorosilane with di-t-butylmethyleneaminolithium (2 and 3 molar equivalents)

In two separate experiments, methyltrichlorosilane (1·50 gm., 10 mmole) was heated in toluene at 110° for several days with two molar equivalents of di-t-butylmethyleneaminolithium (2·94 gm., 20 mmole) and with three molar equivalents of di-t-butylmethyleneaminolithium (4·41 gm., 30 mmole). In each case the only product of reaction was a pale yellow liquid, identified by its i.r. spectrum and boiling point as di-t-butylmethyleneaminomethyldichlorosilane, $^{t}Bu_2C{:}NSiMeCl_2$.

Reaction of Silicon Tetrachloride with di-t-butylmethyleneaminolithium

A mixture of silicon tetrachloride (2·89 gm., 17 mmole) and di-t-butylmethyleneaminolithium (2·50 gm., 17 mmole) in hexane (30 ml.) was refluxed at 80° for 20 hours. After filtration and removal of solvent, the residue was distilled from a greaseless apparatus to give a colourless liquid which was identified as di-t-butylmethyleneaminotrichlorosilane, $^{t}Bu_2C{:}NSiCl_3$, b.p. 96-98° at 0·005 mm. (Found: C,40·3; H,6·2; Cl,37·6; N,4·8%; M,286. $C_9H_{18}Cl_3NSi$ requires C,39·5; H,6·6; Cl,38·6; N,5·1%; M,274). ν_{max} (Liquid film) 2959vs, 2924vs,sh, 2874s, 1754vs,sh, 1742vs,sh, 1729vs, 1668m, 1537w, 1486s, 1468s,sh, 1395ms, 1370s, 1261w, 1235ms, 1202w, 1152w,sh, 1087m,br, 1045s, 1005m, 965s, 949ms, 923s, 890m, 840w, 814vs, 803s, 738w, 641w, 590vs, 562vs, 540vs,br, 522vs, and 489m,br cm^{-1}.

Reaction of Silicon Tetrachloride with di-t-butylmethyleneaminolithium (4 molar equivalents)

The only product obtained after heating a mixture of silicon tetrachloride (1·70 gm., 10 mmole) and di-t-butylmethyleneaminolithium (5·88 gm., 40 mmole) in toluene (20 ml.) for several days was di-t-butylmethyleneaminotrichlorosilane $^{t}Bu_2C{:}NSiCl_3$.

Reaction of Vinyltrichlorosilane with di-t-butylmethyleneaminolithium

A mixture of vinyltrichlorosilane (3·23 gm., 20 mmole) and di-t-butylmethyleneaminolithium (2·94 gm., 20 mmole) in hexane (30 ml.) was stirred at room temperature overnight. After filtration and removal of solvent, the residual yellow liquid was distilled to yield a pale yellow liquid, identified as di-t-butylmethyleneaminovinyldichlorosilane, $^{t}Bu_2C{:}NSi(CH{:}CH_2)Cl_2$, b.p.

64-66° at 0·05 mm. (Found: C,49·2; H,7·9; Cl,26·2; N,5·3%; M,259. $C_{11}H_{21}Cl_2NSi$ requires C,49·5; H,7·9; Cl,26·6; N,5·3%; M,266). ν_{max} (Liquid film) 3062w,sh, 2959s, 2924ms,sh, 2874m,sh, 2801w,sh, 1927vw, 1825vw, 1742vs, 1736vs, 1674m, 1604w, 1534w, 1484m, 1460m,sh, 1401m,sh, 1395m, 1368m, 1261vw, 1235m, 1202w, 1152w,sh, 1081m,br, 1046m, 1005m, 1000m,sh, 967ms, 943w, 915m, 841w, 813ms, 741w, 717ms, 644w, 592ms, 568ms,br, 541m,br, 535m,br, and 492w,br, cm^{-1}

DISCUSSION

The question of N → Si (p → d) π multiple bonding has been extensively studied and several reviews have recently appeared.[244,245] Electron-diffraction studies on silylamine derivatives have been interpreted in terms of substantial double-bond character in the Si-N bonds. Compounds recently reported include: $(H_3Si)_3N$,[246,247] which shows an almost planar arrangement about the central nitrogen; $(H_3Si)_2NN(SiH_3)_2$,[248] which has a planar Si_2NN group; $ClSi(NMe_2)_3$,[249] which has a planar configuration of the nitrogen atoms; $(SiH_3)_2NH$,[246] $(Me_3Si)_2NH$[250] and $(SiH_3)_2N.BF_2$,[250,251] the latter having planar Si_2NB and NBF_2 groups which are slightly twisted with respect to one another; and H_3SiNMe_2,[252] where the Si-N bond length supports some degree of (p → d) π-bonding but the $SiNC_2$ skeleton is non-planar, a result which is in agreement with the relatively high basicity of the nitrogen in this compound. These compounds, together with $[(Me_3Si)_2N]_2Be$,[253] $[(Me_3Si)_2N]_3Al$[229] and $(Me_3SiNSiMe_2)_2$[254] whose structures have been examined by X-ray crystallographic methods, all show marked stereochemical inactivity of the nitrogen lone pairs and relatively short Si-N bond lengths (1.72-1.75Å), results interpreted in terms of substantial N → Si (p → d) π-bonding which will be maximised if the lone pair is in a pure 'p' orbital; similar arguments have been invoked to explain the structural characteristics of aminoboranes (see pages 59-63). Similarly, near-linear M-N-C units (M = Si, Sn), the shape appropriate for optimum N → M π-bonding, have been found in the crystal structures of $Si(NCS)_4$,[255] $Si(NCO)_4$,[256] H_3SiNCS,[257] Me_3SnNCS,[258] $Me_2Sn(NCS)_2$[259,260] and $[(Me_2SnNCS)_2O]_2$,[261] the angles M-N-C varying from 168-176°, although angular units (M-N-C angle ca.154°) apparently exist in gaseous Me_3SiNCS and Me_3SiNCO.[262] It has, however, been noted[263] that although such planar and linear configurations do in theory optimise N → M π-bonding, such bonding is at least possible to some degree in compounds having pyramidal or angular units, such as the pyramidal (by ^{15}N n.m.r. studies) trimethylsilylanilines[264] and the apparently non-linear (by u.v. spectroscopic studies) iminosilanes.[35] The chemical and physical properties of Group IV amines have also given much information regarding the occurrence and degree of N → M π-bonding. Studies reported include: changes in reactivity[245] and basicity[265,266] of Group IV amines in the order $M = Si < Ge < Sn$, explicable in terms of the expected diminution of N → M π-bonding in the order $M = Si > Ge > Sn$; electronic absorption spectra of a number of aminosilanes[267] which indicate that localised N → Si π-bonding can and does occur in a single Si-N bond; vibrational frequencies,[268,269] leading to force constants and hence M-N bond orders; <u>ab initio</u> calculations on trisilylamine,[270] where the energy of the π-bond has been estimated to be as much as 16 $kcal.mole^{-1}$, and on silylamine.[271] Chloroaminosilanes[272] have also recently been studied by ^{1}H n.m.r. techniques and are of special interest as, in theory, both the chloro- and amino-groups can be involved in π-bonding to silicon; the photoelectron spectra of Group IV halides[273,274] have recently provided substantial evidence that (p → d) π-bonding between the halide and the metalloid does occur in all but the carbon halides.

This chapter reports the preparation and some properties of a series of di-t-butylmethyleneaminosilanes, $^{t}Bu_2C{:}NSiR_nCl_{3-n}$ ($R = Me$, $n = 0 \rightarrow 3$; $R =$ vinyl, $n = 1$).

As noted in earlier chapters, the presence of high azomethine stretching frequencies in the i.r. spectra of compounds containing a ketimino-group attached to a co-ordinatively unsaturated metal or metalloid, M, has been interpreted as indicative of the presence of linear $C{=}N{\stackrel{.}{=}}M$ units in such compounds, a view recently confirmed by X-ray crystallographic studies on $Ph_2C{:}NBmesityl_2$[159] (see p.50) and $LiAl(N{:}C^{t}Bu_2)_4$[47a,b] (see p.89). In addition, the simple ^{1}H n.m.r. of the t-butyl groups in the $^{t}Bu_2C{:}N$-residue has been used as a probe to investigate the arrangement of the C=N-M linkage in such compounds. Earlier studies on diphenylmethyleneaminosilanes,[35] whose u.v.[35] and i.r.[12,32] spectra were interpreted in terms of angular C=N-Si units

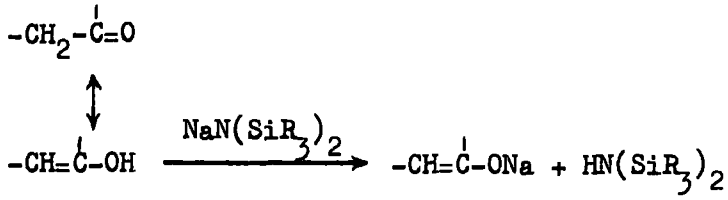
(Figure VI.a), were complicated by their susceptibility to disproportionation, a tendency which it was hoped would be nullified by the bulk of the t-butyl groups. Finally, di-t-butylmethyleneaminotrimethylsilane, $^tBu_2C:NSiMe_3$, was of particular interest as, by analogy with diarylmethyleneaminotrimethylsilanes, it was likely to prove to be a useful intermediate in the synthesis of di-t-butylmethyleneamino-derivatives of other Main Group elements.

Iminosilanes, $R^1R^2C:NSiR_3$, have found use both synthetically, as intermediates in the preparation of other organometallic systems,[275] and industrially, for example, in vulcanisation composites.[276] Compounds with $R^1 = H$ (aldiminosilanes),[277] $R^1 = OSiR_3$ (imidatosilanes),[276,278-281] $R^1 = NR_2$ (amidinosilanes)[282] and $R^1 = RO$, $R^2 = NR_2$[283] have been extensively studied, and various routes to these compounds have recently been reviewed.[284] Essentially two main preparative routes have led to alkylideneaminosilanes (R^1, R^2 = H, alkyl, aryl). The first, the reaction between non-enolisable aldehydes and ketones with sodium bis(trimethylsilyl)amide[285] (Equation VI.1), has been used to prepare iminosilanes, which, in turn, have been reacted with diarylboron halides (Equation VI.2) to give iminoboron derivatives of imines which cannot themselves be prepared (for example, the compounds $R^1R^2C:NBAr_2$ where $R^1 = Ph$, $R^2 = H$ and $R^1 = R^2 = C_{12}H_8$)[53]

$$NaN(SiR_3)_2 + R^1R^2C:O \longrightarrow R^1R^2C:NSiR_3 + NaOSiR_3 \qquad VI.1$$

$$R^1R^2C:NSiR_3 + Ar_2BX \longrightarrow R^1R^2C:NBAr_2 + R_3SiX \qquad VI.2$$

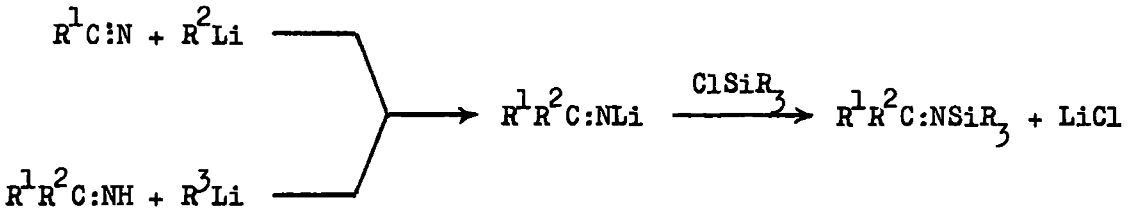
This route to iminosilanes cannot be applied to aldehydes or ketones having hydrogen atoms attached to the α-carbon atom, as the hydroxy proton in the enol form is readily exchanged with the sodium ion of the silyl amide, consequently forming sodium enolate and disilylamine[286] (Equation VI.3)



$$-CH_2-\overset{|}{C}=O \;\updownarrow\; -CH=\overset{|}{C}-OH \xrightarrow{NaN(SiR_3)_2} -CH=\overset{|}{C}-ONa + HN(SiR_3)_2$$

VI.3

The second route, involving reaction between a ketimino-lithium derivative and an organosilicon halide (Equation VI.4), has previously been used, in the main, to prepare diarylketiminosilanes,[12,35] as it too is complicated by the possibility of imine-enamine tautomerism.

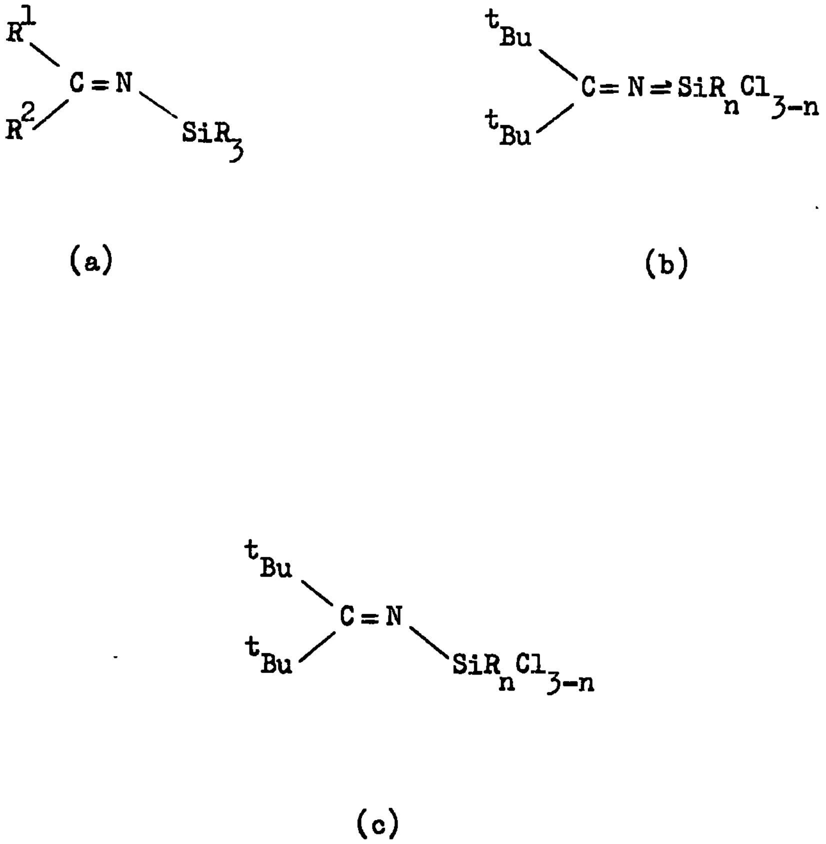


$$\left.\begin{array}{l} R^1C{:}N + R^2Li \\ R^1R^2C{:}NH + R^3Li \end{array}\right\} \longrightarrow R^1R^2C{:}NLi \xrightarrow{ClSiR_3} R^1R^2C{:}NSiR_3 + LiCl$$

VI.4

This route, analogous to that used to prepare aminosilanes by reaction of organosilicon halides with amino-lithium reagents such as $LiNMe_2$[287] and $LiN(SiCl_3)_2$,[288] was employed to prepare the new series of di-t-butylmethyleneaminosilanes, $^tBu_2C{:}NSiR_nCl_{3-n}$. The absence of α-C-attached hydrogens eliminates any complications due to tautomerism and, indeed, these are believed to be the first alkylideneaminosilanes, $R^1R^2C{:}NSiR_3$, where both R^1 and R^2 are alkyl groups, although compounds having perhalogenated alkyl groups R^1 and R^2 have previously been prepared.[35]

FIGURE VI



(a) (b)

(c)

Reactions between di-t-butylmethyleneaminolithium and chlorosilanes Me_nSiCl_{4-n} ($n = 0 \rightarrow 3$) (Equation VI.5) gave pale yellow or colourless liquids of general formula $^tBu_2C{:}NSiMe_nCl_{3-n}$ ($n = 0 \rightarrow 3$). The liquids could be distilled at temperatures up to 100° without disproportionating into bis(alkylideneamino)-silanes.

$$^tBu_2C{:}NLi + Me_nSiCl_{4-n} \longrightarrow {}^tBu_2C{:}NSiMe_nCl_{3-n} + LiCl \qquad VI.5$$

Indeed, attempts to prepare bis-, tris-, and tetrakis(alkylideneamino)silanes from reactions of $^tBu_2C{:}NLi$ with Me_2SiCl_2 (2:1), $MeSiCl_3$ (2:1 and 3:1) and $SiCl_4$ (4:1) resulted only in transfer of one alkylideneamino-group to the silicon, despite the use of vigorous reaction conditions (usually heating the reaction mixture at *ca.* 110° for one day). This is in marked contrast to the behaviour of the analogous $Ph_2C{:}NLi/Me_nSiCl_{4-n}$ ($n = 0 \rightarrow 2$) reaction systems[32,35] where, in all cases (as previously noted for the reaction where n = 2[35]) a disproportionation (Equation VI.6) occurs at or below room temperature, the products being the yellow solids, the bis(diphenylmethyleneamino)silanes, $(Ph_2C{:}N)_2SiMe_nCl_{2-n}$ ($n = 0 \rightarrow 2$).

$$\begin{array}{lcl} 2Ph_2C{:}NLi + 2Me_nSiCl_{4-n} & \longrightarrow & 2[Ph_2C{:}NSiMe_nCl_{3-n}] + 2LiCl \\ & & \quad \big\downarrow \; 20^\circ \qquad\qquad\qquad VI.6 \\ & & (Ph_2C{:}N)_2SiMe_nCl_{2-n} + Me_nSiCl_{4-n} \end{array}$$

$$n = 0 \rightarrow 2$$

Recent work[32] has shown that for the reaction where n = 2, disproportionation of the mono-substituted iminosilane is slow enough at room temperature to permit its characterisation as $Ph_2C{:}NSiMe_2Cl$; attempted distillation or standing for several days at room temperature gives the bis(imino)silane, $(Ph_2C{:}N)_2SiMe_2$.[32] This compound,[32,35] as well as the tris- and tetrakis-derivatives,

$(Ph_2C{:}N)_3SiMe$[35] and $(Ph_2C{:}N)_4Si$,[12] have also been prepared by reaction of $Ph_2C{:}NLi$ with Me_2SiCl_2 (2:1), $MeSiCl_3$ (3:1) and $SiCl_4$ (4:1). Reaction of $^tBu_2C{:}NLi$ with vinyl$SiCl_3$ gave the alkylideneaminosilane, $^tBu_2C{:}NSi(vinyl)Cl_2$ (Equation VI.7).

$$^tBu_2C{:}NLi + (CH_2{:}CH)SiCl_3 \longrightarrow {}^tBu_2C{:}NSi(CH{:}CH_2)Cl_2 + LiCl \qquad VI.7$$

The five new di-t-butylmethyleneaminosilnes all show strong bands in their i.r. spectra at ca.1730 cm^{-1} (Table VI.1), a position seemingly appropriate for assignment as the asymmetric stretching vibration of a linear C=N±Si unit (Figure VI.b) [cf. ν(C=N±B) for a series of di-t-butylmethyleneaminoboranes at ca.1830 cm^{-1}, see p.48]. A series of reported diphenylmethyleneaminosilnes,[12,32,35] on the other hand, show strong bands at ca.1650 cm^{-1}in their i.r. spectra, previously assigned as ν(C:N) of apparently bent C=N-Si links (Figure VI.a) [cf. ν(C=N±B) for $Ph_2C{:}NBmesityl_2$,[12,52,53] whose predicted allene-type structure has been confirmed by X-ray crystallography,[159] at 1792 cm^{-1}]. This absorption at ca.1650 cm^{-1} seems peculiarly insensitive to the number of ketimino groups attached to the silicon atom, ν(C:N) hardly changing in the compounds $(Ph_2C{:}N)_nSiMe_{4-n}$ ($n = 1 \rightarrow 4$), and this in itself suggests that there is little or no (p → d) π-bonding in the N-Si links of these derivatives. Their u.v. spectra, which show little change in the n → π* absorption maxima, have also been interpreted in terms of angular C=N-Si units.[35] (Figure VI.a). The azomethine stretching frequencies of the di-t-butylmethyleneaminosilanes are surprisingly insensitive to the nature of the other substituents on silicon, substitution of Me by Cl having no significant effect. The compound $^tBu_2C{:}NSi(vinyl)Cl_2$ shows ν(C=N±Si) in a similar position to the other four compounds, although a significant change in the N → Si π bond order might have been expected due to a competitive electron back-bonding Si ← Cπ interaction similar to that thought to be present in silylbutadienes[289] and silylethylenes.[290]

The di-t-butylmethyleneaminosilanes also have bands in the regions

899-923 cm^{-1} and 959-967 cm^{-1} in their i.r. spectra (Table VI.1), either of which would seem appropriate for assignment as Si-N stretching vibrations, ν(Si-N), by analogy with similar assignments for silazanes[291] (900-1000 cm^{-1}), N-trimethylsilylaniline[292] (899 cm^{-1}) and other previously reported iminosilanes[35] (900-925 cm^{-1}). The absorption ν(Si-N) in diphenylmethyleneaminesilanes has previously been assigned in the range 905-913 cm^{-1},[35] although re-examination[32] of the i.r. spectra of these compounds has shown that they too possess bands in a second range, 935-939 cm^{-1}.

Further evidence for N ⟶ Si (p ⟶ d) π-bonding in these di-t-butylmethyleneaminosilanes comes from the observed shift of ν(C-D) in the i.r. spectra of mixtures of $CDCl_3$ with the organometallic base, $\Delta\nu[= \nu(\text{C-D})_{\text{Free CDCl}_3} - \nu(\text{C-D})_{\text{mixture}}]$ being *ca.*40 cm^{-1} for all the five new compounds [*cf.* Δν for $^{t}Bu_2C{:}NBRR^1$ *ca.*10 cm^{-1},[31] for Me_3SiNEt_2 64 cm^{-1} and for Me_3CNEt_2 *ca.*100 cm^{-1} [266]].

The ^1H n.m.r. spectra of the compounds were recorded in toluene solution at +33° (Table VI.2) and at temperatures down to -60°. The t-butyl resonances retained their singlet nature on cooling, in contrast to those of the parent ketimine, $^{t}Bu_2C{:}NH$, which split into two resonances (separation 0.17 p.p.m.) of equal area at -60°. These results accordingly indicate either that the alkylideneaminosilanes have linear C=N±Si units (Figure VI.b) and hence the stereochemical requisite for appreciable N ⟶ Si multiple π bonding or that, if angular C=N-Si units are present (Figure VI.c), inversion at nitrogen is so rapid, even at -60°, that the ^1H n.m.r. technique is incapable of distinguishing the magnetically inequivalent t-butyl groups of such a structure.

The mass spectra of all the di-t-butylmethyleneaminosilanes were recorded, and masses, relative intensities and assignments of some of the peaks in two of them ($^{t}Bu_2C{:}NSiMeCl_2$ and $^{t}Bu_2C{:}NSiMe_3$) are shown (in Table VI.3 and VI.4 respectively). All the compounds $^{t}Bu_2C{:}NSiMe_nCl_{3-n}$ (n = 0 ⟶ 3) exhibit similar breakdown patterns, losing Me and/or Cl and C_4H_9 to give such species as $^{t}Bu_2C{:}NSiMeCl$, $^{t}Bu_2C{:}NSiMe_2$, $^{t}Bu_2C{:}NSiCl_2$ and $^{t}BuC{:}NSiMe_nCl_{3-n}$; this latter fragment then invariably loses butene to give $HCNSiMe_nCl_{3-n}$. All other species are caused by cleavage of the Si-N bond giving HCN, ${}^tBuCNH$ and Me_nSiCl_{3-n}, and other fragments caused by their breakdown. The compound ${}^tBu_2C{:}NSi(vinyl)Cl_2$ loses Cl, C_4H_9 and C_4H_8 but not, apparently, $CH{:}CH_2$. In all the spectra, the most abundant fragments are butyl groups.

TABLE VI.1

Azomethine stretching frequencies and suggested Si-N stretching frequencies for the di-t-butylmethyleneaminosilanes

Compound	ν(C:N) cm^{-1}	ν(Si-N) cm^{-1}
$^tBu_2C{:}NSiMe_3$	1735vs	959m 899s
$^tBu_2C{:}NSiMe_2Cl$	1736vs	965ms 910s
$^tBu_2C{:}NSiMeCl_2$	1736vs (1672m)	966ms 914ms
$^tBu_2C{:}NSiCl_3$	1729vs (1668m)	967ms 915m
$^tBu_2C{:}NSi(CH{:}CH_2)Cl_2$	1742vs, 1736vs (1674m)	965s 923s

All the i.r. spectra were recorded as Liquid Films.

TABLE VI.2

^1H n.m.r. spectroscopic results for the di-t-butylmethyleneaminosilanes

Compound	τ Values	
$^tBu_2C{:}NSiMe_3$	8.88s(18)	9.79s(9)
$^tBu_2C{:}NSiMe_2Cl$	8.84s(18)	9.52s(6)
$^tBu_2C{:}NSiMeCl_2$	8.88s(18)	9.40s(3)
$^tBu_2C{:}NSiCl_3$	8.86s(18)	
$^tBu_2C{:}NSi(CH{:}CH_2)Cl_2$	8.87s(18)	4.03s(3)

Spectra recorded at +33° as *ca.*20 wt.% solution in toluene.

$\tau(Me_4Si)$ = 10.00 p.p.m.

s = singlet; relative intensities in parentheses.

TABLE VI.3

Mass spectroscopic results for ${}^{t}Bu_2C:NSiMeCl_2$

m/e	Relative Intensity	Assignment
238	1.5	$Bu_2C:NSiCl_2$
218	5.5	$Bu_2C:NSiMeCl$
196	64	$BuC:NSiMeCl_2$
140	60	$HC:NSiMeCl_2$
113	27	$MeSiCl_2$
84	38	BuC:NH
63	8	SiCl
57	100	Bu
56	9	C_4H_8
41	88	MeCN
36	5	HCl
27	17.5	HCN
15	4	Me

TABLE VI.4

Mass spectroscopic results for ${}^{t}Bu_2C:NSiMe_3$

m/e	Relative Intensity	Assignment
198	2	$Bu_2C:NSiMe_2$
156	8	$BuC:NSiMe_3$
100	6	$HC:NSiMe_3$
84	48	BuC:NH
73	30	Me_3Si
57	100	Bu
56	10	C_4H_8
41	42	MeCN
27	12	HCN
15	5	Me

m/e values for fragments containing chlorine relate to ${}^{35}Cl$ isotopes

APPENDIX I

EXPERIMENTAL TECHNIQUES

1. Experimental Details

Most of the reactions described in this thesis 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 affected in the second limb of the Schlenk tube. In the case of liquid products, a solution of the product was transferred under nitrogen from the Schlenk tube to a greaseless apparatus from which it was distilled. 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 tank of liquid nitrogen, was dried by passage through two traps maintained at -196° and delivered to a 'pig' providing multiple outlets.

Glove Box

Samples for analysis and spectroscopic investigation 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 two furnaces at 400° containing copper wire (to remove traces of oxygen), and back to the box via a second trap at -196°.

Solvents

Pentane, hexane, petroleum ether, diethyl ether, benzene and toluene were dried and stored over extruded sodium. Carbon tetrachloride was dried and stored over phosphorus pentoxide. Chloroform was used freshly distilled from phosphorus oxide.

2. Instrumentation

Infrared Spectra

I.r. spectra in the range 2·5-25 microns were recorded on a Grubb-Parsons Spectromaster. Samples were in the form of Nujol mulls, KBr discs, thin films or solutions in a suitable solvent, as appropriate.

^{1}H n.m.r. spectra

These were recorded on a Perkin-Elmer R.10 spectrometer, operating at 60 MHz. Samples were either pure liquids or solutions in toluene, chloroform or carbon tetrachloride. Tetramethylsilane was usually used as the internal reference standard.

Mass Spectra

These were recorded on an A.E.I. M.S.9 instrument at 70 eV and an accelerating potential of 8 kV, with a source temperature of 150-250^o and electromagnetic scanning. Samples were introduced by direct insertion into the ion source.

Molecular Weights

These were determined either cryoscopically in benzene (where solubility permitted) or by osmometry (where air stability permitted). 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.

3. Analytical Methods

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser. Halogens were determined by fusion of the compound with potassium, followed by volumetric determination of the halide ions.

Lithium was determined by flame photometry. Boron was determined as boric acid after ignition of a weighed sample. Aluminium-attached alkyl groups were determined by measuring the alkane evolved when weighed samples were heated with dilute sulphuric acid; the aluminium content of the hydrolysate was determined by the 8-hydroxyquinoline method.

APPENDIX II

Reaction between Gallium Trichloride and di-t-butylmethyleneaminolithium

A solution of gallium trichloride (3·34 gm., 19 mmole) in ether (10 ml.) was added to a cooled solution (at -196°) of di-t-butylmethyleneaminolithium (2·79 gm., 19 mmole) in hexane (20 ml.). On allowing the reactants to warm up to room temperature, a pale yellow solution was formed and a white solid deposited. After 30 minutes stirring, solvent was removed and the residual yellow solid taken up in hot pentane. As filtration and cooling gave no crystals, the pentane was removed to leave a yellow oil. Addition of further pentane caused a pale yellow solid to be deposited and this was then characterised as dimeric di-t-butylmethyleneaminogallium dichloride, $(^t\mathrm{Bu}_2\mathrm{C{:}NGaCl}_2)_2$, m.p. 71°. (Found: H,6·2; Cl,26·1; Ga,25·3; N,4·7%. $C_{18}H_{36}Cl_4Ga_2N_2$ requires H,6·4; Cl,25·0; Ga,25·0; N,5·0%). ν_{max} (Nujol mull) 1647s, 1592w, 1517m, 1458vs,sh, 1445vs, 1397w, 1368s, 1299w, 1220w,sh, 1205w, 1195w,sh, 1155m, 1085w,br, 1026w,br, 969w,br, 901w, 837m, 797w,br, 727m,br, 645m and 468s cm^{-1}.

The compound proved insufficiently soluble in benzene for determination of its molecular weight, while its mass spectrum contained only organic fragments, presumably arising from its thermal decomposition. The ^1H n.m.r. spectrum of the compound (in $CHCl_3$ solution) shows only a singlet at 8·44τ.

Alkylideneaminogallanes have previously been prepared by two general routes, viz. by re-arrangement of adducts $\mathrm{RC{:}N,GaEt_3}$[117] to give dimeric aldimino derivatives $(\mathrm{RCH{:}NGaEt_2})_2$ (R = Ph, ^{t}Bu), and by thermal decomposition of adducts $\mathrm{Ph_2C{:}NH,GaR_3}$ (R = Me,Et,Ph)[89] to give dimeric ketimino derivatives $(\mathrm{Ph_2C{:}NGaR_2})_2$; similar alkane elimination reactions have been used to prepare aminogallanes of type $(\mathrm{R_2NGaMe_2})_2$[221,222] where, again, the preference for dimeric products is the dominant feature of the pyrolyses.

All alkylideneamino derivatives $(R^1R^2C{:}NMR^3R^4)_2$ (M = Al,Ga) are thought to have $(MN)_2$ four-membered ring structures, confirmed by X-ray crystallography for $({}^tBuCMe{:}NAlMe_2)_2$[151] and $(p\text{-}BrC_6H_4.CPh{:}NAlPh_2)_2$;[172] similar structures have been proposed, (on the basis of their i.r. spectra) for the compounds $({}^tBu_2C{:}NAlCl_2)_2$ [ν(C:N) at 1664 cm^{-1}, see p.78][26] and $[(Me_2N)_2C{:}NAlCl_2]_2$[33] [ν(C:N) at 1647 cm^{-1}, see p.103]. Although the molecular weight and mass spectrum of the compound obtained from the equimolar reaction of ${}^tBu_2C{:}NLi$ with $GaCl_3$ could not be obtained, its azomethine stretching absorption at 1647 cm^{-1} would seem appropriate for a bridging ketimino group [cf. ν(C:N) in the range 1612-1626 cm^{-1} for the derivatives $(Ph_2C{:}NGaR_2)_2$[89] (R = Me,Et,Ph)], so that a similar $(GaN)_2$ four-membered ring structure is proposed for this compound.

The di-t-butylmethyleneaminogallanes $({}^tBu_2C{:}NGaCl_2)_2$, $({}^tBu_2C{:}N)_3Ga$[32] and $LiGa(N{:}C{}^tBu_2)_4$[32] would seem, on the basis of their similar spectroscopic features, to be isostructural with their aluminium analogues which have been discussed in Chapter IV.

APPENDIX III

Reaction between Diphenylchlorophosphine and di-t-butylmethyleneaminolithium

Diphenylchlorophosphine, Ph_2PCl, (3.84 gm., 17 mmole) in toluene (10 ml.) was added by syringe to a cooled (-196°) solution of $^tBu_2C{:}NLi$ (2.50 gm., 17 mmole) in hexane (20 ml.). On warming to 18°, a deep yellow solution was formed and lithium chloride precipitated. After removal of solvents, the yellow residue was taken up in hot pentane and the solution filtered and cooled, to yield yellow needles of di-t-butylmethyleneaminodiphenylphosphine, $^tBu_2C{:}NPPh_2$, m.p. 41°. (Found: C,76.6; H,8.8; N,4.5%; M,340. $C_{21}H_{28}NP$ requires C,77.4; H,8.7; N,4.3%; M,325). ν_{max} (Nujol mull), 1942vw, 1883vw, 1812vw, 1647s, 1617ms, Nujol, 1435s, 1389ms,sh, 1368ms, 1316w, 1305w,sh, 1220ms, 1200s, 1176m,sh, 1160w,sh, 1116ms, 1106ms, 1090m, 1066m, 1044m, 1026m, 1015w,sh, 998w, 976ms, 876m, 848w, 801ms, 790ms, 752s, 746s, 737s, 721s, 694vs, 624w, 602w,br, 568m, 554vs, 532s,br, 508ms and 485m,br.

^1H n.m.r. spectra: in toluene at +33°, a multiplet at 2.29τ and a singlet at 8.68τ.

On cooling the solution down to -80°, the t-butyl resonance remained as a singlet.

: neat liquid at +50°, multiplets at 2.29τ(4) and 2.88τ(6) plus a singlet at 8.65τ(18).

The mass spectrum of the compound shows that it is monomeric in the vapour phase, the highest m/e fragment being at 325. Loss of a C_4H_9 group then occurs after which the N-P bond cleaves so that the remainder of the spectrum consists of the radicals Ph_2P and BuCN, and of fragments due to their breakdown.

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Enough of science and of art;
Close up these barren leaves;
Come forth, and bring with you a heart
That watches and receives.

William Wordsworth.

"The Tables Turned"
(Lyrical Ballads, 1778).