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Aluminium alkyls with heteroatoms.

XVII *. Mass spectrometry of dialkylaluminium-(*N*-methylsilyl)amides

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Abstract

Dialkylaluminium-(*N*-methylsilyl)amides give characteristic mass spectrometric fragments dependent on alkyl or aryl substituents at nitrogen in addition to the methylsilyl group. The mass spectra of these compounds formulated as R^1–$N(R^2)$–AlR^3_2 (R^1 = HMe_2Si, Me_3Si; R^2 = alkyl, Ph; R^3 = alkyl) were interpreted with regard to substituent effects. To verify the given interpretations some energy data are also presented. It is shown that energy data can also reveal the influence of several substituents on mass spectrometric fragmentations.

Introduction

Organic compounds which contain elements of both main groups 5 and 3 tend to form stable ring systems [1]. The known mass spectra of dialkylaluminium-(*N*-dial-

Table 1

Degrees of association of the compounds studied

Compound	R^3	R^3	R^3	Degree of association [a]
1	$SiMe_3$	Me	Me	1.98
2	$SiMe_3$	Me	Et	1.96
3	$SiMe_3$	Me	i-Bu	2.00
4	$SiMe_3$	Me	CH_2SiMe_3	2.00
5	$SiMe_3$	i-Pr	Me	2.06
6	$SiHMe_2$	i-Pr	Et	1.97
7	$SiMe_3$	Ph	Et	2.14
8	$SiMe_3$	Ph	i-Bu	1.5–1.6
9	$SiHMe_2$	t-Bu	Et	1.4–1.6
10	$SiHMe_2$	t-Bu	i-Bu	1.3–1.5

[a] Cryoscopic determination in benzene

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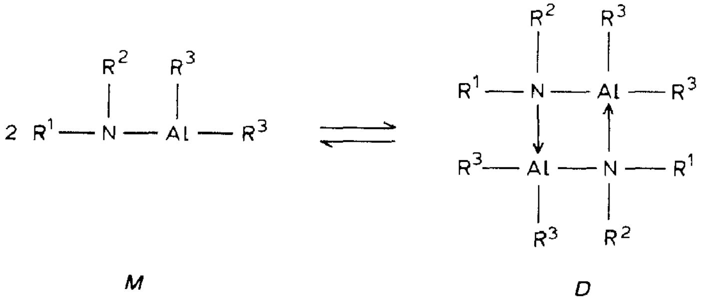
* For part XVI see ref. 4.

kyl)amides are characterized by a base peak resulting from a single Al–C bond cleavage [2,3]. The *m/z* values indicate the association of two molecules which leads to four-membered rings with highly stable Al–N bonds, and molecular ions were not observed. For our novel dialkylaluminium-(*N*-alkyl/aryl-*N*-silyl)amides of general formula R^1–$N(R^2)$–AlR^3_2 (R^1 = HMe_2Si, Me_3Si; R^2 = alkyl, Ph; R^3 = alkyl)., we have obtained NMR data [4] and have determined cryoscopically the molecular weights, which also indicate the existence of four membered N–Al rings (Scheme 1, Table 1).



Scheme 1. Structure of dialkylaluminium-(*N*-alkyl/aryl-*N*-methylsilyl)amides R^1–$N(R^2)$–AlR^3_2 (R^1 = HMe_2Si, Me_3Si; R^2 = alkyl, Ph; R^3 = alkyl; *M* = monomer; *D* = dimer)

Investigations of mass spectrometric fragmentation were expected to characterize the influence by several substituents connected to both the nitrogen and aluminium atoms, on the ring stability of the dimeric dialkylaluminium-(*N*-alkyl/aryl-*N*-silyl)amides. In addition, we will describe the ionization and appearance energies measured for several of our ions.

Results and discussion

Fragmentation reactions

The present *N*-methyl-substituted dialkylaluminium-(*N*-methylsilyl)amides (compounds **1** to **4**) gave the expected base peak due to the loss of an alkyl group from aluminium (compare the mass spectra in Fig. 1 for the compounds studied). All these compounds exist as dimeric, stable four-membered Al–N rings. Equation 1 gives an idea of the dominant primary fragmentation (see also Scheme 2).

$$[D]^{+\cdot} \rightarrow [D - R^3]^+ + {}^{\cdot}R^3 \qquad (1)$$

The molecular ion $[D]^{+\cdot}$ was not observed. As a primary fragmentation this favoured single bond cleavage directs the following fragmentation pathway. Metastable peaks reveal the transannular fragmentation of the $[D - R^3]^+$ ions (Scheme 2) but $[M - R^3]^+$ ions are less abundant in relation to $[D - R^3]^+$. In the spectra of compounds **5** and **6** we found that the abundance of $[D - R^3]^+$ ions does not lead to the base peak. The $[M - R^3]^+$ are the most abundant ions, which indicates the lowered stability of the four-membered ring system. Ring stability can be expressed as the abundance ratio R_s:

$$R_s = [D - R^3]/([M] + [M - R^3] + [M - R^3_2]) \qquad (2)$$

The denominator is calculated by summation of all the monomeric ion abundances (Table 2). Substituents connected to the nitrogen exert a greater influence on ring

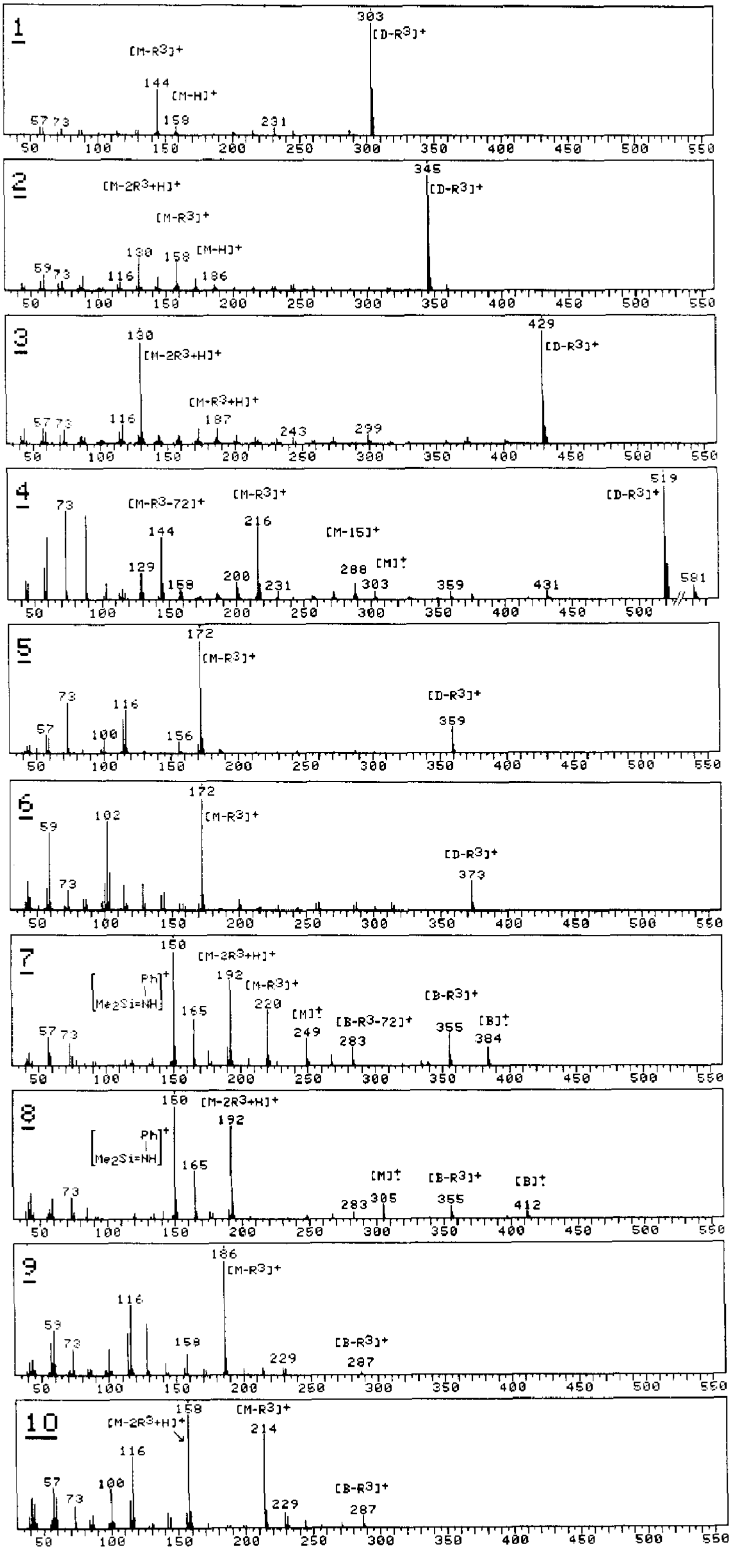
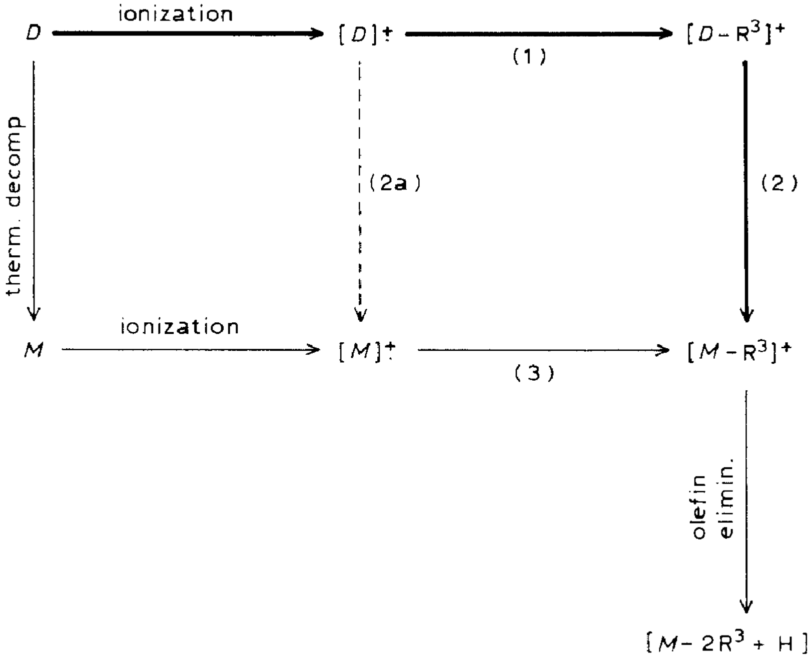


Fig. 1. Mass spectra of dialkylaluminium-(*N*-alkyl/aryl-*N*-methylsilyl)amides R^1–$N(R^2)$–AlR^3_2 (R^1 = HMe_2Si, Me_3Si; R^2 = alkyl, Ph; R^3 = alkyl; ion source: 200 °C; 70 eV).



Scheme 2. Fragmentation pathway of dialkylaluminium-(*N*-alkyl/aryl-*N*-methylsilyl)amides. M = monomer; D = dimer

stability than the substituents at the acceptor atom. Replacement of methyl or ethyl groups at aluminium by i-butyl groups reduces R_s from about 2.0 to 1.1. On the other hand, replacement of methyl with i-propyl at the nitrogen atom reduces R_s from 2.0 to 0.2. This decrease in ring stability is not consistent with the simple theory that a larger $+I$-effect of an alkyl substituent stabilizes the Al–N bond and hence the four-membered ring. We suggest that the unexpected destabilizing effect is because of dominant steric hindrance by the bulky alkyl groups. In connection with this behavior some groups have observed an unexpected change in the basicity of the nitrogen with amines [5,6]. Alkyl substituents with increasing $+I$-effect, contrary to what was expected under the inductive effect, actually lowered the basicity. Interpretation of the NMR and IR data show that this is caused predominantly by steric effects. The mass spectra of compounds **5** and **6** do not exhibit metastable peaks from transannular fragmentations, and thus, reconstruction of the

Table 2

Abundance ratio which characterizes the Al–N ring stability; $R_s = [D - R^3]/([M] + [M - R^3] + [M - R^3_2])$.

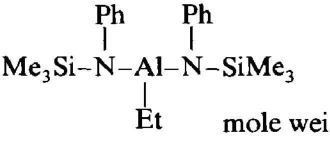
	Compound	R_s
1	$Me_3SiN(Me)AlMe_2$	1.9
2	$Me_3SiN(Me)AlEt_2$	2.1
3	$Me_3SiN(Me)Al(i\text{-}Bu)_2$	1.1
4	$Me_3SiN(Me)Al(CH_2SiMe_3)_2$	1.2
5	$Me_3SiN(i\text{-}Pr)AlMe_2$	0.2
6	$HMe_2SiN(i\text{-}Pr)AlEt_2$	0.2

fragmentation pathway is difficult. Scheme 2 includes all possible pathways leading to $[M-\mathrm{R}^3]^+$ ions. The bold line shows the pathway for compounds **1** to **4**. The main pathway for compounds **5** and **6** is along the thin arrows. The appearance energies observed support our premise, which will be discussed in detail. Reaction 2a (Scheme 2) does not seem to be a relevant fragmentation. Initial results of our study indicated that bulky alkyl substituents at nitrogen destabilize the four-membered Al–N-ring system, which, in turn corresponds with the possibility of thermal dissociation by some of the dimeric molecules before they have even reached the electron beam.

The formation of $[M-\mathrm{R}^3]^+$ is followed by an olefin elimination if alkyl substituents R^3 have more than one carbon atom. Butene elimination especially leads to intense peaks in the spectra of **3**. In the case of compound **4** no olefin elimination is detected because a double bond cannot be formed without skeletal rearrangement. Cleavage of the Si–N bond leads to significant peaks only with compound **1** (m/z 231). A dimethylmethylenesilane molecule is eliminated from the $[D-\mathrm{R}^3]^+$ ion, which seems to be comparable with other olefin eliminations that start from the $[M-\mathrm{R}^3]^+$ precursor ion, and is due to the great stability of the methyl-substituted Al–N-ring which has a low tendency to undergo transannular fragmentations.

The synthesis of *N*-phenyl substituted dialkylaluminium-(*N*-methylsilyl)amides was seen as a chance to lower the basicity of the nitrogen atom without steric complications. It is known that the planar phenyl ring requires much lower steric strain than that for the bulky i-alkyl groups. Indeed, the mass spectra of compounds **7** and **8** show drastically lowered ring stability owing to the influence of the phenyl substituent with its $-M$-effect. We did not detect $[D-\mathrm{R}^3]^+$ ions, which was the case for compounds **1** to **6** but found instead the $[M]^{+\cdot}$ ions and the additional, very intense (nearly 100%B) $[M-\mathrm{R}^3_2]^+$ ions. Only by in-beam measurements did we succeed in providing the existence of the $[D-\mathrm{R}^3]^+$ species. This suggests that the *N*-phenyl compounds are present only to a very low extent as dimers in the gas phase.

Cryoscopically determined degrees of association gave a value of 1.5 for compound **7**, thus showing that approximately 50% of the molecules are already in the monomeric form at the temperature of melting benzene. Up to this point the results obtained correspond to our expectations, but other peaks, which occur in the spectra contradict the molecular structure and known fragmentation pathways (e.g. m/z 384, **7**; m/z 412, **8**). The m/z 384 ion was found by high resolution mass spectrometry to have the formulation $\mathrm{C_{20}H_{33}AlN_2Si_2}$. The difference of 114 mass units between m/z 384 and the molecular ion of the diethylaluminium-(*N*-phenyl-*n*-trimethylsilyl)amide dimer could be regarded as the loss of one molecule of triethylaluminium. The ethylaluminium-bis(*N*-phenyl-*N*-trimethylsilyl)amide *B* (*B* = bis-amide) should result from such an elimination reaction.



$$\mathrm{Me_3Si{-}\overset{Ph}{N}{-}\underset{Et}{Al}{-}\overset{Ph}{N}{-}SiMe_3}$$

mole weight for $B = m/z$ 384

To verify this structure, we synthesized the bis-amide by reaction of one mole of triethylaluminium with two moles of *N*-phenyl-*N*-trimethylsilylamine. The ethylaluminium-bis(*N*-phenyl-*N*-trimethylsilyl)amide gives a mass spectrum similar to the spectrum of **7** with a molecular peak at *m/z* 384 and a $[M-29]^+$ peak at *m/z* 355. The peak ratio was comparable with the $[M]/[M-29]$ ratio of **7**. It is noteworthy that there were no NMR signals in the spectra of compound **7** that support either a dimeric or bis-amide structure. So we conclude that bis-amide formation must be thermally induced at the probe tip during sample evaporation. Thus in practice, bis-amide formation and the competing cleavage of the four-membered ring are complete before the sample vapor has reached the ionization chamber. It is noteworthy that the abundance ratio of $[M]/[B]$ remains constant with changing temperature of the ion source. Both ions are precursors of fragmentations that are comparable to single bond cleavage and to the olefin elimination described for compounds **1** to **6**. For example, compound **7** loses an alkyl substituent of aluminium to give the $[B-R^3]^+$ ion, *m/z* 355 or to $[M-R^3]^+$ ion, *m/z* 220, respectively. Decreased ring stability because of a weaker Al–N bond leads to a reduction in the donor strength of the nitrogen atom to give the highly abundant methylsilylamine ions, *m/z* 165 and *m/z* 150, of $[Me_3SiNHPh]^{+\cdot}$ and $[Me_2SiNHPh]^+$ respectively. On the other hand, the Al–C bond is stabilized because an $-M$ substituent is bonded to the nitrogen atom.

The N-t-butyl substituted compounds **9** and **10** undergo the same thermally induced reaction as that of compounds **7** and **8** during evaporation in the ionization chamber. The $+I$-effect of the t-butyl groups is superimposed by their steric

$$R_c=[M]/([M-R^3]+[M-R^3_2]) \tag{3}$$

influence which apparently lowers the ring stability. The monomer and bis-amide which result are represented by $[M-R^3]^+$ and $[B-R^3]^+$ ions, respectively, whereas molecular ions are not significantly in abundance. Compounds **7** to **10** are good examples of the dominant influence by the N-substituent on the Al–C bond stability, because no competing transannular fragmentation will lead to $[M-R^3]^+$ ions. In general $[M]^{+\cdot}$ ions are most suitable as precursor ions. Consequently, the abundance ratio R_c gives a simple quantitative expression (eq. 3) with regard to Al–C bond stability. Indeed the R_c values (Table 3) show the expected differences between N-phenyl an N-t-butyl compounds. However only small differences were observed between Al-diethyl and -di-i-butyl compounds. There are some complications. In some cases $[M-R^3]^+$ ions and the resultant $[M-R^3_2]^+$ ions may result from the cleavage of an Al–N single bond of the $[B]^{+\cdot}$ precursor ion. There was a metastable peak for such a fragmentation in the spectrum of 7. Small peaks at *m/z* 191 in the spectra of **7** and **8** are also attributable to such Al–N bond cleavage in the $[B-R^3]^+$ ion. Thus decomposition of $[B]^{+\cdot}$ could lower the value of R_c of compounds **7** and **8**, so that the difference in Al–C bond strengths might not give a

Table 3

Abundance ratio which characterizes Al–C bond stability; $R_c=[D-R^3]/([M]+[M-R^3]+[M-R^3_2])$

	Compound	R_c
7	$Me_3SiN(Ph)AlEt_2$	0.19
8	$Me_3SiN(Ph)Al(i\text{-}Bu)_2$	0.11
9	$HMe_2SiN(t\text{-}Bu)AlEt_2$	0.03
10	$HMe_2SiN(t\text{-}Bu)Al(i\text{-}Bu)_2$	0.02

true representation when expressed in terms of the abundance ratios from mass spectrometric fragmentation processes. Because the formation of $[B]^{+\cdot}$ from N-t-butyl compounds is less likely (no ions at *m/z* 150 or *m/z* 165 which would indicate Al–N bond cleavage in a bis-amide), a comparable influence on the R_c values was not expected in this case.

Energy data

The activation energy E_0 of a fragmentation reaction can be evaluated from the ionization energy of the molecule IE(M) and the appearance energy of the product ion AE($[M-R^3]^+$). If the energy of the reverse reaction is negligible, which is primarily the case for single bond cleavages, then the activation energy will give the bond dissociation energy of the molecular ion DE($[M]^{+\cdot}$); in this case for cleavage of the Al–C bond $[M]^{+\cdot} \rightarrow [M-R^3]^+ + \cdot R^3$ [8]. The activation energy of the fragmentation pathway 1 (Scheme 2) was calculated from eq. 4:

$$E_0 = \mathrm{AE}([M-R^3]^+) - \mathrm{IE}(M) = \mathrm{DE}([M]^{+\cdot}) \qquad (4)$$

A relationship between the activation energy and the bond dissociation energy of the neutral fragment is given in eq. 5.

$$E_0 = \mathrm{IE}([M-R^3]^{\cdot}) + \mathrm{DE}(M) - \mathrm{IE}(M) \qquad (5)$$

The dissociation energies of ions are normally not comparable with those of the neutral molecules because the stability of the resulting products and electron affinity of the hypothetical $[M-R^3]^{\cdot}$ radical are included in the bond dissociation energy determined for the ion. But if we compare compounds with bond stabilization effects of substituents which are expected to be larger than the changes in electron affinity, or if both effects are in the same direction bond dissociation energy changes at the ion show the same tendency as that for the neutral molecule. In this respect our results did throw some light on bond relations in dialkylaluminium-(*N*-alkyl/aryl-*N*-methylsilyl)amides. However, in some cases energy data permit reconstruction of the correct fragmentation pathway. The energy data are listed in Table 4. Some difficulties were encountered during our investigation. The ionization energies of dimeric molecules of compounds **1** to **6** could not be measured because molecular ions did not appear, and we were only able to measure the appearance energy values for $[D-R^3]^+$ ions from compounds **1**, **2** and **6**. The

Table 4

Energy data (in eV) for some dialkylaluminium-(*N*-alkyl/aryl-*N*-methylsilyl)amides. AE = appearance energy; IE = ionization energy; E_0 = activation energy; D = dimeric molecule; M = monomeric molecule; B = molecule with bis-amide structure $R^1N(R^2)Al(R^3)N(R^2)R^1$

Compound	AE($[D-R^3]^+$)	IE(M)	AE($[M-R^3]^+$)	E_0 for $[M]^{+\cdot} \rightarrow [M-R^3]^+$
1	9.2	–	10.7	1
2	9.2	–	–	1
6	8.0	8.2	8.8	0.6
7	–	8.5	9.6	1.1
		IE(B)	AE($[B-R^3]^+$)	E_0 for $[B]^{+\cdot} \rightarrow [B-R^3]^+$
7		8.5	10.3	1.8

value for **6** is 0.4 eV (38 kJ/mol) lower than those for **1** and **2**. From the literature we know that the ionization energy for alkylamine varies only from 8.97 eV for CH_3NH_2 to 8.87 eV for n- and i-$C_3H_7NH_2$ [9]. We conclude that the significant difference of the appearance energies of **1** and **2** compared with **6** reflects the tendency of Al–C bond stability to change with type of $[D-R^3]^+$ ion. On the other hand, the same appearance energy of the $[M-R^3]^+$ ion and the $[D-R^3]^+$ ion clearly show that our interpretation of the mass spectra of compounds **5** and **6** is valid. $[M-R^3]^+$ is formed from a real molecular ion $[M]^{+\cdot}$. This is produced by a thermal decomposition of the dimeric molecule before it undergoes fragmentation. Transannular fragmentation leads to a considerably higher appearance energy for $[M-R^3]^+$ such as that found with compound **1** (AE($[D-R^3]^+$) 9.2 eV and AE($[M-R^3]^+$) 10.7 eV). For compound **6**, we were able to determine the activation energy of the single bond cleavage $[M]^{+\cdot} \rightarrow [M-R^3]^+ + \cdot R^3$, viz. 0.6 eV (58 kJ/mol). A similar phenomenon was found for the ionization energies of $[B]^+$; and $[M]^{+\cdot}$ of compound **7**. The values are somewhat higher than the ionization energy IE(M) for **6**. In contrast to the Al–C single bond cleavage, which requires 1.1 eV (106 kJ/mol), the analogous cleavage requires 1.8 eV (173 kJ/mol) if a second *N*-phenyl-*N*-trimethylsilyl group is bonded to ethylaluminium. These results undoubtedly point to the fact that $[B]^{+\cdot}$ is indeed a molecular ion similar to $[M]^{+\cdot}$. Furthermore, has been shown that replacement of alkyl group with an electron-withdrawing phenyl group at the nitrogen atom enhances the activation energy of Al–C bond fragmentation. This energy is lowered, when electron-donating substituents are used. But *N*-phenyl substituents drastically reduce Al–N bond stability as is indicated by the partial thermal dissociation of dimeric dialkylaluminium-(*N*-phenyl-*N*-methylsilyl)amides, even at rather low temperatures. Otherwise bulky i-alkyl groups tend to decrease the Al–N bond stability of the dimers too, in spite of their +*I*-effect, because of their strong steric hindrance which strains the four-membered ring.

Experimental

Mass spectra were recorded on a Varian MAT CH6 mass spectrometer equipped with a direct insertion probe. EI parameters: electron energy 70 eV; source temperatur 200 °C. For the measurement of ionization and appearance energies argon was used as reference.

Compounds **1**–**10** were prepared by reaction of equimolar amounts of AlR^3_3 (or $HAlR^3_2$) with R^1R^2NH as described in detail elsewhere [4].

References

1 R.E. Bowen, K. Gosling, J. Chem. Soc. Dalton, (1974) 964.
2 K. Gosling, J.D. Smith, D.H.W. Warmby, J. Chem. Soc. A, (1969) 1738.
3 J.Z. Nyathi, J.M. Ressmer, J.D. Smith, J. Organomet. Chem., 70 (1974) 35.
4 G. Sonnek, M. Paech, J. Prakt. Chem., 329 (1987) 907.
5 S.W. Jarvie, D. Lewis, J. Chem. Soc., (1963) 4758.
6 E.W. Abel, D.A. Armitage, J. Chem. Soc. A, (1967) 554.
7 E.W. Abel, D.A. Armitage, Trans. Faraday Soc., 62 (1966) 3459.
8 K. Hottmann, Dissertation, Berlin, 1972.
9 R.W. Kiser, Introduction to Mass Spectrometry and its Applications, Prentice-Hall, Englewood Cliffs, NJ, 1965.