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REACTIONS OF SULFURDIIMINES AND SULFINYLANILINES WITH $[AlMe_3]_2$

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Summary

Reaction of sulfurdiimines RN=S=NR and the isoelectronic and structurally analogous sulfinylanilines RN=S=O with $[Me_3Al]_2$ gave the complexes $[Me_2Al\{RNS(Me)NR\}]_2$ (R = 4-MeC_6H_4, 4-ClC_6H_4, 2,6-$Me_2C_6H_3$) and $[Me_2Al\{RNS(Me)O\}]_2$ (R = Me, C_6H_5, 4-MeC_6H_4, 4-ClC_6H_4, 2,6-$Me_2C_6H_3$ and 2,4,6-$Me_3C_6H_2$) in which the S atom is methylated. Reaction of $[Me_2Al\{RNS(Me)NR\}]_2$ with $HgCl_2$ or $SnCl_2$ results in replacement of the methyl groups on the Al atom by Cl to give the dimeric $[Cl_2Al\{RNS(Me)NR\}]_2$ for R = 2,6-$Me_2C_6H_3$.

The dimeric complexes $[Me_2Al\{RNS(Me)X\}]$ (X = O, NR) exist in two conformations which undergo intramolecular interconversion in the case of the sulfurdiimine compounds, and probably also for the sulfinylaniline derivatives. In the latter case intermolecular exchange via a monomeric species also plays a role. This monomer may be observed in dilute solutions. While the sulfinylaniline compounds are stable in solution ($CDCl_3$, pyridine), the sulfurdiimine compounds decompose slowly in $CDCl_3$ and rapidly in pyridine to produce diazoaryls, some RNH_2 and polymeric products. The alcoholysis of the sulfurdiimine-Al complexes also usually give similar products. The possible roles of nitrene N—R and radical RNS—Me intermediates in the decompositions are discussed.

1. Introduction

The coordination of heteroolefins and the relation between their coordination to metal atoms and possible chemical activation has been studied in our

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laboratory mainly with compounds of α-diimines RN=CH—CH=NR [1—5], sulfurdiimines RN=S=NR [6,7] and the analogous sulfinylanilines RN=S=O [7,8] and sulfines [9,10]. While for RNSNR and RNSO, η^1-N, η^1-S and η^2-N=S coordination to metals has been observed, it has been demonstrated that chemical activation is favoured by initial η^2-N=S coordination to low valent electron-rich transition metal atom centres [6,7]. Most commonly the activated N=S bond is ruptured. The RNS, S and NR fragments so formed may then be captured with formation of cluster complexes [6,7]. It has further been demonstrated that chemical activation may also take place by addition of LiR′ or XMgR′ (R′ = alkyl, aryl) across one of the N=S double bonds. In the case of sulfurdiimines this affords the uninegative $[RNS(R')NR]^-$ ligand [11,12], which may then be bonded to Cu^I, Ag^I, Rh^I and Pd^{II} via metathesis reactions [12,13].

Unfortunately, the structural features of the Li and Mg complexes could not be studied in great detail. It was therefore of interest to investigate the reactions of $[Me_3Al]_2$ with RNSNR and RNSO in order to obtain more information about the structural and chemical behaviour of the $[RNS(Me)X]^-$ (X = O, NR) anions, which are isoelectronic with the well studied $[OS(Me)O]^-$ anion [14—17]. The results of this investigation are presented below.

2. Experimental

All manipulations were carried out under dry, oxygen-free nitrogen. The solvents were carefully dried and purified before use. The RNSNR and RNSO compounds were prepared by published procedures [18]. All complexes $[Me_2Al\{RNS(Me)X\}]_2$ (X = O, NR) are soluble in $CHCl_3$, CH_2Cl_2, benzene and toluene, but insoluble in pentane and hexane. The products are all pyrophoric in air and very susceptible to hydrolysis. The analytical data and molecular weights are listed in Table 1 and Table 2, respectively.

Preparation of $[Me_2Al\{RNS(Me)NR\}]_2$ *(R =* $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$ *and* $2,6\text{-}Me_2C_6H_3$*)*

A solution of 25% $[Me_3Al]_2$ in hexane (4.2 cm^3 containing 5 mmol $[Me_3Al]_2$) was added dropwise to a suspension of 10 mmol of RNSNR in

TABLE 1

ANALYTICAL DATA FOR $[Me_2AlRNS(Me)NR]_2$ (I), $[Me_2AlRNS(Me)O]_2$ (II) AND $[Cl_2AlRNS(Me)NR]_2$ (III)

R	Hydrolysable Methyl/Al	Analysis found (calcd.) (%)			
		Al	N	C	H
$4\text{-}MeC_6H_4$ (I)	1.9	8.48(8.58)	8.85(8.91)		
$4\text{-}ClC_6H_4$ (I)	2.0	7.55(7.60)	7.95(7.89)		
$2,6\text{-}Me_2C_6H_3$ (I)	2.0	7.80(7.88)	8.11(8.18)		
C_6H_5 (II)			6.73(6.63)	51.08(51.16)	6.51(6.68)
$4\text{-}MeC_6H_4$			6.20(6.22)	53.00(53.27)	7.34(7.16)
$4\text{-}ClC_6H_3$			5.89(5.70)	42.70(43.98)	5.41(5.33)
$2,6\text{-}Me_2C_6H_3$			5.81(5.85)	54.57(55.20)	7.62(7.58)
$2,4,6\text{-}Me_3C_6H_2$			5.39(5.53)	55.21(56.87)	8.03(7.96)
$2,6\text{-}Me_2C_6H_3$ (III)			7.35(7.31)	53.10(53.27)	5.45(5.52)

TABLE 2

MOLECULAR WEIGHTS OF $[Me_2AlRNS(Me)NR]_2$ (I), $[Me_2AlRNS(Me)O]_n$ (II) AND $[Cl_2AlRNS(Me)NR]_2$ (III) IN BENZENE

R	Concentration (dimer/l)	Molecular weight found (calcd. dimer)
$4\text{-}MeC_6H_4$(I)	2.0×10^{-3}	600 (629)
	1.9×10^{-2}	605
$4\text{-}ClC_6H_4$ (I)	1.9×10^{-3}	715 (710)
	2.1×10^{-2}	675
$2,6\text{-}Me_2C_6H_3$ (I)	9.4×10^{-4}	630 (684)
	1.7×10^{-2}	625
$2,6\text{-}Me_2C_6H_3$ (II)	2.0×10^{-3}	313 (479)
	7.8×10^{-3}	326
	9.0×10^{-3}	358
	2.5×10^{-2}	480
C_6H_5 (II)	3.1×10^{-3}	281 (422)
	5.5×10^{-3}	332
	8.6×10^{-3}	344
	1.3×10^{-2}	415
$4\text{-}ClC_6H_4$ (II)	4.4×10^{-3}	354 (492)
	7.7×10^{-3}	382
	1.4×10^{-2}	404
	1.9×10^{-2}	398
$2,6\text{-}Me_2C_6H_3$ (III)	1.5×10^{-3}	710 (767)
	2.1×10^{-2}	730

pentane at 0° C. At precisely a 1 : 1 molar ratio of Al to ligand the colour of the mixture changed from orange-yellow to white. The suspension was stirred for 24 h at room temperature to dissolve trace impurities. The precipitate was then filtered off, washed with cold pentane and dried under vacuum (yield 80—85%). The products are white, but become yellow-brown on storage at room temperature owing to thermal decomposition. The products are not very stable in $CHCl_3$ solution, since they start to decompose after 1 h at 0° C except for $2,6\text{-}Me_2C_6H_3$ which is much more stable. All products immediately decompose when dissolved in pyridine to give as in the case of $CHCl_3$, RN=NR (~10%), RNH_2 (~3%) and unidentified polymeric material.

Preparation of $[Cl_2Al\{RNS(Me)NR\}]_2$ $(R = 2,6\text{-}Me_2C_6H_3)$

15 cm³ of ether was added to a mixture of 5 mmol $[Me_2Al\{RNS(Me)RN\}]_2$ and 5 mmol of $HgCl_2$ or $SnCl_2$. The mixture was stirred for 30 min, after which the solvent was removed under vacuum. The resulting off-white product was kept under vacuum for 1 h to remove all traces of Me_2Hg. After addition of 20 cm³ of ether the precipitate was filtered off and dried under vacuum (yield 70%). Except for R = $2,6\text{-}Me_2C_6H_3$ the products are insoluble in all common solvents, and this prevented structural characterization.

Preparation of $[Me_2Al\{RNS(Me)O\}]_2$ $(R = Me, C_6H_5, 4\text{-}MeC_6H_4, 4\text{-}ClC_6H_4, 2,6\text{-}Me_2C_6H_3$ *and* $2,4,6\text{-}Me_3C_6H_2)$

A solution of 25% $[Me_3Al]_2$ in hexane containing 5 mmol of $[Me_3Al]_2$ was added dropwise to a solution of RNSO in 20 cm³ pentane at 0° C. At an Al to ligand ratio of 1 : 1 the colour changed abruptly from orange-yellow to white.

After 5 min stirring the precipitate was filtered off, washed with ice-cold pentane and dried under vacuum (yield 70%). The products are stable at room temperature both as solids and in solution, including solutions in pyridine.

Preparation of RN(H)S(Me)O ($R = Me$, C_6H_5, 4-MeC_6H_4, 4-ClC_6H_4, 2,6-$Me_2C_6H_3$ and 2,4,6-$Me_3C_6H_2$)

Excess water was added to a solution of $[Me_2AlRNS(Me)O]_2$ in CH_2Cl_2. After 60 min stirring the suspension was filtered off. The solvent was removed under vacuum and the resulting white powder collected and characterized by ^1H NMR as RNHS(Me)O (Yield 70—90%).

Reaction of $[Me_2Al\{RNS(Me)NR\}]_2$ with t-BuOH

Reaction of $[Me_2Al\{RNS(Me)NR\}]_2$ with t-BuOH in pentane resulted in decomposition, with the formation of RN=NR (25%), RNH_2 (5%) and polymeric material for $R = 4\text{-}MeC_6H_4$ and 4-ClC_6H_4. However, for $R = 2,6\text{-}Me_2C_6H_3$ no RN=NR was formed, but instead a compound of the composition $C_{17}H_{20}N_2S$ (exact mass determination) was isolated in 25% yield. In addition to polymeric material some RNH_2 (5%) was identified.

Analysis

The compounds $[Me_2Al\{RNS(Me)NR\}]_2$, could not be analyzed by standard elemental analytical methods owing to their extreme sensitivity to air. We therefore determined the quantity of methane evolved in the reaction with water. The residue was weighed and analyzed for Al and N (see Table 1).

The analyses of the other compounds has been carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO, Utrecht.

Molecular weight determination, NMR and IR spectroscopy

Molecular weights were determined by cryoscopy in benzene (Table 2). ^1H NMR spectra were recorded on Varian A-60 or T-60 spectrometers, ^{13}C NMR spectra were measured with a Varian CFT-20 or Bruker WP-80 spectrometer. The assignment of the ^{13}C NMR signals was carried out with the help of off-resonance ^1H decoupled ^{13}C NMR spectra. IR spectra of the sulphurinylaniline compounds in KBr discs and Nujol mulls were recorded on a Beckman 425 spectrophotometer.

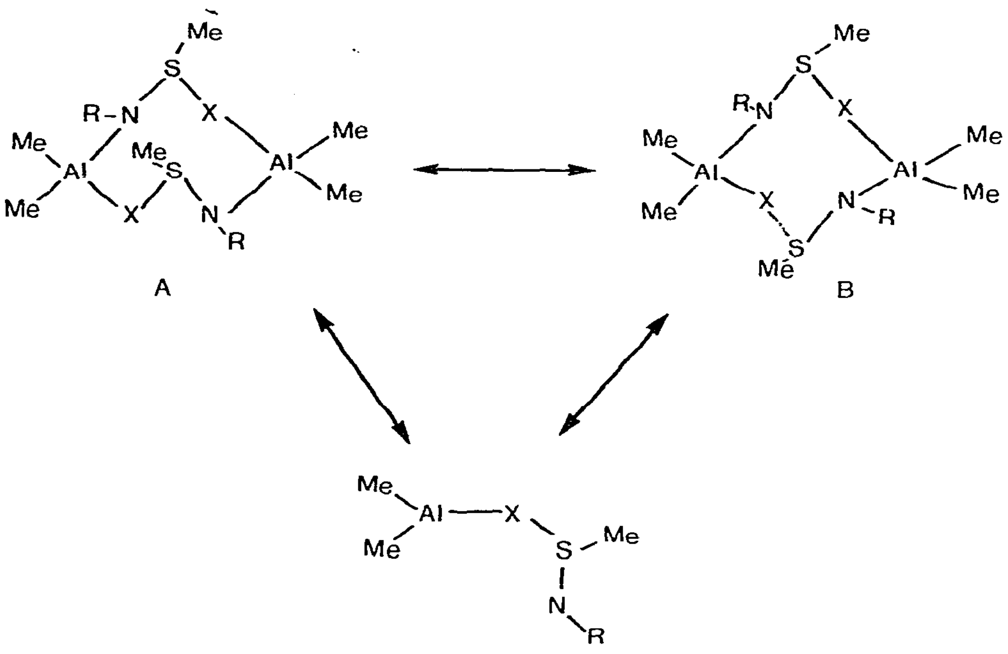
Results

Reaction of RNSNR or RNSO with $[Me_3Al]_2$ in 1 : 1 mol ratio gave white products in good yield. The reactions are very fast, like the corresponding reactions with LiR′ and XMgR′ [12], and may be used for the titration of $[R_3Al]_2$.

Analysis and molecular weight determinations of the white products are consistent with the formulation of these products as $[Me_2Al\{RNS(Me)X\}]_2$ ($X =$ O, NR). (See Tables 1 and 2). The suggested possible structures for these dimers are shown in Fig. 1 (A and B).

$[Me_2\{AlRNS(Me)NR\}]_2$ ($R = 4\text{-}MeC_6H_4$, 4-ClC_6H_4, 2,6-$Me_2C_6H_3$)

Molecular weight determinations in benzene show the complexes to be



(X=O or N-R)

Fig. 1. Two possible structures for $[Me_2Al\{RNS(Me)X\}]_2$ (X = O or NR) and the structure of the monomer $[Me_2Al\{XS(Me)NR\}]$. The R groups have been omitted for clarity.

dimeric with no observable concentration dependence (Table 2). For R = 4-MeC_6H_4 and 4-ClC_6H_4 the ^1H NMR spectrum is temperature dependent and consists of the superimposed resonance patterns of two distinct molecules. One pattern comprises 2 singlets upfield from TMS, one singlet at 2—3 ppm and an A-B multiplet at 6—8 ppm, the other only one singlet upfield from TMS, one singlet at 2—3 ppm and an A-B pattern at 6—8 ppm. At high temperatures (>40° C) the resonance pattern with one singlet upfield from TMS dominates, while at low temperature (—45° C), only the other resonance pattern of two Me resonances upfield from TMS is present (Fig. 2).

The relative intensities of the resonance patterns were concentration independent.

These observations indicate the presence of two conformations in solution which are interconverted slowly on the NMR time scale. The proposed structures (Fig. 1A and B) contain two S-methylated [RNS(Me)NR] ligands bridging the two Al atoms, as suggested for $[M\{RNS(R')NR\}]_2$ [12]. The eight-membered ring may exist in two conformations. One conformation has C_{2v} symmetry, giving to rise to two AlMe resonances upfield from TMS, while the other conformer with C_{2h} symmetry gives rise to only one AlMe signal. Apparently, the C_{2v} conformation is preferred at low temperature and the C_{2h} conformation at high temperatures. At 30°C the ratio C_{2v}/C_{2h} decreases in the order R = 4-MeC_6H_4 > 4-ClC_6H_4.

Mixing of two dimers having different R substituents did not give rise to

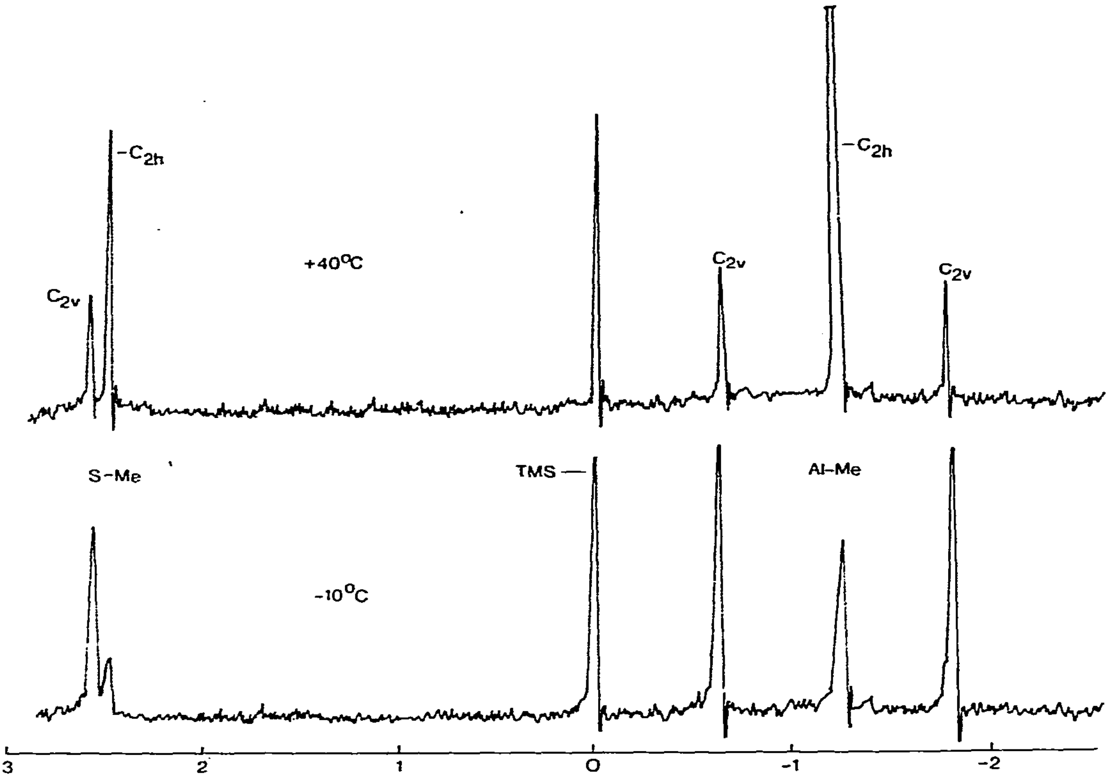


Fig. 2. Temperature dependence of the ^{1}H NMR spectrum of $[Me_2Al\{RNS(Me)NR\}]_2$ (R = 4-ClC_6H_4) in $CDCl_3$.

additional resonances attributable to mixed dimers, thereby excluding the possibility of intermolecular exchange of dimer halves or of ligands. Thus it is concluded that the interconversion between the two conformations is intramolecular.

Another interesting feature of the aluminium complex is that in $CHCl_3$ (or $CDCl_3$) there is a slow and in pyridine a fast decomposition to RN=NR (10%), RNH_2 (<3%) and unidentified polymeric material. Alcoholysis with t-BuOH also afforded RN=NR (25%), RNH_2 (5%) and again unidentified polymeric material, but only for R = 4-ClC_6H_4 and R = 4-MeC_6H_4. For R = 2,6-$Me_2C_6H_3$, however, we obtained no RN=NR, but instead a compound of composition $C_{17}H_{20}N_2S$.

$[Cl_2Al\{RNS(Me)R\}]_2$ (R = 2,6-$Me_2C_6H_3$)

Reaction of $[Me_2Al\{RNS(Me)NR\}]_2$ with $HgCl_2$ yielded a dimeric compound $[Cl_2Al\{RNS(Me)NR\}]_2$ for R = 2,6-$Me_2C_6H_3$, while insoluble materials were obtained for all other R groups. Both the ^{1}H and ^{13}C NMR spectra (Tables 3 and 4) of the dichloroaluminium compound show from 40 to −40°C the presence of only one S—Me resonance and two *ortho* methyl resonances. The *ortho* and *meta* ^{13}C atoms are non-equivalent, while C_1 and the *para* C_4 atoms each give rise to one signal. Therefore, it is concluded that (a) only one conformer is present in solution and (b) the R groups are equivalent, but cannot rotate freely about the N—C bond.

$[Me_2Al\{RNS(Me)O\}]_2$ (R = Me, Ph, 4-ClC_6H_4, 4-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$)

Molecular weight determinations in the case of $[Me_2Al\{RNS(Me)O\}]_n$ indicate that n varies from 1 at low to close to 2 at higher concentrations (Table 2). ^1H and ^{13}C NMR at high concentrations (0.5—1.0 mmol) show two resonance patterns, each consisting of one R, one S—Me and two Al—Me resonances (Fig. 3 and Tables 3 and 4). Molecular models suggest that two ring conformers (with the required symmetry) are possible, i.e. one with S_2 and one with C_2 symmetry (Fig. 1). In analogy to the sulfurdiimine complexes the two outer Al—Me resonances in the ^1H NMR spectra (Fig. 3) are assigned to the C_2 isomer. The assignment is suggested by similarities between both compounds in the temperature dependence and in the influence of the R groups on the con-

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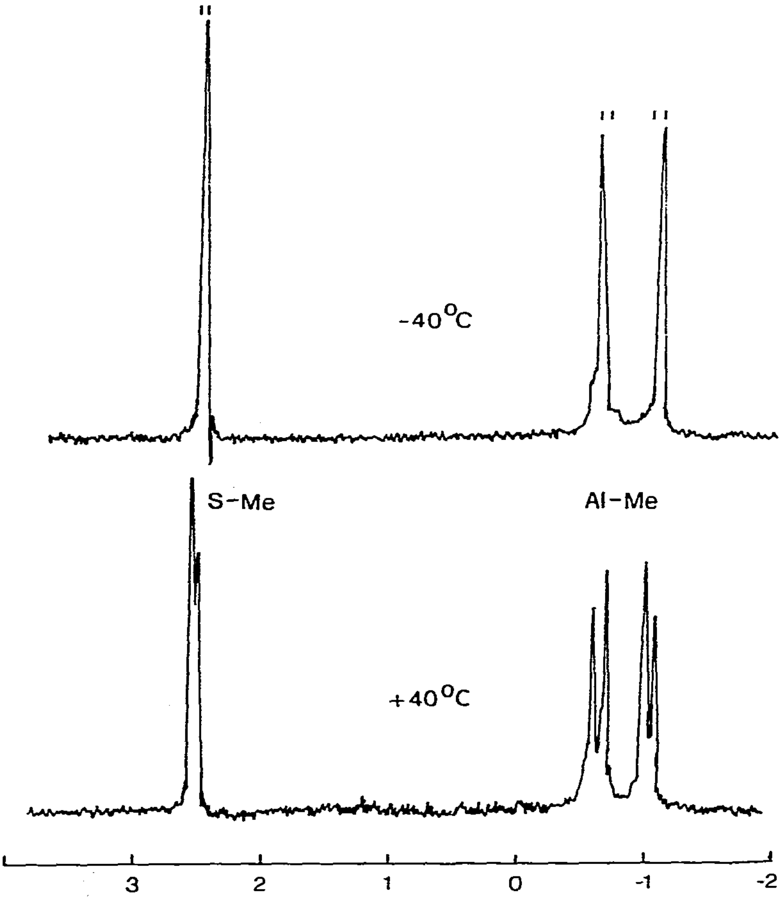

Fig. 3. Temperature dependence of the ^1H NMR spectrum of $[Me_2Al\{RNS(Me)O\}]_n$ (R = C_6H_5) in $CDCl_3$ (0.5 mol/l).

TABLE 3

^{1}H NMR DATA FOR $[Me_2AlRNS(Me)NR]_n$ (I) $[Me_2AlRNS(Me)O]_n$ (II), $[Cl_2AlRNS(Me)NR]_n$ (III) AND RN(H)S(Me)O (IV) IN ppm RELATIVE TO TMS [a, b]

R	Solvent	n	Aryl	Methyl groups				
				2	6	4	Al-Me	S-Me
4-MeC_6H_4 (I)	$CDCl_3$	2	6,93 6,65 [c]	—	—	2,19	—0,70 —1,87(—1,33)	2,51(2,42)
4-ClC_6H_4 (I)	$CDCl_3$	2	7,15 6,70(7,12 6,67 [c])	—	—	—	—0,53 —1,59(—1,10)	2,63(2,56)
2,6-$Me_2C_6H_3$ (I)	$CDCl_3$	2	7,02	2,47	2,47	—	—0,48 —0,74	2,58
4-MeC_6H_4 (III)	$CDCl_3$	2	7,02	—	—	2,39	—1,08 —0,62 (—1,01 —0,71)	2,48
4-MeC_6H_4 (II)	Pyr-d_5	1	7,18 (br)	—	—	2,20	—0,49	2,53
4-MeC_6H_4 (IV)	$CDCl_3$	—	6,76 7,40	—	—	2,25	—	2,74
4-ClC_6H_4 (II)	$CDCl_3$	2	7,23 (br)	—	—	—	—0,68 —1,13 (—0,74 —1,07)	2,46
4-ClC_6H_4 (II)	Pyr-d_5	1	7,29	—	—	—	—0,55	2,53
4-ClC_6H_4 (IV)	$CDCl_3$	—	6,87 7,18 [c]	—	—	—	—	2,81
2,6-$Me_2C_6H_3$ (II)	$CDCl_3$	2	7,03	2.16	2,59	—	—0,70 —1,22 (—0,87 —1,17)	2,42
2,6-$Me_2C_6H_3$ (II)	Pyr-d_5	1	7,10(br)	2.43(br)	2,43(br)	—	—0,58 (br)	2,43(br)
2,6-$Me_2C_6H_3$ (IV)	$CDCl_3$	—	6,90	2.23	2,23	—	—	2,71
2,4,6-$Me_3C_6H_2$ (II)	$CDCl_3$	2	6,86 6,80	2,13	2,52	2,25	—0,74 —1,24 (—0,86 —1,17)	2,41
2,4,6-$Me_3C_6H_2$ (IV)	$CDCl_3$	—	6,79	2.28	2,28	2,21	—	2,76
C_6H_5 (II)	$CDCl_3$	2	7,24 (br)	—	—	—	—0,65 —1,13 (—0,75 —1,05)	2,42(2,46)
C_6H_5 (IV)	$CDCl_3$	—	7,02 (m)	—	—	—	—	2,78
Me (II)	$CDCl_3$	2	2,62(2,64) N—Me	—	—	—	—0,89 —0,77 (—0,86)	2,71(2,75)
Me (II)	Pyr-d_5	1	2,58 N—Me	—	—	—	—0,57	2,71
Me (IV)	$CDCl_3$	—	2,67 N—Me [d]	—	—	—	—	2,52
2,6-$Me_2C_6H_3$ (III)	$CDCl_3$	2	6,63	2,30	2,46	—	—	2,58

[a] Concentration of the samples was 0,5—1 mol/l. [b] Values in parenthesis refer to isomer B, (Fig. 1). [c] J(A—B) = 8—9 Hz, br = broadened, m = multiplet.
[d] J((N)H—Me) = 5 Hz.

TABLE 4

SOME RELEVANT ^{13}C NMR DATA FOR [Me$_2$AlRNS(Me)NR]$_2$ (I); [Me$_2$AlRNS(Me$_2$O)]$_2$ (II) AND [Cl$_2$AlRNS(Me)NR]$_2$ (III) IN CDCl$_3$ [a]

R	Methyl groups			
	2	6	4	S-Me
4-MeC$_6$H$_4$ (II)	—	—	20.47	(36.07)35.52
4-ClC$_6$H$_4$ (II)	—	—	—	36.43(36.03)
2,6-Me$_2$C$_6$H$_3$ (I)	19.60	19.60	—	44.80
2,6-Me$_2$C$_6$H$_3$ (II)	21.61	(19.69)19.52	—	(35.55)35.46
2,6-Me$_2$C$_6$H$_3$ (III)	20.50	19.96	—	41.74
2,4,6-Me$_3$C$_6$H$_2$ (II)	21.48	19.45(19.72)	20.62	35.38(34.92)
C$_6$H$_5$ (II)	—	—	—	(36.66)36.48
Me (III)	(26.11)25.55	[N—Me]	—	(35.76)35.39

[a] Values in parenthesis refer to isomer B (Fig. 1).

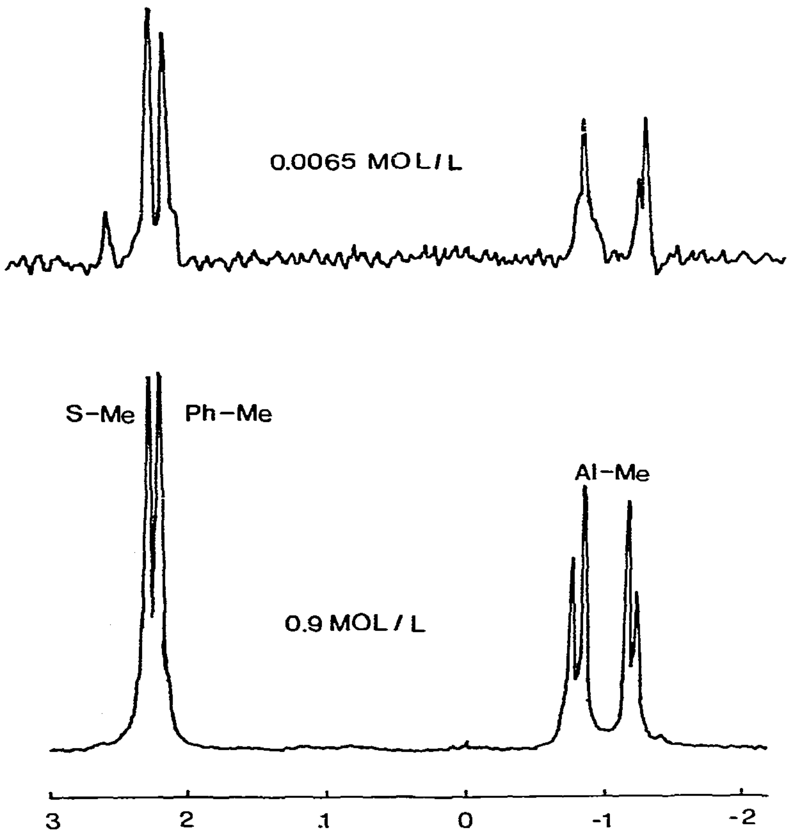

Fig. 4. Concentration dependence of the ^{1}H NMR spectrum of [Me$_2$Al{RNS(Me)O}]$_n$ (R = 4-MeC$_6$H$_4$) in CDCl$_3$.

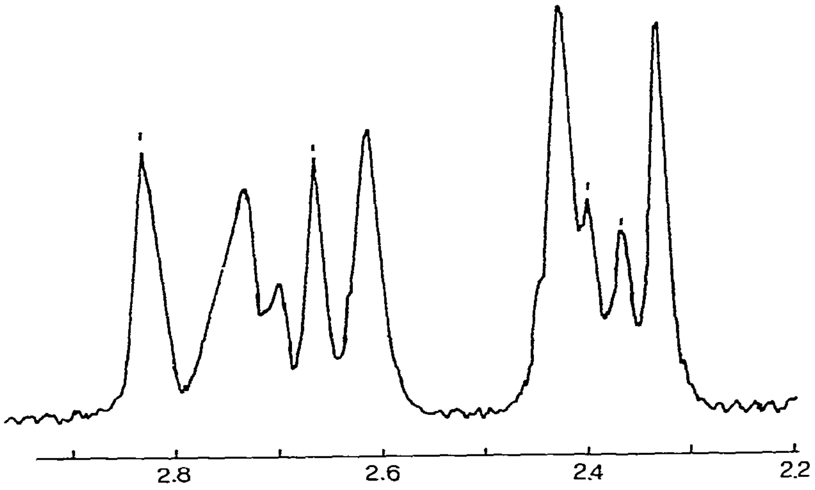

Fig. 5. ^1H NMR spectrum of a 1/1 mixture of $[Me_2Al\{4\text{-}MeC_6H_4)NS(Me)O\}]_n$ and $[Me_2Al\{(Me)NS\text{-}(Me)O\}]_n$ in $CDCl_3$. The marked peaks belong to the mixed dimer.

formational equilibrium constant K (C_2/S_2) (vide infra). K is independent of concentration and decreases in the order R = 2,4,6-$Me_3C_6H_2$ ≈ 2,6-$Me_2C_6H_3$ >> 4-MeC_6H_4 > Me > Ph > 4-ClC_6H_4 at 30° C. For all R groups the conformation with C_2 symmetry is preferred at low temperature and that with S_2 symmetry at high temperatures. The ^1H and ^{13}C NMR spectra further indicate that, as for $[Cl_2Al\{RNS(Me)NR\}]_2$, the rotation of the R group about the N—C bond is blocked for 2,6-$Me_2C_6H_2$ and 2,4,6-$Me_3C_6H_2$ substituents.

^1H NMR spectra at low concentrations (0.005 mol/l) show the appearance of an additional pattern i.e. one resonance at 2—3 ppm and a broad one upfield from TMS, which are respectively assigned to the S—Me and the Al—Me groups of a monomeric species (Fig. 4).

Moreover, the ^1H NMR spectrum of a 1 : 1 mixture of $[Me_2Al\{MeNS\text{-}(Me)O\}]_n$ and $[Me_2Al\{4\text{-}MeC_6H_4NS(Me)O\}]_n$ shows the appearance of additional signals owing to the formation of a mixed dimer (Fig. 5). This indicates that in addition to an intramolecular conformational exchange between the two dimeric conformers there is also an intermolecular exchange between dimer and monomer (Fig. 1).

Addition of pyridine-d_5 to solutions of $[Me_2Al\{RNS(Me)O\}]_n$ in $CDCl_3$ results in the coalescence of the Al—Me signals in the ^1H NMR spectra. In pyridine d_5 alone the coalescence is complete and only one Al—Me resonance was observed. This is consistent with the formation of monomeric $[Me_2Al\{RNS(Me)O\} \cdot \text{pyridine}]$ (Table 3).

For R = 2,6-$Me_2C_6H_3$ and 2,4,6-$Me_3C_6H_2$ the *ortho* methyl peaks coalesced in addition to those of the Al—Me groups, indicating that the rotation of the R groups is no longer blocked in the monomer.

IR spectrum of $[Me_2Al\{RNS(Me)O\}]_2$ and RN(H)S(Me)O

Complete assignment of the vibrational spectra of these compounds was unfortunately impossible due to both their complexity and because their

TABLE 5

IR DATA FOR $[Me_2AlRNS(Me)O]_2$ (II) AND RN(H)S(Me)O (IV) IN cm^{-1} (KBr DISC AND NUJOL MULL)

R	ν(N—S)	ν(CO)	ν(N—Ph)	δ(HCH)	δ(HCS)
$C_6H_5(^{14}N)$ (II)	942	970	1211	1405	1305
C_6H_5 (^{14}N) (IV)	[a]	1056	1229	1404	1302
C_6h_5 (^{15}N) (II)	932	970	1203	1405	1305
C_6H_5 (^{15}N) (IV)	[a]	1056	1225	1404	1302
4-MeC_6H_4 (II)	927	982	1214	1413	1303
4-MeC_6H_4 (IV)	[a]	1027	1227	1405	1299
4-ClC_6H_4 (II)	933	982	1219	1407	1304
4-ClC_6H_4 (IV)	[a]	1058	1237	1390	1305
2,6-$Me_2C_6H_3$ (II)	935	986	1202	1410	1306
2,6-$Me_2C_6H_3$ (IV)	[a]	1056	1202	1405	1310
2,4,6-$Me_3C_6H_2$ (II)	934	986	1202	1412	1308
2,4,6-$Me_3C_6H_2$ (IV)	[a]	1060	1217	1410	1305
Me (II)	927	964	—	1407	1306
Me (IV)	[a]	1044	—	1413	1303

[a] This band is probably hidden under the very intense ν(CO) and C—H (def) at approximately 1000 cm^{-1}.

decomposition in a laser beam prevented recording of their Raman spectra. However, the eight-membered ring vibrations, which may be of interest from a chemical point of view, could readily be assigned by comparison with other Al ring systems and by the use of ^{15}N labeling. Assignment of the S=O stretching and the S—Me bonding vibrations is based on values reported for similar complexes [15] (Table 5). The assignment of ν(N—Ph) is based on ^{15}N labelling and on results derived for RNSO and RNSNR by Meij et al. [19]. ν(N—S) in the complexes is assigned by comparison of the ^{15}N-labelled compounds with those of the non-labelled compounds, and are in accord with the values reported for dimeric $[M\{RNS(R')NR\}]_2$ ($M = Cu^I, Ag^I$) [12], in which there are similar eight-membered rings.

It was impossible to identify the ν(N—S) for RN(H)S(Me)O even with the use of ^{15}N labelling, possibly because this vibration is hidden under the very intense bands at 1000 cm^{-1} (ν(S—O) and δ(CH)). We believe that this is the case since both ν(SO) and ν(N—S) are very close in the Al complexes and are expected to shift by approximately the same amount on going from the metal-coordinated to the non-coordinated situation. As in RNSO, ν(S—O) does not change significantly upon substitution of ^{15}N [19]. The low ^{15}N shift of ν(N—S) in the complex (10 cm^{-1} versus 25 cm^{-1} theoretically) shows that this vibration is not pure N—S in character and as in RNSO, is probably coupled with other vibrations of the R groups.

4. Discussion

It has been shown previously that cumulated double bond systems X=Y=Z such as RN=C=NR [17,23], RN=C=O [17,21,22], O=C=O [17,20], O=S=O [14—17] and S=C=S [17,24], can insert into metal—carbon bonds with formation of dimeric and polymeric materials in which the $[XY(R)Z]^-$ ligand generally behaves as a metal—metal bridging ligand. In the case of the dimeric $[Me_2Al\{XY(Me)Z\}]_2$ the ligands form with the two Al atoms an eight-membered puckered ring, as confirmed by X-ray analysis for $[Me_2M(Me)NC(Me)NMe]_2$ (M = Al, Ga) [23] and $[Me_2AlOC(Ph)NPh]_2$ [25].

Although several authors have reported changes in conformation on going from solution to the solid state, only in one case, namely $[Me_2AlOC(Me)NPh]_2$, has a conformational equilibrium between dimeric conformers been reported [22]. Since this equilibrium is concentration dependent, it appears likely that other processes may also be occurring in this particular case.

Behaviour of $[Me_2Al\{RNS(Me)O\}]_2$ in solution

The temperature and concentration dependence of the ^1H NMR spectrum of $[Me_2Al\{RNS(Me)O\}]_n$ in $CDCl_3$ shows the existence of an equilibrium of two dimeric species and a monomeric compound. The presence of a dimer—monomer equilibrium was further confirmed by the concentration dependence of the molecular weight in benzene. A dimer—monomer equilibrium is consistent with the observation that mixing of two different dimeric complexes (i.e. having different R groups) gives mixed dimers. Although the relative rates of the reactions cannot be estimated, it seems logical to assume, by analogy to the sulfurdiimine systems (vide infra), that there must also be an intramolecular exchange between the two dimeric conformational isomers which is slow on the NMR time scale. Such a ring flipping process, analogous to that occurring for cyclohexane, would be expected to have a sufficiently low activation enthalpy since no bond-breaking is involved.

The structure of the monomer remains doubtful, since the ligand may be bonded via the N or via the O atom. However, since rotation of the R group about the N—C bond is blocked for R = 2,6-$Me_2C_6H_3$ and 2,4,6-$Me_3C_6H_2$ in $CDCl_3$ (in which the complexes are dimeric) and not in pyridine (in which they are monomeric), we suspect, that the [RNS(Me)O] ligand in the monomer is bonded via the O atom. This choice is supported by the X-ray determination of the structure of $[Me_2Al\{OCR(R')NR\}Me_3NO]$ [22] which shows the [OC(R')NR] ligand to be bonded via the O atom to Al.

Behaviour of $[Me_2Al\{RNS(Me)NR\}]_2$ in solution

The temperature- and concentration-dependent ^1H NMR spectra of $[Me_2Al\{RNS(Me)NR\}]_2$, formed from the reaction of $[Me_3Al]_2$ and RN=S=NR, in $CDCl_3$, show that two dimeric conformers exist in solution and are in conformational equilibrium. No evidence was found for a monomeric species at low concentrations, and no mixed dimers were formed upon mixing two differently substituted compounds. Furthermore, it was found that the molecular weights are concentration independent. From these observations it is concluded that the equilibrium between the two dimeric conformers must be intramolecular and involves some kind of ring flipping process.

An interesting point is the stability of the compounds in solvents such as $CDCl_3$, $CHCl_3$, CH_2Cl_2 and pyridine-d_5. Whereas solutions of $[Me_2Al\{RNS(Me)O\}]_n$ are stable for weeks, we found that $[Me_2Al\{RNS(Me)R\}]_2$ decomposes slowly in $CDCl_3$ and rapidly in pyridine-d_5 to afford RN=NR, RNH_2 and unidentified polymeric material, evidencing various parallel decomposition pathways.

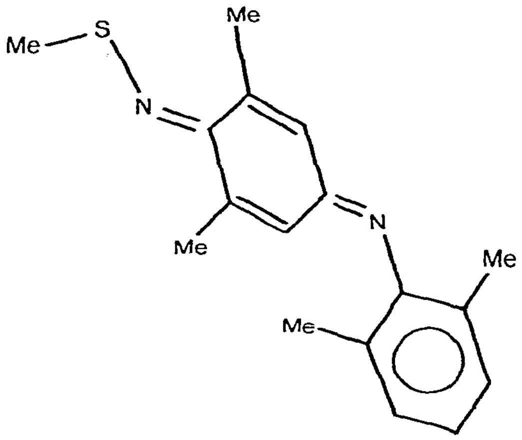

Fig. 6. Structure of the compound prepared by the alcoholysis of $[Me_2Al\{RNS(Me)NR\}]_2$ (R = 2,6-$(Me)_2C_6H_3$).

In view of these results it is relevant to recall that $[Li\{RNS(R')NR\}]$ and $[BrMg\{RNS(R')NR\}]$ are fairly stable in solution. However, the complexes $[M\{RNS(R')NR\}]_2$ ($M = Cu^I, Ag^I$) [12] $[(OC)_2Rh\{RNS(R')NR\}]$ and $[(\eta^3\text{-allyl})Pd\{RNS(R')NR\}]_2$ [12,14] decompose in a highly stereoselective manner in solution into RN=NR (quantitatively) and SR′ fragments. The rate of decomposition depends to some extent on the metal, the type of bonding (bridging or chelate) and strongly on the electronic and steric properties of R and R′. It is concluded that for all these metal complexes the formation of RN=NR proceeds intramolecularly via intermediates which are probably monomeric.

The decomposition of the Al compounds, which is shown by the products to be more complex, indicates the occurrence of both intra- and intermolecular decomposition pathways. The production of RN=NR might proceed intra- or intermolecularly, but the formation of RNH_2 in solution and the production of polymeric material indicates the intervention of nitrene NR intermediates which may react with the complexes themselves or with the solvent. The formation of nitrene intermediates seems to be further supported by the alcoholysis experiments, since alcoholysis of $[Me_2Al\{RNS(Me)NR\}]_2$ with t-BuOH in pentane or $CDCl_3$ again produced, in addition to the expected RNH_2 *, RN=NR and unidentified polymeric material for R = 4-ClC_6H_4 and 4-MeC_6H_4. Furthermore for R = 2,6-$Me_2C_6H_3$ no RN=NR was formed, but instead a 25% yield of a compound of the composition $C_{17}H_{20}N_2S$ was obtained. Preliminary results from a single crystal X-ray determination [26] shows the remarkable structure shown in Figure 6. This structure shows that an NS bond has been cleaved. Formally, combination of an NR fragment and a MeSNR unit, with attachment at the *para* position of the R group, would produce the isolated

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* Hydrolysis of the transition metal complexes of Rh, Pd, Cu and Ag afforded RNH_2 and RN=NR.

complex. It seems highly likely that such compound could only be formed via intermolecular reactions.

In view of the limited information available it is not appropriate to speculate further on possible mechanisms of the various decompositions in relation to the highly stereoselective processes occurring for the transition metal complexes mentioned above. It is, however, noteworthy that coordinated $[RNS(Me)NR]^-$ may not only decompose in solution into NR and S=N fragments when bonded to electron rich metal atoms [6,7], but also when coordinated to highly electropositive metal atoms in high oxidation states.

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