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Synthesis and characterization of alkylaluminum and -gallium derivatives of thiomorpholine. Molecular structures of $\text{Me}_3\text{Al} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$ and $[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2$

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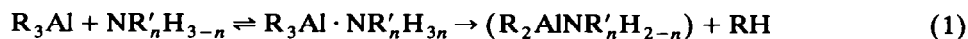
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Abstract

Trialkylaluminum derivatives, R_3Al ($\text{R} = \text{Me}$, Et or ^iBu), react with thiomorpholine, depending upon the conditions and stoichiometry, to give the adducts $\text{R}_3\text{Al} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$ ($\text{R} = \text{Me}$, **1a**; Et , **1b**; ^iBu , **1c**), $\text{R}_3\text{Al} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S} \cdot \text{AlR}_3$ ($\text{R} = \text{Me}$, **2a**; ^iBu , **2b**), the amido derivative $[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2$, **3**, or the bridged amido adduct $[\text{R}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2 \cdot (\text{AlR}_3)_2$ ($\text{R} = \text{Et}$, **4a**; ^iBu , **4b**) and for Me_3Ga the simple addition compound, $\text{Me}_3\text{Ga} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **5**. The resulting compounds have been characterized by ^1H and ^{13}C NMR spectroscopy. The structures of **1a** and **3** were determined by single crystal X-ray diffraction techniques. **1a** and **3** were found to be in the monoclinic cell system, space group $P2_1/c$ (No. 14) with cell constants for **1a**: $a = 8.452(4) \text{ \AA}$; $b = 21.075(4) \text{ \AA}$; $c = 12.267(2) \text{ \AA}$; $\beta = 90.37(2)^\circ$ and $Z = 8$; for **3**: $a = 7.167(1) \text{ \AA}$; $b = 13.547(2) \text{ \AA}$; $c = 16.227(2) \text{ \AA}$; $\beta = 96.74(1)^\circ$ and $Z = 4$ (dimers). The structure of **1a** was refined to a final $R = 6.30\%$ ($R_w = 5.99\%$) based on 2029 observed reflections ($I \geq 3.0\sigma(I)$). The molecule exists as an adduct with an average Al–N bond distance of 2.03 \AA . The structure of **3** was refined to a final $R = 5.93\%$ ($R_w = 4.62\%$) based on 1722 observed reflections ($I \geq 3.0\sigma(I)$). The molecule exists as a dimer with a puckered four-member Al_2N_2 ring. The Al–N bond distances range from 1.96 to 1.99 \AA . ^1H NMR studies showed that formation of the addition complex at nitrogen locks the thiomorpholine ring in the chair conformation which leads to coupling ($^3J = 8\text{--}12 \text{ Hz}$) between the NH proton and the axial protons on the α ring-carbon.

Introduction

The reaction of monodentate amines with trialkyl Group 13 metal derivatives, R_3M , has been studied extensively [1]. Typically the reaction leads to a simple addition compound as shown in eq. 1. If a primary or secondary amine or ammonia is used, a subsequent elimination step may occur leading to amides, imides or ultimately to the aluminum nitride.



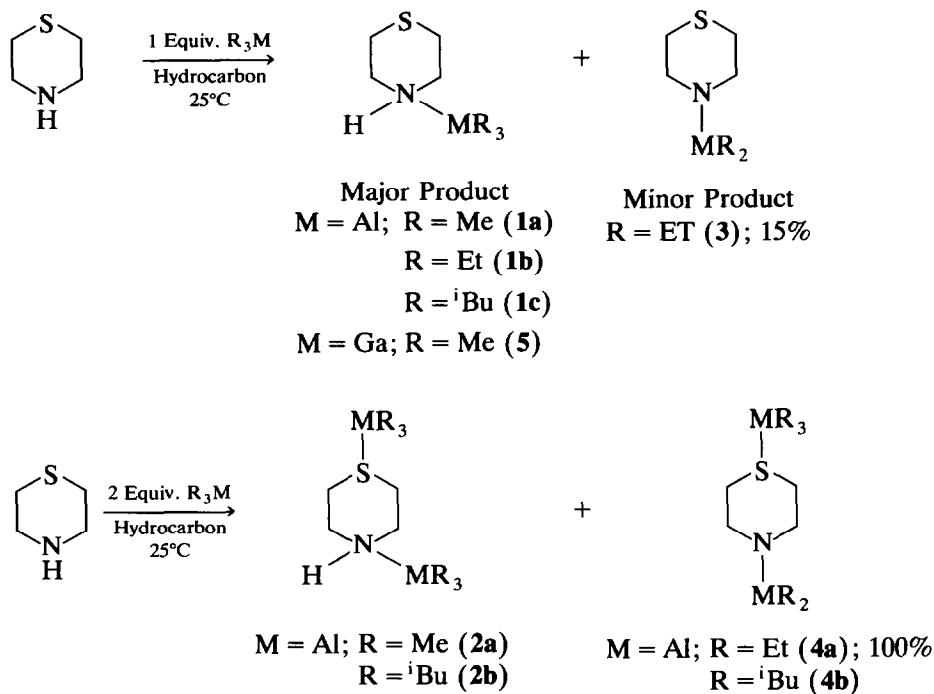
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This decomposition process has been studied by several groups and has been shown to proceed in a stepwise manner leading to small rings and cage structures [2]. In several recent papers, Interrante *et al.* have discussed the decomposition process and have considered the bonding in these systems in detail [3]. Substantially less information is known about the formation and structures of organoaluminum compounds with bifunctional or polyfunctional bases. When a second basic site is present, the additional site may interact with metal alkyls to yield more complex products. Several recent studies have appeared in which compounds containing two or more nitrogen atoms [4], nitrogen and oxygen atoms [5], or nitrogen and sulfur atoms [6] are present. A variety of different structural types have been observed for these products including simple addition compounds, derivatives with two or more types of Al atoms and complexed cage structures. We have now extended this work to include thiomorpholine where both nitrogen and sulfur atoms are present, but unlike earlier studies in our laboratory, the N and S sites in the base are separated so that they may not readily interact with the same metal atom. The reaction of thiomorpholine with trialkylaluminum derivatives yields four different types of products: the 1:1 adduct, the 2:1 adduct, the 1:1 elimination product and the adduct of the elimination product. Two of the new complexes, $\text{Me}_3\text{Al} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **1a**, and $[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2$, **3**, have been characterized by single crystal X-ray diffraction studies. The other products have been characterized by NMR spectral studies.

Results and discussion

When thiomorpholine is allowed to react with R_3M , it yields the adducts $\text{R}_3\text{M} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$ (R = Me, **1a**; Et, **1b**; ¹Bu, **1c**; M = Ga, R = Me, **5**) or $\text{R}_3\text{Al} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S} \cdot \text{AlR}_3$ (R = Me, **2a**; ¹Bu, **2b**), or the alkane elimination product $[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2$, **3**, or the bridged addition compound $[\text{R}_2\text{AlNC}_4\text{H}_8\text{S}] \cdot (\text{AlR}_3)_2$ (R = Et, **4a**; ¹Bu, **4b**). The specific compound(s) formed depends both on the ratio of reactants and the reaction conditions. Small changes in either the reaction conditions or the purity of the reactants affect the product distribution. In a limited study it was also shown that Me_3Ga yielded the addition compound, $\text{Me}_3\text{Ga} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **5**. To obtain the simple addition compounds, **1**, **2** and **5**, mild reaction conditions with the appropriate ratio of R_3M to thiomorpholine are required. The formation of the bridge compounds, **3** and **4**, is favored by increasing the reaction temperature to promote the alkane elimination process. The reaction conditions and characterization of all of these compounds is given in the experimental section. Scheme 1 shows the reaction and products obtained in hydrocarbon solvent at 25°C.

The molecular structure of the addition compound, **1a**, and of the elimination product **3**, have been determined by single crystal X-ray diffraction. ORTEP diagrams of **1a** and **3** are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are listed in Tables 1 and 2. The structure of **1a** consists of a discrete monomeric unit with the aluminum atom in a distorted tetrahedral geometry common for trialkylaluminum addition compounds with the C–Al–C angles all greater than 109° in the R_3Al moiety. The average Al–C and Al–N bond distances (Table 1) are within experimental error of those reported for organoaluminum amine adducts [7]. The thiomorpholine rings are in the chair conformation with



Scheme 1.

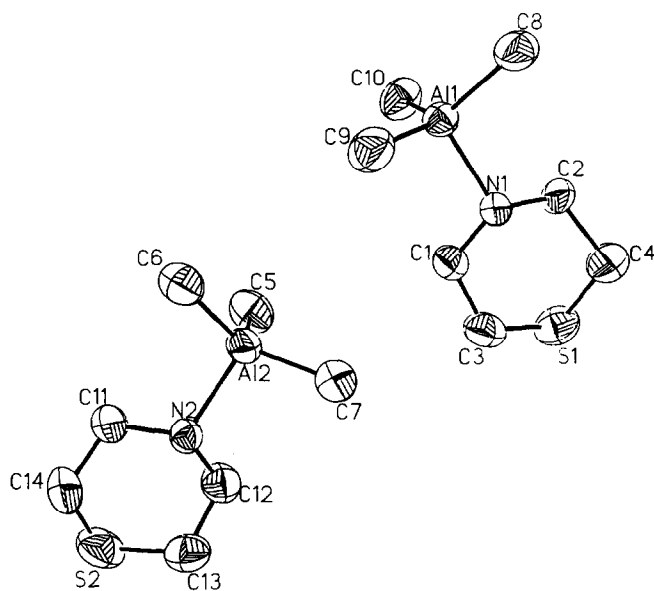


Fig. 1. An ORTEP diagram of $\text{Me}_3\text{Al}\cdot\text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **1a**, showing the atom labeling scheme. Hydrogen atoms are omitted for clarity.

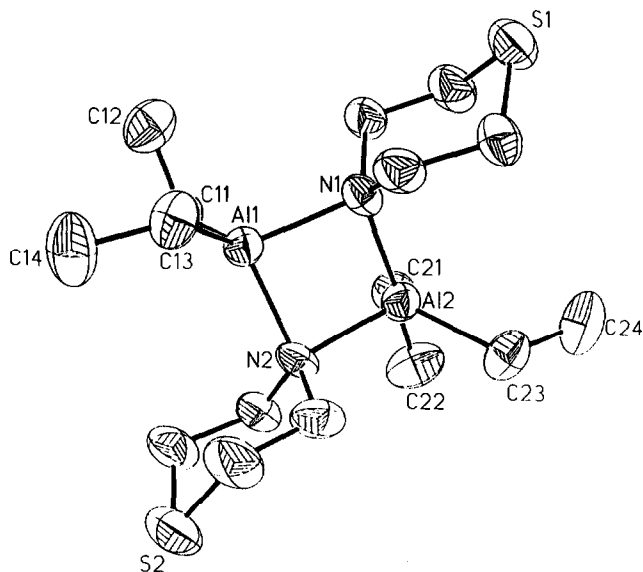


Fig. 2. An ORTEP diagram of $[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2$, **3**, showing the atom labeling scheme. Hydrogen atoms are omitted for clarity.

normal distances and angles. There is no apparent interaction between sulfur and aluminum atoms of adjacent molecules.

Compound **3** exists as a nitrogen-bridged dimer with each asymmetric unit containing a complete dimeric molecule. The central ring is not planar with a root-mean-square deviation of 0.1573 \AA from the plane described by Al1, N1, Al2 and N2. The two aluminum atoms are below the plane by the same amount the two nitrogen atoms are above the plane. An alternative way to describe this is by measuring the angle between the plane described by N1, Al1 and N2 and the plane described by N2, Al2 and N2 which is $25.5(2)^\circ$. This gives rise to a butterfly-shaped molecule uncommon for nitrogen-bridged aluminum compounds [2–4,8]. This

Table 1

Selected bond distances (\AA) and bond angles ($^\circ$) for $\text{Me}_3\text{Al} \cdot \text{N}(\text{HC}_4\text{H}_8\text{S})$, **1a**

<i>Bond distances</i>			
Al2–C6	1.979(6)	Al2–C7	1.967(6)
Al2–C5	1.972(6)	Al2–N2	2.032(4)
Al1–N1	2.030(4)	Al1–C8	1.971(6)
Al1–C9	1.974(6)	Al1–C10	1.967(6)
<i>Bond angles</i>			
Al1–N1–C1	112.2(3)	C5–Al2–C6	114.8(3)
Al1–N1–C2	112.9(3)	C5–Al2–C7	117.4(3)
N1–Al1–C8	103.2(2)	C6–Al2–C7	112.4(3)
N1–Al1–C9	101.4(2)	N2–Al2–C5	104.6(2)
N1–Al1–C10	104.6(2)	N2–Al2–C6	103.4(2)
C8–Al1–C9	112.7(3)	N2–Al2–C7	101.9(2)
C9–Al1–C10	116.9(3)	C8–Al1–C10	115.5(3)

Table 2

Selected bond distances (Å) and angles (°) for $[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2$, **3**

<i>Bond distances</i>			
Al1–C11	1.983(6)	Al2–N1	1.956(5)
Al1–C13	1.974(7)	Al2–C21	1.983(6)
Al1–N1	1.993(5)	Al2–C23	1.968(6)
Al1–N2	1.966(5)	Al2–N2	1.989(5)
Al1–Al2	2.777(3)	N1–N2	2.720(7)
<i>Bond angles</i>			
Al1–C11–C12	112.8(4)	Al2–C21–C22	112.8(4)
Al1–C13–C14	113.2(4)	Al2–C23–C24	114.1(4)
Al1–N1–C15	110.5(4)	Al2–N2–C25	113.4(4)
Al1–N1–C17	113.2(4)	Al2–N2–C27	110.1(4)
Al1–N1–Al2	89.4(2)	C21–Al2–C23	113.6(3)
Al1–N2–Al2	89.2(2)	C21–Al2–N2	110.9(2)
Al1–N2–C25	116.3(4)	C23–Al2–N2	111.9(2)
Al1–N2–C27	117.4(4)	N1–Al2–C21	111.9(2)
C11–Al1–C13	112.4(3)	N1–Al2–C23	117.8(2)
C11–Al1–N1	111.0(2)	N1–Al2–N2	88.0(2)
C11–Al1–N2	111.7(2)	C13–Al1–N1	113.5(2)
C13–Al1–N2	118.2(2)	N1–Al1–N2	87.6(2)

deviation from planarity may result from weak interactions of the thiomorpholine rings with the other ligands, but no detailed analysis of this has been attempted. The remainder of the features of the dimer are normal for organoaluminum compounds. The plane containing the aluminum atoms and the carbons bound to them forms an angle of $89.2(4)^\circ$ with the plane defined by the central ring atoms. The thiomorpholine rings are in the chair conformation, and there appears to be no interaction between sulfur and aluminum atoms. All of the bond distances and angles of the central ring and the metal–carbon parameters (see Table 2) can be compared with those of analogous compounds [2–6,8].

The NMR spectra of these derivatives provide interesting insight into the stability and structure of the molecules in solution. Thiomorpholine gives a complex ^1H NMR spectrum with the NH proton at 1.11 ppm, the SCH_2 protons at 2.28 and those associated with the NCH_2 unit at 2.74 ppm. Under normal conditions no coupling is observed between the NH proton and either the axial or equatorial protons on the thiomorpholine ring because of rapid conformational changes. On complex formation all of these signals are shifted slightly, and the second order splittings are also modified as the chemical shifts and coupling constants change. In **1a–1c**, **2a**, **2b** and **5** the spectra show additional coupling between the NH proton and the ring protons that ranges from 8 to 12 Hz. Furthermore in **2a** and **2b** two distinct sets of resonances for the R_3Al groups are observed, one corresponding to the N-bound and one to the S-bound moieties. This latter feature establishes that no exchange between these sites occurs on the NMR time scale and provides a crude measure of the stability of the adducts.

In order to better understand the coupling interaction between the NH proton and the ring, a series of selective decoupling experiments was carried out and is shown in Fig. 3. Decoupling the signals centered at 2.1 ppm shows that the NH proton is coupled primarily to these protons which are also coupled to the geminal

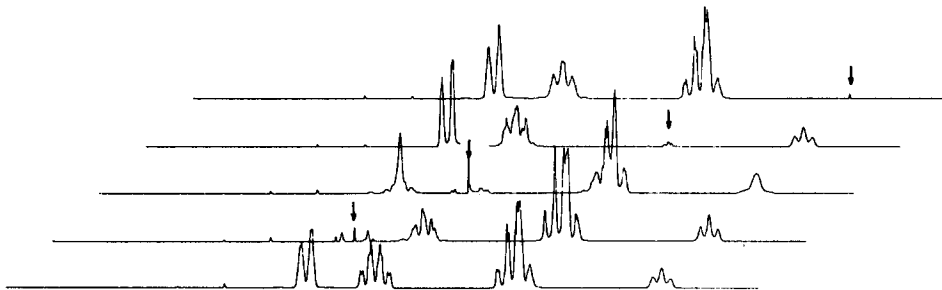


Fig. 3. ^1H NMR spectrum of $\text{Me}_3\text{Al}\cdot\text{N}(\text{H})\text{C}_4\text{H}_8\text{S}\cdot\text{AlMe}_3$, **2a**; full spectrum (bottom); with selective decoupling \downarrow centered on the multiplets with chemical shifts equal to 2.46, 2.14, 1.43 and 0.82 ppm (above).

protons (see Fig. 3). Neither set of protons on this carbon is strongly coupled to those on the carbon α to the S atom.

Examination of the structure of the molecule provides additional insight into this system. In **1a** the dihedral angles $\text{H}-\text{N}-\text{C}-\text{H}$ for the axial and equatorial protons on the α -carbon atom to nitrogen are around 170° and 70° , respectively. Similar angles are to be expected in the bis addition compounds, **2a** and **2b**. Application of the Karplus equation, which relates the dihedral angle to the magnitude of the vicinal coupling constant, predicts a large coupling to the axial protons on the order of 10–12 Hz and near zero for coupling to the equatorial protons [9]. Thus, the resonance centered at 2.1 ppm can be assigned to the axial protons and the other resonances can then be assigned relative to this set of protons. The ^{13}C NMR spectrum shows only single environments for the CH_2 carbon atoms and is consistent with this interpretation.

The conclusions which may be drawn from these observations are that the thiomorpholine ring is locked into the chair conformation on complex formation which permits coupling to occur between the NH proton and the axial protons on the carbon α to the nitrogen atom. Furthermore the stability of the bis complexes is sufficient to prevent rapid exchange of the R_3Al moieties between the nitrogen and sulfur sites on the thiomorpholine ring.

Experimental

General experimental conditions

All solvents were purified and dried by standard techniques [10]. Argon gas was purified by passing through a series of columns containing Deox catalyst, calcium sulfate and phosphorus pentoxide. Trimethylaluminum (Aldrich, 2.0 M solution in toluene), triethylaluminum (Aldrich, 1.9 M solution in toluene), triisobutylaluminum (1.0 M solution in toluene) and thiomorpholine (Aldrich) were used as received. All glassware used in the synthetic work was oven-dried, and standard Schlenk line techniques were employed since the starting materials and new derivatives are both air- and moisture-sensitive, decomposing over a period of minutes in the solid state or in solution on exposure to air. The new species are moderately to very soluble in hydrocarbons such as pentane, benzene and toluene and in the donor solvents such as diethyl ether and tetrahydrofuran. ^1H and ^{13}C

NMR spectra were recorded on a General Electric QE-300 spectrometer at 25°C. The chemical shifts were referenced to the residual protic benzene- d_6 peak ($\delta = 7.15$ ppm) for ^1H spectra and to the center of the benzene triplet ($\delta = 128.0$ ppm) for ^{13}C spectra. Elemental analyses on selected compounds were performed by Galbraith Laboratories, Knoxville, TN.

*Preparation of $\text{Me}_3\text{Al} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **1a***

To 0.5 g (0.49 mL, 4.85 mmol) of thiomorpholine in 20 mL of pentane, Me_3Al (2.4 mL, 4.8 mmol) was added dropwise with stirring. Upon addition of Me_3Al , an exothermic reaction was observed. The resulting solution was then stirred for 2 h. Removal of volatiles *in vacuo* resulted in a white powder in quantitative yield. m.p. 107–108°C. Anal. Found: C 45.98; H 9.9; N 7.69. $\text{C}_7\text{H}_{18}\text{NSAl}$ calc.: C 47.97; H 10.35; N 7.99%. ^1H NMR: -0.55 (s, 9H); 0.92 (NH, broad, 1H); 1.63 (m, splitting = 4.8 Hz, 4H); 2.47 (m, splitting = 3.3 Hz, 4H). $^{13}\text{C}\{^1\text{H}\}$: -9.6 (Al–C); 26.3 (C–S); 45.8 (C–N).

*Preparation of $\text{Et}_3\text{Al} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **1b**, and $[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2$, **3***

In an analogous fashion to **1a**, **1b** and **3** were prepared by the addition of Et_3Al (2.5 mL, 4.8 mmol) to 0.5 g (4.85 mmol) of thiomorpholine. NMR of the crude product showed two products in an 85:15 ratio by integration. The compounds were identified as the amine-adduct (**1b**, 85%) and the alkane-elimination product (**3**, 15%). Compound **3** was selectively recrystallized from a pentane/toluene solution (70:30) to give suitable, X-ray diffraction quality, single crystals. ^1H NMR (**1b**): -0.02 (q, $^3J = 8.2$ Hz, 6H); 1.16 (NH, t, $^3J \cong 8.0$ Hz, 1H); 1.28 (t, $^3J = 8.2$ Hz, 9H); 1.81 (broad, 4H); 2.59 (broad, 4H). $^{13}\text{C}\{^1\text{H}\}$: -1.0 (Al–C–C); 10.5 (Al–C–C); 26.7 (Al–C–C); 46.5 (C–N). ^1H NMR (**3**): -0.03 (q, $^3J = 8.2$ Hz, 4H); 1.27 (t, $^3J = 8.2$ Hz, 6H); 2.20 (broadened m, 4H); 2.82 (broadened m, 4H). $^{13}\text{C}\{^1\text{H}\}$: -0.5 (Al–C–C); 9.4 (Al–C–C); 28.0 (Al–C–S); 49.1 (C–N).

*Preparation of $(^i\text{Bu})_3\text{Al} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **1c***

The same procedure was used to prepare **1c** by the addition of $(^i\text{Bu})_3\text{Al}$ (4.8 mL, 4.8 mmol) to 0.5 g (4.85 mmol) of thiomorpholine. ^1H NMR: -0.02 (d, $^3J = 6.9$ Hz, 6H); 0.96 (NH, t, $^3J \cong 8.0$ Hz, 1H); 1.14 (d, $^3J = 6.6$ Hz, 18H); 1.76 (broad, 4H); 1.97 (m, splitting = 6.6 Hz, 2H); 2.60 (broad, 4H). $^{13}\text{C}\{^1\text{H}\}$: 22.5 (Al–C–C–C); 26.9 (Al–C–C–C); 27.2 (C–S); 29.1 (Al–C–C–C); 46.6 (C–N).

*Preparation of $\text{Me}_3\text{Al} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S} \cdot \text{AlMe}_3$, **2a***

In an analogous fashion to **1a**, compound **2a** was prepared by the addition of Me_3Al (5.0 mL, 10.0 mmol) to 0.5 g (4.85 mmol) of thiomorpholine. m.p. 134–135°C. Anal. Found: C 47.80; H 10.30; N 5.85. $\text{C}_{10}\text{H}_{27}\text{NSAl}_2$ calc.: C 48.56; H 11.00; N 5.66%. ^1H NMR: -0.61 (s, 9H); -0.46 (s, 9H); 0.82 (t, $^3J = 12$ Hz, 1H); 1.50 (m, splitting = 14.4 Hz, 3.0 Hz, 4H); 2.13 (m, splitting = 11.4 Hz, 3.3 Hz, 2H); 2.45 (m, splitting = 14.7 Hz, 2.6 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$: -9.6 (N–Al–C), -8.7 (S–Al–C), 26.6 (C–S), 44.0 (C–N).

*Preparation of $(^i\text{Bu})_3\text{Al} \cdot \text{N}(\text{H})\text{C}_4\text{H}_8\text{S} \cdot \text{Al}(^i\text{Bu})_3$, **2b**, and $[(^i\text{Bu})_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S} \cdot \text{Al}(^i\text{Bu})_3)]_2$, **4b***

The reaction of $(^i\text{Bu})_3\text{Al}$ with thiomorpholine was carried out in the same manner as for **2a** with a 2:1 ratio of $(^i\text{Bu})_3\text{Al}$ to thiomorpholine. This reaction

gave a mixture of products corresponding to the addition compound **2b** and the elimination product **4b**. These were identified by their characteristic NMR spectra but were not isolated. ^1H NMR: d, -0.09 ; d, 0.03 ; d, 0.121 ; d, 0.76 (all are CH_2 α to Al in the ^iBu group) 1.09 overlapping multiplets; 1.7 NH with axial coupling $\cong 12$ Hz; 1.9 overlapping multiplets, 2.47 overlapping multiplets; 2.7 overlapping multiplets. $^{13}\text{C}\{^1\text{H}\}$: 19.4 , 22.1 , 22.5 , 23.0 , 26.0 , 26.4 , 27.1 , 28.0 , 28.1 , 28.5 , 28.7 , 28.8 , 29.1 , 45.7 , 49.4 .

*Preparation of $[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S}\cdot\text{AlEt}_3)]_2$, **4a***

Similarly, **4a** was prepared by the addition of Et_3Al (5.1 mL, 9.70 mmol) to 0.5 g (4.85 mmol) of thiomorpholine. This reaction results primarily in the alkane-elimination, sulfur addition product. ^1H NMR: -0.08 (t, $^3J = 8$ Hz, 6H); 0.15 (q, $^3J = 8$ Hz, 4H); 1.14 (t, $^3J = 8$ Hz, 9H); 1.28 (t, $^3J = 8$ Hz, 6H); 2.18 (broad, 4H); 2.68 (broad, 4H). $^{13}\text{C}\{^1\text{H}\}$: -0.8 (N-Al-C-C); -0.3 (S-Al-C-C); 9.4 (S-Al-C-C), 10.2 (N-Al-C-C), 27.2 (C-S), 49.2 (C-N).

*Preparation of $\text{Me}_3\text{Ga}\cdot\text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **5***

$\text{Me}_3\text{Ga}\cdot\text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **5** was prepared by the addition of Me_3Ga (0.56 g, 0.48 mL, 4.86 mmol) to 0.25 g (2.43 mmol) of thiomorpholine. ^1H NMR: -0.25 (s, 9H); 0.77 (t, broad, 1H); 1.69 (m, splitting = 4.8 Hz, 4H); 2.43 (broad, 4H). $^{13}\text{C}\{^1\text{H}\}$: -6.7 (N-Ga- CH_3), 26.7 (C-S), 46.2 (C-N). Treatment with a 2:1 excess of Me_3Ga did not lead to a stable Ga-S bonded addition compound and under the reaction conditions did not yield an elimination product.

*X-Ray structure determination of $\text{Me}_3\text{Al}\cdot\text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **1a**, and $[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2$, **3***

Crystals of $\text{Me}_3\text{Al}\cdot\text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **1a**, were grown from a pentane solution at -20°C . Crystals of $[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2$, **3**, were obtained from pentane/toluene solution (70:30) at -20°C . In each case a crystal suitable for X-ray diffraction studies was mounted in a thin-walled capillary tube in a dry box, plugged with grease, removed from the dry box, flame sealed, mounted on a goniometer head and placed on a diffractometer for data collection. Parameters from the crystal structure determination are presented in Table 3.

Lattice constants were verified by axial photographs. Compound **1a** was assigned to the space group $P2_1/c$ (No. 14); and the crystal of **3a** was assigned to the space group $P2_1/c$ (No. 14) on the basis of the systematic absences. Data reduction was carried out using the SHELXTL program [11]. The direct method produced acceptable solutions for the structures in all cases placing all of the non-hydrogen atoms. Full-matrix least-squares refinement was carried out using SHELX-76 [12]. The data were corrected for Lorentz and polarization effects and scattering factors for neutral carbon, nitrogen and aluminum atoms were used [13]. Each hydrogen atom was placed with a C-H bond distance of 0.96 Å, and the C-H vector held constant in magnitude and direction, but not position, during subsequent refinement. A few additional cycles of refinement of the data led to a convergence with $R = 6.30\%$ ($R_w = 5.99\%$) for **1a** and $R = 5.93\%$ ($R_w = 4.62\%$) for **3a**. Atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms in **1a** and **3a** are presented in Tables 4 and 5.

Table 3

Experimental parameters for the X-ray diffraction study of $\text{Me}_3\text{Al}\cdot\text{N}(\text{HC}_4\text{H}_8\text{S}, \mathbf{1a})$, and $[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2, \mathbf{3}$

Compound	$\text{Me}_3\text{Al}\cdot\text{N}(\text{HC}_4\text{H}_8\text{S}, \mathbf{1a})$	$[\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})]_2, \mathbf{3}$
Formula	$\text{C}_7\text{H}_{18}\text{NSAl}$	$\text{C}_{16}\text{H}_{36}\text{Al}_2\text{N}_2\text{S}_2$
Mol. weight	175.27	374.57 amu
Crystal habit	Cubic	Rectangular needles
Crystal color	Colorless	Golden
Dimensions (mm)	$0.45 \times 0.38 \times 0.38$	$0.20 \times 0.25 \times 0.35$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Cell constants		
<i>a</i>	8.452(4) Å	7.167(1) Å
<i>b</i>	21.075(4) Å	13.547(2) Å
<i>c</i>	12.267(2) Å	16.227(2) Å
β	90.37(2)°	96.74(1)°
<i>Z</i>	8 (monomers)	4 (dimers)
Volume	2184.89(2.12) Å ³	2124.3(4) Å ³
Density (calc.)	1.065 g cm ⁻³	1.14 g cm ⁻³
Radiation type	Mo- K_{α} $\lambda = 0.71073$ Å, Graphite monochromator	Cu- K_{α} $\lambda = 1.54178$ Å Ni filtered
Temperature	Ambient	Ambient
Type of data collection	$\theta/2\theta$ scan	$\theta/2\theta$ scan, intensities by counter
2θ scan range	6–52°	8–110°
Octants used	<i>h, k, ±l</i>	+ <i>h, + k, ±l</i>
Scan rate	4–10°/min	Variable, 2.0–5.0°/min
Scan width	1.0° below $K_{\alpha 1}$ to 1.0° above $K_{\alpha 2}$	1.0° below $K_{\alpha 1}$ to 1.0° above $K_{\alpha 2}$
Background/scan ratio	0.5	1.0
Standard reflections	3 measured per every 100 reflections, linear decay ~ 1%	3 measured per every 100 reflections, linear decay ~ 5%
Number of data collected	4727	2981
Number of unique reflections	4307	2402, $R_{\text{int}} = 0.0$
Observed reflections	2029 [$F_o \geq 3.00(F)$]	1722 [$F_o \geq 3.00(F)$]
Linear absorption coefficient (μ)	2.87 cm ⁻¹	22.26 cm ⁻¹
<i>F</i> (000)	736 electrons	816 electrons
Absorption correction	Empirical, psi scans	None applied
Number of parameters refined	183	202
Observed/parameter ratio	11:1	8.52:1
$R = \frac{\sum(F_o - F_c)}{\sum F_o }$	6.30%	5.9%
$R_w = \frac{[\sum(F_o - F_c)^2]}{[\sum w F_o ^2]^{1/2}}$	5.99%	4.62%
$w^{-1} = \sigma^2(F_o) + g(F_o)^2$		
Overall shift/e.s.d.	< 0.000	< 0.000
Maximum shift/e.s.d.	0.013	0.001
Secondary extinction	–	Three reflections omitted
Residual electron density	0.34 e/Å ³ 1.09 Å from C2	0.35 e ⁻ /Å ³ , 1.3 Å away from S1

Table 4

Atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms in $\text{Me}_3\text{Al}\cdot\text{N}(\text{H})\text{C}_4\text{H}_8\text{S}$, **1a**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
S1	0.7594(2)	0.07174(9)	0.2501(2)	0.0784(8)
S2	1.2689(2)	0.0604(1)	-0.0011(2)	0.0867(8)
Al1	0.2900(2)	0.15555(8)	0.4747(1)	0.0463(6)
Al2	0.7940(2)	0.14860(9)	0.7825(1)	0.0480(6)
N1	0.4889(4)	0.1439(2)	0.3851(3)	0.040(2)
N2	0.9959(5)	0.1362(2)	0.8708(3)	0.043(2)
C1	0.6077(7)	0.1029(3)	0.4411(4)	0.059(2)
C2	0.4556(6)	0.1222(3)	0.2724(4)	0.061(2)
C3	0.7667(7)	0.1022(3)	0.3866(5)	0.070(3)
C4	0.6118(8)	0.1259(3)	1.1937(5)	0.083(3)
C5	0.7179(7)	0.0619(3)	0.7525(5)	0.074(3)
C6	0.6581(7)	0.1988(3)	0.8810(4)	0.064(2)
C7	0.8698(7)	0.1986(3)	0.6579(4)	0.072(3)
C8	0.1525(7)	0.2065(3)	0.3783(5)	0.074(3)
C9	0.3720(8)	0.2044(3)	0.6001(5)	0.078(3)
C10	0.2160(8)	0.0688(3)	0.5040(5)	0.072(3)
C11	0.9700(7)	0.1120(3)	-0.0158(5)	0.066(3)
C12	1.1138(7)	0.0961(3)	-0.1875(5)	0.064(2)
C13	1.2739(7)	0.0947(3)	-0.1340(5)	0.075(3)
C14	1.1175(9)	0.1114(4)	0.0526(5)	0.086(3)

$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

Table 5

Atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms in $\text{Et}_2\text{Al}(\mu\text{-NC}_4\text{H}_8\text{S})_2$, **3**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Al1	0.8958(3)	0.7371(1)	0.7746(1)	0.0418(8)
C11	0.6389(8)	0.7107(4)	0.7980(4)	0.055(3)
C12	0.6230(9)	0.7042(4)	0.8903(4)	0.072(3)
C13	1.0901(9)	0.6735(4)	0.8329(4)	0.062(3)
C14	1.038(1)	0.5931(4)	0.8280(5)	0.085(4)
N1	0.9449(7)	0.8427(3)	0.7942(3)	0.041(2)
C15	1.1488(9)	0.8553(4)	0.8253(4)	0.056(3)
C16	1.2071(9)	0.9349(3)	0.8325(4)	0.059(3)
C17	0.8293(9)	0.8751(3)	0.8555(4)	0.051(3)
C18	0.8491(9)	0.9561(3)	0.8628(4)	0.064(3)
S1	1.0840(3)	0.9840(1)	0.9044(1)	0.0651(8)
Al2	0.8665(3)	0.8613(1)	0.6766(1)	0.0423(8)
C21	0.5967(8)	0.8874(4)	0.6555(4)	0.053(3)
C22	0.5297(9)	0.8977(4)	0.5638(4)	0.076(4)
C23	1.0298(9)	0.9227(3)	0.6162(4)	0.058(3)
C24	0.982(1)	1.0039(4)	0.6169(5)	0.084(4)
N2	0.9049(7)	0.7561(3)	0.6559(3)	0.042(2)
C25	0.7533(9)	0.7234(3)	0.5981(4)	0.054(3)
C26	0.7723(9)	0.6414(4)	0.5922(4)	0.066(3)
C27	1.0888(9)	0.7446(4)	0.6226(4)	0.056(3)
C28	1.1457(9)	0.6654(4)	0.6161(5)	0.070(3)
S2	0.9793(3)	0.6137(1)	0.5466(1)	0.0771(9)

$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

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Supplementary material available. A listing of the anisotropic thermal parameters, atomic coordinates for the hydrogen atoms and their isotropic thermal parameters, complete listings of bond distances and angles and listings of the observed and calculated structure factors are available for **1a** and **3**.

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