Alkylthiolatoalanes and Alkylthiolatohydridoaluminates

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Dedicated to Prof. Dr. Drs. h. c. Rolf Huisgen on the occasion of his 80th birthday

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Reactions of thiols RSH (R = Et, *i*Pr, *t*Bu) with $AlH_3·NMe_3$ lead to $RSAlH_2·NMe_3$ or $(RS)_2AlH·NMe_3$ compounds, depending on the stoichiometry. Similarly, the 1:1 reaction of $LiAlH_4$ with RSH (R = Et, *i*Pr) in ether produces $LiAlH_3SR$, however, in the case of $NaAlH_4$ and *i*PrSH in THF, ligand exchange of $NaAlH_3(SR)$ to $NaAlH_4$, $NaAlH_2(SR)_2$ and $NaAlH(SR)_3$ occurs. A byproduct of the formation of $LiAlH(StBu)_3$ (**6**), in ether is $[(Et_2O)LiAlH(StBu)_3·LiStBu]_2$ (**7**). Reaction of a 1:1 mixture of $LiAlH_4$ with $AlH_3·NMe_3$ and HS*t*Bu (1:1:5) leads to $LiAlH(StBu)_3·AlH(StBu)_2NMe_3$ (**8**). Compounds **5**, **7** and **8** were characterized by X-ray structure determinations. All molecules contain tetracoordinated Al centers.

Introduction

Aluminum compounds containing aluminum−sulfur bonds are comparatively less well studied than the thermodynamically more stable compounds with Al−O bonds.[1] Therefore, most of them are hydrolytically unstable in spite of the fact that alkanethiols are more acidic than alcohols, even if sulfur is less electronegative than oxygen. This can be readily rationalized by the theory of the HSAB principle. In consonance with this well-known principle is the observation that in dimethylaluminum complexes of thiophene a C-bridging is preferred over an Al−S interaction.[2] However, Al−S bridging in thioalanes is a well-known feature.[3] For instance, Me_2AlSMe is dimeric both in the solution and gas phase, and dimerization occurs via Al−S bonds.[4] However, this compound forms a chain structure in the solid phase.[4] If bulky R groups are introduced as in $Al(SAr)_3$, $RAl(SR)_2$ and $R_2Al(SR)$ (R = *t*Bu, Ar = 2,4,6-$tBu_3C_6H_2$), monomeric arylthioalanes with three-coordinated Al atoms are kinetically stabilized.[5] Not surprisingly, this demonstrates the tendency of oligomerization. So far only a few studies have been concerned with the reaction of thiols with aluminum hydride.[6] For instance, thiomorpholine reacts with $AlH_3·NMe_3$ to produce dimeric $H_2Al[\mu\text{-}N(CH_2)_4S]$, a nitrogen-bridged dimeric substituted alane;[6a] this unit, in the solid state, forms a two-dimensional network via Al−S interactions generating pentacoordinated Al centers.

The reaction of $LiAlH_4$ with $(Et_2HN{-}CH_2{-}CH_2{-}SH)Cl$ yields $AlH(SCH_2CH_2NEt_2)_2$ irrespective of a 1:1 or 1:2 stoichiometry. It is assumed that $H_2AlSCH_2CH_2NEt_2$ is formed in a first stage followed by ligand exchange to give AlH_3 and $AlH(SCH_2CH_2NEt_2)_2$.[6a] Moreover, a number of other thiolatoalanes, H_2AlSR, have been reported.[6b,6c] Alkylthiolatoalanes smell even worse than the thiols, a long-standing experience of the senior author,[7] and this may be a reason why these compounds have not been very attractive for a closer investigation. The purpose of the study reported here was to compare the formation and structures of some thiolatoalanes and thiolatohydridoaluminates with those of organyloxoalanes and alkali metal organyloxohydridoaluminates.[8,9]

Synthesis

Two routes have been employed to prepare alkylthiolatoalanes as depicted in Equation (1) to (3).

$$AlH_3·NMe_3 + RSH \longrightarrow RSAlH_2·NMe_3 + H_2 \qquad \begin{array}{c|ccc} R & Et & iPr & tBu \\ \hline & 1 & 2 & 3 \end{array} \tag{1}$$

$$AlH_3 + tBuSH \longrightarrow \underset{4}{tBuSAlH_2} + H_2 \tag{2}$$

$$AlH_3·NMe_3 + 2\ tBuSH \longrightarrow \underset{5}{(tBuS)_2AlH·NMe_3} + 2\ H_2 \tag{3}$$

Compound **1,** a liquid, fumed in contact with air, solidified at − 20 °C and decomposed on distillation under vacuum. This also holds for the liquid compounds **2** and **3**. Complexed trimethylamine was not released under vacuum; in contrast to alkoxyalane−trimethylamines (particularly with alkyl = Me, Et, *n*Pr)[8,10] which are prone to ligand exchange to give polymeric and insoluble products of various compositions. The alkylthiolatoalanes showed no tendency of this behavior. Solvent-free $tBuSAlH_2$ resulted according to Equation (2). However, the ^{27}Al NMR spectrum of the solution in ether suggests that the compound is present as $tBuSAlH_2·OEt_2$. It looses the coordinated ether in vacuo readily, and the ether-free compound is a moisture-sensitive white powder.

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When $LiAlH_4$ was allowed to react with thiols, the amount of H_2 liberated depended on the stoichiometry involved [Equation (4)].

$$MAlH_4 + n\,RSH \longrightarrow MAlH_{4-n}(SR)_n + nH_2 \qquad M = Li, Na;\ R = Et, iPr, tBu \tag{4}$$

$$2\,NaAlH_2(S\text{-}iPr)_2 \leftrightarrow NaAlH_3(S\text{-}iPr) + NaAlH(S\text{-}iPr)_3 \tag{5}$$

$$2\,NaAlH_3(S\text{-}iPr) \rightarrow NaAlH_4 + NaAlH_2(S\text{-}iPr)_2 \tag{6}$$

1:1 reactions of $LiAlH_4$ with EtSH or *i*PrSH in ether gave a solution which shows only a single ^{27}Al NMR signal at $\delta = 115$; this demonstrates not only the formation of $LiAlH_3(SR)$ but also proves its stability against ligand exchange. For the analogous organyloxyhydridoaluminates this kind of ligand exchange is typical,[9−11] and all members of the series $LiAlH_{4-n}(OR)_n$ can be detected in solution. However, when *i*PrSH was allowed to react with $NaAlH_4$ in THF in a 1:1 ratio the ^{27}Al NMR spectrum reveals the presence of at least three species [$NaAlH_4$, $NaAlH_2(SiPr)_2$ and $NaAlH(SiPr)_3$] in solution, as shown in Equation (5).

Treatment of $LiAlH_4$ in ether with *t*BuSH in a 1:3 ratio yielded compound **6** which was isolated as $Et_2O{\cdot}LiAlH(StBu)_3$. However, in addition to this main product small amounts of crystals separated from the solution, and an X-ray structure analysis proved them to be $(Et_2O){\cdot}LiAlH(StBu)_3{\cdot}LiStBu$ (**7·Et₂O**). Most likely this compound was formed in a reaction sequence described by Equation (7) to (9).

$$LiAlH_4 + 3\,{}^tBuSH \longrightarrow \underset{\textbf{6}}{LiAlH(S^tBu)_3} + 3\,H_2 \tag{7}$$

$$LiAlH(S^tBu)_3 + Et_2O \rightarrow HAl(S^tBu)_2{\cdot}OEt_2 + LiS^tBu \tag{8}$$

$$LiAlH(S^tBu)_3 + LiS^tBu \rightarrow \underset{\textbf{7}}{LiAlH(S\text{-}^tBu)_3\,LiS^tBu} \tag{9}$$

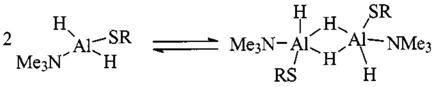
Obviously, $LiAlH(StBu)_3$ behaves as a Lewis acid and adds LiS*t*Bu through its *t*BuS groups. In order to test whether $LiAlH(StBu)_3$ would add an alane as a Lewis base, we employed $(tBuS)_2AlH{\cdot}NMe_3$. As shown in Equation (10) a 1:1 mixture of $LiAlH_4$ and $AlH_3{\cdot}NMe_3$ reacted smoothly with *t*BuSH to produce the compound $LiAlH(StBu)_3{\cdot}AlH(StBu)_2{\cdot}NMe_3$ (**8**). However, the alane acted as a ligand only for the Li center with the formation of Li−S bonds, and no NMe_3 displacement from $(tBuS)_2AlH{\cdot}NMe_3$ occurred.

$$LiAlH_4 + AlH_3{\cdot}NMe_3 + 5\,HS^tBu \rightarrow \underset{\textbf{8}}{LiAlH(S^tBu)_3{\cdot}AlH(S^tBu)_2{\cdot}NMe_3} + 5\,H_2 \tag{10}$$

NMR-Spectroscopic Data

As already indicated, only a single ^{27}Al NMR signal can be observed for the alkylthiolatoalanes **1−5**. Table 1 lists the relevant data.

Compounds **1−3** are tetracoordinated at the Al atom as shown by the low-field resonances. The signals are not very broad, nevertheless no Al−H coupling can be observed. Compound **4**, in ether solution, shows a better shielded Al center than compounds **1−3**. However, in benzene solution the Al nucleus of the ether-free compound **4** exhibits no change in shielding, but an enormous increase in the line width. This is an indication of the association of monomeric molecules in solution, probably through hydrogen bonds [Equation (11)]. If **4** were present in solution with pentacoordinated Al centers, the signal would then appear at an even higher field ($\delta \approx 110-120$). The ^{27}Al NMR spectrum of **4** in benzene solution also shows a low-intensity signal at $\delta = 9$ which points to the presence of a hexacoordinated species.



(11)

In contrast to alkoxyalanes, the shielding of the ^{27}Al nucleus is only marginally influenced by the number of RS substituents (compare **3** with **5**). However, this is not the case for the alkylthiolatohydridoaluminates; here, $\delta(^{27}Al)$ changes in the same manner as for the $AlH_{4-n}(OR)_n^-$ species.[9,11c] A higher degree of RS substitution leads to a successive deshielding of the ^{27}Al nucleus. The solution for the 1:1 reaction of $NaAlH_4$ with *i*PrSH shows three ^{27}Al NMR

Table 1. ^{27}Al NMR spectroscopic data of alkylthiolatoalanes and alkylthiolatohydridoaluminates (δ in ppm, $h_{1/2}$ in Hz)

	1	**2**	**3**	**4**	**5**	**6**	**7**
$\delta^{27}Al$	152	151	147	132	147	136	147
$h_{1/2}$	1053	1126	1103	1510	924	4390	1000
Solvent	C_6D_6	C_6D_6	C_6D_6	Et_2O	C_6D_6	C_6D_6	C_6D_6
δ (^7Li)	−	−	−	−	−	0.26	0.70
Solvent						Ether	C_6D_6
	$LiAlH_3SEt$	$LiAlH_3SiPr$	$LiAlH_2(SiPr)_2$	$LiAlH(StBu)_3$			
$\delta^{27}Al$	115	115	128	131, 133			
Solvent	Ether	Ether	Ether	THF, Ether			

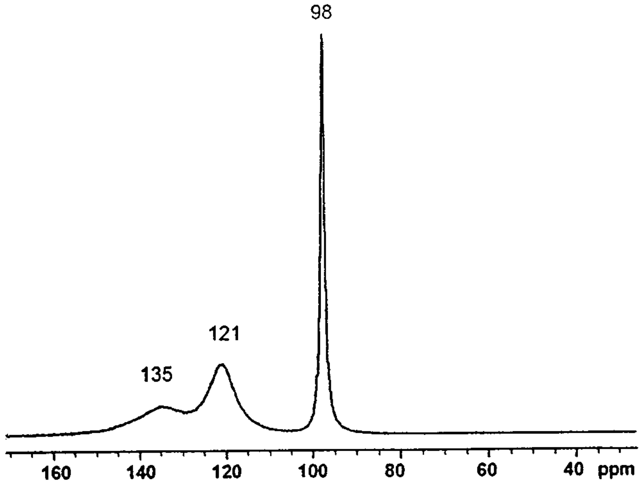


Figure 1. ^{27}Al NMR spectrum of a solution of "$NaAlH_2(S\textit{i}Pr)_2$" in THF to show the presence of various species; signals at δ = 98, 121 and 135 are assigned to $NaAlH_4$, $NaAlH_2(S\textit{i}Pr)_2$ and $NaAlH(S\textit{i}Pr)_3$

signals (see Figure 1). The sharp signal stems from $NaAlH_4$, the signal at δ = 135 is due to $NaAlH(S\textit{i}Pr)_3$ and the signal at δ = 121 due to $NaAlH_2(S\textit{i}Pr)_2$ (exchange). $NaAl(S\textit{i}Pr)_4$ is not present as this would give rise to a sharp and easily detectable signal.

IR Data

Table 2 contains a list of Al−H stretching bands. Compounds **2** and **3** exhibit a strong band in the narrow region 1805−1808 cm^{-1}, and compound **5** a strong and sharp band at 1840 cm^{-1}. Therefore, two electronegative RS groups strengthen the Al−H bond. This is in agreement with the series of compounds $AlH_{3-n}X_n{\cdot}OEt_2$ (X = Cl, Br).[12] Compound **4** shows a band for a terminal Al−H stretching vibration at 1846 cm^{-1}. In addition, there is a strong broad band ranging from 1750 to 1570 cm^{-1}, which is due to an Al−H−Al bridging mode. A band at 1699 cm^{-1} is observed for compound **2** (solid in Nujol mull) which also proves the presence of bridging hydrides. Consequently, this compound does not seem to be present as monomeric $\textit{i}PrSAlH_2{\cdot}NMe_3$, but it is associated through Al−H−Al bridges. This is because the IR data exclude the presence of an Al−(SR)−Al bridge. The Al−H(terminal) stretching vibrations for the hydridoaluminates are found in the 1850-cm^{-1} region, which are associated with tetracoordinated Al centers.

Table 2. Al−H strechting bands (in cm^{-1}) for compounds **2−6** and **8**; for further data see Experimental Section

	2	3	4	5	6	8
νAlH_2	1808	1805	1846	1840	1829	1858, 1782
νAl−H−Al	1699	−	1750−1570	−	−	−

Molecular Structures

The structural features deduced from IR- and NMR-spectroscopic data of compounds **1−5** are ascertained by the determination of the molecular structure of **5** by X-ray structure analysis. This compound crystallizes in space group $P2_1/c$. The Al center is surrounded by two S atoms, one N and one H atom in a distorted tetrahedral array (see Figure 2).

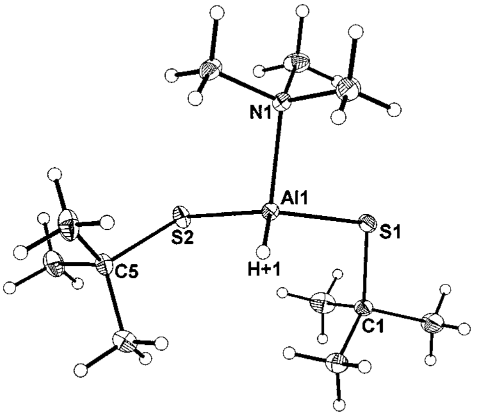


Figure 2. ORTEP plot of the molecular structure of the crystal of $HAl(S\textit{t}Bu)_2{\cdot}NMe_3$ (**5**); thermal ellipsoids are shown on a 25% probability scale; selected bond lengths [Å] and angles [°] (esd values in parentheses): Al1−S1 2.2496(5), Al1−S2 2.2296(5), Al1−N1 2.020(1), Al1−H1 1.50(2), S1−C1 1.861(1), S2−C5 1.863(1); N1−Al1−S1 98.46(3), N1−Al1−S2 106.19(4), S1−Al1−C2 112.00(2), H1−Al1−N1 102.9(6), H1−Al1−S1 118.1(6), H1−Al1−S2 116.2(6), Al1−S1−C1 106.44(4), Al1−S2−C5 108.20(5), C10−N1−C9 109.2(1), C10−N1−C11 108.5(1), C9−N1−C11 107.6(1), C10−N1−Al1 112.70(8), C11−N1−Al1 110.09(8), C9−N1−Al1 108.6(9)

The Al−S bond lengths (average 2.240 Å) are shorter than the Al−S dative bond in $[\textit{t}BuAl(\mu\text{-}OC_6H_4\text{-}2\text{-}SMe)]_2$ [2.778(1) Å].[13] The latter is comparable with the Al−S bond lengths in $AlH(SCH_2CH_2NEt_2)_2$ (average 2.725 Å)[14] with its pentacoordinated Al center. Thus, the difference in bond lengths between the tetracoordinated Al center in **5** and the pentacoordinated Al atom in $AlH(SCH_2CH_2NEt_2)_2$ is ca. 0.49 Å. It is also significantly longer than in the tricoordinated Al compound $Al(SC_6H_2\textit{t}Bu_3)_3$ [2.185(8) Å].[15] Al−S−C bond angles are wider than the H−S−C bond angles in thiols (96−101°).[16]

Crystals obtained from the 1:3 reaction of $LiAlH_4$ with *t*BuSH were suspected to be $LiAlH(S\textit{t}Bu)_3$ but proved to be the ether adduct of dimeric $LiAlH(S\textit{t}Bu)_3{\cdot}LiS\textit{t}Bu$ (**7**) by X-ray structure analysis. The molecular structure as found for the solid state is represented in Figure 3.

The centrosymmetric dimer features a planar central Li_2S_2 ring with open S−Li−S bond angles [103.9(3)°] and rather sharp Li−S−Li angles [76.1(3)°]. Each lithium atom is tetracoordinated, atom Li1 is surrounded by three sulfur atoms and one oxygen atom, while atom Li2 coordinates to four sulfur atoms. It should be noted that the Li−S bonds to the tetracoordinated S4 atom (average 2.429 Å) are slightly shorter than the Li−S bonds to the tricoordinated

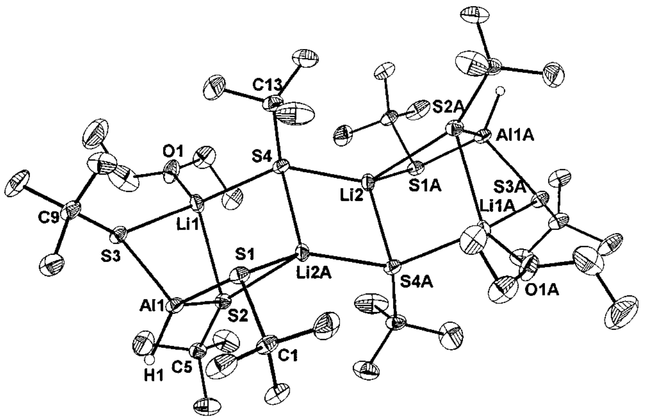


Figure 3. Molecular structure of the crystal of **7·OEt₂**; thermal ellipsoids are depicted on a 25% probability level; hydrogen atoms bonded to C atoms are not shown for clarity; selected atom distances [Å] and bond angles [°] (esd values in parentheses): Al1−H1 1.39(1), Al1−S1 2.259(2), Al1−S2 2.263(2), Al1−S3 2.242(2), Al1−S1 3.250(8), Li1−O1 1.889(9), Li1−S2 2.548(9), Li1−S3 2.563(9), Li1−S4 2.427(9), Li1−Li2A 3.39(1), Li2−Li2A 2.98(2), Li2A−S4 2.404(8), Li2−S1A 2.494(8), Li2−S4A 2.431(8), Li2−S2A 2.803(9), Li2A−S1 2.494(8), Li2A−S2 2.803(9), S1−C1 1.854(5), S2−C5 1.858(5), S3−C9 1.848(5), S4−C13 1.838(5); H1−Al1−S1 112(2), H1−Al1−S2 116(4), H1−Al1−S3 117(4), S1−Al1−S2 102.83(8), S1−Al1−S3 110.16(8), S2−Al1−S3 96.80(7), S1−Li2a−S4 137.6(3), S1−Li2A−S2 89.4(3), O1−Li1−S4 1o8.9(4), O1−Li1−S2 127.5(4), Al1−S1−Li2A 90.2(2), Al1−S2−Li2A 82.7(2), Al1−S2−Li1 84.8(2), Al1−S3−Li1 84.8(2), LI1−S4−Li2 139.1(3), Li1−S4−Li2A 88.4(3), Li2−S4−Li2A 76.1(3)

S atoms. Atom Li1 binds to only two sulfur atoms of the $HAl(StBu)_3^-$ unit, and these bonds are the longest ones (2.548, 2.563 Å) while the bond Li1−S4 adopts an intermediate position (2.494 Å). The shortest Al−S bond is Al1−S2 [2.263(2) Å], atom S2 being tetracoordinated. It features a very large Li2A−S2−C5 bond angle of 155.1(2)°. All S−Al−S bond angles are rather sharp (96−103°), and, consequently, the H−Al−S bond angles are wide (112−117°). This asymmetry for a tetracoordinated Al atom with respect to a tetrahedral array is also present at the Li atoms.

A much simpler molecular structure is observed for compound **8**, $LiAlH(S\mathit{t}Bu)_3 \cdot AlH(S\mathit{t}Bu)_2 \cdot NMe_3$, as shown in Figure 4. One can readily note that it is an addition product of $HAl(S\mathit{t}Bu)_2 \cdot NMe_3$ and $LiAlH(S\mathit{t}Bu)_3$. The metal ions are tetracoordinated and the skeleton of the molecule can be described as a spirocycle with the Li atom at the spiro center. This Li atom coordinates to four sulfur atoms with Li−S bond lengths ranging from 2.489(6) to 2.511(6) Å. There are two pairs of sharp S−Li−S bond angles (88°) and two wide ones (136°). The coordination geometry around both Al atoms is a strongly distorted tetrahedral geometry. The distortion is greater for Al1 than for Al2. At Al2, the S−Al−S bond angles are all different, the smallest one is S3−Al2−S5 with only 97.66(5)°, probably due to the coordination of these S atoms to Li1. In contrast, the angle S3−Al2−S4 is rather wide, 117.49(6)°, while the angle S5−Al2−S4 [109.19(6)°] is almost a perfect tetrahedral angle.

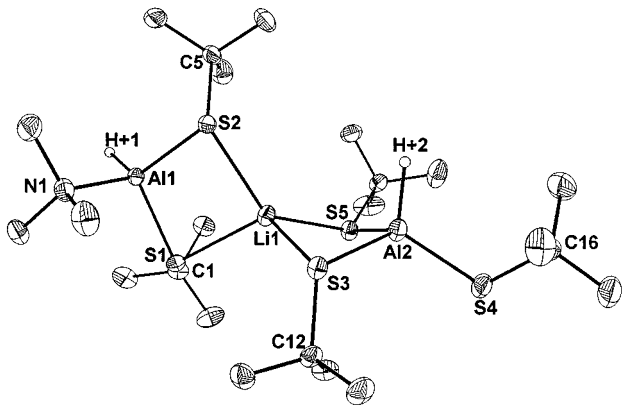


Figure 4. ORTEP presentation of the molecular structure of the crystal of **8**; thermal ellipsoids are drawn on a 25% probability level; H atoms bonded to carbon atoms are omitted for clarity; selected atom distances [Å] and bond angles [°] (esd values in parentheses): Al1−H1 1.48(4), Al1−N1 1.979(3), Al1−S1 2.246(1), Al1−S2 2.243(1), Al2−H2 1.58(4), Al2−S3 2.281(2), Al2−S4 2.237(2), Al2−S5 2.293(2), Li1−S1 2.489(6), Li1−S2 2.551(6), Li1−S3 2.491(6), Li1−S5 2.445(6), S1−C1 1.865(4), S2−C5 1.866(4), S3−C12 1.866(4), S4−C16 1.865(4), S5−C20 1.858(4); N1−Al1−S1 103−7(1), N1−Al1−S2 106.2(1), S1−Al1−S2 103−67(5). Al1−S−Li1 83.5(2), Al1−S2−Li1 82.2(2), S1−Li1−S2 88.8(2), S3−Li1−S5 88.5(2), S1−Li1−S3 109.8(2), S2−Li1−S5 136.5(3), S2−Li1−S3 108.7(2), DS1−Li1−S5 112.9(2), Li1−S5−C20 127.2(2)

Discussion

Although the present study on the interaction of thiols with alane·trimethylamine, $LiAlH_4$ and $NaAlH_4$ is not as complete as analogous studies with alcohols,[8−11] some generalizations can be deduced. As expected, when the thiols, which are more acidic than alcohols, react, the amount of hydrogen evolved and the formation of the products are determined by the stochiometry involved. While AlH_3 in ether reacts with alcohols (ROH) having small R groups (R = Me, Et, Pr), to produce not very well defined products of composition $AlH_{3-n}(OR)_n$, only single-type species $AlH_2(SR) \cdot NMe_3$ and $AlH_2(SR) \cdot NMe_3$, which are stable against ligand exchange at ambient temperatures, are formed in the reaction of alane trimethylamine with thiols. Compound $AlH_2SEt \cdot NMe_3$ associates in the solid state through hydride bridges, and the IR spectra clearly show that there are no Al−S−Al bridging bonds. In contrast, compounds $ROAlH_2$ are characterized by Al−O−Al bridges.[17] This difference can readily be explained by the HASB theory. The softer base H^- is preferred as a bridging ligand over sulfur, and the IR spectra of the compounds $RSAlH_2 \cdot NMe_3$ indeed show the presence of Al−H−Al bridges,[18] while in the case of alkoxyalanes the Al−O bonds are thermodynamically favored. No bands attributable to Al−H−Al vibrations are present for $(\mathit{t}BuS)_2AlH \cdot NMe_3$ (**5**) in agreement with its molecular structure.

Reactions of $MAlH_4$ with RSH have concentrated on the $LiAlH_4$/*t*BuSH and $NaAlH_4$/*i*PrSH systems, particularly on the former. For the first system, the product expected by the stoichiometry of the reaction has been found to be LiAlH(S*t*Bu)$_3$ (**6**). However, in addition, a small amount of the dimeric compound LiAlH(S*t*Bu)$_2$·LiS*t*Bu (**7**) is also formed, demonstrating that LiHAl(S*t*Bu)$_3$, whose structure is still unknown, may act as a Lewis base through its RS groups. This has been verified by the addition of the alane (*t*BuS)$_2$AlH·NMe$_3$ to LiHAl·(S*t*Bu)$_3$ in compound **8**. This is a feature that needs further investigation; a similar behavior is, as yet, unknown in alkoxyaluminate chemistry. However, an investigation of Noyori's reagent[19,20] revealed many unexpected aspects showing that even hexacoordinated aluminates are readily formed.[21] We will report on these results shortly.

It is expected that the Al−S bond length would increase with increasing coordination number, and this can be demonstrated for the compounds investigated. All Al atoms of compounds **5**, **7** and **8** are tetracoordinated while the S atoms have coordination numbers 2, 3 and 4, respectively. Average Al−S bonds are as follows: $\mathrm{Al^{(4)}{-}S^{(2)}}$ = 2.239 Å, $\mathrm{Al^{(4)}{-}S^{(3)}}$ = 2.244 Å, and $\mathrm{Al^{(4)}{-}S^{(4)}}$ = 2.457 Å. In addition, the average Al−S bond length $\mathrm{Al^{(6)}{-}S^{(2)}}$ has been found to be 2.399 Å.[22] (Coordination numbers are set here in superscript). Therefore, we observe an increase in the Al−S bond lengths as the coordination number of sulfur increases. The $\mathrm{Al^{(4)}{-}S^{(2)}}$ bond length is shorter than the $\mathrm{Al^{(6)}{-}S^{(2)}}$ bond lengths by 0.016 Å. This trend was to be expected. Li−S bond lengths give no clear separation between $\mathrm{Li^{(4)}{-}S^{(3)}}$ and $\mathrm{Li^{(4)}{-}S^{(4)}}$, the former span the range from 2.489 to 2.566 Å, the latter from 2.457 to 2.548 Å. These data are in agreement with known structures of lithium thiolates,[23] the shortest being 2.39 Å found in (Et$_2$O)$_2$Li(trip−S)$_2$In(S−trip)$_2$ (trip = 2,4,6-triisopropylphenyl).

Experimental Section

All experiments were performed under anhydrous conditions and dinitrogen using Schlenk techniques. LiAlH$_4$ was supplied by Chemetall GmbH and AlH$_3$·NMe$_3$ prepared form LiAlH$_4$ and [Me$_3$NH]Cl.[24] The thiols used were obtained commercially. − NMR: Jeol GSX 270 and EX 400; standards: AlCl$_3$ in H$_2$O (1 M), C$_6$D$_6$, SiMe$_3$. − IR: Nicolet 20 FT spectrometer (4000−400 cm^{-1}) as Nujol/Hostaflon mulls. − X-ray: Siemens P4 diffractometer with CCD area detector and LT2 low-temperature device. − Elemental analysis: C, H, N in the microanalytical laboratory of the institute; Al complexometrically. Partial hydrolysis was noted in weighing small samples for elemental analysis. This may be the reason for several significant deviations between calculated and found values.

Alkylthiolatoalanes and Lithium(alkylthiolato)hydridoaluminates. − General Procedure: The hydrides (AlH$_3$·NMe$_3$, AlH$_3$ in ether, LiAlH$_4$ or NaAlH$_4$) were dissolved or suspended in toluene, ether or THF. While stirring, a solution of the thiol in the respective solvent was added (1:1, 1:2 ratio), and stirring was continued until gas evolution had ceased. No elemental analysis was performed when ^{27}Al NMR spectra proved that only a single compound was present.

Ethylthiolatoalane·Trimethylamine (1): Prepared from AlH$_3$·NMe$_3$ (0.68 g, 7.63 mmol) in toluene (5 mL), and EtSH (0.47 g, 7.63 mmol) in toluene (4 mL). Addition at −4 °C, 2 h stirring at ambient temperature. An oil remained after stripping off all volatiles in vacuo. This oil solidified on standing to a waxy mass. − ^{27}Al NMR (70 MHz, C$_6$D$_6$): δ = 152 ($h_{1/2}$ = 1053 Hz). − ^{1}H NMR (270 MHz, C$_6$D$_6$): δ = 1.33 [t, ^3J(H,H) = 7.5 Hz, 3 H, CH$_3$CH$_2$S−], 2.00 (s, 9 H, NCH$_3$), 2.67 [q, ^3J(H,H) = 7.5 Hz, 2 H, CH$_3$CH$_2$S−], 4.0 (br, 2 H, AlH$_2$). − ^{13}C NMR (68 Hz, C$_6$D$_6$): δ = 20.9 (CH$_3$CH$_2$S−), 21.5 (br., CH$_3$CH$_2$S−), 46.9 (NCH$_3$).

Isopropylthiolatoalane·Trimethylamine (2): Prepared from AlH$_3$·NMe$_3$ (560 mg, 6.28 mmol) in toluene (10 mL) and *i*PrSH (480 mg, 6.28 mmol) in toluene (5 mL) at 0 °C, 2 h stirring at ambient temperature. All volatiles were removed in vacuo. Yield: 950 mg (92.7%). − ^{27}Al NMR (104 MHz, C$_6$D$_6$): δ = 151 ($h_{1/2}$ = 1126 Hz). − ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.43 [d, ^3J(H,H) = 6.6 Hz, 6 H, CH$_3$(*i*Pr)], 1.97 (s, 9 H, NCH$_3$), 3.25 [qq, ^3J(H,H) = 6.6 Hz, 1 H, CH(*i*Pr)], 4.08 (br., AlH$_2$). − ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 29.7 [CH$_3$(*i*Pr)], 47.0 (NCH$_3$), 32.6 [br., CH(*i*Pr)]. − IR (CsBr): ṽ = 2975 (vs), 2953 (vs), 2916 (vs), 2857 (vs), 1808 (vs, νAlH$_2$), 1699 (m, br., νAlH$_{\mathrm{br}}$), 1480 (vs), 1463 (vs), 1447 (vs), 1406 (m), 1379 (m), 1363 (s), 1244 (s), 1152 (s), 1102 (m), 1050 (m), 1015 (m), 994 (vs), 887 (m), 816 (s), 792 (vs), 746 (vs), 702 (vs), 650 (vs, br), 626 (vs), 552 (s), 501 (s) cm^{-1}.

***tert*-Butylthiolatoalane·Trimethylamine (3):** Prepared from AlH$_3$·NMe$_3$ (1.18 g, 13.2 mmol) in toluene (10 mL) and Me$_3$CSH (1.19 g, 13.2 mmol) in toluene (10 mL) at −15 °C. The resulting solution was stirred for 1 h at 20 °C. After removal of all volatiles, 2.20 g (92.8%) of an oily liquid remained, m.p. 10−15 °C. − ^{27}Al NMR (70 MHz, C$_6$D$_6$): δ = 147 ($h_{1/2}$ = 1103 Hz). − ^{1}H NMR (270 MHz, C$_6$D$_6$): δ = 1.97 [s, 9 H, CH$_3$(*t*Bu)], 1.59 (s, 9 H, NCH$_3$). − ^{13}C NMR (68 MHz, C$_6$D$_6$): δ = 37.1 [CH$_3$(*t*Bu)], 42.4 [br., C$_q$(tBu)], 47.3 (NCH$_3$). − IR (CsBr): ṽ = 2972 (vs), 2957 (vs), 2937 (vs), 2921 (vs), 2894 (s), 2862 (s), 1805 (vs,νAlH$_2$), 1480 (vs), 1462 (vs), 1361 (vs), 1244 (m), 1164 (m), 1156 (m), 1103 (w), 995 (vs), 818 (m), 792 (m, sh), 754 (vs), 732 (s), 705 (vs), 659 (s, br.), 625 (s), 583 (m), 521 (m), 501 (m), 464 (m) cm^{-1}.

***tert*-Butylthiolatoalane (4):** LiAlH$_4$ (25.42 mmol) in Et$_2$O (20 mL) was converted into AlH$_3$ by reaction with AlCl$_3$ (1.17 g, 8.47 mmol), dissolved in ether (20 mL), followed by addition of Me$_3$CSH (3.06 g, 32.9 mmol) in ether (10 mL). After 2 h, the insoluble material was separated and ether removed from the filtrate in vacuo. An oil remained that proved to contain Et$_2$O by NMR spectroscopy. It was treated several times with small amounts of pentane and the residue was then kept in vacuo for several hours. This produced a white powder. Yield: 4.00 g (66.6%). −^{27}Al NMR (70 MHz, Et$_2$O): δ = 132 ($h_{1/2}$ = 1510 Hz), (C$_6$D$_6$): δ = 132 ($h_{1/2}$ = 6632 Hz), 9 ($h_{1/2}$ = 3061 Hz). − ^{1}H NMR (270 MHz, C$_6$D$_6$): δ = 1.58 [s, 9 H, CH$_3$(*t*Bu)], ca. 4.5 (br., AlH$_2$). − ^{13}C NMR (68 MHz, C$_6$D$_6$): δ = 14.7 (CH$_3$), 47.8 [C$_q$(*t*Bu)]. − IR (Nujol, Hostaflon): ṽ = 2962 (vs), 2937 (vs), 2925 (vs), 2900 (vs), 2862 (vs), 1846 (vs, br.)/ca.1750−1570 (s, br.) (νAlH$_n$), 1472 (vs), 1460 (vs), 1395 (s), 1369 (s, sh), 1364 (s), 1159 (m), 810 (vs, br.), 744 (vs, br), 688 (vs, br), 666−600 (vs, br), 576 (s, br) cm^{-1}. − C$_4$H$_{11}$AlS (118.17): calcd. C 40.66, H 9.38; found C 37.62, H 8.50.

Bis(*tert*-butylthiolato)alane·Trimethylamine (5): Prepared from AlH$_3$·NMe$_3$ (920 mg, 10.3 mmol) in toluene (15 mL) and Me$_3$CSH (1.86 g, 20.7 mmol) in toluene (8 mL) at −15 °C. The resulting solution was stirred for 1 h followed by reduction of the volume of the solution by ca. 50%. From this solution crystals separated at −20 °C. Yield: 2.41 g (93.4%), m.p. 62 °C. − ^{27}Al NMR (70 MHz, C$_6$D$_6$): δ = 147 ($h_{1/2}$ = 924 Hz). − ^{1}H NMR (270 MHz, C$_6$D$_6$): δ = 1.71 [s, 18 H, CH$_3$(*t*Bu)], 1.94 (s, 9 H, NCH$_3$). − ^{13}C NMR

(68 MHz, C_6D_6): δ = 37.1 [CH_3(tBu)], 47.3 (NCH_3). − IR (Nujol, Hostaflon): ṽ = 2975 (vs), 2957 (vs), 2938 (vs), 2900 (vs), 2733 (vs), 1840 (vs, νAlH_2), 1482 (vs), 1471 (s), 1458 (s), 1444 (m), 1423 (m), 1406 (s), 1390 (m), 1360 (s), 1245 (s), 1241 (s), 1212 (s), 1166 (vs), 1150 (vs), 1110 (s), 1105 (s), 1024 (m), 997 (vs), 988 (vs), 819 (vs), 657 (vs), 628 (vs), 580 (vs), 528 (vs), 493 (vs), 460 (s) cm^{-1}. − $C_{10}H_{25}AlNS_2$ (250.42): calcd. C 47.96, H 10.06, Al 10.78, N 5.59; found C 46.33, H 8.61, Al 10.45, N 5.31.

Lithium Tris(*tert*-butylthiolato)hydridoaluminate (6) and Its 1:1 Adduct with Lithium *tert*-Butylthiolate (7): A solution of Me_3CSH (4.81 g, 53.3 mmol) in ether (20 mL) was allowed to react with $LiAlH_4$ (17.76 mmol) in ether (20 mL). A slightly turbid solution formed. On keeping the clear solution at 0 °C for several days, a small amount of crystals of $(\mathbf{7})_2$ formed. This was confirmed by X-ray structure analysis. From the filtrate all volatile materials were removed in vacuo, and the residue washed several times with small amounts of pentane. On keeping the solid material under vacuum (10^{-3} Torr) all the ether could be removed from **6**. Yield: 4.75 g (71%), m.p. 136 °C (dec.). − ^{27}Al NMR (70 MHz, C_6D_6): δ = 136 ($h_{1/2}$ = 4392 Hz); (Et_2O): δ = 133 ($h_{1/2}$ = 1782 Hz); (THF): δ = 131 ($h_{1/2}$ = 1535 Hz). − ^{7}Li NMR (105 MHz, Et_2O): δ = 0.26 ($h_{1/2}$ = 64.9 Hz). − ^{1}H NMR (270 MHz, C_6D_6): δ = 1.10 [t, br., ^3J(H,H) = 7.0 Hz, 6 H, $CH_3(Et_2O)$], 1.70 [s, 27 H, CH_3(*t*Bu)], 3.33 [dd, br., ^3J(H,H) = 7.0 Hz, 4 H, $CH_2(Et_2O)$]. − ^{13}C NMR (68 MHz, C_6D_6): δ = 15.1 [$CH_3(Et_2O)$], 36.2 [CH_3(*t*Bu)], 45.1 (C_q), 65.7 [$CH_2(Et_2O)$]. − IR (Nujol, Hostaflon): ṽ = 2973 (vs), 2959 (vs), 2938 (vs), 2921 (vs), 2894 (vs), 2859 (vs), 1829 (vs, νAlH_2), 1472 (s), 1458 (s), 1389 (m), 1362 (vs), 1216 (m), 1187 (m), 1167 (vs), 1153 (vs), 1106 (m), 1097 (s), 1069 (s), 1027 (m), 839 (w), 820 (s), 657 (vs), 613 (vs), 578 (vs) cm^{-1}. − $C_{12}H_{38}AlLiS_3$ (302.47): calcd. C 47.65, H 9.33, Al 8.92; found C 47.16, H 9.30, Al 8.55.

Lithium Pentakis(*tert*-butylthiolato)dihydridodialuminate·Trimethylamine (8): A solution of $LiAlH_4$ (8.08 mmol) in ether (5 mL) was added to a solution of $AlH_3·NMe_3$ (720 mg, 8.08 mmol) in toluene (10 mL), followed by dropwise addition of Me_3CSH (3.64 g, 40.4 mmol), dissolved in toluene (5 mL), at −20 °C. Stirring was continued for 1 h, and ether removed at 10 Torr from the solution. On cooling to −20 °C needles of **8** separated. From the filtrate all volatiles were removed in vacuo giving **8**, m.p. 147−150 °C (dec.). − ^{27}Al NMR (104 MHz, C_6D_6): δ = 147 ($h_{1/2}$ = 998 Hz). − ^{7}Li NMR (105 MHz, C_6D_6): δ = 0.70 ($h_{1/2}$ = 11.0 Hz). − ^{1}H NMR (270 MHz, C_6D_6): δ = 1.72 [s, br., CH_3(*t*Bu)], 1.73 [s, br., CH_3(*t*Bu)], 1.92 (s, NCH_3). − ^{13}C NMR (68 MHz, C_6D_6): δ = 36.4 [br., CH_3(*t*Bu)], 37.1 [CH_3(*t*Bu)], 43.2 (C_q), 47.3 (NCH_3). − IR (Nujol, Hostaflon): ṽ = 2969 (vs), 2957 (vs), 2938 (vs), 2929 (vs), 2894 (vs), 2859 (vs), 1858 (vs)/1782 (vs, νAlH_2), 1481 (s), 1472 (s), 1459 (s), 1446 (w), 1406 (m), 1360 (vs), 1309 (m, br.), 1244 (s, br.), 1236 (vs), 1212 (m), 1166 (vs), 1152 (vs), 1111 (m), 1105 (m), 997 (m), 986 (vs), 815 (s), 653 (vs), 628 (s), 578 (m) cm^{-1}. − $C_{23}H_{56}Al_2S_5LiN$ (567.94): calcd. C 48.64, H 9.94, Al 9.50, N 2.47; found C 46.86, H 9.22, Al 9.13, N 1.86.

Crystal Structure Determinations: Single crystals of compounds **5**, **7**, and **8** were covered with perfluoroether oil, the selected crystal mounted on the tip of a glass fiber and placed on a goniometer head. The goniometer head was then fitted on the support of a Siemens P4 diffractometer equipped with a low-temperature device LTP2 and a CCD area detector. Graphite-monochromated Mo-K_α radiation was used for measurements. Preliminary unit-cell determinations were performed with the reflection data of a total of 75 frames taken in five different orientations of 15 frames each by changing φ by 0.3° increments. Data collection was performed with the program HEMISHERE and 5 s/frame exposure time with two

Table 3. Crystal data and data of collection parameters and results of refinement

Compound	**5**	**7**	**8**
Empirical formula	$C_{11}H_{28}AlNS_2$	$C_{20}H_{47}AlLi_2OS_4$	$C_{23}H_{56}Al_2LiNS_5$
Molecular mass	265.44	472.68	567.89
Crystal size [mm]	0.20 × 0.30 × 0.40	0.3 × 0.5 × 0.5	0.10 × 0.10 × 0.40
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a [Å]	15.1505(1)	15.385(7)	11.646(3)
b [Å]	9.6977(2)	10.709(6)	18.351(3)
c [Å]	11.8115(2)	18.75(1)	17.118(3)
β [°]	110.323(1)	107.542(8)	102.176(8)
V [Å^3]	1627.37(4)	2944.9(27)	3576.1(13)
Z	4	4	4
ρ(calcd.) [Mg/m^3]	1.083	1.066	1.055
μ [mm^{-1}]	0.358	0.360	0.385
F(000)	584	1032	1240
Index range	$-18 \le h \le 18$, $-11 \le k \le 12$, $-14 \le l \le 15$	$-18 \le h \le 16$, $-13 \le k \le 13$, $-24 \le l \le 24$	$-13 \le h \le 13$, $-21 \le k \le 21$, $-19 \le l \le 19$
2θ [°]	57.92	58.42	49.42
T [K]	183(2)	183(2)	193(2)
Refl. collected	8968	16503	16658
Refl. unique	3197	5722	5713
Refl. observed (4σ)	2742	2856	4558
R (int.)	0.0164	0.0864	0.0319
No. variables	149	276	347
Weighting scheme[a] *x*/*y*	0.03910/0.3364	0.0590/7.8456	0.0575/5.6772
GOOF	1.044	1.168	1.060
Final *R*(4σ)	0.0268	0.0537	0.0564
Final *wR*2	0.0685	0.1341	0.1346
Largest residual peak [e/Å^3]	0.265	0.619	1.621

[a] $w^{-1} = \sigma^2F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

different χ settings. Data of a total of 1290 frames were collected and reduced using the program SAINT including absorption correction with the program SADABS. The structures were solved by direct methods (SHELXPLUS).[25] All non-hydrogen atoms were refined anisotropically, H atom positions at Al were taken from the difference Fourier data, and the H atom positions on C were calculated. These were included in the final refinement with a riding model, while the AlH hydrogen atoms were freely refined with fixed isotropic U values in the final cycles of refinement. All refinements proceeded normally. Relevant data are summarized in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143572 (**5**), -143573 (**7**·OEt$_2$), -143574 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] *Chemistry of Aluminium, Gallium, Indium and Thallium* (Ed.: A. J. Downs), Blackie Academic Professional, London, Glasgow, New York, Tokyo, Melbourne, Madras, **1993**, chapter 8.

[2] H. Rahbarnoohi, R. Kumar, M. J. Heeg, J. P. Oliver, *Organometallics* **1994**, *13,* 3300−3308.

[3] D. J. Brauer, G. D. Stucky, J. Am. Chem. *Soc.* **1969**, *91*, 5462−5466.

[4] A. Haaland, O. Stokkeland, J. Weidlein, *J. Organomet. Chem.* **1975**, *94*, 353−360.

[5] R. J. Wehmschulte, K. Ruthlandt-Senge, P. P. Power, *Inorg. Chem.* **1995**, *34*, 2593−2599.

[6] [6a] C. Jones, F. C. Lee, G. A. Koutsantonis, M. G. Gardiner, C. L. Raston, J. Chem. Soc. *Chem. Commun.* **1996**, 829−833. − [6b] W. Marconi, A. Mazzei, F. Bonati, M. de Malde, *Z. Naturforsch, Part B* **1963**, *18,* 3−5. − [6c]A. Mazzei, F. Bonati, W. Marconi, G. Manana, G. Castelfranchi, Ital. Patent 68730; *Chem. Abstr.* **1967**, *66*, P2724.

[7] H. Nöth, Dissertation, University of Munich, **1954**.

[8] A. Schlegel, H. Nöth, H. Schwenk-Kirchner, *Angew. Chem.* **1997**, *109*, 2754−2758.; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2640−2645.

[9] A. Schlegel, J. Knizek, I. Krossing, H. Nöth, W. Ponikwar, *Chem. Eur. J.* **1998**, *4*, 2191−2203.

[10] A. Schlegel, Dissertation, University of Munich, **1999.**

[11] [11a] H. C. Brown, C. J. Shoaf, J. Am. Chem. *Soc.* **1964**, *86*, 1079−1085. − [11b] N. Ya. Turova, M. I. Karporskaya, A. V. Novoselova, *J. Gen. Chem. USSR* **1966**, *47*, 1231−1237. − [11c] L. I. Zakharkin, D. N. Maslin, V. V. Gavrilova, *J. Gen. Chem. USSR* **1966**, *36*, 2000−2006. − [11d] J. Fusek, F. Hanousek, F. Haruda, Coll. Czech. *Chem. Commun.* **1976**, *41*, 187−192.

[12] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsfrequenzen*, G. Thieme Verlag, Stuttgart, New York, **1981.**

[13] D. G. Henndershot, M. Barber, R. Kumar, J. P. Oliver, *Organometallics* **1991**, *10*, 3302−3309.

[14] C. Jones, F. C. Lee, G. A. Koutsantonis, M. G. Gardiner, C. L. Raston, *J. Chem. Soc. Dalton Trans.* **1996**, 829−233.

[15] K. Ruthland-Senge, P. P. Power, *Inorg. Chem.* **1991**, *30*, 2633−2637.

[16] *Interatomic Distances*, Special Publ. No. 18, Royal Soc. Chem., London, **1968**.

[17] M. Veith, S. Faber, H. Wolfanger, V. Huch, *Chem. Ber.* **1996**, *129*, 381−384.

[18] J. L. Atwood, F. R. Bennet, F. M. Elms, C. Jones, C. L. Raston, K. D. Robinson, *J. Am. Chem. Soc.* **1991**, *113*, 8183−8185.

[19] R. Noyori, I. Tomino, M. Yamada, M. Nishizawa, *J. Am. Chem. Soc.* **1984**, *106,* 6709−6716.

[20] R. Noyori, *Pure Appl. Chem.* **1981**, *53*, 2315−2322.

[21] Max Suter, Diploma Thesis, University of Munich, **1999**; A. Schlegel, PhD Thesis, University of Munich, **1999**. See also ref.[10]

[22] H. Nöth, P. Konrad, *Chem. Ber.* **1983**, *116*, 3552−3558

[23] *Lithium Chemistry* (Eds.: A.-M. Sapse, P. v. Rague-Schleyer), J. Wiley Interscience, New York, Chichester, Brisbane, Toronto, Singapore, **1995**., chapter 8.

[24] J. K. Ruff, *Inorg. Synth.* **1967**, *9*, 30−37.

[25] *SHELXPLUS*, *SAINT*, *SMART*, *SADABS*, Siemens Analytical Instrumentation, Madison, **1995**, Version 4.1.

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