Formation of Methylchloroaluminium Alkanethiolates, MeAl(SR)Cl, and Dichloroaluminium Alkanethiolates, Cl₂AlSR, from Methylaluminium Dichloride and Trimethylsilyl Alkanethiolates, Me₃SiSR

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Dedicated to Prof. Dr. Dr. h.c. Max Schmidt on the occasion of his 75th birthday

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Methylchloroaluminium Alkanethiolates, Dichloroaluminium Alkanethiolates

Depending on the reaction conditions methylaluminium dichloride, MeAlCl₂, and trimethylsilyl alkanethiolates, Me₃SiSR, give dichloroaluminium alkanethiolates, Cl₂AlSR with R = Me and Et or methylchloroaluminium alkanethiolates, MeAl(SR)Cl with R = Me, Et, and i-Pr. The reaction pathways are described and IR and ¹H NMR spectroscopic data are presented.

Results and Discussion

Introduction

In an attempt to further examine the reactivity of MeMCl₂ (M = Al, Ga, In) compounds towards trimethylsilyl alkanethiolates, Me₃SiSR, methylaluminium dichloride, MeAlCl₂, has been investigated in some detail. Generally, one can expect reactions of equimolar amounts of MeMCl₂ (M = Al, Ga, In) and Me₃SiSR (R = alkyl, aryl) to form the corresponding MeM(SR)Cl derivatives with three different functional groups attached to the metal atom together with Me₃SiCl as already shown for MeGaCl₂ [1]. The unexpected and interesting behaviour of MeAlCl₂ is reported here.

Synthesis

Strongly depending on the reaction conditions, the interaction of methylaluminium dichloride and trimethylsilyl alkanethiolates at ambient temperature in benzene or n-pentane as solvent leads to the formation of either dichloroaluminium alkanethiolates or methylchloroaluminium alkanethiolates according to eq. (1a) and eq. (1b), respectively:

\[
\text{MeAlCl}_2 + \text{Me}_3\text{SiSR} \rightarrow \text{Cl}_2\text{AlSR} + \text{Me}_3\text{SiCl} \quad (1a)
\]

\[
\text{MeAlCl}_2 + \text{Me}_3\text{SiSR} \rightarrow \text{MeAl}^{+}(\text{SR})^{-} + \text{Me}_3\text{SiCl} \quad (1b)
\]

Via these reaction pathways the two types of aluminium compounds are produced exclusively and in very high yields. The highly air- and moisture sensitive products were characterised by elemental analyses and by their IR as well as ¹H NMR spectra.

For the first step of both reactions a nucleophilic attack of the Lewis bases 1 - 3 at the electrophilic center of the Lewis acid MeAlCl₂ can be expected. The 1:1 adduct intermediates (eq. (2)) were neither detected in situ by means of ¹H NMR spectroscopy, nor could they be isolated under the chosen reaction conditions. This is in contrast to the surprisingly stable Me₃SiSR adducts of the aluminium halides [2].

\[
\text{MeAlCl}_2 + \text{Me}_3\text{SiSR} \rightarrow \text{MeAlCl}_2 \cdot \text{SMe}_3 (\text{R}) \quad (2)
\]

In a second and probably rate determining step, these reactive intermediates are subject to decomposition to give the methylchloroaluminium alkanethiolates 6–8 together with trimethylchlorosilane (eq.(3)).

\[
\text{MeAlCl}_2 \cdot \text{SMe}_3 (\text{R}) \rightarrow \text{MeAl}^{+}(\text{SR})^{-} + \text{Me}_3\text{SiCl} \quad (3)
\]
If an excess of MeAlCl₂ is present and maintained in the reaction mixture throughout the whole reaction time, which can be easily attained by progressive addition of small amounts of the trimethylsilyl alkanethiolate solution, trimethylchlorosilane will react with MeAlCl₂ in competition to reaction (1a) [3]. Thus, MeAlCl₂ serves as a scavenger for trimethylchlorosilane. Tetramethylsilane together with aluminium chloride are formed according to eq.(4):

\[
\text{MeAlCl}_2 + \text{Me}_3\text{SiCl} \rightarrow \text{AlCl}_3 + \text{Me}_4\text{Si} \quad (4)
\]

Then, the thus formed AlCl₃ reacts with the initially formed methylchloroaluminium alkanethiolates 6 and 7 to exchange the thiolate group. The dichloroaluminium alkanethiolates 4 and 5 together with MeAlCl₂ are the reaction products, corresponding to eq.(5):

\[
\text{AlCl}_3 + \text{MeAl(SR)Cl} \rightarrow \text{Cl}_2\text{AlSR} + \text{MeAlCl}_2 \quad (5)
\]

R = Me, Et

The alternative possibility, namely the direct reaction of aluminium chloride with Me₃SiSR cannot be excluded, but seems unlikely because the corresponding Lewis acid-base adducts are neither detectable in the ¹H NMR spectra nor isolable from the reaction mixture.

Test reactions clearly demonstrated that a reaction of 7 with a large excess of Me₃SiCl according to eq.(6)

\[
\text{MeAl(SEt)Cl} + \text{Me}_3\text{SiCl} \rightarrow \text{Cl}_2\text{AlSEt} + \text{Me}_4\text{Si} \quad (6)
\]

\[7\quad 5\]
does not proceed under these reaction conditions. If, however, aluminium chloride is provided in at least catalytic amounts, the exchange reaction will slowly proceed, finally converting 7 quantitatively into 5.

If, on the other hand, an excess of a solution of the trimethylsilyl alkanethiolate in benzene or n-pentane is provided and a solution of MeAlCl₂ in benzene or n-pentane is rapidly added maintaining an excess of Me₃SiSR in the reaction mixture throughout the entire reaction time, the methylchloroaluminium alkanethiolates 6–8 are formed in excellent yields at ambient temperature (eq.(7)):

\[\text{excess Me}_3\text{SiSR} \quad \frac{\text{Me}_2\text{SiSR} + \text{MeAlCl}_2}{\text{MeAl(SR)Cl} + \text{Me}_3\text{SiCl} \quad (7)}\]

R = Me, Et, i-Pr

This particular reaction pathway guarantees an almost quantitative reaction of the two starting components and excludes the competition reaction according to eq.(4). The exchange reaction of aluminium chloride and the methylchloroaluminium alkanethiolates according to eq.(5) is thus easily avoided by this simple modification of the experiment.

**Spectroscopy**

**¹H NMR Spectra**

Some preliminary results of ¹H NMR spectroscopy revealed that in the spectra, which were recorded at ambient temperature, the signals of the alkanethiolate groups are shifted to lower field compared to the signals of the free alkanethiols. All signals are considerably broadened strongly indicating exchange reactions of the title compounds in solution. Especially, the two signal groups observed in the ¹H NMR spectrum of methylchloroaluminium i-propanethiolate suggest dimer/trimer equilibria and/or cis/trans isomerisations [1b, 4]. Moreover, rapid ligand scrambling reactions as shown for one example in eq.(8) cannot be excluded, too:

\[\text{2 MeAl(S-i-Pr)Cl} \rightleftharpoons \text{Al(S-i-Pr)}_2\text{Cl} + \text{Me}_2\text{AlCl} \quad (8)\]

Investigations of this highly interesting behaviour of MeAl(SR)Cl in solution are the subject of further work.

**Conclusion**

Depending on the reaction procedure, methylaluminium dichloride reacts with trimethylsilyl alkanethiols to give either methylchloroaluminium alkanethiolates, MeAl(SR)Cl, or dichloroaluminium alkanethiolates, Cl₂AlSR. For the preparation of methylchloroaluminium alkanethiolates via this exchange reaction it has been found necessary to treat a solution of the trimethylsilyl alkanethiolate with a solution of MeAlCl₂ in such a way that an excess of Me₃SiSR is maintained in the reaction mixture throughout the entire reac-
tion time. Otherwise, only tetramethylsilane and dichloroaluminium alkanethiolates are formed.

**Experimental**

All manipulations involving air- and moisture sensitive materials were carried out by using standard Schlenk techniques under an atmosphere of dry nitrogen. Solvents were dried and distilled prior to use and stored under an inert atmosphere. 

$^1$H NMR spectra were recorded on a Varian T 60 spectrometer using benzene as internal standard. IR spectra were recorded as Nujol mulls or films between CsI and polyethylene plates on a Perkin-Elmer 283 instrument. Al [5], Cl [6], and S [7] were analysed according to established analytical methods, C and H analyses were carried out by a Carlo Erba 1106 instrument.

Trimethylsilyl alkanethiolates were prepared according to published methods [8–12].

**Preparation**

$\text{Al(SEt)}\text{Cl}_2$ (4). To a solution of 1.13 g (10.0 mmol) of methylaluminium dichloride in 20 ml of benzene a solution of 1.62 ml (10.0 mmol) of trimethylsilyl methanethiolate in 20 ml of benzene was slowly added under vigorous stirring at ambient temperature. After stirring for 1 h, the solution was evaporated to dryness in vacuo. An oil remained, which crystallised on cooling. Yield: 1.42 g (98%).

IR (CsI, Nujol mull): $v = 676$ s (CS), 500 vb (AlCl) [15], 341 m (AlS) [14], 310 w, 230 m cm$^{-1}$ [2]. – $^1$H NMR (60 MHz, benzene): $\delta = 1.64$ (s, SMe). – $\text{CH}_3\text{Cl}_2\text{AlS}$ (145.0): calcd. C 8.28, H 2.09, Cl 48.91, Al 18.1, S 21.9.

$\text{Al(Se)}\text{Cl}_2$ (5). A solution of 11.29 g (100 mmol) of $\text{MeAlCl}_2$ in 100 ml of $n$-pentane, 16.2 ml (100 mmol) of trimethylsilyl ethanethiolate in 100 ml of $n$-pentane; same procedure as described for 4. An oil remained, which crystallised on cooling. Yield: 15.8 g (99%).

IR (CsI, Nujol mull): $v = 698$ s, 679 s, (CS), 626 b, 500 vb (AlCl) [13], 364 b (AlS) [14], 277 m cm$^{-1}$ [2]. – $^1$H NMR (60 MHz, benzene): $\delta = 2.75$ (q, SCH$_2$), 0.97 (t, Me). – $\text{CH}_3\text{H}_2\text{Cl}_2\text{AlS}$ (159.0): calcd. C 15.11, H 3.17, Cl 44.59, Al 16.97, S 20.16; found C 15.21, H 3.05, Cl 44.3, Al 17.1, S 21.9.

$\text{MeAl(SEt)}\text{Cl}_2$ (6). To a solution of 4.10 ml (28.7 mmol) of $\text{Me}_2\text{SiSeMe}$ in 20 ml of benzene a solution of 2.70 g (23.9 mmol) of $\text{MeAlCl}_2$ in 20 ml of benzene was poured in one dash under vigorous stirring at ambient temperature. After stirring for 10 min, the solution was evaporated to dryness in vacuo. The remaining oil was dissolved in $n$-pentane and evaporated again to leave a white precipitate. The product was distilled under reduced pressure (0.1 mm) at 130–170 °C to afford a colourless solid. Yield: 2.41 g (81%).

IR (CsI, Nujol mull): $v = 665$ sh (CS), 660 b (AlC) [15], 553 m (AlCl) [13], 484 m, 465 s, 442 w, 412 m (AlS) [14], 367 b, 328 m, 220 m cm$^{-1}$. – $^1$H NMR (60 MHz, benzene): $\delta = -0.28$ (s, AlMe), 1.68 (s, SMe). – $\text{C}_2\text{H}_5\text{ClAlS}$ (124.569): calcd. C 19.28, H 4.86, Cl 28.46, Al 21.66, S 25.74; found C 21.4, H 4.91, Cl 29.1, Al 21.3, S 25.5.

$\text{MeAl(SEt)}\text{Cl}$ (7). A solution of 11.1 ml (68.5 mmol) of $\text{Me}_2\text{SiSe}$ in 75 ml of $n$-pentane, 6.45 g (57.1 mmol) of $\text{MeAlCl}_2$ in 75 ml of $n$-pentane; same procedure as described for 6. A colourless precipitate remained. Yield: 7.50 g (95%).

IR (CsI, Nujol mull): $v = 671$ b, (CS and AlC) [15], 548 m (AlCl) [13], 463 s, 420 m (AlS) [14], 405 sh cm$^{-1}$. – $^1$H NMR (60 MHz, benzene): $\delta = -0.20$ (s, AlMe), 1.02 (t, $\text{CH}_2$Me) 2.66 (q, SCH$_2$). – $\text{C}_3\text{H}_6\text{ClAlS}$ (138.595): calcd. C 26.00, H 5.82, Cl 25.58, Al 19.47, S 23.14; found C 25.8, H 5.71, Cl 25.14, Al 19.0, S 23.1.

$\text{MeAl(SePr)}\text{Cl}$ (8). A solution of 2.11 ml (12.0 mmol) of trimethylsilylethynylithium in 20 ml of $n$-pentane, 1.13 g (10.0 mmol) of $\text{MeAlCl}_2$ in 20 ml of $n$-pentane; procedure as described for 6. A colourless oil remained. Yield: 0.610 g (40%).

IR (CsI, Nujol mull): $v = 665$ b (CS), 655 sh (AlC) [15], 590 m, 548 m (AlCl) [13], 463 b, 441 sh, 395 b (AlS) [14], 350 sh, 305 w, 260 m cm$^{-1}$. – $^1$H NMR (60 MHz, benzene): $\delta = -0.03$ and -0.20 (s, AlMe), 1.18 and 1.35 (d, $\text{CH}_2$Me), 3.55 (d of q, SCH). – $\text{C}_3\text{H}_10\text{ClAlS}$ (152.621): calcd. C 31.48, H 6.61, Cl 23.23, Al 17.68, S 21.01; found C 31.0, H 6.31, Cl 23.4, Al 17.4, S 22.9.

**Reaction of MeAl(SEt)Cl** (7) with AlCl$_3$. To a solution of 0.934 g (6.74 mmol) of MeAl(SEt)Cl in 30 ml of benzene 0.899 g (6.74 mmol) of AlCl$_3$ was added under vigorous stirring. The reaction mixture was heated at reflux for 3 h to give a light red solution. After removing the solvent and MeAlCl$_2$ under reduced pressure the remaining yellow oil was dissolved in 5 ml of $n$-pentane and evaporated again four times. A colourless solid remained. Yield: 1.03 g (96%).

IR (CsI, Nujol mull and PE, Nujol mull): $v = 698$ s, 679 s (CS), 625 b, 501 vb (AlCl), 363 b (AlS), 277 m cm$^{-1}$. – $^1$H NMR (60 MHz, benzene): $\delta = 2.75$ (q, SCH$_2$), 0.97 (t, Me). – $\text{C}_2\text{H}_5\text{AlClS}$ (159.0): calcd. C 15.11, H 3.17, Cl 44.59, Al 16.97, S 20.16; found C 15.13, H 3.21, Cl 44.4, Al 16.7, S 20.3.
MeAl(SEt)Cl (7) and Me₃SiCl: 1.10 g (8.00 mmol) of MeAl(SEt)Cl was stirred for 24 h in 15 ml of Me₃SiCl. After removing the volatiles under reduced pressure a colourless solid remained. Yield: 1.08 g (98%).

IR (CsI, Nujol mull and PE, Nujol mull): ν = 671 b (CS and AlC), 548 vb (AlCl), 463 s, 420 m (AlS), 405 m, sh cm⁻¹. - ¹H NMR (60 MHz, benzene): δ = -0.20 (s, AlMe), 1.02 (t, CH₂Me), 2.66 (q, CH₃). - C₃H₈AlClS (138.595); calcd. C 26.00, H 5.82, Cl 25.58, Al 19.47, S 23.14; found C 25.89, H 5.78, Cl 24.9, Al 19.7, S 23.2.

Reaction of MeAl(SEt)Cl with Me₃SiCl in the presence of catalytic amounts of AlCl₃: 0.71 g (5.13 mmol) of MeAl(SEt)Cl were stirred for 24 h in 15 ml of Me₃SiCl and 0.05 g (0.38 mmol) of AlCl₃. After removing the volatiles under reduced pressure a yellow oil remained which was dissolved in 5 ml of n-pentane and evaporated again four times. A colourless solid remained. Yield: 0.79 g (97%).

IR (CsI, Nujol mull and PE, Nujol mull): ν = 698 s, 679 s (CS), 625 b, 501 vb (AlCl), 363 b (AlS), 277 cm⁻¹. - ¹H NMR (60 MHz, benzene): δ = 2.75 (q, SCH₂), 0.97 (t, Me). - C₂H₅AlCl₂S (159.0); calcd. C 15.11, H 3.17, Cl 44.59, Al 16.97, S 20.16; found C 15.13, H 3.21, Cl 44.4, Al 16.7, S 20.3.

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