ELSEVIER

Journal of Fluorine Chemistry 102 (2000) 17–20

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Reaction of dimethylaluminumfluoride with primary amines RNH_2 ($R = t$-Bu, 2,6-i-$Pr_2C_6H_3$)

Carsten Rennekamp, Andreas Stasch, Peter Müller, Herbert W. Roesky*,
Mathias Noltemeyer, Hans-Georg Schmidt, Isabel Usón

Universität Göttingen, Institut für Anorganische Chemie, Tammannstraße 4, D-37077 Göttingen, Germany

Received 15 April 1999; received in revised form 9 June 1999; accepted 20 July 1999

Dedicated to Professor Paul Tarrant on the occasion of his 85th birthday

---

Abstract

The first few steps of the title reaction of two bulky substituted primary amines with dimethylaluminumfluoride have been investigated in toluene. For RNH_2 ($R = 2,6$-i-$Pr_2C_6H_3$) the formation of an unexpected ring system $(Me_2)Al_4(NHR)_2F_2$ (**1**, $R = 2,6$-i-$Pr_2C_6H_3$) is observed. The reaction was repeated in an NMR tube and monitored by ^{19}F NMR spectroscopy. The product of Me_2AlF and RNH_2 ($R = t$-Bu) offers more information about the initial step of the reaction. During the course of the reaction the $(Me_2AlF)_4$ ring is cleaved and yields the adduct $Me_2AlF{\cdot}NH_2R$ (**2**, $R = t$-Bu), which has a polymeric structure in the solid state. In both reactions no methane evolution was observed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Aluminumfluorides; AlF bond cleavage; Fluorine nitrogen exchange

---

1. Introduction

Though dimethylaluminumfluoride (Me_2AlF) is known since 1957 and its structure is well investigated [1–3] and though it is applicable as a cocatalyst in Ziegler–Natta polymerization reactions or as an additive in MAO [4,5,6], little is known about its chemistry.

Recently, we reported on the synthesis and properties of aminoaluminumfluorides [7]. In this paper, we report on the reactions of Me_2AlF with the bulky primary amines RNH_2 ($R = t$-Bu, 2,6-i-$Pr_2C_6H_3$), which could serve as an alternative approach to aminoaluminumfluorides.

2. Results and discussion

The reaction of RNH_2 ($R = 2,6$-i-$Pr_2C_6H_3$) with Me_3Al is well investigated and leads, depending on the temperature to the adduct $Me_3Al{\cdot}NH_2R$, to a dimer $(Me_2AlNHR)_2$ or to a trimer $(MeAlNR)_3$ [8,9]. Adding RNH_2 to a solution of Me_2AlF in toluene at 0°C in a 1:1 molar ratio leads to the tetrameric $(Me_2)Al_4(NHR)_2F_2$ (**1**) ring system. Single crystals suitable for X-ray analysis of **1** are obtained from the reaction mixture at −2°C over night in 65% yield (Scheme 1, Fig. 1).[1]

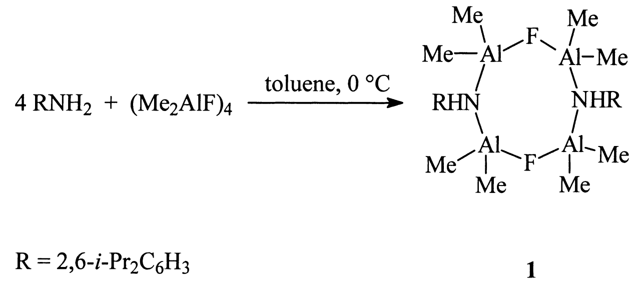
The centrosymmetric eight-membered ring of **1** consists of four aluminum atoms connected by alternating amino groups and fluorine atoms. The molecule can be formally divided into two aminometalane $RNHAlMe_2$ and two dimethylaluminumfluoride fragments. Nevertheless, the bond lengths between Al(1) and Al(2), respectively, and F(1) (181.8(2) pm and 180.8(1) pm) are similar to each other and equal to that found by electron diffraction for Me_2AlF (181 pm) [3]. The bond lengths of Al(1)–N(1A) and Al(2)–N(1) are equal (196.6 pm) within the experimental error. The

---

* Corresponding author. Tel.: +49-5-51-393001; fax: +49-5-51-393373.
E-mail address: hroesky@gwdg.de (H.W. Roesky).

[1] Crystal data for **1**. $C_{32}H_{60}Al_4F_2N_2$, $M = 618.74$, crystal size: $1.0 \times 0.8 \times 0.6\ mm^3$, triclinic, $P\ \bar{1}$, unit cell dimensions: $a = 914.9(2)$ pm, $b = 1013.7(2)$ pm, $c = 2307.5(5)$ pm, $\alpha = 80.34(3)^\circ$, $\beta = 88.74(3)^\circ$, $\gamma = 66.07(3)^\circ$, unit cell volume $1.9260(5)\ nm^3$, $Z = 2$, $\rho_{calc.} = 1.067$ g cm^{-1}, $\mu = 0.152\ mm^{-1}$; total number of reflections measured 7204, unique 6820 ($R_{int} = 0.0657$). Data/restraints/parameters: 6807/1/385. Final R indices: $R1 = 0.0461$, $wR2 = 0.1135$ on data with $I > 2\sigma(I)$ and $R1 = 0.0580$, $wR2 = 0.1280$ on all data, goodness-of-fit $S = 1.042$; ($R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR2 = \left[\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2\right]^{1/2}$, $S = \left[\sum w(F_0^2 - F_c^2)^2 / \sum (n-p)\right]^{1/2}$); weighting scheme $w^{-1} = \sigma^2 (F_0)^2 + (0.029\ P)^2 + 2.057\ P$; $P = [F_0^2 + 2F_c^2]/3$; largest difference peak and hole: 312 and $-244\ e\ nm^{-3}$.

PII: S0022-1139(99)00236-5



Scheme 1.

Al(1)–F(1)–Al(2) angle (157.2(1)°) shows a more linear character compared to the Al–F–Al angle in the Al_4F_4 tetramer of Me_2AlF (146°) [3]. This leads to a shape of this ring which can be described as a distorted chair conformation. The composition of the solid state structure of **1** is confirmed by ^1H NMR, ^{19}F NMR, MS (EI), IR and elemental analysis.

The ^{19}F NMR spectra of the solution after filtration from the crystals of **1** (broad signal between −120 and −180 ppm) did not give any hint for a certain mechanism. Nevertheless, HF elimination of organometal fluorides of group 13 metals in the presence of acidic protons was described for the hydrolysis of Mes_2GaF by Neumüller and Gahlmann [10,11]. In search of an indication for a similar mechanism we repeated the reaction between RNH_2 and Me_2AlF in a 2:1 ratio. However, only crystals of **1** were isolated in 60% yield.

More information was obtained by monitoring the reaction with ^{19}F NMR spectroscopy in a NMR tube at room temperature and recording the spectra after 10, 45 min, 2.5, 4 and 24 h (Fig. 2). During the reaction a decreasing amount of Me_2AlF (−144.8 ppm) and growth of the broad signal (around −158 ppm) was observed, yielding after 24 h the signals assignable to **1** (−144.2 ppm) and unknown byproducts (−145.0 ppm and −147.4 ppm). These observations are a strong evidence for so far unknown fluorine exchange processes. It should be stressed that the Al–F bond cleavage occurs at unexpected mild conditions compared to the thermodynamical stability of the Al–F bond.

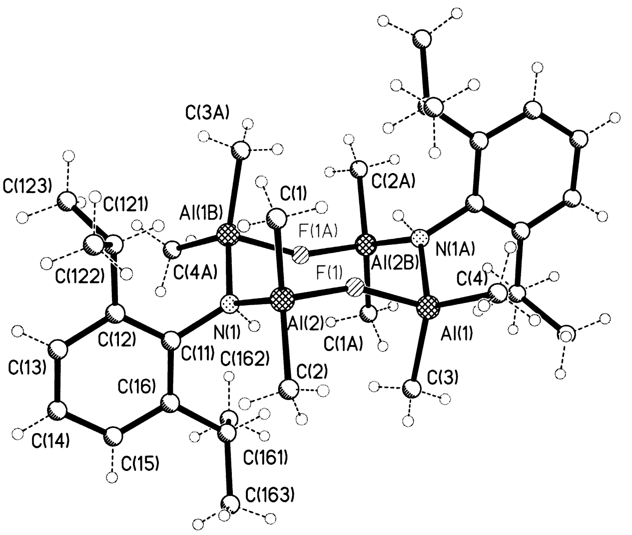


Fig. 1. Molecular structure of **1**. Selected bond lengths (pm) and angles (deg). Al(1)–F(1) 181.8(2), Al(2)–F(1) 180.8(1), Al(2)–C(1) 194.7(3), Al(2)–C(2) 194.9(2), Al(1)–C(3) 195.1(3), Al(1)–C(4) 194.5(2), Al(1)–N(1A) 196.4(2), Al(2)–N(1) 196.6(2); Al(1)–F(1)–Al(2) 157.2(1), Al(2)–N(1)–Al(1B) 120.6(1), N(1)–Al(2)–F(1) 93.5(1), C(1)–Al(2)–C(2) 120.9(1), C(3)–Al(1)–C(4) 121.3(1).

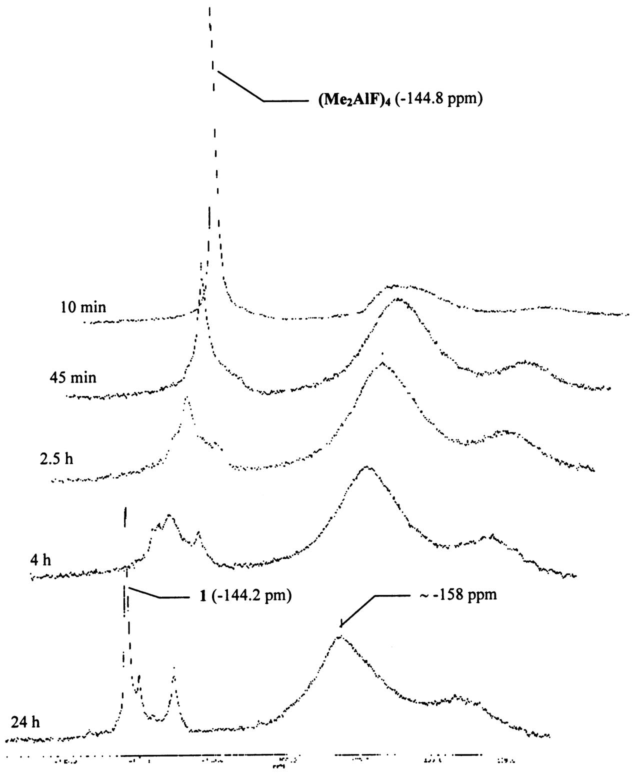


Fig. 2. ^{19}F NMR spectra of the reaction of Me_2AlF and RNH_2 (R = 2,6-i-$Pr_2C_6H_3$) in a NMR tube at room temperature. Spectra recorded after 10, 45 min, 2.5, 4, and 24 h.

To understand the first step of the reaction we repeated the reaction under the same conditions with the less acidic, but also bulky primary amine *t*-$BuNH_2$. After filtration of a white solid the solution was kept at −20°C for 3 weeks. Single crystals suitable for X-ray analysis were formed. The structure is shown in Fig. 3.[2]

---

[2] Crystal data for **2**. $C_6H_{17}AlFN$, $M = 149.19$, crystal size $0.30 \times 0.20 \times 0.20\ mm^3$ monoclinic, $P2_1/n$, unit cell dimensions: $a = 859.9(2)$ pm, $b = 1012.0(2)$ pm, $c = 1155.5(2)$ pm, $\beta = 107.55(3)°$, unit cell volume $0.9588(3)\ nm^3$, $Z = 4$, $\rho_{calc.} = 1.034\ g\ cm^{-1}$, $\mu = 0.158\ mm^{-1}$; total number of reflections measured 12928, unique 2083 ($R_{int} = 0.0235$). Data/restraints/parameters: 2083/2/93. Final R indices: $R1 = 0.0267$, $wR2 = 0.0695$ on data with $I > 2\sigma(I)$ and $R1 = 0.0329$, $wR2 = 0.0723$ on all data, goodnes-of-fit $S = 1.081$; ($R1 = ||F_0| - |F_c||/\Sigma|F_0|$, $wR2 = \left[\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2\right]^{1/2}$, $S = \left[\sum w(F_0^2 - F_c^2)^2/\sum(n-p)\right]^{1/2}$); weighting scheme $w^{-1} = \sigma^2\ (F_0)^2\ + (0.026\ P)^2 + 11.462\ P$; $P = [F_0^2 + 2F_c^2]/3$; largest difference peak and hole: 236 and −180 $e\ nm^{-3}$.

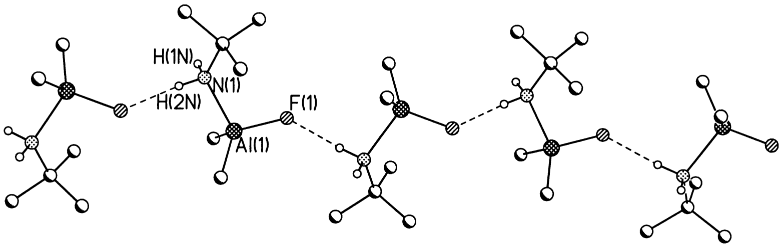


Fig. 3. Molecular structure of **2**. Selected bond lengths (pm) and angle (deg). Al(1)–F(1) 170.30(8), Al(1)–N(1) 198.6(1); F(1)–Al(1)–N(1) 103.9(1).

We observed a cleavage of the Al_4F_4 ring system of Me_2AlF and the formation of the adduct $Me_2AlF{\cdot}NH_2R$ (**2**, R = *t*–Bu). This is in good correspondence with the above mentioned formation of $Me_3Al{\cdot}NH_2R$ (R = 2,6-*i*-$Pr_2C_6H_3$) and with the ^{19}F NMR investigations for **1**. In the solid state structure of **2** hydrogen fluorine bonds F(1)-H(2N) (196.8(1) pm) between the molecules connect the monomeric adducts to long polymeric chains. These hydrogen bonds are longer than in comparable ammonium fluorides and ammonium hydrogendifluorides (about 170 pm) [12,13]. The Al(1)–F(1) bond length (170.30(8) pm) is shorter than the Al–F bond in the Me_2AlF tetramer (181 pm) [3].

A singlet (−155.5 ppm) is observed in the ^{19}F NMR spectrum of **2**. Further results of ^1H NMR, MS (EI), IR measurements as well as elemental analysis are consistent with the solid state structure of **2**.

Fluorine aluminum bonds are replaced by nitrogen aluminum bonds yielding **1**. As far as the thermodynamical stability of the Al–F bond and as far as our recent results on the nitrogen fluorine exchange reactions between metallocene trifluorides and alumazene $(MeAlNR)_3$ (R = 2,6-*i*-$Pr_2C_6H_3$) are concerned [14–16], this observation is unexpected. It can be regarded as an inverted fluorine nitrogen exchange reaction.

Though our primary goal to exploit Me_2AlF as a precursor for the direct synthesis of aminoorganoaluminum fluorides was not achieved, an interesting and so far unknown phenomena was observed. Our present investigations are focused on the sterical and electronical variation of the amines. From these investigations we hope to isolate the missing intermediates between **1** and **2** and to understand the processes better.

3. Experimental

All solvents were purified and dried by standard techniques, and Schlenk line and dry box techniques, respectively, were used. The N_2 inert gas was dried by passing through a combination of three columns containing P_4O_{10}, $CaCl_2$ and Oxisorb (Messer Griesheim GmbH). The chemical shifts were referenced to the residual proton line from C_6D_6 ($\delta = 7.15$ ppm for ^1H NMR). The elemental analysis were performed in the Analytisches Laboratorium des Instituts für Anorganische Chemie, Göttingen. Small variations in the analytical data are due to metal carbide formation in these systems.

DMAF (16% solution in toluene) was used as received from the Witco GmbH, Bergkamen. Di*iso*propylaniline (Aldrich) and *tert*-butylamine was distilled over KOH prior to use and kept in a Schlenk flask at −2°C.

Crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether [17]. Diffraction data were collected on Stoe–Siemens four-circle-diffractometers, in case of **1** coupled to a Siemens CCD area-detector, at 133(2) K, with graphite-monochromated Mo-K_α radiation ($\lambda = 71.073$ pm), performing φ- and ω-scans. The structures were solved by direct methods using SHELXS-97 [18] and refined against F^2 on all data by full-matrix least squares with SHELXL-97 [19]. All non-hydrogen atoms were refined anisotropically. In both structures the hydrogen atoms bonding to N were found in the difference-Fourier-map and refined freely, all other hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

3.1. Reaction of 2,6-diisopropylaniline with dimethylaluminumfluoride

3.24 g (18.3 mmol) 2,6-*i*-$Pr_2C_6H_3NH_2$ dissolved in toluene (15 ml) was added to 8.68 g of a solution of Me_2AlF (16%, 18.3 mmol) in toluene at 0°C, stirred for 1 h at this temperature while no methane evolution was observed and kept at −2°C over night. Colorless single crystals (1.83 g, 65% yield) of **1** were obtained. After decanting the solution with a syringe a suitable crystal for X-ray analysis was taken from the flask and the remaining product was dried in vacuo. The solution was used for ^{19}F NMR spectroscopy. The reaction was repeated in a 2:1 ratio and **1** was obtained (1.70 g, 60% yield related to the Al). Decomp. 120°C; ^1H NMR (200 MHz, C_6D_6): δ −0.72 (d, δ(HF) = 5.8 Hz, 12 H, $AlCH_3$), −0.12 (d, δ(HF) = 5.8 Hz, 12 H $AlCH_3$), 1.10 (m, ^3J (H H) = 6.8 Hz, 24 H, $CH(CH_3)_2$), 3.18 (sept., ^3J (H H) = 6.8 Hz, 2 H, $CH(Me)_2$), 3.48 (sept., ^3J (H H) = 6.8 Hz, 2 H, $CH(Me)_2$), 6.98 (m, 6 H, Ar–*H*); ^{19}F $\{^1H\}$ NMR (90 MHz, C_6D_6): δ −144.2 (s); IR ([cm^{-1}], KBr, Nujol): ν 3255, 1316, 1204, 820, 720; MS (EI) *m*/*e*(%): 618 [M^+, 2], 603 [M^+−Me, 100]; Anal. Calc. for $C_{32}H_{60}Al_4F_2N_2$, Al, 17.44; F, 6.14. Found: Al, 15.78; F, 5.47.

Preparation of **1** in a NMR tube: 0.27 g DMAF (0.56 mmol, 16% solution in toluene) was added dropwise to a solution of 0.10 g (0.56 mmol) 2,6-*i*-$Pr_2C_6H_3NH_2$ in C_6D_6 (0.3 ml) through a septum under shaking at room temperature and ^{19}F NMR spectra were recorded after 10, 45 min, 2.5, 4, and 24 h respectively. After 24 h no change in the spectrum was observed.

3.2. Reaction of tert-butylamine with dimethylaluminumfluoride

A solution of 3.60 g (49.3 mmol) *t*-$BuNH_2$ in toluene (15 ml) was added dropwise to a solution of 23.4 g Me_2AlF (16%, 49.3 mmol) in toluene at 0°C. While stirring the reaction mixture for 1 h at 0°C no methane evolution but precipitation of a white solid was observed. After filtration the clear filtrate was kept at −20°C for 3 weeks. Colorless single crystals of **2** were obtained. After decanting, the remaining residue of the solvent was removed in vacuo and the single crystals were fully characterized. There is no spectroscopical difference between the crystals and the filtrate. 5.89 g (76% yield); decomp. 165°C; ^1H NMR (200 MHz, C_6D_6): δ −0.40 (d, 6 H, $Al(CH_3)_2$), 0.78 (s, 9 H, $C(CH_3)_3$), 2.33 (s, br, NH_2); $^{19}F\{^1H\}$ NMR (90 MHz, C_6D_6): δ −155.5 (m) ppm; IR ([cm^{-1}], KBr, Nujol): v 3266, 3201,1465, 1196, 901, 720; MS (EI) *m*/*e*(%): 149 [M^+, 10], 58 [*t*-$BuNH_2$-Me, 100]; Anal. Calc. for $C_6H_{17}AlFN$ Al, 18.09; F, 12.73. Found: Al, 17.99; F, 12.41.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft, the Witco GmbH, and the Bundesministerium für Bildung und Forschung for financial support. C.R. is grateful to the Fonds der Chemischen Industrie for a fellowship.

References

[1] K. Ziegler, E. Holzkamp, R. Köster, H. Lehmkuhl, Angew. Chem. 67 (1955) 213.

[2] J. Weidlein, V. Krieg, J. Organometal. Chem. 11 (1968) 9.

[3] G. Gundersen, T. Haugen, A. Haaland, J. Organometal. Chem. 54 (1973) 77.

[4] P. Longo, L. Oliva, A. Grassi, C. Pellecchia, Makromol. Chem. 190 (1989) 2357.

[5] A. Winter, V. Dolle, W. Spaleck, Patent EP 0 553 757 A1, 1993.

[6] A. Winter, V. Dolle, W. Spaleck, C.A. (1994) 77929.

[7] S.D. Waezsada, F.-Q. Liu, E.F. Murphy, H.W. Roesky, M. Teichert, I. Usón, H.-G. Schmidt, T. Albers, E. Parisini, M. Noltemeyer, Organometallics 16 (1997) 1260.

[8] K.M. Waggoner, H. Hope, P.P. Power, Angew. Chem. 100 (1988) 1765.

[9] K.M. Waggoner, H. Hope, P.P. Power, Angew. Chem., Int. Ed. Engl. 27 (1988) 1699.

[10] B. Neumüller, F. Gahlmann, Angew. Chem. 105 (1993) 1770.

[11] B. Neumüller, F. Gahlmann, Angew. Chem., Int. Ed. Engl. 32 (1993) 1701.

[12] D. Lux, W. Schwarz, H. Hess, Cryst. Struct. Commun. 8 (1979) 41.

[13] W.A. Denne, M.F. Mackay, J. Cryst. Mol. Struct. 1 (1971) 311.

[14] H. Wessel, C. Rennekamp, H.W. Roesky, M.L. Montero, P. Müller, I. Usón, Organometallics 17 (1998) 1919.

[15] H. Wessel, M.L. Montero, C. Rennekamp, H.W. Roesky, P. Yu, I. Usón, Angew. Chem. 110 (1998) 862.

[16] H. Wessel, M.L. Montero, C. Rennekamp, H.W. Roesky, P. Yu, I. Usón, Angew. Chem., Int. Ed. 37 (1998) 843.

[17] T. Kottke, D. Stalke, J. Appl. Crystallogr. 26 (1993) 615.

[18] G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467.

[19] G.M. Sheldrick, SHELX 97, Universität Göttingen, 1997.