Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Fluorine Chemistry 125 (2004) 1765–1769

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/fluor

Preparation of fluorine compounds of groups 13 and 14: a study case for the diagonal relationship of aluminum and germanium

Herbert W. Roesky*

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

Available online 11 November 2004

Abstract

The synthesis of carbaalanes of composition $[(AlF)_6(AlNMe_3)_2(CR)_6]$ containing terminal fluorine atoms is described. The clusters have in common that the central core consists of eight aluminum and six carbon atoms. Six of the eight aluminum atoms are bearing six terminal fluorine atoms. The fluorination of $(t\text{-BuNCH}_2\text{AlH})_4$ results in the formation of the aggregate $(t\text{-BuNCH}_2\text{AlF})_4$. In group 14, the fluorine containing unsaturated compounds LGeF, LGe=S(F), LGe=Se(F), and $LGe{=}NSiMe_3(F)$ were prepared ($L{=}HC(CMeNAr)_2$), Ar = 2,6-$i\text{Pr}_2\text{C}_6\text{H}_3$ and Ar = 2,6-$\text{Me}_2(\text{C}_6\text{H}_3)$).

© 2004 Elsevier B.V. All rights reserved.

Keywords: Aluminum; Cluster; Surface fluorination; Terminal Al–F bonds; Germanium

> We see in nature not words, but rather only the first letters of words, and if we then wish to read, we discover that the new so-called words are again merely first letters of words.
>
> Georg Christoph Lichtenberg

1. Introduction

Recently we have published an overview on organoaluminum fluorides covering various aspects of this field [1]. Herein, we report on the latest results of group 13 and 14 fluorides discovered in Göttingen. We are interested in the diagonal relationship of aluminum and germanium.

In group 13, fluorine plays an important role and this dates back to the year 1886 when Heroult and Hall discovered the electrolytic process for aluminum production. In recent years, scientists were mainly involved in the environmental problems of this process [2]. The presence of Al–F species for various applications is listed below (Table 1).

For the preparation of the new Al–F compounds we used the fluorinating agents:

Me_3SnF
Ph_3SnF
$n\text{-Bu}_4\text{NHF}_2$
BF_3OEt_2

2. Synthesis of carbaalanes containing terminal fluorine atoms

Diorganoaluminum fluorides of composition $[R_2AlF]_4$ were synthesized by Ziegler from the corresponding chlorides [3,4]. In the solid state, they are forming a tetramer with bridging Al–F–Al bonds. The structure of $(Me_3Si)_3CAlF_2$ containing the bulky $(Me_3Si)_3C$ group consists of a puckered alternating Al–F six-membered ring. Additionally each aluminum atom bears a terminal fluorine atom [5]. For the fluorine–methyl exchange Me_3SnF was used as a mild fluorination reagent [6] (Scheme 1).

These two examples are representative for aluminum fluorine compounds. Fluorine has a preference of forming first an Al–F–Al bond and then a terminal one, when the

---

* Tel.: +49 551 39 3373; fax: +49 551 39 3373.
E-mail address: hroesky@gwdg.de.

0022-1139/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2004.09.018

Table 1
Selected applications of Al–F compounds

1	Catalysts and cocatalysts in polymerization reactions
2	AlF_3 and Na_3AlF_6 in aluminum production
3	AlF_3 for surface modification (m.p. of $AlF_3$1290 °C for comparison $AlCl_3$ m.p. 192.6 °C)
4	Al–F containing compounds are ingredients of tea
5	The gemstone topaz has the composition $Al_2(SiO_4)(F/OH)_2$
6	β-AlF_3 is used for chlorine-fluorine exchange with HF in chlorocarbon systems
7	AlF is one of the interstellar molecules
8	AlF_4^- interferes with the nucleotide binding proteins
9	AlF_4^- has a similar size to that of PO_4^{3-} and mimics the binding site of γ-phosphate to nucleoside diphosphates
10	Al–F compounds are used as precursors for new materials

coordination number around the aluminum is four. Higher coordination numbers at the aluminum atom favour terminal Al–F bonds.

The starting material for the preparation of carbaalanes is $AlH_3 \cdot NMe_3$ (**1**). This compound is prepared from $LiAlH_4$ and $Me_3N \cdot HCl$ [7] (Scheme 2).

The synthesis of the carbaalanes $[(AlH)_6(AlNMe_3)_2(CCH_2R)_6]$ (**2**) (R=Ph) proceeds from six PhC≡CH and eight equivalents of $AlH_3 \cdot NMe_3$ in boiling toluene [8] (Scheme 3).

The first step of the reaction is the formation of $PhC{\equiv}CAlH_2 \cdot NMe_3$ under elimination of hydrogen. An excess of PhC≡CH in this reaction resulted in the trisubstituted product $(PhC{\equiv}C)_3Al \cdot NMe_3$. The conversion of the carbaalanes **2** with $BF_3 \cdot OEt_2$ leads to the corresponding fluorine derivative **3** (Scheme 4) in a 54% yield [9].

In the X-ray single crystal structure the terminal Al–F bond length was found in the range 1.667(3)–1.669(3) Å. The molecular structure of **3** is shown in Scheme 5.

Due to the poor solubility of **3** no satisfying NMR spectra could be recorded. Therefore $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**4**) was prepared from $Me_3SiCH_2C{\equiv}CH$ and **1**. The metathesis of **4** to the fluorine derivative $[(AlF)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**5**) is shown in Scheme 6.

The yield of **5** is more than 90% independently whether $BF_3 \cdot OEt_2$ or Me_3SnF is used as a fluorinating reagent. The ^{19}F NMR resonance of **5** for the terminal fluorine bonds is shifted to the high field region (δ −181.5 ppm). Only the resonance of the tetracoordinated $[Me_4N][AlF_4]$ compound (δ −194.9 ppm) is observed more upfield than that of **5** [1].

3. Fluorination of an $Al_4C_4N_4$ cluster

The cluster $(t\text{-}BuNCH_2AlH)_4$ (**6**) was obtained by hydroalumination of *t*-BuNC with $AlH_3 \cdot NMe_3$ [10]. Compound **6** reacts smoothly with Me_3SnF at room temperature in dichloromethane to form $(t\text{-}BuNCH_2AlF)_4$ (**7**) in 67 % yield (Scheme 7).

The molecular structure of **7** is shown in Fig. 1.

The $Al_4C_4N_4$ core with four F atoms in place of the four H atoms is retained in the tetrafluoro derivative [11]. The four Al atoms form a distorted tetrahedral geometry with D_{2d} symmetry. The terminal Al–F bond lengths (1.659–1.666 Å) are in agreement with those reported in literature. The chemical shift for the ^{19}F NMR terminal fluorine atoms of **7** is −155.7 ppm. A comparison of the chemical shifts for compounds containing terminal Al–F bonds is given in Table 2.

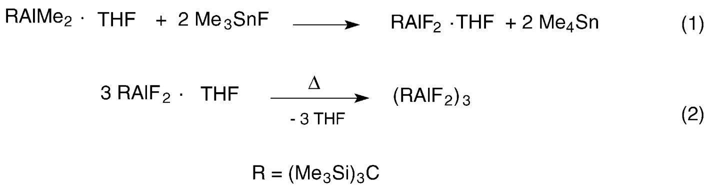
4. Preparation of aluminum compounds containing a formal Al–O double bond stabilized by $B(C_6F_5)_3$

For the stabilization of the aluminum center the ligand $HC[CMeNCH_2CH_2NEt_2]_2H$ (**8**) (LH) was synthesized. The reaction of **8** with $AlMe_3$ yields the $LAlMe_2$ compound **9** (Scheme 8).

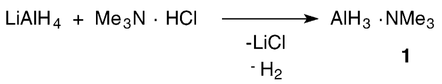
Compound **9** reacts with $(F_5C_6)_3B \cdot H_2O$ at 0 °C in toluene under elimination of methane to $HC[CMeNCH_2CH_2NEt_2]_2Al{=}O \cdot B(C_6F_5)_3$ (**10**) (Scheme 9) [12].

In contrast, when the same reagents were allowed to react in THF at 55 °C for two hours, compound $LAl(C_6F_5)O–B(C_6F_5)_2$ **11** was isolated (Scheme 9). The main difference between compounds **10** and **11** is the Al–O bond length. In **10**, this bond is 1.659(3) Å, the shortest Al–O bond reported so far for a tetracoordinate aluminum atom. The B–O bond length in **10** is 1.444(3) Å.

As expected in compound **11** an isomer of **10**, which was formed by migration of one C_6F_5 group from boron to aluminum, the Al–O (1.780(2) Å) and the B–O bonds (1.311(2) Å) are in the range of those of previously reported compounds [12].



Scheme 1.



$$LiAlH_4 + Me_3N\cdot HCl \xrightarrow[-H_2]{} \underset{\mathbf{1}}{AlH_3\cdot NMe_3}$$

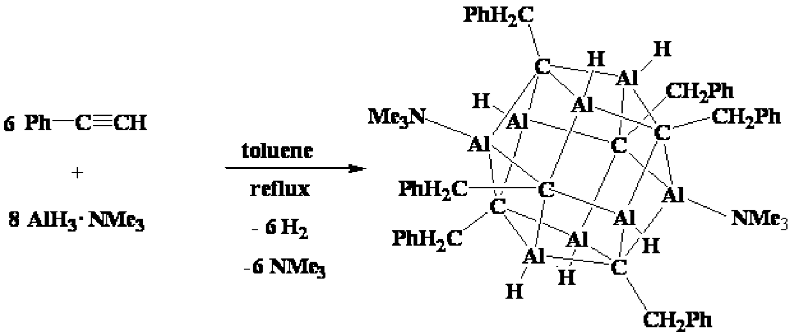
Scheme 2.

5. Preparation of unsaturated germanium and tin fluorine compounds

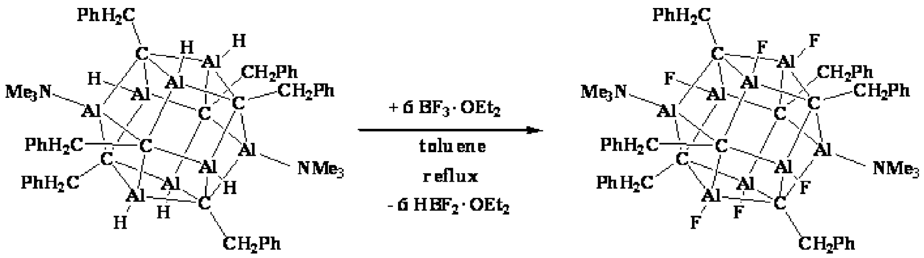
The starting material for the preparation of the unsaturated compounds of germanium is the LGeCl (**12**) (L=HC(CMeNAr)$_2$, Ar = 2,6-i-Pr$_2$C$_6$H$_3$ and Ar = 2,6-Me$_2$C$_6$H$_3$). Compound **12** was obtained from LLi(OEt$_2$) (**13**) and GeCl$_2$·(dioxane) [14]. The β-diketiminato Sn(II) chloride (**14**) was easily prepared in high yield by the reaction of **13** with one equivalent of SnCl$_2$ in diethyl ether [14]. Compound **14** is converted by AgOSO$_2$CF$_3$ to LSn(OSO$_2$CF$_3$) **15** (Scheme 10).

In compound **15**, the backbone of the chelating ligand L is essentially planar and the tin atom is out of the plane (0.65 Å). In **15**, the triflate group is monodentate with a Sn–O bond length of 2.254(2) Å. The ^{19}F NMR of **15** resonates at δ 85.28 ppm [14].

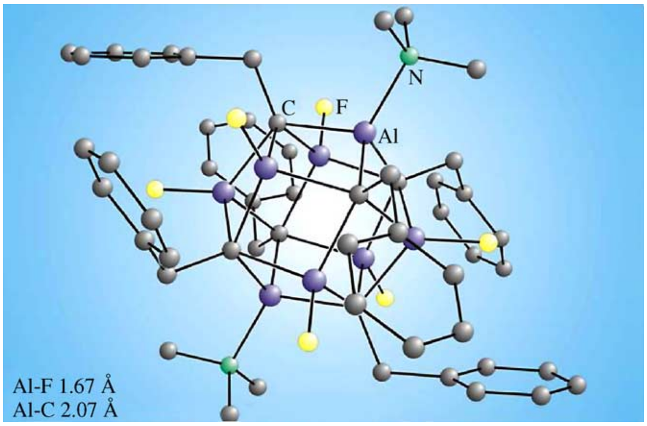
The reactions of LGeCl (**12**) are summarized in Scheme 11 [15–17].



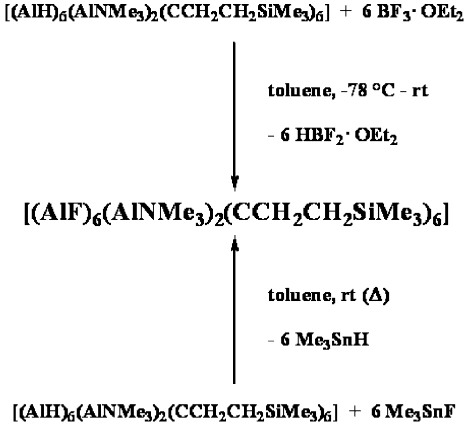
Scheme 3.



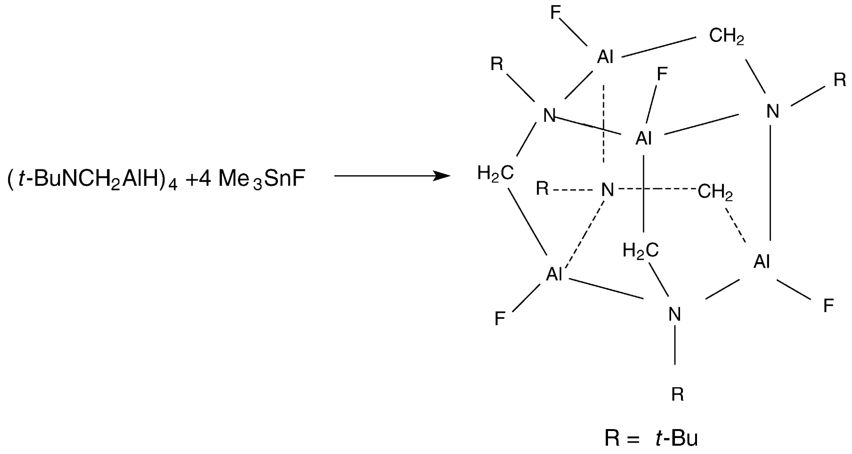
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

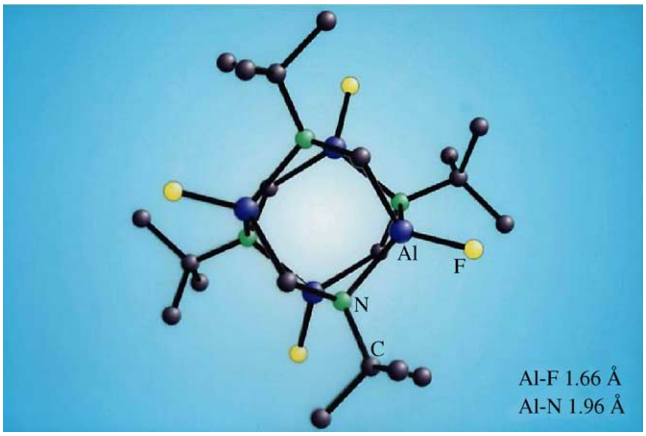
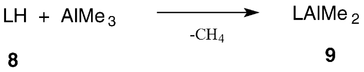


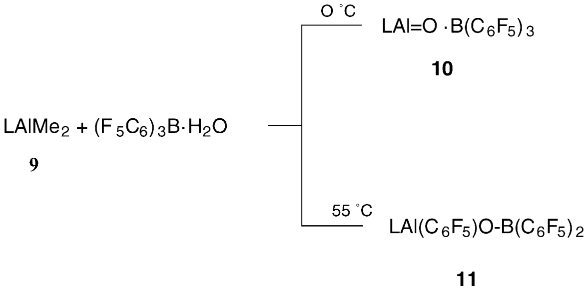
Fig. 1. Molecular structure of $(t\text{-}BuNCH_2AlF)_4$.

Table 2
^{19}F NMR chemical shifts of selected compounds with terminal Al–F bonds

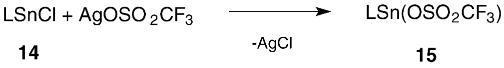
Compound	δ (ppm)
$(Me_3Si)_3CAlF_2\cdot THF$ [5]	−159.2
$(n\text{-}Bu_4N)(Me_2AlF_2)$ [13]	−154.8
$(n\text{-}Bu_4N)((Me_3Si)_3CMeAlF_2)$ [13]	−145.93
$(t\text{-}BuNCH_2AlF)_4$ [11]	−155.7
$[(AlF)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ [9]	−181.5



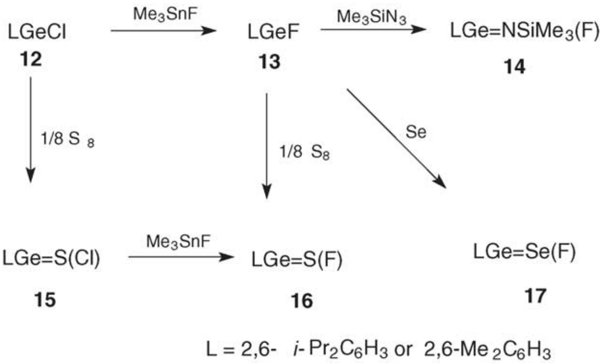
Scheme 8.



Scheme 9.



Scheme 10.



Scheme 11.

The metathesis reactions of LGeCl (**12**) and LGe=S(Cl), respectively, with Me_3SnF give the corresponding fluorides LGeF (**13**) and LGe=S(F) (**16**) in good yield. The latter compound was also accessible by the reaction of LGeF (**13**) with elemental sulfur. The ^{19}F NMR of **13** exhibits a singlet at δ 50.58 ppm. Compound **13** was characterized by single crystal X-ray structural analysis. The Ge(II)–F bond length is 1.805(17) Å and falls in the same range like that of **16**.

The reactions of germylene with trimethylsilyl azide have been well studied and established as a route to compounds containing the Ge=N double bond [18]. Compound **13** reacts with Me_3SiN_3 under elimination of nitrogen and formation of $LGe{=}NSiMe_3(F)$ (**14**). The ^{19}F NMR chemical shift of **14** is found at low field (71.04 ppm) compared with that of the starting material (50.58 ppm).

Compound LGe=Se(F) (**17**) was prepared either from LGeF by oxidative addition of selenium in toluene or by reacting LGe=Se(Cl) with Me_3SnF in dichloromethane [19]. The X-ray single crystal structural analysis of **17** exhibits a Ge–F bond length of 1.758(3) Å comparable with that of LGeF.

In summary, we noticed that compounds with terminal Al–F and Ge–F bonds are easily formed by metathesis reactions. In the case of germanium, the unsaturated compounds LGeF, LGe=S(F), LGe=Se(F) and $LGe{=}NSiMe_3(F)$ are obtained, whereas these systems in aluminum chemistry so far are unknown. The tendency of aluminum is the formation of aggregates rather than forming unsaturated compounds. However, AlF exists in the interstellar space and we have to look for the answer if there will exist compounds of composition FAl=NR, FAl=S and FAl=Se.

Acknowledgement

The financial support for this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. I am very thankful to my coworkers who have contributed to this work; their names are mentioned in the references.

References

[1] J. Pinkas, H.W. Roesky, J. Fluorine Chem. 122 (2003) 125–150.

[2] W. Wilcke, K.U. Totsche, M. Korber, J. Kobza, W. Zech, J. Plant Nutr. Soil Sci. 163 (2000) 503–508.

[3] K. Ziegler, E. Holzkamp, R. Köster, H. Lehmkuhl, Angew. Chem. 67 (1955) 213–214.

[4] K. Ziegler, R. Köster, Liebigs Ann. Chem. 608 (1957) 1–7.

[5] C. Schnitter, K. Klimek, H.W. Roesky, T. Albers, H.-G. Schmidt, C. Röpken, E. Parisini, Organometallics 17 (1998) 2249–2259.

[6] A. Herzog, F.Q. Liu, H.W. Roesky, A. Demsar, K. Keller, M. Noltemeyer, F. Pauer, Organometallics 13 (1994) 1251–1256.

[7] R.A. Kovar, J.O. Callaway, C.H. van Dyke, N.D. Miro, Inorg. Synth. 17 (1975) 36–41.

[8] A. Stasch, M. Ferbinteanu, J. Prust, W. Zheng, F. Cimpoesu, H.W. Roesky, J. Magull, H.-G. Schmidt, M. Noltemeyer, J. Am. Chem. Soc. 124 (2002) 5441–5448.

[9] A. Stasch, H.W. Roesky, D. Vidovic, J. Magull, H.-G. Schmidt, M. Noltemeyer, Inorg. Chem. 43 (2004) 3625–3630.

[10] W. Zheng, A. Stasch, J. Prust, H.W. Roesky, F. Cimpoesu, M. Noltemeyer, H.-G. Schmidt, Angew. Chem. 113 (2001) 3569–3572; W. Zheng, A. Stasch, J. Prust, H.W. Roesky, F. Cimpoesu, M. Noltemeyer, H.-G. Schmidt, Angew. Chem. Int. Ed. 40 (2000) 3461–3464.

[11] Y. Peng, J. Rong, D. Vidovic, H.W. Roesky, T. Labahn, J. Magull, M. Noltemeyer, H.-G. Schmidt, J. Fluorine Chem. 125 (2004) 951–957.

[12] D. Neculai, H.W. Roesky, A.M. Neculai, J. Magull, B. Walfort, D. Stalke, Angew. Chem. 114 (2002) 4470–4472;
D. Neculai, H.W. Roesky, A.M. Neculai, J. Magull, B. Walfort, D. Stalke, Angew. Chem. Int. Ed. 41 (2002) 4294–4296.

[13] H.W. Roesky, A. Stasch, H. Hatop, C. Rennekamp, D.H. Hamilton, M. Noltemeyer, H.-G. Schmidt, Angew. Chem. 112 (2000) 177–179;
H.W. Roesky, A. Stasch, H. Hatop, C. Rennekamp, D.H. Hamilton, M. Noltemeyer, H.-G. Schmidt, Angew. Chem. Int. Ed. 39 (2000) 171–173.

[14] Y. Ding, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, P.P. Power, Organometallics 20 (2001) 1190–1194.

[15] Y. Ding, Q. Ma, H.W. Roesky, R. Herbst-Irmer, I. Usón, M. Noltemeyer, H.-G. Schmidt, Organometallics 21 (2002) 5216–5220.

[16] Y. Ding, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Organometallics 20 (2001) 4806–4811.

[17] Y. Ding, Q. Ma, I. Usón, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, J. Am. Chem. Soc. 124 (2002) 8542–8543.

[18] M. Veith, S. Becker, V. Huch, Angew. Chem. 102 (1990) 186–188;
M. Veith, S. Becker, V. Huch, Angew. Chem. Int. Ed. Engl. 29 (1990) 216–218.

[19] Y. Ding, Q. Ma, H.W. Roesky, I. Usón, M. Noltemeyer, H.-G. Schmidt, Dalton Trans. (2003) 1094–1098.