An Alternative Approach to Al_2O_2 Ring Systems by Unexpected Cleavage of Stable Al−F− and Si−O− Bonds[†]

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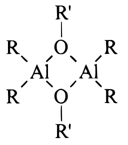
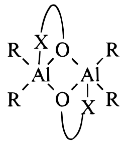
The reaction of dimethyl aluminum fluoride (Me_2AlF, DMAF) with 2,6-diisopropylphenol and triethylcitrate, respectively, leads to the products $(RO)_6Al_4F_2Me_4$ (R = 2,6-*i*-$Pr_2C_6H_3$) (**1**) and $(ROAlFMe)_2$ (R = $C(CH_2COOEt)_2$-(COOEt)) (**2**), containing Al_2O_2 ring systems. Both aluminum-μ-oxo fluorides have been structurally characterized. Fluorine exchange in the reaction of 2,6-diisopropylphenol with DMAF has been monitored using ^{19}F NMR spectroscopy. The proposed processes in solution are confirmed by the solid-state structure of **1**. Compound **1** contains four aluminum centers forming three four-membered ring systems. The two outer cycles consist of bridging −OR groups, whereas the aluminum atoms in the central cycle are connected via fluorine atoms. Two of the aluminum atoms are 4-fold coordinated, and two are 5-fold coordinated. Compound **1** contains a rare four-membered Al_2F_2 ring system. Compound **2** exhibits a dimeric structure, with oxygen rather than fluorine atoms bridging the aluminum atoms. A further carboxy oxygen atom binds coordinatively to one aluminum atom in **2**. The aluminum atoms are 5-fold coordinated. In search of an alternative approach to synthesizing Al_2O_2 ring systems, it has been found that neither DMAF nor trimethyl aluminum (Me_3Al, TMA) reacts with $(Me_3Si)_2O$, whereas the reaction of diisobutyl aluminum hydride (*i*-Bu_2AlH, DIBAH) with $(Me_3Si)_2O$ leads to (*i*-$Bu_2AlOSiMe_3)_2$ (**3**). In compound **3** the aluminum centers in the four-membered Al_2O_2 ring system are only 4-fold coordinated. This is the first example of a structurally characterized aluminum product obtained from $(Me_3Si)_2O$ under cleavage of the Si−O bond.

Introduction

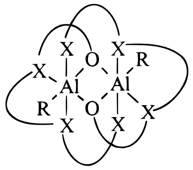
The chemistry of organoaluminum derivatives of group 16 elements has been investigated for many years, and the earlier work is reviewed extensively.[1] The alkoxide compounds form four- or six-membered ring systems,[2] depending on the sterical demand of the organic residues. Nevertheless, the Al_2O_2 ring system is widely found as the central structural unit in numerous aluminumoxo compounds. In the alkoxides with monodentate ligands (type **I**), the aluminum center is usually 4-fold coordinated, although there are some exceptions such as Al(O*i*-Pr)$_3$, which can be attributed to steric reasons.[3] Bidentate or polydentate ligands lead to more complex bridged systems, with two or three coordinative bonds to the aluminum center, increasing its coordination number to five or six (types **II** and **III**).[4] The common synthetic procedure for these compounds is based on the facile elimination reaction illustrated in Scheme 1.[5]



I



II



III

The Al_2O_2 ring system is also an important building block in numerous aluminumoxo compounds obtained from the

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[†] Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday.

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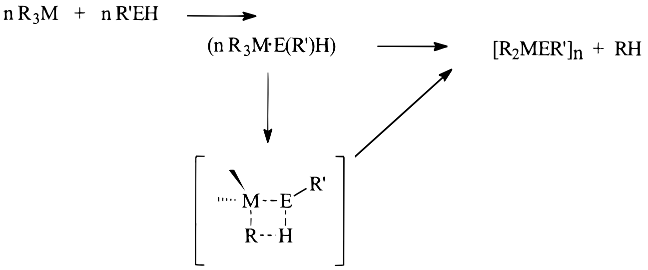
Scheme 1



hydrolysis of triorganoaluminum compounds. Several working groups achieved important progress in this field and presented interesting model compounds for methylaluminoxane (MAO). These compounds consist, depending on the bulkiness of the substituents and the reaction conditions, respectively, of ring or cage frameworks.[6]

Since the early work of Schmidbaur et al. in the 1960s, there is also a high interest in organoaluminum siloxides.[7] These compounds can be synthesized by salt elimination reactions, but our interest was focused on an alternative approach to aluminum siloxides: the cleavage of silicones presented by Barron et al. in 1990 and the cleavage of $(Me_2SiO)_3$ with aluminum dihydrides, yielding the new organoalumoxanes reported by Power et al. in 1997, respectively.[8]

As a new contribution to both fields, we report herein the synthesis of various Al_2O_2 ring systems based on the alcoholysis reaction of DMAF and the cleavage of hexamethyl siloxane with diisobutyl aluminum hydride.

It should be stressed that DMAF was synthesized by Ziegler et al.[9] in 1955, and that except for some structural investigations,[10] little is known about its chemistry. To the best of our knowledge, no structurally characterized aluminum fluoralkoxide is yet reported. For the alcoholysis of DMAF, we chose a mono- and a polydentate ligand and were interested in the coordination behavior of the aluminum in these fluorine-containing molecules. First, reaction of ROH, a compound containing a sterically demanding substituent (R = 2,6-*i*-$Pr_2C_6H_3$), yields a product with an aluminum atom bonded to one oxygen-containing group forming a MeAl(OR)F fragment. Second, we attempted to synthesize a similar aluminum core that was surrounded by chelating electron-donating ligands such as triethylcitrate ($HO[C(CH_2COOEt)_2(COOEt)]$). Citrate proved to be an interesting chelating agent for aluminum systems because of its six potentially coordinating sites.[4e,11]

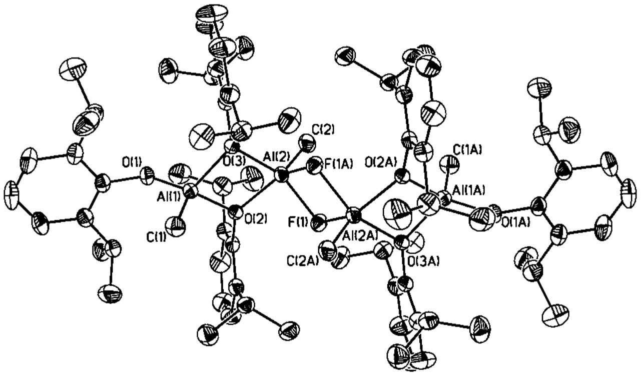
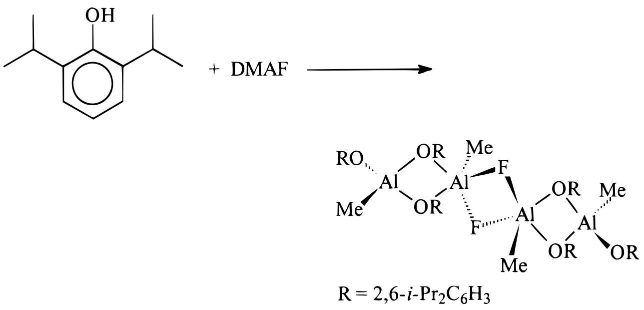


Figure 1. Molecular crystal structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are given in Table 1; for further details of refinement, see Table 4.

Scheme 2



1

(10 %)

To the best of our knowledge, hexamethyldisiloxane has not yet been used as a substrate in the preparation of aluminum siloxides. We tried different ways to obtain the desired product of type **I**, but were successful only with DIBAH.

Results and Discussion

Reaction of DMAF with 2,6-*i*-$Pr_2C_6H_3OH$. The reaction of DMAF with 2,6-*i*-$Pr_2C_6H_3OH$ (Scheme 2) was carried out in a 1:1 molar ratio in toluene at room temperature. Rapid evolution of methane and precipitation of a white insoluble solid were observed after the solution was stirred for 8 h. The solution was filtered; however, the residue could not be characterized because of its insolubility in all common solvents. The filtrate was kept for 2 weeks at −20 °C, and colorless crystals were obtained in a 10% yield suitable for X-ray investigations. The molecular structure of **1** is shown in Figure 1.

The molecule of **1** is centrosymmetric and consists of two $Me_2Al_2(OR)_3F$ fragments, where the fluorine atoms connect the two parts of the molecule. The outer arranged aluminum atoms

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**

Distances			
Al(1)−O(1)	1.7111(18)	Al(1)−O(2)	1.8375(2)
Al(1)−O(3)	1.841(2)	Al(1)−C(1)	1.941(3)
Al(2)−F(1A)	1.812(2)	Al(2)−O(2)	1.871(2)
Al(2)−F(1)	1.879(2)	Al(2)−O(3)	1.912(2)
Al(2)−C(2)	1.917(3)	F(1)−Al(2A)	1.812(2)
Angles			
O(1)−Al(1)−O(2)	112.36(9)	O(1)−Al(1)−O(3)	113.52(9)
O(2)−Al(1)−O(3)	79.17(8)	O(1)−Al(1)−C(1)	115.6(1)
O(2)−Al(1)−C(1)	114.75(1)	O(3)−Al(1)−C(1)	116.3(1)
F(1A)−Al(2)−O(2)	132.09(8)	F(1A)−Al(2)−F(1)	75.56(7)
O(2)−Al(2)−F(1)	89.20(7)	F(1A)−Al(2)−O(3)	90.31(7)
O(2)−Al(2)−O(3)	76.59(7)	F(1)−Al(2)−O(3)	144.89(8)
F(1A)−Al(2)−C(2)	107.68(1)	O(2)−Al(2)−C(2)	119.6(1)
F(1)−Al(2)−C(2)	99.37(1)	O(3)−Al(2)−C(2)	115.6(1)
C(11)−O(1)−Al(1)	133.58(2)	C(21)−O(2)−Al(1)	126.7(1)
C(21)−O(2)−Al(2)	130.85(1)	Al(1)−O(2)−Al(2)	102.05(8)
C(31)−O(3)−Al(1)	128.37(1)	C(31)−O(3)−Al(2)	131.3(1)
Al(1)−O(3)−Al(2)	100.38(8)	Al(2A)−F(1)−Al(2)	104.44(7)

have a 4-fold coordination sphere. The Al(1)−O(1) bond length (1.7111(18) Å) is significantly shorter than those of Al(1)−O(2) (1.8375(2) Å) and Al(1)−O(3) (1.841(2) Å), respectively, as expected for μ-versus μ_3-bridging oxygen atoms. The plane formed by Al(1), O(3), Al(2), and O(2) has angles of O(2)−Al(1 or 2)−O(3) around 79° and Al(2)−O(2 or 3)−Al(3) around 101°. Therefore, the coordination sphere at Al(1) can be described as distorted tetrahedral. In contrast, Al(2) has a distorted trigonal bipyramidal environment. The Al(2)−C(2) equatorial bond length (1.917(3) Å) differs from the distance of Al(1)−C(1) (1.941(3) Å) and is slightly shorter (0.024 Å). The equatorial Al(2)−O(2) bond length (1.871(2) Å) is remarkably shorter than the corresponding axial Al(2)−O(3) bond length (1.912(2) Å). In agreement with this assignment is the short axial Al(2)−F(1A) (1.812(2) Å) in comparison to the equatorial Al(2)−F(1) (1.879(2) Å) bond length. The bond length of Al(2)−F(1A) is comparable to that found by electron diffraction for DMAF (1.808 Å).[10] The different Al−F bond lengths reflect the nonsymmetric coordination between Al(2) and Al(2A) (Table 1).

In the mass spectrum (EI) peaks (634 *m/e*; 58%) are assigned to $M^+/2$ and to $MeAl(OR)_2$ (396 *m/e*; 100%), respectively. The elemental analysis as well as the NMR data are consistent with **1**. The reaction was repeated on an NMR tube scale with a solvent mixture of toluene and C_6D_6 (4:1). ^{19}F NMR spectra were recorded (1 min, 45 min, 165 min, and 1 day) after addition of the alcohol to the DMAF solution. The spectra (Figure 2) show the formation of a first product which could be assigned to the expected fluorine-bridged $[MeAl(OR)F]_x$ ($x = 2, 3, 4$) (−159.7 ppm), which is not stable in solution and forms **1** (−174.4 ppm).[12]

In contrast to previous investigations on aluminates, e.g., Me_3AlF^-, in which a dissociation in the gas phase of the Al−F bond was excluded,[13] our ^{19}F NMR spectra in a toluene/C_6D_6 mixture indicate a fluorine-alkoxy exchange reaction leading to a stable product **1**.

Reaction of DMAF with HO[C(CH$_2$COOEt)$_2$(COOEt)]. The reaction of HO[C(CH$_2$COOEt)$_2$(COOEt)] with DMAF in toluene at room temperature (Scheme 3) leads to methane evolution, and a solution is obtained that remains clear after 24 h of stirring. Colorless crystals of **2** were formed after 4 weeks at −20 °C, suitable for X-ray measurements. After 70% of the solvent was removed, the residue was kept at −20 °C to yield a second crop of **2**.

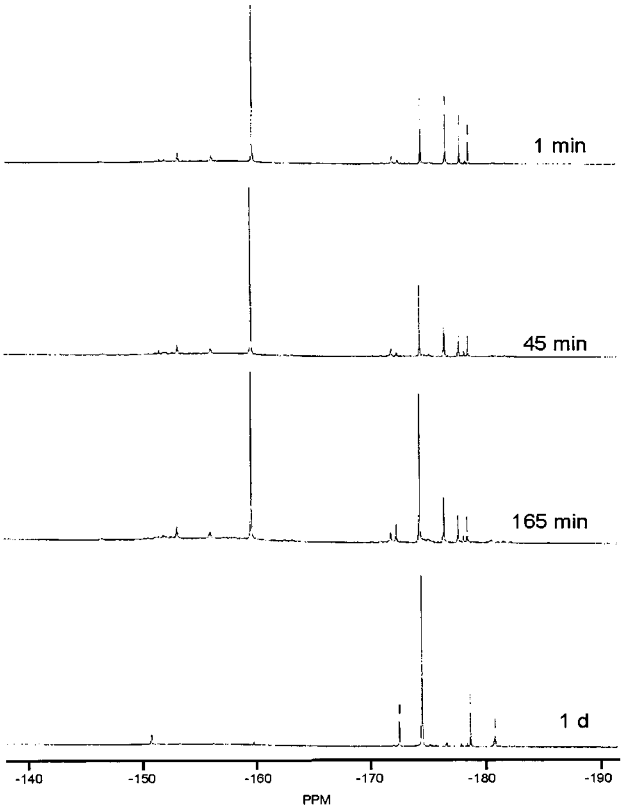
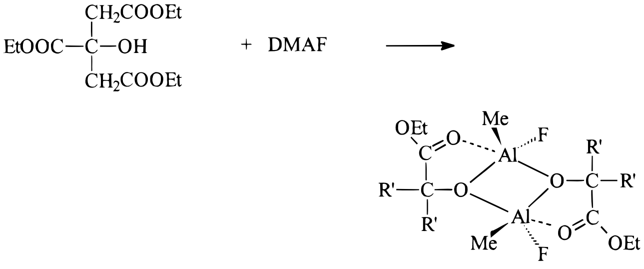


Figure 2. ^{19}F NMR spectroscopical investigations on the reaction of DMAF with 2,6-*i*-$Pr_2C_6H_3OH$ recorded as a function of time (1 min, 45 min, 165 min, 1 day).

Scheme 3



2
(63 %)

R' = CH_2COOEt

The structure of **2** can be regarded as a dimer of MeAl(OR)F having an idealized C_2 symmetry. Although a fluorine bridged dimer was expected, **2** has terminal fluorine atoms in a pseudo-cis conformation and is bridged by oxygen (Figure 3). The aluminum atoms have a 5-fold coordination sphere. A further coordination of an oxygen atom from the citrate ligand is not observed. The central four-membered Al_2O_2 ring is nearly perfectly planar. The values of the bond lengths of Al(1)−F(1) (1.670(4) Å) and Al(2)−F(2) (1.679(4) Å) are slightly longer than in the reported aluminum difluoride ((2,6-*i*-$Pr_2C_6H_3$)N-($SiMe_3$)AlF_2, Al−F (terminal), about 1.64 Å).[12] The bond lengths of Al(1)−C(1) and Al(2)−C(2) are equal within the

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[12] For ^{19}F NMR shifts of aluminum fluorides, see: Waezsada, S. D.; Liu, F.-Q.; Murphy, E. F.; Roesky, H. W.; Teichert, M.; Usón, I.; Schmidt, H.-G.; Albers, T.; Parisini, E.; Noltemeyer, M. *Organometallics* **1997**, *16*, 1260. ^{19}F NMR shifts for 5-fold coordinated alkylalkoxyaluminum fluorides are, to the best of our knowledge, still unknown.

[13] Damrauer, R.; Kremp, M.; Damrauer, N. H.; Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 5218.

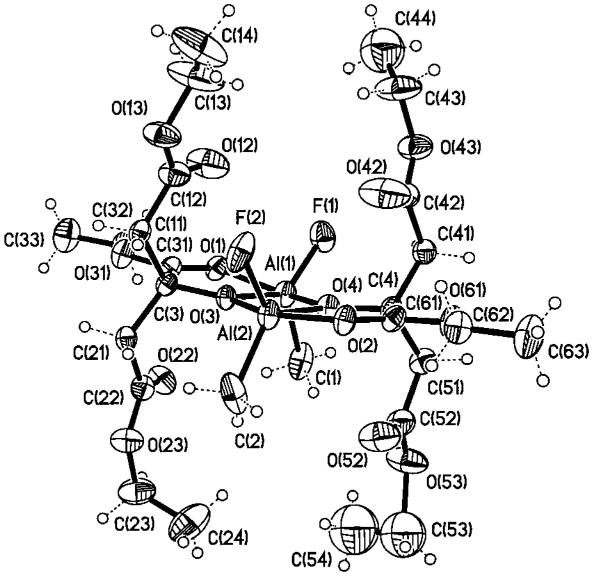

Figure 3. Molecular crystal structure of **2**. Selected bond lengths (Å) and angles (deg) are given in Table 2; for further details of refinement, see Table 4.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**

	Distances		
Al(1)−F(1)	1.670(4)	Al(1)−O(3)	1.863(4)
Al(1)−C(1)	1.902(8)	Al(1)−O(4)	1.916(4)
Al(1)−O(1)	2.045(5)	Al(2)−F(2)	1.679(4)
Al(2)−O(4)	1.859(4)	Al(2)−C(2)	1.909(9)
Al(2)−O(3)	1.935(4)	Al(2)−O(2)	1.987(4)
	Angles		
F(1)−Al(1)−O(3)	127.7(2)	F(1)−Al(1)−C(1)	114.0(3)
O(3)−Al(1)−C(1)	118.2(3)	F(1)−Al(1)−O(4)	96.8(2)
O(3)−Al(1)−O(4)	75.2(2)	C(1)−Al(1)−O(4)	102.8(3)
F(1)−Al(1)−O(1)	90.7(2)	O(3)−Al(1)−O(1)	80.2(2)
C(1)−Al(1)−O(1)	96.9(3)	O(4)−Al(1)−O(1)	153.7(2)
C(31)−O(1)−Al(1)	112.7(4)	F(2)−Al(2)−O(4)	122.7(2)
F(2)−Al(2)−C(2)	114.5(4)	O(4)−Al(2)−C(2)	122.8(4)
F(2)−Al(2)−O(3)	95.9(2)	O(4)−Al(2)−O(3)	74.9(2)
C(2)−Al(2)−O(3)	102.3(3)	F(2)−Al(2)−O(2)	91.6(2)
O(4)−Al(2)−O(2)	81.4(2)	C(2)−Al(2)−O(2)	95.6(3)
O(3)−Al(2)−O(2)	155.5(2)	C(61)−O(2)−Al(2)	113.7(4)
C(3)−O(3)−Al(1)	121.2(3)	C(3)−O(3)−Al(2)	134.0(3)
Al(1)−O(3)−Al(2)	104.4(2)	C(4)−O(4)−Al(2)	120.5(3)
C(4)−O(4)−Al(1)	134.0(3)	Al(2)−O(4)−Al(1)	105.4(2)

experimental error (about 1.90 Å) and in the same range of the 4-fold coordinated aluminum atom Al(1)−C(1) in **1**. The Al(1)−O(3) (1.863(4) Å), Al(2)−O(4) (1.859(4) Å), Al(2)−O(3) (1.935(4) Å), and Al(1)−O(4) (1.916(4) Å) bond lengths show the nonsymmetrical arrangement of the ligand between Al(1) and Al(2). Two five-membered rings (Al(1)−O(3)−C(3)−C(31)−O(1) and Al(2)−O(4)−C(4)−C(61)−O(2)) arrange in such a way that a ladder-shaped core is formed. The Al(1)−O(1) (2.045(5) Å) and Al(2)−O(2) (1.987(4) Å) bond lengths reflect the weak coordinative character of these bonds (Table 2).

Comparing this result with that of **1**, compound **2** can be regarded as a model for an intermediate of the suggested exchange mechanism for **1**. With the attack of a second Lewis basic oxygen-containing fragment, the aluminum is electronically saturated and the terminal fluorine atom could then be abstracted by another Lewis acidic center. Compound **2** is intramolecularly stabilized by the citrate ligand, and, consequently, the abstracting step does not occur. The elemental analysis of **2** is consistent with the composition in the solid state.

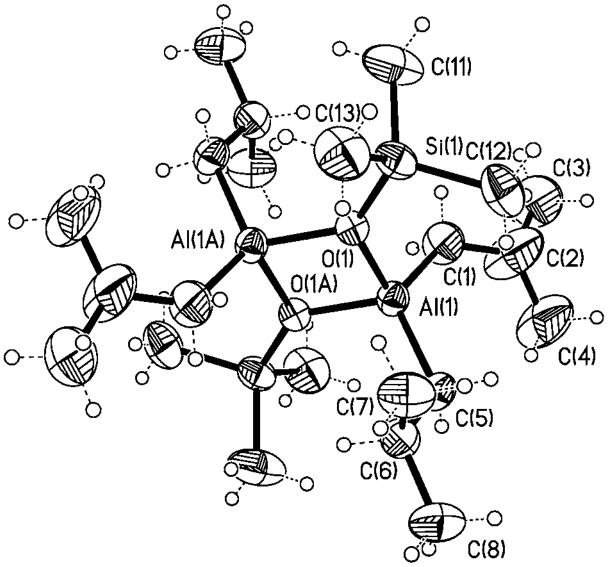

Figure 4. Molecular crystal structure of **3**. Selected bond lengths (Å) and angles (deg) are given in Table 3; for further details of refinement, see Table 4.

In the ^{1}H NMR spectrum we find the expected signals in the range of the protons of the methyl group on the aluminum. ^{19}F NMR measurements give a more complicated picture. Although the doublets found (−173.0 and −181.3 ppm) are in good correlation to the structure of **2**, we find several further signals.[12,14] We suggest assigning these signals to different conformers in solution as illustrated schematically in Scheme 4.

The mass spectrum (EI) shows fragments of the monomer assigned to $M^{+}/2 - Me$ (321 *m*/*e*).

Reaction of TMA, DMAF, and DIBAH with $(Me_3Si)_2O$. In 1997 we reported on the cleavage of THF with aluminum difluorides $RAlF_2$;[15] consequently, we investigated the cleavage of the silyl ether $(Me_3Si)_2O$ with TMA and DMAF, respectively, but we were not successful in the cleavage of the strong Si−O bond. Both reactions were done with mixtures of Me_2Al_x (x = Me, F) without any solvent under reflux (in the case of DMAF/$(Me_3Si)_2O$, for 36 h; in the case of TMA/$(Me_3Si)_2O$, for 14 days), but no reaction was observed in either the ^{29}Si NMR or the ^{1}H NMR spectra.

Heating a mixture of $(Me_3Si)_2O$ and DIBAH without solvent in a 1:1 molar ratio to 130 °C leads to a rapid formation of Me_3SiH (Scheme 5). The mixture was kept at this temperature for 1 h. Storing the product mixture at −2 °C for 8 h leads to the formation of the colorless product **3** in 98% yield.

Compound **3** was dissolved in *n*-hexane and kept for 2 weeks at −20 °C. Single crystals suitable for X-ray crystallography were obtained from this solution. Compound **3** is a centrosymmetric molecule consisting of two oxygen-bridged $R_2AlOSiMe_3$ fragments (Figure 4). The bond lengths of the four-membered ring (Al(1)−O(1) and Al(1)−O(1A), about 1.86 Å) are equal within the experimental error. The value for the Si(1)−O(1) bond length is 1.674(3) Å. The angles in the perfect planar ring are (O(1)−Al(1)−O(1A), 83.85(1)° and for Al(1)−O(1)−

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(14) Temperature-dependent ^{19}F NMR measurements at 40 °C and 60 °C show only broader signals compared to the spectra at room temperature, but no change in the intensities. Nevertheless, the formation of $M^{+}/2-Me$ in the EI mass spectra underlines the suggested species shown in Scheme 4.

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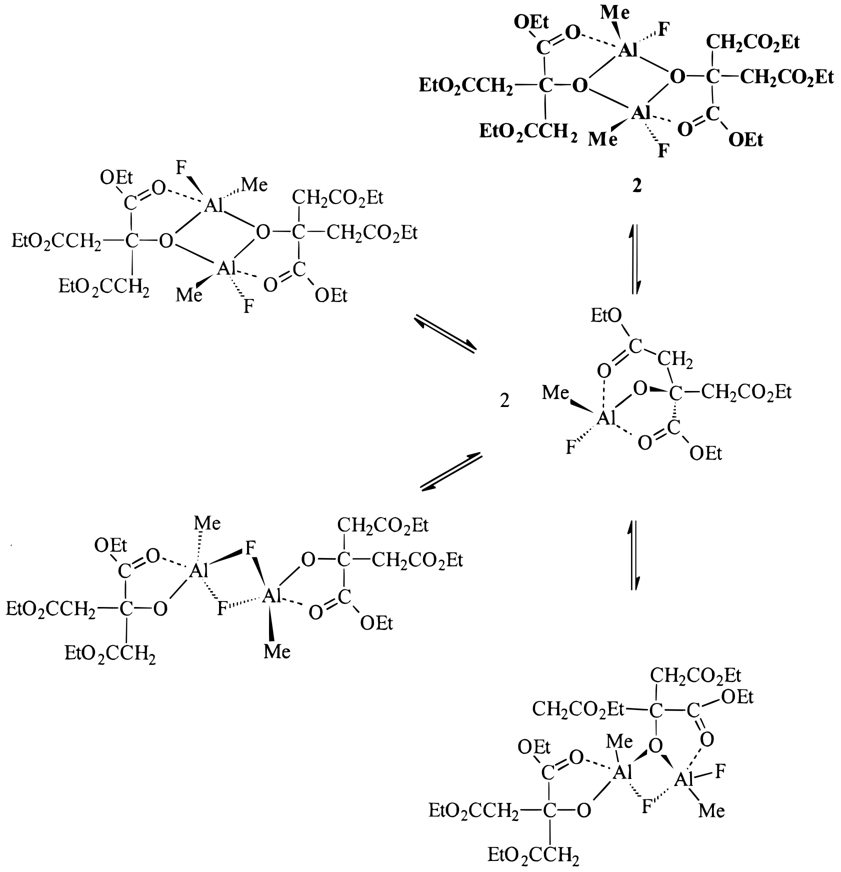
Scheme 4



Scheme 5

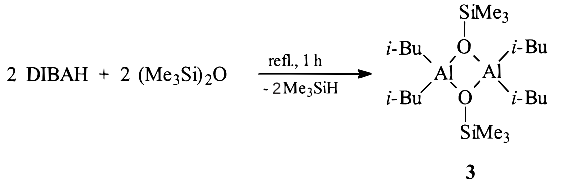


Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3**

Distances			
Si(1)−O(1)	1.674(3)	Al(1)−O(1A)	1.859(3)
Al(1)−O(1)	1.861(3)	Al(1)−C(1)	1.965(4)
Al(1)−C(5)	1.967(4)		
Angles			
O(1)−Si(1)−C(13)	108.5(2)	O(1)−Si(1)−C(11)	109.7(2)
O(1)−Si(1)−C(12)	107.9(2)	O(1A)−Al(1)−O(1)	83.85(1)
O(1A)−Al(1)−C(1)	111.4(2)	O(1)−Al(1)−C(1)	107.5(2)
O(1A)−Al(1)−C(5)	110.4(2)	O(1)−Al(1)−C(5)	115.6(2)
C(1)−Al(1)−C(5)	121.8(2)	Si(1)−O(1)−Al(1A)	132.8(2)
Si(1)−O(1)−Al(1)	130.6(2)	Al(1A)−O(1)−Al(1)	96.15(1)
C(2)−C(1)−Al(1)	127.4(4)	C(6)−C(5)−Al(1)	122.5(3)

Al(1A), 96.15(1)°), in agreement with the expected values for a highly symmetric Al_2O_2 ring system (Tables 3 and 4).

The NMR (^1H, ^{29}Si) data are consistent with the solid-state structure, and a signal for the molecular ion minus one butyl group in the mass spectrum (403 *m*/*e*; 18%) indicates the stability of the ring system in the gas phase. These results are underlined by a correct elemental analysis.

In summary, we have presented **1** and **2** as examples of the new class of flouroaluminum alkoxide ring systems. The route to **1** and **2** is a strong indication for the surprising instability of Al−F bonds if alternative electron donors are introduced. The coordination behavior of the fluorine atoms in these systems is dependent on the environment. In **1** it is serving as bridging element between two aluminum alkoxides; in **2** it is terminal. Nevertheless, in both molecules the fluorine-containing aluminum atom is 5-fold coordinated. The increased Lewis acidity by the fluorine atom might be the reason for the stabilization

Table 4. Crystallographic Data for **1**, **2**, and **3**

Data for **1**	
$C_{76}H_{114}Al_4F_2O_6$	fw 1269.59 g/mol
$a = 10.050(2)$ Å	space group $P2_1/c$
$b = 23.111(5)$ Å	$T = 133(2)$ K
$c = 16.234(3)$ Å	$\lambda = 0.710\ 73$ Å
$\beta = 97.13(3)°$	$\rho_{calc} = 1.127$ Mg/m^3
$V = 3741.6(13)$ Å	$\mu = 0.115$ mm^{-1}
$Z = 2$	R1 = 0.0642
cryst syst monoclinic	wR2 = 0.1327
$S = 1.144$	
Data for **2**	
$C_{26}H_{44}Al_2F_2O_{14}$	fw 672.57 g/mol
$a = 12.173(2)$ Å	space group $P2_12_12_1$
$b = 13.319(3)$ Å	$T = 200(2)$ K
$c = 20.512(4)$ Å	$\lambda = 0.710\ 73$ Å
$V = 3325.7(12)$ Å	$\rho_{calc} = 1.343$ Mg/m^3
$Z = 4$	$\mu = 0.161$ mm^{-1}
cryst syst orthorhombic	R1 = 0.0657
$S = 1.076$	wR2 = 0.1807
Data for **3**	
$C_{22}H_{54}Al_2O_2Si$	fw 460.79 g/mol
$a = 17.090(2)$ Å	space group *Pbca*
$b = 10.260(2)$ Å	$T = 200(2)$ K
$c = 17.521(4)$ Å	$\lambda = 0.710\ 73$ Å
$V = 3072.0(10)$ Å	$\rho_{calc} = 0.992$ Mg/m^3
$Z = 4$	$\mu = 0.186$ mm^{-1}
cryst syst orthorhombic	R1 = 0.0722
$S = 1.065$	wR2 = 0.1912

of these systems. The synthetic approach cleaving $(Me_3Si)_2O$ is surprising. For all compounds we found that the formation of Al_2O_2 ring systems is a strong driving force for the unexpected cleavage of former so-called “stable bonds”. These observations are promising and further investigations in this field will follow.

Experimental Section

General Experimental Procedures. All solvents were purified and dried by standard techniques, and Schlenk line and drybox 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 (δ 7.15 ppm for ^1H NMR). The elemental analyses were performed in the Analytisches Laboratorium des Anorganischen Instituts, Göttingen. Small variations are due to metal carbide formation in these systems.

DMAF (16% solution in toluene) and DIBAH were used as received from the Witco GmbH, Bergkamen. $(Me_3Si)_2O$ (Aldrich) was dried over molecular sieves and always distilled prior to use. Diisopropylphenol (Aldrich) and triethyl citrate (Aldrich) were distilled before use and kept in Schlenk flasks at −2 °C.

X-ray Procedures. A suitable crystal of compound **1** was mounted on a glass fiber in a rapidly cooled perfluoropolyether.[16] Diffraction data were collected on a Stoe−Siemens−Huber four-circle diffractometer coupled to a Siemens CCD area detector at 133(2) K, with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), performing φ and ω scans.

A suitable crystal of compound **2** and **3**, respectively, was mounted on a glass fiber and coated with paraffin oil. Diffraction data were collected on a Siemens−Stoe AED2 four-circle diffractometer.

All structures were solved by direct methods using SHELX-97 and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[17,18] All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The final fractional atomic coordinates are given in the Supporting Information.

Preparation of 1. A solution of 2,6-*i*-$Pr_2C_6H_3OH$ (3.67 g, 20.6 mmol) in toluene (10 mL) was added dropwise to a solution of DMAF (1.56 g, 20.6 mmol) in toluene (30 mL) under methane evolution at room temperature and stirred for 8 h. The reaction mixture was filtered and the remaining white solid (2.94 g, 56%) was dried in vacuo. The filtrate was stored at −20 °C and colorless single crystals were obtained. After the solution was decanted into a second flask, 80% of the solvent was removed in vacuo and the solution kept at −20 °C for further crystallization. From this solution, 0.43 g (10%) was isolated, decomp 120 °C. ^1H NMR (200 MHz, C_6D_6): δ −0.90 (s, 6 H, $AlCH_3$), −0.57 (s, 6 H $AlCH_3$), 1.05 (d, ^3J(H H) = 6.8 Hz, 48 H, $CH(CH_3)_2$), 1.18 (d, ^3J(H H) = 6.8 Hz, 24 H, $CH(CH_3)_2$), 1.42 (sept, ^3J(H H) = 7.1 Hz, 8 H, $CH(Me)_2$), 3.48 (sept, ^3J(H H) = 6.8 Hz, 4 H, $CH(Me)_2$), 7.09 (s, 18 H, Ar−*H*) ppm. ^{13}C NMR (500 MHz, C_6D_6): δ −12.2 (s, $AlCH_3$), 21.3−28.0 (m, $CH(CH_3)_2$), 120.9−149.9 (m, Ar−C) ppm. $^{19}F\{^1H\}$ NMR (90 MHz, C_6D_6): δ −174.5 (s) ppm. IR ([cm^{-1}], KBr, Nujol): ν 1465, 1155, 833, 753. MS (EI) *m/e* (%): 634 [$^1/_2M^+$, 58], 396 [$(MeAlOR_2)^+$, 100]. Anal. Calcd for $C_{76}H_{114}Al_4F_2O_6$: Al, 8.50; F, 2.99. Found: Al, 7.6; F, 2.1.

Preparation of 1 (NMR Tube). A solution of 2,6-*i*-$Pr_2C_6H_3OH$ (0.10 g, 0.56 mmol) in C_6D_6 (0.3 mL) was added dropwise to DMAF (0.27 g, 0.56 mmol, 16% solution in toluene) through a septum under shaking. Gas evolution occurred and the methane was removed using a 2-mL syringe. ^{19}F NMR spectra were recorded after 1 min, 45 min, 165 min, 1 day, and 2 days. After 1 day, no change in the spectrum was observed. $^{19}F\{^1H\}$ NMR (188 MHz, C_6D_6, 1 min reaction time): δ −159.7 (s), −174.4 (s), −176.6 (s), −177.9 (s), −178.7 (s) ppm. $^{19}F\{^1H\}$ NMR (188 MHz, C_6D_6, 45 min): δ −159.7 (s), −174.5 (s), −176.6 (s), −177.9 (s), −178.7 (s) ppm. $^{19}F\{^1H\}$ NMR (188 MHz, C_6D_6, 165 min): δ −159.7 (s), −172.5 (s), −174.4 (s), −176.6 (s), −177.9 (s), −178.7 (s) ppm. $^{19}F\{^1H\}$ NMR (188 MHz, C_6D_6, 1 day): δ −172.5 (s), −174.4 (s), −178.7 (s) ppm.

Preparation of 2. A solution of $HO[C(CH_2COOEt)_2(COOEt)]$ (1.40 g, 5.04 mmol) in toluene (15 mL) was added dropwise to a solution of DMAF (0.38 g, 5.04 mmol) in toluene (40 mL) under methane evolution at room temperature and stirred for 24 h. The solution was kept at −20 °C, and colorless single crystals were obtained. After the solution was decanted into a second flask, 70% of the solvent was removed in vacuo and the solution kept at −20 °C for further crystallization of **2**, 1.07 g (63%) was isolated from this solution, decomp 140 °C. ^1H NMR (250 MHz, C_6D_6): δ [−0.19 (s), −0.20 (s), −0.21 (s), −0.30 (s, 6 H, $AlCH_3$)], 0.75−1.10 (m, 18 H, OCH_2CH_3), 2.60−3.55 (m, 8 H, CH_2-COOEt), 3.75 (m, 12 H, OCH_2CH_3) ppm. $^{19}F\{^1H\}$ NMR (235 MHz, C_6D_6): δ −160.5 (s), −165.0 (s), −167.0 (s), −173.0 (d, *J*(F F) = 24 Hz), −178.5 ppm (s), −181.3 (d, *J*(F F) = 24 Hz) ppm. IR ([cm^{-1}], KBr, Nujol): ν 1466, 1375, 1275, 1082, 1026, 917, 759. MS (EI) *m/e* (%): 321 [1/2 M^+ − Me]. Anal. Calcd for $C_{26}H_{44}Al_2F_2O_{14}$: Al, 8.02; F, 5.65. Found: Al, 7.4; F, 5.6.

Preparation of 3. A mixture of $(Me_3Si)_2O$ (10.0 g, 61.7 mmol) and DIBAH (9.93 g, 61.7 mol) was heated to 130 °C, and Me_3SiH evolution was observed. The reaction mixture was stirred for 1 h at this temperature and then kept at −2 °C for 8 h. A white crystalline solid was formed. 3.00 g of **3** was dissolved in *n*-hexane (10 mL) and the solution stored at −20 °C for 2 weeks. Single crystals suitable for X-ray measurements were obtained, yield 13.9 g (98%), decomp 160 °C. ^1H NMR (250 MHz, C_6D_6): δ 0.22 (d, ^3J(H H) = 7.0 Hz, 8 H, $AlCH_2$-$CHMe_2$), 0.23 (s, 18 H, $Si(CH_3)_3$), 1.14 (d, ^3J(H H) = 6.5 Hz, 24 H, $CH_2CH(CH_3)_2$), 2.02 (dqt, ^3J(H H) = 7.0 Hz, ^3J(H H) = 6.5 Hz, 4 H, $CH_2CH(Me)_2$). ^{29}Si NMR (79 MHz, C_6D_6): δ 18.9 ($Si(CH_3)_3$). IR ([cm^{-1}], KBr, Nujol): ν 1257, 1072, 850, 810, 765. MS (EI) *m/e* (%): 403 [M^+ − Bu, 18], 235 [M^+ − 4 Bu + 3 H, 100]. Anal. Calcd for $C_{26}H_{44}Al_2O_2Si_2$: Al, 11.76; Si, 12.24%. Found: Al, 11.1; Si, 11.3.

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Supporting Information Available: X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Final *R* indices: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$(for $[I > 2\sigma(I)]$), $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ (for all data); goodness of fit $S = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n - p)]^{1/2}$.