Aminodimethylalanes ($R^1R^2NAlMe_2$) as Useful Synthetic Precursors of Aminoalane Difluorides Using Trimethyltin Fluoride: Crystal Structures of (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)$AlMe_2$ and (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)AlF_2†

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Aminodimethylalanes $R^1R^2NAlMe_2$ (R^1 = 2,6-*i*-$Pr_2C_6H_3$, 2,6-$Me_2C_6H_3$; R^2 = $SiMe_3$, Si(*i*-Pr)Me_2, Si(*t*-Bu)Me_2, Si(2,4,6-$Me_3C_6H_2$)Me_2) are prepared in high yield via reaction of the respective amine R^1R^2NH with trimethylaluminum in *n*-hexane. Further reaction of (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)$AlMe_2$ with 2 equiv of trimethyltin fluoride in toluene affords the aminoalane difluoride (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)AlF_2. An X-ray structural determination of (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)$AlMe_2$ shows it to be dimeric with bridging methyl and terminal amino groups. The aminoalane difluoride (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)AlF_2 is trimeric with a six-membered alternating aluminum−fluorine ring. Terminal fluorine atoms are located above and below the ring. Reactions of aminoalanes $R^1R^2NAlMe_2$ with 2 equiv of trimethyltin fluoride in THF yield the monomeric THF adducts $R^1R^2NAlF_2\cdot$THF.

Introduction

As early as 1955, Ziegler and co-workers had pioneered the preparation of dialkylaluminum fluorides. Starting from the corresponding chlorides and using sodium fluoride as a chloro−fluoro exchange reagent, they succeeded in preparing the fluorides for the first time (eq 1).[1] In the intervening 40 years, however, only

$$R_2AlCl + NaF \rightarrow R_2AlF + NaCl \qquad (1)$$

a small number of other dialkylaluminum[2] and some dialkylgallium[3] and -indium fluorides[4] have been synthesized, using fluorinating reagents such as $BF_3\cdot OEt_2$ or alkali-metal fluorides. Attempted fluorination of $EtAlCl_2$ using sodium fluoride was mentioned briefly by Ziegler, but no experimental characterization was presented.[5]

In the past two years, we have reported the facile preparation of groups 4−6[6] and main-group fluorides[7] from their corresponding chlorides using trimethyltin fluoride as the chloro−fluoro exchange reagent. As an extension of our interest in the preparation of main group fluorides, in particular organoaluminum fluorides, we have turned our attention to the synthesis of aminoalane difluorides $R^1R^2NAlF_2$. To the best of our knowledge, compounds of this type have not been described previously. Treatment of aminodimethylalanes with trimethyltin fluoride has proven to be a convenient route to aminoalane difluorides. Herein, we report the synthesis of a series of new aminodimethylalanes and structural characterization of the methyl-bridged aminodimethylalane (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)-$AlMe_2$. Further reaction of (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)$AlMe_2$ with 2 equiv of trimethyltin fluoride affords the first structurally characterized aminoalane difluoride (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)AlF_2.

Results and Discussion

On the basis of our previous successes in the fluorination of main-group chlorides with trimethyltin fluoride, we were somewhat dismayed by the complications encountered in the isolation of a chloride-free product when organoaluminum dichlorides were treated with Me_3SnF. To circumvent this problem, we directed our subsequent efforts toward the reaction of aminodi-

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† Dedicated to Professor Walter Siebert on the occassion of his 60th birthday.

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[1] Ziegler, K.; Holzkamp, E.; Köster, R.; Lehmkuhl, H. *Angew. Chem.* **1955**, 67, 213. Ziegler, K.; Köster, R. *Liebigs Ann. Chem.* **1957**, *608*, 1.

[2] Laubengayer, A. W.; Lengnick, G. F. *Inorg. Chem.* **1966**, *5*, 503. Gundersen, G.; Haugen, T.; Haaland, A. *J. Organometal. Chem.* **1973**, *54*, 77. Krieg, V.; Weidlein, J. *J. Organometal. Chem.* **1970**, *21*, 281. Lehmkuhl, H.; Olbrysch, O.; Nehl, H. *Liebigs Ann. Chem.* **1973**, 708. Schmidbaur, H.; Weidlein, J.; Klein, H.-F.; Eiglmeier, K. *Chem. Ber.* **1968**, *101*, 2268.

[3] Schmidbaur, H.; Klein, H.-F.; Eiglmeier, K. *Angew. Chem.* **1967**, *79*, 821; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 806. Schmidbaur, H.; Klein, H.-F. *Chem. Ber.* **1968**, *101*, 2278. Neumüller, B.; Gahlmann, F. *Z. Anorg. Allg. Chem.* **1992**, *612*, 123. Neumüller, B.; Gahlmann, F. *Angew. Chem.* **1993**, *105*, 1770; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1701.

[4] Neumüller, B.; Gahlmann, F. *J. Organometal. Chem.* **1991**, *414*, 271. Neumüller, B.; Gahlmann, F.; Schäfer, M.; Magull, S. *J. Organometal. Chem.* **1992**, *440*, 263.

[5] Brit. Pat. 779,873, 1957; *Chem. Abstr.* **1957**, *51*, 17981a.

[6] Köhler, K.; Herzog, A.; Steiner, A.; Roesky, H. W. *Angew. Chem.* **1996**, *108*, 331; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 295. Herzog, A.; Liu, F.-Q.; Roesky, H. W.; Demsar, A.; Keller, K.; Noltemeyer, M.; Pauer, F. *Organometallics* **1994**, *13*, 1251. Murphy, E. F.; Yu, P.; Dietrich, S.; Roesky, H. W.; Parisini, E.; Noltemeyer, M. *J. Chem. Soc., Dalton Trans.* **1996**, 1983.

[7] Roesky, H. W.; Herzog, A.; Keller, K. *Z. Naturforsch.* **1994**, *49B*, 981.

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Table 1. Yields, Mp, ^{19}F and ^{29}Si NMR, and Elemental Analyses of 1a–e and 2a–f

			NMR (C_6D_6)		anal. found (calcd) (%)			
complex (no.)	yield %	mp °C	^{29}Si	^{19}F	C	H	N	F
(2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)$AlMe_2$ (**1a**)	92	61	3.71		67.0 (66.8)	10.7 (10.6)	4.6 (4.6)	
(2,6-*i*-$Pr_2C_6H_3$)N{Si(*i*-Pr) Me_2}$AlMe_2$ (**1b**)	88	95–100[a]	7.25		68.1 (68.4)	10.6 (10.88)	4.1 (4.20)	
(2,6-*i*-$Pr_2C_6H_3$)N{Si(*t*-Bu)Me_2}$AlMe_2$ (**1c**)	83	108–114[a]	8.39		68.6 (69.11)	10.7 (11.02)	5.0 (4.03)	
(2,6-$Me_2C_6H_3$)N{Si(*t*-Bu)Me_2}$AlMe_2$ (**1d**)	86	30	6.95		64.2 (65.93)	9.9 (10.37)	4.7 (4.81)	
(2,6-$Me_2C_6H_3$)N{Si(2,4,6-$Me_3C_6H_2$)Me_2}$AlMe_2$ (**1e**)	81	49	−7.08		69.5 (71.34)	9.1 (9.12)	4.0 (3.96)	
(2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)AlF_2 (**2a**)	84	137	6.37	−172.5[b]	57.4 (57.48)	8.1 (8.36)	4.4 (4.47)	11.8 (12.12)
(2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)AlF_2·THF (**2b**)	86	69	5.61	−178.1	59.0 (59.19)	8.9 (8.89)	3.5 (3.63)	9.6 (9.86)
(2,6-*i*-$Pr_2C_6H_3$)N{Si(*i*-Pr)Me_2}AlF_2·THF (**2c**)	97	92	6.52	−177.0	60.0 (60.98)	9.3 (9.26)	3.9 (3.39)	8.8 (9.19)
(2,6-*i*-$Pr_2C_6H_3$)N{Si(*t*-Bu)Me_2}AlF_2·THF (**2d**)	92	127	8.26	−175.1	60.9 (61.79)	9.3 (9.43)	3.4 (3.28)	9.0 (8.89)
(2,6-$Me_2C_6H_3$)N{Si(*t*-Bu)Me_2}AlF_2·THF (**2e**)	84	48	7.44	−175.0	56.9 (58.19)	8.4 (8.68)	3.8 (3.77)	9.9 (10.23)
(2,6-$Me_2C_6H_3$)N{Si(2,4,6-$Me_3C_6H_2$)Me_2}AlF_2·THF (**2f**)	86	96	−7.74	−175.9	62.3 (63.71)	7.7 (7.90)	3.1 (3.23)	8.5 (8.76)

[a] Boiling point at 0.1 Torr. [b] For low-temperature study, see Figure 1 and text.

methylalanes with trimethyltin fluoride. We intended to break an Al–C bond and form an Al–F bond, with the concomitant generation of volatile tetramethyltin. Aminodimethylalanes $RHNAlMe_2$ have been prepared via reaction of the primary amine RNH_2 with trimethylaluminum in refluxing toluene.[8] Using a similar procedure and *n*-hexane as the solvent, we have prepared the series of aminodimethylalanes **1a–e** in high yields (eq 2). Reaction of aminodimethylalane (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)$AlMe_2$ (**1a**) with 2 equiv of trimethyltin fluoride proceeds smoothly in toluene to give the aminoalane difluoride (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)AlF_2 (**2a**, eq 3). Interestingly, aminodimethylalanes **1a–e**, when treated with trimethyltin fluoride in THF yielded the monomeric aminoalane difluoride–THF adducts **2b–f** (eq 4).

$$R^1R^2NH + AlMe_3 \xrightarrow{n\text{-hexane}} \underset{\mathbf{1a-e}}{R^1R^2NAlMe_2} + MeH \qquad (2)$$

a: $R^1 = 2,6\text{-}i\text{-}Pr_2C_6H_3$, $R^2 = SiMe_3$

b: $R^1 = 2,6\text{-}i\text{-}Pr_2C_6H_3$, $R^2 = Si(i\text{-}Pr)Me_2$

c: $R^1 = 2,6\text{-}i\text{-}Pr_2C_6H_3$, $R^2 = Si(t\text{-}Bu)Me_2$

d: $R^1 = 2,6\text{-}Me_2C_6H_3$, $R^2 = Si(t\text{-}Bu)Me_2$

e: $R^1 = 2,6\text{-}Me_2C_6H_3$, $R^2 = Si(2,4,6\text{-}Me_3C_6H_2)Me_2$

$$3R^1R^2NAlMe_2 + 6Me_3SnF \xrightarrow{\text{toluene}} \underset{\mathbf{2a}}{(R^1R^2NAlF_2)_3} + 6SnMe_4 \qquad (3)$$

$$R^1 = 2,6\text{-}i\text{-}Pr_2C_6H_3,\ R^2 = SiMe_3$$

$$R^1R^2NAlMe_2 + 2Me_3SnF \xrightarrow{\text{THF}} \underset{\mathbf{2b-f}}{R^1R^2NAlF_2{\cdot}THF} + 2SnMe_4 \qquad (4)$$

b: $R^1 = 2,6\text{-}i\text{-}Pr_2C_6H_3$, $R^2 = SiMe_3$

c: $R^1 = 2,6\text{-}i\text{-}Pr_2C_6H_3$, $R^2 = Si(i\text{-}Pr)Me_2$

d: $R^1 = 2,6\text{-}i\text{-}Pr_2C_6H_3$, $R^2 = Si(t\text{-}Bu)Me_2$

e: $R^1 = 2,6\text{-}Me_2C_6H_3$, $R^2 = Si(t\text{-}Bu)Me_2$

f: $R^1 = 2,6\text{-}Me_2C_6H_3$, $R^2 = Si(2,4,6\text{-}Me_3C_6H_2)Me_2$

The choice of solvent, thus, enables us to selectively prepare monomeric or higher associated aminoalane difluorides. Compounds **2a–f** are white solids formed in high yield.

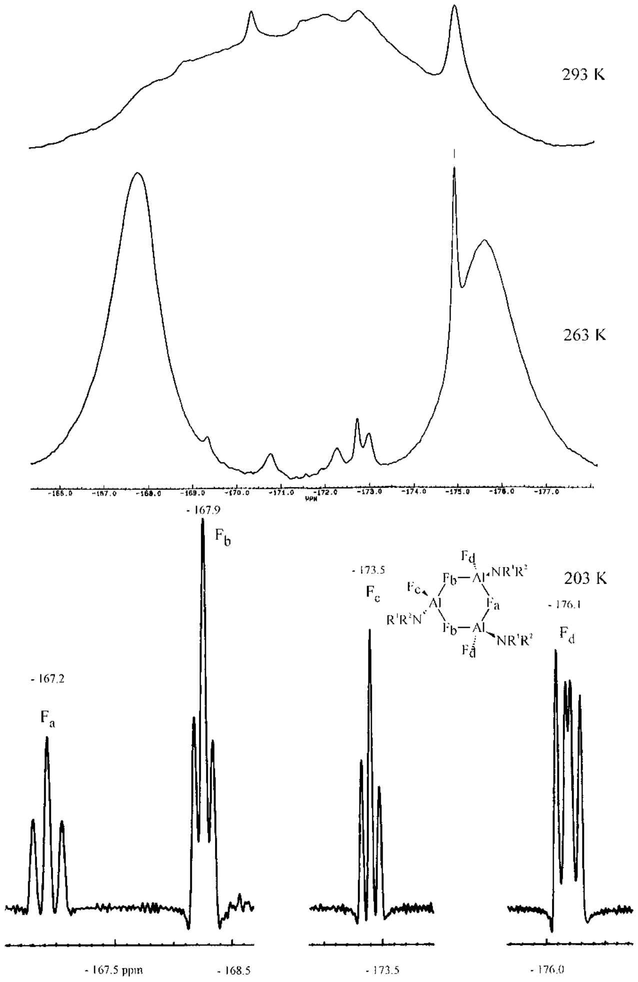

Figure 1. ^{19}F NMR spectrum of (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)-AlF_2 (**2a**) recorded at 293, 263, and 203 K.

Yields, melting points, ^{19}F and ^{29}Si NMR shifts, and chemical analyses for **1a–e** and **2a–f** are given in Table 1. The ^{19}F NMR spectra of (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)AlF_2 (**2a**) recorded at various temperatures (293, 263, and 203 K) in deuterated toluene are shown in Figure 1. At room temperature, rapid interchange of the bridging and terminal fluorines of **2a** leads to coalesence of the signals and a very broad ^{19}F NMR signal is observed. As the temperature is gradually lowered (203 K), resolution of the broad peak into four multiplets is achieved. The four multiplets (−167.1, −167.9, −173.7, and −176.2 ppm) integrate in a 1:2:1:2 ratio, respectively, corresponding to two different types of bridging and terminal fluorine environments (Figure 1). On the

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[8] Power, P. P.; Waggoner, K. M.; Hope, H. *Angew. Chem.* **1988**, *100*, 1765; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699.

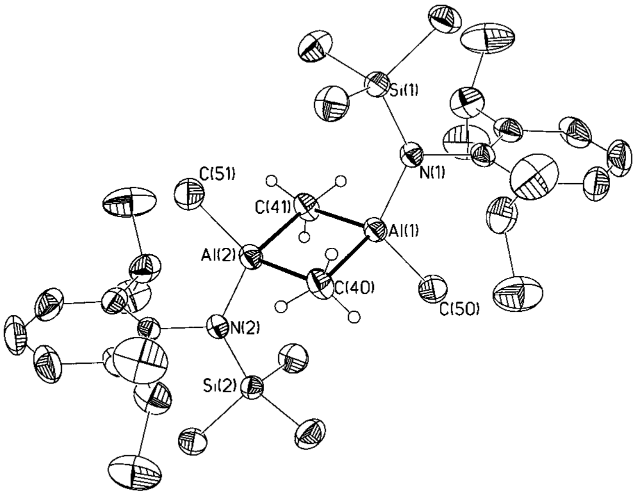

Figure 2. X-ray structure of (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)-$AlMe_2$ (**1a**), with atomic numbering scheme. Hydrogen atoms, except those on the bridging methyl group, have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)$AlMe_2$ (1a) and (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)AlF_2 (2a)

bond lengths		bond angles	
		Compound **1a**	
Al(1)–N(1)	1.823(2)	N(1)–Al(1)–C(50)	116.55(12)
Al(1)–C(50)	1.941(3)	C(41)–Al(1)–C(40)	103.07(12)
Al(1)–C(40)	2.127(3)	Al(1)–C(41)–Al(2)	77.00(10)
Al(1)–C(41)	2.120(3)	N(2)–Al(2)–C(51)	117.00(12)
Al(2)–N(2)	1.818(2)	N(1)–Al(1)–C(50)	116.55(12)
Al(2)–C(51)	1.947(3)	Al(1)–C(40)–Al(2)	77.04(10)
Al(2)–C(40)	2.122(3)		
Al(2)–C(41)	2.131(3)		
		Compound **2a**	
Al(1)–F(1)	1.788(2)	F(2)–Al(1)–F(1)	91.93(11)
Al(1)–F(2)	1.787(2)	F(2A)–Al(2)–F(2)	93.25(14)
Al(1)–F(10)	1.642(2)	Al(2)–F(2)–Al(1)	144.61(13)
Al(2)–F(2)	1.770(2)	Al(1)–F(1)–Al(1A)	134.3(2)
Al(2)–F(20)	1.634(3)		
Al(1)–N(1)	1.771(3)		
Al(2)–N(2)	1.767(3)		

basis of a comparison of the ^{19}F chemical shifts for monomeric **2b**–**f**, which have only terminal fluorines, we assign the triplet (−173.7 ppm) and the doublet of doublets (−176.2 ppm) to terminal fluorines F_C and F_D, respectively.

X-ray Crystallographic. The structure of **1a** with the atom labeling scheme is shown in Figure 2. Selected bond lengths and angles are collected in Table 2. The structure of **1a** consists of a methyl-bridged dimer with a four-membered planar ring (mean deviation 0.008 Å). The Al–C bond lengths in the ring do not differ significantly (2.120(3)–2.131(3) Å) and are comparable with the bond lengths in dimeric trimethylaluminum (2.125(2) Å).[9] In **1a**, the Al–C–Al angle is 77.00(1)°, which is somewhat greater than the corresponding angle in dimeric trimethylaluminum (75.7(1)°). This may be caused by a higher electronic repulsion between the positively charged aluminum centers, due to the higher electron withdrawing properties of the amino groups. The Al–Al distance in **1a** (2.646(1) Å) is only slightly larger than the sum of the covalent radii (2.5 Å), and the C(50)–Al–N(1) angle is 116.55(1)°. In trimethylaluminum the corresponding values are 2.606(2) Å and 123.2(1)°, respectively. The C(50), Al(1), N(1), and Si(1) atoms are coplanar, and the plane through these atoms is orthogonal to both the plane formed by the four-membered Al_2C_2 and the aromatic ring. The aromatic and the four-membered rings form an angle of 13.8(1)°. To our knowledge, this is the first aminoalane that forms methyl bridges instead of dimerizing via nitrogen bridges to remedy the electron deficiency at the metal centers. The related (*N*-(trimethylsilyl)-anilino)dimethylaluminum PhN($SiMe_3$)$AlMe_2$ forms a nitrogen-bridged dimer.[10] The structure of aminoalane difluoride **2a** with the atom labeling scheme is shown in Figure 3, with selected bond distances and angles listed in Table 2. X-ray diffraction analysis of **2a** shows it to be trimeric with a six-membered alternating aluminum–fluorine ring and three terminal fluorine atoms. Two of the terminal fluorine atoms are located above and one below this ring. Consequently, the (*i*-$Pr_2C_6H_3$)N($SiMe_3$) groups occupy the opposite positions. The Al atoms and fluorine atoms F(2) and F(2A) form an almost perfect plane (mean deviation, 0.036 Å),[11] with F(1) located 0.598 Å above this plane. The bridging Al–F bonds in **2a** range from 1.770 to 1.788 Å and are comparable with those found by electron diffraction for $\{Me_2AlF\}_4$ (1.808 Å)[12] or by X-ray diffraction for $\{(Cp^*AlF)_2SiPh_2\}_2$[13] (average Al–F bond length, 1.846 Å). The related $\{(Me_3C)_2SiFNCMe_3\}_2AlCl$ compound[14] is described as an $AlClF_2$ adduct and has, nevertheless, very different structural parameters that are derived from a situation in which, in our opinion, the aluminum center establishes three strong covalent bonds to chlorine and both nitrogen atoms (Al–N, 1.853(4) Å), with two additional weaker donor–acceptor F → Al interactions (Al–F, 2.085(2) Å). The number of compounds

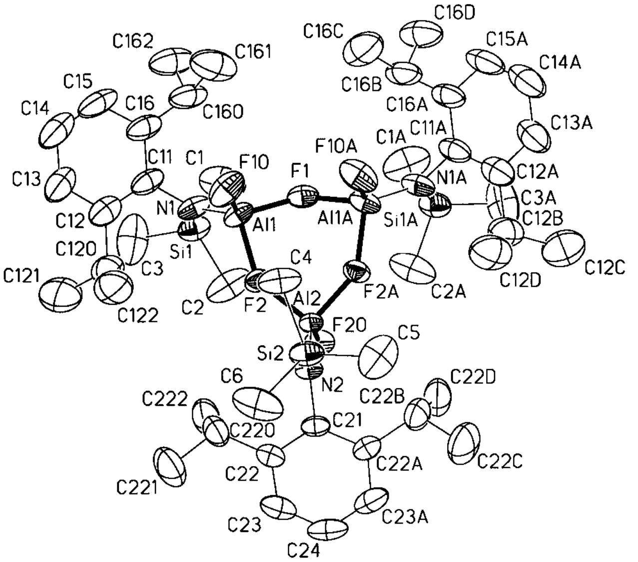

Figure 3. X-ray structure of (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)AlF_2 (**2a**), with atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

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[9] Huffman, J. C.; Streib, W. E . *Chem. Commun.* **1971**, 911.

[10] Roesky, H. W.; Waezsada, S. D.; Parisini, E. Unpublished results.

[11] *SHELXTL-PLUS Software Package for the Determination of Crystal Structure*, Release 5. 03; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994.

[12] Gundersen, G.; Haugen, T.; Haaland, A. *J. Chem. Soc., Chem. Commun.* **1972**, 708.

[13] Schulz, S.; Schoop, T.; Roesky, H. W.; Häming, L.; Steiner, A.; Herbst-Irmer, R. *Angew. Chem.* **1995**, *107*, 1015; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 919.

[14] Clegg, W.; Klingebiel, U.; Niemann, J.; Sheldrick, G. M. *J. Organomet. Chem.* **1983**, *249*, 47.

having terminal Al−F bonds is limited.[15] In **2a**, the terminal Al−F bonds range from 1.634 to 1.642 Å and are comparable to those in AlF_3 (1.63 Å), as determined by electron diffraction.[16] The Al−N distance, 1.77 Å (average), for **2a** is rather short when compared to the aluminum−nitrogen bonds in compounds having four-coordinate Al centers.[17] However, it is in good agreement with the values for compounds containing three-coordinate Al and N centers ($C_{52}H_{96}Al_4N_4Si_4$,[18] 1.781−1.819 Å; $\{CpAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)\}_2$,[19] 1.796−1.811 Å; $\{MeAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)\}_3$,[20] 1.78 Å).

Conclusion and Remarks

On incorporating bulky substituents (R^1, R^2) at the nitrogen in the compounds $R^1R^2NAlMe_2$, we have been able to prepare and structurally characterize the first examples of methyl-bridged aminodimethylalanes. Starting from these aminodimethylalanes, we have succeeded in synthesizing a novel series of aminoalane difluorides using the versatile trimethyltin fluoride reagent. Depending on our choice of reaction solvent, we were able to isolate, selectively, trimeric or monomeric solvated aminoalane difluorides. The trimeric structure is also observed in the gas phase using electron-ionization. To our surprise, under the reported conditions, we have not observed any equilibrium of the type (eq 5) that is normally very common in the case of aluminum-substituted halides. This demonstrates one of the

$$2R^1R^2NAlF_2 \rightleftharpoons (R^1R^2N)_2AlF + AlF_3 \qquad (5)$$

unique properties of this class of compounds. We are currently investigating the preparation of other organoaluminum, -gallium, and -indium fluorides.

Experimental Section

All experiments and manipulations were performed under a nitrogen atmosphere and strictly anhydrous reaction conditions using conventional Schlenk techniques or a drybox. Reagent grade solvents were purified and dried according to standard methods and then distilled under nitrogen prior to use. C_6D_6 and $C_6D_5CD_3$ were trap-to-trap distilled from CaH_2. *Caution*: Aluminum alkyls are extremely air and moisture sensitive and must be handled with the utmost care. This sensitivity and the resulting difficulty in handling these compounds probably is responsible for poor analytical results.

Nuclear magnetic resonance spectra were recorded on a Bruker AM 250 or AS 400 spectrometer. The ^1H , ^{29}Si, and ^{19}F NMR chemical shifts are quoted in parts per million (ppm) downfield from external standards, TMS and $CFCl_3$, respectively. Electron-ionization mass spectra (data reported as *m/z*) were obtained on Finnigan MAT 8230 and Varian MAT CH5 spectrometers. Melting points were determined on a HWS SG 3000 melting point apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratory (Göttingen, Germany) or in our institute.

Synthesis of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)AlMe_2$ (1a). A solution of $AlMe_3$ (50 mmol, 2 M in *n*-hexane) was added dropwise to an ice-cooled solution of $(2,6\text{-}i\text{-}Pr_2C_6H_3)(SiMe_3)NH$ (12.50 g, 50 mmol) in *n*-hexane (60 mL) with vigorous stirring. The ice bath was removed, and the reaction mixture was stirred for 1 h at room temperature and then, finally, refluxed for 1 h to drive the reaction to completion. The solvent was removed *in vacuo*, yielding the white crystalline product **1a**. Yield: 14.05 g (92%). Mp: 61 °C. ^1H NMR (C_6D_6): δ −0.55 (s, 6H, $AlMe_2$), 0.15 (s, 9H, $SiMe_3$), 1.10 (d, $J = 6.9$ Hz, 6H, *i*-Pr), 1.23 (d, $J = 6.9$ Hz, 6H, *i*-Pr), 3.50 (sept, $J = 6.9$ Hz, 2H, CH), 7.05−7.00 (m, 3H, aromatic). ^{29}Si NMR (C_6D_6): δ 3.71. MS (EI, 70 eV): *m/z* 305 (M^+, 20), 290 ($[M - Me]^+$, 100), 249 ($[M - AlMe_2]^+$, 28). Anal. Calcd for $C_{17}H_{32}AlNSi$: C, 66.83; H, 10.56; N, 4.58. Found: C, 67.0; H, 10.7; N, 4.6.

$(2,6\text{-}i\text{-}Pr_2C_6H_3)N\{Si(i\text{-}Pr)Me_2\}AlMe_2$ (1b). $AlMe_3$ (30 mmol, 2.0 M in *n*-hexane) was added dropwise to a stirred solution of $2,6\text{-}i\text{-}Pr_2C_6H_3\{Si(i\text{-}Pr)Me_2\}NH$ (8.33 g, 30 mmol) in *n*-hexane (60 mL) at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then refluxed for 1 h. Removal of the *n*-hexane solvent under reduced pressure, followed by vacuum distillation of the residual liquid, yielded the colorless product **1b**. Yield: 8.73 g (87%). Bp: 95−100 °C, 0.1 Torr. ^1H NMR (C_6D_6): δ −0.52 (s, 6H, $AlMe_2$), 0.06 (s, 6H, $SiMe_2$), 1.01 (s, 7H, *i*-Pr), 1.09 (d, $J = 6.9$ Hz, 6H, *i*-Pr), 1.23 (d, $J = 6.9$ Hz, 6H, *i*-Pr), 3.52 (sept, $J = 6.9$ Hz, 2H, CH), 7.04 (s, 3H, aromatic). ^{29}Si NMR (C_6D_6): δ 7.25. MS (EI, 70 eV): *m/z* 333 (M^+, 4), 318 ($[M - Me]^+$, 8). Anal. Calcd for $C_{19}H_{36}AlNSi$: C, 68.41; H, 10.88; N, 4.20. Found: C, 68.1; H, 10.6; N, 4.1.

$(2,6\text{-}i\text{-}Pr_2C_6H_3)N\{Si(t\text{-}Bu)Me_2\}AlMe_2$ (1c). **1c** was prepared by the procedure described for **1b**. $AlMe_3$ (28 mmol, 2.0 M in *n*-hexane) was added to a solution of $2,6\text{-}i\text{-}Pr_2C_6H_3\{Si(t\text{-}Bu)Me_2\}NH$ (8.16 g, 28 mmol) in *n*-hexane (50 mL) at 0 °C. Removal of the solvent under reduced pressure, followed by vacuum distillation of the residue, yielded the colorless liquid product **1c**. Yield: 8.10 g (83%). Bp: 108−114 °C, 0.1 Torr. ^1H NMR (C_6D_6): δ −0.49 (s, 6H, $AlMe_2$), 0.07 (s, 6H, Me_2Si), 1.03 (s, 9H, *t*-Bu), 1.09 (d, $J = 6.9$ Hz, 6H, *i*-Pr), 1.23 (d, $J = 6.9$ Hz, 6H, *i*-Pr), 3.61 (sept, $J = 6.9$ Hz, 2H, CH), 7.03 (s, 3H, aromatic). ^{29}Si NMR (C_6D_6): δ 8.39. MS (EI, 70 eV): *m/z* 347 (M^+, 21), 332 ($[M - Me]^+$, 100). Anal. Calcd for $C_{20}H_{38}AlNSi$: C, 69.11; H, 11.02; N, 4.03. Found: C, 68.6; H, 10.7; N, 5.0.

$(2,6\text{-}Me_2C_6H_3)N\{Si(t\text{-}Bu)Me_2\}AlMe_2$ (1d). **1d** was prepared by the procedure described for **1a**. $AlMe_3$ (60 mmol, 2.0 M in *n*-hexane) was added to a solution of $2,6\text{-}i\text{-}Pr_2C_6H_3\{Si(t\text{-}Bu)Me_2\}NH$ (14.13 g, 60 mmol) in *n*-hexane (80 mL) at 0 °C. Removal of the solvent *in vacuo* afforded the white crystalline compound **1d**. Yield: 15.0 g (86%). Mp: 30 °C. ^1H NMR (C_6D_6): δ −0.63 (s, 6H, $AlMe_2$), 0.15 (s, 6H, Me_2Si), 0.87 (s, 9H, *t*-Bu), 2.16 (s, 6H, *o*-Me), 6.81−7.01 (m, 3H, aromatic). ^{29}Si NMR (C_6D_6): δ 6.95. MS (EI, 70 eV): *m/z* 291 (M^+, 1), 276 ($[M - Me]^+$, 1), 234 ($[M - AlMe_2]^+$, 100). Anal. Calcd for $C_{16}H_{30}AlNSi$: C, 65.93; H, 10.37; N, 4.81. Found: C, 64.2; H, 9.9; N, 4.7.

$(2,6\text{-}Me_2C_6H_3)N\{Si(2,4,6\text{-}Me_3C_6H_2)Me_2\}AlMe_2$ (1e). **1e** was prepared by the procedure described for **1a**. $AlMe_3$ (25 mL, 2.0 M in *n*-hexane) was added to a solution of $(2,6\text{-}i\text{-}Pr_2C_6H_3\{Si(2,4,6\text{-}Me_3C_6H_2)Me_2\}NH$ (14.88 g, 50 mmol) in *n*-hexane (80 mL). Removal of the solvent yielded the white crystalline product **1e**. Yield: 14.25 g (81%). Mp: 49 °C. ^1H NMR (C_6D_6): δ −0.69 (s, 6H, $AlMe_2$), 0.45 (s, 6H, Me_2Si), 2.03 (s, 3H, *p*-Me), 2.31 (s, 6H, *o*-Me), 2.47 (s, 6H, *o*-Me), 6.70−7.08 (m, 5H, aromatic). ^{29}Si NMR (C_6D_6): δ −7.08. MS (EI, 70 eV): *m/z* 338 ($[M - Me]^+$, 100), 297 ($[M - AlMe_2]^+$, 16). Anal. Calcd for $C_{21}H_{32}AlNSi$: C, 71.34; H, 9.12; N, 3.96. Found: C, 69.5; H, 9.1; N, 4.0.

$(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)AlF_2$ (2a). A suspension of **1a** (0.92 g, 3.0 mmol) and Me_3SnF (1.10 g, 6.0 mmol) in toluene (60 mL) was stirred at room temperature for 12 h, until all of the reactants had dissolved. The solvent and volatile $SnMe_4$ were removed *in vacuo*. Recrystallization of the residue from

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(15) Bukovec, P. *Monatsh. Chem.* **1983**, *114*, 277. Herron, N.; Thorn, D. L.; Harlow, R. L.; Davidson, F. *J. Am. Chem. Soc.* **1993**, *115*, 3028.

(16) Shanmugasunderan, G.; Nagarajan, G. *Z. Phys. Chem.* **1969**, *240*, 363.

(17) Schulz, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Organomet. Chem.* **1995**, *493*, 69.

(18) Schulz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. M. *Angew. Chem.* **1994**, *106*, 1052; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 969.

(19) Fisher, J. D.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 271.

(20) Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem.* **1988**, *100*, 1765; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699.

n-hexane gave analytically pure **2a**. Yield: 0.79 g (2.5 mmol, 84%). Decomposition onset: 137 °C. ^{1}H NMR (C_6D_6): δ 0.15 (s, 9H, $SiMe_3$), 1.22 (d, $J = 6.7$ Hz, 6H, *i*-Pr), 1.25 (d, $J = 6.7$ Hz, 6H, *i*-Pr), 3.64 (sept, $J = 6.9$ Hz, 2H, CH), 7.04 (s, 3H, aromatic). ^{19}F NMR (C_6D_6, 293 K): δ −172.5. ^{19}F NMR (C_6D_5-CD_3, 203 K): δ −167.2 (t, $J = 22.6$ Hz, 1F), −167.9 (t, $J = 14.5$ Hz, 2F), −173.5 (t, $J = 14.5$ Hz, 1F), −176.1 (dd, $J = 22.6$ Hz, 2F). ^{29}Si NMR (C_6D_6): δ 6.37. MS (EI, 70 eV): *m/z* 939 ($[M_3]^+$, 5%), 626 ($[M_2]^+$, 10%), 313 ($[M]^+$, 5%). Anal. Calcd for $C_{15}H_{26}AlF_2NSi$: C, 57.48; H, 8.36; N, 4.47; F, 12.12. Found: C, 57.4; H, 8.1; N, 4.4; F, 11.8.

(2,6-*i*-Pr$_2$C$_6$H$_3$)N(SiMe$_3$)AlF$_2$·THF (2b). Compound **2a** (0.94 g, 3.0 mmol) was stirred in THF (20 mL) at room temperature for 0.5 h. Removal of the THF *in vacuo*, followed by recrystallization of the residue from *n*-hexane, yielded the colorless crystalline product **2**·THF, **2b**. Yield: 0.99 g (86%). Mp: 69 °C. ^{1}H NMR (C_6D_6): δ 0.32 (s, 9H, $SiMe_3$), 0.89 (m, 4H, THF), 1.28 (d, $J = 6.9$ Hz, 6H, *i*-Pr), 1.32 (d, $J = 6.9$ Hz, 6H, *i*-Pr), 3.58 (m, 4H, THF), 3.88 (sept, $J = 6.9$ Hz, 2H, CH), 7.11 (s, 3H, aromatic). ^{19}F NMR (C_6D_6): δ −178.1. ^{29}Si NMR (C_6D_6): δ 5.61. Anal. Calcd for $C_{19}H_{34}AlF_2NOSi$: C, 59.19; H, 8.89; N, 3.63; F, 9.86. Found: C, 59.0; H, 8.9; N, 3.5; F, 9.6.

(2,6-*i*-Pr$_2$C$_6$H$_3$)N{Si(*i*-Pr)Me$_2$}AlF$_2$·THF (2c). A solution of **1b** (1.67 g, 5.0 mmol) in THF (30 mL) was added to a suspension of Me_3SnF (1.83 g, 10.0 mmol) in THF (40 mL). The mixture was then stirred for 6 h at room temperature, until all of the solids had dissolved. The solvent was removed *in vacuo*, and the residue was recrystallized from *n*-hexane, affording colorless crystals of **2c**. Yield: 2.01 g (97%). Mp: 92 °C. ^{1}H NMR (C_6D_6): δ 0.24 (s, 6H, $SiMe_2$), 0.88 (m, 4H, THF), 1.21−1.35 (m, 18H, *i*-Pr), 3.52 (m, 4H, THF), 3.95 (sept, $J = 6.9$ Hz, 2H, CH), 7.02−7.13 (m, 3H, aromatic). ^{19}F NMR (C_6D_6): δ −177.0. ^{29}Si NMR (C_6D_6): δ 6.52. Anal. Calcd for $C_{21}H_{38}AlF_2NOSi$: C, 60.98; H, 9.26; N, 3.39; F, 9.19. Found: C, 60.0; H, 9.3; N, 3.9; F, 8.8.

(2,6-*i*-Pr$_2$C$_6$H$_3$)N{Si(*t*-Bu)Me$_2$}AlF$_2$·THF (2d). Compounds **2d**−**f** were prepared according to the procedure described for **2c**. **1c** (1.74 g, 5.0 mmol) in THF (30 mL) was added to a suspension of Me_3SnF (1.83 g, 10.0 mmol) in THF (40 mL). Workup of the reaction mixture gave the colorless crystalline product **2d**. Yield: 1.96 g (4.6 mmol, 92%). Mp: 127 °C. ^{1}H NMR (C_6D_6): δ 0.22 (s, 6H, Me_2Si), 0.84 (m, 4H, THF), 1.23 (d, $J = 6.8$ Hz, 6H, *i*-Pr), 1.30 (s, 9H, *t*-Bu), 1.31 (d, $J = 6.8$ Hz, 6H, *i*-Pr), 3.39 (m, 4H, THF), 4.05 (sept, $J = 6.8$, 2H, CH), 7.05 (m, 3H, aromatic). ^{19}F NMR (C_6D_6): δ −175.1. ^{29}Si NMR (C_6D_6): δ 8.26. Anal. Calcd for $C_{22}H_{40}AlF_2NOSi$: C, 61.79; H, 9.43; N, 3.28; F, 8.89. Found: C, 60.9; H, 9.3; N, 3.4; F, 9.0.

(2,6-Me$_2$C$_6$H$_3$)N{Si(*t*-Bu)Me$_2$}AlF$_2$·THF (2e). A suspension of Me_3SnF (1.83 g, 10.0 mmol) in THF (40 mL) was added to a solution of **1d** (1.46 g, 5.0 mmol) in THF (30 mL). The mixture was stirred for 6 h at room temperature. The crude product was recrystallized from *n*-hexane to give colorless crystals of **2e**. Yield: 1.56 g (84%). Mp: 48 °C. ^{1}H NMR (C_6D_6): δ 0.33 (s, 6H, Me_2Si), 0.91 (m, 4H, THF), 1.19 (s, 9H, *t*-Bu), 2.46 (s, 6H, *o*-Me), 3.31 (m, 4H, THF), 6.81−7.00 (m, 3H, aromatic). ^{19}F NMR (C_6D_6): δ −175.0. ^{29}Si NMR (C_6D_6): δ 7.44. Anal. Calcd for $C_{18}H_{32}AlF_2NOSi$: C, 58.19; H, 8.68; N, 3.77; F, 10.23. Found: C, 56.9; H, 8.4; N, 3.8; F, 9.9.

(2,6-Me$_2$C$_6$H$_3$)N{Si(2,4,6-Me$_3$C$_6$H$_2$)Me$_2$}AlF$_2$·THF (2f). A solution of **1e** (1.77 g, 5.0 mmol) in THF (30 mL) was added to a suspension of Me_3SnF (1.83 g, 10.0 mmol) in THF (40 mL). Yield: 1.87 g (86%) of colorless crystals. Mp: 96 °C. ^{1}H NMR (C_6D_6): δ 0.65 (s, 6H, Me_2Si), 0.78 (m, 4H, THF), 2.10 (s, 3H, *p*-CH_3), 2.30 (s, 6H, *o*-Me), 2.47 (s, 6H, *o*-Me), 3.33 (m, 4H, THF), 6.73−6.93 (m, 5H, aromatic). ^{19}F NMR (C_6D_6): δ −175.9. ^{29}Si NMR (C_6D_6): δ −7.74. Anal. Calcd for $C_{23}H_{34}AlF_2NOSi$: C, 63.71; H, 7.90; N, 3.23; F, 8.76. Found: C, 62.3; H, 7.7; N, 3.1; F, 8.5.

Table 3. Crystal Data and Structure Refinement Details for 1a and 2a

	1a	**2a**
formula	$C_{34}H_{64}Al_2N_2Si_2$	$C_{45}H_{78}Al_3F_6N_3Si_3$
fw	611.03	940.31
cryst dimens, mm	0.5 × 0.5 × 0.5	0.75 × 0.40 × 0.40
cryst syst	monoclinic	orthorhombic
space group (No.)	$P2_1/n$ (No. 14)	*Pnma* (No. 62)
a, Å	13.608(3)	26.810(2)
b, Å	18.688(4)	24.964(2)
c, Å	15.356(3)	8.271(1)
β, deg	99.37(3)	
V, Å^3	3853(1)	5535.4(9)
Z	4	4
D_{calcd}, g cm^{-3}	1.053	1.128
μ, mm^{-1}	0.161	0.184
F(000)	1344	2016
T, (K)	187(2)	153(2)
no. of refns measd	7429	12805
no. of indep. reflns	5679	3676
2θ range, deg	5−47	7−45
R_{int}	0.0408	0.0529
no. of data/no. of params	5671/415	3676/364
no. of restraints	40	276
R1 ($I > 2\sigma(I)$)	0.0505	0.0485
wR2 (all data)	0.1333	0.1361
g_1	0.0521	0.0636
g_2	3.6520	4.4778
largest diff peak	0.326	0.246
largest diff hole (e·A^{-3})	−0.272	−0.280

X-ray Structure Determinations for 1a and 2a. Data for **1a** were collected at −80 °C on a Stoe-Siemens-AED diffractometer with monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Data for **2a** were collected at −120 °C on a Stoe-Siemens-AED2 diffractometer with monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The structures of **1a** and **2a** were solved by direct methods using SHELXS-90/96.[21] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the bridging methyl groups in **1a** were refined freely, with restraints for the 1,2- and 1,3-distances and are disordered over two sets of positions that are rotated around 60° with an occupancy of 0.5. For all of the other hydrogen atoms, the riding model was used. The structures were refined against F^2, with a weighting scheme of $w^{-1} = \sigma^2 (F_o^2) + (g_1P)^2 + g_2P$, with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-93/SHELXL-96.[22] The R values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{0.5}$. Figures 2 and 3 (hydrogen atoms omitted) show 50% probability displacement ellipsoids. Crystal data and structure refinement details are listed in Table 3. The two $SiMe_3$ sites in **2a** are severely disordered; the one corresponding to Si(2) to such an extent that it was regarded as not fulfilling the mirror plane. Both sites were modeled with the help of ADP- and distance restraints.

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Supporting Information Available: Details of the X-ray crystal structure analysis of **1a** and **2a** with listings of bond lengths and angles, positional parameters, and thermal parameters, labeled ORTEP diagrams, and NMR spectra of those compounds whose elemental analysis was outside the acceptable range (32 pages). Ordering information is given on any current masthead page.

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(21) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(22) Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Göttingen, 1993. Sheldrick, G. M. *SHELXL-96*; University of Göttingen, Göttingen, 1996.