Synthesis and Characterization of Tris(trimethylsilyl)methyl Halide Derivatives of Aluminum: Potential Precursors for Low-Valent Aluminum Compounds. Crystal Structures of [{$(Me_3Si)_3CAlF_2$}$_3$], [$(Me_3Si)_3CAlX_2\cdot THF$] (X = Cl, Br, I), and [{$(THF)_2K(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3$}$_2$]†

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The novel bulky alkylaluminum dihalogenides [$(Me_3Si)_3CAlX_2\cdot THF$] (X = F, **1**; X = Cl, **4**; X = Br, **5**; X = I, **6**) and dialkylaluminum halogenides [$(Me_3Si)_3CAl(Me)X\cdot THF$] (X = Cl, **8**; X = Br, **9**; X = I, **10**) have been prepared by reaction of the mixed trialkylalane [$(Me_3Si)_3CAlMe_2\cdot THF$] with Me_3SnX (X = F, Cl) and X_2 (X = Br, I) in a 2:1 and 1:1 molar ratio, respectively. The coordinated THF molecule of compound **1** can be removed by heating in vacuo to yield the trimeric solvent-free organoaluminum difluoride [{$(Me_3Si)_3CAlF_2$}$_3$] (**2**). Compound **2** shows no cocatalytic activity with group 4 metallocenes for ethylene polymerization. Reaction of [$(Me_3Si)_3CAlF_2\cdot THF$] (**1**) with potassium fluoride gave the unusual coordination compound [{$(THF)_2K(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3$}$_2$] (**3**). The molecular structures of compounds **2**−**6** have been determined by X-ray structure analysis. Compound **2** is the first structurally characterized organoaluminum difluoride, and **6** is the first structurally characterized organoaluminum diiodide.

Introduction

The importance of group 4 metallocene catalysts (Ziegler-type) is growing rapidly. These compounds could probably be the next generation of Ziegler-type catalysts used in the chemical industry for α-olefin polymerizations. To obtain a catalytically active system, a highly Lewis-acidic cocatalyst is added to the metallocene complex.

On the basis of the theory of Dyachkovskii the role of the cocatalyst is always to generate and stabilize (as a contact ion pair) the catalytically active 14-electron cation $(Cp'_2MR)^+$ (R = H, Me, Benz) or the 10-electron cation $(Cp'MR_2)^+$ (R = Me, Benz) (M = Ti, Zr, Hf; Cp′ = Cp, Cp*, Ind) in olefin polymerization reactions. This assumption was confirmed by many groups[1] and is today widely accepted.

Examples for such cocatalytically active species, which were strongly investigated in the past few years by many groups, are alumoxanes,[2] especially methylalumoxane (MAO), triphenylcarbenium salts of weakly coordinating anions,[3] or $B(C_6F_5)_3$.[4] However, compounds of aluminum with the C_6F_5 ligand have been shown to be explosive[5] and are very difficult to handle. On the other hand, organoaluminum difluorides should have a very high Lewis acidity and could be promising reagents to generate such catalytically active cations with group 4 metallocenes (eq 1). However, knowledge

$$RAlF_2 + Cp_{4-x}MX_x \rightleftharpoons [Cp_{4-x}MX_{x-1}]^+[RAlF_2X]^- \text{ (M = Ti, Zr, Hf; X = F, Cl, Me)} \quad (1)$$

of the synthetic methods leading to organoaluminum difluorides and the properties of these compounds is

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† Dedicated to Prof. Hans Bock on the occasion of his 70th birthday.

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limited to just a few patents,[6] and no spectroscopic data are available for such compounds. We have recently reported on the synthesis of some aminoalane difluorides by the reaction of the corresponding aminodimethylalanes with trimethyltin fluoride.[7] Interest in alkylaluminum difluorides has prompted us to extend the use of this method to the synthesis of this new class of compounds. Due to the high tendency of forming of AlF_3, bulky substituents at the aluminum center are necessary for the kinetic stabilization of such compounds.

The tris(trimethylsilyl)methyl group (trisyl ligand) can be regarded as a very bulky ligand having stabilizing electronic properties.[8] A complex of composition $[Li\{(Me_3Si)_3CAlF_3\}\cdot THF]_4$ was recently synthesized by Eaborn et al.[9] using the reaction of $[Li\{(Me_3Si)_3CAlH_3\}\cdot 2\,THF]$ and HF. However, this complex is inappropriate to serve as a cocatalyst in olefin polymerization reactions due to the coordinated THF molecule.

Presently, there is growing interest in the chemistry of the heavier group 13 halides.[10] Sterically hindered neutral organohalide derivatives of Al, Ga, and In are the key starting materials for a variety of compounds having unusual bonding and oxidation states as well as unique structures.[11] Using the trisyl ligand, it was possible to synthesize the low-valent tetrameric species $[\{MC(SiMe_3)_3\}_4]$ of gallium,[12] indium,[13] and thallium[14] by reaction of the low-valent precursor $Ga_2Br_4\cdot$dioxane, InBr and TlCp with trisyllithium, respectively. However, the corresponding chemistry of aluminum is rather unknown, or in a very few cases, compounds are available only under enormous preparative difficulties.[11a] We have recently reported on a facile synthesis of the aluminum(I) compound $[(Cp^*Al)_4]$ by reduction of $[Cp^*AlCl(\mu\text{-}Cl)]_2$ using potassium in toluene.[15] Herein, we report on the easy syntheses of some trisylaluminum halide derivatives which could serve as potential precursors for synthesizing low-valent trisylaluminum compounds.

Experimental Section

General Considerations. All experiments were performed using standard Schlenk techniques under dry nitrogen atmosphere due to the extreme sensitivity of the reactants and products toward air and moisture. A Braun MB 150-GI drybox was used to store the compounds and to prepare the samples for spectroscopic characterizations. All solvents were dried over sodium/benzophenone, freshly distilled and degassed prior to use. Trimethyltin chloride, bromine, iodine, and potassium fluoride were purchased from Aldrich Chemical Co.; $[(Me_3Si)_3CAlMe_2\cdot THF]$[16] and trimethyltin fluoride[17] were prepared as described in the literature.

Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. It is well-known that the analysis for carbon in group 13 compounds is often low due to the generation of metal carbides.[18] In compounds containing silicon, the deficit is increased further by formation of silicon carbide. NMR spectra were recorded on a Bruker AM 200 and Bruker AM 250 and were externally referenced to tetramethylsilane and $CFCl_3$, respectively. FT-IR spectra were measured on a Bio-Rad FTS-7 as Nujol mulls between KBr plates in the range of 4000−400 cm^{-1} (abbreviations used: vs, very strong; s, strong; m, medium) and EI mass spectra on Finnigan MAT 8230 or Varian MAT CH 5 instruments. Melting points were measured in sealed glass tubes and were not corrected.

Preparation of $[(Me_3Si)_3CAlF_2\cdot THF]$ (1). A solution of trimethyltin fluoride (1.01 g, 5.54 mmol) in THF (20 mL) was slowly added at room temperature to a solution of $[(Me_3Si)_3CAlMe_2\cdot THF]$ (1.00 g, 2.77 mmol) in THF (20 mL). After 15 h of stirring at room temperature, the solvent was removed from the clear slightly yellow solution in vacuo. The residue was washed with pentane (10 mL) to yield compound **1** (0.81 g, 79%) as a colorless solid, mp 152 °C. ^1H NMR (200.13 MHz, C_6D_6): δ 3.79 (m_c, 4 H, OCH_2CH_2), 0.91 (m_c, 4 H, OCH_2CH_2), 0.42 (s, 27 H, $SiCH_3$). ^{19}F NMR (188.32 MHz, C_6D_6): δ −159.17 (s). ^{29}Si NMR (49.63 MHz, C_6D_6): δ −3.1 (s). MS (70 eV): *m/e* 281 (M − THF − Me, 10), 277 (M − THF − F, 9), 201 ($C(SiMe_3)_3$ − 2 Me, 100). IR (Nujol mull): 1292 (m), 1262 (s), 1253 (s), 1075 (m), 1058 (m), 993 (m), 861 (vs), 800 (m), 721 (s), 675 (s), 648 (m), 608 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{35}AlF_2OSi_3$ (368.68): C, 45.61; H, 9.57. Found: C, 44.8; H, 9.5.

Preparation of $[\{(Me_3Si)_3CAlF_2\}_3]$ (2). Compound **1** (3.00 g, 8.14 mmol) was heated for 8 h in vacuo (10^{-2} mbar) to 200 °C. The resulting yellow residue was extracted with *n*-hexane (60 mL) to yield compound **2** (1.67 g, 69%) as a slightly yellow solid, mp > 320 °C. ^1H NMR (200.13 MHz, C_6D_6): δ 0.38 (s, 27 H, $Si(CH_3)_3$). ^{19}F NMR (188.32 MHz, C_6D_6): δ −149.60 (s (br)). ^{19}F NMR (188.32 MHz, toluene-d_8): δ −149.68 (s (br)). ^{29}Si NMR (79.46 MHz, C_6D_6): δ −3.1 (s). MS (70 eV): *m/e* 873 (M − Me, 1), 577 ($[(Me_3Si)_3CAlF_2]_2$ − Me, 52), 281 ($[(Me_3Si)_3CAlF_2]$ − Me, 17), 201 ($C(SiMe_3)_3$ − 2 Me, 100). IR (Nujol mull): 1295 (m), 1255 (vs), 1011 (s), 852 (vs), 840 (vs), 802 (s), 754 (m), 720 (m), 705 (m), 675 (s), 649 (m), 618 (m), 571 (s). Anal. Calcd for $C_{30}H_{81}Al_3F_6Si_9$ (889.71): C, 40.50; H, 9.18. Found: C, 40.6; H, 9.1.

Preparation of $[\{(THF)_2K(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3\}_2]$ (3). To a suspension of potassium fluoride (3.00 g, 51.6 mmol) in THF (20 mL) was slowly added at room temperature a solution of **1** (2.00 g, 5.42 mmol) in THF (40 mL). The suspension was stirred for 18 h at room temperature

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and then refluxed for 2 h. After the solvent was removed in vacuo the residue was washed with *n*-hexane (10 mL) to yield compound **3** (1.53 g, 71%) as a colorless solid, mp > 320 °C. Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from THF at −26 °C. ^{1}H NMR (200.13 MHz, C_6D_6): δ 3.57 (m$_c$, 4 H, OCH_2CH_2), 1.42 (m$_c$, 4 H, OCH_2CH_2), 0.38 (s, 27 H, $Si(CH_3)_3$). ^{19}F NMR (188.32 MHz, C_6D_6): δ −160.43 (s(br)). ^{19}F NMR (188.32 MHz, toluene-d_8): δ −160.18 (s (br)). ^{29}Si NMR (79.46 MHz, C_6D_6): δ −3.3 (s). IR (Nujol mull): 1287 (m), 1257 (vs), 1248 (vs), 1056 (s), 863 (vs), 850 (s), 799 (s), 756 (s), 705 (s), 674 (vs), 624 (s), 614 (s) cm^{-1}. Anal. Calcd for $C_{56}H_{140}Al_4F_{10}K_2O_4Si_{12}$ (1590.91): C, 42.28; H, 8.87. Found: C, 41.5; H, 8.5.

Testing of the Cocatalytic Activity of [{(Me$_3$Si)$_3$CAlF$_2$}$_3$] (2) with Group 4 Metallocenes. Testing of ethylene polymerization was carried out in a 250 mL glass reactor by saturating toluene (100 mL) with ethylene (1 bar) at room temperature. A solution of [{$(Me_3Si)_3CAlF_2$}$_3$] **(2)** (0.50 mmol) and the metallocene (1.50 mmol) (Cp^*TiF_3, $Cp^*{}_2ZrF_2$ ($Cp^* = C_5Me_5$), Cp_2ZrCl_2 and Cp_2ZrMe_2) in toluene (20 mL) was injected, and the mixture was stirred at room temperature while ethylene was vigorously bubbled through the solution. After 30 min, the ethylene supply was turned off and ethanol (10 mL) was added. Under these conditions, no polymer was obtained after workup.

Preparation of [(Me$_3$Si)$_3$CAlCl$_2$·THF] (4). To a solution of [$(Me_3Si)_3CAlMe_2$·THF] (9.03 g, 25.0 mmol) in toluene (100 mL) was slowly added a solution of trimethyltin chloride (9.98 g, 50.1 mmol) in toluene (50 mL) at room temperature. After the reaction mixture was stirred for 15 h at room temperature, all volatiles were removed in vacuo and the yellow residue was washed with pentane (2 × 50 mL) to yield compound **4** (9.16 g, 91%) as a colorless solid, mp 245 °C. ^{1}H NMR (200.13 MHz, C_6D_6): δ 3.93 (m, 4 H, OCH_2CH_2), 0.92 (m, 4 H, OCH_2CH_2), 0.45 (s, 27 H, $Si(CH_3)$). ^{29}Si NMR (79.46 MHz, C_6D_6): δ −3.1 (s). MS (70 eV): *m/e* 387 (M − Me, 2), 315 (M − THF − Me, 20), 201 ($C(SiMe_3)_3$ − 2 Me, 100). IR (Nujol mull): 1264 (s), 1254 (vs), 988 (m), 922 (m), 854 (vs), 835 (m), 795 (s), 722 (m), 670 (s), 481 (s), 454 (s), 389 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{35}AlCl_2OSi_3$ (401.59): C, 41.87; H, 8.79. Found: C, 41.4; H, 8.8.

Preparation of [(Me$_3$Si)$_3$CAlBr$_2$·THF] (5). A solution of bromine (2.6 g, 16.0 mmol) in toluene (30 mL) was slowly added dropwise to a solution of [$(Me_3Si)_3CAlMe_2$·THF] (2.9 g, 8.0 mmol) in toluene (50 mL) at 0 °C. After the solution was stirred for 2 h at room temperature, the methyl bromide was removed in vacuo. Crystallization at −26 °C and filtration gave product **5** (2.5 g, 65%) as colorless crystals, mp 130 °C (dec). ^{1}H NMR (250.13 MHz, C_6D_6): δ 3.99 (m, 4 H, OCH_2CH_2), 0.91 (m, 4 H, OCH_2CH_2), 0.47 (s, 18 H, $Si(CH_3)$), 0.46 (s, 9 H, $Si(CH_3)$). ^{29}Si NMR (49.69 MHz, C_6D_6): δ −3.2 (s). MS (70 eV): *m/e* 403 (M − THF − Me, 4), 201 ($C(SiMe_3)$ − 2 Me, 100). IR (Nujol mull): 1253 (vs), 1151 (s), 1094 (s), 1029 (s), 1009 (s), 986 (s), 920 (s), 851 (vs), 804 (vs), 719 (s), 671 (s), 468 (s), 414 (vs), 400 (vs). Anal. Calcd for $C_{14}H_{35}AlBr_2OSi_3$ (490.48): C, 34.4; H, 7.2. Found: C, 34.4; H, 7.2.

Preparation of [(Me$_3$Si)$_3$CAlI$_2$·THF] (6). Iodine (7.04 g, 27.7 mmol) in toluene (100 mL) was slowly added to a solution of [$(Me_3Si)_3CAlMe_2$·THF] (5.00 g, 13.9 mmol) in toluene (30 mL) at room temperature. The purple reaction mixture was stirred overnight and then refluxed for 2 h. After filtration of the slightly brown solution through Celite, the solvent was removed in vacuo and the brownish residue recrystallized from toluene (60 mL) to yield compound **6** as slightly brown crystals (4.00 g). Reducing the mother liquor (30 mL) and crystallization at −26 °C gave another crop of crystals (3.2 g, overall yield 89%), mp 202 °C. ^{1}H NMR (200.13 MHz, C_6D_6): δ 4.09 (m, 4 H, OCH_2CH_2), 0.95 (m, 4 H, OCH_2CH_2), 0.50 (s, 27 H, $Si(CH_3)$). ^{29}Si NMR (79.46 MHz, C_6D_6): δ −2.9 (s). MS (70 eV): *m/e* 497 (M − THF − Me, 65), 385 (M − THF − I, 80), 201 ($C(SiMe_3)_3$ − 2 Me, 100). IR (Nujol mull): 1350 (m), 1285 (m), 1263 (vs), 1253 (vs), 982 (s), 920 (s), 840 (vs), 815(vs), 789 (vs), 749 (s), 711 (s), 667 (vs), 641 (s), 615 (m), 402 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{35}AlI_2OSi_3$ (584.58): C, 28.76; H, 6.04. Found: C, 29.0; H, 6.0.

Preparation of [{(Me$_3$Si)$_3$CAlMe(μ-F)}$_2$] (7). To a suspension of trimethyltin fluoride (0.51 g, 2.77 mmol) in THF (20 mL) was slowly added at room temperature a solution of [$(Me_3Si)_3CAlMe_2$·THF] (1.00 g, 2.77 mmol) in THF (20 mL). After 15 h of stirring at room temperature, the solvent was removed from the clear slightly yellow solution in vacuo. The residue was washed with pentane (5 mL) to yield 0.71 g of a mixture of [$(Me_3Si)_3CAlMe_2$·THF], [$(Me_3Si)_3CAlF_2$·THF] (**1**), and [{$(Me_3Si)_3CAlMe(\mu$-F)}$_2$] **(7),** which could not be separated by crystallization. ^{1}H NMR (200.13 MHz, C_6D_6): δ 3.79 (m$_c$, OCH_2CH_2 of **1**), 3.53 (m$_c$, OCH_2CH_2 of [$(Me_3Si)_3CAlMe_2$·THF]), 0.98 (m$_c$, OCH_2CH_2 of [$(Me_3Si)_3CAlMe_2$·THF]), 0.91 (m$_c$, OCH_2CH_2 of **1**), 0.42 (s, $SiCH_3$ of **1**), 0.41 (s, $SiCH_3$ of **7**), 0.39 (s, $SiCH_3$ of [$(Me_3Si)_3CAlMe_2$·THF]), −0.37 (s, $AlCH_3$ of [$(Me_3Si)_3CAlMe_2$·THF]), −0.41 and −0.43 (2 s, $AlCH_3$ of **7**). ^{19}F NMR (188.32 MHz, C_6D_6): δ −151.80 (s, **7**), − 159.09 (s, **1**). ^{29}Si NMR (49.69 MHz, C_6D_6): δ −3.2 (s, **1**), −3.97 and 4.01 (2 s, **7**), −4.4 (s, [$(Me_3Si)_3CAlMe_2$·THF]).

Preparation of [(Me$_3$Si)$_3$CAl(Me)Cl·THF] (8). Trimethyltin chloride (0.55 g, 2.77 mmol) in toluene (20 mL) was slowly added to a solution of [$(Me_3Si)_3CAlMe_2$·THF] (1.00 g, 2.77 mmol) in toluene (20 mL) at room temperature. After the reaction mixture was stirred at room temperature for 15 h, the solvent was removed in vacuo. The slightly yellow residue was washed with pentane (7 mL) to yield product **8** (0.83 g, 79%) as a colorless solid, mp 211 °C. ^{1}H NMR (200.13 MHz, C_6D_6): δ 3.88 (m$_c$, 2 H, OCH_2CH_2), 3.59 (m$_c$, 2 H, OCH_2CH_2), 0.98 (m$_c$, 4 H, OCH_2CH_2), 0.42 (s, 27 H, $SiCH_3$), −0.22 (s, 3 H, $AlCH_3$). ^{29}Si NMR (49.69 MHz, C_6D_6): δ −3.9 (s). MS (70 eV): *m/e* 293 (M − THF − Me, 50), 273 (M − THF − Cl, 15), 201 ($C(SiMe_3)_3$ − 2 Me, 100). IR (Nujol mull): 1350 (m), 1285 (m), 1251 (vs), 1191 (m), 1097 (m), 1047 (m), 994 (s), 920 (s), 853 (vs), 788 (vs), 751 (s), 722 (s), 667 (vs), 613 (s), 606 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{38}AlClOSi_3$ (381.17): C, 47.27; H, 10.05. Found: C, 47.0; H, 10.0.

Preparation of [(Me$_3$Si)$_3$CAl(Me)Br·THF] (9). Bromine (0.66 g, 4.16 mmol) in toluene (20 mL) was slowly added at room temperature to a solution of [$(Me_3Si)_3CAlMe_2$·THF] (1.50 g, 4.16 mmol) in toluene (20 mL). After the solution was stirred for 15 h at room temperature, all volatiles were removed in vacuo. The yellow residue was washed with pentane (10 mL) to yield compound **9** (1.34 g, 76%) as a colorless solid, mp 266 °C. ^{1}H NMR (200.13 MHz, C_6D_6): δ 3.92 (m$_c$, 2 H, OCH_2CH_2), 3.58 (m$_c$, 2 H, OCH_2CH_2), 0.97 (m$_c$, 4 H, OCH_2CH_2), 0.43 (s, 27 H, $SiCH_3$), −0.10 (s, 3 H, $AlCH_3$). ^{29}Si NMR (49.69 MHz, C_6D_6): δ −3.8 (s). MS (70 eV): *m/e* 339 (M − THF − Me, 30), 273 (M − THF − Br, 15), 201 ($C(SiMe_3)$ − 2 Me, 100). IR (Nujol mull): 1351 (m), 1284 (m), 1251 (vs), 1192 (m), 992 (m), 919 (m), 853 (vs), 836 (vs), 789 (vs), 750 (s), 666 (vs), 605 (s), 393 (m) cm^{-1}. Anal. Calcd for $C_{15}H_{38}AlBrOSi_3$ (425.62): C, 42.33; H, 9.00. Found: C, 41.8; H, 8.9.

Preparation of [(Me$_3$Si)$_3$CAl(Me)I·THF] (10). To a solution of [$(Me_3Si)_3CAlMe_2$·THF] (1.00 g, 2.77 mmol) in toluene (20 mL) was slowly added a solution of iodine (0.70 g, 2.77 mmol) in toluene (40 mL) at room temperature. The resulting colorless reaction mixture was stirred at room temperature for 18 h. After filtration of the solution through Celite, all volatiles were removed in vacuo. The yellow residue was washed with pentane (10 mL) to yield compound **10** (1.04 g, 79%) as a slightly yellow solid, mp 229 °C. ^{1}H NMR (200.13 MHz, C_6D_6): δ 3.95 (m$_c$, 2 H, OCH_2CH_2), 3.55 (m$_c$, 2 H, OCH_2CH_2), 1.00 (m$_c$, 4 H, OCH_2CH_2), 0.43 (s, 27 H, $Si(CH_3)_3$), 0.07 (s, 3 H, $AlCH_3$). ^{29}Si NMR (49.69 MHz, C_6D_6): δ −3.8 (s). MS (70 eV): *m/e* 385 (M − THF − Me, 65), 273 (M − THF − I, 60), 201 ($C(SiMe_3)_3$ − 2 Me, 100). IR (Nujol mull): 1350 (m), 1283 (m), 1259 (vs), 1251 (vs), 1193 (s), 1103 (m), 1046 (m), 991 (s), 960 (m), 923 (m), 850 (vs), 835 (vs), 789 (vs), 749 (s),

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [{(Me$_3$Si)$_3$CAlF$_2$}$_3$] (2)

Al(1)−F(1)	1.657(5)	Al(1)−F(4)	1.795(4)
Al(1)−F(6)	1.812(4)	Al(1)−C(1)	1.943(6)
Al(2)−F(2)	1.681(5)	Al(2)−F(4)	1.795(4)
Al(2)−F(5)	1.812(4)	Al(2)−C(2)	1.939(6)
Al(3)−F(3)	1.671(5)	Al(3)−F(5)	1.802(4)
Al(3)−F(6)	1.815(4)	Al(3)−C(3)	1.943(6)
C(1)−Al(1)−F(1)	119.6(2)	C(1)−Al(1)−F(4)	120.0(2)
C(1)−Al(1)−F(6)	116.0(2)	F(1)−Al(1)−F(4)	99.4(2)
F(1)−Al(1)−F(6)	105.8(2)	F(4)−Al(1)−F(6)	91.40(17)
C(2)−Al(2)−F(2)	121.7(2)	C(2)−Al(2)−F(4)	118.8(2)
C(2)−Al(2)−F(5)	116.3(2)	F(2)−Al(2)−F(4)	99.3(2)
F(2)−Al(2)−F(5)	103.6(2)	F(4)−Al(2)−F(5)	91.96(18)
C(3)−Al(3)−F(3)	117.7(2)	C(3)−Al(3)−F(5)	116.8(2)
C(3)−Al(3)−F(6)	120.4(2)	F(3)−Al(3)−F(5)	105.8(2)
F(3)−Al(3)−F(6)	101.3(2)	F(5)−Al(3)−F(6)	90.57(18)
Al(1)−F(4)−Al(2)	144.6(2)	Al(1)−F(6)−Al(3)	130.3(2)
Al(2)−F(5)−Al(3)	145.2(2)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [{(THF)$_2$K(Me$_3$Si)$_3$CAlF$_2$(μ-F)F$_2$AlC(SiMe$_3$)$_3$}$_2$] (3)

Al(1)−C(1)	1.954(3)	Al(1)−F(1)	1.821(2)
Al(1)−F(11)	1.672(2)	Al(1)−F(12)	1.672(2)
Al(2)−C(2)	1.957(3)	Al(2)−F(1)	1.817(2)
Al(2)−F(21)	1.672(2)	Al(2)−F(22)	1.677(2)
Al(3)−C(3)	1.964(3)	Al(3)−F(3)	1.818(2)
Al(3)−F(31)	1.672(1)	Al(3)−F(32)	1.678(2)
Al(4)−C(4)	1.962(3)	Al(4)−F(3)	1.823(2)
Al(4)−F(41)	1.673(2)	Al(4)−F(42)	1.673(2)
K(1)−F(12)	2.717(2)	K(1)−F(21)	2.740(2)
K(1)−F(32)	2.734(2)	K(1)−F(41)	2.653(2)
K(1)−O(130)	2.713(3)	K(1)−O(140)	2.765(3)
K(2)−F(11)	2.610(2)	K(2)−F(22)	2.860(2)
K(2)−F(31)	2.709(2)	K(2)−F(42)	2.698(2)
K(2)−O(150)	2.788(3)	K(2)−O(160)	2.705(3)
C(1)−Al(1)−F(1)	114.3(1)	C(1)−Al(1)−F(11)	113.5(1)
C(1)−Al(1)−F(12)	118.5(1)	F(1)−Al(1)−F(11)	102.9(1)
F(1)−Al(1)−F(12)	100.1(1)	F(11)−Al(1)−F(12)	105.5(1)
C(2)−Al(2)−F(1)	114.7(1)	C(2)−Al(2)−F(21)	115.1(1)
C(2)−Al(2)−F(22)	118.4(1)	F(1)−Al(2)−F(21)	103.0(1)
F(1)−Al(2)−F(22)	99.1(1)	F(21)−Al(2)−F(22)	104.3(1)
C(3)−Al(3)−F(3)	115.1(1)	C(3)−Al(3)−F(31)	114.8(1)
C(3)−Al(3)−F(32)	117.9(1)	F(3)−Al(3)−F(31)	103.3(1)
F(3)−Al(3)−F(32)	99.1(1)	F(31)−Al(3)−F(32)	104.4(1)
C(4)−Al(4)−F(3)	113.9(1)	C(4)−Al(4)−F(41)	114.4(1)
C(4)−Al(4)−F(42)	118.0(1)	F(3)−Al(4)−F(41)	102.9(1)
F(3)−Al(4)−F(42)	99.9(1)	F(41)−Al(4)−F(42)	105.7(1)
Al(1)−F(1)−Al(2)	126.2(1)	Al(3)−F(3)−Al(4)	125.7(1)
Al(1)−F(11)−K(2)	118.7(1)	Al(1)−F(12)−K(1)	144.8(1)
Al(2)−F(21)−K(1)	107.6(1)	Al(2)−F(22)−K(2)	147.3(1)
Al(3)−F(31)−K(2)	108.4(1)	Al(3)−F(32)−K(1)	151.4(1)
Al(4)−F(41)−K(1)	122.3(1)	Al(4)−F(42)−K(2)	143.4(1)
F(12)−K(1)−F(21)	71.2(1)	F(12)−K(1)−F(32)	107.4(1)
F(12)−K(1)−F(41)	103.3(1)	F(12)−K(1)−O(130)	81.9(1)
F(12)−K(1)−O(140)	158.4(1)	F(21)−K(1)−F(32)	114.1(1)
F(21)−K(1)−F(41)	173.4(1)	F(21)−K(1)−O(130)	83.3(1)
F(21)−K(1)−O(140)	102.3(1)	F(32)−K(1)−F(41)	70.6(1)
F(32)−K(1)−O(130)	162.0(1)	F(32)−K(1)−O(140)	94.1(1)
F(41)−K(1)−O(130)	92.5(1)	F(41)−K(1)−O(140)	81.5(1)
O(130)−K(1)−O(140)	76.9(1)	F(11)−K(2)−F(22)	71.0(1)
F(11)−K(2)−F(31)	178.4(1)	F(11)−K(2)−F(42)	108.8(1)
F(11)−K(2)−O(150)	88.7(1)	F(11)−K(2)−O(160)	77.8(1)
F(22)−K(2)−F(31)	110.4(1)	F(22)−K(2)−F(42)	111.0(1)
F(22)−K(2)−O(150)	158.5(1)	F(22)−K(2)−O(160)	94.2(1)
F(31)−K(2)−F(42)	71.3(1)	F(31)−K(2)−O(150)	89.8(1)
F(31)−K(2)−O(160)	101.4(1)	F(42)−K(2)−O(150)	81.6(1)
F(42)−K(2)−O(160)	154.7(1)	O(150)−K(2)−O(160)	74.1(1)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [(Me$_3$Si)$_3$CAlX$_2$·THF] (X = Cl, 4; X = Br, 5; X = I, 6)

	3	4	5
Al(1)−C(1)	1.975(2)	1.975(6)	1.981(4)
Al(1)−O(1)	1.883(2)	1.886(5)	1.891(3)
Al(1)−X(1)	2.154(1)	2.311(1)	2.564(1)
C(1)−Si(1)	1.899(2)	1.905(8)	1.906(3)
C(1)−Si(2)	1.910(2)	1.891(8)	1.912(4)
C(1)−Si(3)	1.894(2)	1.918(7)	1.908(2)
C(1)−Al(1)−O(1)	114.8(1)	115.1(1)	115.5(2)
C(1)−Al(1)−X(1)	116.4(1)	116.9(1)	117.8(1)
O(1)−Al(1)−X(1)	100.0(1)	100.0(1)	100.0(1)
X(1)−Al(1)−X(2)	106.7(8)	105.5(1)	102.8(1)
Al(1)−C(1)−Si(1)	109.7(1)	108.9(2)	109.9(2)
Al(1)−C(1)−Si(2)	106.5(1)	109.0(2)	107.5(2)
Al(1)−C(1)−Si(3)	110.6(1)	109.0(2)	110.4(1)
Si(1)−C(1)−Si(2)	109.8(1)	111.4(3)	109.9(1)
Si(1)−C(1)−Si(3)	110.4(1)	108.9(2)	109.7(2)
Si(2)−C(1)−Si(3)	109.7(1)	109.5(3)	109.3(2)

719 (s), 669 (vs), 654 (s), 612 (s), 605 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{38}AlIOSi_3$ (472.62): C, 38.12; H, 8.10. Found: C, 37.6; H, 8.0.

Crystal Structure Solution and Refinement for 2−6 (Table 4). Data for structures **1**, **2**, and **6** were collected on a Stoe-Siemens-Huber four-circle diffractometer and for structures **3**, **4**, and **5** on a Stoe-Siemens-Huber four-circle diffractometer equipped with a Siemens SMART CCD area detector. Mo Kα radiation (λ = 0.710 73 Å) was used in all cases. A semiempirical absorption correction for structures **3**, **4**, and **5** was performed using the program SADABS[19] and for **6** using the program XPREP.[20]

All structures were solved by direct methods (SHELXS-96)[21] and refined against F^2 using SHELXL-97.[22] All heavy atoms were refined anisotropically, unless stated otherwise. Hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atom.

Compound **1** crystallizes in the space group *Pbcn*, which is uniquely defined by the systematic absences. Refinement is problematic, though, as there is extensive disorder, which cannot be modeled satisfactorily. The residual electron density is as high as 3 eA^{-3} in several places and *R*1 does not drop below 0.27. Therefore, we cannot discuss bond lengths and angles and do not deposit coordinates.

In structure **2**, two of the three (Me$_3$Si)$_3$C groups are disordered over two sets of positions, each with occupancies of 9:1. Chemically equivalent 1,2- and 1,3-distances in the disordered parts were restrained to be equal, and rigid-bond and similarity restraints were used for the anisotropic displacement parameters in the disordered groups. U_{iso} for the minor components in the disordered parts were set to fixed values. There is a molecule of *n*-hexane present in the crystal lattice. Bond lengths and angles for the solvent molecule were restrained to standard values, and a common isotropic thermal parameter was refined.

The structures of compounds **4**, **5**, and **6** are isomorphic. The (Me$_3$Si)$_3$C group in these compounds and the coordinated THF molecule in compounds **4** and **6** are disordered about the mirror plane, and all chemically equivalent 1,2- and 1,3-distances in the ligands were restrained to be equal. In compound **5**, the C1 and C1A positions are disordered. Anisotropic refinement of the disordered parts of the structure was possible by using similarity and rigid-bond restraints. We believe that the choice of space group *Pbcm* is correct, instead of its noncentrosymmetric counterpart *Pbc*2$_1$ (alternative setting of *Pca*2$_1$, No. 29), as the disorder is present in the acentric space group as well.

In the structure of **3**, three of the four (Me$_3$Si)$_3$C groups are disordered about two sets of positions with occupancies of 9:1, 8:2, and 8:2. The carbon atoms of the minor component of the first (Me$_3$Si)$_3$C group were refined with one common isotropic

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(19) Sheldrick, G. M. *SADABS, Program for absorption correction of Siemens area detector data*; University of Göttingen: Göttingen, Germany, 1996.

(20) *XPREP V 5.05*, Siemens Analytical X-ray instruments.

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

(22) Sheldrick, G. M. *SHELXL, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table 4. Crystallographic Data for Compounds 1−6

compound	**1**	**2**	**3**	**4**	**5**	**6**
empirical formula	$C_{14}H_{35}AlF_2Si_3$	$C_{36}H_{95}Al_3F_6Si_9$	$C_{56}H_{140}F_{10}K_2O_4Si_{12}$	$C_{14}H_{35}AlCl_2OSi_3$	$C_{14}H_{35}AlBr_2OSi_3$	$C_{14}H_{35}AlI_2OSi_3$
fw	368.66	975.90	1590.88	401.57	490.49	584.47
temp (K)	193(2)	213(2)	193(2)	193(2)	163(2)	213(2)
cryst size (mm)	0.50 × 0.50 × 0.50	0.70 × 0.40 × 0.10	0.50 × 0.50 × 0.50	0.60 × 0.50 × 0.50	0.40 × 0.20 × 0.15	0.50 × 0.50 × 0.50
cryst syst	orthorhombic	triclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	*Pbcn*	$P\bar{1}$	$P2_1/n$	*Pbcm*	*Pbcm*	*Pbcm*
a (Å)	26.984(6)	9.144 (5)	17.230(3)	12.541(11)	12.560(3)	12.553(3)
b (Å)	11.684(4)	13.541(7)	23.993(5)	13.247(13)	13.360(3)	13.985(3)
c (Å)	13.556(4)	24.638(4)	22.199(4)	13.501(11)	13.445(3)	13.813(3)
α (deg)	90	99.54(8)	90	90	90	90
β (deg)	90	99.21(4)	95.25(3)	90	90	90
γ (deg)	90	97.53(2)	90	90	90	90
cell vol ($Å^{3)}$	4340(3)	2931(2)	9139(3)	2243(3)	2256(1)	2425(1)
Z	8	2	4	4	4	4
ρ_c (g mm^{-3})	1.129	1.106	1.156	1.189	1.444	1.601
μ (mm^{-1})	0.270	0.291	0.355	0.487	3.790	2.777
F(000)	1600	1060	3424	864	1008	1152
2θ range (deg)		7.04−43.10	5.52−46.52	4.48−48.80	5.38−49.42	7.02−50.10
no. of data measd, unique		10 869, 6732 ($R_{int} = 0.0462$)	69 150, 13 117 ($R_{int} = 0.0437$)	18 712, 1928 ($R_{int} = 0.0293$)	17 830, 2224 ($R_{int} = 0.0336$)	4444, 2231 ($R_{int} = 0.0186$)
R,[a] $wR2$[b] ($I > 2\sigma(I)$)		0.0857, 0.2203	0.0445, 0.0985	0.0296, 0.0789	0.0564, 0.1212	0.0256, 0.0624
R, $wR2$ (all data)		0.1196, 0.2560	0.0621, 0.1072	0.0341, 0.0818	0.0628, 0.1243	0.0285, 0.0642
goodness of fit, S[c]		1.042	1.090	1.101	1.319	1.133
weight factors *a*, *b*[d]		0.1311/12.2886	0.0397/7.7591	0.0404/0.7040	0.0038/15.326	0.0241/3.1857
no. of refined params		553	1043	181	163	179
min/max transm factors		0.972/0.822	0.697/0.894	0.630/0.772	0.429/0.302	0.22/0.29
restraints		2757	3951	108	111	164
largest diff peak/hole (e $Å^{-3}$)		0.2269/−0.666	0.365/−0.258	0.231/−0.193	0.442/−0.502	0.489/−0.849

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2]/\sum(n - p)]^{1/2}$. [d] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [F_o^2 + 2F_c^2]/3$.

thermal parameter. There is also disorder in several of the coordinated THF molecules. Chemically equivalent 1,2- and 1,3-distances in the disordered parts were restrained to be equal using similarity and rigid-bond restraints.

Results and Discussion

On the basis of our previous successes in the fluorination of aminodimethylalanes with trimethyltin fluoride, we started our experiments with the dimethyltrisylalane [$(Me_3Si)_3CAlMe_2$·THF]. We intended to cleave the weaker Al−CH_3 bonds and form two Al−F bonds with the concomitant generation of volatile tetramethyltin. Reaction of the trialkylalane [$(Me_3Si)_3CAlMe_2$·THF] with 2 equiv of trimethyltin fluoride in THF proceeds smoothly to give the organoaluminum difluoride−THF adduct [$(Me_3Si)_3CAlF_2$·THF] (**1**) in good yields (eq 2).

$$[(Me_3Si)_3CAlMe_2\cdot THF] + 2Me_3SnF \xrightarrow[-2Me_4Sn]{THF} \underset{\mathbf{1}}{[(Me_3Si)_3CAlF_2\cdot THF]} \quad (2)$$

In contrast to our previously reported aminoalane difluorides,[7] which could be prepared in either toluene or THF solution, the reactions of [$(Me_3Si)_3CAlMe_2$·THF] with trimethyltin fluoride in toluene or *n*-hexane gave only mixtures of several compounds, as shown by NMR spectroscopy.

Compound **1** is a white air- and moisture-sensitive solid and was characterized by ^1H, ^{19}F, and ^{29}Si NMR, mass, and IR spectroscopy as well as elemental analysis (see Experimental Section). The spectroscopic methods indicate a monomeric species with 4-fold coordination at the aluminum center. Crystals of compound **1** suitable for X-ray diffraction analyses were obtained from THF at −26 °C. Unfortunately, extensive disorder in the crystals was always observed (see Experimental Section). For this reason, it is not appropriate to discuss the structure in detail. However, the monomeric nature of **1** can be recognized.

As proposed by Ziegler and co-workers,[23] dialkylaluminum fluorides form no stable complexes with ethers. The same behavior is observed for compound **1**, which can be converted to the THF-free product by heating in vacuo (10^{-2} mbar) to 200 °C for several hours (eq 3).

$$\underset{\mathbf{1}}{[(Me_3Si)_3CAlF_2\cdot THF]} \xrightleftharpoons[\text{THF, 25 °C}]{\text{200 °C, 0.01 mbar−THF}} \underset{\mathbf{2}}{{}^1/_3[\{(Me_3Si)_3CAlF_2\}_3]} \quad (3)$$

After workup, we obtained the solvent-free trisylaluminum difluoride [$\{(Me_3Si)_3CAlF_2\}_3$] (**2**), as shown by ^1H NMR spectroscopy. However, this dissociation reaction is reversible. If compound **2** is stirred for several hours in THF at room temperature, the THF-adduct **1** could be obtained in quantitative yield after removal of the solvent in vacuo (eq 3).

As observed for the previously reported aminoalane difluoride [$\{(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)AlF_2\}_3$],[7] the ^{19}F NMR spectrum of [$\{(Me_3Si)_3CAlF_2\}_3$] (**2**) in deuterated toluene recorded at room temperature shows only one broad singlet (−149.68 ppm), indicating rapid interchange of the bridging and terminal fluorine atoms and, therefore, coalescence of the signals. As the temperature is gradually lowered to 183 K, resolution of the

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(23) Ziegler, K.; Köster, R. *Liebigs Ann. Chem.* **1957**, *608*, 1.

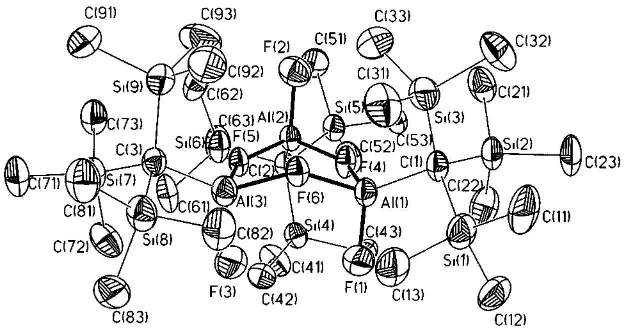

Figure 1. Crystal structure of [{(Me$_3$Si)$_3$CAlF$_2$}$_3$] (**2**), with anisotropic displacement parameters depicting 50% probability. All of the hydrogen atoms of the molecule have been omitted for clarity.

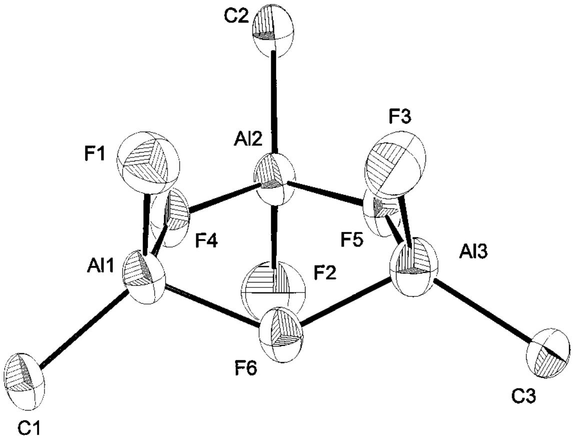

Figure 2. Central core of [{(Me$_3$Si)$_3$CAlF$_2$}$_3$] (**2**), with anisotropic displacement parameters depicting 50% probability. The organic ligands except for the *ipso*- carbon atoms have been omitted for clarity.

broad signal into several complex overlapping multiplets in the range from −147.0 to −151.5 ppm is observed. However, in contrast to [{(2,6-*i*-Pr$_2$C$_6$H$_3$)N(SiMe$_3$)AlF$_2$}$_3$] (four separated multiplets at −167.1, −167.9, −173.7, and −176.2 ppm in the ratio 1:2:1:2),[7] a clear interpretation of the complex spectrum was not possible. The signal with the highest mass in the EI mass spectrum ($m/e = 873$) could be assigned to the fragment ion of the trimeric difluoride [{(Me$_3$Si)$_3$CAlF$_2$}$_3$] with loss of one methyl group.

Crystals suitable for X-ray diffraction studies were obtained from *n*-hexane by cooling the solution (−26 °C). The structure of the alkylaluminum difluoride **2** with the atom-labeling scheme is shown in Figure 1 and the central core of the molecule in Figure 2. Selected bond distances and angles are listed in Table 1. Compound **2** crystallizes in the triclinic crystal system, space group $P\bar{1}$. X-ray diffraction analysis of **2** shows it to be trimeric with a six-membered alternating aluminum−fluorine ring and three terminal fluorine atoms, similar to that observed in the aminoalane difluoride [{(2,6-*i*-Pr$_2$C$_6$H$_3$)N(SiMe$_3$)AlF$_2$}$_3$].[7] The Al$_3$(μ-F)$_3$ ring takes up a flat boat conformation comparable to that of the gallium hydroxide [{(Me$_3$Si)$_3$CGaMe(μ-OH)}$_3$][16] with two of the terminal fluorine atoms located above and one below this ring. This may be caused by the large steric demand of the ligands at the metal centers. In the boat conformation, all trisyl groups can adopt the favorable equatorial position with only two of the trisyl groups on one side of the ring. In contrast, the chair conformation demands that in the 1,3,5-trisubstituted compounds all three equatorial ligands are located on the same side of the ring, which may be impossible for the extremely bulky trisyl group. The bridging Al−F bonds in **2** range from 1.795 to 1.815 Å and are comparable with those found by electron diffraction for [Me$_2$AlF]$_4$ (1.808 Å)[24] or by X-ray diffraction for [{(2,6-*i*-Pr$_2$C$_6$H$_3$)N(SiMe$_3$)AlF$_2$}$_3$] (1.770−1.788 Å)[7] and [{(Cp*-AlF)$_2$SiPh$_2$}$_2$] (average 1.846 Å).[25] Only a few compounds containing terminal Al−F bonds have been structurally characterized.[26] In **2**, the terminal Al−F bonds range from 1.657 to 1.681 Å and are somewhat longer than those in [{(2,6-*i*-Pr$_2$C$_6$H$_3$)N(SiMe$_3$)AlF$_2$}$_3$] (1.634−1.642 Å)[7] and AlF$_3$ (1.63 Å),[27] as determined by electron diffraction. The Al−C distance (average 1.942 Å) is distinctly shorter than that in the starting material [(Me$_3$Si)$_3$CAlMe$_2$·THF] (2.030 Å)[16] due to the strong electron-withdrawing properties of the three fluorine atoms coordinated at each aluminum center.

We examined the cocatalytic activity of [{(Me$_3$Si)$_3$CAlF$_2$}$_3$] (**2**) in the presence of several group 4 metallocenes (Cp*TiF$_3$, Cp$^*_2$ZrF$_2$, Cp$_2$ZrCl$_2$ and Cp$_2$ZrMe$_2$) for ethylene polymerization. The experiments were carried out in ethylene-saturated toluene solutions (1 bar) at room temperature. However, under these conditions, no formation of polyethylene was observed. One possible explanation for this could be the great steric hindrance of the bulky substituents at the aluminum center which does not allow the formation of a catalytically active complex (eq 1) with the bulky metallocene derivatives. The high fluorine acceptor ability of the aluminum difluoride is demonstrated by the formation of the unusual coordination compound [{(THF)$_2$K(Me$_3$Si)$_3$CAlF$_2$(μ-F)F$_2$AlC(SiMe$_3$)$_3$}$_2$] (**3**) by the reaction of [(Me$_3$Si)$_3$CAlF$_2$·THF] (**1**) (compound **2** exists in THF solutions only as the solvated complex **1**) using excess potassium fluoride (eq 4).

$$\underset{\mathbf{1}}{4[(\mathrm{Me_3Si})_3\mathrm{CAlF_2{\cdot}THF}]} + 2\mathrm{KF} \xrightarrow{\mathrm{THF}} \underset{\mathbf{3}}{[\{(\mathrm{THF})_2\mathrm{K}(\mathrm{Me_3Si})_3\mathrm{CAlF_2}(\mu\text{-F})\mathrm{F_2AlC}(\mathrm{SiMe_3})_3\}_2]} \quad (4)$$

Compound **3** was characterized by ^{1}H, ^{19}F, and ^{29}Si NMR and IR spectroscopies as well as elemental analysis (see Experimental Section). The ^{19}F NMR spectrum of **3** in toluene-d_8 shows only one broad singlet (−160.18 ppm), indicating rapid interchange of the bridging and terminal fluorine atoms and, therefore, coalescence of the signals. As the temperature is gradually lowered to 183 K, the signal becomes much broader but no clear resolution in the different signals is observed.

Single crystals suitable for X-ray diffraction analysis were obtained from THF (−26 °C). The crystal structure of compound **3** is shown in Figure 3 and the central

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

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[27] Shanmugasunderan, G.; Nagarajan, G. *Z. Phys. Chem.* **1969**, *240*, 363.

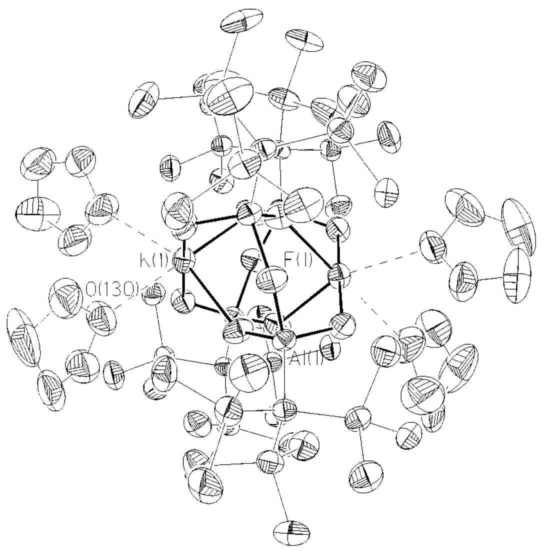

Figure 3. Crystal structure of $[\{(THF)_2K(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3\}_2]$ (**3**), with anisotropic displacement parameters depicting 50% probability. All of the hydrogen atoms of the molecule have been omitted for clarity.

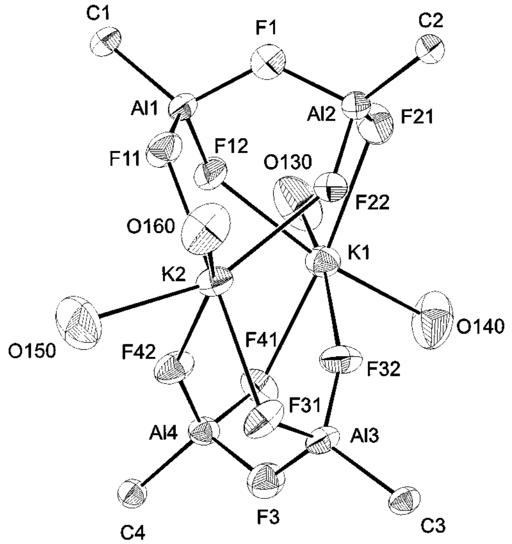

Figure 4. Central core of $[\{(THF)_2K(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3\}_2]$ (**3**), with anisotropic displacement parameters depicting 50% probability. The organic ligands except for the *ipso*- carbon atoms have been omitted for clarity.

core of the molecule in Figure 4. Selected bond lengths and angles are given in Table 2. Compound **3** crystallizes in the monoclinic system, space group $P2_1/n$. The central core of **3** is built up by two $[(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3]^-$ anions connected by two potassium cations. Each aluminum atom is coordinated to one carbon and to three fluorine atoms and each potassium ion to four fluorine atoms and two THF molecules. The two $[(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3]^-$ anions are in a gauche conformation with an angle of 33° between the planes defined by C1/Al1/F1 and C2/Al2/F1 or C3/Al3/F3 and C4/Al4/F3. For this reason, one of the terminal fluorine atoms at each aluminum center can coordinate one potassium ion in an axial and the other terminal fluorine atom the second potassium ion in an equatorial position.

The average aluminum–carbon distance (1.960 Å) is distinctly shorter than that in $[(Me_3Si)_3CAlMe_2\cdot THF]$ (2.030 Å) but somewhat longer than that in the difluoride **2** (average 1.942 Å). The Al–F(terminal) distances (average 1.674 Å) are comparable with those in $[Li\{(Me_3Si)_3CAlF_3\}\cdot THF]_4$ (1.687 Å)[9] but somewhat longer than those in $[\{(Me_3Si)_3CAlF_2\}_3]$ (**2**) (average 1.670 Å), $[\{(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)AlF_2\}_3]$ (average 1.637 Å),[7] and AlF_3 (1.63 Å).[27] Similarly, the Al–F(bridging) distances in **3** (average 1.819 Å) are longer than those in the difluorides **2** (average 1.805 Å) and $[\{(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)AlF_2\}_3]$ (average 1.782 Å).[7] The K–F distances cover a wide range (2.610–2.860 Å) but are comparable to those in crystalline potassium fluoride (2.664 Å).[28] The coordination sphere of the potassium ion is completed by four THF molecules, so that each potassium ion has a distorted octahedral environment with two fluorine atoms in the axial positions. The K–O distances are in the range of 2.706–2.788 Å and are comparable to the K–O distances in $[(C_4H_8)K_2\cdot 3\,THF]$ (2.665–2.846 Å)[29] and $[K(C_5(CH_2C_6H_5)_5)\cdot 3\,THF]$ (average 2.735 Å).[30] We are currently studying the fluorine acceptor ability of $[\{(Me_3Si)_3CAlF_2\}_3]$ (**2**) using other fluorides.

The trisylaluminum dichloride $[(Me_3Si)_3CAlCl_2]$ (without coordinated solvent) was first prepared in low yield by Eaborn et al.[31] using the reaction of trisyllithium $[(Me_3Si)_3CLi\cdot 2\,THF]$ and aluminum trichloride. However, we were not able to reproduce this reaction and observed only products from cleavage reactions of ether.[32] On the other hand, the reaction of solvent-free trisyllithium $[(Me_3Si)_3CLi]$ with aluminum trichloride yields the alkyltrichlorometalate $[Li\{Cl_3AlC(SiMe_3)_3\}]$ rather than the alkylaluminum dichloride $[(Me_3Si)_3CAlCl_2]$ as described by Weidlein et al.[33]

However, as observed for the synthesis of $[(Me_3Si)_3CAlF_2\cdot THF]$ (**1**) using trimethyltin fluoride, the compound $[(Me_3Si)_3CAlCl_2\cdot THF]$ (**4**) can be prepared in excellent yields by reaction of $[(Me_3Si)_3CAlMe_2\cdot THF]$ with trimethyltin chloride as a mild transfer reagent in a 1:2 molar ratio with the elimination of tetramethylstannane, which can be easily removed in vacuo (eq 5).

$$[(Me_3Si)_3CAlMe_2\cdot THF] + 2Me_3SnCl \xrightarrow[-2Me_4Sn]{\text{toluene}} \underset{\mathbf{4}}{[(Me_3Si)_3CAlCl_2\cdot THF]} \quad (5)$$

The reactions of $[(Me_3Si)_3CLi\cdot 2\,THF]$ with $AlBr_3$ and AlI_3 gave, in all cases, only brown oils, which could not be identified. In contrast the reactions of $[(Me_3Si)_3CAlMe_2\cdot THF]$ with bromine and iodine in a 1:2 molar ratio give, in good yields, the corresponding alkylaluminum dihalogenides $[(Me_3Si)_3CAlX_2\cdot THF]$ (X = Br, **5**; X = I, **6**) with the elimination of volatile methyl bromide and iodide, respectively (eq 6).

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(28) Wells, A. F. *Structural Inorganic Chemistry*, 3rd ed.; Oxford University Press: London, 1962.

(29) Hu, N.; Gong, L.; Jin, Z.; Chen, W. *J. Organomet. Chem.* **1988**, *352*, 61.

(30) Lorberth, J.; Shin, S.-H.; Wocadlo, S.; Massa, W. *Angew. Chem.* **1989**, *101*, 793; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 735.

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(32) The same observations were described by Uhl and co-workers, see: Hiller, W.; Layh, M.; Uhl, W. *Angew. Chem.* **1991**, *103*, 339; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 324.

(33) Schaller, F.; Schwarz, W.; Klinkhammer, K. W.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1455.

$$\begin{array}{l}[(Me_3Si)_3CAlMe_2{\cdot}THF] + 2X_2 \xrightarrow[-2MeX]{\text{toluene}} \\ \qquad\qquad [(Me_3Si)_3CAlX_2{\cdot}THF] \\ \qquad\qquad \mathbf{5}\ X = Br \\ \qquad\qquad \mathbf{6}\ X = I \end{array} \quad (6)$$

In the case of the dibromide **5**, complete elimination of methyl bromide is reached after stirring at room temperature for 2 h, whereas the synthesis of the diiodide requires additional refluxing in toluene for 2 h.

Compounds **4**, **5**, and **6** have been fully characterized by ^1H and ^{29}Si NMR, mass, and IR spectroscopies as well as elemental analyses (see Experimental Section). The spectroscopic methods indicate monomeric species with 4-fold coordination of the aluminum centers. In contrast to the aluminum difluoride **1**, the aluminum dichloride $[(Me_3Si)_3CAlCl_2{\cdot}THF]$ (**5**) can be sublimed without dissociation in vacuo at 130 °C while the derivatives of the higher congeners $[(Me_3Si)_3CAlX_2{\cdot}THF]$ (**5**, X = Br; **6**, X = I) decompose with formation of a complex mixture of products under similar conditions.

Crystals of compounds **4**, **5**, and **6** suitable for X-ray diffraction analyses were obtained from toluene (−26 °C). The structure of **6** is shown in Figure 5 (compounds **4** and **5** are isostructural to **6**), and selected bond lengths and angles for **4**, **5**, and **6** are given in Table 3.

Compounds **4**, **5**, and **6** crystallize in the orthorhombic system (space group *Pbcm*). The aluminum atom in all three compounds is coordinated to one carbon atom, two halogen atoms, and one oxygen atom. The Al−C and Al−O distances are nearly equal in all three compounds (Al−C 1.977 Å, Al−O 1.887 Å, all on average) and are in good agreement with those observed for $[MesAlCl_2{\cdot}THF]$ (Al−C 1.969 Å, Al−O 1.852 Å),[10a] $[2,6\text{-}Mes_2C_6H_3AlCl_2{\cdot}OEt_2]$ (Al−C 1.992 Å, Al−O 1.877 Å),[10b] $[TripAlBr_2{\cdot}OEt_2]$ (Al−C 1.976 Å, Al−O 1.865 Å),[10a] and $[2,4,6\text{-}Ph_3C_6H_2AlBr_2{\cdot}OEt_2]$ (Al−C 1.983 Å, Al−O 1.868 Å)[10b] but distinctly shorter than those in the starting material $[(Me_3Si)_3CAlMe_2{\cdot}THF]$ (Al−C 2.030 Å, Al−O 1.968 Å)[16] due to the higher positive charge of the aluminum atom caused by the electron-withdrawing halide atoms. The main difference between the three structures lies in the aluminum−halide distances which increase, as expected, in the order **4** (2.154 Å) < **5** (2.311 Å) < **6** (2.564 Å) but are comparable to those in $[MesAlCl_2{\cdot}THF]$ (Al−Cl 2.148 Å),[10a] $[2,6\text{-}Mes_2C_6H_3AlCl_2{\cdot}OEt_2]$ (Al−Cl 2.1399 Å),[10b] $[TripAlBr_2{\cdot}OEt_2]$ (Al−Br 2.311 Å),[10a] and $[2,4,6\text{-}Ph_3C_6H_2AlBr_2{\cdot}OEt_2]$ (Al−Br 2.300 Å).[10b] No crystallographic data for aluminum diiodides are available, but the Al−I distance in **6** (2.564 Å) is in good agreement with that in $[Me_2AlI{\cdot}NMe_3]$ (2.580 Å),[34] which is the only other example of a structurally characterized neutral organoaluminum iodide.

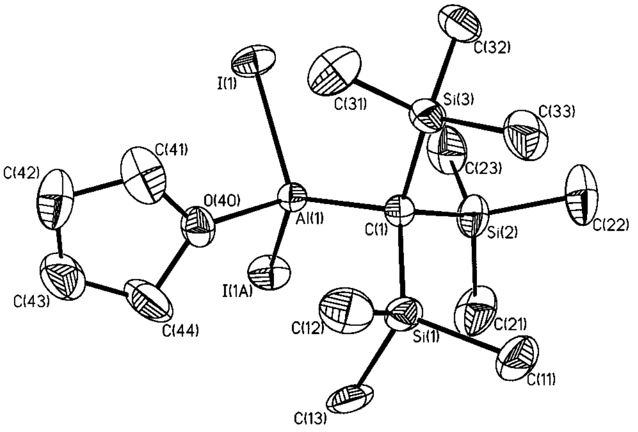

Figure 5. Crystal structure of $[(Me_3Si)_3CAlI_2{\cdot}THF]$ (**6**), with anisotropic displacement parameters depicting 50% probability. All of the hydrogen atoms of the molecule have been omitted for clarity.

Reaction of $[(Me_3Si)_3CAlMe_2{\cdot}THF]$ with 1 equiv of trimethyltin fluoride in THF gave, after workup, a white solid, which was identified by ^1H, ^{19}F, and ^{29}Si NMR spectroscopy and mass spectroscopy as a mixture of $[(Me_3Si)_3CAlMe_2{\cdot}THF]$, $[(Me_3Si)_3CAlF_2{\cdot}THF]$ (**1**), and a third compound, which is presumably *cis*/*trans*-$[\{(Me_3Si)_3CAlMe(\mu\text{-}F)\}_2]$ (**6**) (three singlets in the ^1H NMR spectrum at 0.41, −0.41, and −0.43 ppm in the ratio 54:3:3, one singlet in the ^{19}F NMR spectrum at −151.80 ppm, two singlets in the ^{29}Si NMR spectrum at −3.97 and −4.01 ppm in the ratio 1:1). Unfortunately, we were not able, at this time, to separate this mixture by fractional crystallization or sublimation or to obtain pure compounds by variation of the reaction conditions. The coordination of the THF molecule in an intermediate compound $[(Me_3Si)_3CAl(Me)F{\cdot}THF]$ could not be very strong, resulting in equilibria with rapid exchange reactions (eq 7). In contrast, the reaction of $[(Me_3Si)_3CAlMe_2{\cdot}THF]$ with trimethyltin chloride (eq 8), bromine, or iodine (eq 9) in a 1:1 molar ratio gave, in good yields, only the dialkylaluminum halides $[(Me_3Si)_3CAl(Me)X{\cdot}THF]$ (X = Cl, **7**; X = Br, **8**; X = I, **9**), respectively, rather than mixtures of compounds as observed above.

$$\begin{array}{c}2[(Me_3Si)_3CAlMe_2{\cdot}THF] + 2Me_3SnF \xrightarrow[-2Me_4Sn]{\text{THF}} \\ 2[(Me_3Si)_3CAl(Me)F{\cdot}THF] \rightarrow \\ [\{(Me_3Si)_3CAlMe(\mu\text{-}F)\}_2] + 2THF \rightleftharpoons \\ \mathbf{7} \\ [(Me_3Si)_3CAlMe_2{\cdot}THF] + [(Me_3Si)_3CAlF_2{\cdot}THF] \\ \mathbf{1}\end{array} \quad (7)$$

$$\begin{array}{l}[(Me_3Si)_3CAlMe_2{\cdot}THF] + Me_3SnCl \xrightarrow[-Me_4Sn]{\text{toluene}} \\ \qquad\qquad [(Me_3Si)_3CAl(Me)Cl{\cdot}THF] \\ \qquad\qquad\qquad \mathbf{8}\end{array} \quad (8)$$

$$\begin{array}{l}[(Me_3Si)_3CAlMe_2{\cdot}THF] + X_2 \xrightarrow[-MeX]{\text{toluene}} \\ \qquad\qquad [(Me_3Si)_3CAl(Me)X{\cdot}THF] \\ \qquad\qquad \mathbf{9}\ X = Br \\ \qquad\qquad \mathbf{10}\ X = I\end{array} \quad (9)$$

The slightly yellow compounds **7**−**9** are air- and moisture-sensitive solids and were fully characterized by ^1H and ^{29}Si NMR, mass, and IR spectroscopies as well as elemental analyses (see Experimental Section). A remarkable feature of all three compounds is the signal pattern of the coordinated THF molecule in the ^1H NMR spectra. It shows, in all three cases, two multiplets in a 1:1 ratio for the protons at the α-C atoms and one multiplet with double intensity for the protons at the β-C atoms of the THF molecule. These data

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[34] Atwood, J. L.; Milton, P. A. *J. Organomet. Chem.* **1973**, *52*, 275.

suggest that the chirality of the Al center is preserved in solution so that the protons at the α-carbons are diastereotopic. Unfortunately, we were not able, at this time, to obtain suitable crystals of these compounds for X-ray structure analysis.

Conclusions and Remarks

The novel bulky tris(trimethylsilyl)methylaluminum halides [$(Me_3Si)_3CAlX_2\cdot THF$] (X = F, Cl, Br, I) and [$(Me_3Si)_3CAl(Me)X\cdot THF$] (X = Cl, Br, I) can be prepared by reaction of the mixed trialkylalane [$(Me_3Si)_3CAlMe_2\cdot THF$] using Me_3SnX (X = F, Cl) and X_2 (X = Br, I) in a 1:2 and 1:1 molar ratio, respectively. We are currently investigating the reductions of these halide derivatives using alkaline metals. From the reduction of the diiodide [$(Me_3Si)_3CAlI_2\cdot THF$], we obtained the red crystalline product [$\{(Me_3Si)_3CAl\}_4$]. However, these results will be reported elsewhere.

The solvated difluoride [$(Me_3Si)_3CAlF_2\cdot THF$] can be converted to the solvent-free product [$\{(Me_3Si)_3CAlF_2\}_3$] by heating in vacuo. The compound [$\{(Me_3Si)_3CAlF_2\}_3$] shows no cocatalytic activity with group 4 metallocenes in ethylene polymerization reactions. However, the high fluorine acceptor properties of this difluoride were demonstrated by the formation of the unusual coordination compound [$\{(THF)_2K(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3\}_2$]; we are currently studying the fluorine acceptor properties of this difluoride with other fluorine donor compounds.

The synthetic methods adopted here are likely to be quite general and can possibly be extended for the preparation of other aluminum halides, especially new Al−F compounds. Furthermore, the presence of easily reducible aluminum halides offer possible access to low-valent aluminum compounds.

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Supporting Information Available: Tables of crystal data, non-hydrogen fractional coordinates and *U* values, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and *U* values of **2**−**6** (58 pages). Ordering information is given on any current masthead page.

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