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Reactions of Group 4 Metal Cyclopentadienyl Trifluorides with a Trimeric Iminoalane

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Summary: Reaction of CpMF_3 ($M = \text{Ti}, \text{Zr}$) with $[\text{MeAlN}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)]_3$ leads to fluorine–nitrogen exchange and the formation of isostructural adamantane-like cages. This reaction proceeds with activation of metal–fluorine bonds and can be regarded as a new route to aluminum-containing mixed group 4 amido-fluorides.

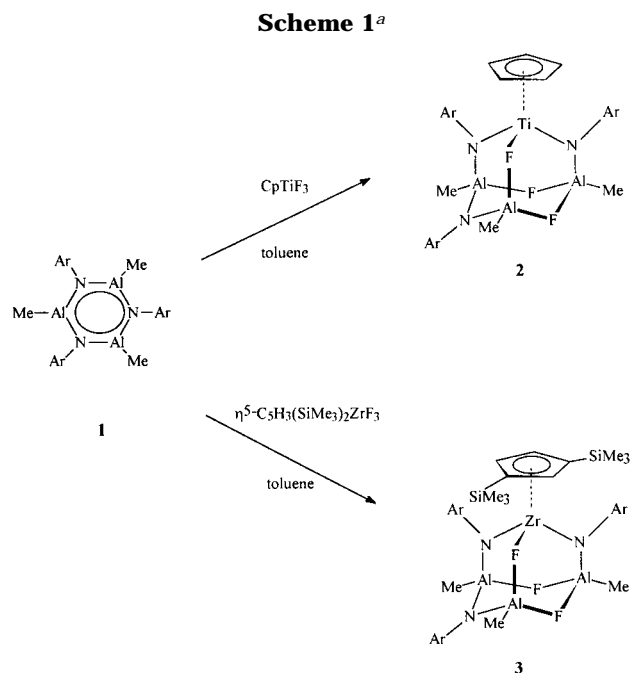
In recent years, the activation of a variety of C–F,¹ Si–F,² and P–F³ bonds has been described. It is assumed that the dissociation of these bonds can be markedly facilitated using an electrophilic support. In this respect, metallocenes of group 4 elements have been intensively investigated in the past few years.^{4,5} Reactions of organometallic fluorides of group 4 with alkyl derivatives of aluminum are of particular interest with regard to the mechanism of homogeneous catalysis for the polymerization of olefins. The formation of adducts of group 4 metallocene halides with AlMe_3 is assumed to be the first step of activation of a polymerization catalyst when AlMe_3 -containing methylaluminoxane (MAO) is used. The subsequent methylation of the metallocene centers is markedly facilitated by the electrophilic support.

To understand the catalytic activity of these compounds, it is necessary to examine whether a selective activation of the metal–fluorine bond and exchange for alkyl and amino groups, respectively, is possible using aluminum compounds.

Recently, we reported on adducts of a titanium fluoride oxide with AlMe_3 containing activated Ti–F bonds.⁶ These products are formed as intermediates in the methylation of compounds with sterically crowded titanium centers.

Herein, we report the reaction of an alumazene⁷ (**1**) with CpTiF_3 and $\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{ZrF}_3$.

The reaction of a suspension of **1** and CpTiF_3 in toluene at room temperature gives a color change from



slightly orange to bright red until all of the solid has dissolved (Scheme 1). The color change is typical for nitrogen-containing titanium compounds and for Ti–F activation,⁶ respectively. Compounds **2** and **3** can be isolated in analytically pure form after recrystallization from *n*-hexane. The compounds were characterized by elemental analysis and mass, IR, and NMR spectroscopic measurements.^{8,9} Furthermore, the molecular structures have been determined by X-ray crystallography, Figures 1 and 2.¹⁰

Both structures **2** and **3** are very similar with slight geometrical differences derived from the somewhat longer bond distances for Zr as compared to Ti and the more bulky substituents on the Cp ligand in the case of **3**. The adamantane-like cores of the molecules are built from one $\text{Al}_3\text{F}_2\text{N}$, one MAl_2FN_2 , and two $\text{MAl}_2\text{F}_2\text{N}$ six-membered rings in a chair conformation with μ_2 -bridging F and N atoms. Each aluminum atom is methyl substituted, and a 2,6-*i*Pr₂C₆H₃-ligand binds to each nitrogen atom. The metal on top of the cage (Ti in **2**, Zr in **3**) binds to $\eta^5\text{-C}_5\text{H}_5$ (**2**) and $\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2$ (**3**), respectively. All metal atoms are distorted tetrahedrally coordinated: The endocyclic angles are in the range from 91.9(1)° (F(2)–Al(3)–N(3)) to 115.7(1)° (N(1)–Al(3)–N(3)) in **2** and 91.80(6)° (F(3)–Zr(1)–N(2))

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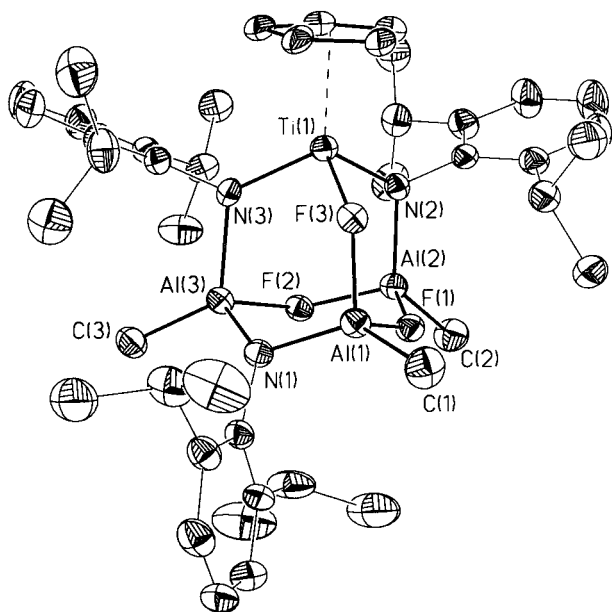


Figure 1. X-ray structure of **2** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Ti(1)–N(2) 1.905(3), Ti(1)–N(3) 1.875(3), Ti(1)–F(3) 2.028(2), Al(1)–N(1) 1.799(3), Al(1)–F(1) 1.825(2), Al(1)–F(3) 1.773(2), Al(2)–N(2) 1.846(3), Al(2)–F(1) 1.791(2), Al(2)–F(2) 1.766(2), Al(3)–N(1) 1.827(3), Al(3)–N(3) 1.934(3), Al(3)–F(2) 1.896(2).

to 117.41(8)° (N(1)–Al(3)–N(3)) in **3** and are smaller than the exocyclic ones which vary from 107.3(2)° (F(1)–Al(1)–C(1)) to 129.5(2)° (N(1)–Al(1)–C(1)) in **2** and 106.17(9)° (F(1)–Al(1)–C(1)) to 130.8(1)° (N(1)–Al(1)–C(1)) in **3**.

In summary, reactions of group 4 metal cyclopentadienyl trifluorides lead to intramolecular fluorine–nitrogen exchange, activation of metal–fluorine bonds, and the formation of isostructural adamantane-like

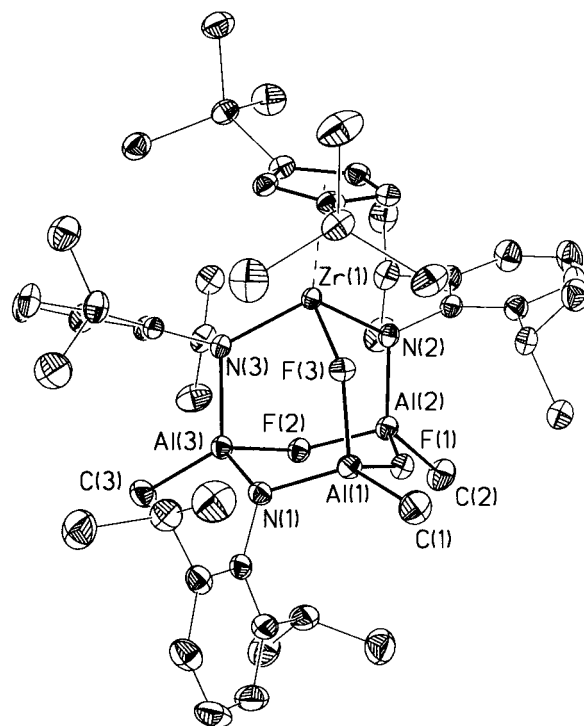


Figure 2. X-ray structure of **3** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Zr(1)–N(2) 2.051(2), Zr(1)–N(3) 1.998(2), Zr(1)–F(3) 2.125(1), Al(1)–N(1) 1.786(2), Al(1)–F(1) 1.812(1), Al(1)–F(3) 1.786(1), Al(2)–N(2) 1.848(2), Al(2)–F(1) 1.795(1), Al(2)–F(2) 1.766(1), Al(3)–N(1) 1.829(2), Al(3)–N(3) 1.944(2), Al(3)–F(2) 1.903(1).

cages. Moreover, the reported synthesis is a new route to aluminum-containing mixed group 4 amidofluorides.

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(8) **2**: A solution of **1** (980 mg, 1.5 mmol) in toluene (30 mL) was added to a suspension of CpTiF₃ (255 mg, 1.5 mmol) in toluene (50 mL). The mixture was then stirred for 36 h at room temperature, until all of the solids had dissolved. The solvent was removed *in vacuo*, and the residue was treated with *n*-hexane (30 mL), affording **2** as a red compound. Yield: 860 mg (70%). Mp: 180 °C. ¹H NMR (C₆D₆): δ (ppm) –1.04 (d, AlCH₃, 3 H), –0.65 (m, AlCH₃, 3 H), –0.45 (m, AlCH₃, 3 H), 1.13–1.42 (m, CH₃(*i*Pr), 36 H), 3.00 (sept, CH(*i*Pr), 1 H), 3.25 (sept, CH(*i*Pr), 1 H), 3.60 (sept, CH(*i*Pr), 1 H), 3.85 (sept, CH(*i*Pr), 2 H), 4.10 (sept, CH(*i*Pr), 1 H), 5.84 (s, CpH, 2 H), 5.97 (s, CpH, 1 H), 6.18 (s, CpH, 1 H), 6.60 (s, CpH, 1 H), 7.05 (m, arom H, 9 H). ¹⁹F NMR (C₆D₆): δ (ppm) –158.8 (d, 1 F), –133.3 (m, 1 F), –131.8 (m, 1 F). MS EI (*m/z*): 162 (ArH, 100). IR (ν, cm^{–1}): 1587, 1425, 1307, 1252, 1229, 1207, 1167, 1107, 1038, 1019, 930, 888, 870, 818, 796, 781, 760, 733, 714, 686, 641, 600, 570, 533. Anal. Calcd for C₄₄H₆₅Al₃F₃N₃Ti: C, 64.3; H, 7.9; N, 5.1. Found: C, 63.8; H, 8.0; N, 5.1. **3**: A solution of **1** (980 mg, 1.5 mmol) in toluene (30 mL) was added dropwise to a solution of η⁵-C₅H₄(SiMe₃)₂ZrF₃ (540 mg, 1.5 mmol) in toluene (50 mL). The mixture was then stirred for 12 h at room temperature. The solvent was removed *in vacuo*, and the residue was treated with *n*-hexane (30 mL), affording **3** as a slightly yellow product. Yield: 1.21 g (80%). Mp: 236 °C. ¹H NMR (C₆D₆): δ (ppm) –1.20 (m, AlCH₃, 3 H), –0.65 (m, AlCH₃, 3 H), –0.50 (m, AlCH₃, 3 H), 0.25 (s, Si(CH₃)₃, 18 H), 1.13–1.34 (m, CH₃(*i*Pr), 36 H), 3.25 (sept, CH(*i*Pr), 3 H), 4.00 (sept, CH(*i*Pr), 3 H), 6.05 (m, CpH, 1 H), 6.60 (m, CpH, 1 H), 7.05 (m, arom H, 9 H), 7.40 (m, CpH, 1 H). ¹⁹F NMR (C₆D₆): δ (ppm) –137.5 (m, 1 F), –132.5 (m, 1 F), –126.4 (m, 1 F). MS EI (*m/z*): 1007 (M⁺, 20), 162 (ArH, 100). IR (ν, cm^{–1}): 1617, 1589, 1425, 1383, 1310, 1260, 1202, 1167, 1088, 1074, 1019, 919, 892, 838, 799, 766, 724, 707, 680, 640, 612, 556, 473, 432. Anal. Calcd for C₅₀H₈₁Al₃F₃N₃Zr: C, 59.5; H, 8.0; N, 4.2. Found: C, 58.7; H, 7.9; N, 4.1. It is known in the literature that the analysis of carbon in aluminum compounds is often incorrect due to the generation of noncombustible aluminum carbide.⁹

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(10) The crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether.¹¹ 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 (λ = 0.710 73 Å), performing φ and ω scans. The structures were solved by direct methods using SHELXS-96¹² and refined against F² on all data by full-matrix least squares with SHELXL-97.¹³ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The disordered Cp ring in **2** was modeled with the help of similarity restraints for 1–2 and 1–3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The final fractional atomic coordinates are given in the Supporting Information. Crystallographic data for **2**: C₄₄H₆₅Al₃F₃N₃Ti, M = 821.83, crystal size: 0.30 × 0.10 × 0.05 mm³, triclinic, *P*1, unit cell dimensions *a* = 9.284(2) Å, *b* = 13.236(3) Å, *c* = 20.435(4) Å, α = 75.53(3)°, β = 85.01(3)°, γ = 69.77(3)°, unit cell volume 2281.4(8) Å³, Z = 2, ρ_{calcd} = 1.196 g cm^{–3}, μ = 0.290 mm^{–1}; total number of reflections measured 42 698, unique 7675 (*R*_{int} = 0.0710). Data/restraints/parameters: 7675/236/547. Final *R* indices: *R*1 = 0.0682, *wR*2 = 0.1091 on data with *I* > 2σ(*I*) and *R*1 = 0.1032, *wR*2 = 0.1246 on all data, goodness-of-fit *S* = 1.216; weighting scheme *w*^{–1} = σ²(*F*_o)² + (0.0049)*P*² + 4.4342*P*, largest difference peak and hole 0.596 and –0.475 e Å^{–3}. Crystallographic data for **3**: C₅₀H₈₈Al₃F₃N₃Zr, M = 1052.64, crystal size 0.40 × 0.20 × 0.20 mm³ triclinic, *P*1, unit cell dimensions *a* = 12.488(3) Å, *b* = 12.638(3) Å, *c* = 20.838(8) Å, α = 91.42(2)°, β = 90.88(2)°, γ = 117.524(9)°, unit cell volume 2914(2) Å³, Z = 2, ρ_{calcd} = 1.200 g cm^{–3}, μ = 0.319 mm^{–1}; total number of reflections measured 44 920, unique 13 269 (*R*_{int} = 0.0383). Data/restraints/parameters: 13269/0/620. Final *R* indices: *R*1 = 0.0388, *wR*2 = 0.0765 on data with *I* > 2σ(*I*) and *R*1 = 0.0536, *wR*2 = 0.0825 on all data, goodness-of-fit *S* = 1.094. (*R*1 = Σ||*F*_o| – |*F*_c||/Σ|*F*_o|, *wR*2 = [Σ*w*(*F*_o² – *F*_c²)²/Σ*w*(*F*_c²)²]^{1/2}, *S* = [Σ*w*(*F*_o² – *F*_c²)²/Σ(*n* – *p*)]^{1/2}); weighting scheme *w*^{–1} = σ²(*F*_o)² + (0.0144)*P*² + 3.0498*P*, *P* = [*F*_o² + 2*F*_c²]/3; largest difference peak and hole: 0.405 and –0.303 e Å^{–3}.

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Supporting Information Available: Text giving details of the X-ray crystal structure studies and tables of crystal structure determination data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compounds **2** and **3** (18 pages). Ordering information is given on any current masthead page.

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