Reactions of Group 4 Metal Cyclopentadienyl Trifluorides with a Trimeric Iminoalane

Helge Wessel, Carsten Rennekamp, Herbert W. Roesky,* Mavis L. Montero, Peter Müller, and Isabel Usón

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany

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Summary: Reaction of CpMF₃ (M = Ti, Zr) with [MeAlN(2,6-iPr₂C₆H₃)]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, Si–F, and P–F 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. 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 AlMe₃ is assumed to be the first step of activation of a polymerization catalyst when AlMe₃-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 AlMe₃ containing activated Ti–F bonds. These products are formed as intermediates in the methylation of compounds with sterically crowded titanium centers.

Herein, we report the reaction of an alumazene (1) with CpTiF₃ and η⁵-C₅H₅(SiMe₃)₂ZrF₃.

The reaction of a suspension of 1 and CpTiF₃ 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, 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. Furthermore, the molecular structures have been determined by X-ray crystallography, Figures 1 and 2.

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 AlF₂N, one MAI₂FN₂, and two MAI₂F₂N six-membered rings in a chair conformation with η⁵-bridging F and N atoms. Each aluminum atom is methyl substituted, and a 2,6-iPr₂C₆H₃-ligand binds to each nitrogen atom. The metal on top of the cage (Ti in 2, Zr in 3) binds to η⁵-C₅H₅ (2) and η⁵-C₅H₅(SiMe₃)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)) in 3.

Scheme 1

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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(1) 1.896(2).

Figure 1. X-ray structure of 2 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(1) 1.903(1).

In summary, reactions of group 4 metal cyclopendadienyl trifluorides lead to intramolecular fluorine-nitrogen exchange, activation of metal–fluorine bonds, and the formation of isosctructural adamantane-like cages. Moreover, the reported synthesis is a new route to aluminum-containing mixed group 4 amidofluorides.

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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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