Formation of [Cp$_2$Ti(μ_2-F)$_2$AlEt$_2$]$_2$ and [Cp(C$_5$H$_4$)Ti(μ_2-H)AlEt$_2$]$_2$ in the Reaction of Cp$_2$TiF$_2$ with AlEt$_3$. Structure of [Cp$_2$Ti(μ_2-F)$_2$AlEt$_2$]$_2$

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Introduction

In the past four decades organometallic titanium and zirconium chlorides, in combination with organoaluminum compounds, have been used extensively as catalysts in the polymerization of olefins.[1] Examples include the reaction of titanocene dichlorides with trialkylaluminum compounds AlR$_3$ (R = Et, Me), which lead to the interesting compounds Cp$_2$Ti(μ_2-Cl)$_2$AlEt$_2$ and Tebbe's reagent, Cp$_2$Ti(μ_2-CH$_2$)(μ_2-Cl)AlMe$_2$.[2] The corresponding fluorides of titanium and zirconium have attracted less attention to date.[3] Because of the extreme electronegativity of fluorine, the M−F bond (M = Ti, Zr, Al) is highly polar and hence also very strong. A characteristic feature of fluoride ligands, as compared to chloride substituents, is the high tendency to bridge metal centers, which leads to a variety of interesting complexes.[4] Recently it was shown that group 4 organometallic fluorides together with methylaluminoxane (MAO) as cocatalyst are active catalysts for the polymerization of ethylene and styrene.[5] Previously, we described the reaction of Cp*ZrF$_3$ with stoichiometric amounts of AlMe$_3$ as well as the facile formation of the Al$_6$Zr$_3$ cluster [(Cp*Zr)$_3$-Al$_6$Me$_8$(μ_3-CH)$_5$(μ_2-CH$_2$)$_2$] with excess AlMe$_3$.[6] The reactions of organotitanium fluorides with alkyl aluminum compounds, however, have not been reported until now. In this report, we describe our preliminary results concerning the reactions of titanocene difluoride with triethylaluminum.

Results and Discussion

Synthesis of 2 and 3. The reaction of Cp$_2$TiF$_2$ (**1**) with AlEt$_3$ in toluene in a 1:1 molar ratio at room temperature proceeds with evolution of gas and reduction of Ti(IV) to Ti(III) to yield complex **2** (eq 1). Compound **2** is blue in color and air and
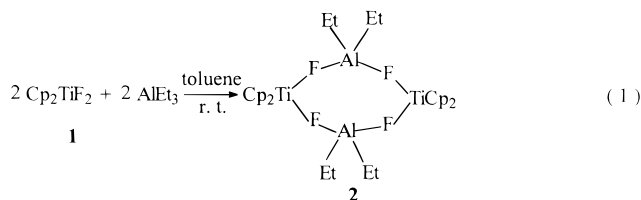
moisture sensitive and decomposes without melting above 135 °C. The mass spectrum of **2** shows the monomeric parent ion [EI-MS: *m/e* 301 (M$^+$)]. The ^{1}H and ^{19}F NMR spectra of compound **2** were recorded at room temperature. Due to the paramagnetism of the titanium(III) oxidation state,[7] the ^{1}H NMR signals are broad and unresolved. The chemical shifts resonate for the cyclopentadienyl ring at 6.3 ppm, for the methyl group at 1.34−1.23 ppm and for the methylene group at 0.95−0.78 ppm. However, no signal was observed in the ^{19}F NMR spectrum.

Moreover, if **1** is reacted with an excess of AlEt$_3$ (greater than 2 equiv) at room temperature, a purple solution develops and **3** is obtained after recrystallization from *n*-hexane (eq 2a).
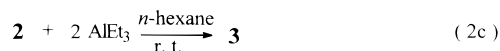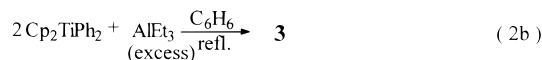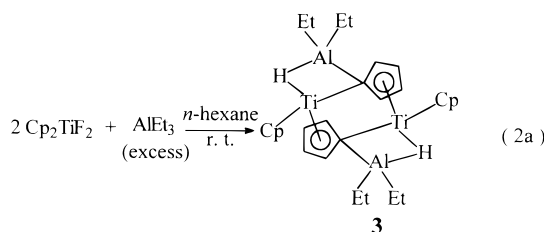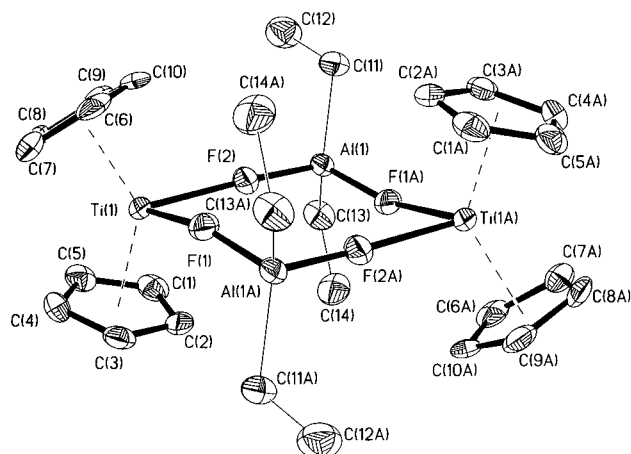

On the basis of the spectral properties of **3** in solution and an X-ray structure analysis, **3** is identical to the compound previously synthesized by Tebbe via another route (eq 2b) under more forcing conditions.[8] Alternatively, **3** can be obtained by the reaction of **2** with a slight excess of AlEt$_3$ at room temperature in yields higher than that of route 2a (eq 2c).

In the mass spectrum of **3** the highest fragment is observed at *m/e* 408 (M$^+$ − 4Et) exhibiting the correct isotope pattern. In the ^{1}H and ^{13}C NMR spectra of **3**, one signal for the protons and carbons of the C$_5$H$_5$ ring and four proton signals and five carbon signals for the C$_5$H$_4$ ring are observed, respectively. The hydrogens displaced from the rings are metal-coordinated and shifted to high field (δ −7.01). However, the X-ray structure analysis shows that compound **3** is an unsymmetrical molecule exhibiting nonequivalent ethyl groups, leading to two triplets for the protons in the ^{1}H NMR spectrum as well as two carbon signals in the ^{13}C NMR spectrum for the methyl, two multiplets for the protons, and a broad carbon signal for the methylene group.

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Figure 1. Molecular structure of [Cp$_2$Ti(μ_2-F)$_2$AlEt$_2$]$_2$.

Table 1. Crystallographic Data for [Cp$_2$Ti(μ_2-F)$_2$AlEt$_2$]$_2$

empirical formula	C$_{28}$H$_{40}$Al$_2$F$_4$Ti$_2$	formula weight	602.36
a, Å	10.901(2)	space group	$P2_1/n$ (No. 14)
b, Å	8.004(2)	T, K	133(2)
c, Å	17.812(4)	λ, Å	0.710 73
β, deg	106.10(3)	ρ_{calcd}, g cm^{-3}	1.340
V, Å^3	1493.3(5)	μ, cm^{-1}	6.34
Z	4	R1^a	0.0482
		wR2^b	0.1186

^{a} R1 $= \Sigma|F_o - F_c|/\Sigma|F_o|$. ^{b} wR2 $= [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

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

Bond Distances			
Ti(1)−F(2)	2.0956(15)	Ti(1)−F(1)	2.1063(15)
Al(1)−F(2)	1.7342(16)	Al(1)−F(1A)	1.7364(16)

Angles			
F(2)−Ti(1)−F(1)	78.53(7)	F(2)−Al(1)−F(1A)	100.18(8)
Al(1A)−F(1)−Ti(1)	160.13(9)	Al(1)−F(2)−Ti(1)	169.08(10)

Recently, we reported for the first time that Ti−F bonds can be activated using AlMe$_3$.[9] Moreover, Buchwald et al. found that the unprecedented conversion of Ti−F to Ti−H bonds with phenylsilane can be utilized in the development of highly enantioselective catalyst systems for the hydrosilylation of imines.[10] The results of this note showed that the Ti−F bonds can be easily activated using AlEt$_3$ and converted to the Ti−H bonds that are involved in the activation of the C−H bonds. Furthermore, investigations of substituted-Cp-ring titanium fluorides reacting with alkylaluminum compounds are in progress.

X-ray Crystal Structure of 2. Complex **2** (Figure 1) crystallizes as blue crystals from toluene. Crystallographic data and selected bond distances and angles are listed in Tables 1 and 2, respectively. The single-crystal X-ray structure analysis shows **2** to be the condensation product of two molecules of each of the starting materials with the concomitant loss of two ethyl groups from each aluminum. The core of complex **2** may be described as a nonplanar eight-membered ring consisting of two titanium atoms (as Cp$_2$Ti units), two aluminum atoms (as AlEt$_2$ units), and four bridging fluorine atoms. The four metal atoms and two of the fluorine atoms (F(2) and F(2A)) describe a plane (rms deviation 0.016 Å), while the other two fluorine

atoms lie 0.31 Å above and below this plane, respectively. The Cp and ethyl ligands are found both above and below the average Al$_2$F$_4$Ti$_2$ plane. Both the Ti and Al atoms have distorted tetrahedral coordination environments. The Ti−Ti distance (5.841 Å) indicates no metal−metal bond to be formed. The Ti−F (2.10 Å) and Al−F (1.73 Å) average bond distances are comparable to those in compound (Cp$_2$TiF$_2$)$_3$Al (**4**) (Ti−F 2.09 Å, Al−F 1.81 Å, average, respectively).[11] However, all F−Ti−F (78.53°), F−Al−F (100.18°), and Al−F−Ti (160.13°, 169.08°) angles in **2** are larger than those found in complex **4** (F−Ti−F (68.29°), F−Al−F (80.91°), Al−F−Ti (105.40°)).

Experimental Section

General Data. All experimental manipulations were carried out under an atmosphere of dinitrogen rigorously excluding air and moisture. Solvents were purified according to conventional procedures and were freshly distilled prior to use. Compound **1** was prepared as previously described.[12] IR spectra were recorded on a Bio-Rad FTS-7 spectrometer. Mass spectra were obtained on Finnigan MAT 8230 and Varian MAT CH5 spectrometers. Elemental analyses were performed at the analytical laboratory of the Institute of Inorganic Chemistry of Göttingen University.

NMR spectra were recorded on a Bruker AM 250 spectrometer. TMS was used as the reference for ^{1}H and ^{13}C NMR.

Synthesis of 2. To a suspension of **1** (0.432 g, 2 mmol) in toluene (30 mL) was added an equimolar amount of AlEt$_3$ (2 mL, 1.0 M solution in *n*-hexane) via syringe at room temperature. A slow gas evolution took place, and the suspension dissolved and turned into a green-blue solution. The solution was further stirred for 1 h. Then the volume of the solution was reduced slowly under vacuum (15 mL) and kept at −20 °C for 1 week. Blue crystals of **2** were obtained by filtration and washed with cold *n*-hexane. Yield: 0.38 g (63%). Anal. Calcd for C$_{14}$H$_{20}$AlF$_2$Ti: C, 55.78; H, 6.64; F, 12.62. Found: C, 55.61; H, 6.73; F, 12.40. Mp: >135 °C dec; MS (EI): *m/e* 301 [Cp$_2$TiF$_2$AlEt$_2$] (2), 272 [Cp$_2$TiF$_2$AlEt] (5), 197 [Cp$_2$TiF] (15), 178 [Cp$_2$Ti] (100). IR (Nujol) (cm^{-1}): 1305 m, 1262 m, 1022 s, 1013 s, 802 s, 722 s, 615 s.

Preparation of 3. **1** (0.864 g, 4 mmol) was suspended in *n*-hexane (50 mL), and AlEt$_3$ (10 mL, 1.0 M solution in *n*-hexane) was added dropwise over 30 min. The suspended solid dissolved, and the color of the solution changed from yellow to dark blue and finally purple. After the mixture was stirred at room temperature overnight, the solvent and volatile reaction products were removed in vacuo. The purple residue was extracted with *n*-hexane (10 mL), and dark purple crystals were obtained at −25 °C. Yield: 0.58 g (55%). Anal. Calcd for C$_{28}$H$_{40}$Al$_2$Ti$_2$: C, 63.83; H, 7.60. Found: C, 63.68; H, 7.72. Mp: >155 °C dec. MS (EI): *m/e* 408 [M$^+$ − 4Et] (100). ^{1}H NMR (C$_6$D$_6$, ppm): δ 5.06 (C$_5$H$_5$); 6.90, 5.82, 4.89, 4.24 (C$_5$H$_4$); 1.51, 1.36 (CH$_3$) (tr, J_{HH} = 8 Hz); 0.71−0.66, 0.54−0.45 (CH$_2$) (mult), metal hydride −7.01. ^{13}C NMR (C$_6$D$_6$, ppm): δ 102.2 (C$_5$H$_5$); 150.9, 132.6, 125.1, 109.9, 107.5 (C$_5$H$_4$); 10.7,10.5 (CH$_3$); 4.7 (CH$_2$).

Reaction of 2 with AlEt$_3$. **2** (0.30 g, 0.5 mmol) in *n*-hexane (30 mL) was added dropwise to an excess amount of AlEt$_3$ (1.2 mL, 1.2 mmol) using a syringe at room temperature. The color changed from light blue green to dark blue and finally purple. After removal of the volatiles in vacuo, the residue was washed with cold *n*-hexane and a dark purple solid was obtained in 65% yield (0.17 g). The solid is identical to compound **3** using MS (EI) and ^{1}H NMR for the characterization.

X-ray Structure Analysis of 2. A blue crystal (dimensions 0.4 × 0.1 × 0.1 mm^3) suitable for X-ray diffraction studies was selected. The diffraction data were collected (at 133 K) on a Siemens/Stoe/Huber four-circle diffractometer (Mo Kα λ = 0.710 73 Å) equipped with a Siemens CCD area detector. Crystallographic data: fw = 602.36, monoclinic, space group $P2_1/n$, a = 10.901(2) Å, b = 8.004(2) Å, c =

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17.812(4) Å, $\beta = 106.10(3)°$, $V = 1493.3(5)$ Å^3, $Z = 4$, $F(000) = 628$, and μ(Mo Kα) = 0.634 mm^{-1}; 17 829 measured reflections, 3031 unique ($R_{int} = 0.055$) used for the structure solution and refinement of 210 parameters with the help of 188 restraints. $R1 = \sum|F_o - Fc|/\sum|F_o| = 0.0482$ ($I > 2\sigma(I)$), $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2} = 0.1186$ (all data); minimum/maximum residual electron density $-0.623/0.486$ e Å^{-3}. The structure was solved by direct methods using the program SHELXS-90/96[13] and refined on all data by full-matrix least squares on F^2 with SHELXL-93/96.[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement in idealized positions. One of the Cp ligands was disordered, occupying two different sites, and was refined with the help of similarity restraints for bond distances, angles and displacement parameters, and rigid bond restraints on the anisotropic displacement parameters.

Supporting Information Available: Crystal data, atomic positional and thermal parameters, and selected interatomic distances and angles for complex **2** (4 pages). Ordering information is given on any current masthead page.

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