Difference in Reactivity of Cyclopentadienyltitanium Fluorides and Chlorides Using AlR_3 (R = Me, Et): Syntheses and Structures of Ti(III)−F(Cl)−Al Compounds $(\eta^5\text{-}C_5Me_5)_2Ti_2(\mu\text{-}Cl)_6Al_2Me_4$, $(\eta^5\text{-}C_5Me_5)_2Ti_2(\mu\text{-}F)_8Al_4Me_8$, and $[(\eta^5\text{-}C_5H_4Me)_2Ti(\mu\text{-}F)_2AlEt_2]_2$[†]

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Received November 9, 1998

The reaction of Cp^*TiX_3 [X = Cl (**1a**), F (**1b**), $Cp^* = \eta^5\text{-}C_5Me_5$] with an excess of $AlMe_3$ afforded the methylated products Cp^*TiCl_2Me (**2a**) and $(Cp^*TiF_2Me)(AlMe_2F)$ (**2b**), respectively, whereas under thermal conditions the reduced titanium species $Cp^*{}_2Ti_2(\mu\text{-}Cl)_6Al_2Me_4$ (**3**) and $Cp^*{}_2Ti_2(\mu\text{-}F)_8Al_4Me_8$ (**4**) were obtained in moderate yields. The reduction of Ti(IV) to Ti(III) is observed when Cp'_2TiF_2 ($Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4Me$, Cp*) and Cp^*TiF_3 are treated with $AlEt_3$, leading to $[Cp'_2Ti(\mu\text{-}F)_2AlEt_2]_2$ [$Cp' = \eta^5\text{-}C_5H_5$ (**5**), $\eta^5\text{-}C_5H_4Me$ (**6**), Cp* (**7**)] and $Cp^*{}_2Ti_2(\mu\text{-}F)_8Al_4Et_8$ (**8**), respectively. The crystal structures of complexes **3**, **4**, and **6** have been determined by X-ray single-crystal structure analyses. The core of structure **3** is described as a chair conformation. The environments of the Al and Ti atoms in **3** are distorted tetrahedral and pseudo square pyramidal, respectively. The single-crystal structure analysis of **4** shows an octahedral metal core for Al_4Ti_2 with the Ti atoms occupying trans positions. The core of complex **6** is a nonplanar eight-membered ring consisting of two titanium atoms, two aluminum atoms, and four bridging fluorine atoms.

Introduction

Metallocene complexes of titanium and zirconium ($CpTiCl_3$, Cp^*TiCl_3, and $CpZrCl_3$ ($Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$)), with methylaluminoxane (MAO) as cocatalyst are known as very active systems for the polymerization of olefins.[1] The investigation of the titanium system by ESR identified the presence of trivalent titanium. The reduction of titanium atoms was interpreted by the formation of a hydride species which is involved in the alkylation of titanium(IV) chloride.[1a] Obviously MAO plays a crucial role in the formation of the active catalytic site, of which the oxidation state may exert a significant influence on the catalyst performance.[2] Attempts to isolate well-defined reduced titanium species from $CpTiCl_3$ and Cp^*TiCl_3/MAO systems were unsuccessful so far.[1a,2d] In this connection, however, it is known that cyclopentadienyltitanium chlorides can be easily reduced from Ti(IV) to Ti(III) species using $AlEt_3$.[2a,3] For example the reaction of Cp_2TiCl_2 and $Cp'TiCl_3$ (Cp′ = Cp, Cp*) with $AlEt_3$ or Et_2AlCl resulted in the formation of compounds $Cp_2Ti(\mu\text{-}Cl)_2AlEtX$[3a,b] and $Cp'Ti[(\mu\text{-}Cl)_2AlEt_2][(\mu\text{-}Cl)_2AlEtX]$[3c] (X = Et or Cl). In fact, only a few reductive reactions of cyclopentadienyltitanium chlorides with $AlMe_3$ have been investigated, and very seldom well-defined products were isolated.[4] In addition, the products of the reaction of cyclopentadienyltitanium fluorides with MAO have recently been found to exhibit a high catalytic activity for the polymerization of olefins, especially for that of styrene in a syndiotactic manner. The activity of the fluorides is improved by a factor of 30 when compared to the corresponding chlorides.[2d,5] However, the reactions of organotitanium fluorides with alkylaluminum have attracted less attention to date. There has been a long debate about the interaction of the alkylaluminum with the transition metal center and its ligands with regard to the mechanism of this homogeneous catalysis for the polymerization of olefins.[1d,2] Therefore, obtaining well-defined Ti(Zr)−Al complexes by treating organometallics of group 4 halides with alkylaluminum has

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[†] Dedicated to Professor C. N. R. Rao on the occasion of his 65th birthday.

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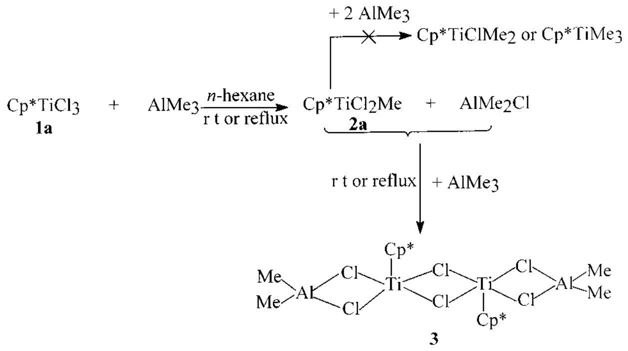
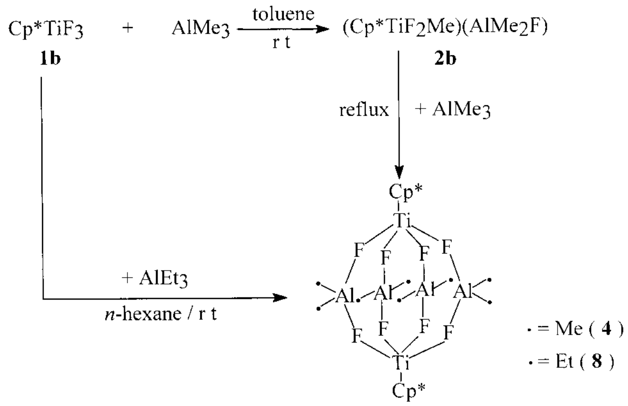
10.1021/om9809163 CCC: $18.00 © 1999 American Chemical Society
Publication on Web 04/09/1999

Scheme 1



Scheme 2



become one of our research interests. Previously, we have shown that reaction of Cp^*MF_3 (M = Zr, Hf) with $AlMe_3$ in a 1:1 molar ratio leads to a selective exchange of fluorine atoms for methyl groups, and the byproduct $AlMe_2F$ acts as a ligand bridging two transition metals.[6a] Furthermore, activation of C−H bonds is observed when an excess of $AlMe_3$ is reacted with Cp^*MF_3 along with the formation of the fluorine-free cluster $[(Cp^*M)_3Al_6Me_8(\mu_3\text{-}CH)_5(\mu_2\text{-}CH_2)_2]$.[6] The oxidation state of the metal (M = Zr, Hf), however, remains unchanged. The analogous reaction of the corresponding titanium halides Cp^*TiX_3 (X = Cl, F) with $AlMe_3$, however, has not been fully studied. Herein, we describe the results of the reduction of Cp^*TiX_3 by $AlMe_3$ and the investigation on the reduction of Cp^*TiF_3, $Cp^*_2TiF_2$, and $(\eta^5\text{-}C_5H_4Me)_2TiF_2$ using $AlEt_3$ to complete our earlier preliminary results concerning the reaction of Cp_2TiF_2 with $AlEt_3$.[7]

Results and Discussion

Preparation of 3 and 4. It is known that Cp^*TiCl_3 (**1a**) can be easily methylated by using 1 equiv of $AlMe_3$ to yield Cp^*TiCl_2Me (**2a**) in *n*-hexane.[8] Surprisingly, reacting **1a** with 2 equiv or an excess of $AlMe_3$ did not yield the expected product $Cp^*TiClMe_2$ or Cp^*TiMe_3; instead compound **2a** in a 60% yield and a dark green crystalline product identified as $Cp^*_2Ti_2(\mu\text{-}Cl)_6Al_2Me_4$ (**3**) in low yield (10%) are isolated. This suggests that further methylation of **2a** by using an excess of $AlMe_3$ is not possible (Scheme 1). Heating the reaction mixture resulted in improving the yield of **3** to 25%. Compound **3** was isolated from the reaction mixture at room temperature and compound **2a** at −20 °C. Compound **3** is air and moisture sensitive. It decomposes without melting at 200 °C. The most intense peaks in the mass spectrum of **3** are observed at *m*/*e* 508 ($M^+ - 2AlMe_2Cl$, 40%) and 253 (Cp^*TiCl_2, 100%). The ^1H NMR spectrum of **3** was recorded at room temperature and exhibits a sharp signal (1.75 ppm) for Cp*-ring protons and a broad signal at relatively higher field (−0.88 ppm) for Al−Me groups.

Attempts to methylate the corresponding fluoride Cp^*TiF_3 (**1b**) using $AlMe_3$ were unsuccessful. In fact, when **1b** was reacted with various molar ratios of $AlMe_3$ at room temperature, a yellow oil-like product was formed after removal of the volatiles. The ^1H and ^{19}F NMR spectra show a mixture of products including Cp^*TiF_2Me and $AlMe_2F$, which aggregate to form an adduct identified as $(Cp^*TiF_2Me)(AlMe_2F)$ (**2b**). When **1b** was heated under reflux with 2 equiv of $AlMe_3$ in toluene for 24 h, compound $Cp^*_2Ti_2(\mu\text{-}F)_8Al_4Me_8$ (**4**) resulted in a 30% yield as green crystals (Scheme 2).

Compound **4** is very air and moisture sensitive. It decomposes at 230 °C without melting. The most intense peak in the mass spectrum of **4** is at *m*/*e* 202 (Cp^*TiF, 100%) and the molecular ion fragment is at *m*/*e* 731 ($M^+ - Me$, 10%). The ^1H NMR spectrum of **4** at room temperature exhibits broad and unresolved signals probably due to the paramagnetic interaction between Ti(III) and ^{19}F atoms.[9] The protons of the pentamethylcyclopentadienyl ring resonate at 2.10 ppm, and the protons of the Al−Me at relatively higher field (−0.44 to −0.62 ppm). The ^{19}F NMR spectrum of **4** is silent. The reduction of Ti(IV) to Ti(III) in compounds **3** and **4** is evidenced by the greenish color of the products. This observation is in agreement with the solid-state structure showing titanium atoms having oxidation state 3. In this connection, Atwood has recently provided an example of such behavior. Reacting $CpTiCl_3$ with $AlMe_3$ in the presence of 18-crown-6 resulted in the formation of $[CpTiCl\cdot 18\text{-crown-}6]^+[AlCl_2Me_2]^-$.[4b] In this study the reaction of **1a** and **1b** with $AlMe_3$ leads to the formation of **3** and **4**, respectively, where $AlMe_2X$ (X = Cl, F) is coordinating to the Ti(III) atoms through the halide atoms forming a four-membered ring in **3** and an eight-membered ring in **4** (Schemes 1 and 2). Surprisingly, it was not possible to obtain compound **4** at room temperature similar to **3**. This is probably due to the higher reduction potential of **1b** compared to **1a**.

As it has been shown so far, only monomethylation of **1a** and **1b** has been observed, yielding **2a** and **2b**, respectively. This obviously indicates that **2a** and **2b** are possible intermediates for the formation of **3** and **4**, respectively. However, the reduction mechanism (**2a** and **2b** to **3** and **4**) is still unclear. A plausible explanation might be given similar to the system (Cp_2TiCl_2/$AlMe_3$ or Cp^*TiCl_3/MAO) involving bridging moieties such as methene or hydrides.[1a,4a]

Preparation of 6, 7, and 8. The reduction of Ti(IV) to Ti(III) using $AlEt_3$ via the β-hydrogen transfer

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Scheme 3

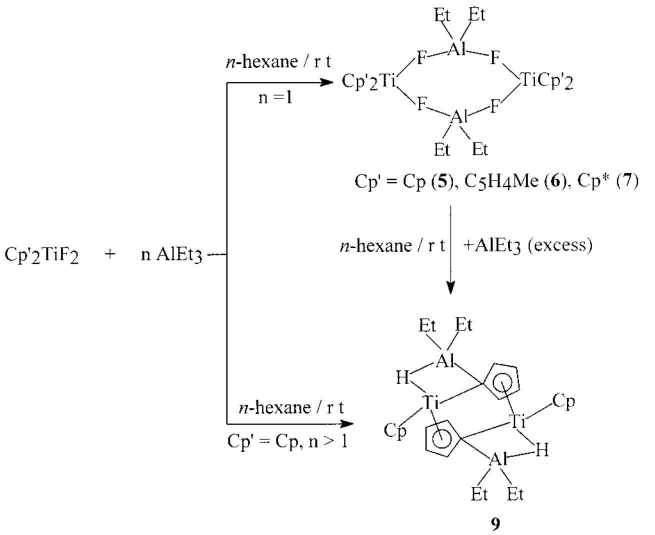

Table 1. Crystallographic Data for 3, 4, and 6

	3	4	6
chemical formula	$C_{24}H_{42}Al_2Cl_6Ti_2$	$C_{28}H_{54}Al_4F_8Ti_2$	$C_{32}H_{48}Al_2F_4Ti_2$
fw	693.04	746.43	658.46
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 12)	$C2/c$ (No. 12)
T, °C	−123	−140	−140
λ, Å	0.710 73	0.710 73	0.710 73
a, Å	9.852(2)	17.143(3)	24.340(4)
b, Å	15.099(3)	15.078(3)	7.916(1)
c, Å	11.767(2)	15.257(3)	20.128(4)
β, deg	112.09(1)	97.61(3)	121.518(2)
V, Å^3	1621.9(6)	3909.1(1)	3306(1)
Z	2	4	4
ρ_{calcd}, g cm^{-3}	1.419	1.268	1.323
μ, mm^{-1}	1.054	0.553	0.579
$R1^a$	0.0520	0.0355	0.0477
$wR2^b$	0.1408	0.0979	0.1178

[a] $R1 = \sum|F_o - F_c|/\sum|F_o|$ $[I > 2\sigma(I)]$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$ (all data).

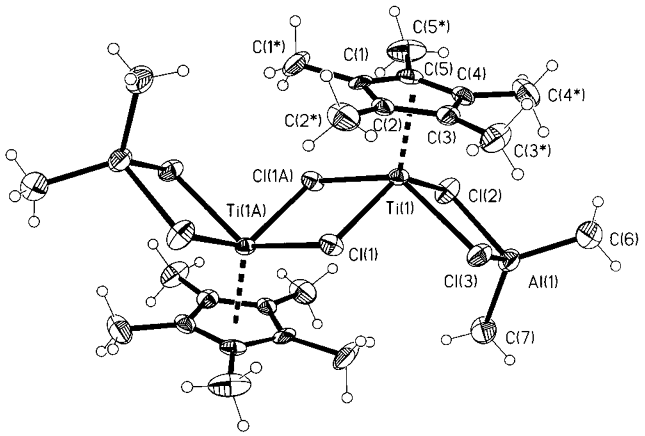

Figure 1. Molecular structure of $(\eta^5\text{-}C_5Me_5)_2Ti_2(\mu\text{-}Cl)_6Al_2Me_4$ (**3**).

mechanism is demonstrable.[2] This explains the facile reduction of $CpTiCl_3$, Cp^*TiCl_3, and Cp_2TiCl_2 using $AlEt_3$ in equimolar ratio leading to the formation of the complexes $Cp'Ti(\mu\text{-}Cl)_4Al_2Et_4$[3c] (Cp′ = Cp, Cp*) and $Cp_2Ti(\mu\text{-}Cl)_2AlEt_2$, respectively.[3a] However, the reduction of cyclopentadienyltitanium fluorides using $AlEt_3$ is still in the beginning stages. We have recently reported our preliminary results on the reduction of Cp_2TiF_2 with $AlEt_3$, which resulted in the formation of $[Cp_2Ti(\mu\text{-}F)_2AlEt_2]_2$ (**5**).[7] The F atoms in **5** exhibit completely different coordination modes when compared to the corresponding chlorides.[3a,5b] The reaction of $(\eta^5\text{-}C_5H_4Me)_2TiF_2$, $Cp^*_2TiF_2$, and Cp^*TiF_3 with $AlEt_3$ in a 1:1 molar ratio at room temperature leads to the formation of blue crystals for $[(\eta^5\text{-}C_5H_4Me)_2Ti(\mu\text{-}F)_2AlEt_2]_2$ (**6**) and $[Cp^*_2Ti(\mu\text{-}F)_2AlEt_2]_2$ (**7**) (Scheme 3) and green crystals for $Cp^*_2Ti_2(\mu\text{-}F)_8Al_4Et_8$ (**8**) (Scheme 2) in moderate yields at low temperature (−20 °C). Compounds **5**−**8** are air and moisture sensitive. They have been characterized by MS, IR, and elemental analyses. The signals in the ^1H and ^{19}F NMR spectra of **5**−**8** are broad and unresolved. Compounds **5**, **6**, and **7** decompose at 135, 120, and 105 °C, respectively. The decreasing of the decomposition point might be possibly related to the substituents on the Cp-ring. A similar observation has been made for compound **8** (190 °C) and compound **4** (230 °C), where **8** has ethyl and **4** has methyl substituents. The mass spectra of **6** and **7** indicate on the basis of their molecular ion peaks that they are monomeric in the gaseous state [EI-MS: m/e 300 ($M^+ - Et$, 8%), 225 ($(C_5H_4Me)_2TiF$, 100%) for **6**, and 412 ($M^+ - Et$, 10%), 337 (Cp^*_2TiF, 60%), and 317 (Cp^*_2Ti, 100%) for **7**]. The similar behavior of **6** and **7** in the gaseous state might suggest that compound **7** has a structure similar to **6**. The mass spectrum of **8** exhibits fragment ions [EI-MS: m/e 828 ($M^+ - Et$, 8%), 202 (Cp^*TiF, 100%)] which are similar to those observed in compound **4**.

Furthermore, when $(\eta^5\text{-}C_5H_4Me)_2TiF_2$, $Cp^*_2TiF_2$, and Cp^*TiF_3 are allowed to react with more than 2 equiv of $AlEt_3$, new deep red crystals are isolated. The identification of these species is in progress. We have shown that the reaction of Cp_2TiF_2 with an excess of $AlEt_3$ gave a stable hydride compound $[Cp(C_5H_4)Ti(\mu\text{-}H)AlEt_2]_2$ (**9**)[7] in good yield (Scheme 3). This indicates that the reduction of cyclopentadienyltitanium fluorides from Ti(IV) to Ti(III) using $AlEt_3$ is more facile when compared to $AlMe_3$. In addition it is reasonable to propose that the formation of the titanium(III) hydride species occurs through a β-hydrogen transfer process. Although the reduction of Cp^*TiF_3 using $AlMe_3$ is still ambiguous, it might occur in a similar fashion through the α-hydrogen transfer process,[4a,10] or alternatively it might involve free radicals since the reduction is promoted under thermal conditions.

In summary, we have shown that the monoalkylation of Cp^*TiX_3 (X = Cl and F) by $AlMe_3$ is the first step in the reaction followed by the reduction of Ti(IV) to Ti(III). The formation of the reduced chloride species **3** is more facile compared to that of the fluoride **4** due to the lower reduction potential of **1a** than that of **1b**. The resulting aggregates of Ti(III)−X−methylaluminum complexes are well-characterized. Finally the reduction of titanium fluorides is facile by involving the β-hydrogen transfer process. Some of the intermediates and the final Ti(III)−X−ethylaluminum products were isolated and characterized.

Structural Aspects. The solid-state structures of **3**, **4**, and **6** were determined by single-crystal X-ray structure analysis (Table 1). Compound **3** crystallizes as dark green crystals from n-hexane. The molecular structure of **3** is shown in Figure 1. Selected bond distances and angles are listed in Table 2. Compound **3** is a tetra-

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 3

Ti(1)−Cl(1)	2.463(1)	Ti(1)−Cl(1A)	2.482(1)
Ti(1)−Cl(2)	2.554(1)	Ti(1)−Cl(3)	2.544(1)
Ti(1A)−Cl(1)	2.482(1)	Al(1)−Cl(2)	2.264(2)
Al(1)−Cl(3)	2.264(2)	Al(1)−C(6)	1.941(5)
Al(1)−C(7)	1.945(5)		
Cl(1)−Ti(1)−Cl(1A)	79.8(4)	Cl(1)−Ti(1)−Cl(3)	83.2(5)
Cl(1)−Ti(1)−Cl(2)	131.9(5)	Cl(1A)−Ti(1)−Cl(2)	80.8(4)
Cl(1A)−Ti(1)−Cl(3)	132.0(5)	Cl(3)−Ti(1)−Cl(2)	78.0(4)
Ti(1)−Cl(1)−Ti(1A)	100.2(4)	Cl(2)−Al(1)−Cl(3)	90.2(7)
Al(1)−Cl(3)−Ti(1)	96.0(6)	Al(1)−Cl(2)−Ti(1)	95.7(6)
C(6)−Al(1)−Cl(2)	111.2(2)	C(6)−Al(1)−C(7)	120.1(2)
C(6)−Al(1)−Cl(3)	111.9(2)	C(7)−Al(1)−Cl(2)	109.3(2)
C(7)−Al(1)−Cl(3)	110.0(2)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 4

Ti(1)−F(1)	2.066(6)	Ti(1)−F(2)	2.052(7)
Ti(1) −F(3)	2.058(7)	Ti(1)−F(4)	2.074(6)
Al(1)−F(4)	1.759(5)	Al(2)−F(1)	1.756(6)
Al(3)−F(2)	1.748(7)	Al(2A)−F(3)	1.771(7)
F(2)−Ti(1)−F(3)	80.2(2)	F(2)−Ti(1)−F(1)	79.9(2)
F(1)−Ti(1)−F(3)	128.9(3)	F(2)−Ti(1)−F(4)	129.0(3)
F(4)−Ti(1)−F(3)	78.0(2)	F(1) −Ti(1)−F(4)	79.1(2)
F(4)−Al(1)−F(4A)	96.6(4)	F(1)−Al(2)−F(3A)	95.4(3)
F(2)−Al(3)−F(2A)	94.7(5)	F(4)−Al(1)−F(4A)	96.6(4)
Al(2)−F(1)−Ti(1)	146.7(3)	Al(3)−F(2)−Ti(1)	147.7(4)
Al(2A)−F(3)−Ti(1)	145.8(4)	Al(1)−F(4)−Ti(1)	145.9(3)

nuclear complex in which two [Cp*TiCl(μ-Cl)$_2$AlMe$_2$] moieties are bridged by the Cl atoms in an asymmetric arrangement. Compound **3** is a centrosymmetric molecule with the center of inversion in the center of the Ti(μ-Cl)$_2$Ti plane and with the 2-fold axis going through the bridging Cl(1) and Cl(1A). The four-membered Al(1)(μ-Cl)$_2$Ti(1), Ti(1)(μ-Cl)$_2$Ti(1A), and Al(1A)(μ-Cl)$_2$Ti(1A) rings are planar with small deviations from planarity (rms deviation 0.02, 0.01, and 0.02 Å). The core of complex **3** is described as a chair conformation consisting of three four-membered rings. The Al atoms have a distorted tetrahedral coordination sphere, while the environment of the Ti atoms is pseudo square pyramidal. The average bond distance of Ti−Cl−Ti (Ti−Cl, 2.47 Å) is slightly shorter than that of Ti−Cl−Al (Ti−Cl, 2.54 Å). Both of them are longer than those in compound [CpTiCl·18-crown-6][AlCl$_2$Me$_2$] (Ti−Cl, 2.34 Å).[4b] The Al−Cl (2.26 Å) and Al−C (1.94 Å) average bond distances are comparable to those in compound Cp$_2$Ti(μ-Cl)$_2$AlEt$_2$ (Al−Cl, 2.5 Å, Al−C 1.94 Å). The average Ti−Cl−Ti (100°) angle is slightly larger than that of Al−Cl−Ti (95°). While the Cl−Al−Cl (90°) angle is larger than the Cl−Ti−Cl (79°) one.

Green single crystals of compound **4** are obtained from toluene. The X-ray single-crystal structure analysis shows **4** to crystallize in the monoclinic space group *C*2/*c* with half a molecule in the asymmetric unit. The other half is generated by the 2-fold axis through Al(1) and Al(3). The selected bond distances and angles are listed in Table 3. The core of structure **4** consists of a Al$_4$Ti$_2$ octahedron with the two Ti atoms occupying trans positions. The edges of the octahedron are μ-bridged by eight F atoms, which are somewhat displaced from their ideal geometrical positions; thus, a Al$_4$F$_8$Ti$_2$ cage is formed (Figure 2). This cage has a noncrystallographic 4-fold axis through both the Ti atoms and no mirror plane through the four Al atoms. A Cp* ligand completes the coordination sphere of Ti, which is a square pyramid (Cp*TiF$_4$). The tetrahedral coordination sphere of Al is completed by two methyl groups; 50% of the cage in the crystal of **4** is disordered about the Ti(1)−Ti(1A) pseudo axis by 45°. It is interesting to note that the C atoms of the Al−methyl groups are not directly involved in the disorder; only the Al atoms which are connected to them change and the methyl H atoms are disordered. In compound **4** the average Ti−F bond distance is 2.06 Å (average Al−F 1.76 Å) and is comparable to those determined in compound **6** (Ti−F 2.11 Å and Al−F 1.74 Å, average) and [Cp$_2$Ti(μ-F)$_2$]$_3$Al[11] (Ti−F 2.09 Å, Al−F 1.81 Å, average), whereas the average F−Al−F (95.5°) angle is smaller than that in **6** (103°). It is interesting to note that there are two types of F−Ti−F angles in **4** (average 80.1° and 128.9°). Both are larger than that in **6** (average 77°).

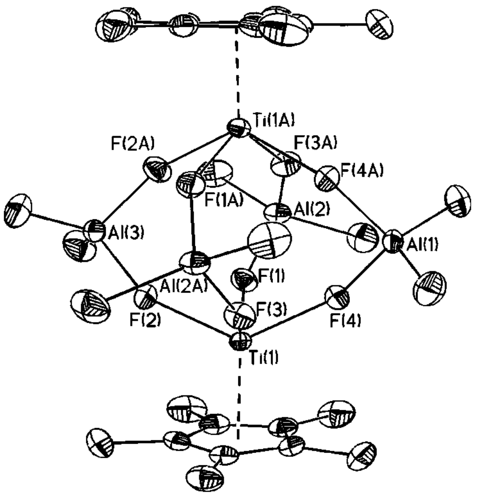

Figure 2. Molecular structure of (η^5-C$_5$Me$_5$)$_2$Ti$_2$(μ-F)$_8$Al$_4$Me$_8$ (**4**).

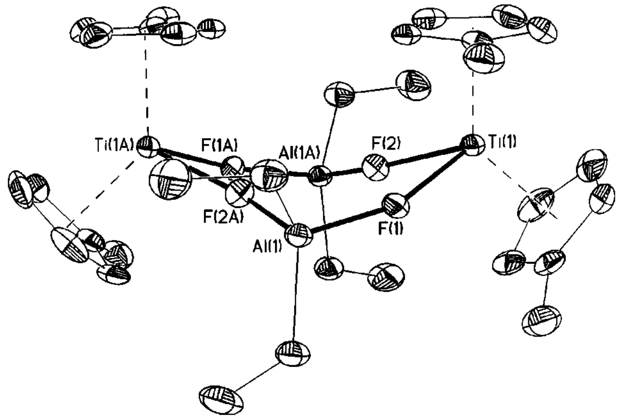

Figure 3. Molecular structure of [(η^5-C$_5$H$_4$Me)$_2$Ti(μ-F)$_2$AlEt$_2$]$_2$ (**6**).

Complex **6** crystallizes as blue crystals from toluene. The single-crystal X-ray structure analysis shows **6** consists of two molecules of each of the starting materials with the loss of one ethyl group from each aluminum (Figure 3). Selected bond distances and angles are listed in Table 4. The core of complex **6** is a nonplanar eight-membered ring consisting of two titanium atoms (as

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Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 6

Ti(1)−F(1)	2.119(2)	Ti(1)−F(2)	2.113(2)
Al(1)−F(1)	1.749(2)	Al(1)−F(2A)	1.741(2)
Al(1A)−F(2)	1.741(2)	Al(1)−C(11)	1.974(4)
Al(1)−C(13)	1.965(4)		
F(2)−Ti(1)−F(1)	76.68(7)	F(2A)−Al(1)−F(1)	102.9(1)
Al(1A)−F(2)−Ti(1)	162.9(1)	Al(1)−F(1)−Ti(1)	154.0(1)
F(1)−Al(1)−C(11)	108.2(1)	F(1)−Al(1)−C(13)	108.0(1)
F(2A)−Al(1)−C(11)	106.0(1)	F(2A)−Al(1)−C(13)	110.0(1)
C(13)−Al(1)−C(11)	120.4(2)		

Cp_2Ti units), two aluminum atoms (as $AlEt_2$ units), and four bridging fluorine atoms, respectively. Both the Ti and Al atoms have distorted tetrahedral coordination spheres. In compound **5** four of the metal atoms and two of the fluorine atoms form a plane, whereas in compound **6** the corresponding four metal atoms and two of the fluorine atoms (F(2) and F(2A)) are far away from planarity. Instead, the $Al_2F_4Ti_2$ core of **6** shows a boatlike conformation (Figure 3). The Ti−Ti distance (5.865 Å) indicates that no metal−metal interaction is found in compound **6**. The Ti−F (2.11 Å) and Al−F (1.74 Å) average bond distances are comparable with those in compound **5** (Ti−F 2.09 Å, Al−F 1.73 Å, average respectively).[7] In **6** the average angles of F−Al−F (102.8°), F−Ti−F (76.7°), and Al−F−Ti (153.9° and 162.9°) are comparable with those in **5** (F−Al−F 100.1°, F−Ti−F 78.5°, and Al−F−Ti 160.1°, 169.1°).

Experimental Section

General Data. All experimental manipulations were carried out under an atmosphere of dinitrogen rigorously excluding air and moisture using Schlenk techniques. Solvents were purified according to conventional procedures and were freshly distilled prior to use. Compounds **1a**,[12] **1b**,[13] (η^5-$C_5H_4Me)_2TiF_2$,[14] and $Cp^*{}_2TiF_2$[14] were prepared as previously described. $AlMe_3$ and $AlEt_3$ were purchased from Aldrich. 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, University of Göttingen. NMR spectra were recorded on a Bruker AM 250 spectrometer.

Synthesis of $Cp^*{}_2Ti_2(\mu\text{-}Cl)_6Al_2Me_4$ (3). To a suspension of Cp^*TiCl_3 (0.58 g, 2 mmol) in *n*-hexane (50 mL) was added $AlMe_3$ (2.5 mL, 5 mmol, 2.0 M in toluene) by a syringe at room temperature. A clear greenish-yellow solution was obtained upon stirring the reaction mixture overnight at ambient temperature. After reducing the volume to about 15 mL, dark green crystals of compound **3** could be obtained in 10% (0.07 g) yield at room temperature along with an orange-yellow crystalline compound **2a** obtained in a 60% (0.32 g) yield by cooling at −10 °C. When the green solution was heated under reflux for 12 h, a brown oil-like product deposited from a brown-green solution on the bottom of the flask upon cooling the flask to room temperature. The dark green solution was transferred by a syringe and then concentrated to about 15 mL. The dark green crystals of **3** could be isolated in a 25% yield (0.17 g) at ambient temperature along with orange crystals of **2a**, which were obtained in a 40% (0.21 g) yield by cooling at −10 °C. Mp: >200 °C (dec). EI-MS *m/e* (%): 508 ($M^+ - 2AlMe_2Cl$, 40), 253 (Cp^*TiCl_2, 100). ^1H NMR (C_6D_6) δ (ppm): 1.75 (30 H, Cp*), −0.88 (12 H, Al−Me). IR (Nujol) (cm^{-1}): 1278 m, 1162 m, 1054 s, 902 s, 850 s, 741 s, 665 s, 533 s. Anal. Calcd for $C_{24}H_{42}Al_2Cl_6Ti_2$: C, 41.5; H, 6.1; Cl, 30.7. Found: C, 42.1; H, 6.3; Cl, 30.2.

Synthesis of $Cp^*{}_2Ti_2(\mu\text{-}F)_8Al_4Me_8$ (4). To a solution of **1b** (0.48 g, 2 mmol) in toluene (40 mL) was added $AlMe_3$ (2 mL, 4 mmol, 2 M solution in toluene) dropwise using a syringe. The reaction mixture was allowed to stir at room temperature to give an orange-yellow solution, which turned to brown-yellow upon heating under reflux overnight. After filtration and partial removal of the solvent in vacuo, compound **4** was obtained in the form of green crystals in a yield of 30% (0.15 g) based on **1b**. Mp: >230 °C (dec). EI-MS *m/e* (%): 713 ($M^+ - Me$, 10), 655 ($M^+ - Me - AlMe_2F$, 15), 221 (Cp^*TiF_2, 90), 202 (Cp^*TiF, 100). IR (Nujol) (cm^{-1}): 2002 w, 1945 w, 1592 m, 1488 m, 1429 s, 1220 s, 1146 s, 1078 s, 988 s, 940 s, 755 s, 716 s, 695 s, 553 s, 530 s. Anal. Calcd for $C_{28}H_{54}Al_4F_8Ti_2$: C, 32.2; H, 7.2; F, 20.4. Found: C, 32.8; H, 7.3; F, 20.1.

Synthesis of $[(\eta^5\text{-}C_5H_4Me)_2Ti(\mu\text{-}F)_2AlEt_2]_2$ (6). To a suspension of (η^5-$C_5H_4Me)_2TiF_2$ (0.49 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 a syringe at room temperature, causing a slow gas evolution. 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 **6** were obtained in 37% yield (0.11 g) by filtration and washed with cold *n*-hexane (5 mL). Mp: >120 °C (dec). EI-MS *m/e* (%): 300 ($M^+ - Et$, 8), 225 ($(C_5H_4Me)_2TiF$, 100). IR (Nujol) (cm^{-1}): 1036 m, 984 m, 950 m, 859 m, 799 s, 722 s, 649 s. Anal. Calcd for $C_{32}H_{48}Al_2F_4Ti_2$: C, 58.4; H, 7.3; F, 11.5. Found: C, 57.9; H, 7.3; F, 11.0.

Synthesis of $[Cp^*{}_2Ti(\mu\text{-}F)_2AlEt_2]_2$ (7). To a suspension of $Cp^*{}_2TiF_2$ (0.71 g, 2 mmol) in *n*-hexane (30 mL) was added an equimolar amount of $AlEt_3$ (2 mL, 1.0 M solution in *n*-hexane) via a syringe at room temperature. The mixture was further stirred overnight. Reducing the solvent to about 10 mL and cooling the solution at −20 °C for 1 week produced air-sensitive, blue crystals of **7** in 35% yield (0.3 g). Mp: >105 °C (dec). EI-MS *m/e* (%): 412 ($M^+ - Et$, 10), 337 ($Cp^*{}_2TiF$, 60), and 317 ($Cp^*{}_2Ti$, 100). IR (Nujol) (cm^{-1}): 1261 m, 1101 s, 1059 s, 1024 s, 799 m, 722 s, 640 s. Anal. Calcd for $C_{48}H_{80}Al_2F_4Ti_2$: C, 65.3; H, 9.1; F, 8.6. Found: C, 65.7; H, 9.4; F, 8.2.

Synthesis of $Cp^*{}_2Ti_2(\mu\text{-}F)_8Al_4Et_8$ (8). To a suspension of **1b** (0.48 g, 2 mmol) in *n*-hexane (30 mL) was added $AlEt_3$ (2 mL, 1.0 M solution in *n*-hexane) dropwise via a syringe at room temperature. The color changed from orange to dark red at once. The mixture was further stirred for 2 h to give a brown-yellow solution. After removal of the volatiles, the residue was dissolved in *n*-hexane (10 mL) and cooled to −20 °C to give green crystals of compound **8** in a 27% (0.15 g) yield. Mp: >190 °C (dec). EI-MS *m/e* (%): 828 ($M^+ - Et$, 8), 799 ($M^+ - 2Et$, 25), 221 (Cp^*TiF_2, 90), 202 (Cp^*TiF, 100). IR (Nujol) (cm^{-1}): 1108 m, 1098 m, 1024 m, 721 s, 660 s, 636 s, 612 s. Anal. Calcd for $C_{36}H_{70}Al_4F_8Ti_2$: C, 50.3; H, 8.2; F, 17.7. Found: C, 50.8; H, 8.3; F, 17.9.

X-ray Crystallography. Single crystals of compounds **3**, **4**, and **6** suitable for X-ray diffraction studies were selected and mounted on a glass fiber in a rapidly cooled perfluoropolyether.[15] The diffraction data of **3** were collected on a Stoe-Siemens-AED2 four-circle diffractometer at 150(2) K, using Mo Kα radiation ($\lambda = 0.710\,73$ Å), performing $2\theta/\omega$ scans. The data for **4** and **6** 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 ($\lambda = 0.710\,73$ Å), performing φ and ω scans. The structures were solved by direct methods using the program SHELXS-97[16] and refined against F^2 on all data by full-matrix least-squares with

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SHELXL-97.[17] 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 disorder in **4** and the Cp* ring 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 occupancies for the disordered parts were refined and eventually set at the convergence value.

Acknowledgment. This work was supported by the Göttinger Akademie der Wissenschaften, the Witco GmbH, and the Deutsche Forschungsgemeinschaft. M.A.S. thanks the Alexander von Humboldt Foundation, Bonn, for a research fellowship.

Supporting Information Available: Listings of X-ray crystallographic data, atomic coordinates and equivalent isotropic displacement parameters for all non-hydrogen atoms, hydrogen positional and thermal parameters, anisotropic displacement parameters, and bond distances and angles for the structures of **3**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9809163

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