Reactions of Organotitanoxane Fluorides with AlR_3 (R = Me, Et, CH_2Ph) and Me_3SiCl: X-ray Crystal Structures of $[C_5Me_5Ti(\mu\text{-}O)]_4F[(\mu\text{-}F)AlMe_3]_3$, $[C_5Me_5Ti(\mu\text{-}O)]_4F_3[(\mu\text{-}F)Al(CH_2Ph)_3]$, $[C_5Me_5Ti(\mu\text{-}O)Et]_4$, and $(C_5Me_5)_4Ti_4O_5X_2$ (X = Cl and F)[†]

Peihua Yu, Thomas Pape, Isabel Usón, Musa A. Said, Herbert W. Roesky,*
Mavis L. Montero, Hans-Georg Schmidt, and Alojz Demsar

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

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A new pentamethylcyclopentadienyl titanoxane fluoride $(C_5Me_5)_4Ti_4O_5F_2$ (**1b**) has been synthesized from $(C_5Me_5)_4Ti_4O_5Cl_2$ using the fluorinating reagent Me_3SnF. The fluorination of organotitanoxane chlorides proceeds via a proposed intermediate similar to the four-membered ring $Ti(\mu\text{-}Cl)(\mu\text{-}F)Sn$ and the bridged $Ti(\mu\text{-}F)ClSnMe_3$ species. The reactions of **1b** and $[C_5Me_5Ti(\mu\text{-}O)F]_4$ with AlR_3 (R = Me, Et, CH_2Ph) afforded the thermally unstable adducts $[C_5Me_5Ti(\mu\text{-}O)]_4F_{4-n}[(\mu\text{-}F)AlR_3]_n$ ($n = 1-4$), which proceed with selective exchange of fluorine atoms for alkyl groups to give an eight-membered alkylated ring compound $[C_5Me_5Ti(\mu\text{-}O)R]_4$. The reactions of **1b** and $[C_5Me_5Ti(\mu\text{-}O)F]_4$ with Me_3SiCl result in exchange of fluorine for chlorine atoms. Moreover, using an excess of Me_3SiCl leads to a novel oxygen−chlorine exchange reaction to give $C_5Me_5TiCl_3$. The crystal structures of complexes $(C_5Me_5)_4Ti_4O_5X_2$ (X = Cl (**1a**), F (**1b**)), $[C_5Me_5Ti(\mu\text{-}O)]_4F[(\mu\text{-}F)AlMe_3]_3$ (**2b**), $[C_5Me_5Ti(\mu\text{-}O)]_4F_3[(\mu\text{-}F)Al(CH_2Ph)_3]$ (**3a**), and $[C_5Me_5Ti(\mu\text{-}O)Et]_4$ (**4**) have been determined by X-ray diffraction studies. Both chlorides and fluorides in **1a** and **1b**, respectively, are oriented to the exo position of their "butterfly" structures. The bond lengths of the terminal fluorines ($Ti-F_t$) in compounds **2b** and **3a** are discussed with respect to the deviation from the bond lengths of the bridging fluorines ($Ti-F_b-Al$). The structure of **4** displays a nonplanar Ti_4O_4 ring conformation as shown in **2b** and **3a**.

Introduction

Organometallic fluorides are of special interest since M−F bonds play a key role in the cleavage and formation of C−F bonds, i.e., C−F bond activation.[1] The presence of open coordination sites facilitates the first step of any catalytic cycle which involves substrate coordination at the metal center.[2] Therefore, as part of our research efforts in this complementary line, we are interested in using the organotitanoxane fluorides as starting materials.[3] In fact organotitanoxane fluorides have attracted less attention to date due to the absence of a general synthetic method. For example, to the best of our knowledge, the compound $[C_5Me_5Ti(\mu\text{-}O)F]_4$ is the only confirmed organotitanoxane fluoride structure which was prepared using two methods: (a) by treating $C_5Me_5TiF_3$ with $(Bu_3Sn)_2O$ and (b) by reacting $[C_5Me_5Ti(\mu\text{-}O)Cl]_3$ with Me_3SnF.[4,5a] The latter has become a versatile method particularly in the conversion of group 4−6 and also main group chlorides to the corresponding organometallic fluorides.[5]

Reactions of $C_5Me_5TiF_3$ with alkali metals and their fluorides lead to a variety of Ti−F−alkali metal clusters,[1a,6] and in general the reactions of $C_5Me_5MF_3$ with AlR_3 (M = Zr, Hf; R = alkyl) in different stoichiometries result in the activation of C−H bonds as well as the formation of zirconium− and hafnium−aluminum clusters $[(C_5Me_5M)_3Al_6Me_8(\mu_3\text{-}CH)_5(\mu_2\text{-}CH_2)_2]$.[7] As a potential new type of olefin polymerization catalyst, however, organotitanoxane compounds have attracted less attention to date. Few investigations have been carried out on the alkylation reactions of organotitanoxane halides with alkylaluminum compounds, which are of great interest in establishing the highly reactive homogeneous group 4 metallocene/alumoxane type of olefin polymerization catalysts.[8]

[†] Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday.

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Table 1. Crystallographic Data for **1a,b, 2b, 3a,** and **4**

	1a	**1b**	**2b**	**3a**	**4**
formula	$C_{40}H_{60}Cl_2O_5Ti_4$	$C_{40}H_{60}F_2O_5Ti_4$	$C_{49}H_{87}Al_3F_4O_4Ti_4$	$C_{61}H_{81}AlF_4O_4Ti_4$	$C_{48}H_{80}O_4Ti_4$
fw	882.51	850.48	1087.55	1173.11	912.89
cryst syst	monoclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$C2/m$ (No. 12)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	18.404(4)	10.872(2)	22.593(5)	14.625(3)	22.985(5)
b (Å)	16.524(3)	11.892(3)	14.073(3)	14.798(3)	22.254(5)
c (Å)	14.893(3)	17.678(4)	23.134(5)	17.948(4)	23.307(5)
α (deg)	90	86.04(3)	90	67.630(10)	90
β (deg)	98.87(3)	86.68(1)	107.23(3)	81.610(10)	113.57(3)
γ(deg)	90	68.11(1)	90	89.85(2)	90
V (Å^3)	4475.1(2)	2114.7(8)	7025(2)	3547.6(13)	10927(4)
Z	4	2	8	2	8
ρ_{calcd} (g cm^{-3})	1.374	1.336	1.204	1.270	1.214
T (°C)	−73	−70	−20	−140	−140
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ (cm^{-1})	8.49	7.76	5.27	5.03	6.04
R1^a	0.0396	0.0362	0.0524	0.0577	0.0485
wR2^b	0.1113	0.0988	0.1377	0.1368	0.1112

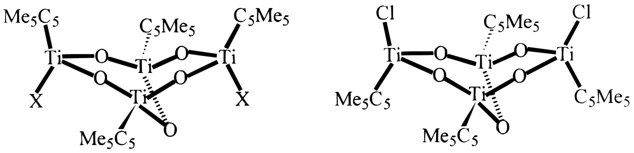
[a] $R1 = \sum|F_o - F_c|/\sum F_o|$ $[I > 2\sigma(I)]$. [b] $wR2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$ (all data).

Recently we have reported on preliminary results where we have shown that the Ti−F bonds of $[C_5Me_5Ti(\mu\text{-}O)F]_4$ can be activated using $AlMe_3$ to form a thermally unstable, almost linear-bridged Ti−F−Al adduct, $[C_5Me_5Ti(\mu\text{-}O)(\mu\text{-}F)AlMe_3]_4$.[9] This example provides intriguing insight into the oxygen or fluorine abstraction from $[C_5Me_5Ti(\mu\text{-}O)F]_4$ by using various alkylaluminum compounds to obtain the unknown eight-membered alkylated ring compound $[C_5Me_5Ti(\mu\text{-}O)R]_4$. Such reactions are interesting because they are expected to throw light on the C−H bond activation similar to those observed in several corresponding six-membered-ring compounds $[C_5Me_5Ti(\mu\text{-}O)R]_3$.[10] It should be mentioned here that despite intensive research on methylaluminoxane (MAO), which is the most effective cocatalyst in olefin polymerization,[11] MAO has not been fully characterized and has the undesirable property of exhibiting variable composition.[12]

We report herein the detailed preparation and the first step in the fluorination reaction of a new organotitanoxane fluoride $(C_5Me_5)_4Ti_4O_5F_2$ (**1b**), the chlorine−fluorine and oxygen−chlorine exchange reactions of organotitanoxane fluoride when treated with Me_3SiCl, the reactions of the compound $[C_5Me_5Ti(\mu\text{-}O)F]_4$ and **1b** with AlR_3, and the formation of a novel alkylated compound $[C_5Me_5Ti(\mu\text{-}O)Et]_4$ along with the single-crystal X-ray structures of $(C_5Me_5)_4Ti_4O_5X_2$ [X = Cl (**1a**), F (**1b**)], $[C_5Me_5Ti(\mu\text{-}O)]_4F_{4-n}[(\mu\text{-}F)AlR_3]_n$ [R = Me, $n = 3$ (**2b**); R = CH_2Ph, $n = 1$ (**3a**)], and $[C_5Me_5Ti(\mu\text{-}O)Et]_4$ (**4**) (Table 1).

Results and Discussion

Synthesis and Structural Aspects of Organotitanoxane Fluoride and Chloride. Although the first eight-membered-ring organotitanoxane fluoride $[C_5Me_5Ti(\mu\text{-}O)F]_4$ can be prepared in high yield by reaction of $[C_5Me_5Ti(\mu\text{-}O)Cl]_3$ with Me_3SnF (eq 1),[5a] the fluorine−chlorine exchange mechanism pathway is still unclear in the ring expansion from a six- to an eight-membered ring. Furthermore, attempts to isolate $[C_5Me_5TiF_2]_2(\mu\text{-}O)$ by the same method were unsuccessful (eq 2); only $[C_5Me_5Ti(\mu\text{-}O)F]_4$ was detected along with $C_5Me_5TiF_3$.



A [X = Cl(**1a**), F(**1b**)] B

Figure 1. (A) View of the molecular structure of **1a** and **1b**. (B) Klemperer's proposition for complex **1a**.

$$4[C_5Me_5Ti(\mu\text{-}O)Cl]_3 + 12Me_3SnF \xrightarrow[\text{room temp}]{\text{toluene}} 3[C_5Me_5Ti(\mu\text{-}O)F]_4 + 12Me_3SnCl \quad (1)$$

$$4[C_5Me_5TiCl_2]_2(\mu\text{-}O) + 16Me_3SnF \xrightarrow[\text{room temp}]{\text{toluene}} [C_5Me_5Ti(\mu\text{-}O)F]_4 + 4C_5Me_5TiF_3 + 16Me_3SnCl \quad (2)$$

We have chosen $(C_5Me_5)_4Ti_4O_5Cl_2$ (**1a**), which has a rigid conformation, as a starting material. The structure of **1a** has not been confirmed by X-ray crystallography to date.[13] The reaction of **1a** in a 1:2 molar ratio with Me_3SnF in toluene results in the formation of a pale yellow crystalline compound which does not melt below 360 °C. The compound was characterized by elemental analysis, mass spectrometry, and ^1H and ^{19}F NMR spectroscopy, which are in agreement with $(C_5Me_5)_4Ti_4O_5F_2$ (**1b**). Both **1a** and **1b** have been established by X-ray diffraction studies and exhibit a "butterfly" structure (Figures 1A, 2, and 3).

The Cl(F) bound to the "terminal" titanium atoms are oriented to the exo position rather than to the endo one as proposed by Klemperer for **1a** (Figure 1B).[14] The average Ti−O bond lengths are 1.840 and 1.830 Å in **1a** and **1b**, respectively. The O−Ti−Cl(F) angles fall in the range of 103.3−104.6°. The Ti−Cl bond distance in **1a** (average 2.28 Å) is longer than those

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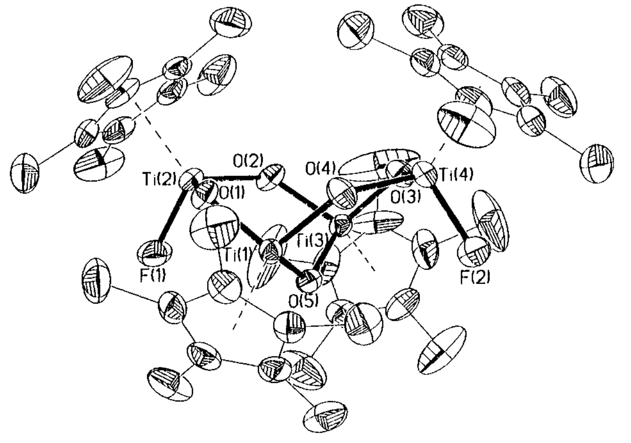


Figure 2. Molecular structure of $(C_5Me_5)_4Ti_4O_5F_2$ (**1b**).

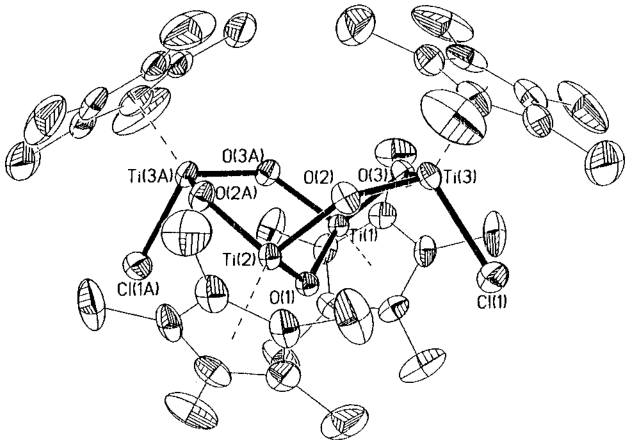


Figure 3. Molecular structure of $(C_5Me_5)_4Ti_4O_5Cl_2$ (**1a**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1a**

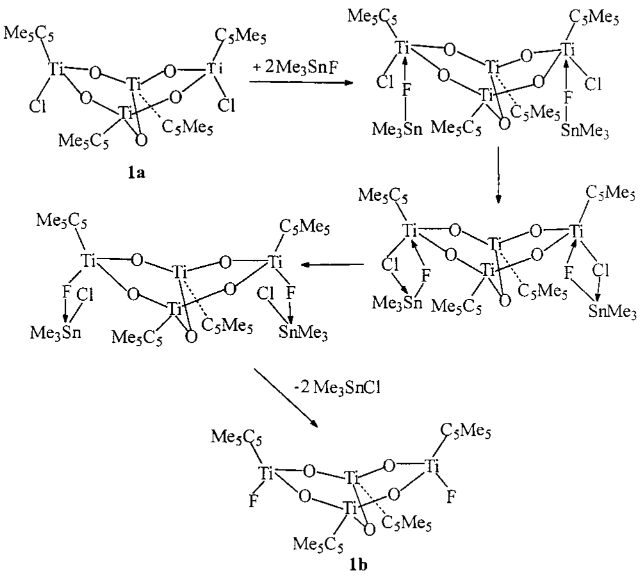
Ti(1)−O(1)	1.8392(18)	Ti(1)−O(3)	1.8594(14)
Ti(2)−O(1)	1.8361(19)	Ti(2)−O(2)	1.8579(15)
Ti(3)−O(2)	1.8110(14)	Ti(3)−O(3)	1.8111(14)
Ti(1)−O(3A)	1.8594(14)	Ti(2)−O(2A)	2.368(3)
Ti(3)−Cl(1)	2.2847(7)		
O(1)−Ti(1)−O(3A)	102.05(6)	O(1)−Ti(1)−O(3)	102.05(6)
O(3)−Ti(1)−O(3A)	105.07(9)	O(1)−Ti(2)−O(2)	101.86(6)
O(1)−Ti(2)−O(2A)	101.86(6)	O(2)−Ti(2)−O(2A)	105.09(10)
O(2)−Ti(3)−O(3)	105.10(7)	O(2)−Ti(3)−Cl(1)	103.43(6)
O(3)−Ti(3)−Cl(1)	103.32(5)	Ti(1)−O(3)−Ti(3)	127.57(8)
Ti(1)−O(1)−Ti(2)	122.52(10)	Ti(2)−O(2)−Ti(3)	127.84(8)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1b**

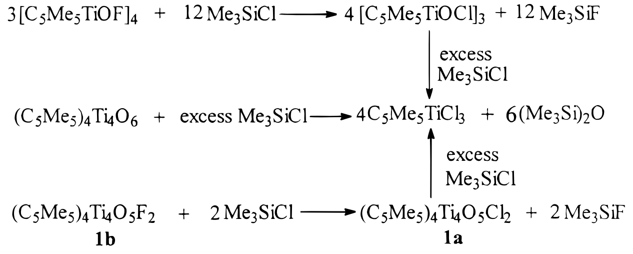
Ti(1)−O(1)	1.842(2)	Ti(1)−O(4)	1.8404(19)
Ti(1)−O(5)	1.834(2)	Ti(2)−O(1)	1.8192(19)
Ti(2)−O(2)	1.8146(19)	Ti(3)−O(3)	1.8434(19)
Ti(3)−O(2)	1.848(2)	Ti(3)−O(5)	1.8405(18)
Ti(4)−O(3)	1.8186(19)	Ti(4)−O(4)	1.8256(19)
Ti(2)−F(1)	1.8247(18)	Ti(4)−F(2)	1.8125(19)
O(5)−Ti(1)−O(4)	102.19(9)	O(5)−Ti(1)−O(1)	101.96(8)
O(4)−Ti(1)−O(1)	105.46(9)	O(2)−Ti(2)−O(1)	105.57(9)
O(3)−Ti(4)−O(4)	105.44(9)	O(5)−Ti(3)−O(3)	101.90(8)
O(5)−Ti(3)−O(2)	101.57(8)	O(3)−Ti(3)−O(2)	105.41(10)
Ti(2)−O(1)−Ti(1)	126.69(11)	Ti(2)−O(2)−Ti(3)	126.92(10)
Ti(4)−O(3)−Ti(3)	126.98(10)	Ti(4)−O(4)−Ti(1)	126.68(11)
Ti(1)−O(5)−Ti(3)	123.02(10)	F(2)−Ti(4)−O(3)	103.68(10)
F(2)−Ti(4)−O(4)	103.80(10)		

of Ti−F (average 1.83 Å) in **1b** and $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (average 1.845 Å)[4b] (Tables 2 and 3).

Scheme 1



Scheme 2



The fact that the chlorine atoms are oriented to the outer direction indicates that the fluorinating reagent Me_3SnF attacks the “terminal” titanium atoms of **1a** from the outer direction leading to **1b** and keeping the same conformation by chlorine−fluorine exchange via a proposed intermediate similar to the four-membered-ring $Ti(\mu\text{-}F)(\mu\text{-}Cl)Sn$ and $Ti(\mu\text{-}F)ClSnMe_3$ species (Scheme 1). In a previous paper we showed that a corresponding zirconium compound keeping the $ClSnMe_3$ coordinated to the zirconium center via $Zr(\mu\text{-}F)ClSnMe_3$ could be isolated.[5b] Therefore, it is likely that the reactions in eqs 1 and 2 proceed via the rearrangement of the ring to afford the thermodynamically more stable compound $[C_5Me_5Ti(\mu\text{-}O)F]_4$.

The chlorine−fluorine exchange reactions have been reported in connection with the preparation of silyhydrazine ring systems and mixed fluoro−chloro derivatives of group 4 elements, using Me_3SiCl as an exchange reagent.[15] We have also found that not only the fluorine atoms but also the oxygen atoms in the organotitanoxane fluoride can be replaced by chlorine atoms when treated with an excess of Me_3SiCl. When the compounds $[C_5Me_5Ti(\mu\text{-}O)F]_4$ and **1b** were allowed to react with stoichiometric amounts of Me_3SiCl in toluene, $[C_5Me_5TiOCl]_3$ and **1a** were formed. However, when $[C_5Me_5Ti(\mu\text{-}O)F]_4$, **1a**, **1b**, $[C_5Me_5TiOCl]_3$, or $(C_5Me_5)_4Ti_4O_6$ was reacted with an excess of Me_3SiCl, the quantitative formation of $C_5Me_5TiCl_3$ resulted (Scheme 2). The driving force of these reactions is attributed to the formation of the very strong Si−F and Si−O bonds in Me_3SiF and $(Me_3Si)_2O$.

It is worth mentioning here that the oxygen−chlorine exchange reaction has recently become useful for developing

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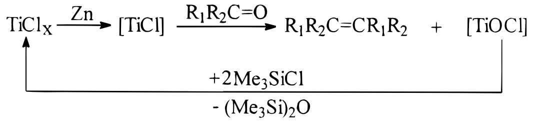
Scheme 3



carbonyl coupling reactions (McMurry reaction)[16] by using low-valent titanium catalysts which can be obtained by the reduction of $TiCl_x$ ($x = 3, 4$). The latter can be recovered directly from titanium oxides or oxychlorides treated with Me_3SiCl (Scheme 3).[17]

Alkylaluminum Adducts of Organotitanoxane Fluorides and Structural Aspects. Substitution reactions can be carried out using organotitanoxane chlorides. $[C_5Me_5Ti(\mu\text{-}O)Cl]_3$ was partially or completely alkylated by using stoichiometric amounts of the corresponding organolithium or Grignard reagent to afford a series of trinuclear complexes $[C_5Me_5Ti(\mu\text{-}O)]_3Cl_nR_{3-n}$ ($n = 0, 1, 2$).[10]

Our initial attempts to alkylate the organotitanoxane fluoride $[C_5Me_5Ti(\mu\text{-}O)F]_4$ using LiMe in a 1:4 molar ratio gave a pale yellow solid very soluble in *n*-hexane, which decomposes without melting at 340 °C. The highest fragment observed in the EI-MS was *m/e* 872 (M^+), which corresponds to $[C_5Me_5Ti(\mu\text{-}O)F]_4$. The ^1H NMR spectrum exhibits two different types of signals (δ 1.94 (C_5Me_5) and 1.29 (LiMe) ppm). The ^{19}F NMR is shifted from a sharp signal for $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (64.6 ppm) to a broad one (−203.8 ppm). This implies the formation of stable Ti−F−Li bridged complexes which can only be formulated as $[C_5Me_5Ti(\mu\text{-}O)(\mu\text{-}F)]_4[LiMe]_x$ ($x = 1{-}4$) since the elemental analysis could not assign the value of *x*. Attempts to obtain a single crystal of this product to determine the molecular structure were unsuccessful. Subsequently, we investigated the reaction of $[C_5Me_5Ti(\mu\text{-}O)F]_4$ with $AlMe_3$ in a 1:4 molar ratio in toluene at −20 °C. A bright red solution formed soon after mixing, from which red crystals of $[C_5Me_5Ti(\mu\text{-}O)(\mu\text{-}F)AlMe_3]_4$ (**2a**) were obtained (Scheme 4).[9] The ^{19}F NMR experiment in toluene-d_8 at −20 °C has shown that the signal of the starting material $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (δ 64.6 ppm) disappeared within ca. 20 min and was replaced by two sharp signals (intensity 1:1) at high field (δ −132.6, −136.5 ppm) with respect to $CFCl_3$. This indicates that the four terminal fluorines are coordinated to $AlMe_3$ and the eight-membered ring Ti_4O_4 becomes nonplanar, as already confirmed by the crystal structure analyses in our earlier report.[9] Moreover, it was found that compound **2a** slowly decomposes at −10 °C, leading to an orange product, which has been confirmed as a new compound, $[C_5Me_5Ti(\mu\text{-}O)]_4F[(\mu\text{-}F)AlMe_3]_3$ (**2b**) (Figure 4), by means of X-ray crystallography.

It was possible to synthesize **2b** by treating $[C_5Me_5Ti(\mu\text{-}O)F]_4$ with $AlMe_3$ in a 1:3 molar ratio in toluene at −10 °C (Scheme 4). The ^{19}F NMR experiment at −10 °C showed that the original signal (δ 64.6 ppm) is replaced by three signals (intensity 2:1:1) (δ −135.0, −130.5, 100.8 ppm), which is consistent with the structure containing three bridging $Ti{-}F_b{-}Al$ bonds and one terminal $Ti{-}F_t$ bond. The X-ray structure analyses shows that the terminal $Ti{-}F_t$ bond length (1.823 Å) is shorter than those in the bridging position (average $Ti{-}F_b$ 1.958Å and $Al{-}F_b$ 1.884 Å). The bond distances of the bridging fluorines are comparable with the corresponding distances in compound **2a** (average $Ti{-}F_b$ 1.959 Å and $Al{-}F_b$ 1.896 Å),[9] while the $Ti{-}F_b{-}Al$ bond angle on one side of the ring Ti_4O_4 [Ti(3)−F(3)−Al(3) 173.7°] is slightly different from that on the other side [Ti(2)−F(2)−Al(2) 177.9°, Ti(4)−F(4)−Al(4) 175.4°] (Table 4).

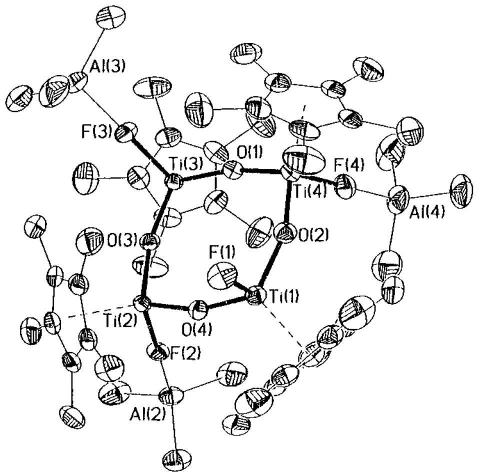


Figure 4. Molecular structure of $[C_5Me_5Ti(\mu\text{-}O)]_4F[(\mu\text{-}F)AlMe_3]_3$ (**2b**).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **2b**

Ti(1)−F(1)	1.823(3)	Ti(2)−F(2)	1.959(2)
Ti(3)−F(3)	1.963(2)	Ti(4)−F(4)	1.953(3)
Ti(1)−O(2)	1.849(3)	Ti(1)−O(4)	1.844(3)
Ti(2)−O(3)	1.840(3)	Ti(2)−O(4)	1.795(3)
Ti(3)−O(3)	1.815(3)	Ti(3)−O(1)	1.824(3)
Ti(4)−O(1)	1.827(3)	Ti(4)−O(2)	1.790(3)
Al(2)−F(2)	1.879(3)	Al(3)−F(3)	1.892(3)
Al(4)−F(4)	1.882(3)		
Al(2)−F(2)−Ti(2)	177.94(15)	Al(3)−F(3)−Ti(3)	173.72(16)
Al(4)−F(4)−Ti(4)	175.43(18)	F(1)−Ti(1)−O(2)	104.62(13)
F(1)−Ti(1)−O(4)	103.32(13)	F(3)−Ti(3)−O(1)	104.01(12)
F(3)−Ti(3)−O(3)	105.47(12)	F(4)−Ti(4)−O(1)	102.93(13)
F(4)−Ti(4)−O(2)	102.88(13)	O(4)−Ti(1)−O(2)	104.51(13)
O(3)−Ti(3)−O(1)	105.21(13)	O(2)−Ti(4)−O(1)	106.29(13)
Ti(3)−O(1)−Ti(4)	165.60(17)	Ti(1)−O(2)−Ti(4)	161.79(18)
Ti(3)−O(3)−Ti(2)	162.47(17)	Ti(2)−O(4)−Ti(1)	162.77(17)

Crystals of both **2a** and **2b** are unstable and decompose quickly at room temperature even under nitrogen atmosphere to afford an orange yellow solid, which has been characterized by ^1H and ^{19}F NMR spetroscopy and hence formulated as $[C_5Me_5Ti(\mu\text{-}O)]_4F_2[(\mu\text{-}F)AlMe_3]_2$ (**2c**) (Scheme 4). Compound **2c** was synthesized independently by reacting $[C_5Me_5Ti(\mu\text{-}O)F]_4$ with 2 molar equiv of $AlMe_3$. The ^1H NMR of **2c** demonstrates the presence of two different signals for C_5Me_5 and another for $AlMe_3$, while its ^{19}F NMR shows one signal at low field (δ 95.4 ppm, with respect to $CFCl_3$) for the terminal fluorine and another at high field (δ −113.1 ppm) for the bridging fluorine. Dissolving **2c** in THF leads to the starting material $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (Scheme 4) without adduct formation.

Attempts to obtain a suitable single crystal of **2c** for X-ray analysis have been unsuccessful so far. It is interesting to note that reacting $[C_5Me_5Ti(\mu\text{-}O)F]_4$ with only 1 molar equiv of $AlMe_3$ proceeds differently, to give a mixture of the starting material and **2c**, and not the expected product $[C_5Me_5Ti(\mu\text{-}O)]_4F_3[(\mu\text{-}F)AlMe_3]$. That is possibly attributed to the smaller steric hindrance of methyl groups in $AlMe_3$. Hence, when $[C_5Me_5Ti(\mu\text{-}O)F]_4$ was allowed to react with stoichiometric amounts of AlR_3 having more bulky R groups, the formation of the alkylaluminum adducts $[C_5Me_5Ti(\mu\text{-}O)]_4F_3[(\mu\text{-}F)AlR_3]$ [R = CH_2Ph (**3a**), Et (**3b**)] became much more facile (Scheme 5).

The low stability of complexes **3a** and **3b** was confirmed by the absence of the molecular peaks in their mass spectra. The MS contains only the starting material $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (*m/e*

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(16) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513.

(17) Fürstner, A.; Hupperts, A. *J. Am. Chem. Soc.* **1995**, *117*, 4468.

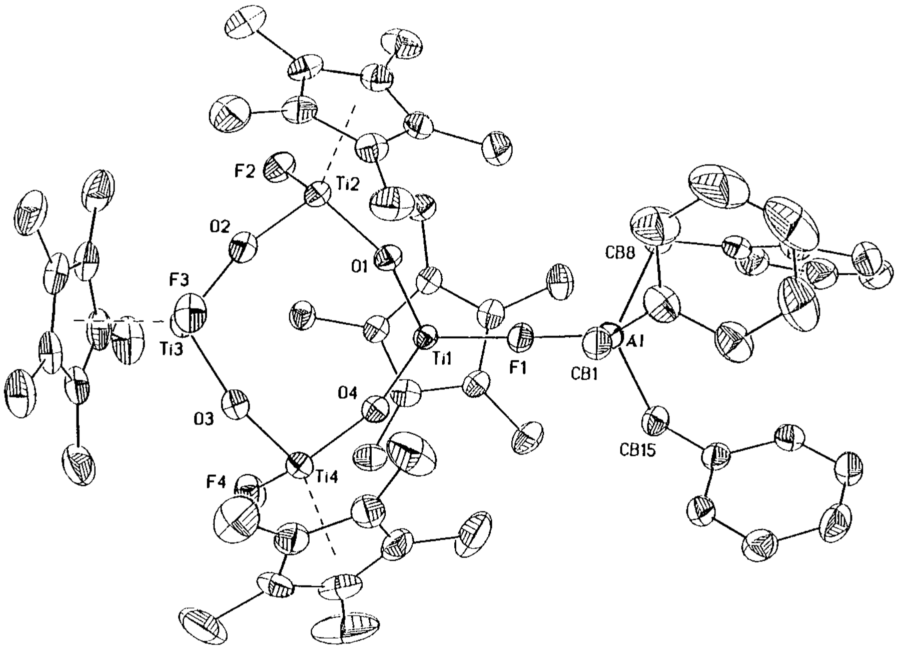
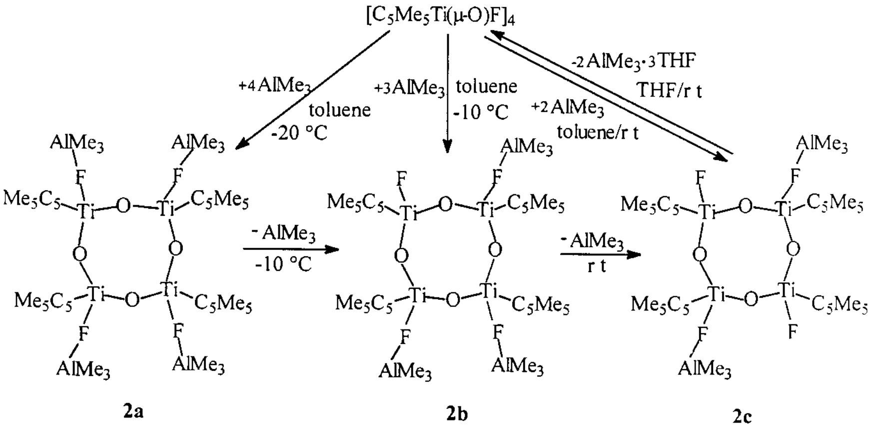


Figure 5. Molecular structure of $[C_5Me_5Ti(\mu\text{-}O)]_4F_3[(\mu\text{-}F)Al(CH_2Ph)_3]$ (**3a**).

Scheme 4



Scheme 5

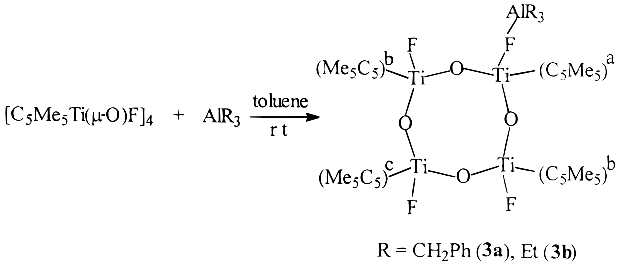


Table 5. Selected Bond Lengths (Å) and Angles (deg) for **3a**

Ti(1)−F(1)	1.982(2)	Ti(2)−F(2)	1.825(2)
Ti(3)−F(3)	1.853(2)	Ti(4)−F(4)	1.817(2)
Al−F(1)	1.838(2)	Ti(1)−O(1)	1.796(2)
Ti(1)−O(4)	1.796(2)	Ti(2)−O(1)	1.843(2)
Ti(2)−O(2)	1.807(3)	Ti(3)−O(2)	1.815(3)
Ti(3)−O(3)	1.816(3)	Ti(4)−O(3)	1.808(3)
Ti(4)−O(4)	1.848(2)	Al−(CB1)	1.998(4)
Al−C(B15)	1.994(4)	Al−(CB8)	1.995(4)
Ti(1)−F(1)−Al	178.16(13)	F(1)−Ti(1)−O(1)	101.01(10)
F(1)−Ti(1)−O(4)	104.85(10)	F(2)−Ti(2)−O(1)	104.12(10)
F(2)−Ti(2)−O(2)	103.21(11)	F(3)−Ti(3)−O(3)	103.56(11)
F(3)−Ti(3)−O(2)	104.09(11)	F(4)−Ti(4)−O(3)	102.59(11)
F(4)−Ti(4)−O(4)	105.93(11)	O(1)−Ti(1)−O(4)	105.76(11)
O(2)−Ti(2)−O(1)	106.23(11)	O(3)−Ti(3)−O(2)	104.42(11)
O(4)−Ti(4)−O(3)	106.30(11)	Ti(1)−O(1)−Ti(2)	159.49(15)
Ti(2)−O(2)−Ti(3)	165.46(15)	Ti(4)−O(3)−Ti(3)	163.09(16)
Ti(1)−O(4)−Ti(4)	162.36(15)	F(1)−Al−C(B1)	104.46(13)
F(1)−Al−C(B8)	107.11(14)	F(1)−Al−C(B15)	101.29(13)

872). The complexes were characterized by ^1H and ^{19}F NMR spectroscopy to show three different types of C_5Me_5 groups [$(C_5Me_5)^a$, $(C_5Me_5)^b$, and $(C_5Me_5)^c$ (see Scheme 5)] and a series of signals in ^{19}F NMR which is consistent with two different types of terminal fluorines and one bridging fluorine. The X-ray analysis of compound **3a** confirms (Figure 5) the structure suggested by NMR spectroscopy and shows nearly linear bridging of $Ti-F_b-Al$ (average $Ti-F_b$ 1.982 Å, $Al-F_b$ 1.838 Å, and $Ti-F_b-Al$ 178.16°); this is slightly different from the bridging in compound **2a** (average $Ti-F_b$ 1.959 Å, $Al-F_b$ 1.896 Å, and $Ti-F_b-Al$ 175.7°) and in compound **2b** (average $Ti-F_b$ 1.958 Å, $Al-F_b$ 1.884 Å, and $Ti-F_b\text{-}Al$ 175.3°). The terminal fluorine $Ti-F_t$ bond (1.853 Å) on the opposite side of the bridging $Ti-F_b-Al$ fluorine is longer than the adjacent ones (average 1.821 Å) (Table 5).

The thermal decomposition of $[C_5Me_5Ti(\mu\text{-}O)]_4F_{4-n}[(\mu\text{-}F)AlMe_3]_n$ ($n = 2-4$) does not afford the corresponding methylated compounds $[C_5Me_5Ti(\mu\text{-}O)]_4F_{4-n}Me_n$; however, the mass

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **4**

Ti(1A)−O(1A)	1.824(2)	Ti(2A)−O(1A)	1.824(2)
Ti(1A)-O(4A)	1.8236(19)	Ti(2A)-O(2A)	1.8236(19)
Ti(3A)-O(2A)	1.8300(19)	Ti(3A)-O(3A)	1.838(2)
Ti(4A)-O(3A)	1.824(2)	Ti(4A)-O(4A)	1.8263(19)
Ti(1A)-C(1EA)	2.140(3)	Ti(2A)-C(3EA)	2.143(3)
Ti(3A)-C(5EA)	2.127(3)	Ti(4A)-C(7EA)	2.161(3)
C(1EA)-C(2EA)	1.469(3)	C(3EA)-C(4EA)	1.489(3)
C(5EA)-C(6EA)	1.479(3)	C(7EA)-C(8EA)	1.483(3)
O(1A)-Ti(1A)-O(4A)	107.96(9)	O(1A)-Ti(1A)-C(1EA)	95.92(10)
O(4A)-Ti(1A)-C(1EA)	100.82(10)	O(1A)-Ti(2A)-O(2A)	108.78(9)
O(1A)-Ti(2A)-C(3EA)	97.76(10)	O(2A)-Ti(2A)-C(3EA)	100.00(10)
O(2A)-Ti(3A)-O(3A)	108.92(9)	O(2A)-Ti(3A)-C(5EA)	99.38(11)
O(3A)-Ti(3A)-C(5EA)	100.02(11)	O(3A)-Ti(4A)-O(4A)	108.57(9)
O(3A)-Ti(4A)-C(7EA)	99.73(9)	O(4A)-Ti(4A)-C(7EA)	98.14(9)
Ti(1A)-O(1A)-Ti(2A)	161.48(11)	Ti(2A)-O(2A)-Ti(3A)	160.05(11)
Ti(4A)-O(3A)-Ti(3A)	160.28(11)	Ti(1A)-O(4A)-Ti(4A)	161.44(11)

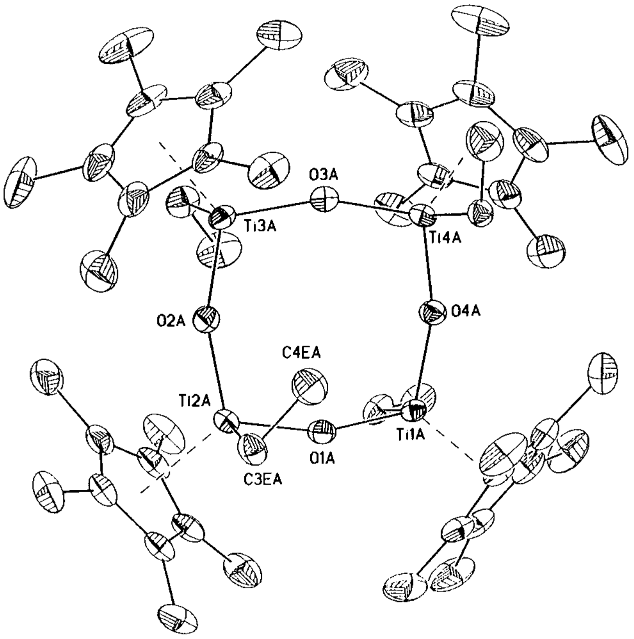
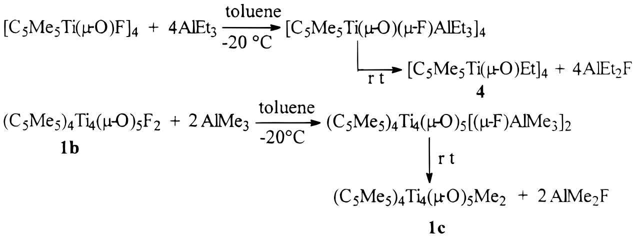


Figure 6. Molecular structure of $[C_5Me_5Ti(\mu\text{-}O)Et]_4$ (**4**).

Scheme 6



spectra reveal that the decomposition of **2a**, **2b**, and **2c** leads to a mixture of products containing fluorine atoms and methyl groups: MS *m/e* 845 $[C_5Me_5Ti(\mu\text{-}O)]_4FMe_2$ and *m/e* 849 $[C_5Me_5Ti(\mu\text{-}O)]_4F_2Me$, respectively. This may suggest that the formation of a cationic organotitanoxane fluoride occurs by partial abstraction of the fluorine from $[C_5Me_5Ti(\mu\text{-}O)F]_4$ under thermal conditions similar to that observed by Coville and coworkers.[18] Furthermore, when $[C_5Me_5Ti(\mu\text{-}O)F]_4$ was reacted with 4 molar equiv of $AlMe_3$ at room temperature, a brown-yellow solution was formed and resulted in an oil-like product. Attempts to isolate any pure compound from this reaction mixture were unsuccessful. In contrast, when $[C_5Me_5Ti(\mu\text{-}O)F]_4$ was reacted with 4 molar equiv of $AlEt_3$ in toluene at room temperature, the novel tetranuclear alkylated complex $[C_5Me_5Ti(\mu\text{-}O)Et]_4$ (**4**) (Scheme 4) was obtained in moderate yield. Compound **4** was characterized by elemental analysis, MS, NMR spectroscopy, and finally X-ray crystallography. This compound is thermally stable at room temperature although sensitive to air and moisture. The proton signals in the ^1H NMR spectrum are seen at δ 1.98 (C_5Me_5), 1.82−1.71 (CH_3), and 1.39−1.28 (CH_2) ppm. The structure of **4** has a nonplanar Ti_4O_4 ring conformation (Figure 6) as found in **2a**, **2b**, and **3a**. In compound **4** the four oxygen atoms lie in a plane (mean deviation from the plane 0.006 Å) whereas the four titanium atoms are alternately positioned above and below the plane (0.141 Å). The Ti−O bond lengths, which fall in the range 1.826−1.841 Å (Table 6), are longer than those in $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (average 1.816 Å),[4b] due to the replacement of four fluorine atoms by four ethyl groups. The bond distances of $Ti-C_2H_5$, which fall in the range 2.127−2.161 Å, are comparable with those observed for $Ti-CH_3$ bonds in $[C_5Me_5Ti(\mu-O)Me]_3$ (2.08−2.10 Å). We should mention here that although the $Ti-F_t$ bond distances in $(C_5Me_5)_4Ti_4O_5F_2$ (**1b)** (average 1.819 Å) are slightly shorter than those in $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (1.845 Å),[4b] compound **1b** was easily methylated by using 2 molar equiv of $AlMe_3$ to yield the methylated product $(C_5Me_5)_4Ti_4O_5Me_2$ (**1c**) (Scheme 6). Compound **1c** was synthesized independently by Mena et al. using a different procedure.[13] The ^{19}F NMR monitoring studies on the reaction of $[C_5Me_5Ti(\mu\text{-}O)F]_4$ and **1b** with $AlEt_3$ and $AlMe_3$ performed in toluene-d_8 at −40 °C show that the signals of the starting material $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (δ 64.6) and **1b** (δ 54.5) are replaced by two sharp signals (δ −132.2, −134.3) for the former and a sharp signal (δ −122.5) for the latter. This suggests that the compound $[C_5Me_5Ti(\mu\text{-}O)F]_4$ and **1b** are alkylated by alkylaluminum compounds to form the corresponding adducts as intermediates, in which one of the alkyl groups is transferred from aluminum to titanium to give **4** and **1c**, respectively, along with the elimination of R_2AlF. This phenomenon occurs after the reaction mixture is kept in a Schlenk flask at room temperature overnight (Scheme 6).

Furthermore, it was found that when compound $[C_5Me_5Ti(\mu\text{-}O)F]_4$ was allowed to react with an excess of $GaMe_3$, the reaction mixture afforded only $[C_5Me_5Ti(\mu\text{-}O)]_4F_3[(\mu\text{-}F)GaMe_3]$ (**5**). This is probably because $GaMe_3$ is electron rich compared to $AlMe_3$. Compound **5** is unstable and easily reverts to $[C_5Me_5Ti(\mu\text{-}O)F]_4$ at room temperature. A partial X-ray structure done on this sample shows that it is as formulated above; however, a good set of data could not be collected.

Conclusions and Outlook. We have shown that organotitanoxane chlorides can be easily fluorinated by Me_3SnF via a

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(18) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1.

four-membered-ring Ti(μ-F)(μ-Cl)Sn intermediate, and organotitanoxane fluorides can be converted to the corresponding chlorides and even further to the oxygen-free organotitanium chlorides by using an excess of Me_3SiCl. Due to the electron deficiency of alkylaluminum compounds, they exhibit electrophilic reactions with organotitanoxane fluorides, giving the corresponding alkylaluminum adducts with different stoichiometric ratios. The adducts react further to yield novel alkylated compounds.

Finally, from our experience in this field, it is reasonable to expect that an organotitanoxane−AlR_3 compound may have action and utility similar to those of the metallocene−methylaluminoxane system. This investigation is in progress.

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled under nitrogen and degassed prior to use. Melting points were determined in sealed capillaries and were not calibrated. ^1H and ^{19}F NMR spectra ($CDCl_3$, C_6D_6, or toluene-d_8 solution) were recorded on an AS-400 Bruker or an AM-200 Bruker spectrometer. Chemical shifts are reported in parts per million with reference to external TMS or $CFCl_3$. Mass spectra were obtained on a Finnigan MAT 8230 and a Varian MAT CH5 spectrometer. Elemental analyses were carried out by the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen.

The starting materials $[C_5Me_5TiOCl]_3$,[19a] $(C_5Me_5)_4Ti_4O_6$,[19b] $[C_5Me_5Ti(\mu\text{-}O)F]_4$,[5a] Me_3SnF,[5a] and $Al(CH_2Ph)_3$[20] were prepared according to the literature methods. Me_3SiCl, $AlMe_3$, and $AlEt_3$ were purchased from Aldrich Chemical Co. and used as received.

$(C_5Me_5)_4Ti_4O_5Cl_2$ (1a). The known organotitanoxane chloride **1a** was prepared in a better yield using the following modified procedure.[14] A mixture of $(C_5Me_5)_4Ti_4O_6$ (4.14 g, 5 mmol) and $TiCl_4{\cdot}2THF$ (0.835 g, 2.5 mmol) in toluene (40 mL) was stirred at room temperature overnight. The reaction mixture was subsequently filtered and dried in vacuo to afford a yellow solid. The yellow solid obtained was washed with *n*-hexane to yield 82% (3.62 g) of analytically pure **1a**. Mp: 350−353 °C. EI-MS: *m/e* (%) 882 [M^+] (8), 747 [$M^+-C_5Me_5$] (100). ^1H NMR and analytical data are similar to those previously reported.

$(C_5Me_5)_4Ti_4O_5F_2$ (1b). A suspension of **1a** (3.53 g, 4 mmol) and Me_3SnF (1.46 g, 8 mmol) in toluene (40 mL) was stirred at room temperature overnight and filtered. The volatiles were removed under reduced pressure to afford a yellow solid. The product was purified by recrystallization from toluene to yield 85% (2.89 g). Mp: >350 °C dec. EI-MS: *m/e* (%) 850 [M^+] (6), 715 [$M^+-C_5Me_5$] (100). ^1H NMR ($CDCl_3$; ppm): δ 2.00 and 1.94 (1:1). ^{19}F NMR ($CDCl_3$; ppm): δ 54.5. Anal. Calcd for $C_{40}H_{60}F_2O_5Ti_4$: C, 56.47; H, 7.06; F, 4.47. Found: C, 56.2; H, 7.1; F, 4.7.

$(C_5Me_5)_4Ti_4O_5Me_2$ (1c). **1c** was prepared by reacting **1b** (0.85 g, 1 mmol) with $AlMe_3$ (1 mL, 2 mmol) in toluene (15 mL) at 0 °C; a bright-red solution formed soon after mixing and turned into orange yellow after 1 h of stirring at room temperature. The solution was concentrated to 5 mL and cooled (−10 °C) to yield 80% (0.67 g) of **1c**. The ^1H NMR and MS spectra are identical to those described in the literature.[13]

$[C_5Me_5Ti(\mu\text{-}O)(\mu\text{-}F)AlMe_3]_4$ (2a). To a solution of $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (0.87 g, 1 mmol) in toluene (15 mL) with stirring was added $AlMe_3$ (2 mL, 2.0 M in toluene) at once using a syringe at −20 °C. A bright-red solution formed immediately. The reaction mixture was stirred for 5 min and subsequently cooled (−20 °C) to yield 52% (0.6 g) of red crystals of **2a**. The solution of compound **2a** is unstable and decomposes slowly at −10 °C to give orange crystals, which were characterized as $[C_5Me_5Ti(\mu\text{-}O)]_4F[(\mu\text{-}F)AlMe_3]_3$ (**2b**) by NMR spectroscopy.

$[C_5Me_5Ti(\mu\text{-}O)]_4F[(\mu\text{-}F)AlMe_3]_3$ (2b). Compound **2b** was prepared by treating $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (0.872 g, 1 mmol) with $AlMe_3$ (1.5 mL, 3 mmol) in toluene (15 mL) at −10 °C for 10 min. The color changed from yellow to orange during the addition. Orange crystals were isolated in 60% (0.65 g) yield by cooling the solution (−10 °C). The crystals decompose within 10 min at room temperature even under a nitrogen atmosphere to afford an orange yellow solid which was identified as $[C_5Me_5Ti(\mu\text{-}O)]_4F_2[(\mu\text{-}F)AlMe_3]_2$ (**2c**) by NMR spectroscopy.

$[C_5Me_5Ti(\mu\text{-}O)]_4F_2[(\mu\text{-}F)AlMe_3]_2$ (2c). Compound **2c** was prepared by reacting $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (0.872 g, 1 mmol) with $AlMe_3$ (1 mL, 2 mmol) in toluene (15 mL) at 0 °C. The reaction mixture was stirred for 20 min to give an orange yellow solution. The solution subsequently was cooled (−10 °C) to yield 45% (0.46 g) of an orange yellow microcrystalline solid **2c**. Mp: >250 °C dec. EI-MS: *m/e* (%) 864 [$M^+-2AlMe_2F$] (8), 710 [$M^+ - 2AlMe_2F - F - C_5Me_5$] (100). ^1H NMR (C_6D_6; ppm): δ 2.08 (s, 30 H, C_5Me_5), 2.10 (s, 30 H, C_5Me_5), and −0.81 (s, 18 H, $AlMe_3$). ^{19}F NMR (C_6D_6; ppm): (95.4 and −113.1 (1:1). Anal. Calcd for $C_{46}H_{78}Al_2F_4O_4Ti_4$: C, 54.43; H, 7.68; F, 7.48. Found: C, 54.9; H, 7.8; F, 7.2.

$[C_5Me_5Ti(\mu\text{-}O)]_4F_3[(\mu\text{-}F)Al(CH_2Ph)_3]$ (3a). A mixture of $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (0.872 g, 1 mmol) and $Al(CH_2Ph)_3$ (0.3 g, 1 mmol) in toluene (20 mL) was stirred at room temperature overnight. The reaction mixture obtained was filtered and subsequently cooled (−10 °C) to yield 40% (0.47 g) of yellow crystals **3a**. Mp: 175−178 °C. EI-MS: *m/e* (%) 872 [$M^+ - Al(CH_2Ph)_3$] (10), 91 [CH_2Ph] (100). ^1H NMR ($CDCl_3$; ppm): δ 7.18−6.85 (m, 15 H, C_6H_5), 2.10 (s, 15 H, C_5Me_5), 2.09 (s, 30 H, C_5Me_5), 2.08 (s, 15 H, C_5Me_5), and 1.70 (s, 6 H, CH_2). ^{19}F NMR ($CDCl_3$; ppm): δ 90.69, 87.25, and −133.95 (2:1:1). Anal. Calcd for $C_{61}H_{81}AlF_4O_4Ti_4$: C, 62.46; H, 6.91; F, 6.48. Found: C, 62.5; H, 6.9; F, 6.8.

$[C_5Me_5Ti(\mu\text{-}O)]_4F_3[(\mu\text{-}F)AlEt_3]$ (3b). To a solution of $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (0.872 g, 1 mmol) in toluene (15 mL) was added $AlEt_3$ (1 mL, 1.0 M in *n*-hexane) through a syringe at 0 °C. The resulting pale orange yellow solution was left at room temperature overnight and subsequently cooled (−10 °C) to yield 30% (0.30 g) of analytically pure **3b**. Mp: 240−243 °C. EI-MS: *m/e* (%) 872 [$M^+ - AlEt_3$] (6), 497 [$M^+ - AlEt_3 - C_5Me_5TiF_3$] (100). ^1H NMR (C_6D_6; ppm): δ 2.11 (s, 15 H, C_5Me_5), 2.09 (s, 30 H, C_5Me_5), 2.07 (s, 15 H, C_5Me_5), 1.70−1.69 (tr, 9 H, CH_3), and 0.43−0.55 (qt, 6 H, CH_2). ^{19}F NMR (C_6D_6; ppm): δ 96.50, 92.81, and −121.35 (2:1:1). Anal. Calcd for $C_{46}H_{75}AlF_4O_4Ti_4$: C, 55.98; H, 7.60; F, 7.71. Found: C, 56.0; H, 7.4; F, 7.0.

$[C_5Me_5Ti(\mu\text{-}O)Et]_4$ (4). To a solution of $[C_5Me_5Ti(\mu\text{-}O)F]_4$ (0.87 g, 1 mmol) in toluene (15 mL) was added $AlEt_3$ (4 mL, 1.0 *M* in *n*-hexane) through a syringe at −10 °C. The yellow color of the reaction mixture changed to bright-red soon after the addition was completed and then turned to brown yellow with stirring at room temperature overnight. After removal of the volatiles and recrystallization of the residue from *n*-hexane, yellow pale crystals of **4** in 40% (0.36 g) yield were obtained. Mp: > 260 °C dec. EI-MS: *m/e* (%) 883 [$M^+ - Et$] (8), 823 [$M^+ - Et - 2C_2H_6$] (100). ^1H NMR (C_6D_6; ppm): δ 1.98 (60 H, C_5Me_5), 1.82−1.71 (tr, 12 H, CH_3), and 1.39−1.28 (qt, 8 H, CH_2). Anal. Calcd for $C_{48}H_{80}O_4Ti_4$: C, 63.16; H, 8.77. Found: C, 62.9; H, 8.7.

Fluorine(oxygen)−Chlorine Exchange Reaction of $[C_5Me_5Ti(\mu\text{-}O)F]_4$, 1a, 1b, $[C_5Me_5Ti(\mu\text{-}O)Cl]_3$ and $(C_5Me_5)_4Ti_4O_6$ Using Me_3SiCl. All reactions were carried out following the same procedure and under the same conditions. A representative example is the following: To a solution of **1b** (0.85 g, 1 mmol) in toluene (15 mL) was added Me_3SiCl (0.22 g, 2 mmol) at room temperature. The reaction mixture was stirred for 3 h, and the volatiles were removed under reduced pressure to give a yellow solid. The yellow solid was washed with *n*-hexane (10 mL) to yield 95% (0.83 g) of analytically pure **1a** . Furthermore, treating **1a** or **1b** (1 mmol) in toluene (15 mL) with an excess of Me_3SiCl (10 mmol) by stirring at room temperature for 3 h resulted in a red reaction mixture. The volatiles were removed subsequently to yield 95% of $C_5Me_5TiCl_3$.

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Measurement of the ^{19}F NMR. Compound [$C_5Me_5Ti(\mu\text{-}O)F]_4$ or **1b** (0.1 mmol) was placed in an NMR tube and dissolved in toluene-d_8 cooled at −40 °C, and the corresponding molar amount of $AlEt_3$ (or $AlMe_3$) was added to this solution through a syringe. The sample was placed in a cooling bath maintained at −40 °C, and the progress of the reaction was monitored by ^{19}F NMR spectroscopy at the same temperature. The signal of the starting material disappeared soon after mixing; two sharp signals (−132.2 and −134.3 ppm) resulted from the reaction with $[C_5Me_5Ti(\mu\text{-}O)F]_4$, and one sharp signal (−122.5 ppm) resulted from the reaction with **1b**.

Crystallographic Analysis. Crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether.[21] Diffraction data for **1a**, **1b**, and **2b** were collected on a Siemens/Stoe AED2 four-circle diffractometer performing $2\theta/\omega$ scans. Data for **4** and **5** were collected on a Siemens/Stoe Huber four-circle diffractometer coupled to a Siemens CCD area detector [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[22] and refined using F^2 on all data by full-matrix least squares with SHELXL-97.[23] 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 methyl groups in **5** were 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.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures **1a**, **1b**, **2b**, **3a**, and **4** are available on the Internet only. Access information is given on any current masthead page.

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