Synthesis and Structure of the First Non-Metallocene Ti^{III} Fluoride Complex LTiF$_2$·2Me$_3$SnCl Supported by a β-Diketiminato Ligand

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Dedicated to Professor F. A. Kuznetsov on the occasion of his 70th birthday

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The Ti^{III} dichloride complex LTiCl$_2$ (**1**) and the first non-metallocene Ti^{III} fluoride complex LTiF$_2$·2Me$_3$SnCl (**2**) supported by the β-diketiminato ligand 2-{[2-(diethylamino)ethyl]amino}-4-{[2-(diethylamino)ethyl]imino}pent-2-ene have been synthesized. Elemental analysis, mass spectrometry and X-ray structural analysis show that **1** is monomeric, neutral, and free of solvent and lithium salt. The complex adopts a pseudo-octahedral geometry with the two chlorine atoms arranged in *trans* position to each other. Compound **1** is soluble in common organic solvents and thermally surprisingly robust. Complex **2** was prepared using Me$_3$SnF as a fluorinating agent. X-ray structural analysis revealed that complex **2** consists of the LTiF$_2$ unit and two molecules of Me$_3$SnCl coordinated through a fluorine bridge to the titanium center. The fluorine atoms in **2** are located in *trans* positions to each other and the geometry around the titanium atom is distorted octahedral. Elemental analysis and mass spectrometry proved that **2** releases the coordinated Me$_3$SnCl under vacuum or during sublimation.

Introduction

The chemistry of trivalent titanium fluorides has proven to be a promising area of research with far-reaching results. At the moment this area is restricted mainly to cyclopentadienyl-substituted complexes. During the last decade our group has been successful in obtaining and structurally characterizing several Ti^{III} fluoride complexes, namely large clusters[1,2] based on fluorine-bridged organometallic units and the tetranuclear complexes [{[C$_5$H$_4$(SiMe$_3$)]$_2$TiF$_2$}$_3$M] (M = Ti,[3] Ga,[3] Al[4]) with the four-membered MF$_2$Ti rings surrounded by the central metal atom in a propeller like fashion. Furthermore, the dimeric titanium complex [(C$_5$H$_4$Me)$_2$TiF]$_2$[5] has been prepared from the corresponding chlorine derivative.

There is widespread interest in the chemistry of low-valent titanium fluorine species from several perspectives, including synthetic methodology, and structural and theoretical implications. More pertinent to this study, however, is the high catalytic activity displayed by pentamethylcyclopentadienyl-substituted titanium fluorides in combination with methylaluminoxane (MAO) in the polymerization of styrene:[6] β-diketiminato complexes of Ti^{III} with the general formula LTiCl$_2$,[7,8] in the presence of excess methylaluminoxane[7] or B(C$_6$F$_5$)$_3$,[8] catalyse the homopolymerization of ethylene and the copolymerization of ethylene with α-olefins. Thus, our interest in the chemistry of titanium fluoride complexes stems from the potential use of Ti^{III} fluoride complexes supported by a new β-diketiminato ligand as a novel olefin polymerisation catalyst.

Mono β-diketiminato Ti^{III} dichlorides are accessible from TiCl$_3$ and the corresponding LiL salt in THF.[8] Access to a fluoride complex of Ti^{III} is possible by the reaction of trimethyltin fluoride with the corresponding chloride complex in non-aqueous solvents.[5]

Herein we report the synthesis and characterization of the new β-diketiminato Ti^{III} dichloride complex LTiCl$_2$ (**1**) [L = Et$_2$NCH$_2$CH$_2$NC(Me)CHC(Me)NCH$_2$CH$_2$NEt$_2$] and the first non-metallocene, neutral, solvent-free Ti^{III} fluoride complex LTiF$_2$·2Me$_3$SnCl (**2**).

Results and Discussion

The titanium complex **1** was prepared in a one-step synthesis from titanium trichloride and stoichiometric amounts of the lithium salt of the ligand in THF (Scheme 1). The

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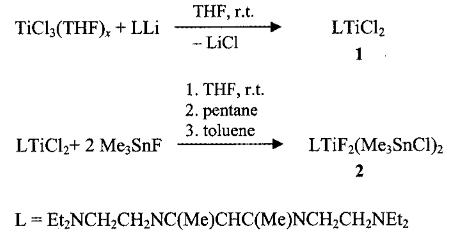
reaction proceeds at room temperature within 2 h and crystals are easily obtained from the original solution in high yield. Compound **1** is soluble in toluene, THF and dichloromethane, and can be recrystallized from toluene and THF. Complex **1** is thermally stable and can be refluxed in THF without observing any appreciable decomposition. Solid compound **1**, and especially its solution, are air-sensitive, but crystals of **1** are stable in a glove box for one month.



Scheme 1. Synthesis of the complexes **1** and **2**

The melting point of **1** is in the range 144−145 °C. Mass spectrometry and elemental analysis show that compound **1** is monomeric, solvent-free and contains no lithium chloride. Complex **1** exhibits a signal of the molecular ion $[M]^+$ in the EI-MS as well as strong fragments of $[C_5H_{12}N]^+$ and $[C_6H_{14}N]^+$ due to the decomposition of the titanium complex during the EI-MS experiment.

These properties indicate that **1** is a versatile starting material for studying the chemistry of low-valent titanium compounds.

Reaction of **1** with 2 equiv. of Me_3SnF in THF affords a clear solution. After evaporation of the solvent and washing with pentane, the residue was extracted with toluene. Initial addition of toluene caused the precipitate to dissolve, but after several minutes some solid deposited again. This solid is insoluble in toluene and THF and contains titanium, fluorine and non-stoichiometric amounts of the ligand. Complex **2** was purified by crystallization from toluene (Scheme 1). It should be pointed out that crystals of **2** are poorly soluble in toluene and can be obtained from the toluene solution. Complex **2** has good solubility in dichloromethane. Solutions of **2** and the solid are air-sensitive, but crystals of **2** can be kept in the glove box for several months.

The melting point of **2** is in the range 149−151 °C. Elemental analysis shows that complex **2** contains two molecules of Me_3SnCl. The composition was confirmed by EI-MS spectrometry. In the temperature range from room temp. to 120 °C $[Me_3SnCl]^+$ and several other fragments are observed. The elimination of Me_3SnCl ceases at 120 °C and in the temperature range from 155 to 200 °C compound **2** exhibits the molecular ion of $[LTiF_2]^+$.

Complex **2** decomposes and eliminates Me_3SnCl on standing under vacuum over a long period of time at 100−120 °C. The elemental analysis, however, shows that the remaining product does not correspond to the pure fluoride complex $LTiF_2$. Thus, by standing under vacuum it is possible to remove almost all coordinated Me_3SnCl, although the residue is not a pure fluoride complex. Further purification by sublimation at 150−160 °C resulted in a brown powder. The elemental analysis of the sublimate revealed that it is essentially $LTiF_2$. The EI-MS spectrum of this sublimate exhibits the molecular ion $[LTiF_2]^+$ and its corresponding fragments. Unfortunately, all the attempts to recrystallize this product were unsuccessful. Initially, this compound dissolved in toluene, but after several hours an amorphous precipitate deposited from solution.

Complexes **1** and **2** are paramagnetic and exhibit strong broadened proton NMR resonances ($\Delta\nu_{1/2}$ ranged from 50 to 1000 Hz); a fluorine resonance of **2** was not observed. A resonance at $\delta = 0.6$ ppm in the ^1H NMR spectrum of **2** in CD_2Cl_2 can be assigned to Me_3SnCl.

X-ray Structural Analysis of $LTiCl_2$

A summary of the crystallographic data and refinement parameters for the structure of **1** is given in Table 2. Selected bond lengths and angles are listed in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1** and **2**

Complex 1			
Ti−N(1)	2.065(2)	N(1)−Ti−N(2)	90.26(7)
Ti−N(2)	2.074(2)	N(1)−Ti−Cl(2)	92.75(7)
Ti−Cl(2)	2.372(1)	Cl(2)−Ti−Cl(1)	173.34(2)
Ti−Cl(1)	2.372(1)	N(1)−Ti−N(3)	170.24(7)
Ti−N(3)	2.434(2)	Cl(2)−Ti−N(3)	88.55(6)
Ti−N(4)	2.454(2)	N(1)−Ti−N(4)	79.84(8)
		Cl(2)−Ti−N(4)	87.57(6)
		N(3)−Ti−N(4)	109.89(6)
Complex 2			
Ti(1)−F(1)	1.912(2)	F(1)−Ti(1)−F(1A)	169.03(1)
Ti(1)−F(1A)	1.912(2)	F(1)−Ti(1)−N(1)	94.31(1)
Ti(1)−N(1)	2.077(3)	N(1)−Ti(1)−N(1A)	89.37(2)
Ti(1)−N(2)	2.373(3)	F(1)−Ti(1)−N(2)	88.70(9)
Sn(1)−C(13)	2.112(4)	N(1)−Ti(1)−N(2)	79.99(1)
Sn(1)−Cl(1)	2.462(1)	N(1)−Ti(1)−N(2A)	169.28(1)
Sn(1)−F(1)	2.559(4)	N(2)−Ti(1)−N(2A)	110.67(1)
		Sn(1)−F(1)−Ti(1)	148.20(1)
		C(13)−Sn(1)−C(12)	114.88(2)
		C(13)−Sn(1)−Cl(1)	96.28(1)
		Cl(1)−Sn(1)−F(1A)	176.60(2)
		C(12)−Sn(1)−F(1A)	84.20(9)

Single crystals of **1** suitable for X-ray diffraction analysis were obtained by recrystallization from THF. $LTiCl_2$ crystallizes in the orthorhombic space group $Pna2_1$. The X-ray structural analysis proves that compound **1** is free of solvent and lithium salt and monomeric in the solid state (Figure 1).

In this complex the ligand coordinates to the metal center through the four nitrogen atoms. All four nitrogen atoms and the titanium atom are in the same plane. The geometry of this complex is similar to those of the praseodymium complexes $LPrX_2$ (X= Cl, Br)[9] containing the same ligand. The chlorine atoms in **1** are almost perpendicular to the equatorial plane, with the Cl(2)−Ti−Cl(1) angle [173.34(2)°] (Table 1) indicating that each chlorine atom is

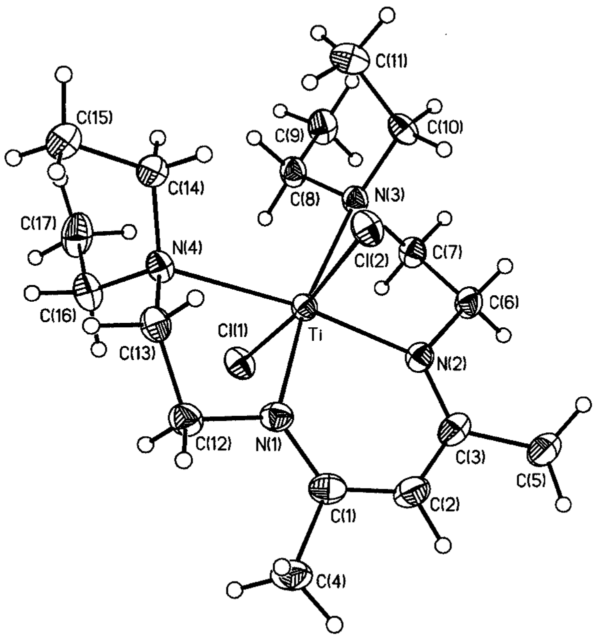


Figure 1. ORTEP drawing (50% thermal probability ellipsoids) of the crystal structure of **1** with atomic numbering scheme

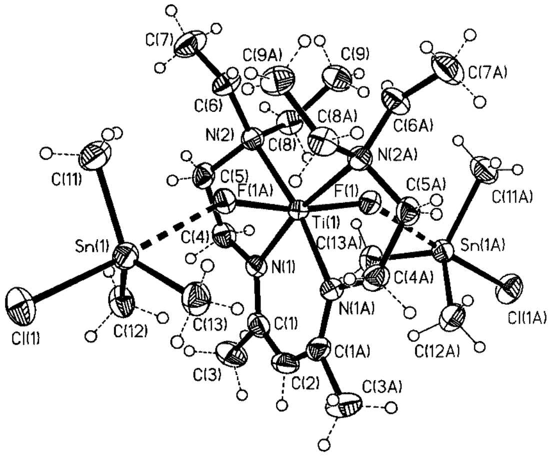


Figure 2. ORTEP drawing (50% thermal probability ellipsoids) of the crystal structure of **2** with atomic numbering scheme

slightly tilted towards the pendant arm. For this complex the titanium atom lies slightly out of the plane of the diimine ligand framework. The coordination number at the titanium atom in **1** is six and the geometry around the metal atom is pseudo-octahedral.

The Ti−N bonds of the pendant arm are longer than those of the backbone, as for the distances in the praseodymium complex $LPrX_2$ (X = Cl, Br),[9] due to the coordinative and covalent character involved in different bonding modes. The Ti−Cl bond length is similar to those found in the literature for β-diketiminato complexes of Ti^{III} (Ti−Cl 2.395 Å[7]).

X-ray Structural Analysis of $LTiF_2$·$2Me_3SnCl$

A summary of the crystallographic data and refinement parameters for the structure of **2** is given in Table 2. Selected bond lengths and angles are listed in Table 1.

Single crystals of **2** suitable for X-ray diffraction analysis were obtained by crystallization from toluene. Complex **2** crystallizes in the monoclinic space group *C*2/*c*. The X-ray structural analysis reveals that compound **2** consists of an $LTiF_2$ unit and two coordinated molecules of Me_3SnCl. Trimethyltin chloride is coordinated through a fluoride bridge to the titanium center (Figure 2). The Sn−F distances [Sn(1)−F(1) 2.559(5) Å] in **2** are considerably longer than those in tin fluoride complexes [Sn−F 2.041(5)[10] Å, 2.126(3)[11] Å for five-coordinate tin] and are similar to those found for [(acac)$_2$(η^5-C_5Me_5)Zr(μ-F)$SnMe_3Cl$] [Sn−F 2.462(2) Å],[12] where Me_3SnCl is coordinated by a fluorine bridge to the zirconium center. Each Me_3SnCl molecule is tilted slightly towards the pendant arm of the $LTiF_2$ unit [Sn(1)−F−Ti(1) 148.20(1)°] due to repulsion between Me_3SnCl and the ethyl groups of the backbone of the β-diketiminato ligand. The coordination number at the tin atom in **2** is five and the geometry around the tin is pseudo-trigonal-bipyramidal. The fluorine and chlorine atoms in the Me_3SnFCl unit are almost in *trans* positions to each other [F(1)−Ti−Cl(1) 176.60(2)°] (Table 1).

In complex **2** the β-diketiminato ligand coordinates to the titanium center through the four nitrogen atoms. All four nitrogen atoms and the titanium atom lie in the same plane. The fluorine atoms in **2** are almost perpendicular to the equatorial plane [F(1)−Ti−F(1)#1 169.03(1)°] (Table 1) and each fluorine atom is tilted slightly towards the pendant arm. The coordination number at the titanium atom in **2** is six and the geometry around the metal atom is distorted octahedral.

The Ti−N bonds of the pendant arm are longer than those of the backbone, like those in complex **1** and $LPrX_2$ (X = Cl, Br).[9] The Ti−F bond is shorter than that found in the literature for titanium(III) fluoride complexes [Ti−F 1.975(1),[4] 2.094(1),[4] 2.092(2)[5] Å].

Conclusion

We have reported the synthesis and characterization of the Ti^{III} dichloride $LTiCl_2$ and the Ti^{III} fluoride complex $LTiF_2$·$2Me_3SnCl$ supported by the β-diketiminato ligand 2-{[2-(diethylamino)ethyl]amino}-4-{[2-(diethylamino)ethyl]imino}pent-2-ene. Compound **2** is easily prepared. It has been shown for the first time that Me_3SnF is a good fluorinating reagent for non-metallocene Ti^{III} compounds. Elemental analysis, mass spectrometry and X-ray structural analysis show that **2** is monomeric. Moreover, **2** is thermally unstable and gives off Me_3SnCl under vacuum. The uncoordinated $LTiF_2$ aggregates in toluene solution and therefore we were not able to obtain reliable results in polymerization reactions.

Experimental Section

General Remarks: All operations were performed using standard Schlenk line and dry box techniques under purified nitrogen or argon. Anhydrous titanium trichloride was of commercial reagent quality. The compound LH [L = $Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$] was prepared by a known method.[9,13,14] The purity of LH was checked by elemental analysis, and ^1H and ^{13}C NMR spectroscopy. Me_3SnF was prepared by a literature method.[15] The purity of Me_3SnF was checked by elemental analysis and was found to contain less than 1% chlorine. Toluene, pentane and THF were dried with Na/benzophenone and distilled under nitrogen prior to use. C_6D_6 and [D$_8$]THF were dried with Na and degassed. CD_2Cl_2 was dried with CaH_2 and degassed. ^1H NMR spectra were recorded using a Bruker AM 200 spectrometer. Chemical shifts are reported in δ units downfield from Me_4Si with the solvent as the reference signal. Mass spectra were recorded using a Finnigan MAT 8230 instrument, and elemental analyses were carried out at the Analytical Laboratories of the Institute of Inorganic Chemistry at the University of Göttingen. Melting points were determined in sealed capillary tubes under nitrogen and are not corrected.

Synthesis of Complexes

$LTiCl_2$: LH (1.2 g, 1.28 mL, 4.0 mmol) was added to dry THF (30 mL) in a 50-mL Schlenk flask. The mixture was cooled to −78 °C and a solution of LiMe (2.52 mL; 1.6 M, 4.0 mmol) in Et_2O was added dropwise. The reaction mixture was stirred for 1 h at −78 °C, allowed to warm to room temperature and stirred at room temp. until methane evolution had ceased. This solution was added dropwise to a suspension of $TiCl_3$ (0.62 g, 4.0 mmol) in THF (30 mL) at room temp. in a 100-mL Schlenk flask. Then, the reaction mixture was stirred overnight. The suspension was filtered and concentrated. Finally, the resulting solution was left at −26 °C for 2 d. The red crystals that formed were separated by filtration, washed with pentane (20 mL) and dried in vacuo. Yield of $LTiCl_2$ (1.10 g, 66%). M.p. 144−145 °C. $C_{17}H_{35}Cl_2N_4Ti$ (414.3): calcd. C 49.28, H 8.45, N 13.53; found C 49.20, H 8.39, N 13.45. EI-MS: *m/z* (%) = 414 (6.4) [M^+], 378 (1.2) [LTiCl], 349 (0.6) [LTiCl − C_2H_6], 327 (1.0) [$M^+ - C_5H_{12}N$], 100 (4.0) [$C_6H_{14}N$], 86 (100.0) [$C_5H_{12}N$].

$LTiF_2{\cdot}2Me_3SnCl$: A mixture of $LTiCl_2$ (1.0 g, 2.4 mmol) and Me_3SnF (0.88 g, 4.8 mmol) in a 100-mL Schlenk flask was stirred in THF (40 mL) until all the precipitate dissolved (2 h). Then, the

Table 2. Crystallographic data of the X-ray diffraction studies of **1** and **2**

	1	**2**
Empirical formula	$C_{17}H_{35}Cl_2N_4Ti$	$C_{23}H_{53}Cl_2F_2N_4Sn_2Ti$
M_r	414.29	779.86
Temperature [K]	133(2)	200(2)
Radiation Used (λ [Å])	Mo-K_α (0.71073)	Mo-K_α (0.71073)
Crystal description	red plates	green block
Crystal size [mm]	0.8 × 0.8 × 0.2	1.00 × 0.80 × 0.6
Crystal system	orthorhombic	monoclinic
Space group	$Pna2_1$	$C2/c$
a [Å]	20.582(4)	10.736(2)
b [Å]	9.488(2)	17.181(3)
c [Å]	10.700(2)	18.294(4)
α [°]	90	90
β [°]	90	104.18(3)
γ [°]	90	90
V [Å^3]	2089.6(7)	3271.5(1)
Z	4	4
F (000)	884	1564
$\rho_{calcd.}$ [g·cm^{-3}]	1.317	1.579
μ [mm^{-1}]	0.672	1.946
Total reflections	16494	4650
Unique reflections	3566	2838
R(int)	0.0541	0.0506
Scan range Θ [°]	1.98 to 24.76	3.57 to 24.97
Completeness to Θ_{max} [%]	99.7	98.8
Index ranges	$-24 \le h \le 24$	$-12 \le h \le 12$
	$-11 \le k \le 9$	$-20 \le k \le 20$
	$-12 \le l \le 12$	$-21 \le l \le 21$
Data/restrains/parameters	3566/1/224	2838/0/161
$R1$,[a]	0.0308, 0.0736	0.0294, 0.0762
$R1$,[a] $wR2$ (all data)[c] [d]	0.0334, 0.0743	0.0323, 0.0781
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2 [e]	1.010	1.111
Max./min. electr. dens. [e·Å^{-3}]	0.591/−0.270	1.134/−0.640

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] Denotes the value of the residual considering only the reflections with $I > 2\sigma(I)$. [c] $wR2$ [$I > 2\sigma(I)$]$wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)/3$. [d] Denotes the value of the residual considering all the reflections. [e] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/[(n - p)^{1/2}]]$, n: number of data, p: parameters used.

THF was evaporated under vacuum, and the residue was washed portionwise (20 mL) with pentane. The residue was extracted with toluene (30 mL), the suspension was filtered and concentrated to approximately 7 mL. Finally, the resulting solution was left undisturbed for 3 d at room temp. The green crystals that formed were separated by filtration and washed with pentane (10 mL). Yield of $LTiF_2 \cdot 2Me_3SnCl$ (0.54 g, 29%). M.p. 149−151 °C. $C_{23}H_{53}Cl_2F_2N_4Sn_2Ti$ (779.0): calcd. C 35.38, H 6.80, N 7.18; found C 35.40, H 6.78, N 7.16. EI-MS ($T < 120$ °C): *m*/*z* (%) = 200 (5) [Me_3SnCl], 185 (100) [Me_2SnCl], 165 (54) [Me_3Sn], 155 (35) [SnCl], 134 (24) [MeSn], 119 (18) [Sn]; ($T > 155$ °C): *m*/*z* (%) = 381 (12) [M^+], 362 (1) [$LTiF]^+$, 333 (0.5) [$LTiF^+ - C_2H_6$], 309 (0.5) [$M^+ - NC_4H_{10}$], 295 (7) [$M^+ - C_5H_{12}N$], 100 (4.0) [$C_6H_{14}N$], 86 (100.0) [$C_5H_{12}N$].

Sublimation Experiment: Complex **2** (0.265 g, 0.34 mmol) was kept under vacuum at 90−110 °C for 6 h, until evolution of Me_3SnCl ceased. The amount of residue was 0.15 g (calcd. yield of the pure $LTiF_2$ 0.13 g). M.p. 152−156 °C. $C_{17}H_{35}F_2N_4Ti$ (381.5): calcd. C 53.54, H 9.19, N 14.70; found C 49.09, H 8.43, N 13.00. EI-MS: *m*/*z* (%) = 381 (12) [M^+], 362 (1) [LTiF], 333 (0.5) [$LTiF^+ - C_2H_6$], 309 (0.5) [$M^+ - NC_4H_{10}$], 295 (8) [$M^+ - C_5H_{12}N$], 100 (14) [$C_6H_{14}N$], 86 (100.0) [$C_5H_{12}N$]. This residue was sublimed at 150−160 °C to give 0.09 g of a dark brown powder. M.p. 122−123 °C. $C_{17}H_{35}F_2N_4Ti$ (381.5): calcd. C 53.54, H 9.19, N 14.70; found C 52.88, H 9.18, N 13.96. EI-MS: *m*/*z* (%) = 397 (1.5), 381 (6) [M^+], 362 (1) [LTiF], 333 (0.5) [$LTiF^+ - C_2H_6$], 309 (0.5) [$M^+ - NC_4H_{10}$], 295 (8) [$M^+ - C_5H_{12}N$], 210 (30) [$L^+ - C_5H_{12}N$], 100 (52) [$C_6H_{14}N$], 86 (100.0) [$C_5H_{12}N$].

X-ray Crystallographic Study: Crystal data and experimental conditions are listed in Table 2. Selected bond lengths and bond angles with standard deviations in parentheses are presented in Table 1. Intensity data for the crystal structure of $LTiCl_2$ were collected with a Stoe image-plate IPDS II-system. Data for the crystal structure of $LTiF_2 \cdot 2Me_3SnCl$ was collected with a Stoe−Siemens four-circle diffractometer. All structures were solved by direct methods (SHELXS-97) and refined against F^2 using SHELXS-97.[16] The heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to U_{iso} of the parent atoms. CCDC-189244 (**1**) and -189245 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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