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Preparation of the hydrocarbon-soluble trifluoro complex $LTiF_3$ with a β-diketiminato ligand

Grigory B. Nikiforov [a], Herbert W. Roesky [a,*], Peter G. Jones [b]

[a] *Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany*
[b] *Institut für Anorganische Chemie und Analytische Chemie der Technischen Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany*

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Dedicated to Professor Valentin Mitkin on the occasion of his 60th birthday.

Abstract

The β-diketiminato fluoride complex ($LTiF_3$) (**1**) (L = HC(CMeN(2,6-$i$$Pr_2C_6H_3$))$_2$, "NacNac") has been obtained using two synthetic routes, interaction of TiF_4 and NacNacK·2THF in toluene and interaction of $LTiCl_3$ and 3 equiv. of Me_3SnF in toluene. The trifluoro complex ($LTiF_3$) (**1**) is soluble in the non-polar solvents toluene and hexane and moderately active in polymerization of ethylene; the activity is higher than that of $LTiMe_3$ and comparable with that of the oxo-bridged complexes LTiCl(μ-O)$_2$TiClL and LTiMe(μ-O)$_2$TiMeL·toluene. Compound **1** was characterized by single crystal X-ray structural analysis, elemental analysis, NMR spectroscopy, and mass spectrometry. Complex **1** in the solid state is a centrosymmetric dimer containing two $LTiF_2$ moieties connected by two bridging fluorines, whereas C_6D_6 and CD_3CN solutions of **1** contain the monomeric complex at room temperature.

Keywords: Titanium(IV); Fluoride; β-Diketiminato complex; Fluorine bridged complex; Olefin polymerization

1. Introduction

Titanium fluoride complexes have been attracting continuous attention for use in several fields including synthetic methodology [1,2], theoretical studies [3] and catalysis. The catalytic activity of Ti(IV) fluoride complexes has been documented in asymmetric organic synthesis [4] and olefin polymerization [5]. The corresponding chloride complexes are less active [4a,d,e,5b].

Most of the known titanium fluoride complexes are supported by the cyclopentadienyl or substituted cyclopentadienyl ligands [1,6,7]. These complexes are usually soluble in less polar solvents such as toluene and hexane, which is important for catalytic applications. The compound $CpTiF_3$ is active in syndiospecific styrene polymerization in the presence of methylaluminoxane (MAO) [5b]. Non-cyclopentadienyl Ti(IV) fluoride complexes, in contrast, are normally only soluble in donor solvents or halogenated alkanes, although there are a few exceptions such as $[(Me_2N)_2TiF_2]_4$ [8], $[(Me_2N)_2TiF_2]_6$ [9], [n-Bu_4N][(iPrO)$_3$Ti(μ-F)$_2$(μ-OiPr)Ti(OiPr)$_3$] [10], and [(THF)$_2$Li(μ-F)$_2$Ti(OR$_f$)$_2$(μ-F)]$_2$ [11]. Therefore, it is highly desirable to expand this family of compounds and to study the influence of the fluorine atom in these complexes on the activity for polymerization reactions. Herein we report the synthesis using two different routes, characterization, and catalytic properties of a toluene- and hexane-soluble Ti(IV) trifluoro complex supported by the bulky β-diketiminato ligand (L = HC(CMeN(2,6-$i$$Pr_2C_6H_3$))$_2$, "NacNac").

2. Results and discussion

2.1. Synthesis and characterization

The complex ($LTiF_3$) (**1**) was obtained using two synthetic routes, interaction of TiF_4 and NacNacK·2THF [12] in toluene and reaction of $LTiCl_3$ with 3 equiv. of Me_3SnF in toluene (Scheme 1). The L^2K_2 [13], and dark brown product **1** (isolated yield of **1** was ca. 10%) were isolated in the first reaction. Despite the low yield of **1**, this reaction is of fundamental

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* Corresponding author.
E-mail address: hroesky@gwdg.de (H.W. Roesky).

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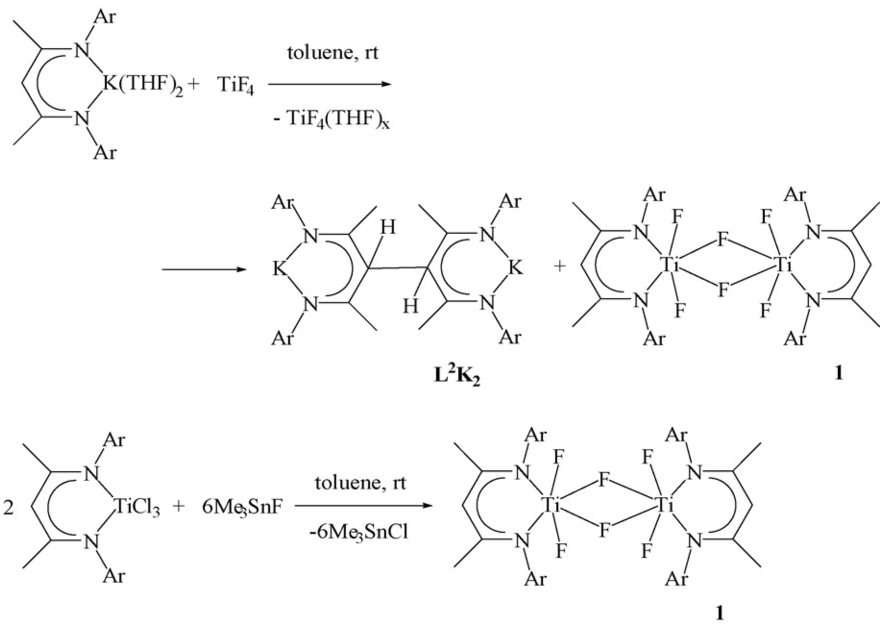

Scheme 1. Ar = 2,6-iPr$_2$C$_6$H$_3$.

importance because it shows that the Ti(IV) fluoride complex can be obtained in toluene solution directly from TiF_4 and the potassium salt of the ligand. In contrast, the reaction of $LiOCPh(CF_3)_2$ in boiling toluene produced only the alkoxide $Ti(OCPh(CF_3)_2)_4$ [11].

The second reaction afforded **1** in 90% isolated yield, showing that Me_3SnF is a good fluorinating agent for non-cyclopentadienyl Ti(IV) complexes.

Complex **1** is thermally stable (decomp. 197 °C) and does not change its appearance on storage in sealed ampoules at room temperature for several months. The largest cation detected in the mass spectrum of **1** corresponds to $[LTiF_3]^+$ (m/z 522). Further cations are formed by elimination of F, CH_4, and iPr from $[LTiF_3]^+$. The ^{19}F NMR spectrum of **1** dissolved in C_6D_6 or CD_3CN showed one resonance at room temperature (rt), while the proton spectra exhibited resonances attributed to the NacNac moiety. Thus, the NMR data are consistent with the presence of the $LTiF_3$ monomer in C_6D_6 and CD_3CN solution at room temperature. The low temperature (230 K) ^{19}F NMR spectrum of **1** in CD_3CN exhibited a mixture of complexes including the $[Ti_4F_{18}]^{2-}$ anion [14], an unassigned fluoride-bridged complex and the $LTiF_3$. A solution of **1** in toluene-d_8 allowed a study of the equilibria over a wide temperature range. Only one ^{19}F NMR resonance of the monomeric $LTiF_3$ was observed in the temperature range from 300 K to 230 K in a toluene solution, while below 220 K resonances of monomeric $LTiF_3$ and dimeric $(LTiF_3)_2$ are detected. The relative intensities of both complexes depended on the temperature, and allowed the determination of the thermodynamic equilibrium constants ($2LTiF_3 \leftrightarrows (LTiF_3)_2$) using $\ln(K) = -\Delta H/RT + \Delta S/R$ (Fig. 1). The determined data are $\Delta H = -5.8(7)$ kJ mol^{-1}, $\Delta S = -24(4)$ J mol^{-1} K^{-1}, $\Delta G^{298} = +1.4$ kJ mol^{-1}, $\Delta G^{183} = -1.4$ kJ mol^{-1}.

The single crystal structure of **1** has been determined by X-ray crystallographic methods. Complex **1** is an inversion-symmetric dimer in the solid state and contains two $LTiF_2$ moieties, connected by two bridging fluorine atoms. The Ti(IV) center is located in a distorted octahedral environment, formed by two terminal and two bridging fluorine atoms and two nitrogen atoms of the NacNac ligand (Fig. 2). The Ti atom lies 0.71 Å out of the NNCCC plane; the angle between this plane and the TiN_2 plane is 28°. It is noteworthy that the trichloride complex $LTiCl_3$ with the similar ligand [17] is monomeric with the Ti(IV) center in a distorted square pyramidal environment.

The Ti–N and Ti–F bond lengths in **1** are in the normal range [6,15,16]. Ti–F$_{terminal}$ distances are almost equal, while the Ti–(μ-F) bond lengths (1.9733(15) and 2.0679(15) Å) differ somewhat. The Ti–N distances are also slightly different from each other (2.077(2) Å and 2.028(2) Å), the shorter Ti–(μ-F) is

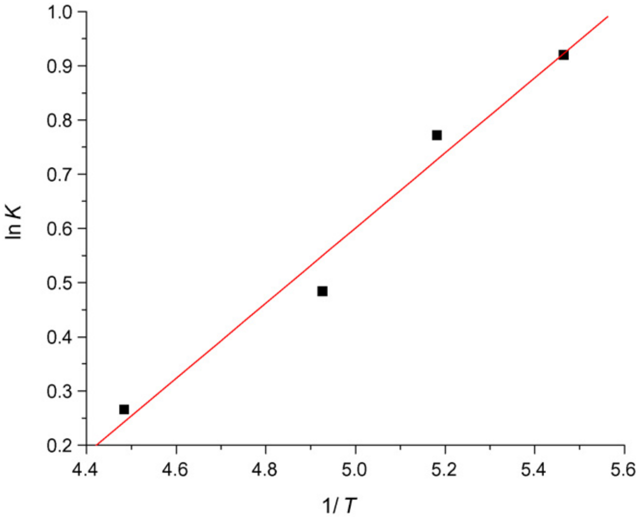

Fig. 1. Eyring plot for the disappearance of $LTiF_3$ vs. time; $(\mathbf{1})_0 = 1.53 \times 10^{-2}$ mol/L, $1/\ln(K) = -2.9(4) + 693(82)\ (1/T)$.

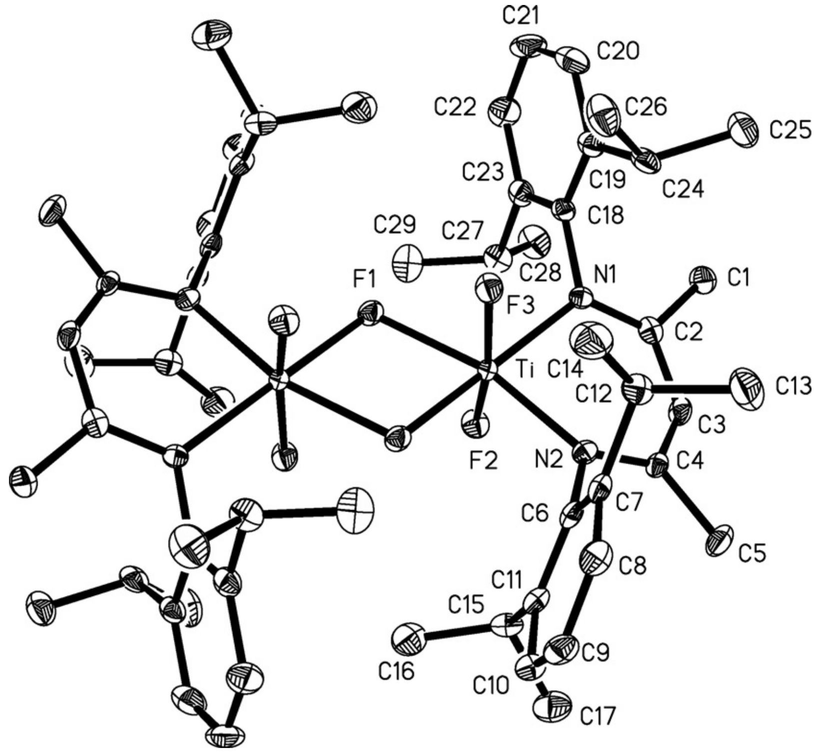

Fig. 2. Molecular structure of **1** with the selected labelled atoms. Ellipsoids represent 50% probability level. Selected bond distances (Å) and angles (°): Ti–F(3) 1.8012(15), Ti–F(2) 1.8047(15), Ti–F(1)#1 1.9733(15), Ti–N(2) 2.028(2), Ti–F(1) 2.0679(15), Ti–N(1) 2.077(2), F(3)–Ti–F(2) 165.40(8), F(3)–Ti–F(1)#1 89.26(7), F(3)–Ti–N(2) 100.27(8), F(2)–Ti–N(2) 93.03(8), F(3)–Ti–F(1) 82.50(7), F(2)–Ti–F(1) 86.26(7), N(2)–Ti–F(1) 164.69(8), F(3)–Ti–N(1) 87.27(8). Symmetry transformation used to generate equivalent atoms #1: $-x + 1/2$, $-y + 1/2$, $-z + 1$.

located *trans* to the longer Ti–N bond, consistent with the *trans* effect in octahedral complex of d^0 transition metals [3b–f].

2.2. Polymerization experiments

The trifluoro complex ($LTiF_3$) (**1**) is moderately active in polymerization of ethylene, although the activity is definitely higher than that of $LTiMe_3$ and comparable with that of the oxo-bridged complexes $LTiCl(\mu\text{-}O)_2TiClL$ and $LTiMe(\mu\text{-}O)_2TiMe$-L·toluene [17]. The trichloride complex $LTiCl_3$ and the dichloride complex $LTiCl_2$ are inactive in the polymerization of ethylene. A similar trend of activities in polymerization of styrene was observed for the chloride, alkyl, oxo-bridged and fluoride complexes supported by the cyclopentadienyl ligand [5a,b]. The high activity of the oxo-bridged cyclopentadienyl complexes has been explained by the oxygen effect. It enhances the Lewis acidity at the metallic centers in the oxo-bridged complexes and in turn leads to an increase in the catalytic activity. The most electronegative element fluorine might also enhance the Lewis acidity at the Ti(IV) center in **1** compared to that of $LTiCl_3$ and $LTiMe_3$, which might result in an increase of the catalytic activity.

3. Conclusion

Complex ($LTiF_3$) (**1**) has been obtained using two synthetic routes, reaction of TiF_4 and NacNacK·2THF in toluene and interaction of $LTiCl_3$ with 3 equiv. of Me_3SnF in toluene. The first method allowed facile generation of the Ti(IV) fluoride complex in toluene by reaction of TiF_4 with NacNacK·2THF, while the second method afforded complex **1** in high yield. Complex **1** is a dimer in the solid state, and the monomer was the only detected species in C_6D_6 and CD_3CN solution, respectively at room temperature. The stabilization of **1** can be rationalized by the facile formation of the Ti → (μ-F)–Ti coordinative bond, whose energy is higher than that of Ti → (μ-Cl)–Ti. Consequently, the corresponding trichloride complex $LTiCl_3$ is a monomeric species in the solid state. The trifluoro complex ($LTiF_3$) (**1**) is moderately active in polymerization of ethylene; the activity is higher than that of $LTiMe_3$ and $LTiCl_2$, and comparable with those of the oxo-bridged complexes $LTiCl(\mu\text{-}O)_2TiClL$ and $LTiMe(\mu\text{-}O)_2TiMe$-L·toluene. The increased activity is attributed to the higher electronegativity of fluorine, compared to that of Me, Cl, and oxygen. Therefore the fluorine atom attached to the titanium enhances the Lewis acidity of the Ti(IV) center.

4. Experimental

All operations were performed under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and MBrown MB-150B inert atmosphere glove box. Solvents toluene, hexane, and tetrahydrofuran were dried over Na/benzophenone and distilled under nitrogen prior to use. C_6D_6 was dried over K and degassed, CD_3CN was dried over CaH_2 and distilled prior to use. The compounds LH with the ligand $L = (2,6\text{-}i\text{Pr}_2C_6H_3NC(Me))_2CH$, NacNacH), Me_3SnF, $LTiCl_3$ were prepared by known literature methods [17–20]. The purity of all compounds was checked by ^{1}H and ^{13}C NMR spectra. TiF_4 (Acros Organics 99%) was used as received. KH suspension in mineral oil (Acros Organics) was filtered and then thoroughly washed with *n*-hexane. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using Bruker Avance DPX 200, Bruker Avance DRX 500, and Varian INOVA-600 spectrometers. Chemical shifts are reported in δ ppm to high frequency of Me_4Si with the solvent as the reference signal. Mass spectra were recorded using a Finnigan MAT 8230 mass spectrometer, and elemental analyses were carried out at the Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen. Melting points were measured in sealed capillary tubes under nitrogen and were not corrected.

4.1. Compound $(LTiF_3)_2$ (**1**)

Toluene (50 mL) was added to solid $LTiCl_3$ (0.88 g, 1.5 mmol) and Me_3SnF (0.85 g, 4.6 mmol). The resulting solution was stirred for 16 h at room temperature, then filtered and all volatiles were removed under vacuum. The resulted solid was washed with *n*-hexane (3× 10 mL). Yield of **1** 0.71 g (90%). Elemental analysis $C_{29}H_{41}F_3N_2Ti$: calcd. C 66.67, H 7.85, N 5.36; found C 66.81, H 7.94, N 5.24. mp 197 °C. EI-MS: m/z (%) = 522 (25) $[M]^+$, 503 (45) $[M-F]^+$, 487 (5) $[M–F–CH_4]^+$, 482 (20) $[M-2HF]^+$, 479 (25) $[M-i\text{Pr}]^+$. 417 (100) $[L]^+$. ^{1}H NMR (200.131 MHz, C_6D_6, rt), δ (ppm) = 7.15–6.90 (m, 6H, aryl), 5.13 (s, 1H, $C(CH_3)C\mathit{H}C(CH_3)$), 3.16 (sept, 4H, J = 6.70 Hz, $C\mathit{H}Me_2$), 1.43 (d, 6H, J = 6.70 Hz, $CH\mathit{Me}_2$), 1.39 (s, 6H, $C(C\mathit{H}_3)CHC(C\mathit{H}_3)$), 1.10 (d, 6H, J = 6.70 Hz, $CH\mathit{Me}_2$). ^{13}C NMR (50.33 MHz, C_6D_6, rt), δ (ppm) = 167.29 ($\mathit{C}(CH_3)CH\mathit{C}(CH_3)$), 148.13 ($\mathit{C}_6H_3$), 141.68 ($\mathit{C}_6H_3$), 124.35 ($\mathit{C}_6H_3$), 103.56 ($C(CH_3)\mathit{C}HC(CH_3)$, 28.84 ($\mathit{C}HMe_2$), 25.08 ($CH\mathit{Me}_2$), 24.94 ($C(\mathit{C}H_3)CHC(\mathit{C}H_3)$, 24.46 ($CH\mathit{Me}_2$). ^{19}F NMR (188.34 MHz, C_6D_6, rt), δ (ppm) = 247.9 ($\Delta\omega_{1/2}$ = 332 Hz). Complex **1** in toluene-d_8. ^{19}F NMR (470.65 MHz, toluene-d_8, rt), δ (ppm) = 246.6 (s, $LTiF_3$). ^{19}F NMR (470.65 MHz, toluene-d_8, 183 K), δ (ppm) = 243.3 (s, $LTiF_3$), 241.8 (br, 4F, F terminal of $(LTiF_3)_2$), 3.6 (br, 2F, F bridging of $(LTiF_3)_2$). Complex **1** in CD_3CN. ^{19}F NMR (188.34 MHz, CD_3CN, rt), δ (ppm) = 209.1 (s, $LTiF_3$). ^{19}F NMR (188.34 MHz, CD_3CN, 230 K), δ (ppm) = 261.6 (m, F_{terminal}, $[Ti_4F_{18}]^{2-}$), 417–405 (br, weak), 232.9 (m, oligomer, unassigned), 220.0 (m, oligomer, unassigned), 204.9 (br, $\Delta\omega_{1/2}$ = 1093 Hz, $LTiF_3$), −14.2 (br, oligomer, unassigned), −22.1 (br, oligomer, unassigned), −24.68 (br, μ-F, $[Ti_4F_{18}]^{2-}$).

4.2. Reaction of $LK{\cdot}THF_x$ with TiF_4

Dry THF (50 mL) was added to a mixture of LH (1.41 g, 3.4 mmol) and KH (0.135 g, 3.4 mmol) in a 100 mL Schlenk flask. The mixture was stirred until all KH dissolved and then the THF was removed under vacuum leaving a solid residue ($LK{\cdot}THF_x$, $x \approx 2$ according to ^{1}H NMR [12]). The TiF_4 (0.418 g, 3.4 mmol) was added to this residue together with 50 mL of toluene. A dark brown color appeared upon addition of toluene. The resulting suspension was stirred for 5 days and then filtered. The toluene was removed under vacuum and the resulting solid was dissolved in *n*-hexane. Finally the *n*-hexane solution was concentrated and left at 0 °C for 3 days. During this time a colorless solid and small dark crystals of **1** deposited. Compound **1** was separated from the colorless solid by washing with *n*-hexane (5× 5 mL). Yield of **1** 0.2 g (10%), Analytical data for **2**. mp 306 °C, decomposition. EI-MS: m/z (%) = 835 (75) $[M-2K]^+$, 792 (10) $[M^+-2K–i\text{Pr}]$, 658 (100) $[M^+-2K–C_6H_3(i\text{Pr})_2–Me]$, 643 (20) $[M^+-2K–C_6H_3(i\text{Pr})_2–C_2H_6]$, 614 (5) $[M^+-2K–C_6H_3(i\text{Pr})_2–i\text{Pr}–CH_4]$ 481 (70) $[M^+-2K–2C_6H_3(i\text{Pr})_2–C_2H_6]$, 457 (15) $[M^+-2K–2C_6H_3(i\text{Pr})_2–C_4H_6]$. ^{1}H NMR (200.13 MHz, C_6D_6, rt), δ (ppm) = 7.18–7.05 (m, 12H, $C_6\mathit{H}_3$), 5.91 (s, 2H, $C(CH_3)C\mathit{H}C(CH_3)$), 3.16 (br, 4H, $C\mathit{H}Me_2$), 2.86 (sept, 4H, J = 6.85 Hz, $C\mathit{H}Me_2$), 2.20 (s, 12H, $C(C\mathit{H}_3)CHC(C\mathit{H}_3)$), 1.23–1.08 (m, 24H, $CH\mathit{Me}_2$).

4.3. Polymerization of ethylene

In a 500 mL Schlenk flask containing 60 mL of toluene, MAO, and then catalyst were combined (MAO:metal = 500:1,

Table 1

Ethylene polymerization data for the complex **1**, activity of $LTiMe_3$, $LTiCl(\mu\text{-}O)_2TiClL$, and $LTiMe(\mu\text{-}O)_2TiMeL{\cdot}$toluene is given for comparison

Complex	Co-catalyst: MAO[a]		T_m[b] (°C)	
	25 °C	80 °C	25 °C	80 °C
$(LTiF_3)_2$ (**1**)	6.4×10^{3}[c]	8.2×10^3	122.0	123.0
$LTiMe_3$ [17]	1×10^{3}[b]	–	123.7	–
$LTiCl(\mu\text{-}O)_2TiClL$ [17]	1×10^3	7×10^3	125.8	122.2
$LTiMe(\mu\text{-}O)_2TiMeL{\cdot}$toluene [17]	$1–4 \times 10^3$	$4–8 \times 10^3$	123.4	119.9
$TiBz_4$[d]	1.4×10^4	1×10^4	126.2	123.5
$ZrBz_4$[e]	3.8×10^3 2.5×10^3	2.8×10^4	121.0	123.5

[a] Conditions: time, 2 h; pressure, 1 bar, Al:Ti and Al:Zr, 500:1; volume, 60 mL; 15–20 μmol of complex was used in different runs.

[b] Determined by DSC.

[c] Activity, g(polymer)/mol catalyst h bar.

[d] $TiBz_4$.

[e] $TiBz_4$ and $ZrBz_4$ were studied as references under the same conditions. Polymerization of ethylene using $TiBz_4$ was studied in Ref. [24]. The reported activity of $TiBz_4–AlEt_2Cl$ in *n*-heptane solution 7×10^3 g(polymer)/(mol catalyst h bar) [25]. The reported activity of $ZrBz_4$–MAO in *n*-heptane solution at 50 °C was 5.2×10^7 g(polymer)/(mol catalyst h) ($P(C_2H_4) = 3$ kg cm^{-2}, time 0.5 h) [26]. The activity of $ZrBz_4$ is $\sim 10^3$ times lower in our case than in Ref. [20], the same reference reported activity of Cp_2ZrMe_2 2.97×10^7 g(polymer)/(mol catalyst) (Al:Zr = 10,000), while the reported activity of Cp_2ZrMe_2 was 1.02×10^6 g(polymer)/(mol catalyst h bar) (Al:Zr = 400) in toluene solution [27].

15–20 μmol of catalyst). The resulting mixture was stirred for 15 min, then the solution was degassed, and finally the system was connected to an ethylene atmosphere (1 bar pressure). After stirring the resulting suspension for an appropriate time, the mixture was added to a solution of ethanol and aqueous HCl. The polyethylene (PE) was collected by filtration, washed with ethanol, then with *n*-hexane and finally dried. The results are shown in Table 1.

4.4. X-ray crystallography

X-ray data were collected on a Bruker APEX2 CCD diffractometer. The data were reduced (SAINT) [21] and corrected for absorption (SADABS) [22]. The structure was solved by direct methods, and refined against F^2 with anisotropic non-hydrogen atoms. Hydrogen atoms were included using rigid methyl groups or with a riding model. All calculations were carried out using SHELXTL software [23]. Crystal data for **1** ($C_{58}H_{82}F_6N_4Ti_2$) at 100(2) K: $M_r = 1045.08$, crystal dimensions 0.19 mm × 0.08 mm × 0.08 mm, monoclinic, space group $C2/c$, $a = 24.1842(19)$ Å, $b = 15.3141(12)$ Å, $c = 14.6800(10)$ Å, $\beta = 96.698(3)^\circ$, $V = 5399.8(7)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.286$ g cm^{-3}, $\mu = 0.357$ mm^{-1}, of the 60,284 reflections measured ($1.58 < \theta < 26.37^\circ$), 5533 were independent ($R_{int.} = 0.0911$). Refinement led to $wR2 = 0.1283$ (all data), $R1 = 0.0485$ (for reflections with $I > 2\sigma(I)$), data/parameters 5533/326, GooF = 1.03. CCDC-669769 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] The complex $[Cp^*_2Ti_2F_7]$ has been extensively employed as complexing agent for metal cations such as:
(a) $[Na]^+$, $[Mg]^{2+}$ F.Q. Liu, A. Kuhn, R. Herbst-Irmer, D. Stalke, H.W. Roesky, Angew. Chem., Int. Ed. Engl. 33 (1994) 555–556,;
F.Q. Liu, A. Kuhn, R. Herbst-Irmer, D. Stalke, H.W. Roesky, Angew. Chem. 106 (1994) 577–578;
(b) $[Li]^+$ A. Pevec, F. Perdih, J. Kosmrlj, B. Modec, H.W. Roesky, A. Demsar, Dalton Trans. (2003) 420–425;
(c) A. Demsar, A. Pevec, L. Golic, S. Petricek, A. Petric, H.W. Roesky, Chem. Commun. (1998) 1029–1030;
(d) $[Ca]^{2+}$ A. Pevec, A. Demsar, V. Gramlich, S. Petricek, H.W. Roesky, Dalton Trans. (1997) 2215–2216;
(e) A. Demsar, A. Pevec, S. Petricek, L. Golic, A. Petric, M. Björgvinsson, H.W. Roesky, Dalton Trans. (1998) 4043–4047;
(f) P. Yu, P. Müller, H.W. Roesky, M. Noltemeyer, A. Demsar, I. Usón, Angew. Chem., Int. Ed. 38 (1999) 3319–3321 $[Zn]^{2+}$;
P. Yu, P. Müller, H.W. Roesky, M. Noltemeyer, A. Demsar, I. Usón, Angew. Chem. 111 (1999) 3518–3520;
(g) $[La]^{3+}$, F. Perdih, A. Demsar, A. Pevec, S. Petricek, I. Leban, G. Giester, J. Sieler, H.W. Roesky, Polyhedron 20 (2001) 1967–1971.
(h) $[Nd]^{3+}$, $[Pr]^{3+}$ A. Pevec, M. Mrak, A. Demsar, S. Petricek, H.W. Roesky, Polyhedron, 22 (2003) 575–579;
(i) M.G. Walawalkar, R. Murugavel, H.W. Roesky, Eur. J. Solid State Inorg. Chem. 1 (1996) 943–955;
(j) F.Q. Liu, D. Stalke, H.W. Roesky, Angew. Chem., Int. Ed. Engl. 34 (1995) 1872–1874;
F.Q. Liu, D. Stalke, H.W. Roesky, Angew. Chem. 107 (1995) 107–109.

[2] Microporous Ti(IV) fluorophosphates have been prepared from Ti(IV) fluoride complexes in the presence of a donor ligand.
(a) C. Serre, G. Férey, J. Mater. Chem. 9 (1999) 579–584;
(b) Y. Fu, Y. Liu, Z. Shi, Y. Zou, W. Pang, J. Solid State Chem. 162 (2001) 96–102.

[3] (a) A. Beste, O. Oliver, A. Gerhard, G. Frenking, Eur. J. Inorg. Chem. (1999) 2037–2045;
(b) B.J. Coe, S.J. Glenwright, Coord. Chem. Rev. 203 (2000) 5–80;
(c) V.A. Palkin, T.A. Kuzina, Russ. J. Coord. Chem. 21 (1995) 162–164;
(d) D.S. Dyer, R.O. Ragsdale, Chem. Commun. (1966) 601–602;
(e) D.S. Dyer, R.O. Ragsdale, Inorg. Chem. 8 (1969) 1116–1120;
(f) E. Turin, R.M. Nielson, A.E. Merbach, Inorg. Chim. Acta 134 (1987) 67–78.

[4] (a) S. Mizuta, N. Shibata, S. Ogawa, H. Fujimoto, S. Nakamura, T. Toru, Chem. Commun. (2006) 2575–2577;
(b) B.L. Pagenkopf, E.M. Carreira, Chem.-Eur. J. 5 (1999) 3437–3442;
(c) E.D. Burke, N.K. Lim, J.L. Gleason, Syn. Lett. 3 (2003) 390–392;
(d) M. Bandini, P.G. Cozzi, L. Negro, A. Umani-Ronchi, Chem. Commun. (1999) 39–40;
(e) L. Anastasia, E. Giannini, G. Zanoni, G. Vidari, Tetrahedron Lett. 46 (2005) 5803–5806;
(f) J.W. Bode, D.R. Gauthier, E.M. Carreira, Chem. Commun. (2001) 2560–2561;
(g) M. Braun, W. Kotter, Angew. Chem., Int. Ed. 43 (2004) 514–517;
M. Braun, W. Kotter, Angew. Chem. 116 (2004) 520–523.

[5] (a) X. Qian, J. Huang, Y. Qian, J. Organomet. Chem. 689 (2004) 1503–1510;
(b) W. Kaminsky, S. Lenk, V. Scholz, H.W. Roesky, A. Herzog, Macromolecules 30 (1997) 7647–7650.

[6] (a) E.F. Murphy, R. Murugavel, H.W. Roesky, Chem. Rev. 97 (1997) 3425–3468;
(b) H.W. Roesky, I. Haiduc, Dalton Trans. (1999) 2249–2264.

[7] A. Herzog, F.-Q. Liu, H.W. Roesky, A. Demsar, K. Keller, M. Noltemeyer, F. Pauer, Organometallics 13 (1994) 1251–1256.

[8] (a) W.S. Sheldrick, J. Fluor. Chem. 4 (1974) 415–421;
(b) D.A. Straus, M. Kamigaito, A.P. Cole, R.M. Waymouth, Inorg. Chim. Acta 349 (2003) 65–68.

[9] C. Santamaria, R. Beckhaus, D. Haase, W. Saak, R. Koch, Chem.-Eur. J. 7 (2001) 622–626.

[10] D. Chakraborty, S. Horchler, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Inorg. Chem. 39 (2000) 3995–3998.

[11] A. Decken, G.B. Nikiforov, J. Passmore, Dalton Trans. 26 (2007) 4149–4159.

[12] U. Fekl, W. Kaminsky, K.I. Goldberg, J. Am. Chem. Soc. 125 (2003) 15286–15287.

[13] The NMR spectra of this compound are different from those of $\{NacNacK\}_\infty$, hence it could be a dimer, $\{L^2K\}_2$ according to the literature data. W. Clegg, E. K. Cope, A.J. Edwards, F.S. Mair, Inorg. Chem. 37 (1998) 2317–2319.

[14] A. Decken, H.D.B. Jenkins, C. Knapp, G.B. Nikiforov, J. Passmore, J.M. Rautiainen, Angew. Chem., Int. Ed. 44 (2005) 7958–7961;
A. Decken, H.D.B. Jenkins, C. Knapp, G.B. Nikiforov, J. Passmore, J.M. Rautiainen, Angew. Chem. 117 (2005) 8172–8175.

[15] See bond lengths in:
(a) D. Fenske, E. Hartmann, K. Dehnicke, Z. Naturforsch. B43 (1988) 1611–1615 $[LTiCl_2(\mu\text{-}Cl)]_2$ (Ti–N 2.072, 1.986 Å, L-benzamidinato ligand $(NSiMe_3)_2CPh)$);
(b) J.R. Hagadorn, J. Arnold, Organometallics 17 (1998) 1355–1368, $L_2Ti(NCMe_3)$ (Ti–N 2.152(2) and 2.156(3) Å L-PhC$(NSiMe_3)_2$);
(c) D.P. Steinhuebel, S.J. Lippard, Inorg. Chem. 38 (1999) 6225–6233,

$L_2Ti(CH_2SiMe_3)_2$, Ti–N 2.006(2), 2.045(3) Å, $L_2TiCl(CH_2SiMe_3)$ Ti–N 2.087(2), 2.091(2) Å L-aminotroponiminate ligand).

[16] (a) G.B. Nikiforov, C. Knapp, J. Passmore, A. Decken, J. Fluor. Chem. 127 (2006) 1398–1404;
(b) A. Decken, G.B. Nikiforov, J. Passmore Dalton Trans. 36 (2006) 4328–4334;
(c) A. Decken, E.G. Ilyin, H.D.B. Jenkins, G.B. Nikiforov, J. Passmore Dalton Trans. (2005) 3039–3050;
(d) T.S. Cameron, A. Decken, E.G. Ilyin, G.B. Nikiforov, J. Passmore, Eur. J. Inorg. Chem. (2004) 3865–3872;
(e) E.G. Ilyin, G.B. Nikiforov, G.G. Aleksandrov, H.W. Roesky, Y.A. Buslaev, Dokl. Chem. 376 (2001) 58–62;
E.G. Ilyin, G.B. Nikiforov, G.G. Aleksandrov, H.W. Roesky, Y.A. Buslaev, Translated from Dokl Akad. Nauk 376 (2001) 772–776;
(f) E.G. Ilyin, G.B. Nikiforov, G.G. Aleksandrov, Dokl. Chem. 396 (2004) 111–115;
E.G. Ilyin, G.B. Nikiforov, G.G. Aleksandrov, Translated from Dokl. Akad. Nauk 396 (2004) 500–504;
(g) E.G. Ilyin, G.G. Aleksandrov, G.B. Nikiforov, Yu.A. Buslaev, Dokl. Chem. 376 (2001) 25–28;
E.G. Ilyin, G.G. Aleksandrov, G.B. Nikiforov, Yu.A. Buslaev, Translated from Dokl Akad. Nauk 376 (2001) 351–355.

[17] G.B. Nikiforov, H.W. Roesky, P.G. Jones, R.B. Oswald, M. Noltemeyer, Dalton Trans. (2007) 4149–4159.

[18] (a) K. Zerche, K.H. Thiele, Z. Anorg. Allg. Chem. 612 (1992) 155–160;
(b) J. Giesemann, E. Ernst, A. Ernst, J. Ulbricht, Makromol. Chem.-Macromol. Chem. Phys. 187 (1986) 1737–1744;
(c) J. Giesemann, A. Brandt, J. Ulbricht, Acta Polym. 34 (1983) 623–626.

[19] J.C.W. Chien, J.T.T. Hsieh, J. Polym. Sci. Polym. Chem. Ed. 14 (1976) 1915–1932.

[20] E. Giannetti, G.M. Nicoletti, R. Mazzocchi, J. Pol. Sci., Pol. Chem. Ed. 23 (1985) 2117–2133.

[21] G. Bai, S. Singh, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, J. Am. Chem. Soc. 127 (2005) 3449–3455.

[22] E. Krause, Ber. Dtsch. Chem. Ges. 51 (1918) 1447–1456.

[23] M. Stender, R.J. Wright, B.E. Eichler, J. Prust, M.M. Olmstead, H.W. Roesky, P.P. Power, Dalton Trans. (2001) 3465–3469.

[24] (a) W.K. Johnson, J. Org. Chem. 25 (1960) 2253–2254;
(b) L.E. Levchuk, J.R. Sams, F. Aubke, Inorg. Chem. 11 (1972) 43–50.

[25] SAINT 6.02, 1997–1999, Bruker AXS Inc., Madison, Wisconsin, USA.

[26] SADABS, G. Sheldrick, 1999, Bruker AXS Inc., Madison, Wisconsin, USA.

[27] SHELXTL 5.1, G. Sheldrick, 1997, Bruker AXS Inc., Madison, Wisconsin, USA.