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Journal of Fluorine Chemistry 129 (2008) 376–381

JOURNAL OF FLUORINE CHEMISTRY

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

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Received 12 December 2007; received in revised form 22 January 2008; accepted 22 January 2008
Available online 9 February 2008

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-iPr$_2$C$_6$H$_3$))$_2$, “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$_4$N][(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-iPr$_2$C$_6$H$_3$))$_2$, “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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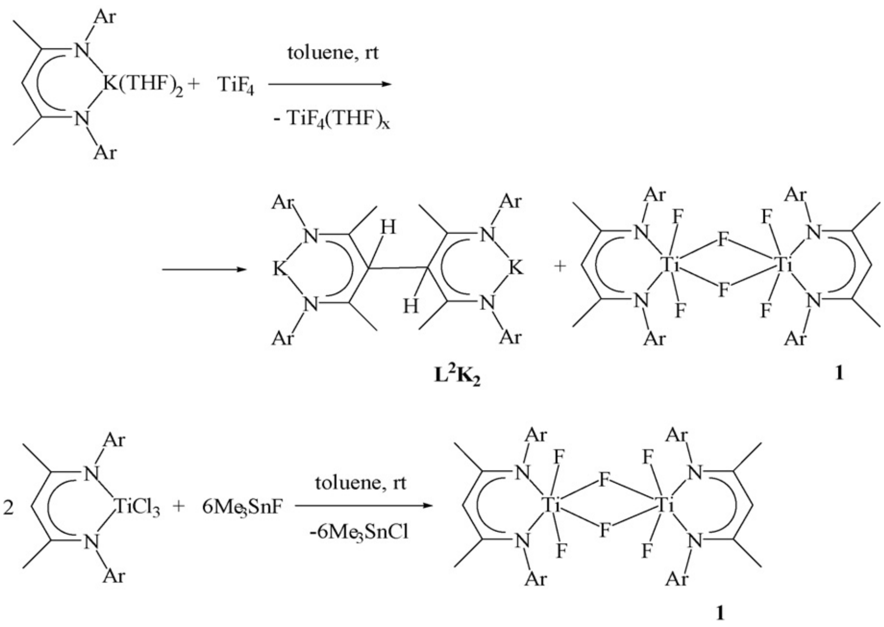
doi:10.1016/j.jfluchem.2008.01.016



Scheme 1. Ar = 2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$.

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 *i*Pr 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 $\Delta H = -5.8(7)\ \mathrm{kJ\ mol^{-1}}$, $\Delta S = -24(4)\ \mathrm{J\ mol^{-1}\ K^{-1}}$, $\Delta G^{298} = +1.4\ \mathrm{kJ\ mol^{-1}}$, $\Delta G^{183} = -1.4\ \mathrm{kJ\ mol^{-1}}$.

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

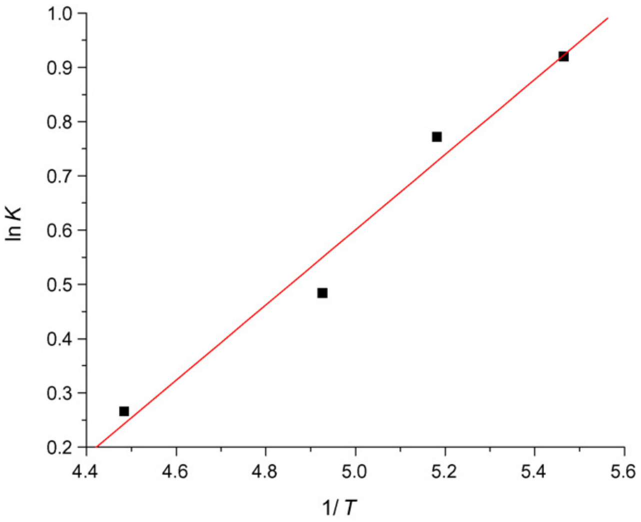


Fig. 1. Eyring plot for the disappearance of $LTiF_3$ vs. time; $(\mathbf{1})_0 = 1.53 \times 10^{-2}$ mol/L, $1/\ln(K) = -2.9(4) + 693(82)\ (1/T)$.