

## Preparation and Properties of some 2,2,2-Trifluoroethoxy Derivatives of Titanium

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*The synthesis and characterization of some compounds of titanium(IV) with the formula  $TiX_{4-x}(OR_f)_x$  (where  $x = 2, 3$  for  $X = Cl$ ;  $x = 1, 2$  for  $X =$  isopropoxy and  $OR_f = 2,2,2$ -trifluoroethoxy,  $OCH_2CF_3$ ) and their adducts with a nitrile ( $CH_3CN$ ,  $C_2H_5CN$ ) and the alcohol  $R_fOH$  are reported. Using an acidity scale based on NMR data, the ligand, 2,2,2-trifluoroethoxy is compared with other ligands such as chlorine and isopropoxy and the following decreasing order of electron donor ability,  $OR > OR_f > Cl$ , is obtained. Attempts to prepare alkylated compounds  $RTi(OR_f)_3$  ( $R = CH_3, C_6H_5CH_2$ ) from  $TiCl(OR_f)_3$  are reported and the cleavage of the titanium carbon bond in these compounds is found to take place readily by action of nucleophilic agents. The reactivity of the titanium oxygen bond of  $Ti-OR_f$  is tested towards some substitution and insertion reactions.*

### Introduction

The use of titanium derivatives as catalysts in organic synthesis and polymerization continues to attract considerable attention [1–4]. From a comparison of experimental data previously reported, it may be suspected that the chemical environment of titanium in the catalyst is of major importance.

As part of a general study of a Lewis acidity scale based on NMR and of an experimental correlation between this scale and chemical reactivity towards addition, substitution and insertion reactions, we have examined in this work the influence of the fluoroethoxy ligand  $OCH_2CF_3$  ( $= OR_f$ ).

Although the first fluoroalkoxy derivative of titanium  $Ti(OR_f)_2(AcAc)_2$  ( $AcAc =$  acetylacetonato) has been known for some time [5], the preparation of two mixed chloro fluoroethoxy  $TiCl_3OR_f$  and  $TiCl_2(OR_f)_2$  has only recently been reported [6, 7] and the alkoxo and alkyl analogues  $TiX_{4-x}(OR_f)_x$  ( $X = OR$  such as isopropoxy or  $X = R$  such as methyl, benzyl) have not yet been described.

We now report the synthesis of several new chloro and alkoxo derivatives and by using the NMR scale the electronic properties of the ligand  $OR_f$  may be

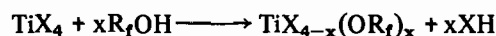
characterized and compared with  $Cl$  and  $OR$ . Then the reactivity of these species is studied. Addition reactions lead to the formation of 1:1 adducts, for example with alcohol and nitriles. Substitution of the ligand  $OR_f$  may be obtained by action of acetyl chloride or acetylacetone. Insertion reactions are exemplified in the case of phenyl isocyanate.

Moreover, a special interest is paid to alkyl derivatives such as  $RTi(OR_f)_3$  ( $R =$  alkyl) as possible active non-halogenated catalysts in polymerization of olefins. In previous work, we have prepared monocyclopentadienyl compounds  $CpTi(OR_f)_3$  and  $Cp(CH_3)Ti(OR_f)_2$  ( $Cp = \eta^5$ -cyclopentadienyl) and found they were efficient in polymerization of methylmethacrylate [8]. We now present attempts to prepare  $CH_3Ti(OR_f)_3$  and  $C_6H_5CH_2Ti(OR_f)_3$  and preliminary investigations on the reactivity of the  $Ti-C$  bond in these derivatives.

### Preparation and Characterization of $TiCl_{4-x}(OR_f)_x$ and $Ti(OR_f)_{4-x}(OR_f)_x$ and Some of Their Adducts

#### Synthesis

The fixation of the ligand 2,2,2-trifluoroethoxy ( $OCH_2CF_3 = OR_f$ ) on titanium may be obtained by action of the alcohol  $R_fOH$  on titanium tetrachloride  $TiCl_4$  or tetraalkyl titanate  $Ti(OR)_4$  (here  $OR = OCH(CH_3)_2 = OiPr$ ) according to the general scheme:



used for the previously reported preparation of  $TiCl_3(OR_f)$  and  $TiCl_2(OR_f)_2$  [6, 7]. This way proved convenient to synthesize the derivatives  $TiCl_2(OR_f)_2$  (I),  $TiCl(OR_f)_3$  (II) and  $Ti(OR_f)_2(OR_f)_2$  (III), but  $Ti(OR_f)_4$  cannot be obtained even using a large excess of  $R_fOH$ .

In the case of  $Ti(OR)_3(OR_f)$  (IV) better yields were obtained from methyl or alkylamido derivatives by the reactions:



TABLE I.  $^1\text{H}$  and  $^{19}\text{F}$  NMR Data<sup>a</sup> of Compounds  $\text{TiX}_{4-x}(\text{OCH}_2\text{CF}_3)_x$ .

Compound	$^1\text{H}$				$^{19}\text{F}$
	$\text{OCH}(\text{CH}_3)_2$	$\text{OCH}(\text{CH}_3)_2$	$\text{OCH}_2\text{CF}_3$	$J_{\text{H-F}}$	$\text{OCH}_2\text{CF}_3$
$\text{TiCl}_2(\text{OR}_f)_2$ (I)			4.95	8.4	+3.4
$\text{TiCl}(\text{OR}_f)_3$ (II)			4.92	7.9	+3.2
$\text{Ti}(\text{O}i\text{-Pr})_2(\text{OR}_f)_2$ (III)	4.80	1.30	4.65	8.7	+3
$\text{Ti}(\text{O}i\text{-Pr})_3(\text{OR}_f)$ (IV)	4.67	1.25	4.65	8.4	+3.4
$\text{CF}_3\text{CH}_2\text{OH}^b$			3.93	7.0	-1.0

<sup>a</sup>Chemical shifts in ppm downfield with respect to TMS for  $^1\text{H}$ , to  $\text{CF}_3\text{CO}_2\text{H}$  for  $^{19}\text{F}$  in  $\text{CCl}_4$  solvent;  $J_{\text{H-F}}$  coupling constant in Hz. <sup>b</sup>Measured as neat liquid.

TABLE II.  $^1\text{H}$  NMR Data of  $\text{Ti}(\text{O}i\text{-Pr})_{4-x}(\text{OR}_f)_x$  ( $x = 1, 2$ ) and Related Derivatives.

Compound		$\text{CH}(\text{CH}_3)_2$	$\text{CH}(\text{CH}_3)_2$	Ref.
$\text{Ti}(\text{O}i\text{-Pr})_4$	Monomer	4.58	1.23	[9]
$\text{Ti}(\text{O}i\text{-Pr})_3(\text{OR}_f)$	Monomer	4.67	1.25	
$\text{Ti}(\text{O}i\text{-Pr})_2\text{Cl}_2$	Dimer	4.94	1.50	[10]
$\text{Ti}(\text{O}i\text{-Pr})_2(\text{OR}_f)_2$	Dimer	4.80	1.30	

In fact, in the course of these syntheses we frequently observed the formation of an adduct by fixation of the alcohol  $\text{R}_f\text{OH}$  on  $\text{TiX}_{4-x}(\text{OR}_f)_x$  and such 1:1 adducts may be isolated in the case of (I), (II) and (III). Their dissociation takes place under mild conditions and the components are recovered.

Other Lewis complexes may be readily obtained. For example, by reaction with nitriles ( $\text{CH}_3\text{CN}$  and  $\text{C}_2\text{H}_5\text{CN}$ ), 1:1 adducts have been prepared from (I) and (II).

#### Physical and Spectroscopic Characterization

Molecular weights were determined cryoscopically: (IV) proved to be a monomer, (I) and (II) are dimerized and (III) is a trimer, suggesting that fluoroalkoxy groups are able to form bridged bonds as alkoxy groups usually do.  $^1\text{H}$  and  $^{19}\text{F}$  NMR parameters of  $\text{TiX}_{4-x}(\text{OR}_f)_x$  are collected in Table I. As in other systems previously reported [9, 10], the chemical shifts  $\delta\text{CH}$  and  $\delta\text{CH}_3$  of the isopropoxy group (Table II) may be used to estimate the shielding induced by the other ligands attached to the metal atom. A progressive downfield shift is thus observed by replacement of OR by  $\text{OR}_f$  and of  $\text{OR}_f$  by Cl. This suggests a decreasing order of electron donor ability:  $\text{OR} > \text{OR}_f > \text{Cl}$ .

The same order is obtained following the chemical shift of  $^1\text{H}$  and  $^{13}\text{C}$  of cyclopentadienyl in  $\text{CpTiX}_3$  ( $\text{X} = \text{Cl}, \text{OC}_2\text{H}_5, \text{OR}_f$ ) [8].

The NMR spectra of 1:1 adducts of (I) and (II) with propionitrile were recorded while the insoluble complexes with acetonitrile cannot be studied. A special interest was paid to  $^1\text{H}$  chemical shifts in the

TABLE III.  $^1\text{H}$  Chemical Shifts of Nitrile in  $\text{TiCl}_{4-x}(\text{OR}_f)_x \cdot \text{C}_2\text{H}_5\text{CN}$  ( $x = 0, 2, 3$ ).

Compound	$\delta\text{CH}_2$	$\delta\text{CH}_3$	$\delta\text{CH}_2 - \delta\text{CH}_3$
$\text{C}_2\text{H}_5\text{CN}$	2.33	1.23	1.10
$\text{TiCl}(\text{OR}_f)_3 \cdot \text{C}_2\text{H}_5\text{CN}$	2.52	1.30	1.22
$\text{TiCl}_2(\text{OR}_f)_2 \cdot \text{C}_2\text{H}_5\text{CN}$	2.65	1.37	1.28
$\text{TiCl}_4 \cdot \text{C}_2\text{H}_5\text{CN}^a$	2.77	1.44	1.33

<sup>a</sup>Unpublished results.

nitrile collected in Table III, which may be used as an acidity scale for the series  $\text{TiCl}_{4-x}(\text{OR}_f)_x$ . The progressive deshielding observed as the number of chlorine atoms is increased indicates that OR is a better electron donor than Cl. Since similar adducts cannot be obtained from  $\text{TiCl}_2(\text{OR})_2$  or  $\text{TiCl}(\text{OR})_3$  owing to their poor Lewis acidity the decreasing order of electron donor ability  $\text{OR} > \text{OR}_f > \text{Cl}$  is confirmed.

#### Preparation and Characterization of the Alkyl Derivatives $\text{RTi}(\text{OR}_f)_3$ (with $\text{R} = \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5$ )

##### Synthesis

We have prepared alkyltitanium derivatives of formula  $\text{RTi}(\text{OR}_f)_3$  starting from (II) and using Grignard or methyl lithium as alkylating agents as shown in eq. 1 and 2:

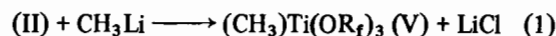
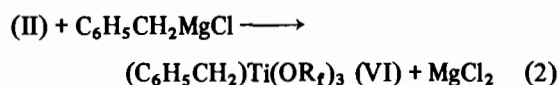


TABLE IV.  $^1\text{H}$  NMR Chemical Shifts of  $\text{RTi}(\text{OR}_f)_3$ .

Compound	Solvent	$\delta$ Ti-CH <sub>3</sub>	$\delta$ Ti-CH <sub>2</sub>	$\delta$ OCH <sub>2</sub> CF <sub>3</sub>
$(\text{C}_6\text{H}_5\text{CH}_2)\text{Ti}(\text{OR}_f)_3$ <sup>a</sup>	$\text{CH}_2\text{Cl}_2$		2.9	4.7
$(\text{CH}_3)\text{Ti}(\text{OR}_f)_3 \cdot \text{CH}_3\text{CN}$	$\text{CH}_2\text{Cl}_2$	1.25		4.72
$(\text{CH}_3)\text{Ti}(\text{OR}_f)_3 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$	$\text{CCl}_4$	1.40		4.75

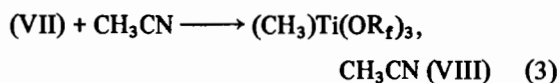
<sup>a</sup> Resonance of the phenyl ring protons in 2-6 and 3-4-5 position are observed at 7.22 and 7.42 p.p.m.



(V) in ethereal solution forms a complex of formula  $(\text{CH}_3)\text{Ti}(\text{OR}_f)_3 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  (VII); the instability of those compounds prevented any analytical investigation.

#### Spectroscopic Characterization

Compounds (V) and (VI) and some of their adducts have been characterized by NMR spectroscopy (Table IV). In complex (VII), ether can be displaced by action of a nitrile. The new 1, 1 complex (VIII) has been obtained (eq. 3):



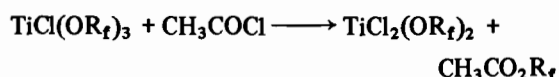
Reactions involving the cleavage of the titanium-carbon bond have been investigated using nucleophilic agents such as  $\text{HN}(\text{C}_2\text{H}_5)_2$  and  $\text{R}_f\text{OH}$ . Evolution of  $\text{CH}_4$  is characterized in both cases by I.R. spectroscopy. By these means a mono dialkylamido derivative can be obtained and this convenient pathway to obtain  $\text{Ti}(\text{OR}_f)_4$  can be retained.

#### Reactivity

##### Substitution of $\text{OR}_f$

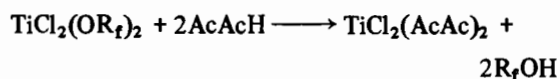
###### By chlorine

(II) is reacted with  $\text{CH}_3\text{COCl}$  and (I) is obtained following the reaction:



###### By a chelating Agent

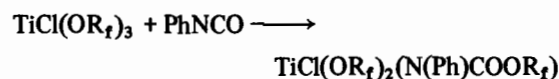
Treatment of (I) with acetylacetone gives the fluoroalcohol following the reaction:



A similar reaction is obtained with  $\text{TiCl}_2(\text{OR})_2$  [11].

#### Insertion

Insertion of phenyl isocyanate is a well known reaction of alkoxides of various transition metals [12]. In (II) a mono insertion takes place in the Ti- $\text{OR}_f$  bond following the reaction:



This is confirmed by analytical data (Experimental) and I.R. spectra.

#### Experimental

Rigorous precautions were taken to exclude moisture in experiments and manipulations were carried out in nitrogen atmosphere. Solvents were dried by conventional techniques.

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded respectively on Perkin-Elmer R<sub>12</sub> and R<sub>10</sub> spectrometers. I.R. data were obtained using a Perkin-Elmer Model 557 spectrophotometer and KBr discs.

Elemental analyses (C, H, Cl, F, Ti) were performed by the "Service Central de Microanalyse du C.N.R.S." (Table V).

Molecular weight determinations were made cryoscopically in  $\text{C}_6\text{H}_6$ . Conductivity measurements were obtained from  $\text{C}_6\text{H}_6$  solutions using a Philips PW 950 conductivity bridge and a conductivity cell with platinum electrode.  $\text{CH}_3\text{Ti}(\text{OiPr})_3$  and  $\text{Ti}(\text{NEt}_2)(\text{OiPr})_3$  were prepared according to literature methods [13, 14].

#### Preparation of Bis(2,2,2-trifluoroethoxy)dichlorotitanium (I)

$\text{R}_f\text{OH}$  (168 mmol) was added dropwise with constant stirring on  $\text{TiCl}_4$  (84 mmol) in solution in 10 ml  $\text{CH}_2\text{Cl}_2$ . The yellow mixture was refluxed during 4 hr and HCl evolved. A crystalline product appears when the solution is allowed to cool to room temperature. The solid was filtered, washed with petroleum ether (40-50 °C), dried under vacuum and recrystallised from benzene and identified as  $\text{TiCl}_2(\text{OCH}_2\text{CF}_3)_2$  (yield 80%). Cryoscopic measurements at different concentrations found: 480, 485, 515, 540, 580 (required for the monomer: 316.9).

TABLE V. Analytical Data.

	%Ti exp (calc)	%C exp (calc)	%H exp (calc)	%N exp (calc)	%Cl exp (calc)	%F exp (calc)
TiCl <sub>2</sub> (OR <sub>f</sub> ) <sub>2</sub> (I)	15.0 (15.1)	15.1 (15.1)	1.2 (1.3)		19.7 (22.4)	35.1 (36.0)
TiCl(OR <sub>f</sub> ) <sub>3</sub> (II)	12.5 (12.6)	19.5 (18.9)	1.6 (1.6)		7.0 (9.3)	45.5 (45.0)
Ti(Oi-Pr) <sub>2</sub> (OR <sub>f</sub> ) <sub>2</sub> (III)	13.1 (13.1)	31.0 (33.0)	4.6 (4.9)		— —	32.0 (31.3)
Ti(Oi-Pr) <sub>3</sub> (OR <sub>f</sub> ) (IV)	14.7 (14.8)	41.3 (40.8)	7.1 (7.1)			17.7 (17.6)
TiCl <sub>2</sub> (OR <sub>f</sub> ) <sub>2</sub> ·R <sub>f</sub> OH	11.8 (11.5)	17.2 (17.3)	1.7 (1.7)		17.2 (17.1)	39.5 (41.0)
TiCl(OR <sub>f</sub> ) <sub>3</sub> ·R <sub>f</sub> OH	10.3 (10.0)	19.7 (20.0)	1.6 (1.9)			46.0 (47.4)
Ti(Oi-Pr) <sub>2</sub> (OR <sub>f</sub> ) <sub>2</sub> ·R <sub>f</sub> OH	11.1 (10.3)	31.1 (31.0)	4.5 (4.5)			34.6 (36.8)
TiCl <sub>2</sub> (OR <sub>f</sub> ) <sub>2</sub> ·CH <sub>3</sub> CN	13.6 (13.4)	20.2 (20.1)	2.1 (2.0)	4.2 (4.0)	18.9 (19.8)	29.8 (29.8)
TiCl <sub>2</sub> (OR <sub>f</sub> ) <sub>2</sub> ·C <sub>2</sub> H <sub>5</sub> CN	12.4 (12.9)	24.9 (22.6)	2.8 (2.4)	4.0 (3.8)	17.2 (19.1)	28.3 (30.6)
TiCl(OR <sub>f</sub> ) <sub>3</sub> ·CH <sub>3</sub> CN	12.0 (11.4)	22.0 (22.8)	2.1 (2.1)	3.3 (3.3)	9.4 (8.4)	38.5 (40.5)
TiCl(OR <sub>f</sub> ) <sub>3</sub> ·C <sub>2</sub> H <sub>5</sub> CN	12.4 (11.0)	23.9 (24.8)	2.5 (2.5)	3.1 (3.2)	8.8 (8.2)	37.4 (39.3)
TiCl(OR <sub>f</sub> ) <sub>2</sub> (N(Ph)COOR <sub>f</sub> )	9.6 (9.6)	31.1 (31.2)	2.2 (2.2)	2.9 (2.8)	7.7 (7.1)	34.1 (34.3)

When using an excess of R<sub>f</sub>OH (R<sub>f</sub>OH/TiCl<sub>4</sub> ≈ 3), a white solid has been isolated and analyses confirmed the formula TiCl<sub>2</sub>(OR<sub>f</sub>)<sub>2</sub>·R<sub>f</sub>OH.

#### Preparation of Chlorotris(2,2,2-trifluoroethoxy)titanium (II)

A similar method using 180 mmol of R<sub>f</sub>OH and 30 mmol of TiCl<sub>4</sub> with a refluxing time of 12 hr gave a white solid. Analyses of this compound confirm the formula TiCl(OR<sub>f</sub>)<sub>3</sub>·R<sub>f</sub>OH.

Vacuum distillation (90 °C/0.01 mm Hg) of this complex furnishes TiCl(OR<sub>f</sub>)<sub>3</sub>. Cryoscopic measurements at different concentrations found: 1028, 1029, 1051, 1140 (required for the monomer: 380.4).

#### Preparation of Bis(isopropoxy)bis(2,2,2-trifluoroethoxy)titanium (III)

To Ti(OiPr)<sub>4</sub> (10 mmol) in 10 ml CH<sub>2</sub>Cl<sub>2</sub> was added dropwise with constant stirring R<sub>f</sub>OH (40 mmol). After refluxing of 12 hr, a crystalline product is isolated when the solution is cooled. Analyses of this solid confirm the formula Ti(OiPr)<sub>2</sub>(OR<sub>f</sub>)<sub>2</sub>·R<sub>f</sub>OH. When heating this complex at 60 °C under

0.01 mm Hg, Ti(OiPr)<sub>2</sub>(OR<sub>f</sub>)<sub>2</sub> has been obtained. Cryoscopic measurements at different concentrations found: 858, 818, 827 (required for the monomer: 363.9).

#### Preparation of (2,2,2-Trifluoroethoxy)tris(isopropoxy)titanium (IV)

R<sub>f</sub>OH (48 mmol) was added dropwise with constant stirring respectively to CH<sub>3</sub>Ti(OiPr)<sub>3</sub> (4.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> or to Ti(NEt<sub>2</sub>)(Oiso Pr)<sub>3</sub> (4.8 mmol) in C<sub>6</sub>H<sub>6</sub> cooled at 4 °C. After refluxing for 0.5 hr the mixture was distilled at 55 °C/0.07 mm Hg, and a colourless liquid is collected as Ti(OiPr)<sub>3</sub>(OR<sub>f</sub>). Cryoscopic measurements at different concentrations found: 396, 409, 391, 398, 393 (required for the monomer: 323.9).

#### Preparation of the Complexes of TiCl<sub>n</sub>(OR<sub>f</sub>)<sub>4-n</sub> with Aliphatic Nitriles

These complexes are prepared by mixing solutions in CH<sub>2</sub>Cl<sub>2</sub> of TiCl<sub>n</sub>(OR<sub>f</sub>)<sub>4-n</sub> with an excess (100 %) of an aliphatic nitrile. Solid products are isolated and analysis confirms the 1:1 ratio.

I.R. data confirm the coordination of nitrile through its nitrogen atom ( $\nu_{\text{C}=\text{N}} = 2245 \text{ cm}^{-1}$  in RCN and  $\nu_{\text{C}=\text{N}} = 2285 \text{ cm}^{-1}$  in the complex [15]).

#### Action of $\text{LiCH}_3$ on (II)

A cooled ethereal solution of  $\text{LiCH}_3$  (15.8 mmol) was added dropwise with constant stirring on a  $\text{TiCl}(\text{OR}_f)_3$  (15.8 mmol) solution in ether at  $-18^\circ\text{C}$ . The orange solution is filtered and after removal of the solvent, a solid residue is obtained. The instability of this solid does not allow analytical investigation.

#### Action of $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$ on (II)

$\text{TiCl}(\text{OR}_f)_3$  (15.7 mmol) in ether was added to  $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$  (15.7 mmol) in solution in ether at  $35^\circ\text{C}$ . After addition, 31.4 mmol of dioxan was added to precipitate the magnesium salt. After filtration, the solvent was removed and a viscous instable product is obtained.

#### Action of $\text{PhNCO}$ on (II)

$\text{PhNCO}$  (8.2 mmol) was added with constant stirring at  $0^\circ\text{C}$  on (II) in  $\text{C}_6\text{H}_6$  (5 ml). After 30 mn refluxing time, the mixture is allowed to warm to room temperature. A pale yellow solid is isolated. In I.R. spectrum  $\nu_{\text{N}=\text{C}=\text{O}}$  at  $2260\text{--}80 \text{ cm}^{-1}$  disappears and is replaced by  $\nu_{\text{C}=\text{O}}$  at  $1740 \text{ cm}^{-1}$ .

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