

A FLUOROALKOXY LIGAND IN ORGANOMETALLIC CHEMISTRY OF TITANIUM(IV): SYNTHESIS AND REACTIVITY OF SOME MONOCYCLOPENTADIENYL FLUOROALKOXY DERIVATIVES

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Summary

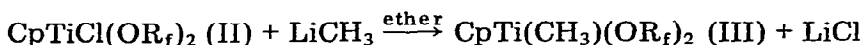
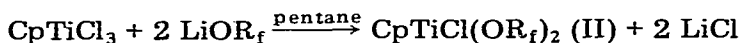
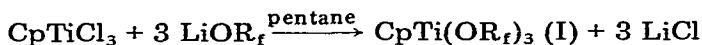
Monocyclopentadienyl derivatives of titanium(IV) containing the fluoroalkoxy group $\text{OCH}_2\text{CF}_3 = (\text{OR}_f)$ have been synthesized: $\text{CpTi}(\text{OR}_f)_3$ (I), $\text{CpTiCl}(\text{OR}_f)_2$ (II) and $\text{CpTi}(\text{CH}_3)(\text{OR}_f)_2$ (III). Their IR and ^1H , ^{13}C and ^{19}F NMR spectra are reported and compared with those of related chloro and alkoxy compounds. Their reactions have been examined and (III) was found to be an efficient catalyst for the polymerization of methyl methacrylate.

Introduction

Interest in introducing new ligands in organometallic derivatives of titanium stems from the role of the chemical environment of the transition metal on its catalytic activity in polymerization of olefins. Among others, non-halogenated complexes are of special interest [1]. We report below the preparation and properties of some monocyclopentadienyl derivatives of titanium(IV) containing the fluoroethoxy group OCH_2CF_3 .

Results and discussion

The following equations depict the method used for the introduction of the fluoroalkoxy group ($\text{OR}_f = \text{OCH}_2\text{CF}_3$) and the methyl group into monocyclopentadienyl complexes of titanium(IV) starting from CpTiCl_3



In the infrared spectra, assignments can be made by comparison with spectra of previously reported related complexes [2,3] (Table 1).

^1H , ^{13}C and ^{19}F NMR data for the new complexes are collected in Table 2, while in Table 3, ^1H and ^{13}C chemical shifts of the methyl and cyclopentadienyl groups in (I), (II), and (III) are compared with published data for related derivatives. It is noteworthy that on introduction of the fluorinated alkoxy OR_f , resonances are shifted downfield with respect to the non fluorinated ligand OR (R = Et, i-Pr) and almost reach the values obtained for chlorinated derivatives.

The reactivity of the ligand OR_f in substitution and insertion reactions have been explored, and the following reactions were found to take place very readily:

Replacement of OR_f by Cl by the action of CH_3COCl

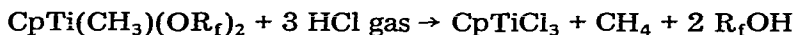
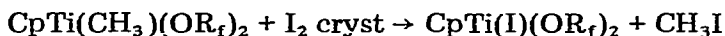


Insertion of phenylisocyanate giving urethane



More attention has been paid to the reactivity of the σ titanium—carbon bond of $\text{Ti}-\text{CH}_3$ in (III), since this type of bond is considered to play a predominant role in catalytic polymerization of olefins [6].

Displacement of CH_3 by halogens or OR_f was found to occur, as follows:



The polymerisation of methylmethacrylate in 40/1 ratio was found to take place at room temperature in presence of (I) and (III), giving a high polymer (molecular weight $\approx 10^6$) soluble in common solvents [7].

TABLE 1

MAIN IR ABSORPTION BANDS OF $\text{CpTi}(\text{CH}_3)\text{X}_2$ AND CpTiX_3 ($\text{X} = \text{OCH}(\text{CH}_3)_2, \text{OCH}_2\text{CF}_3$) IN THE REGION $1100-400 \text{ cm}^{-1}$

$\text{CpTi}(\text{CH}_3)\text{X}_2$		CpTiX_3		$\text{CF}_3\text{CH}_2\text{OH}$	Assign- ment
X =	X =	X =	X =		
$\text{OCH}(\text{CH}_3)_2$	OCH_2CF_3	$\text{OCH}(\text{CH}_3)_2$	OCH_2CF_3		
1020	1020	1022	1020		Cp ring Ti—CH ₃ Ti—O
508	509				
632—578	700—597	610—590	695—595		
	957		957	945	} OCH_2CF_3
	820		825	830	
	630		620	660	
	530		520	545	
	395		420	420	

TABLE 2

 ^1H , ^{19}F AND ^{13}C NMR DATA OF COMPLEXES (I), (II), (III)^a

		$\text{CpTi}(\text{OR}_f)_3$ (I)	$\text{CpTiCl}(\text{OR}_f)_2$ (II)	$\text{CpTi}(\text{CH}_3)(\text{OR}_f)_2$ (III)
^1H	$\delta(\text{CH}_3)$ (Int)			0.82 (3)
	$\delta(\text{CH}_2\text{CF}_3)$ (Int)	4.47 (6.1)	4.62 (4.1)	4.43 (3.9)
	$\delta(\text{C}_5\text{H}_5)$ (Int)	6.45 (5)	6.62 (5)	6.24 (5)
^{19}F	$\delta(\text{CF}_3)$ ($^3J(\text{CH}-\text{C}-\text{F})$)	1.3 (9.6)		1.3 (9.6)
	^{13}C			
	$\delta(\text{CH}_3)$ ($^1J(\text{C}-\text{H})$)			46.4 (145)
	$\delta(\text{CH}_2)$ ($^1J(\text{C}-\text{H})$)	74.2 (146)		73 (146)
	($^2J(\text{C}-\text{C}-\text{F})$)	(35)		(34)
	$\delta(\text{CF}_3)$ ($^1J(\text{C}-\text{F})$)	125 (279)		125 (281)
	$\delta(\text{C}_5\text{H}_5)$ ($^1J(\text{C}-\text{H})$)	117.0 (175)		114.3 (172)

^a δ in ppm downfield with respect to TMS for ^1H and ^{13}C , $\text{CF}_3\text{CO}_2\text{H}$ for ^{19}F ; J coupling constant in Hz; (Int) relative intensity of the peaks.

TABLE 3

 ^1H AND ^{13}C CHEMICAL SHIFTS OF C_5H_5 AND CH_3 BONDED TO TITANIUM IN (I), (II), (III) AND RELATED COMPLEXES

Compound	$\delta(^1\text{H})$		$\delta(^{13}\text{C})$		Ref.
	$\delta(\text{CH}_3)$	$\delta(\text{C}_5\text{H}_5)$	$\delta(\text{CH}_3)$	$\delta(\text{C}_5\text{H}_5)$	
$\text{CpTi}(\text{OR})_3$ ^a		6.22		112.3	4
$\text{CpTiCl}(\text{OR})_2$ ^a		6.44		114.7	4
$\text{CpTi}(\text{OR}_f)_3$ ^b		6.45		117.0	
$\text{CpTiCl}(\text{OR}_f)_2$ ^b		6.62			
CpTiCl_3		7.05		123.1	4
$\text{CpTi}(\text{CH}_3)(\text{OR})_2$ ^c	0.47	6.02	35.0	111.5	2
$\text{CpTi}(\text{CH}_3)(\text{OR}_f)_2$ ^b	0.82	6.24	46.4	114.3	
$\text{CpTi}(\text{CH}_3)\text{Cl}_2$	1.80	6.75			5

^a $\text{R} = \text{CH}_2\text{CH}_3$. ^b $\text{R}_f = \text{CH}_2\text{CF}_3$. ^c $\text{R} = \text{CH}(\text{CH}_3)_2$.

Experimental

Infrared spectra were recorded on a Perkin—Elmer spectrophotometer (model 557) as neat liquids between KBr discs. ^1H NMR spectra were recorded on a Perkin—Elmer R 12 spectrophotometer using CCl_4 as solvent and TMS as internal standard. ^{13}C NMR spectra were recorded on a Fourier transform spectrometer Bruker WH 90, using C_6D_6 solutions with TMS as internal standard. Molecular weight determinations were carried out cryoscopically in C_6H_6 . All experiments were carried out with exclusion of moisture and using dry solvents.

Preparation of LiOR_f

Upon treatment of neat R_fOH with commercial LiBu in hexane, at -80°C , butane is evolved and LiOR_f obtained as a white solid.

Preparation of CpTi(OR_f)₃ (I)

CpTiCl₃ (5.8 g, 26 mmol) in C₆H₆ solution is added dropwise to a C₆H₁₂ suspension of 79 mmol of LiOR_f, at -25°C . The mixture is stirred for 1 h and allowed to warm to room temperature. Lithium salt is filtered off, the solvent evaporated off, and the residual yellow liquid distilled, b.p. $72^{\circ}\text{C}/10^{-2}$ mmHg. Yield: 70%, $M(\text{exp}) = 410$, (calc) = 410. Anal.: Found: C, 33.0; H, 2.88; F, 39.5; Ti, 11.68. Calcd. for C₁₁H₁₁F₉O₃Ti: C, 32.2; H, 2.68; F, 41.7; Ti, 11.68%.

Preparation of CpTiCl(OR_f)₂ (II)

The same procedure, using 15 mmol of CpTiCl₃ and 30 mmol of R_fOH, gives a yellow liquid, yield 90%.

Preparation of CpTi(CH₃)(OR_f)₂ (III)

(II) (5.2 g, 15 mmol) in diethyl ether is added to 15 mmol of LiCH₃ at -10°C . After 1 h stirring, the solution is allowed to warm to room temperature. Lithium salt is filtered off. After removal of the solvent, the residual yellow liquid is vacuum distilled, b.p. $63^{\circ}\text{C}/0.02$ mmHg. Yield: 70%, $M(\text{exp})$ 315, (calc) 326. Anal.: Found: C, 36.83; H, 3.80; F, 35.08; Ti, 15.0. Calcd. for C₁₀H₁₂F₆O₂Ti: C, 36.82; H, 3.68; F, 35.0; Ti, 14.7%.

Reaction of (I) with CH₃COCl

Acetyl chloride (0.5 g, 6.4 mmol) is added at room temperature to a solution of (I) in equimolecular ratio (2.6 g in 5 ml CCl₄). The ester CH₃CO(OR_f) and the solvent are evaporated off, and (II) is characterized by its NMR spectrum.

Reaction of (I) with C₆H₅NCO

Phenyl isocyanate (0.65 g, 5.45 mmol) in 5 ml of pentane is added to a solution of (I) in equimolecular ratio (2.22 g in 5 ml of pentane) at 0°C . After 2 h refluxing the solvent is removed and a viscous liquid obtained. In the IR spectrum, the characteristic band of free ligand $\nu(\text{N}=\text{C}=\text{O})$ at $2260\text{--}2280\text{ cm}^{-1}$ has disappeared and a new band at 1700 cm^{-1} , due to $\nu(\text{C}=\text{O})$, is observed.

Reaction of (III) with I₂

Iodine crystals are added to a solution of (III) in CCl₄ directly in the NMR tube. A new peak immediately appears at 2.1 ppm corresponding to CH₃I. Four days are necessary for complete disappearance of the CH₃Ti peak (δ 0.82 ppm). The cyclopentadienyl resonance is shifted downfield (δ 6.45 ppm).

Reaction of (III) with HCl:

Gaseous HCl is slowly bubbled into 4 mmol of (III) in CCl₄ (5 ml). Evolution of gas is observed and crystals separate. Elimination of CH₃ (as methane) and formation of R_fOH (δ_{CH_2} 3.87 ppm, δ_{OH} 2.35 ppm) and CpTiCl₃ (δ_{Cp} 7.05 ppm) is confirmed by the NMR spectrum of the solution.

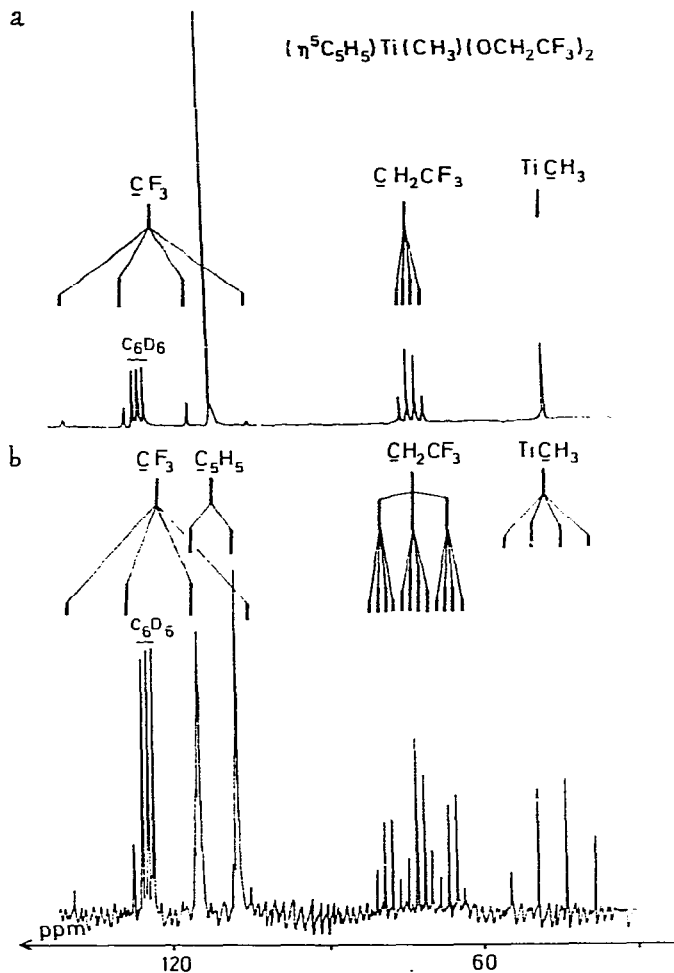


Fig. 1. ^{13}C NMR spectra (at 22.625 MHz) of $\text{CpTi}(\text{CH}_3)(\text{OR}_f)_2$ (III) in C_6D_6 , (a) non-gated (b) gated.

Reaction of (III) with $\text{CF}_3\text{CH}_2\text{OH}$

2,2,2-Trifluoroethanol (0.40 g, 4 mmol) in 1 ml of CCl_4 is added to a solution of (III) in equimolar ratio (1.30 g in 5 ml of CCl_4) at room temperature. The formation of (I) with elimination of CH_4 is confirmed by the NMR spectrum.

Polymerisation of methylmethacrylate

Methylmethacrylate (2.8 g, 20 mmol) is added dropwise at room temperature to 0.17 g (0.5 mmol) of (III) in 40/1 ratio. After 12 h stirring a solid polymer is obtained (molecular weight M 1.19×10^6 , viscosity, η 2.16 dl/g, yield 100% towards monomer, soluble in common solvents). The same procedure is followed using (I) as catalyst; the polymerization takes place more slowly and is complete after 4 days (M 0.78×10^6 , η 1.56 dl/g). Further details of the IR and NMR data will be published later [7].

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