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THE PREPARATION AND PROPERTIES OF MONOCYCLOPENTADIENYLMETHYLDIALKOXYTITANIUM

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Summary

Monocyclopentadienylmethyldialkoxytitanium, $CpTi(CH_3)(OR)_2$, with R = ethyl and iso-propyl, have been prepared and their IR, ^1H and ^{13}C NMR and mass spectra have been recorded and discussed. The reactions with iodine, alcohol, gaseous oxygen and sulfur dioxide have been studied. With this last reagent, a novel double insertion occurs, with both the methyl and cyclopentadienyl groups being converted into sulfinate groups.

Introduction

The role of the titanium—carbon σ bond in catalytic synthesis, exemplified in the Ziegler polymerisation process, is now well accepted. It thus seemed of interest to investigate the influence of the number and nature of other groups attached to the titanium upon the ability of the Ti—C bond to be cleaved and we have studied methyltitanium derivatives containing alkoxy groups or π-cyclopentadienyl as other ligands.

Little work has been carried out on methyltitanium alkoxides [1] which were first synthesized by Clauss [2] in 1968, except for recent NMR studies [3,4]. Moreover, while numerous alkyl compounds of bis(cyclopentadienyl)titanium are known, covering the range of Cp_2TiR_2 or Cp_2TiRX formulae (with R = alkyl, X = Cl, Br, etc.) [1], the only alkyl compound of monocyclopentadienyltitanium so far reported is $CpTi(CH_3)_3$ [5], which was found more reactive toward hydrolysis and alcoholysis than the bis(cyclopentadienyl) compound $Cp_2Ti(CH_3)_2$.

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Results and discussion

Synthesis

We have prepared a new series of monocyclopentadienylmethyltitanium derivatives, of formula $CpTi(CH_3)(OR)_2$ (with OR = ethoxy or isopropoxy), starting from $CpTi(OR)_3$ or $CpTiCl(OR)_2$ and using CH_3MgI, $LiCH_3$ or $Al(CH_3)_3$ as methylating agents as shown in eq. 1 and 2.

$$\left.\begin{array}{l} CpTi(OR)_3 + CH_3MgI \\ CpTiCl(OR)_2 + LiCH_3 \end{array}\right\} \longrightarrow \underset{(I)}{CpTi(CH_3)(OR)_2} \tag{1}$$

$$CpTi(OR)_3 + Al(CH_3)_3 \rightarrow \underset{(II)}{[CpTi(CH_3)OR_2,\ Al(CH_3)_2OR]} \tag{2}$$

In the last case, removal of the solvent left a brown liquid which appeared to be the monomeric bimetallic complex II (involving bridging alkoxy Ti—O(R)—Al), the properties of which will be described in a separate paper. In the other two cases the product I was isolated as a monomeric yellow liquid by vacuum distillation, in 20—45% yield. Attempts to make the t-butoxy compound in the same way have failed.

Spectroscopic data

The spectroscopic properties of these new compounds I can be compared with those of organotitanium derivatives previously studied and especially with monocyclopentadienyltitaniumtrialkoxides, $CpTi(OR)_3$ III, and methyltitaniumtrialkoxides, $CH_3Ti(OR)_3$ (IV) [6]. The main IR frequencies in the range 1200—400 cm^{-1} are listed in Table 1.

TABLE 1

INFRARED ABSORPTION BANDS OF $CpTi(CH_3)(OR)_2$, $CpTi(OR)_3$ AND $(CH_3)Ti(OR)_3$ IN THE REGION 1200—400 cm^{-1}

$CpTi(CH_3)(OEt)_2$ (I)	$CpTi(OEt)_3$ [a] (III)	$(CH_3)Ti(OEt)_3$ [b] (IV)	Assignment
805	806		cyclopentadienyl ring
1020	1022		
420	425		Ti—Cp
505		510	Ti—CH_3
570—635	595—615	580—630	Ti—OEt terminal or bridged in IV
1070	1070	1070	
1110	1110	1100—1150	
		820—920	
$CpTi(CH_3)(O\text{-}i\text{-}Pr)_2$ (I)	$CpTi(O\text{-}i\text{-}Pr)_3$ [c] (III)	$(CH_3)Ti(O\text{-}i\text{-}Pr)_3$ [b] (IV)	
802	805		cyclopentadienyl ring
1020	1022		
508		510	Ti—CH_3
578—632	590—610	575—640	Ti—O-i-Pr terminal or bridged in IV
1130	1127	1120	
		825	
		940	

[a] From ref. 7. [b] These stubstances are known to be associated according to ref. 8. [c] From ref. 9.

TABLE 2

NMR DATA: CHEMICAL SHIFTS (δ, ppm) OF ^{1}H IN $CpTi(CH_3)(OR)_2$ AND RELATED DERIVATIVES [a]

Compound	Ref.	$\delta(CH_3Ti)$	$\delta(CpTi)$	Alkoxy group	
				$\delta(H\alpha)$	$\delta(H\beta)$
$CpTi(CH_3)(OEt)_2$		0.48	6.04	4.16	1.11
$CpTi(OEt)_3$	10		6.22	4.20	1.12
$(CH_3)Ti(OEt)_3$ [b]	4	0.65		4.41	1.29
$CpTi(CH_3)(O\text{-}i\text{-}Pr)_2$		0.47	6.02	4.43	1.12
$CpTi(O\text{-}i\text{-}Pr)_3$	10		6.25	4.50	1.13
$(CH_3)Ti(O\text{-}i\text{-}Pr)_3$ [b]	3–4	0.57		4.75	1.35
$CpTi(CH_3)_3$ [c]	11	0.30	6.25		
$Cp_2Ti(CH_3)_2$	12	−0.06	5.90		

[a] In ppm downfield with respect to TMS as internal standard measured in solution in CCl_4. [b] These substances are known to be associated according to ref. 8. [c] In solution in THF.

TABLE 3

NMR DATA: ^{13}C CHEMICAL SHIFTS [a] AND COUPLING CONSTANTS (J(C—H)) [b] IN $CpTi(CH_3)(O\text{-}i\text{-}Pr)_2$ AND RELATED DERIVATIVES

Compound	Ref.	CH_3Ti		CpTi	
		$\delta(^{13}C)$	J(C—H)	$\delta(^{13}C)$	J(C—H)
$CpTi(CH_3)(O\text{-}i\text{-}Pr)_2$ [c]		35.0	124	111.5	172
$CpTi(OEt)_3$	13			112.3	
$(CH_3)Ti(O\text{-}i\text{-}Pr)_3$ [d]		42.9	123		
$(CH_3)Ti(NEt_2)_3$	14	30.0			
Cp_2TiCl_2	15			121.3	
Cp_2TiPh_2	15			116.8	

[a] In ppm downfield with respect to TMS as standard. [b] In Hertz ±2 Hz. [c] Measured as neat liquid; for the alkoxy group $\delta(C\alpha)$ 77.6 ppm (with J(C—H) 141) and $\delta(C\beta)$ 26.7 ppm (with J(C—H) 127). [d] Measured as neat liquid; for the alkoxy group $\delta(C\alpha)$ 76.3 ppm (with J(C—H) 139) and $\delta(C\beta)$ 25.1 ppm (with J(C—H) 125).

TABLE 4

MASS SPECTRUM OF $CpTi(CH_3)(O\text{-}i\text{-}Pr)_2$

Ion	m/e	Relative intensity (70 eV)
M^+	246	1.5
$M-CH_3^+$	231	25
$M-OiPr^+$	187	10
$C_5H_5TiO^+$	129	36
$TiOC_3H_7^+$	107	100
$TiC_3H_7^+$	91	52
$C_5H_6^+$	66	14
$C_5H_5^+$	65	20

TABLE 5

COMPARISON BETWEEN SOME CHARACTERISTIC FRAGMENTATION PEAKS OF $CpTi(CH_3)(O\text{-}i\text{-}Pr)_2$, $CpTi(O\text{-}i\text{-}Pr)_3$ AND $(CH_3)Ti(O\text{-}i\text{-}Pr)_3$. Intensities (70 eV) are relative to the peak $M - O\text{-}i\text{-}Pr^+$ (I 100)

Ion	$CpTi(CH_3)(O\text{-}i\text{-}Pr)_2$ (I)		$CpTi(O\text{-}i\text{-}Pr)_3$ [a] (III)		$(CH_3)Ti(O\text{-}i\text{-}Pr)_3$ (IV)	
	m/e	I	m/e	I	m/e	I
M^+	246	15	290	23	240	5
$M - CH_3^+$	231	250			225	290
$M - O\text{-}i\text{-}Pr^+$	187	100	231	100	181	100
$M - C_5H_5^+$	181	≈0	225	31		

[a] In good agreement with ref. 16.

Of the ^1H and ^{13}C NMR data, shown in Table 2 and Table 3, the most noteworthy result is the shielding of the nuclei of the methyl group bonded to titanium in I in comparison with that in IV. This suggests that the cleavage of the Ti—C bond by nucleophilic attack might be more difficult for I than for IV, but much easier than for $Cp_2Ti(CH_3)_2$.

Additional arguments relating to the bond cleavages in these molecules come from mass spectrometry. In Table 4 the mass spectral characteristics of $CpTi(CH_3)(O\text{-}i\text{-}Pr)_2$ are summarized, together with suggested assignments. For comparison with other derivatives and especially with III and IV, in Table 5, we show the intensity of some characteristic peaks, relative to $M - OR^+$, which is present in every case. It is noteworthy that the intensity of the molecular ion is lower in derivatives in which a methyl group is bonded to titanium though this effect is less obvious in compound I than in IV. Concurrently the peak corresponding to $M - CH_3^+$ is observed in both compounds but is slightly more marked in IV than in I. Finally, we can note that the peak $M - C_5H_5^+$ (the intensity of which was discussed by Nesmeyanov [15] for the series $CpTi(OEt)_{3-x}Cl_x$) is much less intense when a methyl has replaced an alkoxy group. It thus seems likely that in I the Ti—CH_3 bond would be more readily cleaved than the Ti—Cp linkage in the same compound, but slightly less readily cleaved than the Ti—CH_3 bond in compound IV. This has been shown to be the case by some chemical tests, including substitution and insertion reactions.

Chemical properties

Reactions involving the cleavage of the titanium—carbon σ bond have been reviewed [17]. The present work is especially concerned with the reactions 3—6.

$$\equiv TiCH_3 \xrightarrow{+I_2} \equiv TiI + ICH_3 \qquad (3)$$

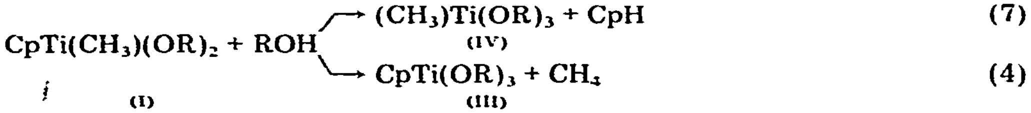
$$\equiv TiCH_3 \xrightarrow{+ROH} \equiv TiOR + CH_4 \qquad (4)$$

$$\equiv TiCH_3 \xrightarrow{+\frac{1}{2}O_2} \equiv TiOCH_3 \qquad (5)$$

$$\equiv TiCH_3 \xrightarrow{+SO_2} \equiv Ti(O_2SCH_3) \qquad (6)$$

Substitution by iodine as in eq. 3 was observed in every case previously investigated as well for $(CH_3)_4Ti$ and CH_3TiCl_3 [18] as for $Cp_2Ti(CH_3)_2$ [19]. It takes place instantly and quantitatively for compounds I, as is clearly demonstrated by the NMR spectra.

The substitution by alcohols (eq. 4) and the insertion of an oxygen atom (eq. 5), do not occur with $Cp_2Ti(CH_3)_2$ [19] although they are known for less stable derivatives such as CH_3TiCl_3 [18], and even $CH_3Ti(OR)_3$ [4,6]. From the NMR data in Table 2 and Table 3 and more specifically from the intermediate shielding of the nuclei of the methyl group in $CpTi(CH_3)(OR)_2$ (I), an intermediate reactivity may be expected for the compounds I. In fact, after bubbling oxygen into the neat liquids or their solutions in benzene or carbon tetrachloride at room temperature, compounds I were recovered unchanged even after several hours. (Attempts at photocatalysed oxygenation have also been unsuccessful.). Alcohols are known to react with $CpTi(OR)_3$ compounds with the replacement of the cyclopentadienyl group [20], and so in a stoichiometric mixture of I with this reagent, two reactions are possible (eq. 7 and 4).



$$\underset{(I)}{CpTi(CH_3)(OR)_2} + ROH \begin{cases} \rightarrow \underset{(IV)}{(CH_3)Ti(OR)_3} + CpH & (7) \\ \rightarrow \underset{(III)}{CpTi(OR)_3} + CH_4 & (4) \end{cases}$$

In practice the reaction proceeds according to eq. 4 as was expected after the mass spectroscopy data. It was followed by measuring the volume of methane evolved and by observing the NMR spectra and it was found to take place more slowly than in the cases previously reported. Thus in a typical experiment, I was transformed into III in ca. 75% yield in 6 days, while, under similar conditions, IV was completely converted into titanate within an hour [6]. More precise kinetic studies are in progress.

We conclude that the CH_3—Ti bond in the compounds $CpTi(CH_3)(OR)_2$, has intermediate stability between the corresponding bonds in $Cp_2Ti(CH_3)_2$ (less reactive) and $(CH_3)Ti(OR)_3$ (more reactive) toward nucleophilic reagents; in agreement with the predictions from the spectroscopic data.

Sulfur dioxide is known to react with alkylbis(cyclopentadienyl)titanium compounds to yield *O*-sulfinates $Cp_2Ti(O_2SCH_3)_2$ and $Cp_2Ti(O_2SCH_3)Cl$ [21]. Insertion of SO_2 into the Ti—CH_3 bonds of $(CH_3)TiCl_3$ and $(CH_3)TiBr_3$ has also been reported [22] and we have recently obtained the *O*-sulfinate $(CH_3SO_2)Ti(OR)_3$ by action of SO_2 on $(CH_3)Ti(OR)_3$ [6].

Treatment of $CpTi(CH_3)(OR)_2$ with SO_2, in CCl_4 or C_6H_6, at room temperature yielded a sulfinated compound with a ^1H NMR methyl peak characteristic of methane *O*-sulfinate (δ 2.32 ppm) and a C_5H_5 peak shifted downfield (δ 6.45 ppm). After several hours, a precipitate appeared and its analysis revealed that two molecules of SO_2 had been fixed. Studies of the mechanism of this double insertion, previously unknown for titanium, are still in progress, but we tentatively formulate the product as $(C_5H_5SO_2)Ti(O_2SCH_3)(OR)_2$, by analogy with the insertion of SO_2 also into the zirconium—cyclopentadienyl bond, which yields the sulfinated product $Cp(C_5H_5SO_2)Zr(O_2SCH_3)Cl$ [21].

Experimental

IR spectra were recorded on a Perkin—Elmer 457 or a Perkin—Elmer 225 spectrophotometer as neat liquids or (for solid samples) as Nujol mulls between KBr discs. ^1H NMR spectra were recorded on a Perkin—Elmer R 12 at 60 MHz. Fourier transform ^{13}C NMR spectra were recorded on a Bruker WH 90 at 22.625 MHz. Mass spectra were performed by the Analytical Laboratory of CNRS on a AEI MS 30 at 80°C (ionizing voltage 70 eV).

All reactions were carried out under dry argon using dry degassed solvents. $CpTi(OR)_3$, $CpTiCl(OR)_2$ and $(CH_3)Ti(OR)_3$ were prepared by published procedures [9,2].

Preparation of CpTi(CH₃)(O-i-Pr)₂ (Ia)

0.07 mol of neat $CpTi(O\text{-}i\text{-}Pr)_3$ is added dropwise to a solution of CH_3MgI in anhydrous ether (0.07 mol in 250 ml) at —10°C. The mixture is stirred for 1 h at room temperature and magnesium salts are filtered off. Ether is removed under reduced pressure and anhydrous hexane (200 ml) is added in order to precipitate the remaining magnesium salts. The solution is decanted, and the hexane removed. The residual liquid is distilled twice to give $CpTi(CH_3)(O\text{-}i\text{-}Pr)_2$ in 44% yield as a yellow-orange liquid, b.p. 48°C/0.1 mmHg d_4^{20} 1.027. (Found: C, 57.11; H, 8.82; Ti, 19.84. $C_{12}H_{22}O_2Ti$ calcd.: C, 58.86; H, 8.91; Ti, 19.52%.)

Ia can also be made by adding, in equimolar ratio at —10°C, either $CpTiCl(O\text{-}i\text{-}Pr)_2$ to a solution of $LiCH_3$ in ether, or $CpTi(O\text{-}i\text{-}Pr)_3$ in benzene on ethereal CH_3MgI, but the yield in both the cases is only 20%.

Preparation of CpTi(CH₃)(OEt)₂ (Ib)

Compound Ib was obtained by the same method as Ia as an orange liquid, b.p. 32°C/0.05 mmHg, d_4^{20} 1.059. (Found: C, 55.40; H, 8.10, Ti, 20.85; mol.wt. (cryoscopy in benzene) 215. $C_{10}H_{18}O_2Ti$ calcd.: C, 55.07; H, 8.26; Ti, 21.98%; mol. wt. 218.)

Reaction of Ib with iodine

Some iodine crystals are added to a solution of Ib in CCl_4 directly in the NMR tube. ^1H NMR spectrum immediately shows a new peak (δ 2.15 ppm) corresponding to CH_3I, while the peak of the methyl bonded to titanium (δ 0.48 ppm) disappears and the cyclopentadienyl resonance is shifted downfield (δ 6.5 ppm).

Reaction of Ia with alcohol

0.36 g of isopropyl alcohol (6.1 mmol) in CCl_4 (0.7 ml) is added to a solution of Ia in equimolar ratio (1.5 g in 3 ml CCl_4) with stirring at room temperature. The volume of methane evolved is measured and characterized by its IR spectrum. After 6 days, this volume was 115 ml (calcd. for 100% yield: 148 ml). The ^1H NMR spectrum shows the formation of $CpTi(OR)_3$.

Reaction of Ib with sulfur dioxide

SO_2 is slowly bubbled with stirring into 3 mmol of Ib in benzene (7 ml) cooled in ice. After 5 min., the ^1H NMR spectrum showed a new peak at δ 2.32 ppm, the intensity of which progressively increased while the intensity of the methyl bonded to titanium progressively decreased. Similarly a new C_5H_5 peak has appeared and increased at δ 6.45 ppm. After 1 h, the solution became cloudy and after several hours, precipitation occurred. The solvent and excess of SO_2 were removed and the residue was pumped dry to give a yellow insoluble solid. (Found: C, 33.12; H, 4.79; Ti, 14.20; S, 19.72. $C_{12}H_{22}O_2Ti(SO_2)_2$ calcd.: C, 34.68; H, 5.20; Ti, 13.84; S, 18.49%.)

From reaction in CCl_4 either at 0°C or at room temperature, the same product was obtained a little more quickly. (Found: C, 34.30; H, 4.70; Ti, 13.87; S, 17.30%.)

Reaction of Ia with sulfur dioxide

The reaction was carried out as described for Ib. An insoluble yellow solid was again obtained (Found: C, 37.29; H, 5.45; Ti, 13.07; S, 17.55. $C_{10}H_{18}O_2Ti(SO_2)_2$ calcd.: C, 38.50; H, 5.88; Ti, 12.83; S, 17.11%.)

The IR of the products show strong absorption in the S—O stretching region 850—1040 cm^{-1}, with maxima at 1020, 965, 935, 915, 890, 850 cm^{-1}.

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