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$(\eta^5\text{-}C_5H_5)TiCl_2(OC_6H_4X)$: SYNTHESIS AND PROPERTIES ($X = NO_2$, Cl, CH_3)

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Summary

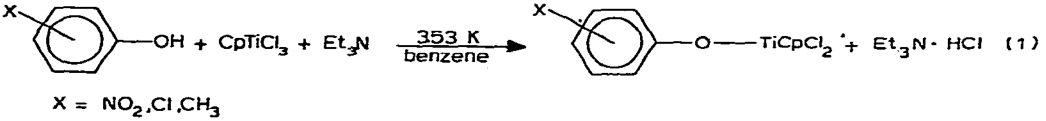
The compounds $(\eta^5\text{-}C_5H_5)TiCl_2(OC_6H_4X)$, where $X = NO_2$, Cl, CH_3, have been obtained from the reaction of $CpTiCl_3$ with suitable substituted phenols in 1 : 1 ratio. Some of the IR and NMR bands of the compounds correlate directly with Hammett σ factors.

Introduction

Organotitanium compounds are known as catalysts for the polymerization [1,2] and hydrogenation[3,4] of olefins and dienes. The synthesis and investigation of titanium compounds with ligands which have varied but known inductive effects can help to explain the influence of these effects on the catalytic activity of titanium compounds. With this aim we undertook the synthesis and investigation of the compounds $CpTiCl_2(OC_6H_4X)$ where $X = NO_2$, Cl, CH_3.

Results

Substituted and unsubstituted phenols react with $CpTiCl_3$ in 1 : 1 ratio giving phenoxytitanium compounds as follows:



Reactions were carried out in benzene at 353 K. Et_3N was used as a HCl-complexing agent. When the reaction was complete (after 4 h) the reaction mixture was concentrated under vacuum and at brown oil was obtained, from which yellow or red crystals precipitated when hexane was added.

The analytical properties of the products are listed in Table 1. The yield of $Et_3N \cdot HCl$ (97—99%) for each reaction demonstrates that reaction 1 go to com-

TABLE 1

ANALYTICAL PROPERTIES OF $CpTiCl_2(OC_6H_4X)$ COMPOUNDS

Compound	Melting point (K)	Yield of $(Et)_3N\cdot HCl$ (%)	Yield of product (%)	Analysis, Found (calcd.) (%)				Colour
				C	N	H	Cl	
$CpTiCl_2(OC_6H_4NO_2$-*p*)	400—401	99,0	48	40,5 (41,0)	4,35 (4,30)	2,90 (2,80)	21,5 (22,0)	light yellow
$CpTiCl_2(OC_6H_4NO_2$-*m*)	408—410	98,5	56	41,4 (41,0)	4,50 (4,30)	3,01 (2,80)	19,9 (22,0)	light yellow
$CpTiCl_2(OC_6H_4NO_2$-*o*)	331—333	97,0	31	39,4 (41,0)	3,94 (4,30)	2,80 (2,80)	21,8 (22,0)	yellow
$CpTiCl_2(OPh)$	316—318	99,0	42	46,7 (47,6)	—	3,46 (3,60)	24,4 (25,6)	yellow orange
$CpTiCl_2(OC_6H_4CH_3$-*p*)	334—336	97,5	51	49,4 (49,5)	—	3,96 (4,12)	22,6 (24,4)	red
$CpTiCl_2(CO_6H_4CH_3$-*m*)	343—347	98,0	38	49,3 (49,5)	—	4,11 (4,12)	22,2 (24,4)	orange
$CpTiCl_2(OC_6H_4CH_3$-*o*)	331	98,0	26	49,3 (49,5)	—	4,16 (4,12)	23,3 (24,4)	red
$CpTiCl_2(OC_6H_4Cl$-*p*)	349—351	99,0	41	42,0 (42,3)	—	3,01 (2,90)	32,2 (34,3)	yellow
$CpTiCl_2(OC_6H_4Cl$-*m*)		98,5	not obtained					
$CpTiCl_2(OC_6H_4Cl$-*o*)	336—340	98,0	5	41,5 (42,3)	—	3,05 (2,90)	32,8 (34,3)	yellow

TABLE 2

IR BANDS OF $CpTiCl_2(OC_6H_4X)$ ($X = NO_2, CH_3$) (cm^{-1})

Compound	Cp				Ti—Cl	Ti—O—R					
	1440	1380	1020	830	415	1415	1250	1100	1070	600	480
$CpTiCl_2(OC_6H_4NO_2$-*p*)	1442	1378	1021	825	412	1420	1267	1115	1070	609	495
$CpTiCl_2(OC_6H_4NO_2$-*m*)	1438	1385	1022	820	410	1418	1260	1110	1080	606	488
$CpTiCl_2(OC_6H_4NO_2$-*o*)	1438	1380	1021	829	417	1417	1263	1115	1070	607	485
$CpTiCl_2(OPh)$	1440	1370	1022	815	420	1416	1265	1105	1070	601	480
$CpTiCl_2(OC_6H_4CH_3$-*p*)	1440	1380	1021	825	415	1415	1260	1102	1071	599	477
$CpTiCl_2(OC_6H_4CH_3$-*m*)	1440	1387	1022	835	413	1416	1265	1103	1086	600	479
$CpTiCl_2(OC_6H_4CH_3$-*o*)	1439	1385	1021	830	417	1415	1263	1103	1072	600	472

pletion. The purification procedure decreases the total yield at products to 40% or even lower (the *m*-chlorophenol derivative was not separated from the reaction mixture).

Direct reactions between phenols and $CpTiCl_3$ were also carried out in benzene at room temperature and in refluxing benzene without Et_3N, but yields after purification were less that 10%. All products obtained are hydrolysed and oxidized slightly in air to pink amorphous solids. The colour of the products can be directly related with the electron-donor properties of the phenoxy ligand more donating phenoxy ligands, which have CH_3 groups, give red compounds, whereas more accepting phenoxy ligands, which have NO_2 groups, give yellow compounds.

IR spectra

The IR spectra of the compounds synthesised show typical bands of the cyclopentadienyl ring, the Ti—Cl bond and the Ti—O—C groups [5,6]. Their frequences are presented in Table 2 for every compound obtained. Phenoxy substituents (NO_2, CH_3) shift to larger wave numbers the 1380 and 830 cm^{-1} bands slighty shift to smaller wave numbers the 1440 and 1020 cm^{-1} bands and shift the Ti—Cl (415 cm^{-1}) bands to smaller wave numbers. The Ti—O—C bands at 490, 600 and 1115 cm^{-1} are shifted to the higher frequency range with increasing electron-accepting ability of the phenoxy ligand. The band at 1415 cm^{-1} shows the tendency.

UV spectra

A band at ≈220 nm of the phenoxy ring and a weak band of the cyclopentadienyl ring at ≈300 nm are observed in the UV spectra of the compounds obtained (Table 3). For all compounds there are no changes observed in the band positions, thus the phenoxy ring substituents do not influence the HOMO and LUMO orbitals of the cyclopentadienyl rings.

TABLE 3

UV BANDS OF $CpTiCl_2(OC_6H_4X)$ COMPOUNDS

X	*p*-NO_2	*m*-NO_2	*o*-NO_2	H	*p*-CH_3	*m*-CH_3	*o*-CH_3
band ≈ 230 nm	230	232	230	231	230	224	230
band ≈ 300 nm	307	300	300	300	300	300	300

TABLE 4

^1H NMR SPECTRAL DATA [a]

X	Cp ring signals (τ)	Ph ring signals (τ)
p-NO_2	2.92(5H, d)	1.89(4H, d)
m-NO_2	3.01(5H, s)	2.39(4H, q)
o-NO_2	2.93(5H, s)	2.41(4H, 3q)
H	3.01(5H, s)	2.99(5H, m)
p-CH_3	3.02(5H, s)	3.14(4H, m)
m-CH_3	3.02(5H, s)	3.06(4H, m)
o-CH_3	3.05(5H, s)	3.05(4H, m)

[a] s = singlet, d = doublet, q = quartet, m = multiplet.

^{1}H NMR spectra

The titanium compounds investigated have two groups of signals: of the phenoxy rings at $\tau = 2$—3 and of the cyclopentadienyl ring at $\tau \approx 3$. The parameters of those signals are presented in Table 4.

The cyclopentadienyl ring signals are always seen as singlets but the phenoxy ring signals have a more or less complicated structure. It is seen that the phenoxy substituents shift the phenoxy proton signals to the lower field region when its electron-acceptor properties increase. This is also the case for the cyclopentadienyl ring protons.

Discussion

The positions of the cyclopentadienyl and the Ti—Cl IR bands of the compounds obtained depend on the positions of the —CH_3 or —NO_2 groups on the phenoxy ring and not on their electron-acceptor or -donor properties. The positions of the Ti—O—R group bands at 1415, 1110, 600 and 480 cm^{-1} depend on the electron-acceptor or -donor properties of —CH_3 and —NO_2 on the phenoxy ring. Further, a straight correlation between Hammett factors and the wave numbers exists, see Fig. 1. Also a direct correlation between the phenoxy proton ^{1}H NMR signals and the Hammett factors is observed, see Fig. 2.

The lack of inductive influence of the phenoxy substituants on the cyclopentadienyl ring (UV, IR spectra) and Ti—Cl bond (IR spectra) suggests that this

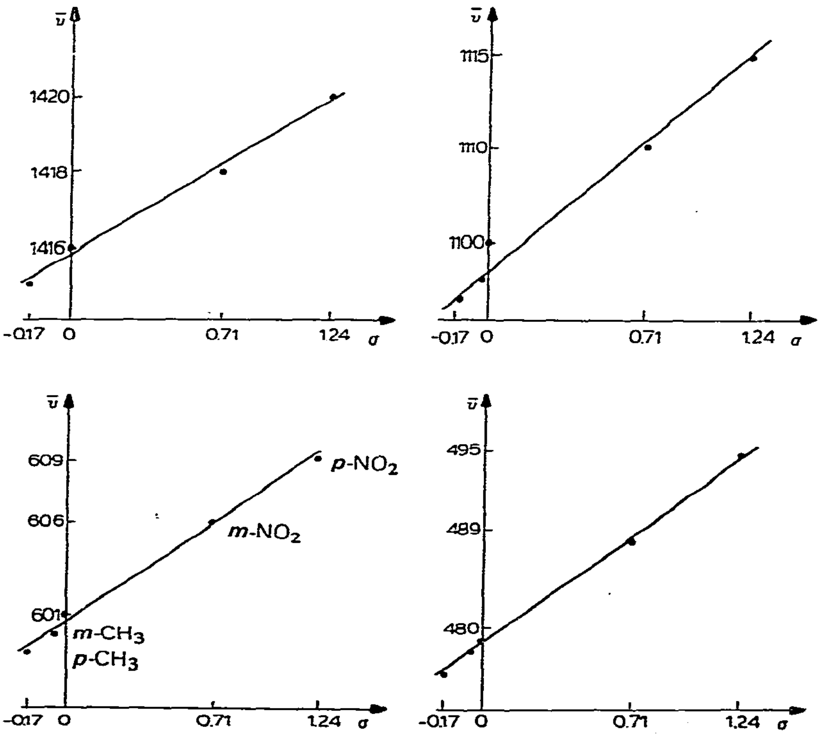


Fig. 1. Correlations between positions of IR bands of $CpTiCl_2(OC_6H_4X)$ and Hammett σ factors of X.

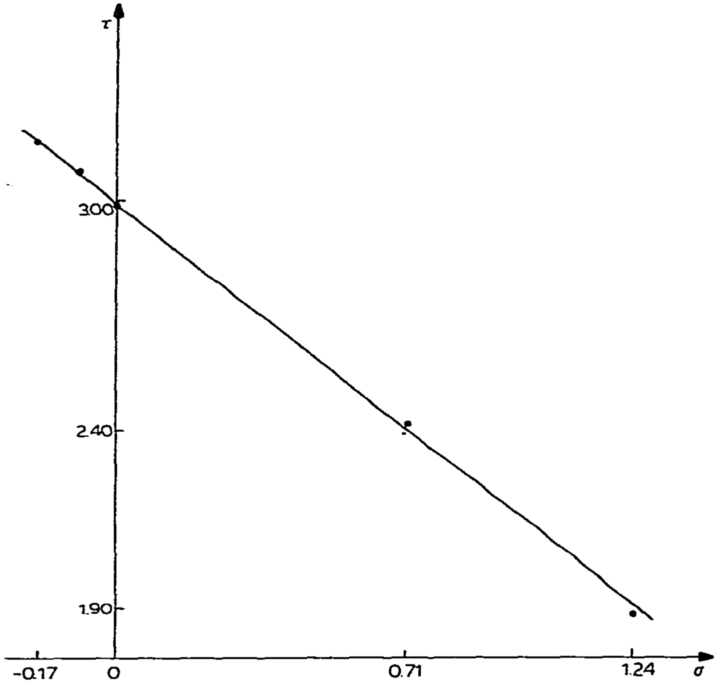


Fig. 2. Correlation between ^1H NMR signals of the phenoxy group protons of $CpTiCl_2(OC_6H_4X)$ and Hammett σ factors of X.

inductive influence stops at the titanium atom and is not transferred to the other ligands bonded to the titanium ion. However, since the C—O—Ti group bands depend on the Hammett factors of the phenoxy ring substituants, we may expect a correlation of the Hammett factors with the catalytic activity of these compounds.

Experimental

All operations were carried out under an inert atmosphere. The solvents benzene (POChem-pure) and hexane (Reachem-pure) were boiled with $LiAlH_4$ and distilled from 5A molecular sieve before use. $CpTiCl_3$ (Stream-pure) and phenols were crystallized or distilled directly before reaction.

NMR investigations were carried out on a BN 487C 80 MHz spectrometer, UV spectra were recorded on a Specord UV-VIS instrument and IR spectra were recorded on Carl Zeiss Jena UR-10 instrument (as KBr discs).

Preparation of $CpTiCl_2(OC_6H_4X)TiCl_2$

To a 0.1 *N* refluxing benzene solution of 5 mmol $CpTiCl_3$ and 8 mmol of Et_3N a 0.1 *N* benzene solution of 5 mmol of phenol was added over 4 h. The reaction mixture was then refluxed for 0.5 h, and allowed to cool to room temperature. The precipitate of $Et_3N \cdot HCl$ formed was filtred off and the brown or yellow solution obtained was concentrated under vacuum. The resulting dark brown oil was refluxed in hexane for 1 h. After 12 h cooling a crystalline product precipitated was filtered off and dried for 4 h under vacuum.

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