

## SYNTHESIS AND SOME CHARACTERISTICS OF DI- $\pi$ -CYCLOPENTADIENYL- $\sigma$ -ORGANOTITANIUM(IV) CHLORIDES

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(Received October 10th, 1969)

### SUMMARY

A series of organotitanium compounds of structure  $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{R})\text{Cl}$  was prepared, where the R ligand was attached by a  $\sigma$ -Ti-C bond. In studying the properties of these compounds, the following observations were made. The  $\sigma$ -Ti-C bond absorbs in the infrared at about 460 to 465  $\text{cm}^{-1}$ . It is apparently a weak, but otherwise normal, covalent bond. In contrast to many other metal atoms, the titanium atom has little effect on the C-H bonds in the  $\sigma$ -bonded ligand. The Ti-Cl bond has ionic character and, in compounds where steric crowding may be important, may form chloride ions even in non-polar solvents.

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### INTRODUCTION

Only a few monoalkylated derivatives of di- $\pi$ -cyclopentadienylnitium dichloride have been synthesized<sup>1-12</sup>, and very limited data on the properties or characteristics of these organotitanium derivatives have been reported. Because it has been suggested that the monoalkyl derivatives,  $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{R})\text{Cl}$  (where R = alkyl), might be a part, at least, of an active olefin polymerization site in Ziegler-Natta catalysis (see refs. 13-17 for example), it was decided to synthesize and thoroughly characterize a series of these compounds. This paper reports primarily the synthetic and spectral work.

### EXPERIMENTAL

#### *Synthesis of compounds of structure $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{R})\text{Cl}$*

The procedure of Long and Breslow<sup>1</sup> was used with the following modification in work-up procedure. Instead of centrifuging the reaction mixture, the reaction solvent was removed on a rotary evaporator at ambient temperature and purified by crystallization from n-hexane or 70 to 30 hexane/toluene mixtures, at 25 to  $-70^\circ$  under argon. Hexane alone was an adequate solvent except for the vinyl, benzyl, and phenethyl derivatives. After precipitation or crystallization was complete, the mother liquor was removed and the solid was dried for one hour at  $10^{-4}$  mm at ambient temperature and stored under argon at  $-78^\circ$ . The yields, although low, seemed limited

mostly by the stability of the compounds in the recrystallization solvent and the rapidity of the work-up procedure. The hexane solutions frequently decomposed to give brown insoluble materials during the recrystallization procedure, although solutions in toluene were more stable; the ethyl derivative was stable for over a year at ambient temperature in degassed toluene solution in a sealed vial. Moreover, the purified ethyl compound did not react with oxygen or moisture within 1 h in toluene at ambient temperature. The benzyl compound smelled of benzaldehyde even after two crystallizations and decomposed rapidly in air even as a solid. The other solid materials could be handled in air for short periods at ambient temperature with only slow loss of purity. This loss of purity was associated with the appearance of an OH band in the infrared spectra.

#### *General comments*

Di- $\pi$ -cyclopentadienyltitanium dichloride was purchased from Arapahoe Chemical Co. (Denver, Colo.) and was recrystallized from toluene. Phenylmagnesium chloride and methylmagnesium chloride were obtained as solutions in tetrahydrofuran from Alfa Inorganics (Beverly, Mass.) and ethylmagnesium chloride came from Fisher-Scientific (Fairlawn, N. J.). The other original reagents were prepared from magnesium (used as received from Fisher-Scientific) and the appropriate alkyl halides which were dried over calcium chloride before use.

All solvents were of analytical or reagent grade, and were purged with, and stored under argon after the following additional purification steps. Dichloromethane was passed through a 3A molecular sieve. Tetrahydrofuran was dried over anhydrous calcium chloride. Hexane and toluene were passed through columns of silica gel and 3A molecular sieves. Toluene was then stored over sodium ribbon.

Melting points were measured in an argon atmosphere on a differential scanning calorimeter (Perkin-Elmer 1-B, Norwalk, Conn.) scanning at 10° per minute. Correction factors based on the melting points of pure compounds were applied, and melting points are believed to be accurate to within  $\pm 0.5^\circ$ .

Infrared spectra were obtained on a Perkin-Elmer model 221 double beam spectrophotometer using KBr discs. NMR spectra were recorded in deuteriochloroform on Varian Models A-60 and HR-100 (Walnut Creek, Calif.). UV and visible spectra were recorded on a Cary Model 14 spectrophotometer (Monrovia, Calif.) using toluene and dichloromethane as solvents.

#### RESULTS

The melting points, elemental assay, and color observations are summarized in Table 1. Several points deserve specific comment.

All of the compounds decompose thermally. Three (methyl, vinyl, and phenyl) decomposed so extensively in the solid state, that no melting behavior of the pure compounds could be observed. The literature<sup>4</sup> melting point for the methyl derivative is the point at which its decomposition products melt in air.

Discrepancies exist between the data in Table 1 and the literature on both the ethyl<sup>1</sup> and propyl<sup>4</sup> derivatives. The ethyl compound was reported to melt about 4° higher than we found; the lower value, given in the table, was confirmed by repeated syntheses as well as by other workers<sup>1,8</sup>. The data on the propyl derivative given here

TABLE 1

ELEMENTAL ANALYSES ON COMPOUNDS OF STRUCTURE  $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{R})\text{Cl}$ 

R	M.p. (°C)	Analyses, found (calcd.) (%) <sup>a</sup>			
		C	H	Ti	Color
CH <sub>3</sub> <sup>b</sup>	91.6 <sup>c</sup>	57.66 (57.76)	5.80 (5.73)	21.17 (20.96)	Orange-yellow
C <sub>2</sub> H <sub>5</sub> <sup>b</sup>	88.7	59.24 (59.41)	6.24 (6.23)	19.92 (19.74)	Red-brown
n-C <sub>3</sub> H <sub>7</sub> <sup>b</sup>	74.5	60.61 (60.84)	6.68 (6.67)	18.62 (18.66)	Red-brown
n-C <sub>4</sub> H <sub>9</sub>	84.7			18.00 (17.70)	Red-brown
iso-C <sub>4</sub> H <sub>9</sub>	70.5	61.97 (62.12)	7.06 (7.08)	17.45 (17.70)	Red-brown
n-C <sub>5</sub> H <sub>11</sub>	52.0	63.14 (63.28)	7.22 (7.44)	16.63 (16.83)	Red-brown
neo-C <sub>5</sub> H <sub>11</sub>	95.0			16.70† (16.83)	Grey-brown
CH <sub>2</sub> =CH	153 <sup>d</sup>			19.97† (19.91)	Red-brown
Ph	121 <sup>d</sup>			16.50† (16.50)	Orange-yellow
PhCH <sub>2</sub>	107			15.40 (15.70)	Blue-black
PhCH <sub>2</sub> CH <sub>2</sub>	139	67.75 (67.83)	6.14 (6.01)	14.76 (15.03)	Red-brown

<sup>a</sup> Analyses by Galbraith Laboratories Inc. (Knoxville, Tenn.) except where marked †, in which case an X-ray fluorescence method was used in our laboratories. <sup>b</sup> Hydrolysis of these compounds with concd. HCl gave quantitative yields of the RH alkane relevant to ligand R. The alkane was identified by gas chromatography and mass spectrometry. <sup>c</sup> First-order reversible crystal phase transition without melting. <sup>d</sup> Does not melt, decomposition visible at this temperature.

are consistent with the data on other n-alkyl derivatives; the literature values<sup>4</sup> are divergent.

The pertinent alkyl C-H bands which were consistently observable in the infrared spectra are listed in Table 2. In contradistinction to many organometallics, the C-H frequencies in these compounds were quite normal. There was also very little shift in methyl C-H absorption frequency from compound to compound. Those for the methyltitanium compound suggest a shorter C-H bond than usual and for the isobutyl derivative a slightly longer C-H bond than usual. The methylene C-H absorption frequencies for the ethyl and isobutyl compounds were shifted slightly from the average. The spectra also showed all of the previously reported frequencies assigned to cyclopentadienyl ligands in compounds of this type<sup>19-22</sup>.

The far infrared spectra of organotitanium compounds are still the subject of debate<sup>22-26</sup>. Pertinent data from both the literature and the present study are summarized in Table 3. It appears that the band at 375 to 395 cm<sup>-1</sup> is due to a Ti-Cl bond, the band at 410 to 417 cm<sup>-1</sup> is due to the Ti-( $\pi\text{-C}_5\text{H}_5$ ) function, and the  $\sigma$ -Ti-C bond absorbs at 459 to 465 cm<sup>-1</sup>. The absorption at roughly 550 to 600 cm<sup>-1</sup>

TABLE 2

SOME INFRARED ABSORPTION FREQUENCIES FOR COMPOUNDS OF STRUCTURE  $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{R})\text{Cl}$ 

R	Frequencies ( $\text{cm}^{-1}$ )				
	CH <sub>3</sub> stretching		CH <sub>2</sub> stretching		CH def. sym.
	asym.	sym.	asym.	sym.	
CH <sub>3</sub>	2985	2900			1362
C <sub>2</sub> H <sub>5</sub>	2940	2885	2910	2840	1365
n-C <sub>3</sub> H <sub>7</sub>	2960	2865	2930	2850	1375
n-C <sub>4</sub> H <sub>9</sub>	2960	2870	2930	2850	1375
iso-C <sub>4</sub> H <sub>9</sub>	2955	2860	2909		1380, 1365
n-C <sub>5</sub> H <sub>11</sub>	2960	2870	2930	2860	1375
neo-C <sub>5</sub> H <sub>11</sub>	2960	2870	2930	2860	1360
PhCH <sub>2</sub>			2925	2860	1370
PhCH <sub>2</sub> CH <sub>2</sub>			2945	2863	1375
			2900	2820	
CH <sub>2</sub> =CH <sup>a</sup>	2930 <sup>b</sup>	2858 <sup>b</sup>			

<sup>a</sup> Vinyl C=C stretch at 1635 and 1438  $\text{cm}^{-1}$ ; vinyl C=C out-of-plane deformation at 880  $\text{cm}^{-1}$ . <sup>b</sup> These frequencies are those of the vinyl C-H stretching modes.

TABLE 3

FAR INFRARED ABSORPTION FREQUENCIES FOR SOME ORGANOTITANIUM COMPOUNDS

Compound	Frequency ( $\text{cm}^{-1}$ )		Ref.
(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> Ti	609	413	22
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiF <sub>2</sub>		416	22
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl <sub>2</sub>	590	412	395, 356 This work
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl <sub>2</sub>	595	415	22
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiBr <sub>2</sub>		417	22
C <sub>3</sub> H <sub>5</sub> TiCl <sub>3</sub>	486	414	22
CH <sub>3</sub> TiCl <sub>3</sub>	550	464	391
CH <sub>3</sub> TiCl <sub>3</sub>	540	459	25
(CH <sub>3</sub> ) <sub>2</sub> TiCl <sub>2</sub>	550	462, 427	396
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(CH <sub>3</sub> )Cl	586	465	410 375 This work
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(C <sub>2</sub> H <sub>5</sub> )Cl	600	465	405 379 This work

has been ascribed to both the cyclopentadienyl ring<sup>22</sup> and to Cl-Ti-Cl asymmetrical stretching<sup>23-24</sup>. Of immediate interest is the confirmation of the assignment of the Ti-C stretching frequency. Gray<sup>23</sup> tentatively made this assignment, in contradiction to other workers<sup>25-26</sup>, based on a study of CD<sub>3</sub>TiCl<sub>3</sub>. It is clear from Table 3 that this band must be the stretching vibration of the  $\sigma$ -Ti-C bond since it is absent in  $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ , but appears in its monoalkyl derivatives.

Table 4 summarizes the data from the UV-visible spectra. Of considerable interest is the fact that three compounds, the neopentyl, phenyl, and benzyl derivatives, had an absorption at about 250  $\mu$  which was very strong and which did not obey Beer's law. There was a rapid increase in absorption as the concentration was increased from 0 to 0.1 mmoles per liter. Above this range, a linear increase in absorption with concentration was seen up to a solution strength of 5 mmoles per liter.

TABLE 4  
SPECTROPHOTOMETRIC DATA IN THE ULTRAVIOLET AND VISIBLE REGIONS FOR COMPOUNDS OF STRUCTURE  $(C_5H_5)_2Ti(R)Cl$

R	$\lambda$ (m $\mu$ )		$\lambda$ (m $\mu$ )		$\lambda$ (m $\mu$ )	
	log $\epsilon$		log $\epsilon$		log $\epsilon$	
	CH <sub>2</sub> Cl <sub>2</sub>	Toluene	CH <sub>2</sub> Cl <sub>2</sub>	Toluene	CH <sub>2</sub> Cl <sub>2</sub>	Toluene
CH <sub>3</sub>	520 2.05	1.93	440 2.73	2.70	300	3.73
C <sub>2</sub> H <sub>5</sub>	520	2.70	440	2.76	No band	No band
n-C <sub>3</sub> H <sub>7</sub>	520 2.38	2.40	440 2.58		247 3.30	247 3.30
			435	2.57	Not measured	Not measured
iso-C <sub>4</sub> H <sub>9</sub>	500 2.55	2.49	430 2.66		300	3.78
			425	2.72		245 3.30
n-C <sub>4</sub> H <sub>9</sub>						
n-C <sub>5</sub> H <sub>11</sub>	500 2.55	2.47	434 2.73	2.64	300	3.83
neo-C <sub>5</sub> H <sub>11</sub>	520 2.05		390 3.42		No band	No band
PhCH <sub>2</sub>	520	No band	382	3.57	279	4.06
PhCH <sub>2</sub> CH <sub>2</sub>	520	2.45	445	2.68	267 3.30	252 4.26 <sup>a</sup>
Ph	485 2.62		395 3.25		280	250 3.36
	484	2.56				245 4.49 <sup>a</sup>
Cl	515	2.31	Not measured		Not measured	Not measured
						232 3.40
						231 3.32
						Not measured
						233 3.38
						233 3.38
						231 3.40
						No band
						No band
						232 3.46
						No band

<sup>a</sup> Beer's Law was not obeyed. Extinction coefficients were taken from the slope of the line of optical density vs. concentration at above 0.1 mmole/l concentration. The line did not pass through the origin.

All other absorptions of all compounds listed in Table 4 did obey Beer's law.

The NMR spectroscopic characteristics (the shifts being relative to tetramethylsilane absorption) are shown in Table 5. The methyl protons absorbed at

TABLE 5

NMR DATA FOR COMPOUNDS OF STRUCTURE  $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{R})\text{Cl}$  IN DEUTEROCHLOROFORM

R	Proton ratio			$\text{C}_5\text{H}_5$ (ppm)	$\text{C}_6\text{H}_5$ (ppm)	$\text{CH}_2$ (ppm)	$\text{CH}_3$ (ppm)
		Theor.	Found				
$\text{CH}_3$	$\pi\text{-C}_5\text{H}_5/\text{CH}_3$	3.33	3.19	6.34			0.72
$\text{C}_2\text{H}_5$	$\pi\text{-C}_5\text{H}_5/\text{others}$	2.00	2.26	6.30		1.64	1.23
$n\text{-C}_3\text{H}_7$	$\pi\text{-C}_5\text{H}_5/\text{others}$	1.33	1.42	6.19		1.58 <sup>a</sup>	0.73
$n\text{-C}_4\text{H}_9$	$\pi\text{-C}_5\text{H}_5/\text{CH}_3$	3.33	3.45	6.16		1.58 <sup>a</sup>	0.79
$i\text{-C}_4\text{H}_9$	$\pi\text{-C}_5\text{H}_5/\text{CH}_3$	1.70	1.67	6.23		1.58 <sup>a</sup>	0.75
$n\text{-C}_5\text{H}_{11}$	$\pi\text{-C}_5\text{H}_5/\text{others}$	0.91	0.90	6.20		1.61 <sup>a</sup>	0.83
$\text{neo-C}_5\text{H}_{11}$	$\pi\text{-C}_5\text{H}_5/\text{others}$	1.11	1.00	6.52		2.31	0.91
Ph				6.33	6.85		
$\text{PhCH}_2$				6.53	7.18	2.92	
$\text{PhCH}_2\text{CH}_2$	$\pi\text{-C}_5\text{H}_5/\text{C}_6\text{H}_5$	2.0	1.95	6.26	7.10	2.75, 1.85	
$\text{CH}_2=\text{CH}$				6.58		6.48, 6.44, 6.31 <sup>b</sup>	

<sup>a</sup> The absorptions for the sets of methylene protons were not resolved but were centered about this frequency. <sup>b</sup> These frequencies are those of a complex band attributable to the vinyl hydrogens.

about 0.7 to 0.9 ppm with the exception of those in the ethyl derivative which absorbed at 1.23 ppm. The latter absorption frequency is upfield from those for the  $\beta$ -hydrogens in the other  $n$ -alkyl compounds and is therefore due to some peculiarity of the ethyl compound itself. The methylene protons generally absorbed at 1.5 to 1.6 ppm irrespective of whether they were  $\alpha$  to the titanium atom or not and in some cases the absorptions were not resolved. The peaks due to the methylene protons of the neopentyl, benzyl and phenethyl compounds however, appeared further downfield. The phenethyl compound gave separate bands for each of its sets of methylene protons, the downfield absorption probably being due to the protons adjacent to the benzene ring. The latter set of methylene protons and those in the benzyl compound appear to be deshielded relative to those in ethylbenzene or to methyl protons in toluene.

Absorptions caused by the cyclopentadienyl protons in these compounds generally occurred close to 6.2 ppm. Exceptions are the benzyl, phenyl, neopentyl and vinyl compounds, in which the cyclopentadienyl protons are deshielded relative to the others. The absorptions of the vinyl group of the vinyl derivative indicate that it may be conjugated with the titanium  $d$ -orbitals.

## DISCUSSION

Several authors have commented on the bonding in organic derivatives of tetravalent titanium<sup>5,27-29</sup>. Molecular orbital theory<sup>5,28</sup> has predicted that the  $sd^3$  hybridization in the titanium gives gerade orbitals which are directional and allow very little  $d_\pi\text{-}p_\pi$  bonding between a  $\sigma$ -bonded ligand and the titanium. However, this theory seems to be both supported by one set of NMR data for titanocene derivatives

and refuted by another. Unusual hyperconjugative effects have been postulated<sup>30</sup> for  $(C_5H_5)_2Ti(CH_3)Cl$ .

The spectroscopic data obtained by us suggest that in most of the compounds there is very little difference in the nature of the  $\sigma$ -Ti-C bond from compound to compound. The methyl compound seems to be very similar to the other n-alkyl compounds and, if anything, the shift to a higher frequency for the C-H stretching is in the opposite direction to that expected for conjugation. Furthermore, the presence of the titanium atom does not seem to have much effect on the adjacent C-H bonds relative to C-H bonds in alkanes. The unexpected appearance of the C-H deformation at its "normal" position near  $1365\text{ cm}^{-1}$  in the infrared spectrum has been commented on by Gray<sup>23</sup>, who was puzzled that it was not below  $1200\text{ cm}^{-1}$  as in most other organometallics. The position of this deformation can be understood if the  $\sigma$ -Ti-C bond is weak. The far infrared position of the Ti-C stretching frequency is similarly explainable.

Three compounds of the series, the neopentyl, phenyl, and benzyl derivatives, are abnormal. The deshielding of all protons suggests that the titanium atom is a center of positive charge. The intense, shifted, UV band which did not obey Beer's Law suggests either association or dissociation of the absorbing species.

Facile ionization of the Ti-Cl bond in methyl and ethyl derivatives in acetonitrile solution was indicated by an immediate precipitation of silver chloride (identified) when silver nitrate was added. The promotion of such ionization in compounds of this type by aluminum alkyls has been postulated previously<sup>15,31</sup>. These three anomalous compounds all have a bulky  $\sigma$ -bonded ligand. Therefore, we postulate that these compounds are ionized, even in non-polar solvents, for steric reasons.

#### ACKNOWLEDGEMENTS

The authors gratefully acknowledge the analytical assistance of G. L. Roberts, R. M. Fritz, J. O. Owens, V. V. Vickroy, J. D. Stroud, and P. Berger, and the laboratory assistance of H. S. Lawless.

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