Journal of Organometallic Chemistry, 334 (1987) 341–345
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The crystal structure of tetrachloro(diethylphthalate)titanium(IV)

Józef Utko, Piotr Sobota★ and Tadeusz Lis

Institute of Chemistry, University of Wrocław, 14, Joliot-Curie, 50-383 Wrocław (Poland)

(Received April 7th, 1987)

Abstract

The crystal structure of $[C_6H_4(OCOC_2H_5)_2TiCl_4]$, which in the presence of activators is a good catalyst for olefin polymerization, has been determined by X-ray diffraction methods and refined by full-matrix least-squares techniques to $R = 0.045$ for 2000 independent non-zero reflexions. Crystals are orthorhombic, space group *Pnma*, with four molecules in a cell of dimensions: a 11.45(1), b 14.07(1), c 10.56(1) Å. The structure consists of discrete molecules possessing crystallographic m (C_s) point symmetry. The Ti atoms are octahedrally coordinated by four chlorine atoms and two carbonyl oxygen atoms of diethylphthalate. The chelating ligand atoms together with the titanium atom form a seven-membered ring with the Cl and Ti atoms located above the benzene ring.

Introduction

The higher activity of the Ziegler–Natta catalyst for ethylene and propylene polymerization, has been based mainly on reaction between magnesium, titanium, and organoaluminium compounds.

Extremely active catalysts for propylene polymerization were prepared by trituration of $MgCl_2$ with ethyl benzoate, followed by treating the product with $TiCl_4$ [1]. Polypropylene produced by this method is mainly in the isotactic form. The high isotactic index is maintained because of the addition of ethyl benzoate. The influence of this ester on the stereospecific course of the propylene polymerization reaction has not been explained as yet. Hence, the study of interaction between esters and titanium and magnesium compounds is fundamental. It was found, that the reaction of $TiCl_4$ with esters, depending on reaction conditions produced two types of compounds: dimer $[(L)Cl_3Ti(\mu\text{-}Cl)_2TiCl_3(L)]$, where $L = CH_3OCOC_2H_5$ [2], or $C_2H_5OCOC_6H_4OCH_3$ [3] and monomer *cis*-$[TiCl_4(C_6H_5OCOC_2H_5)_2]$ [4].

We have started the examination of reaction between $TiCl_4$ and diethylphthalate. That ester was found to have basic influence on the specific propylene polymeriza-

0022-328X/87/$03.50

tion process. We believe that $C_6H_4(OCOR)_2$ compounds with titanium could be used as models for the study of the mutual interaction between esters and aluminium organometallic compounds. The X-ray crystal structure of the 1 : 1 adduct between $TiCl_4$ and $C_6H_4(OCOC_2H_5)_2$ is described here.

Experimental

All manipulations were carried out under N_2 using dried solvents and Schlenk techniques. Anhydrous $TiCl_4$ and diethylphthalate were commercial materials. Microanalyses were performed at the University of Wrocław.

Tetrachloro(diethylphthalate)titanium(IV)

To 5 cm^3 of $TiCl_4$ (8.63 g; 45 mmol) was added dropwise 8.96 cm^3 (10.1 g; 90 mmol) of diethylphthalate and stirred into 150 cm^3 n-hexane under N_2. After 1 h the yellow precipitate was filtered off and washed with n-hexane (3 × 15 cm^3) to give the compound, which is soluble in CH_2Cl_2, in 95% yield. The IR spectrum shows a stretching ν(C=O) mode at 1640(vs,br) cm^{-1} and ν(Ti–Cl) at 390(vs) cm^{-1}, 368(vs) cm^{-1} and 320(w) cm^{-1}. The compound is diamagnetic. The ^1H NMR spectrum shows the triplet at 1.62 ppm and the doublet at 4.85 ppm typical of diethylphthalate. Crystals suitable for the structure determination were grown by slow diffusion of n-hexane into a solution of the title compound in CH_2Cl_2.

X-Ray crystal structure determination

Crystal data. $C_{12}H_{14}Cl_4O_4Ti$, $M = 411.8$, a 11.45(1), b 14.07(1), c 10.56(1) Å, $U = 1701$ Å^3, D_m(by flotation) = 1.61 g cm^{-3}, $Z = 4$, $D_c = 1.61$ g cm^{-3}, $F(000) =$

Table 1

The final positional and thermal parameters for tetrachloro(diethylphthalate)titanium(IV) [a]

Atom	x	y	z	B_{eq} or B_{iso}
Ti	0.23013(6)	0.25	0.07631(6)	1.70(4)
Cl(1)	0.36662(9)	0.25	0.23546(10)	2.38(7)
Cl(2)	0.06650(11)	0.25	−0.04820(10)	3.10(8)
Cl(3)	0.31536(8)	0.12889(6)	−0.02478(8)	3.57(6)
O(1)	0.1378(2)	0.1559(2)	0.1885(2)	2.12(14)
O(2)	0.0581(2)	0.0595(2)	0.3298(2)	2.59(15)
C(1)	0.1365(3)	0.2005(2)	0.4109(3)	1.87(18)
C(2)	0.1629(4)	0.1522(3)	0.5227(4)	2.91(24)
C(3)	0.1928(4)	0.2008(3)	0.6323(3)	3.74(29)
C(4)	0.1105(3)	0.1395(2)	0.2996(3)	1.84(17)
C(5)	0.0350(4)	−0.0090(3)	0.2262(4)	3.24(27)
C(6)	−0.0763(5)	0.0150(4)	0.1604(5)	4.63(38)
H(2)	0.164(3)	0.097(3)	0.525(3)	2.7(8)
H(3)	0.222(4)	0.167(3)	0.704(4)	5.0(11)
H(51)	0.117(3)	−0.012(3)	0.164(3)	2.6(7)
H(52)	0.038(4)	−0.059(3)	0.273(4)	4.6(10)
H(61)	−0.080(4)	0.076(4)	0.106(4)	5.7(11)
H(62)	−0.104(6)	−0.026(5)	0.123(6)	10.0(20)
H(63)	−0.138	0.017(4)	0.229(5)	8.6(17)

[a] For non-H atoms $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

832, space group *Pnma*, Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 11.5$ cm^{-1}, $T = 297 \pm 1$ K.

A sample 0.7 × 0.5 × 0.6 mm was cut from large crystal and sealed in a capillary. The Weissenberg photographs showed the crystal to be orthorhombic. From the extinction rules there are two possible space groups *Pnma* and $Pn2_1a$. The intensity data were recorded on a Syntex $P2_1$ automated diffractometer with graphite-monochromatized Mo-K_α radiation. Intensities were measured by 2θ–ω scan up to $2\theta = 60°$. The intensities of two standard reflexions, monitored after every 50 scan intensities, showed no evidence of crystal decay. 2454 reflections were collected of which 2000 with $I > 1.96\sigma(I)$ were used for the structure analysis. The structure was solved by the heavy-atom method. The Ti atoms were found from the Patterson map, and the centrosymmetric space group *Pnma* was assumed. All other atoms were found from successive difference-Fourier syntheses. An absorption correction following the DIFABS procedure [5] was applied on isotropically refined data; minimum and maximum absorption corrections were 0.848 and 1.267 respectively. Full matrix least-squares refinement was carried out on the positional and anisotropic (isotropic for H) thermal parameters and gave final $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.045$ and $R_w = (\Sigma W \Delta F^2 / \Sigma W F_o^2)^{1/2} = 0.047$, where $w = 1/\sigma^2(F_o)$. Neutral-atom scattering factors were taken from [6]. The Ti, Cl, O and C scattering factors were corrected for real and imaginary components. Most calculations were performed on a NOVA 1200 computer with a locally modified Syntex XTL/XTLE programs [7]. Maximum $\Delta/\sigma = 0.35$, $\Delta(\rho)_{max}$ in final difference synthesis was 0.4 e/Å^3. The final atomic parameters are listed in Table 1.

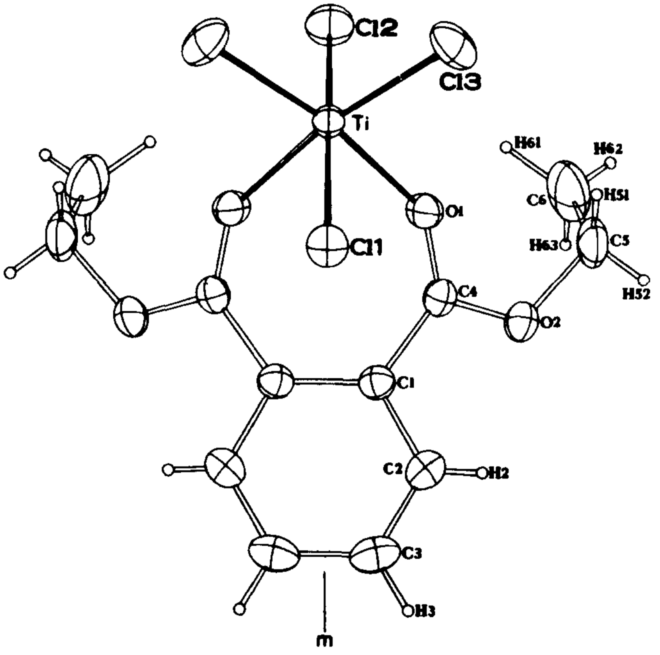

Fig. 1. The molecular structure and numbering scheme of $[C_6H_4(OCOC_2H_5)_2TiCl_4]$.

Table 2

Selected bond lengths (Å) and angles (°) for tetrachloro(diethylphthalate)titanium(IV)[a]

Ti–Cl(1)	2.295(2)	Ti–Cl(2)	2.289(2)
Ti–Cl(3)	2.235(2)	Ti–O(1)	2.068(3)
C(1)–C(1′)	1.394(4)	C(1)–C(2)	1.396(4)
C(2)–C(3)	1.387(5)	C(3)–C(3′)	1.386(5)
C(1)–C(4)	1.485(4)	C(4)–O(1)	1.236(3)
C(4)–O(2)	1.314(3)	C(5)–O(2)	1.483(4)
C(5)–C(6)	1.490(7)	C–H	0.76(7)–1.14(4)
Cl(1)–Ti–Cl(2)	168.0(1)	Cl(1)–Ti–Cl(3)	93.0(1)
Cl(1)–Ti–O(1)	85.9(1)	Cl(2)–Ti–Cl(3)	94.8(1)
Cl(2)–Ti–O(1)	84.9(1)	Cl(3)–Ti–Cl(3′)	99.4(1)
Cl(3)–Ti–O(1)	90.5(1)	Cl(3)–Ti–O(1′)	170.1(1)
O(1)–Ti–O(1′)	79.7(1)	Ti–O(1)–C(4)	142.5(2)
C(4)–O(2)–C(5)	117.3(3)	C(2)–C(1)–C(1′)	119.2(3)
C(4)–C(1)–C(1′)	125.3(3)	C(2)–C(1)–C(4)	115.5(3)
C(1)–C(2)–C(3)	121.3(4)	C(2)–C(3)–C(3′)	119.5(4)
O(1)–C(4)–O(2)	120.4(3)	O(1)–C(4)–C(1)	126.3(3)
O(2)–C(4)–C(1)	113.2(3)	O(2)–C(5)–C(6)	110.5(4)

[a] Atoms marked with a prime are related to those at x, y, z by a mirror plane at $x, \frac{1}{4}, z$.

Results and discussion

The structure of $[C_6H_5(OCOC_2H_5)_2TiCl_4]$ molecule is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. Titanium and two chlorine atoms lie on the mirror plane and hence the whole molecule has *m* symmetry. In the molecule four Cl atoms and two O atoms of the ligand carbonyl groups form the distorted octahedron around the titanium atom. The molecule of the diethylphthalate is coordinated to titanium atom via the carbonyl oxygen atoms. The chelate ligand and the titanium atom form the seven-membered ring. The benzene ring is planar and is almost coplanar with the plane formed by C(1), C(1′), C(4) and C(4′) which

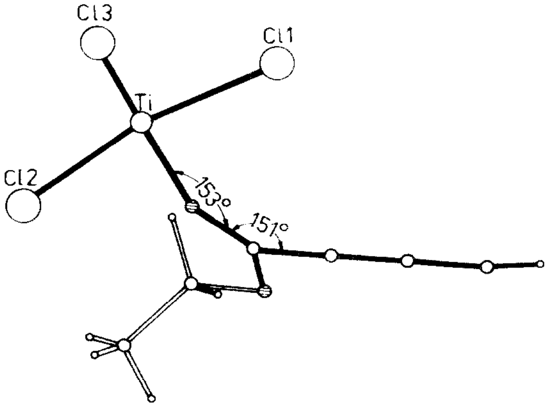

Fig. 2. View of the molecule showing the angles between the seven-membered ring planes and position of Cl and Ti atoms above the benzene ring.

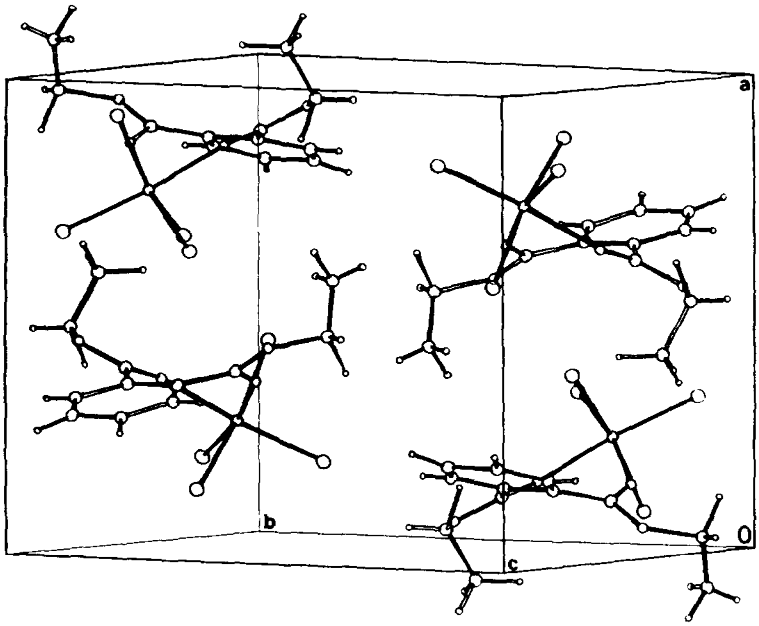

Fig. 3. View of the crystal packing for $[C_6H_4(OCOC_2H_5)_2TiCl_4]$.

is inclined towards the plane C(4), C(4′), O(1), O(1′) by 151° (Fig. 2). The plane formed by Ti, O(1), O(1′) is at an angle of 153° to the C(4), C(4′), O(1), O(1′) plane. The plane C(1), C(1′), C(4), C(4′) forms an angle of 145° with the plane composed of O(1), C(1), C(4), O(2) atoms. The angle of torsion, C(6)–C(5)–O(2)–C(4), is $-84(4)^\circ$. Thus the methyl group is directed almost vertically towards the C(4)–O(1) bond. The Ti–Cl distances vary somewhat but are similar to the terminal Ti–Cl distance in the $[TiCl_4(CH_3OCOC_2H_5)]_2$ [2] and $[TiCl_4(C_2H_5OCOC_6H_4\text{-}OCH_3)]_2$ [3], complexes found previously. The C=O bond length in the coordinated carbonyl group in $[C_6H_4(OCOC_2H_5)_2TiCl_4]$ is 1.236(3) Å and thus very close to the C=O bond length 1.23(1) Å of the free carbonyl group [8].

References

1 P.D. Gavens, M. Botrrill, J.W. Kelland and J. McMeeking, Comprehensive Organometallic Chemistry Vol. 3 (1982) 475.
2 L. Brun, Acta Crystallogr., 20 (1966) 739.
3 I.W. Bassi, M. Calcaterra and J. Intrito, J. Organomet. Chem., 127 (1977) 305.
4 E. Rytter, O. Nirisen, M. Ystenens, Poster at International Symposium "Transition Metal Catalyzed Polymerization" June 16–20, 1986 in Akron, OH.
5 N. Walker and D. Stuart, Acta Crystallogr., A39 (1983) 158.
6 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, Vol. 4, 1968.
7 Syntex XTL/XTLE Structure Determination System, Syntex Analytical Instruments, Cupertino, 1976.
8 O. Kennard, D.G. Watson, F.H. Allen, N.W. Isaacs, W.D.S. Motherwell, R.C. Pettersen and W.G. Tawn, in Molecular Structures and Dimensions, Vol. A1(S3), Oosthoek, Utrecht, (1972).
9 M.W. Lister and L.E. Sutton, Trans. Faraday Soc., 37 (1941) 393.