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$TiCl_4$ diester complexes: relationships between the crystal structures and properties of Ziegler–Natta catalysts

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Abstract

The crystal structures of seven diester · $TiCl_4$ complexes, where diester is $CH_2(CO_2CH_2CH_3)_2$ (**1**), $(CH_3)_2C_2(CO_2CH_2CH_3)_2$ (**2**), $(CH_3CH_2)_2C(CO_2CH_2CH_3)_2$ (**3**), *cis*-$C_2H_2(CO_2CH_2CH_3)_2$ (**4**), *cis*-$CHCCH_3(CO_2CH_2CH_3)_2$ (**5**), *o*-$C_6H_4(CO_2CH_3)_2$ (**6**) and *cis*-1,2-$C_6H_{10}[CO_2CH_2CH(CH_3)_2]_2$ (**7**), have been determined by X-ray diffraction studies. All the diesters form monomeric complexes with $TiCl_4$, and the titanium atom is coordinated by four chlorine atoms and two carbonyl oxygen atoms of diester in the *cis* position. Correlation structure with catalytic behaviour have been investigated.

1. Introduction

The performance of $MgCl_2$-supported Ziegler–Natta catalysts has been markedly improved by using suitable Lewis bases as internal and external donors. It is generally accepted that both internal and external donors are necessary to obtain a catalyst showing high stereospecificity and activity in α-olefin polymerization processes [1–5] The separate functions of the two Lewis bases used in the preparation of the Ziegler–Natta catalysts have been the subject of many unresolved questions [2].

We have determined the crystal structures of seven $TiCl_4$ · diester complexes in order to throw light on the variations in the isospecific activity of various mono- or di-esters in the propylene polymerization [5] when these are used as internal donors in the catalyst preparation. The new structures are compared with those previously described for diester complexes [6].

2. Experimental details

All reactions were carried out under N_2 in dried solvents by use of standard inert atmosphere techniques.

$TiCl_4$ and diacids or their anhydrides were obtained from Aldrich-Chemie GmbH & Co. KG, and the diesters were prepared by standard esterification procedures [7,8] with *p*-toluene sulfonic acid as catalyst starting from diacids or their anhydrides and alcohols. After esterification the products were vacuum distilled to give a chemical purity of > 99.5%. All the diesters are liquids, and they were dried and stored under activated molecular sieves.

2.1. X-Ray crystal structure determination

The moisture sensitive crystals were covered with dried viscous hydrocarbon grease in Hilgenberg glass capillaries under N_2.

Details of crystal parameters, data collection parameters and refined data for complexes **1**–**7** are summarized in Table 1. Data were collected on a Nicolet R3m

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diffractometer using graphite monochromatized Mo Kα radiation. An ω-scan mode with scan speed 2.49–29.29° min^{-1} was used. Intensities were corrected for Lorenz, polarization and background effects. An empirical absorption correction was applied (except for **4**), based on ψ-scans.

Titanium and chlorine atoms were located by the direct methods of the SHELXTL-PLUS [9] program package. Carbon and oxygen atom coordinates were determined by Fourier synthesis. Titanium, chlorine, carbon and oxygen atoms were anisotropically refined for all the structures.

Hydrogen atoms were placed in calculated positions (C–H = 0.96 Å, $U = 0.08$) and not refined. In **4** the hydrogens on C11 and C12 were refined isotropically, but in **5** the hydrogen on C11 was not located. Selected bond lengths, bond angles, torsion angles and non-bonded distances are listed in Tables 2–4, and atomic coordinates in Tables 5–11.

Complete lists of bond lengths and angles and lists of thermal parameters and structure factors for all seven compounds are available from the authors.

2.2. *Preparation of $TiCl_4$ · diester complexes*

2.2.1. *[$CH_2(CO_2CH_2CH_3)_2TiCl_4$] (1)*

$TiCl_4$ (5 cm^3, 8.65 g; 46 mmol) was added dropwise to a solution of 7.37 g (46 mmol) of $CH_2(CO_2CH_2CH_3)_2$ in 200 cm^3 of n-heptane and the mixture was stirred under N_2 at 293 K. After 0.5 h a yellow precipitate was filtered off, washed five times with 50 cm^3 of n-heptane, and dried under vacuum. Crystals suitable for the structure determination were grown by slow

TABLE 1. Crystallographic data for compounds **1**–**7** [a]

	1	**2**	**3**	**4**	**5**	**6**	**7**
Formula weight	349.9	389.9	405.9	357.8	374.9	383.9	474.1
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	*Pbca*	$P2_1/n$	$P2_1/c$	*Pnma*	*P*-1
a (pm)	774.7(5)	987.9(6)	855.5(3)	817.5(7)	964.5(7)	1884.7(4)	928.2(5)
b (pm)	1824.8(13)	977.5(7)	1666.4(7)	1855(2)	1200.0(8)	1178.5(2)	1148.7(7)
c (pm)	991.0(5)	1802.1(12)	2594.6(6)	986.3(9)	1436.4(15)	689.4(10)	2256.0(2)
α (°)	90.00	90.00	90.00	90.00	90.00	90.00	96.63(5)
β (°)	91.23(5)	100.02(5)	90.00	94.77(7)	100.04(7)	90.00	97.37(5)
γ (°)	90.00	90.00	90.00	90.00	90.00	90.00	102.03(4)
U (nm^3)	1.4006(15)	1.714(2)	3.699(2)	1.491(2)	1.637(2)	1.5312(5)	2.308(3)
Z	4	4	8	4	4	4	4
D_{calc} (g cm^{-3})	1.659	1.511	1.458	1.594	1.521	1.665	1.364
$F(000)$	704	792	1664	680	756	768	984
No. centering reflections	25	25	25	25	25	25	25
Centering 2θ	14–25	13–26	10–25	15–30	11–25	11–25	10–24
2θ limits	5–50	5–50	5–50	5–50	5–50	5–50	5–50
h, k, l range	10, 22, ±12	12, 12, ±22	11, 20, 31	9, 12, ±11	12, 15, ±18	9, 15, 23	12, ±14, ±27
No. of unique reflections	2472	3004	3253	2626	2845	1412	7987
Obs. data [$I \geq 3\sigma(I)$]	1795	1740	–	1790	–	–	–
Obs. data [$I \geq 2\sigma(I)$]	–	–	1340	–	1079	1007	2185
μ (mm^{-1})	1.37	1.13	1.05	1.28	1.18	1.26	0.85
No. of parameters	145	172	181	162	163	91	451
R	0.0426	0.0360	0.0724	0.0492	0.0670	0.0435	0.0769
R'	0.0429	0.0372	0.0651	0.0500	0.0612	0.0445	0.0692
G(weight)	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
Goodness of fit	1.4680	1.0766	1.4251	1.7194	1.3769	1.3027	1.5030

$R = (\Sigma \| F_o | - | F_c \|)/\Sigma F_o |$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w |F_o|^2]^{1/2}$, and goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o = number of observed reflections and N_v = number of variables. Weighting scheme used of form $w^{-1} = [\sigma^2(F) + gF^2]$.

[a] $TiCl_4$(diethyl malonate) (**1**)
$TiCl_4$(diethyl isopropylidenemalonate) (**2**)
$TiCl_4$(diethyl diethylmalonate) **3**
$TiCl_4$(diethyl maleate) (**4**)
$TiCl_4$(diethyl citraconate) (**5**)
$TiCl_4$(dimethyl phthalate) (**6**)
$TiCl_4$(*cis*-1,2-di-isobutylcyclohexanoate) (**7**)

diffusion of n-heptane into a solution of complex in CH_2Cl_2.

2.2.2. $[(CH_3)_2C_2(CO_2CH_2CH_3)_2TiCl_4]$ (2)

The synthesis and crystallization procedures were the same as in complex **1** except that 9.21 g (46 mmol) of $(CH_3)_2C_2(CO_2CH_2CH_3)_2$ were used.

2.2.3. $[(CH_3CH_2)_2C(CO_2CH_2CH_3)_2TiCl_4]$ (3)

As for the synthesis of complex **1**, but 9.95 g (46 mmol) of $(CH_3CH_2)_2C(CO_2CH_2CH_3)_2$ were used.

2.2.4. $[cis\text{-}C_2H_2(CO_2CH_2CH_3)_2TiCl]$ (4)

As for the synthesis of complex **1**, but 7.73 g (46 mmol) of *cis*-$C_2H_2(CO_2CH_2CH_3)_2$ were used.

2.2.5. $[cis\text{-}CHCCH_3(CO_2CH_2CH_3)_2TiCl_4]$ (5)

As for the synthesis of complex **1**, but 8.52 g (46 mmol) of *cis*-$CHCCH_3(CO_2CH_2CH_3)_2$ were used.

2.2.6. $[O\text{-}C_6H_4(CO_2CH_3)_2TiCl_4]$ (6)

$TiCl_4$ (5 cm^3, 8.65 g; 46 mmol) was added dropwise to a solution of 8.93 g (46 mmol) of *o*-$C_6H_4(CO_2CH_3)_2$ in 200 cm^3 of n-heptane and the mixture was stirred under N_2 at 293 K. After 0.5 h a yellow orange precipitate was filtered off, washed five times with 50 cm^3 of n-heptane, and dried under vacuum. Because the complex was only slightly soluble in CH_2Cl_2 at room temperature, crystals suitable for the structure determination were obtained by dissolving *ca.* 1 g of complex in 20 cm^3 CH_2Cl_2 at 323 K and then cooling the solution in a refrigerator at 253 K. Yellow orange crystals separated overnight.

2.2.7. $[cis\text{-}1,2\text{-}C_6H_{10}\{CO_2CH_2CH(CH_3)_2\}_2TiCl_4]$ (7)

As for the synthesis of complex **1**, but 13.08 g (46 mmol) of *cis*-1,2-$C_6H_{10}\{CO_2CH_2CH(CH_3)_2\}_2$ were used.

2.3. Catalyst preparation

The catalyst was prepared on a $MgCl_2 \cdot 3EtOH$ support. Two treatments of the support with $TiCl_4$, followed by washing of the catalyst with heptane and drying were carried out as previously described [10c]. The internal donor/$MgCl_2$ molar ratio was 0.075 in the first titanation step unless otherwise stated.

2.4. Polymerization procedure in heptane

A solution of 25 mg of catalyst in 50 ml of heptane was added to a 2 l reactor containing 5 mmol $AlEt_3$ in 1 l of dry heptane. (Cyclohexyl)(methyl)(dimethoxy)silane was used as the external donor and the $AlEt_3$/silane molar ratio was 20 in the propylene polymerization.

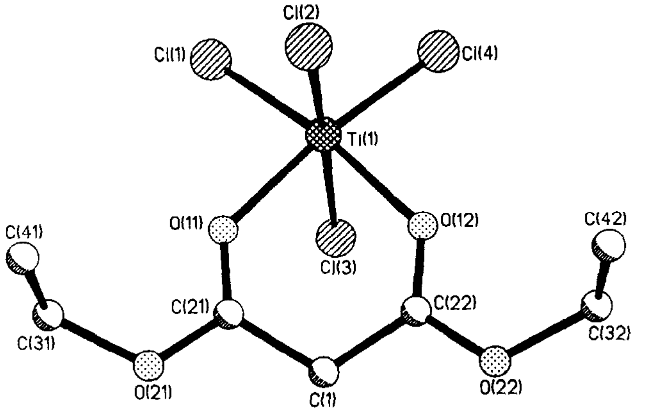

Fig. 1. The molecular structure and numbering scheme of $[CH_2(CO_2CH_2CH_3)_2TiCl_4]$ (1).

Approximately 17 mmol of hydrogen were added to the reactor and the propylene pressure was raised to 10 bar at 70°C. The reaction time was 3 h. The polymer was filtered off and dried. A sample from the liquid phase was examined to determine the amount of dissolved polymer. The polypropylene isotactic index (I.I.) was given by the total amount of heptane-insolubles.

3. Results and discussion

3.1. Structure of $TiCl_4$(diethyl malonate) (1), $TiCl_4$(diethyl isopropylidenemalonate) (2), $TiCl_4$(diethyl diethylmalonate) (3), $TiCl_4$(diethyl maleate) (4), $TiCl_4$(diethyl citraconate) (5), $TiCl_4$(dimethyl phthalate) (6) and $TiCl_4$(cis-1,2-di-isobutyl cyclohexanoate) (7)

Structures and the numbering scheme for these compounds are shown in Figs. 1–7. Selected bond

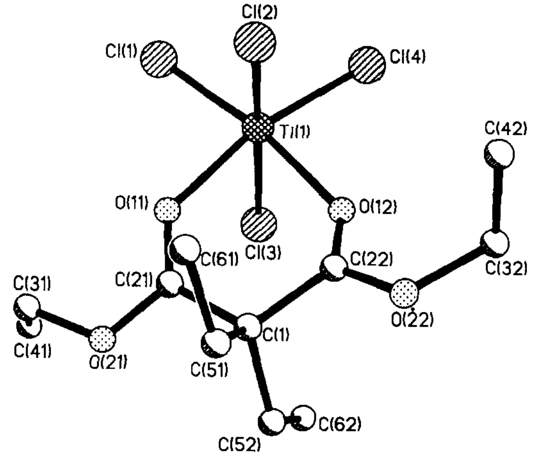

Fig. 2. The molecular structure and numbering scheme of $[(CH_3)_2C_2(CO_2CH_2CH_3)_2TiCl_4]$ (2).

TABLE 2. Selected bond lengths (pm) for compounds **1**–**10**

	1	**2**	**3**	**4**	**5**	**6**	**7a**	**7b**	mean	**8** [6a]	**9** [6b]	**10** [6c]
Ti(1)–Cl(1)	223.9(2)	224.2(2)	221.8(4)	223.2(3)	223.8(5)	222.6(2)	223.4(6)	221.4(6)	223.0	–	223.8(3)	221.5(2)
Ti(1)–Cl(2)	227.3(2)	229.8(2)	228.5(4)	227.6(3)	226.5(5)	229.0(2)	230.5(6)	230.7(6)	228.7	228.9(2)	228.2(3)	228.1(2)
Ti(1)–Cl(3)	230.4(2)	230.2(2)	231.7(4)	228.3(3)	231.0(5)	230.3(2)	230.3(6)	230.8(7)	230.4	229.5(2)	230.5(3)	229.0(2)
Ti(1)–Cl(4)	222.5(2)	224.5(2)	224.2(4)	223.9(3)	224.2(6)	222.6(2)	222.0(6)	222.6(6)	223.3	223.5(2)	223.8(3)	224.1(2)
Ti(1)–O(11)	210.9(3)	209.9(4)	209.2(8)	208.7(4)	206.8(10)	209.1(3)	209.8(13)	206.5(14)	208.9	–	209.3(7)	207.8(3)
Ti(1)–O(12)	213.6(3)	211.8(3)	211.9(7)	209.8(4)	209.7(9)	209.1(3)	209.0(12)	206.2(15)	210.1	206.8(3)	211.3(7)	213.0(3)
O(11)–C(21)	122.9(5)	123.8(6)	121.9(15)	123.4(7)	124.4(16)	122.8(5)	123(3)	118(3)	122.5	–	124.2(13)	122.7(6)
O(12)–C(22)	122.3(5)	123.8(6)	121.2(13)	123.2(6)	121.9(16)	122.8(5)	123(2)	122(4)	122.5	123.6(3)	122.6(12)	123.0(5)
O(21)–C(21)	130.3(5)	129.8(6)	130.4(16)	129.2(8)	131.4(18)	130.4(5)	131(3)	130(3)	130.3	–	130.8(13)	130.3(5)
O(22)–C(22)	130.5(5)	131.2(5)	130.8(13)	130.0(7)	131.8(17)	130.4(5)	130(2)	128(3)	130.3	131.4(3)	129.8(12)	130.1(4)
O(21)–C(31)	146.9(6)	148.3(6)	145.2(18)	147.5(9)	144.9(21)	147.6(6)	147(3)	140(4)	145.9	–	147.4(12)	147.9(6)
O(22)–C(32)	148.2(6)	148.2(6)	146.6(14)	146.3(8)	143.4(18)	147.6(6)	144(2)	142(3)	145.8	148.3(4)	147.2(12)	146.2(6)
C(1)–C(21)	149.8(6)	149.2(7)	152.9(16)	–	–	–	–	–	150.6	–	–	–
C(1)–C(22)	149.3(6)	149.1(7)	153.7(16)	–	–	–	–	–	150.7	–	–	–
C(11)–C(21)	–	–	–	147.5(9)	147.4(19)	149.7(6)	150(3)	160(4)	150.9	–	148.9(15)	148.1(6)
C(12)–C(22)	–	–	–	147.9(9)	149.9(17)	149.7(6)	150(3)	150(3)	149.5	148.5(4)	149.3(15)	147.6(6)
C(11)–C(12)	–	–	–	130.7(10)	134.0(19)	140.3(8)	152(3)	157(4)	142.8	139.4(4)	143.3(16)	–
O(11)–O(12) [a]	271.7	266.0	265.9	271.9	267.6	267.0	272.3	267.9	268.8	264.6	268.9	

[a] Non-bonded.

TABLE 3. Selected bond angles (°) for compounds **1**–**10**

	1	**2**	**3**	**4**	**5**	**6**	**7a**	**7b**	mean	**8** [6a]	**9** [6b]	**10** [6c]
Cl(1)–Ti(1)–Cl(2)	94.4(1)	94.3(1)	93.9(1)	92.6(1)	95.2(2)	94.1(1)	94.6(2)	94.6(2)	94.2	–	92.4(2)	93.3(1)
Cl(1)–Ti(1)–Cl(3)	95.1(1)	94.3(1)	94.1(1)	94.9(1)	93.4(2)	94.1(1)	95.3(2)	94.8(2)	94.5	–	93.4(2)	92.6(1)
Cl(2)–Ti(1)–Cl(3)	165.5(1)	169.3(1)	167.8(1)	167.9(1)	168.3(2)	167.5(1)	165.2(2)	165.7(2)	167.1	168.0(1)	170.8(2)	170.6(1)
Cl(1)–Ti(1)–Cl(4)	97.7(1)	99.7(1)	100.0(1)	98.3(1)	99.3(2)	98.7(1)	98.4(2)	99.1(2)	98.9	99.4(1)	100.9(2)	101.2(1)
Cl(2)–Ti(1)–Cl(4)	95.2(1)	93.3(1)	94.7(1)	94.4(1)	93.7(2)	94.1(1)	95.0(2)	95.1(2)	94.4	94.8(1)	94.2(2)	92.4(1)
Cl(3)–Ti(1)–Cl(4)	94.3(1)	91.5(1)	93.0(1)	93.8(1)	92.8(2)	94.1(1)	94.4(2)	94.0(2)	93.5	93.0(1)	91.6(2)	93.6(1)
Cl(1)–Ti(1)–O(11)	91.0(1)	88.2(1)	91.7(2)	91.3(1)	91.4(3)	91.0(1)	89.8(4)	90.5(4)	90.6	–	90.6(3)	90.3(1)
Cl(2)–Ti(1)–O(11)	83.8(1)	86.7(1)	87.2(2)	84.7(1)	85.5(3)	83.8(1)	84.7(4)	84.9(5)	85.2	–	87.4(3)	85.0(1)
Cl(3)–Ti(1)–O(11)	85.1(1)	87.3(1)	83.3(2)	85.8(1)	86.4(3)	86.6(1)	84.4(4)	84.2(5)	85.4	–	85.5(3)	87.7(1)
Cl(4)–Ti(1)–O(11)	171.3(1)	172.1(1)	168.0(2)	170.4(1)	169.4(3)	170.2(1)	171.8(4)	170.4(5)	170.5	170.1(1)	168.3(3)	168.4(1)
Cl(1)–Ti(1)–O(12)	170.6(1)	166.2(1)	169.8(2)	172.1(1)	171.3(3)	170.2(1)	170.8(4)	171.4(4)	170.3	–	169.2(3)	169.8(1)
Cl(2)–Ti(1)–O(12)	84.3(1)	83.0(1)	84.1(2)	84.9(1)	84.4(2)	83.8(1)	83.5(4)	84.5(5)	84.1	84.9(1)	83.0(3)	86.0(1)
Cl(3)–Ti(1)–O(12)	84.4(1)	87.2(1)	86.5(2)	86.3(1)	86.0(2)	86.6(1)	85.0(4)	84.7(5)	85.8	85.9(1)	90.1(3)	86.9(1)
Cl(4)–Ti(1)–O(12)	91.7(1)	93.9(1)	90.2(2)	89.4(1)	89.4(3)	91.0(1)	90.7(4)	89.5(4)	90.7	90.5(1)	89.2(3)	89.0(1)
O(11)–Ti(1)–O(12)	79.6(1)	78.2(1)	78.3(3)	81.0(2)	79.9(4)	79.4(2)	81.1(5)	81.0(6)	79.8	79.7(1)	79.5(3)	79.6(2)
Ti(1)–O(11)–C(21)	133.4(3)	131.6(3)	134.9(7)	144.9(4)	143.0(9)	144.7(3)	136.3(12)	138.4(19)	138.4	–	138.7(7)	142.1(3)
Ti(1)–O(12)–C(22)	132.6(3)	129.1(3)	135.3(7)	145.5(4)	144.5(8)	144.7(3)	137.4(11)	139.1(15)	138.5	142.5(2)	139.6(7)	139.3(3)
O(11)–C(21)–O(21)	122.7(4)	122.1(4)	122.5(10)	122.0(5)	118.7(12)	120.6(4)	117.8(17)	124.5(25)	121.4	–	121.8(10)	122.0(4)
O(12)–C(22)–O(22)	121.8(4)	121.5(4)	122.4(10)	121.8(5)	120.7(11)	120.6(4)	1228.8(17)	126.4(20)	122.3	120.4(3)	122.0(10)	121.8(4)
C(21)–O(21)–C(31)	118.3(3)	117.2(4)	118.1(10)	118.8(5)	118.9(12)	117.2(3)	119.1(17)	115.4(17)	117.9	–	118.4(8)	118.8(4)
C(22)–O(22)–C(32)	118.1(3)	118.5(4)	118.9(8)	117.8(4)	117.8(11)	117.2(3)	118.3(12)	116.1(18)	117.8	117.3(3)	117.8(8)	119.5(4)
O(11)–C(21)–C(1)	124.3(4)	121.4(4)	126.4(12)	–	–	–	–	–	124.0	–	–	–
O(12)–C(22)–C(1)	124.7(4)	123.9(4)	126.5(10)	–	–	–	–	–	124.0	–	–	–
O(21)–C(21)–C(1)	113.0(3)	116.4(4)	110.9(10)	–	–	–	–	–	113.4	–	–	–
O(22)–C(22)–C(1)	113.4(3)	114.5(4)	111.2(9)	–	–	–	–	–	113.0	–	–	–
C(21)–C(1)–C(22)	113.2(3)	111.6(4)	110.1(9)	–	–	–	–	–	111.6	–	–	–
O(11)–C(21)–C(11)	–	–	–	127.0(6)	130.1(13)	126.3(4)	126.6(19)	128.4(23)	127.7	–	127.3(10)	126.6(4)
O(12)–C(22)–C(12)	–	–	–	126.0(5)	128.6(12)	126.3(4)	125.0(18)	122.6(22)	125.7	126.3(3)	125.7(10)	127.2(4)
O(21)–C(21)–C(11)	–	–	–	111.0(5)	111.2(11)	113.1(4)	115.5(20)	106.4(18)	111.4	–	110.9(9)	111.3(4)
O(22)–C(22)–C(12)	–	–	–	112.1(5)	110.6(11)	113.1(4)	111.9(14)	110.9(23)	111.7	113.2(3)	112.3(9)	111.0(4)
C(12)–C(11)–C(21)	–	–	–	129.2(6)	128.7(11)	124.8(2)	113.6(17)	108.9(18)	121.0	–	122.4(10)	124.4(4)
C(11)–C(12)–C(22)	–	–	–	128.5(6)	124.6(11)	124.8(2)	117.6(13)	117.6(22)	122.6	125.3(3)	123.6(10)	124.6(4)

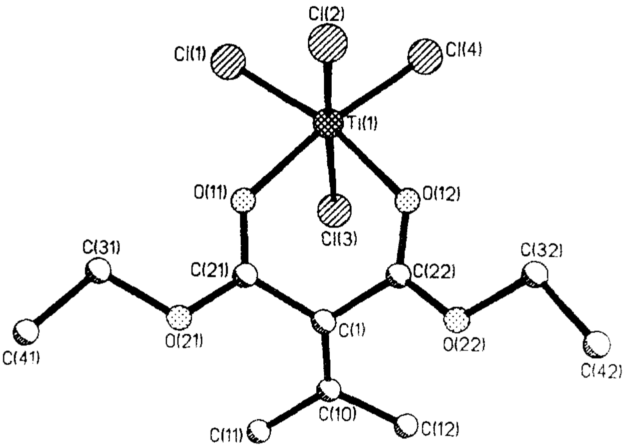

Fig. 3. The molecular structure and numbering scheme of $[(CH_3CH_2)_2C(CO_2CH_2CH_3)_2TiCl_4]$ (**3**).

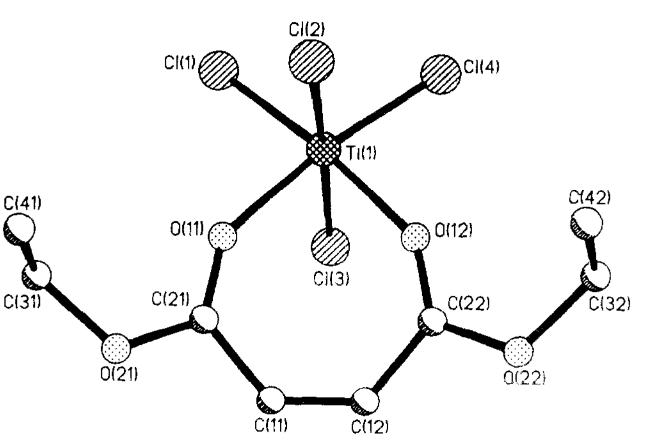

Fig. 4. The molecular structure and numbering scheme of [*cis*-$C_2H_2(CO_2CH_2CH_3)_2TiCl_4$] (**4**).

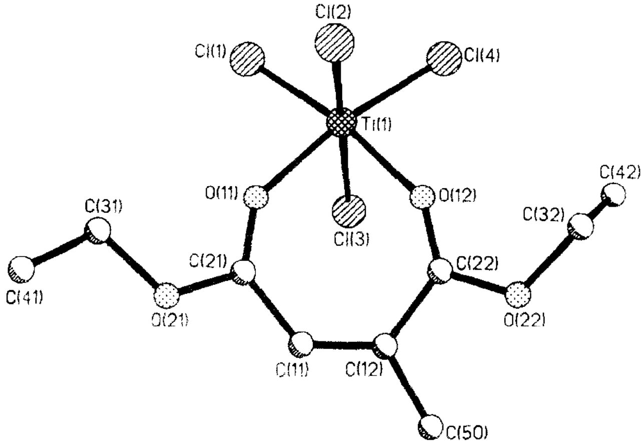

Fig. 5. The molecular structure and numbering scheme of [*cis*-$CHCCH_3(CO_2CH_2CH_3)_2TiCl_4$] (**5**).

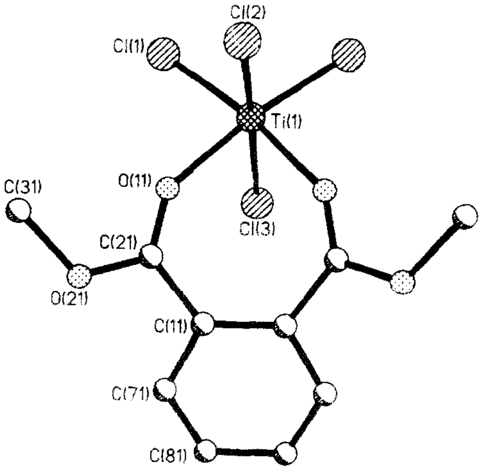

Fig. 6. The molecular structure and numbering scheme of [*o*-$C_6H_4(CO_2CH_3)_2TiCl_4$] (**6**).

TABLE 4. Activity and isotactic index for the donors in compounds **1**, **2**, **3**, **4**, **5** and **7** [a]

	1	**2**	**3**	**4**	**5**	**7**
Activity [b]	300	303	305	542	876	332
I.I. (%)	87.0	91.7	90.5	95.6	97.5	89.6

[a] $TiCl_4$(diethyl malonate) (**1**)
$TiCl_4$(diethyl isopropylidenamalonate) (**2**)
$TiCl_4$(diethyl diethylmalonate) (**3**)
$TiCl_4$(diethyl maleate) (**4**)
$TiCl_4$(diethyl citraconate) (**5**)
$TiCl_4$(dimethyl phthalate) (**6**)
$TiCl_4$(*cis*-1,2-di-isobutylcyclohexanoate) (**7a**)
$TiCl_4$(*cis*-1,2-di-isobutylcyclohexanoate) (molecule b) (**7b**)
$TiCl_4$(diethyl phthalate) [6a] (**8**)
$TiCl_4$(di-isobutyl phthalate) [6b] (**9**)
$TiCl_4(o\text{-}C_6H_4(CO_2CH_2CH_2Ph)_2$ (**10**)
[b] Activity, kg PP/g Ti.

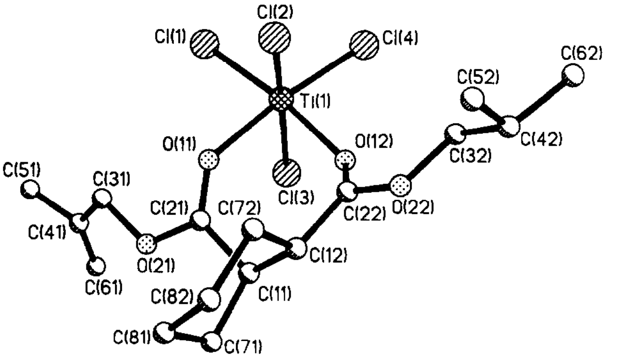

Fig. 7. The molecular structure and numbering scheme of [*cis*-1,2-$C_6H_{10}\{CO_2CH_2CH(CH_3)_2\}_2TiCl_4$] (7).

lengths, bond angles, torsion angles and non-bonding distances are listed in Tables 2–4.

In all the structures four chlorine atoms and two oxygen atoms of the ligand carbonyl groups form a distorted octahedron around the titanium atom. The molecule of diester is coordinated to the titanium atom via two carbonyl oxygen atoms. The chelate ligand and the titanium atom form a six-membered ring in compounds **1**–**3**. In compounds **4**–**7** the corresponding chelate ring is seven-membered. In compounds **1** and **2** titanium two chlorine atoms and one or two carbon atoms lie in the mirror plane. In structures **4** and **6** the mirror plane goes through a titanium and two chlorine atoms.

The crystal structures were determined in order to look for structural trends in chelating diesters that could be related to the catalytic activity of the compounds. The catalytic studies, which will be fully described later [10], show (Tables 4 and 12) that both activity and isotactic index decrease in the order **5** > **9** ≥ **8** > **4** > **6** > **2** > **7** ≥ **3** > **1**, when these donors are used in the preparation of $TiCl_4/MgCl_2$ supported catalysts.

General conclusions from the diester structures and catalytic investigations are as follows:
All the diesters increase the catalyst stereoselectivity and activity. In the absence of an internal donor the catalyst activity and stereoselectivity were 149 kg PP/g Ti and 77.7%, respectively.

A diester with a seven-membered chelate ring (**9**, **8**, **5** and **6**) is a better donor than the three with six-membered rings (**1**, **2** and **3**). Among the seven-membered chelates, the catalytic properties of diesters that have both carbonyl groups in *cis* position and attached to double bond or an aromatic ring are better than those of any of the other diesters. The only exception is the isotactic index for **7**. This suggests that the steric hindrance of a cyclohexyl ring weakens the coordinating ability of a diester and thus the blocking of aspecific sites on the $MgCl_2$ surface. A more appropriate stereochemistry of the isopropylidene group may also explain why the isotactic index of a catalyst with a diester in compound **2** is slightly better than that of **1** and **3**.

TABLE 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) for $TiCl_4$(diethyl malonate)

Atom	*x*	*y*	*z*	U_{eq} [a]
Ti(1)	996(1)	3347(1)	3483(1)	33(1)
Cl(1)	−840(1)	2747(1)	2101(1)	47(1)
Cl(2)	6(2)	2812(1)	5389(1)	60(1)
Cl(3)	2668(2)	3804(1)	1782(1)	55(1)
Cl(4)	−538(2)	4369(1)	3696(2)	68(1)
O(11)	2721(3)	2452(2)	3486(3)	37(1)
O(12)	2999(3)	3759(2)	4789(3)	42(1)
O(21)	5069(4)	1761(2)	3733(3)	46(1)
O(22)	5527(3)	3938(2)	5810(3)	44(1)
C(1)	5423(5)	3012(2)	4175(4)	40(1)
C(21)	4265(5)	2388(2)	3772(4)	36(1)
C(22)	4520(5)	3594(2)	4948(4)	36(1)
C(31)	4068(6)	1104(3)	3372(6)	61(2)
C(32)	4771(6)	4534(3)	6623(5)	54(2)
C(41)	3271(9)	787(3)	4592(6)	85(2)
C(42)	3943(8)	4228(3)	7841(6)	72(2)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

An increase in the alcohol carbon chain length in the phthalate diesters is accompanied by an increase in the catalyst activity (Table 12). This is possibly due to the low dielectric constant of longer alkyl chain phthalates and their inability to react with bulk $MgCl_2$.

In all the structures Ti–Cl(2) (av. 228.7 pm) and Ti–Cl(3) (av. 230.4 pm) distances are slightly longer than the distances Ti–Cl(1) (av. 223.0 pm) and Ti–Cl(4) (av. 223.3 pm) that are *trans* to the oxygen atoms. Compound **3** contains both the shortest Ti–Cl bond (221.8(4) pm) and the longest Ti–Cl bond (231.7(4) pm). An even shorter Ti–Cl bond is found in [*o*-$C_6H_4(CO_2CH_2CH_2Ph)_2Cl_4Ti$] (Table 2). However, the

TABLE 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) $TiCl_4$(dimethyl phthalate)

Atom	*x*	*y*	*z*	U_{eq} [a]
Ti(1)	4024(1)	2500	2569(2)	37(1)
Cl(1)	4402(1)	3933(1)	737(2)	74(1)
Cl(2)	5012(1)	2500	4504(3)	71(1)
Cl(3)	2901(1)	2500	1255(3)	70(1)
O(11)	3629(2)	3633(3)	4638(5)	52(1)
O(21)	3133(2)	4741(3)	6817(4)	50(1)
C(21)	3139(2)	3820(3)	5768(6)	39(1)
C(11)	2496(2)	3095(3)	6062(6)	38(1)
C(71)	1856(2)	3678(4)	6340(6)	46(1)
C(81)	1227(2)	3098(4)	6538(7)	54(2)
C(31)	3717(3)	5556(4)	6518(8)	57(2)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) for $TiCl_4$(1,2-di-isobutyl cyclohexanoate)

Atom	x	y	z	U_{eq} [a]
Ti(1)	1826(4)	6965(3)	3072(1)	58(2)
Cl(1)	2211(6)	6112(5)	3902(2)	100(3)
Cl(2)	2240(6)	5402(4)	2428(2)	80(2)
Cl(3)	876(6)	8471(4)	3531(2)	83(2)
Cl(4)	4097(6)	8115(4)	3135(2)	87(2)
O(11)	−400(15)	5991(10)	2904(5)	63(6)
O(12)	1130(13)	7573(10)	2269(5)	65(6)
O(21)	−2622(15)	5956(12)	3136(6)	101(7)
O(22)	766(14)	7203(10)	1262(5)	69(6)
C(11)	−2109(21)	6853(15)	2260(7)	61(9)
C(12)	−1341(20)	6643(13)	1712(6)	47(7)
C(21)	−1635(27)	6218(16)	2773(8)	67(10)
C(22)	308(22)	7148(15)	1782(9)	54(9)
C(31)	−2213(23)	5406(19)	3673(9)	105(12)
C(32)	2332(22)	7692(16)	1256(8)	80(10)
C(41)	−2829(65)	5772(41)	4138(14)	351(49)
C(42)	2605(22)	7454(20)	616(8)	81(10)
C(51)	−2709(47)	5118(27)	4638(11)	377(47)
C(52)	2282(28)	6191(22)	391(10)	156(16)
C(61)	−3367(34)	6697(36)	4287(13)	249(34)
C(62)	4206(21)	8016(19)	559(7)	105(12)
C(71)	−3835(24)	6489(17)	2044(8)	79(10)
C(72)	−1738(19)	5314(15)	1426(7)	65(9)
C(81)	−4326(19)	5166(17)	1749(7)	73(9)
C(82)	−3426(22)	4886(15)	1228(8)	76(9)
Ti(1a)	7968(4)	1111(3)	1938(1)	61(2)
Cl(1a)	5990(6)	−203(5)	2092(2)	100(3)
Cl(2a)	7400(6)	2731(4)	2487(2)	90(3)
Cl(3a)	9111(6)	−328(4)	1533(2)	91(3)
Cl(4a)	7071(6)	1519(5)	1041(2)	101(3)
O(11a)	9131(17)	912(12)	2749(6)	89(7)
O(12a)	9957(18)	2297(12)	1919(6)	86(7)
O(21a)	9639(19)	1558(16)	3729(7)	124(9)
O(22a)	12193(15)	2475(13)	1621(7)	108(8)
C(11a)	11343(28)	2607(25)	3189(10)	118(14)
C(12a)	12126(25)	2326(21)	2628(10)	109(13)
C(21a)	9917(34)	1530(28)	3175(10)	107(16)
C(22a)	11294(33)	2340(20)	2010(9)	87(12)
C(31a)	8340(38)	743(25)	3805(9)	131(17)
C(32a)	11544(26)	2544(20)	1025(9)	112(13)
C(41a)	7928(56)	1472(63)	4497(29)	350(57)
C(42a)	12505(28)	2246(22)	562(11)	109(13)
C(51a)	6685(37)	334(29)	4591(12)	228(26)
C(52a)	11984(27)	2500(22)	−17(10)	153(17)
C(61a)	8389(63)	996(53)	4609(18)	997(128)
C(62a)	12609(28)	983(23)	573(10)	144(16)
C(71a)	12497(31)	2898(17)	3732(9)	111(14)
C(72a)	12752(27)	1264(15)	2686(8)	95(12)
C(81a)	13203(28)	1847(26)	3816(10)	145(16)
C(82a)	13866(26)	1478(22)	3246(11)	126(14)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for $TiCl_4O_4C_{11}H_{20}$

Atom	x	y	z	U_{eq} [a]
Ti(1)	−46(2)	538(1)	3853(1)	52(1)
Cl(3)	−1555(3)	−266(2)	3321(1)	64(1)
Cl(4)	−550(4)	1647(2)	3393(1)	77(1)
Cl(2)	1838(4)	1125(2)	4350(1)	81(1)
Cl(1)	−1877(4)	643(2)	4454(1)	81(1)
O(11)	708(9)	−564(5)	4149(3)	59(3)
O(12)	1846(8)	261(4)	3357(3)	52(3)
O(21)	1302(9)	−1856(5)	4140(3)	78(4)
O(22)	4229(8)	−94(4)	3122(3)	58(3)
C(11)	2887(12)	−1052(7)	3618(5)	53(4)
C(21)	1492(14)	−1118(8)	3984(4)	55(5)
C(22)	2904(13)	−223(7)	3359(4)	45(4)
C(31)	77(18)	−2017(10)	4513(6)	113(8)
C(32)	4462(14)	672(7)	2855(5)	75(5)
C(41)	−1202(22)	−2245(12)	4318(8)	219(14)
C(42)	5019(16)	1288(7)	3213(5)	99(6)
C(51)	4383(15)	−1228(8)	3930(5)	84(6)
C(52)	2837(14)	−1693(7)	3173(5)	73(5)
C(61)	4613(14)	−687(8)	4370(6)	100(7)
C(62)	1498(18)	−1614(7)	2799(5)	101(7)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Ti–Cl distances do not show trends that can be related to catalytic behaviour.

The Ti–O(11) and Ti–O(12) distances vary somewhat, but are close to those found in previously characterised $TiCl_4$ · diester complexes. In the compounds with a six-membered chelate ring the bonds are slightly longer (av. 211.2 pm) than those in the compounds with seven-membered rings (av. 208.5 pm). Also compound **3** has shorter Ti–O bonds (av. 210.6 pm) than **1** (av. 212.3 pm), which is less active, but no such trend can be seen for the seven-membered chelate compounds. In fact of the phthalates **9** and **8** the more

TABLE 9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for $TiCl_4 \cdot C_8O_4H_{12}$

Atom	x	y	z	U_{eq} [a]
Ti(1)	1400(1)	3339(1)	3413(1)	35(1)
Cl(1)	−360(2)	2735(1)	1981(1)	52(1)
Cl(2)	429(2)	2815(1)	5273(2)	59(1)
Cl(3)	2900(2)	3789(1)	1754(2)	60(1)
Cl(4)	−65(2)	4350(1)	3572(2)	63(1)
O(11)	3049(4)	2477(2)	3501(4)	46(1)
O(12)	3222(4)	3769(2)	4807(4)	48(1)
O(22)	5301(5)	4246(2)	6080(4)	54(1)
O(21)	4985(5)	1645(2)	3526(4)	59(1)
C(11)	5931(7)	2793(4)	3874(7)	54(2)
C(12)	6013(7)	3420(4)	4482(7)	52(2)
C(21)	4513(7)	2306(3)	3621(5)	46(2)
C(22)	4707(7)	3810(3)	5131(6)	44(2)
C(31)	3730(10)	1078(4)	3279(9)	83(3)
C(32)	4140(9)	4661(4)	6820(7)	64(2)
C(41)	3179(15)	801(5)	4530(11)	131(5)
C(42)	3488(11)	4221(5)	7875(9)	91(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE 10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) for $TiCl_4$(citraconic acid, diethylester)

Atom	x	y	z	U_{eq} [a]
Ti(1)	3390(3)	555(2)	7275(2)	51(1)
Cl(1)	4310(4)	-1061(3)	6898(2)	76(2)
Cl(2)	5094(5)	901(3)	8539(3)	80(2)
Cl(3)	1703(4)	583(3)	5919(2)	68(1)
Cl(4)	1870(5)	-97(3)	8159(3)	86(2)
O(11)	4647(10)	1443(7)	6510(6)	61(4)
O(12)	2730(9)	2182(7)	7503(5)	54(4)
O(21)	5811(11)	2490(8)	5650(5)	73(4)
O(22)	1708(10)	3820(8)	7559(6)	72(4)
C(11)	3585(14)	3139(10)	5717(8)	48(5)
C(12)	2566(14)	3487(9)	6174(8)	45(5)
C(21)	4671(15)	2283(11)	6005(9)	51(5)
C(22)	2351(14)	3065(12)	7121(8)	49(5)
C(31)	6978(19)	1715(15)	5835(15)	124(10)
C(32)	1497(21)	3575(15)	8502(10)	101(9)
C(41)	8065(21)	2154(17)	5470(15)	165(14)
C(42)	305(21)	2823(15)	8538(12)	129(11)
C(50)	1575(15)	4390(12)	5768(9)	73(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 11. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) for $TiCl_4$(diethyl isopropylidenemalonate)

Atom	x	y	z	U_{eq} [a]
Ti(1)	699(1)	1222(1)	8488(1)	36(1)
Cl(1)	2057(1)	475(1)	9538(1)	53(1)
Cl(2)	1722(1)	-120(1)	7697(1)	48(1)
Cl(3)	-697(1)	2485(2)	9126(1)	55(1)
Cl(4)	1870(1)	3100(1)	8260(1)	56(1)
O(11)	-600(3)	-448(3)	8575(2)	40(1)
O(12)	-824(3)	1472(3)	7514(2)	40(1)
O(21)	-2495(3)	-1659(3)	8592(2)	46(1)
O(22)	-2857(3)	1331(3)	6761(2)	44(1)
C(1)	-2743(5)	521(5)	8003(3)	39(2)
C(10)	-3945(5)	960(6)	8166(3)	50(2)
C(11)	-4625(5)	359(7)	8774(3)	60(2)
C(12)	-4696(6)	2189(7)	7794(4)	76(3)
C(21)	-1866(5)	-566(5)	8423(3)	41(2)
C(22)	-2060(5)	1171(5)	7417(3)	49(2)
C(31)	-1631(5)	-2782(5)	8972(3)	50(2)
C(32)	-2230(5)	1789(6)	6114(3)	49(2)
C(41)	-2549(7)	-3797(6)	9242(4)	81(3)
C(42)	-3369(6)	1863(7)	5452(3)	68(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 12. Activity and isotactic index for phthalate diesters, (o-$C_6H_4(CO_2R)_2$) (where R = methyl (**6**), ethyl (**8**), isobutyl (**9**) and isodecyl)

	$R = CH_3$	C_2H_5	$^iC_4H_9$	$^iC_{10}H_{21}$
Activity, kg PP/g Ti	367	420	523	750
I.I. (%)	97.3	97.9	96.1	95.6

active **9** has the longer Ti–O bonds. The average O(11)–C(21) and O(12)–C(22) bond lengths are 122.5 and 122.5 pm, respectively.

The plane formed by atoms O(11), O(12), C(21) and C(22) is inclined towards the plane C(21), C(1), C(22) in compounds **1** and **2** and towards the plane C(11), C(12), C(21), C(22) in compounds **4**, **5** and **6**. In molecule **6** the benzene ring is almost planar.

Ti–O–C bond angles are significantly lower in compounds **1–3** (Ti–O(11)–C(21) av. 133.3° and Ti–O(12)–C(22) av. 132.3°), which have six-membered chelate rings, than in compounds **4–7** (Ti–O(11)–C(21) av. 141.5° and Ti–O(12)–C(22) av. 142.2°), in which the rings are seven-membered. Interestingly, the wide Ti–O–C bond angle seems to correlate well with the catalyst performance. This suggests that a wider metal–O–C bond angle improves the coordination of a diester on the surface of the $MgCl_2$ support.

The average O(11)–Ti–O(12) angles are also slightly narrower in compounds **1–3**, but there is overlap in the primary data. There are differences in the non-bonded O(11)–O(12) distances (from 2.65 to 2.72 Å), but no correlation can be seen with the chelate ring size or catalyst performance.

It has been shown by Chien *et al.* [5d] that *only ortho*-phthalates work well when the catalyst is prepared using *ortho*-, *meta*- or *para*-phthalates as internal donors. This, considered along with the structural and preliminary propylene polymerization data presented in this paper, suggest that, besides a suitable stereochemistry, a good diester donor must also have the appropriate distance between the metal and chelating carbonyl oxygen atoms to be able to interact effectively with the catalyst/support surface.

According to the modelling studies of $MgCl_2$ surface, mentioned above, bidentate diesters are able to poison selectively only the *single* four-coordinate Mg atoms on the $MgCl_2$ (110) surface [10b]. This prevents the formation of aspecific catalyst sites with $TiCl_4$ and four-coordinate Mg atoms [5e]. *Meta*- and *para*-phthalate diesters fail to work well as internal donors because the distance of carbonyl oxygen atoms is > 5 Å. Compounds with this distance are not able to form a chelate with Mg atoms on the $MgCl_2$ (110) surface.

4. Conclusions

The common feature in the structure of complexes **4–6**, which form a seven-membered chelate ring, is a *cis*-OCC=CCO substructure in the donor molecule. According to the experimental data (Tables 4 and 12) the compounds with this substructure are more active in catalysis. Compared to malonates the activity is in some cases about two times higher. The isotacticity of the product in polypropene synthesis is also higher. In the case of a single group of these internal donors, *e.g.* phthalate diesters, the performance of a stereospecific catalyst is highly dependent on the amount of donor used in the catalyst preparation [10]. The poisoning of surface sites on a catalyst support is also related to the alcohol carbon chain length and branching in the diester. Thus, in addition to the stereochemistry, the dielectric constant of a diester is of equal importance for the formation of a high yield $TiCl_4/MgCl_2$ supported catalyst. Chadwick *et al.* [13] have noticed that use of a too high or too low titanation temperature in the catalyst preparation step can also markedly decrease the catalyst activity.

It should be noted that although certain structure parameters correlate with catalytic behaviour, these correlations are not valid if the chelate ring size and/or the alcohol carbon chain length or branching is changed [10b]. However, for seven-membered chelates the high C=O–Ti angles seem to be associated with good activity and isotacticity, in contrast to the six-membered chelates which have lower C=O–Ti angles.

Furthermore, it has been suggested by IR studies [11a] and solid state ^{13}C CP MAS NMR spectroscopy [11b], that the carbonyl groups in the internal donor form a complex with the coordinatively unsaturated Mg surface atoms and *not* with the surface Ti atoms. This, together with the experimental data presented in this paper, suggest that the selective poisoning of four-coordinate Mg atoms by a bidentate ligand (*e.g.* diester) on the $MgCl_2$ (110) surface is the main effect in the chemistry of donors in $TiCl_4/MgCl_2$ supported stereospecific catalysts. According to preliminary polymerization results [10] in stereoselective propylene polymerization, a diester with *cis*-OCC=CCO substructure seems to be the best choice when a diester type of internal donor is used for the catalyst preparation.

A deeper understanding of the conformation of coordinated diester molecules will assist in the modelling of $TiCl_4/MgCl_2$ surface and diester interactions.

We should note that since the above was written, it has been claimed in two recent patent applications [12] that organic bidentate ligands having a *cis*-OCC=CCO substructure are very effective promoters for a polypropylene catalyst even when the compound is not a diester.

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