The synthesis of olefin polymerization precatalysts: $[TiCl_4(C_4H_7OCH_2CO_2CH_3)]$ and $[(C_4H_7OCH_2CO_2Et)_2Mg(\mu\text{-}Cl)_2TiCl_4] \cdot 2CH_2Cl_2$. Crystal structures and properties

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Abstract

Direct reactions of $TiCl_4$ or of a 1:1 mixture of $TiCl_4$ and $MgCl_2$ with chiral tetrahydrofurfuryl $C_4H_7OCH_2CO_2CH_3$ and $C_4H_7OCH_2CO_2Et$ esters, respectively, gave $[TiCl_4(C_4H_7OCH_2CO_2CH_3)]$ (1) and $[(C_4H_7OCH_2CO_2Et)_2Mg(\mu\text{-}Cl)_2TiCl_4] \cdot 2CH_2Cl_2$ (2) which are good precatalysts for ethylene polymerization. The crystal structures of 1 and 2 have been solved by X-ray methods. In 1 the titanium atom is octahedrally coordinated by four chlorine atoms and two oxygen atoms of the chelate tetrahydrofurfuryl acetate ligand. In the heterobimetallic complex 2, formed by slightly distorted edge-sharing octahedra, the titanium and magnesium atoms are separated by Ti ··· Mg of 3.725(16) Å and linked through two bridging Cl atoms.

Key words: Titanium; Magnesium; Polymerization

1. Introduction

The addition of Lewis bases such as ethers or aromatic esters to Ziegler-Natta catalytic systems results in higher efficiency of polyethylene or high isotacticity of polypropylene, respectively. It follows that titanium complexes with ether-esters ligand ought to be universal precatalysts for both ethylene and propylene polymerization. In our investigations we have used the chiral tetrahydrofurfuryl esters, which include the thf residues besides the ester group. Hence, the interaction between ester molecules and $TiCl_4$ or $MgCl_2$ and the mechanism of titanium-magnesium molecular complex formation was the subject of our studies. The crystal structures and catalytic properties of $[TiCl_4(C_4H_7OCH_2CO_2CH_3)]$ (1) and $[(C_4H_7OCH_2CO_2Et)_2Mg(\mu\text{-}Cl)_2TiCl_4] \cdot 2CH_2Cl_2$ (2) have been investigated.

2. Experimental section

All reactions were carried out under dinitrogen in dried solvents by Schlenk-tube techniques. Anhydrous $TiCl_4$ was obtained commercially. The $[MgCl_2(thf)_2]$ complex was obtained by literature methods [1]. The tetrahydrofurfuryl acetate and propionate were made in our laboratory by a standard procedure [2] *viz.* reactions of tetrahydrofurfuryl alcohol with acetic or propionic acid, respectively, in presence of *p*-toluenesulfonic acid. IR spectra were recorded on a Perkin-Elmer 180 Spectrometer.

2.1. *Tetrachloro(tetrahydrofurfuryl acetate)titanium(IV) 1*

To 1.5 ml of $TiCl_4$ (2.56 g, 13.5 mmol) in 50 ml, 1.85 ml of tetrahydrofurfuryl acetate (1.95 g, 13.5 mmol) was added dropwise. The mixture was stirred under N_2. The solution was filtered off and the volume was reduced *in vacuo* to 20 ml and left at 276 K for crystallization. After 48 h, the yellow crystals were filtered off and washed with n-hexane (2 × 5 ml). Yield: 4 g, 88.9%. Anal. Found: Cl, 42.1; Ti, 14.0. Calc. for $C_7H_{12}Cl_4O_3Ti$: Cl, 42.4; Ti, 14.3%. Good quality crystals, suitable for X-ray examination were taken directly from the post-reaction mixture.

2.2. *Di-μ-chlorobis(tetrahydrofurfuryl propionate)magnesium(II)tetrachlorotitanium(IV)dichloromethane (1/2) (2)*

To a suspension of 1.68 g of $[MgCl_2(thf)_2]$ (7.2 mmol) in a mixture of 50 ml CH_2Cl_2 and 30 ml of

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TABLE 1. Principal interatomic distances (Å), bond angles (°) and torsion angles for complex **1**

Ti–Cl(1)	2.308(1)	Ti(2)–Cl(3)	2.231(1)
Ti–Cl(2)	2.258(1)	Ti(2)–Cl(4)	2.227(2)
Ti–O(1)	2.143(2)	Ti(2)–O(2)	2.033(3)
O(1)–C(1)	1.456(6)	O(2)–C(6)	1.226(5)
O(1)–C(4)	1.462(5)	C(6)–C(7)	1.473(6)
C(1)–C(2)	1.415(7)	O(3)–C(6)	1.288(5)
C(2)–C(3)	1.452(8)	O(3)–C(5)	1.457(5)
C(3)–C(4)	1.524(6)	C(4)–C(5)	1.496(6)
Cl(1)–Ti–Cl(2)	168.20(5)	Cl(3)–Ti–O(2)	91.63(9)
Cl(1)–Ti–Cl(3)	92.99(5)	Cl(4)–Ti–O(1)	90.21(9)
Cl(1)–Ti–Cl(4)	93.37(6)	Cl(4)–Ti–O(2)	172.20(9)
Cl(1)–Ti–O(1)	84.81(8)	O(1)–Ti–O(2)	82.14(10)
Cl(1)–Ti–O(2)	84.51(8)	Ti–O(1)–C(1)	122.8(3)
Cl(2)–Ti–Cl(3)	94.69(5)	Ti–O(1)–C(4)	127.3(3)
Cl(2)–Ti–Cl(4)	94.73(6)	O(2)–C(6)–O(3)	121.7(4)
Cl(2)–Ti–O(1)	86.59(8)	O(3)–C(5)–C(4)	113.8(4)
Cl(2)–Ti–O(2)	86.33(8)	O(2)–C(6)–C(7)	122.6(4)
Cl(3)–Ti–Cl(4)	95.98(7)	C(5)–O(3)–C(6)	118.1(4)
Cl(3)–Ti–O(1)	173.55(9)		
Ti–O(2)–C(6)–C(7)	−102.6(6)	O(2)–C(6)–O(3)–C(5)	2.9(6)
Ti–O(2)–C(6)–O(3)	78.7(6)	C(6)–O(3)–C(5)–C(4)	−74.9(5)

1,2-$C_2H_4Cl_2$, 0.8 ml of $TiCl_4$ (1.33 g, 7.0 mmol) was added. Then 2.1 ml of tetrahydrofurfuryl propionate (2.22 g, 13.9 mmol) was added dropwise to the suspension. The post-reaction mixture was stirred under N_2 up to complete dissolution of the solid. The volume of the solution was reduced *in vacuo* to 40 ml and left at 276 K for crystallization. After a week the yellow crystals were filtered off and washed with n-hexane (3 × 5 ml). Yield: 3.8 g, 90.4%. Anal. Found: Cl, 45.0; Ti, 6.4; Mg, 3.3. Calc. for $C_{16}H_{28}Cl_6O_6TiMg \cdot 2CH_2Cl_2$: Cl, 46.0; Ti, 6.2; Mg, 3.2%. The crystals were always twinned. Crystals for X-ray examination were cut along the plane of twinning and mounted in a glass capillary.

3. Results and discussion

3.1. Synthesis and Structure of $[TiCl_4(C_4H_7OCH_2CO_2CH_3)]$ (1)

The addition of tetrahydrofurfuryl acetate to $TiCl_4$ in CH_2Cl_2 gave a yellow air – sensitive compound

TABLE 2. Final atomic parameters with esd's in parentheses for complex **1**

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.12901(9)	0.12032(3)	0.30236(8)	0.0323(4)	0.0401(4)	0.0349(3)	0.0015(3)	0.0088(3)	−0.0002(3)
C11	0.10796(16)	0.21868(4)	0.37898(14)	0.0639(7)	0.0383(6)	0.0681(7)	0.0020(5)	0.0245(6)	0.0074(5)
C12	0.21115(18)	0.02519(5)	0.26588(15)	0.0712(8)	0.0487(7)	0.0767(8)	−0.0137(6)	0.0293(6)	0.0059(6)
C13	0.01459(18)	0.14107(6)	0.02562(13)	0.0597(8)	0.1079(11)	0.0384(6)	0.0129(6)	−0.0004(5)	−0.0088(7)
C14	−0.15062(15)	0.09546(5)	0.32669(15)	0.0404(6)	0.0564(7)	0.0851(8)	0.0069(6)	0.0269(6)	−0.0012(5)
O1	0.2672(4)	0.10570(11)	0.5689(3)	0.0491(17)	0.0444(17)	0.0341(14)	0.0058(11)	0.0106(12)	−0.0067(13)
O2	0.3980(4)	0.14310(12)	0.3153(3)	0.0325(16)	0.0615(19)	0.0390(14)	−0.0026(13)	0.0117(12)	−0.0068(14)
O3	0.6232(4)	0.18365(13)	0.5298(3)	0.0490(18)	0.0705(21)	0.0403(15)	−0.0080(14)	0.0123(13)	−0.0167(16)
C1	0.2076(8)	0.0592(2)	0.6624(6)	0.1152(48)	0.0876(40)	0.0586(31)	0.0351(27)	0.0053(31)	−0.0452(36)
C2	0.3454(9)	0.0573(2)	0.8272(6)	0.1141(48)	0.0823(40)	0.0488(29)	0.0193(26)	0.0262(30)	0.0033(36)
C3	0.4462(8)	0.1141(3)	0.8586(5)	0.0862(41)	0.1239(50)	0.0339(25)	0.0080(27)	0.0125(25)	−0.0220(36)
C4	0.4232(6)	0.1406(2)	0.6849(4)	0.0476(25)	0.0568(27)	0.0290(19)	−0.0048(18)	0.0072(17)	−0.0051(20)
C5	0.6009(6)	0.1357(2)	0.6399(5)	0.0406(24)	0.0708(32)	0.0361(22)	0.0068(20)	0.0013(18)	0.0026(22)
C6	0.5188(5)	0.1821(2)	0.3719(5)	0.0357(23)	0.0497(25)	0.0461(22)	−0.0036(19)	0.0199(18)	0.0060(19)
C7	0.5569(6)	0.2293(2)	0.2645(5)	0.0669(31)	0.0561(30)	0.0638(29)	0.0077(22)	0.0356(25)	−0.0063(24)
Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H1	0.1955(8)	0.0164(2)	0.5991(6)	0.15	H4	0.3828(6)	0.1872(2)	0.6819(4)	0.08
H11	0.0707(8)	0.0704(2)	0.6727(6)	0.15	H5	0.7237(6)	0.1349(2)	0.7546(5)	0.10
H2	0.4442(9)	0.0213(2)	0.8318(6)	0.15	H51	0.5954(6)	0.0934(2)	0.5756(5)	0.10
H21	0.2799(9)	0.0489(2)	0.9222(6)	0.15	H7	0.4627(6)	0.2240(2)	0.1351(5)	0.10
H3	0.5958(8)	0.1071(3)	0.9282(5)	0.15	H71	0.5334(6)	0.2727(2)	0.3114(5)	0.10
H31	0.3875(8)	0.1430(3)	0.9321(5)	0.15	H72	0.7033(6)	0.2261(2)	0.2687(5)	0.10

The anisotropic temperature factors are expressed as $\exp[-2\Pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)]$.

formulated as [$TiCl_4(C_4H_7OCH_2CO_2CH_3)$] (**1**).

$$TiCl_4 + C_4H_7OCH_2CO_2CH_3 \xrightarrow{CH_2Cl_2} [TiCl_4(C_4H_7OCH_2CO_2CH_3)] \qquad (1)$$

The IR spectrum shows a band at 1606s [ν(C=O)] and a band at 370vs cm^{-1} due to ν(Ti–Cl). The complex **1** is soluble in halogenated hydrocarbons and insoluble in hydrocarbons. The structure of the [$TiCl_4(C_4H_7OCH_2CO_2CH_3)$] molecule is shown in Fig. 1. Selected bond lengths, bond angles and torsion angles are listed in Table 1. In the molecule of **1** four Cl atoms and two O atoms of the ligand form the distorted octahedron around the titanium atom. The molecule of the tetrahydrofurfuryl acetate is coordinated to the titanium atom via the carbonyl oxygen atom and the oxygen atom of the thf ring. The chelate ligand and the titanium atom form the seven-membered ring. The Ti–Cl and Ti–O distances (see Table 2) are similar to the Ti–Cl and Ti–O distances observed in [$TiCl_4\{o\text{-}C_6H_4(CO_2R)_2\}$] [3,4]. The Ti–O(2)–C(6)–C(7) torsion angle is −102.(6)°. That value indicates that the Ti atom remains out of the O(2), C(6), O(3), C(7) plane. The carbonyl group O(2)–C(6) is almost synperiplanar to the O(3)–C(5) bond. The five-membered ring of the ester molecule has an envelope conformation [5,6]. The chiral carbon atom C(4) is located above the plane through the O(1), C(5), C(3) atoms. In this complex, intramolecular contacts are observed. The chlorine atom Cl(1) is 3.184(4) Å from the C(6) atom. This distance is much shorter than similar distances of 3.232(7) and 3.299(4) Å found previously in [$TiCl_4\{o\text{-}C_6H_4(CO_2R)_2\}$] complexes [7,8].

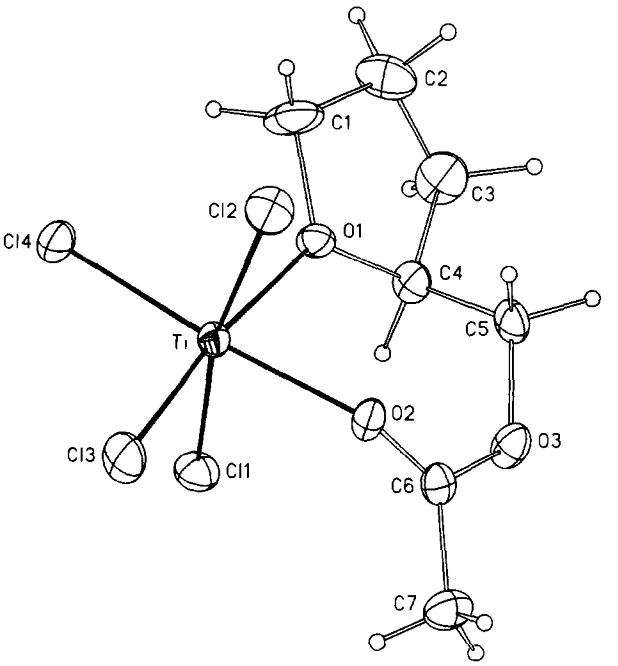

Fig. 1. Structure and the numbering scheme of the [$TiCl_4(C_4H_7OCH_2CO_2CH_3)$] molecule.

3.2. Synthesis and structure of [$(C_4H_7OCH_2CO_2Et)_2Mg(\mu\text{-}Cl)_2TiCl_4$] · $2CH_2Cl_2$ (2)

Our efforts to prepare the titanium-magnesium compound have been successful. The compound [$(C_4H_7OCH_2CO_2Et)_2Mg(\mu\text{-}Cl)_2TiCl_4$] · $2CH_2Cl_2$ (**2**) was obtained in the direct reaction between $TiCl_4$, [$MgCl_2(thf)_2$] and tetrahydrofurfuryl propionate at the molar ratio of 1 : 1 : 2.

$$[MgCl_2(thf)_2] + TiCl_4 + 2[C_4H_7OCH_2CO_2Et] \longrightarrow [(C_4H_7OCH_2CO_2Et)_2Mg(\mu\text{-}Cl)_2TiCl_4] \cdot 2CH_2Cl_2 + 2thf \qquad (2)$$

The IR spectrum has a band at 1678s, br cm^{-1} [ν(C=O)], bands at 1030s and 980s cm^{-1} due to ν(COC) and a band at 380vs cm^{-1} due to ν(Ti–Cl). The structure of di-μ-chlorobis(tetrahydrofurfuryl propionate) magnesium(II)tetrachlorotitanium(IV) is depicted in Fig. 2. Selected bond lengths and bond angles are listed in Table 3. In the [$(C_4H_7OCH_2CO_2Et)_2Mg(\mu\text{-}Cl)_2TiCl_4$] complex the titanium atom is located 3.724(2) Å from the magnesium atom. These two atoms are bridged by two Cl atoms. The two bridging and four terminal Cl atoms form the distorted octahedron around the Ti atom. The terminal Ti–Cl(2) and Ti–Cl(3) bond lengths of 2.292(2) and 2.250(2) Å are shorter than the bridging Ti–Cl(1) distances of 2.463(2) Å. The Ti–Cl distances and Ti–Cl–Mg bond angles are similar to those observed in the [$(CH_3CO_2Et)_4Mg(\mu\text{-}Cl)_2TiCl_4$] complex [9]. The magnesium atom in **2** is octahedrally coordinated by two bridging Cl atoms and four oxygen atoms. The carbonyl and etheral oxygens of the two tetrahydrofurfuryl propionate molecules act as donor atoms towards magnesium. Thus the Mg atom and the two chelate ligands form a seven-membered ring.

The Mg–Cl bridge distance is 2.488(2) Å, which is similar to the corresponding value in [$(CH_3CO_2Et)_4Mg(\mu\text{-}Cl)_2TiCl_4$] and to the Mg–Cl distance of 2.502(4) Å in [$Mg_2(\mu\text{-}Cl)_3(thf)_6$]$^+$ cation [10]. The magnesium atom is located 2.057(3) Å from the carbonyl oxygen O(1). The Mg–O(2) distance of 2.063(2) Å is similar to the Mg–O distances in the [$Mg_2(\mu\text{-}Cl)_3(thf)_6$]$^+$ cation. The Mg–O(1)–C(6) bond angle is 141.8(4)°. It is almost the same as the value of Ti–O(2)–C(6) bond angle [141.11(25) Å] in complex **1**. The Mg–O(1)–C(6)–C(7)

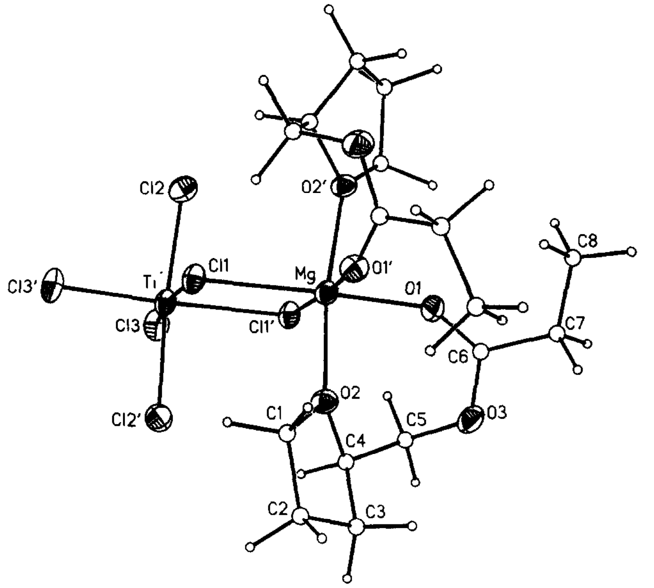

Fig. 2. Structure and the numbering scheme of the $[(C_4H_7OCH_2CO_2Et)_2Mg(\mu\text{-}Cl)_2TiCl_4]$ molecule.

torsion angle is −138.4(6)°. The O(1)–C(6)–O(3)–C(5) torsion angle of 11(5)° is much higher than the corresponding torsion angle of 2.9(6)° in $[TiCl_4(C_4H_7OCH_2\text{-}CO_2CH_3)]$. The five-membered ring of the coordinated to magnesium atom $C_4H_7OCH_2(CO_2Et)$ molecule has the twist conformation with the C(2) and C(3) atoms moved above and below the plane of the ring.

3.3. *Crystallography*

Crystal data for **1**. Yellow crystals, $C_7H_{12}Cl_4O_3Ti$, M = 333.884, monoclinic, space group $P2_1/n$, a = 7.441(3), b = 22.325(6), c = 8.365(3) Å, β = 109.64(3)°, Z = 4, U = 1309(1) Å^3, D_c = 1.694(1) g cm^{-1}, D_m = 1.685 g cm^{-1}, $F(000)$ = 672, T = 300(1) K, μ = 1.44 mm^{-1}.

Crystal data for **2**. Yellow crystals, $C_{16}H_{28}Cl_6O_6MgTi \cdot 2CH_2Cl_2$, M = 771.194, monoclinic, space group $C2/c$, a = 13.510(5), b = 16.003(4), c = 15.907(8) Å and β = 106.33(4)°, Z = 4, U = 3300(3), D_c = 1.552 g cm^{-1}, D_m = 1.489 g cm^{-1}, $F(000)$ = 1568, T = 300(1) K, μ = 1.11 mm^{-1}.

Data collection and processing. Preliminary data were recorded by photographic methods. Intensities were collected using a Kuma KM4 four-circle diffractometer in the ω-2Θ mode (with crystals of dimensions 0.3 × 0.3 × 0.4 for **1** and 0.4 × 0.4 × 0.3 mm for **2**) and Mo Kα radiation. The crystals were cut and sealed in glass capillaries. For both crystals the intensities of three standard reflections, monitored every 100 intensity scans, showed no evidence of crystal decay. 2782 (4° < 2θ < 56°) and 4359 (4° < 2θ < 56°) reflections were measured for **1** and **2**, respectively, from which 1697 and 2258 with $I > 3.0\sigma(I)$ were used for calculations. The structures were solved by the Patterson method and refined by full matrix least-squeres calculations using SHELX76 [11]. Neutral atom scattering factors were from ref. 12; real and imaginary components of anomalous dispersion were included for all non-H

TABLE 3. Principal interatomic distances (Å), bond angles (°) and torsion angles for complex **2**

Ti–Mg	3.724(2)	Mg–Cl(1)	2.488(2)
Ti–Cl(1)	2.463(2)	Mg–O(1)	2.057(3)
Ti–Cl(2)	2.292(2)	Mg–O(2)	2.063(2)
Ti–Cl(3)	2.250(2)	O(1)–C(6)	1.211(6)
O(2)–C(1)	1.436(5)	O(3)–C(5)	1.435(6)
O(2)–C(4)	1.453(4)	O(3)–C(6)	1.304(5)
C(1)–C(2)	1.464(7)	C(4)–C(5)	1.489(7)
C(2)–C(3)	1.503(8)	C(6)–C(7)	1.483(7)
C(3)–C(4)	1.484(7)	C(7)–C(8)	1.477(8)
Cl(1)–Ti–Cl(1′)	82.95(6)	Mg–O(2)–C(1)	123.0(3)
Cl(1)–Ti–Cl(2)	88.21(6)	Mg–O(2)–C(4)	127.5(3)
Cl(1)–Ti–Cl(3)	172.39(7)	Mg–O(1)–C(6)	141.8(4)
Cl(2)–Ti–Cl(3)	92.49(6)	O(2)–C(4)–C(5)	111.8(4)
Cl(1)–Mg–Cl(1′)	81.93(6)	O(3)–C(6)–O(1)	123.5(5)
Cl(1)–Mg–O(1)	176.17(10)	O(3)–C(6)–C(7)	112.7(4)
Cl(1)–Mg–O(2)	92.96(9)	C(3)–C(4)–C(5)	117.8(4)
O(1)–Mg–O(1′)	88.95(12)	C(4)–C(5)–O(3)	115.7(4)
O(1)–Mg–O(2)	85.70(12)	C(5)–O(3)–C(6)	118.1(4)
O(2)–Mg–Cl(1)	92.96(9)	C(6)–C(7)–C(8)	116.1(5)
O(2)–Mg–O(2′)	170.39(11)		
Mg–O(1)–C(6)–O(3)	42.4(6)	C(6)–O(3)–C(5)–C(4)	−90.1(5)
Mg–O(1)–C(6)–C(7)	−138.4(6)	O(3)–C(5)–C(4)–O(2)	60.1(5)
O(1)–C(6)–C(7)–C(8)	6.8(6)	O(3)–C(5)–C(4)–C(3)	−59.7(5)

[a] Primed atoms are related to unprimed by: $-x$, y, $0.5-z$.

atoms. The hydrogen atoms were put in calculated positions with d(C–H) = 1.08 Å and introduced as fixed contributors in the final stage of refinement. A weighting scheme of the form $w = 1/\sigma^2(F_O)$ was applied for both structures. Final R and R_w values are 0.034 and 0.030 for **1** and 0.044 and 0.035 for complex **2**. The R_{int} values are 0.019 and 0.020 for compounds **1** and **2**, respectively. For the last cycle of the refinement the maximum value of the ratio Δ/σ was 0.033 for **1** and 0.075 for **2**. The final difference map showed a general background within −0.30 and 0.27 and −0.33 and 0.38 for **1** and **2**, respectively. The highest peaks on the difference-Fourier map in the proximity of C(9), Cl(4) and Cl(5) atoms suggested a small disorder of the dichloromethane molecule and marked as C(9′), Cl(4′) and Cl(5′) atoms. They were refined isotropically with constraints d[C(9′)–Cl(4′)] = 1.75, d[C(9′)–Cl(5′)] = 1.75 and d[Cl(4′)–Cl(5′)] = 2.90 Å. The final refined occupation factor for the dichloromethane molecule was 0.24. No hydrogen atom was put for the C9′ atom. Final atomic coordinates, selected bond lengths, bond angles and torsion angles are in Tables 1–4. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

3.4. Polymerization studies

The results of ethylene polymerization tests on $[TiCl_4(C_4H_7OCH_2CO_2CH_3)]$ are shown in Table 5. The catalyst was prepared by milling a hexane slurry of $[MgCl_2(thf)_2]$ and the investigated compound. Triethylaluminium was the cocatalyst. The catalytic activity of the compound **1** (73.3 kg polyethylene per g Ti h^{-1}) is lower than that of the $[Ti_2(\mu\text{-}Cl)_2Cl_4\{o\text{-}C_6H_4(CO_2\text{-}Et)_2\}_2]$ dimeric species (126.7 kg polyethylene per g Ti h^{-1}) [13]. Instead, only 21.1 and 11.6 kg polyethylene per g Ti h^{-1} were obtained under the same conditions

TABLE 4. Final atomic parameters with esd's in parentheses for complex **2**

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.00	0.14210(6)	0.25	0.0612(7)	0.0432(5)	0.0525(6)	0.00	0.0314(5)	0.00
Mg	0.00	−0.09065(10)	0.25	0.0519(11)	0.0460(10)	0.0412(10)	0.00	0.0197(9)	0.00
C11	−0.08503(8)	0.02681(6)	0.30532(6)	0.0630(6)	0.0470(5)	0.0586(6)	−0.0012(5)	0.0368(5)	−0.0017(5)
C12	0.013232(9)	0.13376(7)	0.37678(7)	0.0726(8)	0.0784(7)	0.0600(6)	−0.0052(6)	0.0234(6)	−0.0107(7)
C13	0.08602(10)	0.23426(7)	0.19004(8)	0.0909(9)	0.0553(6)	0.0889(8)	0.0100(6)	0.0545(8)	−0.0049(6)
C14	0.22199(18)	0.42011(18)	0.36382(18)	0.1003(17)	0.1569(24)	0.1230(22)	−0.0173(17)	0.0623(15)	−0.0303(15)
C15	0.03141(26)	0.44267(24)	0.4107(3)	0.1445(24)	0.1478(25)	0.2112(40)	−0.0617(26)	0.1123(25)	−0.0357(20)
O1	0.07183(21)	−0.18228(15)	0.19798(16)	0.0649(19)	0.0551(16)	0.0509(16)	−0.0058(14)	0.0222(14)	0.0071(15)
O2	−0.11885(20)	−0.10145(16)	0.13602(15)	0.0527(17)	0.0659(17)	0.0390(14)	0.0012(13)	0.0177(13)	−0.0012(14)
O3	0.00733(24)	−0.21113(18)	0.05964(17)	0.094(3)	0.0662(19)	0.0455(17)	−0.0102(15)	0.0247(17)	0.0016(18)
C1	−0.2255(3)	−0.1037(4)	0.1347(3)	0.044(3)	0.151(6)	0.066(4)	0.000(4)	0.013(3)	−0.013(4)
C2	−0.2865(4)	−0.1153(4)	0.0436(3)	0.069(4)	0.116(5)	0.081(4)	−0.008(4)	0.013(3)	0.000(4)
C3	−0.2095(4)	−0.1322(3)	−0.0066(3)	0.079(4)	0.098(4)	0.054(3)	−0.004(3)	0.011(3)	−0.016(4)
C4	−0.1130(4)	−0.0924(3)	0.0466(2)	0.077(4)	0.075(3)	0.040(3)	0.004(3)	0.017(3)	−0.003(3)
C5	−0.0135(3)	−0.1244(3)	0.0364(2)	0.085(4)	0.073(3)	0.044(3)	0.007(3)	0.032(3)	0.006(3)
C6	0.0567(3)	−0.2308(3)	0.1373(3)	0.069(4)	0.060(3)	0.060(3)	−0.006(3)	0.032(3)	0.005(3)
C7	0.0934(5)	−0.3186(3)	0.1460(3)	0.154(6)	0.071(4)	0.089(4)	−0.002(3)	0.039(4)	0.045(4)
C8	0.1407(4)	−0.3486(3)	0.2362(4)	0.089(4)	0.084(4)	0.122(5)	0.013(4)	0.019(4)	0.024(4)
C9	0.1208(7)	0.3721(5)	0.3947(8)	0.120(8)	0.094(6)	0.209(11)	−0.016(7)	0.111(8)	−0.024(6)
Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H1	−0.2471(3)	−0.0458(4)	0.1597(3)	0.20	H51	0.0478(3)	−0.0882(3)	0.0791(2)	0.15
H11	−0.2399(3)	−0.1546(4)	0.1743(3)	0.20	H7	0.1498(5)	−0.3264(3)	0.1101(3)	0.25
H2	−0.3298(4)	−0.0595(4)	0.0184(3)	0.15	H71	0.0288(5)	−0.3587(3)	0.1161(3)	0.25
H21	−0.3398(4)	−0.1668(4)	0.0373(3)	0.15	H8	0.1640(4)	−0.4128(3)	0.2330(4)	0.20
H3	−0.2344(4)	−0.1068(3)	−0.0721(3)	0.15	H81	0.2073(4)	−0.3112(3)	0.2678(4)	0.20
H31	−0.1976(4)	−0.1987(3)	−0.0106(3)	0.15	H82	0.0849(4)	−0.3450(3)	0.2732(4)	0.20
H4	−0.1188(4)	−0.0266(3)	0.0309(2)	0.10	H9	0.1543(7)	0.3519(5)	0.4615(8)	0.30
H5	−0.0110(3)	−0.1137(3)	−0.0300(2)	0.15	H91	0.0908(7)	0.3180(5)	0.3552(8)	0.30
C9′ [a]	0.1169(15)	0.4009(20)	0.3317(5)	0.142(12)					
C14′ [a]	0.2189(7)	0.3753(7)	0.4234(7)	0.154(5)					
C15′ [a]	0.0243(7)	0.4630(7)	0.3596(7)	0.138(4)					

The anisotropic temperature factors are expressed as $\exp[-2\Pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)]$.

[a] The occupancy factor C9′, C14′ and C15′ is 0.24.

TABLE 5. Polymerization of ethylene with $[TiCl_4(C_4H_7OCH_2CO_2CH_3)]$-$MgCl_2$-$AlEt_3$ catalyst in depending on the titanium concentration

	[Ti] mmol dm^{-3}	Productivity/kg polyethylene per g Ti h^{-1}
1	0.05	29.7
2	0.025	51.4
3	0.015	63.0
4	0.01	73.3

Polymerization conditions: $[Al] = 30$ mmol dm^{-3}, Ti:Mg = 1:12, P ethylene = 0.5 MPa, in hexane.

when monomeric $[TiCl_3(thf)_3]$ and $[TiCl_4(thf)_2]$ were used as precatalysts, respectively. The catalytic efficiency of the complex **2** (28.0 kg polyethylene per g Ti h) is comparable with the activity of the $[(thf)_4Mg(\mu\text{-}Cl)_2TiCl_4]$ compound, and is higher than that of $[Mg(thf)_6][TiCl_5(thf)]_2$ and $[Mg_2(\mu\text{-}Cl)_3(thf)_6][TiCl_5(thf)]$ salts, 16.9 and 12.1 kg polyethylene per g Ti h^{-1}, respectively.

We are currently trying to separate the racemate of tetrahydrofurfuryl esters to elucidate how the presence of chiral ligands in the Ziegler-Natta catalytic system influences the polymer isotacticity. Our results will be discussed in a forthcoming paper.

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