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Ionization of $TiCl_4$ and $MgCl_2$ during the Formation of a High-Activity α-Olefin Polymerization Catalyst. Crystal Structures of [*cis*-$\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti][SbCl_6]_2\cdot CH_2Cl_2$ and $[Mg\{C_2H_4(CO_2Et)_2\}_3][MgCl_4]\cdot 2CH_2Cl_2$

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The *cis*-dichlorobis(diethyl succinate)titanium(IV) bis(hexachloroantimonate(V))−dichloromethane(1/1) salt, [*cis*-$\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti][SbCl_6]_2\cdot CH_2Cl_2$ (**1**), was prepared by direct reaction of $TiCl_4$, diethyl succinate, and $SbCl_5$ in CH_2Cl_2. *catena*-(*μ*-Diethyl succinate-*O*,*O′*)bis(diethyl succinate-*O*,*O′*)magnesium(II) tetrachloromagnesate(II)−dichloromethane(1/2), $[Mg\{C_2H_4(CO_2Et)_2\}_3][MgCl_4]\cdot 2CH_2Cl_2$ (**2**), was formed by substitution of ethyl acetate in $[MgCl_2(CH_3CO_2Et)]$ for diethyl succinate. Both species have been structurally characterized. Complex **1** crystallized in the space group *Pnn*2, with $a = 16.178(5)$, $b = 12.784(4)$, and $c = 10.427(2)$ Å. Compound **2** belongs to the *C*2/*c* space group with $a = 26.121(6)$, $b = 10.086(2)$, $c = 17.947(4)$ Å and $\beta = 116.76(3)°$. In the [*cis*-$\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti]^{2+}$ cation, the titanium atom is octahedrally coordinated by two mutually *cis* chlorine atoms and four carbonyl oxygen atoms of two chelating diethyl succinate molecules. The $([Mg\{C_2H_4(CO_2Et)_2\}_3]^{2+})_\infty$ cation in the crystalline state is a linear polymer formed by the $[Mg\{C_2H_4(CO_2Et)_2\}_2]^{2+}$ units linked by other diethyl succinate ligands. In this cation, each magnesium atom is octahedrally coordinated by six carbonyl oxygen atoms of ethyl succinate molecules. Catalytic activity was found for ethylene polymerization by **1**.

Introduction

The high reactivity and isospecifity in α-olefin polymerizations of group 4 metallocene/methylalumoxane homogeneous catalysts are attributed to the presence of cationic $[M(Cp)_2R]^+$ (M = Ti, Zr, Hf) species.[1] Such cations could be simply formed by ion transfer, e.g. in the reaction between titanocene dichloride and methylaluminum dichloride.[2]

$$Ti(Cp)_2Cl_2 + Al(Me)Cl_2 \rightarrow [Ti(Cp)_2Me][AlCl_4] \quad (1)$$

The alternative routes to $[M(Cp)_2R]^+$ are halide elimination using sodium tetraphenylborate,[3] oxidation of a titanium(III) species by silver tetraphenylborate,[4] and protolysis with elimination of methane of $[Ti(Cp)_2Me_2]$ using $[HNR_3][BPh_4]$ where R = CH_3,[5] Et,[6] or *n*-Bu.[7] The use of ethylaluminum ethoxide, dimethylaluminum methoxide, or diethylaluminum methoxide in the reaction with $[VCl_3(THF)_3]$ leads to the $[V_2(\mu\text{-}Cl)_3(THF)_6][AlR_2Cl_2]$ salt.[8] Therefore it could be expected that also in the heterogeneous modern highly active polypropylene $MgCl_2/TiCl_3/AlEt_3$ catalyst[9] ionic species are present. The enhancement of isospecific activity of such catalysts is strongly dependent on an electron donor such as a carboxylic acid diester. It has been found that *o*-phthalate $C_6H_4(CO_2R)_2$ diesters yield with $TiCl_4$ the monomeric $[o\text{-}C_6H_4(CO_2R)_2Cl_4Ti]$[10] compounds but with $TiCl_3$ the dimeric $[Ti_2(\mu\text{-}Cl)_2Cl_4\{o\text{-}C_6H_4(CO_2Et)_2\}_2]$[11] complexes are formed. These compounds are good precatalysts for α-olefin polymerization processes.[12] The product of direct reaction between a titanium diester compound and an organoaluminum compound is difficult to isolate in pure crystalline form. Alternatively, we have investigated the possibility of the formation of the $[(diester)Cl_3Ti]^+$ cation using $SbCl_5$ as a chlorine-abstracting agent toward $[(diester)Cl_4Ti]$. The chloride transfer between $TiCl_4$ and $SbCl_5$ in donor solvents, as a convenient synthetic route to discrete ionic titanium species is already well documented.[13−15]

$$TiCl_4 + SbCl_5 + 3CH_3CN \rightarrow [(CH_3CN)_3Cl_3Ti][SbCl_6] \quad (2)$$

The reactivity of $MgCl_2$ toward a diester (both are catalyst components) and the influence of organic esters on $MgCl_2$ ionization have been a matter of our interest as well.[16] Here we describe a new simple high-yield method of synthesis leading to the [*cis*-$\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti][SbCl_6]_2\cdot CH_2Cl_2$ and $[Mg\{C_2H_4$-

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Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) with Esd's in Parentheses for Compound **1**[a]

Sb−Cl(2)	2.376(6)	Ti−Cl(1)	2.175(8)
Sb−Cl(3)	2.364(5)	Ti−O(1)	1.972(10)
Sb−Cl(4)	2.353(6)	Ti−O(2)	2.063(11)
Sb−Cl(5)	2.350(6)	O(1)−C(1)	1.244(19)
Sb−Cl(6)	2.341(6)	O(2)−C(2)	1.224(20)
Sb−Cl(7)	2.364(5)	C(9)−Cl(8)	1.630(21)
Cl(2)−Sb−Cl(3)	90.4(2)	Cl(1)−Ti−Cl(1′)	96.1(3)
Cl(2)−Sb−Cl(4)	89.1(3)	Cl(1)−Ti−O(1)	97.7(4)
Cl(2)−Sb−Cl(5)	90.0(3)	Cl(1)−Ti−O(1′)	92.4(4)
Cl(2)−Sb−Cl(6)	91.4(3)	Cl(1)−Ti−O(2)	91.9(4)
Cl(2)−Sb−Cl(7)	178.8(2)	Cl(1)−Ti−O(2′)	171.5(4)
Cl(3)−Sb−Cl(4)	179.4(3)	O(1)−Ti−O(1′)	164.8(5)
Cl(3)−Sb−Cl(5)	89.8(2)	O(1)−Ti−O(2)	83.4(5)
Cl(3)−Sb−Cl(6)	89.5(2)	O(1)−Ti−O(2′)	85.0(5)
Cl(3)−Sb−Cl(7)	90.5(2)	O(2)−Ti−O(2′)	80.4(5)
Cl(4)−Sb−Cl(5)	89.9(3)	Ti−O(1)−C(1)	148.3(11)
Cl(4)−Sb−Cl(6)	90.8(3)	Ti−O(2)−C(2)	139.7(12)
Cl(4)−Sb−Cl(7)	90.0(3)	Cl(8)−C(9)−Cl(8′)	119.5(14)
Cl(5)−Sb−Cl(6)	178.5(3)		
Cl(5)−Sb−Cl(7)	89.1(2)		
Cl(6)−Sb−Cl(7)	89.5(2)		

Ti−O(1)−C(1)−O(3)	16(2)
Ti−O(1)−C(1)−C(3)	−173(3)
Ti−O(2)−C(2)−O(4)	168.7(9)
Ti−O(2)−C(2)−C(4)	85(3)
C(1)−O(3)−C(5)−C(6)	−155(3)
C(2)−O(4)−C(7)−C(8)	111(3)
O(1)−C(1)−O(3)−C(5)	−1(3)
O(1)−C(1)−C(3)−C(4)	−6(4)
O(2)−C(2)−O(4)−C(7)	100(2)
O(2)−C(2)−C(4)−C(3)	−31(3)
C(1)−C(3)−C(4)−C(2)	−41(4)

[a] Primed atoms are related to unprimed by 2 − *x*, 1 − *y*, *z*.

$(CO_2Et)_2\}_3][MgCl_4]\cdot 2CH_2Cl_2$ salts and report the details of their X-ray structures.

Results and Discussion

Synthesis and Characterization of [*cis*-$\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti][SbCl_6]_2\cdot CH_2Cl_2$ (1). The direct reaction of $TiCl_4$ with diethyl succinate and $SbCl_5$ in a 1:2:2 molar ratio in CH_2Cl_2 yields an air-sensitive, yellow compound of composition $TiCl_4\cdot 2SbCl_5\cdot 2C_2H_4(CO_2Et)_2\cdot CH_2Cl_2$, which can be stored under N_2.

$$TiCl_4 + 2C_2H_4(CO_2Et)_2 + 2SbCl_5 \xrightarrow{CH_2Cl_2} \underset{\mathbf{1}}{[\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti][SbCl_6]_2\cdot CH_2Cl_2} \quad (3)$$

The new species **1** is diamagnetic. The IR spectrum shows stretching ν(C=O) modes at 1555 (vs), 1565 (s), 1584 (vs), 1615 (s), and 1635 (s) cm^{-1} characteristic for coordinated ester molecules and bands at 400 (m), 431 (s), 463 (s), and 490 (m) cm^{-1} due to ν(Ti−Cl) and ν(Ti−O) vibrations. An intense sharp band at 342 cm^{-1} is characteristic for the $[SbCl_6]^-$ anion; *cf.* K[$SbCl_6$] with a ν(Sb−Cl) of 346 cm^{-1}.[15] The crystalline compound **1** is insoluble in hydrocarbons, and it is unstable in tetrahydrofuran, immediately undergoing decomposition, and as the result [$TiCl_4(THF)_2$] is formed. The composition of **1** and its IR spectrum suggested the compound to be a salt. This was confirmed by an X-ray structural study.

X-ray Diffraction Study of 1. The results are presented in Table 1 and Figure 1. Crystals of **1** consist of [*cis*-$\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti]^{2+}$ cations and $[SbCl_6]^-$ anions in a 1:2 ratio. There is half of a nonassociated dichloromethane molecule in the asymmetric unit (the C(9) carbon atom from this molecule lies on the 2-fold axis). The solvent dichloromethane molecule in the unit cell results from crystallization. In the cation, the titanium atom is octahedrally coordinated by two mutually *cis* chlorine atoms and four carbonyl oxygen atoms from two diester molecules. The central atom lies on the 2-fold axis, which causes the cation as a whole to possess C_2 symmetry. Each diester molecule is coordinated to the Ti atom by two carbonyl oxygen atoms. The Ti−Cl(1) bond length of 2.175(8) Å is significantly shorter than those [average 2.252(2) Å] in $[C_2H_4(CO_2CH_2CH_2OPh)_2Cl_4Ti]$[17] and similar (within the range of standard deviations) to those found in $[(CH_3CN)_3Cl_3Ti]^+$ [average 2.186(5) Å].[15] In the six-coordinate cation (Figure 1), the independent Ti−O(carbonyl) distances are 1.972(10) and 2.063(11) Å and are shorter than the corresponding Ti−O bond lengths [2.113(2) and 2.088(5) Å] in $[C_2H_4(CO_2CH_2CH_2OPh)_2Cl_4Ti]$. The carbonyl group C(1)−O(1) remains in the preferred conformation, synperiplanar to the C(5)−O(3). The plane through O(1), C(1), O(3), C(3) and the plane through O(2), C(2), O(4), C(4) form an angle of 49(2)°. In the crystal, no short inter- and intramolecular contacts are observed.

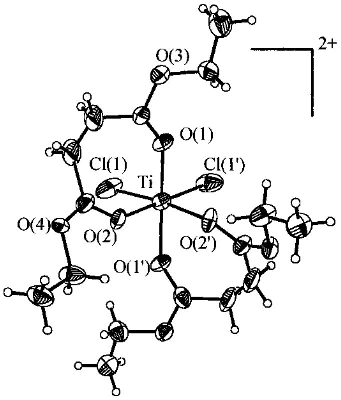

Figure 1. View of the $[\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti]^{2+}$ cation.

The hexachloroantimonate(V) counterions possess a geometry close to an ideal octahedron. Observed bond lengths and bond angles (see Table 1) are similar to earlier observed values for the same anion.[15]

Synthesis and Characterization of [Mg$\{C_2H_4(CO_2Et)_2\}_3][MgCl_4]\cdot 2CH_2Cl_2$ (2). The formation of $[Mg(THF)_6]^{2+}$, $[MgCl(THF)_5]^+$, $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$, and $[MgCl_4]^{2-}$ ions from $[MgCl_2(THF)_2]$ in tetrahydrofuran is well documented.[16] The $[MgCl_2(CH_3CO_2Et)]$ compound in the presence of the diethyl succinate at a 2:3 ratio in dichloromethane gave a colorless air-sensitive compound formulated as $2MgCl_2\cdot 3C_2H_4(CO_2Et)_2\cdot 2CH_2Cl_2$ (**2**).

$$2[MgCl_2(CH_3CO_2Et)] + 3C_2H_4(CO_2Et)_2 \xrightarrow{CH_2Cl_2} \underset{\mathbf{2}}{[\{C_2H_4(CO_2Et)_2\}_3Mg][MgCl_4]\cdot 2CH_2Cl_2} + 2CH_3CO_2Et \quad (4)$$

Its IR spectrum presents the ν(Mg−Cl) stretching band at 370 (vs, br) cm^{-1}, which is typical for the $[MgCl_4]^{2-}$ anion, as well as a ν(C=O) vibration at 1678 cm^{-1} characteristic for coordinated diethyl succinate molecules. The crystalline compound **2** has low solubility in halogenated solvents and is unstable in THF because the magnesium atom easily undergoes solvation and the complex $[MgCl_2(THF)_2]$ is formed immediately. The presence of $[MgCl_4]^{2-}$ in the IR and the composition of **2** suggested the species to be a salt.

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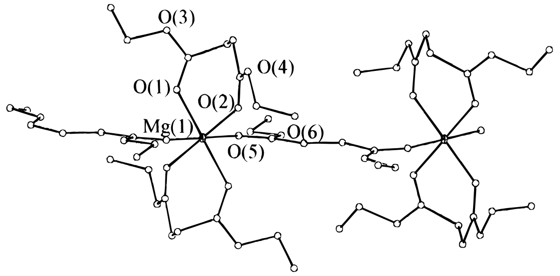

Figure 2. View of the $([Mg\{C_2H_4(CO_2Et)_2\}_3]^{2+})_\infty$ cation.

Table 2. Selected Bond Lengths (Å); Bond Angles (deg), and Torsion Angles (deg) with Esd's in Parentheses for Complex **2**[a]

Mg(1)−O(1)	2.037(4)	Mg(2)−Cl(2)	2.310(3)
Mg(1)−O(2)	2.045(4)	O(1)−C(1)	1.213(6)
Mg(1)−O(5)	2.044(3)	O(2)−C(2)	1.198(7)
Mg(2)−Cl(1)	2.333(2)	O(5)−C(9)	1.226(6)

O(1)−Mg(1)−O(2)	92.4(2)	Cl(1)−Mg(2)−Cl(2′)	118.3(1)
O(1)−Mg(1)−O(5)	89.3(2)	Cl(2)−Mg(2)−Cl(2′)	103.8(1)
O(2)−Mg(1)−O(5)	93.7(2)	Mg(1)−O(1)−C(1)	132.4(4)
Cl(1)−Mg(2)−Cl(1′)	102.1(1)	Mg(1)−O(2)−C(2)	138.5(4)
Cl(1)−Mg(2)−Cl(2)	107.6(1)	Mg(1)−O(5)−C(9)	145.4(4)

Mg(1)−O(1)−C(1)−C(3)	−1.3(7)
Mg(1)−O(2)−C(2)−C(4)	−45.9(8)
Mg(1)−O(1)−C(1)−O(3)	178.8(6)
Mg(1)−O(2)−C(2)−O(4)	132.1(9)
Mg(1)−O(5)−C(9)−C(10)	−5.6(7)
Mg(1)−O(5)−C(9)−O(6)	178.1(6)
O(1)−C(1)−O(3)−C(5)	1.8(8)
O(1)−C(1)−C(3)−C(4)	−74.3(6)
O(2)−C(2)−O(4)−C(7)	3.3(8)
O(2)−C(2)−C(4)−C(3)	−7.3(7)
C(1)−C(3)−C(4)−C(2)	78.7(7)
O(5)−C(9)−O(6)−C(11)	−5.1(8)
C(9)−C(10)−C(10′)−C(9′)	−175.0(6)

[a] Primed atoms are related to unprimed by −*x*, *y*, 0.5 − *z*.

X-ray Diffraction Study of 2. The geometry of the $([Mg\{C_2H_4(CO_2Et)_2\}_3]^{2+})_\infty$ cation in **2** is presented in Figure 2. The results are shown in Table 2. The cation of salt **2** in the crystalline state is a linear polymer formed by $[\{C_2H_4(CO_2Et)_2\}_2Mg]^{2+}$ units linked by other diethyl succinate ligands. Diethyl succinate ligands are coordinated to magnesium atoms by carbonyl oxygen atoms. The magnesium atoms in the polymeric cation are six-coordinated and occupy the center of symmetry. The Mg−O(carbonyl) bond lengths were found to be 2.037(4), 2.045(4), and 2.044(3) Å and are similar to the Mg−O(carbonyl) distances of 2.053(4) Å of the coordinated ethyl acetate molecules in $[Mg(CH_3CO_2Et)_6]^{2+}$.[18] The O(1)−C(1), O(2)−C(2), and O(5)−C(9) carbonyl bonds are in the preferred synperiplanar conformation relative to the O(3)−C(5), O(4)−C(7), and O(6)−C(11) bonds, respectively. The non-associated dichloromethane molecules in the unit cell result from the crystallization. In the crystal, no short inter- or intramolecular contacts are observed.

The $[MgCl_4]^{2-}$ anions exist in the structure as a counterions. The four-coordinated Mg atom from the anion lies on the 2-fold axis. The independent Mg−Cl distances are 2.333(2) and 2.310(3) Å and are similar to the Mg−Cl bond lengths [2.326(2) Å] in the previously reported $[MgCl_4]^{2-}$ anion in $[NBu_4]_2[MgCl_4]\cdot 2THF$.[19] The $[MgCl_4]^{2-}$ anions have distorted tetrahedral geometry with Cl(1)−Mg(2)−Cl(1′), Cl(1)−Mg(2)−Cl(2), Cl(1)−Mg(2)−Cl(2′), and Cl(2)−Mg(2)−Cl(2′) bond angles equal 102.1(1), 107.6(1), 118.3(1), and 103.8(1)°, respectively.

Table 3. Polymerization of Ethylene with Titanium/Diester Complex−$MgCl_2$−$AlEt_3$ Catalysts[a]

compound	productivity, kg of polyethylene/(g of Ti·h)
$[C_2O_4(Me)_2Cl_4Ti]$[b]	19.0
$[CH_2(CO_2Et)_2Cl_4Ti]$[b]	26.4
$[C_2H_4(CO_2Et)_2Cl_4Ti]$[b]	31.0
$[C_2H_4(CO_2CH_2CH_2OPh)_2Cl_4Ti]$[b]	22.3
$[C_3H_6(CO_2Me)_2Cl_4Ti]$[b]	24.1
$[o\text{-}C_6H_4(CO_2Et)_2Cl_4Ti]$[b]	18.3
$[\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti][SbCl_6]_2\cdot CH_2Cl_2$[c]	14.1

[a] Polymerization conditions: $[Ti]_0 = 0.05$ mmol/dm^3; Mg:Ti = 10:1; $P_{ethylene} = 0.6$ MPa; *n*-hexane used as a catalytic medium. [b] [Al] = 25 mmol/dm^3. [c] [Al] = 20 mmol/dm^3.

Polymerization Studies. The results of the ethylene polymerization test on $[cis\text{-}\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti][SbCl_6]_2\cdot CH_2Cl_2$ and six related compounds are shown in Table 3. The catalyst was prepared by milling an *n*-hexane slurry of $MgCl_2$ and one of the compounds listed. Triethylaluminum was the cocatalyst. The highest activity [31 kg of PE/(g of Ti·h)] for $[C_2H_4(CO_2Et)_2Cl_4Ti]$ was reached at Mg:Ti = 10 and $[Ti]_0 = 0.05$ mmol dm^{-3}. In contrast, the catalytic activity for **1** at [Al] = 20 mmol was about 2 times lower [14.1 kg of PE/(g of Ti·h)] than that of $[C_2H_4(CO_2Et)_2Cl_4Ti]$. In our opinion, the incorporation of $AlEt_3$ with $[SbCl_6]^-$ anions was responsible for the low catalytic activity in the ethylene polymerization. Our efforts to replace the $[SbCl_6]^-$ anion by another, e.g $[BF_4]^-$ or $[PF_6]^-$, are unsuccessful.

We supposed that the structure of $[cis\text{-}\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti]^{2+}$ is maintained in the **1**−$MgCl_2$ catalyst assembly. Note that $TiCl_4/MgCl_2/AlEt_3$ with a diester as an internal and an external donor is used as a commercial catalyst.

Conclusions

These results cannot be explained simply, but some generalizations can be considered. The $TiCl_4$ and $MgCl_2$ compounds undergo ionization in the presence of diethyl succinate in dichloromethane to afford salts **1** and **2**. In reaction 4, $MgCl_2$ is simultaneously a Cl^- donor and acceptor. In reaction 3, $TiCl_4$ is a Cl^- donor under treatment with a diester, which is used as internal and external donor for the preparation of the olefin polymerization catalyst, and gives the $[\{C_2H_4(CO_2Et)_2\}_2Cl_2Ti]^{2+}$ cation. Hence ionization of $MgCl_2$ and $TiCl_4$ under the influence of a diester during the formation of an α-olefin polymerization catalyst could be also expected. How all of the components are incorporated in the catalyst can only be answered by further studies.

Experimental Section

Preparation and Characterization of Compounds. All manipulations were carried out under dinitrogen by use of a standard Schlenk system and vacuum line. The compounds $TiCl_4$, $SbCl_5$, and $AlEt_3$ were commercial materials. $[MgCl_2(CH_3CO_2CH_2CH_3)]$ was obtained by substitution of THF in $[MgCl_2(THF)_2]$ by ethyl acetate under reflux. Solvents were dried and purified by standard techniques. Infrared spectra were obtained using a Perkin-Elmer 180 spectrometer.

Synthesis of *cis*-Dichlorobis(diethyl succinate)titanium(IV) Bis(hexachloroantimonate(V))−Dichloromethane(1/1) (1). To 1 mL of $TiCl_4$ (1.7 g, 9.1 mmol) in 60 mL of CH_2Cl_2 was added dropwise 1.5 mL (9.0 mmol) of diethyl succinate. The yellow solution was stirred for 1 h at room temperature, and 1.15 mL (9.1 mmol) of $SbCl_5$ was added dropwise. The resultant solution was filtered, and the volume was reduced under vacuum to 40 mL. After 24 h, the yellow needle-shaped crystals were filtered off and washed with *n*-hexane (3 × 5

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mL). Yield: 4.5 g (68.6%). Anal. Calc for $C_{17}H_{30}Cl_{16}O_8Sb_2Ti$: Cl, 39.4; Ti, 3.3. Found: Cl, 38.7; Ti 3.2. IR (Nujol, cm^{-1}): 1648 (vs, br), 1635 (s), 1615 (s), 1584 (vs), 1565 (s), 1555 (vs), 490 (m), 463 (s), 431 (s), 400 (m).

Synthesis of *catena*-(*μ*-Diethyl succinate-*O,O′*)bis(diethyl succinate)magnesium(II) Tetrachloromagnesate(II)−Dichloromethane-(1/2) (2). To a suspension of 1.2 g (6.5 mmol) of $[MgCl_2(CH_3CO_2Et)]$ in 100 mL of dichloromethane was added 5.5 mL (33.1 mmol) of diethyl succinate. The mixture was stirred at room temperature till the complete dissolution of $[MgCl_2(CH_3CO_2Et)]$, and the volume was reduced under vacuum to 50 mL. After 2 weeks, the colorless crystals were filtered off and washed with *n*-hexane (3 × 5 mL). Yield: 2.2 g (38.3%). Anal. Calc for $C_{26}H_{46}Cl_8O_{12}Mg_2$: Cl, 32.1; Mg 5.5. Found: Cl, 30.9; Mg, 5.1. IR (Nujol, cm^{-1}): 1678 (vs, br), 1552 (vs), 1536 (vs), 1514 (vs), 488 (s), 478 (s), 454 (m), 438 (m).

Polymerization Test. A slurry of $MgCl_2$ (30 mmol) in *n*-hexane was milled under argon in a glass mill (capacity 250 mL, with 20 balls of diameter 5−15 mm) at room temperature for 6 h. Then the titanium compound (3 mmol) and 50 mL of *n*-hexane were added, and the mixture was milled for 24 h. The sample of the precatalyst suspension (containing 0.01% titanium) was activated with 20 mmol of $AlEt_3$ for 15 min at 323 K under argon to form a highly active catalyst. The polymerization of ethylene was carried out at 323 K in a steel stainless 1 dm^3 reactor equipped with a stirrer, in *n*-hexane at an ethylene pressure of 0.6 MPa. The polymerization was quenched with a 5% solution of HCl in methanol (150 mL), and the polymer was filtered off, washed with methanol, and dried under vacuum.

X-ray Data Collection and Refinement of the Structures (Table 4). Data Collection and Processing. Preliminary data for both crystals were obtained from Weissenberg photographs. Intensities were collected using a Kuma KM4 four-circle diffractometer in the $\omega-2\theta$ mode (with crystals of dimensions 0.5 × 0.3 × 0.3 mm for **1** and 0.6 × 0.5 × 0.4 mm for **2**) and Mo Kα radiation. The crystals were cut from large crystals. Cell parameters were obtained from a least-squares fit of the setting angles of 25 reflections in the range $20° < 2\theta < 27°$ for **1** and **2**. The data collection was performed at $T = 270.0(5)$ K for **1** and $T = 180.0(5)$ K for **2** using an Oxford System Cryostream Cooler. The higher temperature of data collection for **1** was used because of a phase transformation occuring at approximately 180 K for crystals of **1**. The measurement performed at a temperature closer to the temperature of phase transformation enhances thermal parameters of all atoms. The mentioned phase transformation presumably causes rearrangement of the $[SbCl_6]^-$ anion. For both crystals, the intensities of three standard reflections, monitored every 100 intensity scans, showed no evidence of crystal decay. Totals of 3316 ($4° < 2\theta < 57°$) and 8801 ($4° < 2\theta < 56°$) reflections were measured for **1** and **2**, respectively, from which 1137 and 2111 independent reflections with $I > 3.0\sigma(I)$ were used for calculations. The structures were solved by the Patterson method and refined by full-matrix least-squares calculations using SHELXL93.[20] The number of refined parameters was 199 for **1** and 219 for **2**. Neutral-atom scattering factors and anomalous dispersion terms used in the refinement were taken from ref 21; real and imaginary components of anomalous dispersion were included for all non-H atoms. The hydrogen atoms were placed in calculated positions with $d(C-H) = 1.08$ Å and introduced as fixed contributors in the final stage of refinement. The CH_2Cl_2 molecule in **1** lies on the 2-fold axis. Absorption corrections following the DIFABS[22] procedure were applied for **2**: minimum and maximum absorption corrections were 0.876 and 1.038. Weighting schemes of the forms $w = 1/\sigma^2(F_o^2) + (0.0383P)^2 + 4.51P$ and $w = 1/\sigma^2(F_o^2) + (0.0362P)^2 + 27.97P$ (where P is defined as $(F_o^2 + 2F_c^2)/3$) were applied for **1** and **2**, respectively. For the last cycle of the refinement, the maximum value of the ratio Δ/σ was below 0.005 Å for **1** and **2**. The final difference map showed a general background within −0.30 and 0.47 for **1** and −0.42 and 0.48 e Å^{-3} for **2**. Final R_1 and R_{2w} for the inverted structure of **1** are 0.0368 and 0.0874, respectively.

Table 4. Crystal Data and Structure Refinement Details for Complexes **1** and **2**

	1	**2**
empirical formula	$C_{17}H_{30}Cl_{16}O_8Sb_2Ti$	$C_{26}H_{46}Cl_8O_{12}Mg_2$
M_r	1441.01	882.848
T/K	270.0(5)	180.0(5)
crystal system	orthorhombic	monoclinic
space group	*Pnn*2	*C*2/*c*
a, Å	16.178(5)	26.121(6)
b, Å	12.784(4)	10.086(2)
c, Å	10.427(2)	17.947(4)
α, deg	90.0	90.0
β, deg	90.0	116.76(3)
γ	90.0	90.0
V, Å^3	2157(2)	4222(2)
Z	2	4
D_c, g·cm^{-3}	1.880(1)	1.389(2)
D_m, g·cm^{-3}	1.895	1.365
λ (Mo Kα), Å	0.710 71	0.710 71
μ, mm^{-1}	2.45	0.61
$F(000)$	1184	1832
no. of reflns collected	3316	8801
min h; max h	0; 22	0; 34
min k; max k	0; 18	0; 13
min l; max l	0; 14	−23; 21
no. of unique reflns	1137	2111
goodness-of-fit on F^2	1.170	1.055
final R_1[a]	0.0361	0.0583
r_{2w}[b]	0.0859	0.1270

[a] $R_1 = \Sigma(F_o + f_c)/\Sigma F_o$. [b] $R_{2w} = \{\Sigma[w(F_o^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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Supporting Information Available: Tables giving final atomic coordinates of all atoms and anisotropic thermal parameters for non-H atoms for **1** and **2** (5 pages). Ordering information is given on any current masthead page.

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