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Ionization of YCl_3 in Tetrahydrofuran. Crystal Structures of the [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] Salt and Polymeric $[YCl_3{\cdot}2THF]_\infty$ Compounds

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The [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] salt (**1**) and polymeric $[YCl_3{\cdot}2THF]_\infty$ (**2**) were prepared by recrystallization of $YCl_3{\cdot}3.5THF$ from tetrahydrofuran (THF) and from dichloromethane, respectively. Both species have been structurally characterized. Complex **1** crystallizes in the space group $C2/c$ with $a = 12.503(4)$ Å, $b = 11.493(3)$ Å, $c = 27.212(8)$ Å, and $\beta = 91.41(3)°$. Compound **2** belongs to the space group $P\bar{1}$ with $a = 8.248(3)$ Å, $b = 8.408(3)$ Å, $c = 9.993(4)$ Å, $\alpha = 83.89(4)°$, $\beta = 67.73(3)°$, and $\gamma = 86.02(3)°$. In the [*trans*-$YCl_2(THF)_5]^+$ cation of **1**, the yttrium atom is seven-coordinated by five pentagonal oxygen atoms of THF molecules and two *trans* chlorine atoms. The structure of **2** includes seven-coordinated Y(III) centers (separated by Y···Y distances of 4.422(1) and 4.436(1) Å), which are linked by double chlorine bridges to form the polymeric species. Two THF molecules and one terminal chlorine atom complete the pentagonal bipyramidal coordination sphere of the yttrium atom. Catalytic activity was found for ethylene polymerization by **1** and **2**.

Introduction

The coordination chemistry of yttrium, after being neglected compared to that of other second-row transition elements, has now become a subject of considerable attention. It was recently reported that yttrium complexes generate extremely active, living, ring-opening polymerization systems[1] as well as catalysts of α-olefin polymerization.[2] There is a lack of Y(III) species soluble in nonaqueous solvents and suitable as starting materials for the preparation of catalysts and Y(III) complexes. The most widely used are the compounds formulated as $YCl_3{\cdot}3THF$[3] and $YCl_3(THF)_x$.[4] However, the number of ^{89}Y NMR resonances of the former compound did not match the expected solid state structure corresponding to $[YCl_3(THF)_3]^3$. The IR spectra of these species also do not agree with those of similar $[MCl_3(THF)_3]$ (M = Sc, Ti, V, Cr) compounds.[5−7]

Here we describe a new simple high-yield method of synthesis leading to the [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] salt and the polymeric $[YCl_3{\cdot}2THF]_\infty$ compounds and report the details of their X-ray crystal structures.

Results and Discussion

Synthesis and Characterization of [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] (1). The direct reaction of anhydrous YCl_3 with tetrahydrofuran under reflux yields a colorless compound of composition $YCl_3{\cdot}3.5THF$ (**1**), which can be stored under

$$2YCl_3 + 7THF \xrightarrow{THF} \underset{\mathbf{1}}{[\mathit{trans}\text{-}YCl_2(THF)_5][\mathit{trans}\text{-}YCl_4(THF)_2]}$$

N_2. The IR spectrum shows bands at 222 (s), 264 (vs), and 298 (s) cm^{-1} assigned to ν(Y−Cl) and ν(Y−O) vibrations and expected bands due to ν_{as}(C−O−C) and ν_s(C−O−C) of coordinated THF molecules at 1015 (vs), 1035 (s), and 865 (vs, br) cm^{-1}. The crystalline compound **1** has low solubility in THF and is unstable, immediately undergoing decomposition on exposure to either air or moisture to give a new unidentified product. The composition of **1** suggested the compound to be a salt. This was confirmed by an X-ray structural study.

Table 1. Final Atomic Coordinates with Esd's in Parentheses for [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] (**1**)

atom	*x*	*y*	*z*
Y(1)	0.00	0.06851(10)	0.25
Y(2)	0.25	0.25	0.00
Cl(1)	0.18995(16)	0.06893(21)	0.28670(7)
Cl(2)	0.32792(19)	0.20385(23)	0.08734(8)
Cl(3)	0.05648(17)	0.21408(20)	0.02786(8)
O(1)	0.00	−0.1396(7)	0.25
O(2)	−0.0783(5)	0.0040(5)	0.32358(17)
O(3)	−0.0275(5)	0.2352(5)	0.30017(18)
O(4)	0.2347(5)	0.4434(5)	0.01943(20)
C(1)	−0.0662(10)	−0.2146(11)	0.2198(5)
C(2)	−0.0369(12)	−0.3306(11)	0.2281(6)
C(3)	−0.0240(9)	0.0069(12)	0.3708(4)
C(4)	−0.0816(8)	−0.0736(10)	0.4024(4)
C(5)	−0.1852(10)	−0.0975(12)	0.3778(4)
C(6)	−0.1827(8)	−0.0472(10)	0.3293(4)
C(7)	−0.1284(8)	0.2788(10)	0.3148(4)
C(8)	−0.1062(8)	0.3815(9)	0.3465(4)
C(9)	0.0107(9)	0.3834(9)	0.3565(4)
C(10)	0.0524(9)	0.3151(10)	0.3172(5)
C(11)	0.1428(8)	0.5164(10)	0.0104(4)
C(12)	0.1527(10)	0.6167(11)	0.0434(5)
C(13)	0.2635(8)	0.6177(10)	0.0614(4)
C(14)	0.3148(7)	0.5092(9)	0.0455(4)

X-ray Diffraction Study of 1. The results are presented in Table 3 and Figure 1. Crystals of **1** consist of the [*trans*-$YCl_2(THF)_5]^+$ cations and the [*trans*-$YCl_4(THF)_2]^-$ anions in a 1:1 ratio. In the [*trans*-$YCl_2(THF)_5]^+$ cation, the yttrium atom is seven-coordinated with five pentagonal oxygen atoms of the THF molecules and two *trans*-coordinated chlorine atoms. The O(1), O(3), and O(3′) oxygen atoms and the yttrium atom are coplanar. The O(2) and O(2′) atoms are −0.458(5) and 0.485(5) Å out of the plane, respectively. In the [*trans*-$YCl_2(THF)_5]^+$ cation, the Y(1)−Cl(1) distance of 2.555(3) Å is comparable

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Table 2. Final Atomic Coordinates with Esd's in Parentheses for $[YCl_3{\cdot}2THF]_\infty$ (**2**)

atom	*x*	*y*	*z*
Y	0.99488(9)	−0.24140(8)	0.93145(8)
Cl(1)	0.89944(27)	0.07161(20)	0.89515(22)
Cl(2)	0.92866(29)	−0.53830(20)	0.87731(23)
Cl(3)	1.30343(27)	−0.24011(31)	0.75606(26)
O(1)	0.9168(7)	−0.2113(6)	0.7193(6)
O(2)	0.7091(7)	−0.2554(6)	1.0911(6)
C(1)	0.7488(13)	−0.1611(15)	0.7135(11)
C(2)	0.7642(14)	−0.1659(15)	0.5592(11)
C(3)	0.9141(18)	−0.2647(21)	0.4962(14)
C(4)	1.0211(14)	−0.2746(12)	0.5832(10)
C(5)	0.6643(16)	−0.2001(19)	1.2299(14)
C(6)	0.5144(17)	−0.2811(21)	1.3231(13)
C(7)	0.4410(13)	−0.3534(15)	1.2352(12)
C(8)	0.5582(13)	−0.3232(19)	1.0889(12)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses for [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] (**1**)

Y(1)−Cl(1)	2.555(3)	C(4)−C(5)	1.470(14)
Y(1)−O(1)	2.391(7)	C(5)−C(6)	1.439(14)
Y(1)−O(2)	2.369(5)	O(3)−C(7)	1.424(11)
Y(1)−O(3)	2.382(6)	O(3)−C(10)	1.426(12)
Y(2)−Cl(2)	2.599(3)	C(7)−C(8)	1.484(15)
Y(2)−Cl(3)	2.588(3)	C(8)−C(9)	1.481(14)
Y(2)−O(4)	2.293(6)	C(9)−C(10)	1.435(14)
O(1)−C(1)	1.439(13)	O(4)−C(11)	1.440(11)
C(1)−C(2)	1.399(17)	O(4)−C(14)	1.429(11)
O(2)−C(3)	1.438(10)	C(11)−C(12)	1.464(16)
O(2)−C(6)	1.444(11)	C(12)−C(13)	1.459(15)
C(3)−C(4)	1.463(14)	C(13)−C(14)	1.473(14)
O(1)−Y(1)−O(2)	71.8(2)	Cl(1)−Y(1)−O(3)	85.5(2)
O(1)−Y(1)−O(3)	143.5(2)	Cl(2)−Y(2)−Cl(3)	88.2(1)
O(2)−Y(1)−O(3)	72.5(2)	Cl(2)−Y(2)−O(4)	91.1(2)
Cl(1)−Y(1)−O(1)	90.1(2)	Cl(3)−Y(2)−O(4)	90.2(2)
Cl(1)−Y(1)−O(2)	94.0(2)		

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses for $[YCl_3{\cdot}2THF]_\infty$ (**2**)[a]

Y−Y′	4.422(1)	C(1)−C(2)	1.507(15)
Y−Y″	4.436(1)	C(2)−C(3)	1.430(20)
Y−Cl(1)	2.718(2)	C(3)−C(4)	1.431(19)
Y−Cl(2)	2.739(2)	O(2)−C(5)	1.426(15)
Y−Cl(3)	2.541(3)	O(2)−C(8)	1.412(14)
Y−O(1)	2.404(6)	C(5)−C(6)	1.430(20)
Y−O(2)	2.347(6)	C(6)−C(7)	1.429(19)
O(1)−C(1)	1.439(13)	C(7)−C(8)	1.453(16)
O(1)−C(4)	1.467(11)		
Y−Cl(1)−Y′	108.5(1)	Y−Cl(2)−Y″	108.2(1)
Cl(1)−Y−Cl(1′)	71.5(1)	Cl(2)−Y−Cl(3)	94.9(1)
Cl(1)−Y−Cl(2)	140.5(1)	Cl(2)−Y−O(1)	72.0(2)
Cl(1)−Y−Cl(3)	100.1(1)	Cl(2)−Y−O(2)	82.4(2)
Cl(1)−Y−O(1)	73.4(2)	Cl(3)−Y−O(1)	84.4(2)
Cl(1)−Y−O(2)	82.3(2)	Cl(3)−Y−O(2)	177.2(2)
Cl(2)−Y−Cl(2′)	71.8(1)	O(1)−Y−O(2)	94.9(2)

[a] The primed atoms are related to the unprimed atoms by $2 - x$, $1 - y$, $2 - z$. The Y″ atom is related to Y atom by $2 - x$, $-1 - x$, $2 - z$.

to Y−Cl bond lengths in the six-coordinated *mer*-octahedral $[YCl_3(C_6H_{10}O_2)_3]$[2] [2.590(1), 2.574(1), 2.604(1) Å] and in seven-coordinated pentagonal bipyramidal $[YCl_3(DME)_2]$ [2.599(2), 2.603(2), 2.597(2) Å] with chlorine ligands in the axial positions.[8] The Y(1)−O(2), Y(1)−O(1), and Y(1)−O(3) distances of 2.369(5), 2.391(7), and 2.382(6) Å, respectively, are comparable. The average Y−O(THF) bond length [2.387(5) Å] in the [*trans*-$YCl_2(THF)_5]^+$ cation is similar to the Y−O(THF) distance [2.41(1) Å] in the seven-coordinated $[Y(OCMe_3)Cl(THF)_5]^+$ cation.[9] In the [*trans*-$YCl_4(THF)_2]^-$ anion, the yttrium atom is six-coordinated with four square-planar chlorine atoms and two *trans* THF molecules. The distances Y(2)−Cl(2) = 2.599(3) and Y(2)−Cl(3) = 2.588(3) Å in the anion are slightly longer than the Y(1)−Cl(1) [2.555(3) Å] distance in the cation. The Y(2)−O(4) bond length of 2.293(6) Å in [*trans*-$YCl_4(THF)_2]^-$ is shorter than Y(1)−O(1,2,3) distances in [*trans*-$YCl_2(THF)_5]^+$. The differences in Y−O bond lengths in **1** are consistent with the relative *trans* influences of oxygen atoms. The structure of [*trans*-$YCl_4(THF)_2]^-$ is similar to those of the [*trans*-$TiCl_4(THF)_2]^-$ and [*trans*-$MoCl_4(THF)_2]^-$ anions.[10,11]

Synthesis and Characterization of $[YCl_3{\cdot}2THF]_\infty$ (2). The dimeric $[M_2(\mu\text{-}Cl)_2Cl_4(THF)_4]$ compounds (M = Ti, V) were prepared by recrystallization of $[MCl_3(THF)_3]$ (M = Ti, V) from dichloromethane.[12] Our effort to prepare the yttrium species with the $Y_2(\mu\text{-}Cl)_2$ unit was successful. When the [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] salt was dissolved in CH_2Cl_2 and the solvent was evaporated to dryness, the species of composition $YCl_3{\cdot}2THF$ (**2**) was isolated. Compound **2**, like **1**, decomposes upon exposure to air or moisture. Species **2** dissolved in THF immediately gives compound **1**. Compound **2** is very soluble in halogenated solvents and insoluble in hydrocarbons. Direct recrystallization of **2** from halogenated solvents or by slow diffusion of *n*-hexane into a solution of **2** in CH_2Cl_2 yielded an oil product. To decrease the solubility of **2**, $[TiCl_4(THF)_2]$ was added in 1:1 molar ratio in CH_2Cl_2. It was expected that both compounds would crystallize simultaneously and the colorless crystals of **2** could be separated from the yellow crystals of $[TiCl_4(THF)_2]$. These efforts were successful, and the mixture of colorless and yellow crystals of compositions $YCl_3{\cdot}2THF$ and $TiCl_4{\cdot}2THF$ precipitated from the solution. The species were separated by hand. The elementary analysis and IR spectrum show that the colorless crystals and species **2** are the same compound. The IR spectrum shows bands due to ν_{as}(C−O−C) and ν_s(C−O−C) and bands at 292 (vs), 228 (m), and 208 (vs) cm^{-1} attributed to ν(Y−Cl) and ν(Y−O).

X-ray Diffraction Study of 2. The structure of **2** includes seven-coordinated Y(III) centers linked by double chlorine bridges to form a polymer. Two THF molecules and one terminal chlorine atom complete the pentagonal bipyramidal coordination sphere of the yttrium atoms (Figure 2). Selected bond lengths and bond angles are listed in Table 4. In the complex one of the two coordinated THF molecules and the Cl(3) chlorine atoms are in axial positions. The remaining four chlorine atoms and one THF molecule are equatorial. All THF rings have twist conformations. The Y••Y distances of 4.422(1) and 4.436(1) Å are well outside metal−metal bond lengths and are much longer than those found in $[YCl_3(THF)_3Y_3(OR)_7O]$ [3.816(4) and 3.387(3) Å].[8] The Y−μ-Cl distances of 2.718(2) and 2.739(2) Å in **2** are generally close to the $Y{-}Cl_{bridge}$ bond lengths measured in $[YCl_3(THF)_3Y_3(OR)_7O]$ [2.751(5) and 2.778(5) Å]. The bridging Y−Cl(1)−Y′ and Y−Cl(2)−Y″ bond angles of 108.5(1) and 108.2(1)° are much greater than the Y−Cl−Y bond angles in $[YCl_3(THF)_3Y_3(OR)_7O]$ (87.3°).

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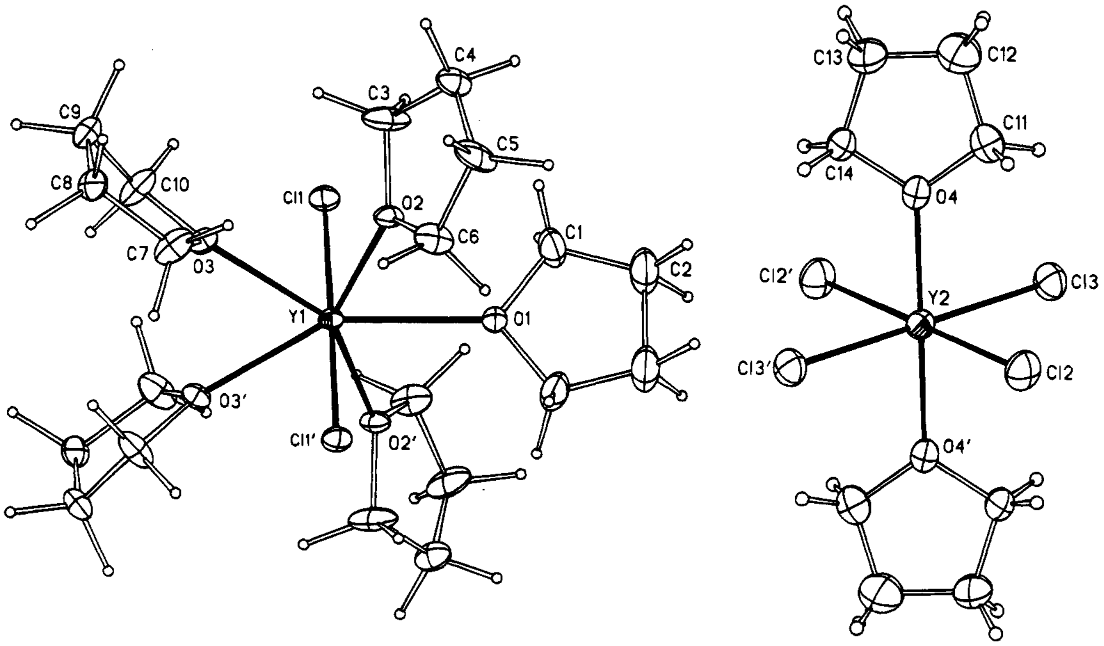

Figure 1. Structures of the $[trans\text{-}YCl_2(THF)_5]^+$ cation and the $[trans\text{-}YCl_4(THF)_2]^-$ anion.

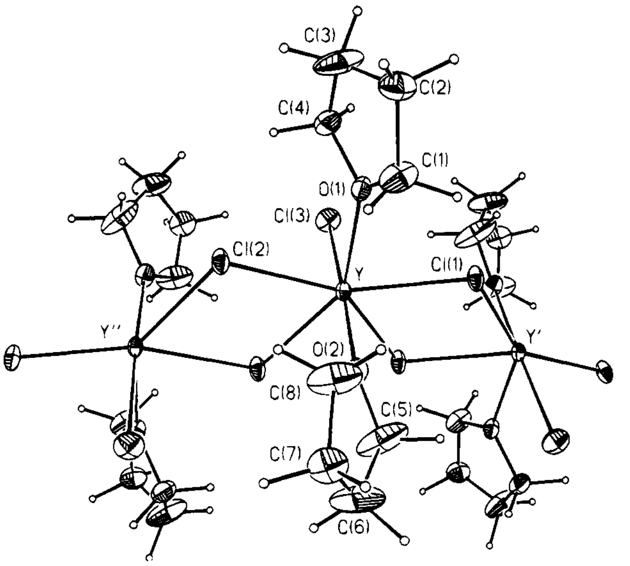

Figure 2. View of the $[YCl_3{\cdot}2THF]$ crystal structure.

Polymerization Studies. The ethylene polymerization catalyst was prepared by milling the *n*-hexane slurry of $[MgCl_2(THF)_2]$ with **1** or **2**. Triethylaluminum was used as the cocatalyst. The highest activity [5 kg of PE/(g of Y·h)] for **1** was reached at Mg:Y = 10 and $[Y]_0 = 0.01$ mmol dm^{-3}. Instead, only 2 kg of PE/(g of Y·h) was obtained when **1** was used without $[MgCl_2(THF)_2]$. The catalytic activity of **2** at the same conditions is about 2 times higher [9.8 kg of PE/(g of Y·h)] than that of **1**.

Conclusions

The results show that the behaviors of YCl_3 and $AlCl_3$ in THF are similar because they form $[trans\text{-}YCl_2(THF)_5][trans\text{-}YCl_4(THF)_2]$ and $[AlCl_2(THF)_4][AlCl_4]$[13] salts but different from the behaviors of $ScCl_3$ and $YbCl_3$, which form molecular $[ScCl_3(THF)_3]$[5] and $[YbCl_3(THF)_2]_2$[14] compounds, respectively. The "$YCl_3(THF)_3$"[3] compound and complex **1** were prepared differently. For the first compound the ^{89}Y NMR spectrum showed four resonances, while complex **1** would be expected to have only two resonances. Therefore, "$YCl_3(THF)_3$" and compound **1** are probably not the same compound. The combination of yttrium and ligands prefers to form the polymetallic species **2** in CH_2Cl_2. Preliminary results of ethylene polymerization tests on **1** and **2** show their low activity compared to 21 kg of PE/(g of Ti·h) when $[TiCl_3(THF)_3]$ was used as precatalyst.[12] In our opinion, the low incorporation of $AlEt_3$ with **1** and **2** species was responsible for their low catalytic activity in ethylene polymerization processes.

Experimental Section

Preparation and Characterization of Compounds. All manipulations were carried out under dinitrogen by use of a standard Schlenk system and vacuum line. YCl_3 was commercial material. Solvents were dried and purified by standard techniques. IR spectra were obtained on a Perkin-Elmer 180 spectrometer.

Synthesis of *trans*-Dichloropentakis(tetrahydrofuran)yttrium(III) *trans*-Tetrachlorobis(tetrahydrofuran)yttrate(III) (1). To a suspension of 7.85 g (40 mmol) of anhydrous YCl_3 in 100 cm^3 of *n*-hexane was added dropwise 30 cm^3 of THF. The mixture was stirred for 4 h at room temperature. Next, the white powder was filtered off and washed with *n*-hexane (3 × 5 cm^3). Then, it was dissolved under reflux in 100 cm^3 of THF. The resultant solution was filtered, and the volume was reduced under vacuum to 80 cm^3. After 24 h, the colorless crystals were filtered off and washed with *n*-hexane (3 × 5 cm^3). Anal. Calc for $C_{28}H_{56}Cl_6O_7Y_2$: Cl, 23.7; Y, 20.0. Found: Cl, 23.7; Y, 20.2. IR (Nujol, cm^{-1}): 1350 (m), 1300 (w), 1254 (w), 1185 (w), 1040 (sh), 1018 (vs), 960 (w), 925 (m), 866 (vs, br), 725 (w), 680 (m), 298 (s), 264 (vs), 222 (s). Good-quality crystals, suitable for X-ray examination, were taken directly from the postreaction mixture.

Synthesis of *catena*-Trichlorobis(tetrahydrofuran)yttrium(III) (2). The salt $[trans\text{-}YCl_2(thf)_5][trans\text{-}YCl_4(thf)_2]$ (6.3 g, 7.0 mmol) was dissolved in CH_2Cl_2 (60 cm^3), and the mixture was stirred to complete dissolution of the solid. The solution was filtered and evaporated to dryness in vacuo. Yield: 4.2 g (88%). Anal. Calc for $C_8H_{16}Cl_3O_2Y$: Cl, 31.2; Y, 26.1. Found: Cl, 31.4; Y, 26.4. IR (Nujol, cm^{-1}): 1344 (m), 1298 (w), 1248 (w), 1180 (w), 1038 (sh), 1020 (sh), 1008 (vs),

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Table 5. Summary of Crystallographic Data for [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] (**1**) and $[YCl_3(THF)_2]_\infty$ (**2**)

	1	**2**
empirical formula	$C_{28}H_{56}Cl_6O_7Y_2$	$C_8H_{16}Cl_3O_2Y$
M	895.292	339.485
cryst syst	monoclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$
a (Å)	12.503(4)	8.248(3)
b (Å)	11.493(3)	8.408(3)
c (Å)	27.212(8)	9.993(4)
α (deg)	90.00	83.89(4)
β (deg)	91.41(3)	67.73(3)
γ (deg)	90.00	86.02(3)
V ($Å^3$)	3909(2)	638(5)
Z	4	2
d(calc)	1.521(1)	1.769(1)
d(mes)	1.517	1.750
μ (mm^{-1})	3.37	5.07
radiation, γ (Å)	Mo Kα, 0.710 69	Mo Kα, 0.710 69
T (K)	300(1)	300(1)
$2\theta_{max}$ (deg)	56	56
no. of obsd reflcns	5182	2991
no. of unique reflcns	1210	1617
R^a	0.034	0.049
$R_w{}^b$	0.041	0.061

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(|F_o|)^2]^{1/2}$.

956 (w), 922 (m), 864 (vs, br), 740 (w), 676 (m), 292 (vs), 228 (m), 208 (vs). A solution of 5.5 g (6.1 mmol) of $YCl_3{\cdot}2THF$ and 2.0 g (5.9 mmol) of $[TiCl_4(THF)_2]$ in 40 cm^3 of CH_2Cl_2 was stirred to complete dissolution of the solid. After 2 weeks, a mixture composed of colorless crystals and a small amount of yellow crystals was obtained by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of the mixture of **2** and $[TiCl_4(THF)_2]$. These crystals were separated by hand. Good-quality colorless crystals for X-ray examination were also taken directly from the postreaction mixture. The Weissenberg photographs showed the yellow crystals to be the known [*cis*-$TiCl_4(THF)_2$] compound.[15]

Polymerization Test. A slurry of $[MgCl_2(THF)_2]$ (30 mmol) in *n*-hexane was milled under argon in a glass mill (capacity 250 cm^3; with 20 balls of 5−15 mm diameter) at room temperature for 6 h. Then yttrium compound **1** (or **2**) (3 mmol) and 50 cm^3 of hexane were added and the mixture was milled for 24 h. The sample of precatalyst suspension (containing 0.01% ytrrium) was activated with 20 mmol of $AlEt_3$ for 15 min at 323 K under argon. The polymerization of ethylene was carried out at 323 K in a steel stainless 1 dm^3 reactor with a stirrer, in *n*-hexane at ethylene pressure 0.5 MPa. The polymerization was quenched with 5% solution of HCl in methanol (150 cm^3), and the polymer was filtered off, washed with methanol, and dried under vacuum.

X-ray Data Collection and Refinement of the Structures (Table 5). Crystal Data for 1: Colorless crystals, $C_{28}H_{56}Cl_6O_7Y_2$, $M = 895.292$, monoclinic, space group *C*2/*c*, $a = 12.503(4)$ Å, $b = 11.493(3)$ Å, $c = 27.212(8)$ Å, $\beta = 91.41(3)°$, $Z = 4$, $V = 3909(2)$ $Å^3$, $D_c = 1.521(1)$ $g{\cdot}cm^{-3}$, $D_m = 1.517$ $g{\cdot}cm^{-3}$, $F(000) = 1840$, $T = 300(1)$ K, $\mu = 3.37$ mm^{-1}.

Crystal Data for 2: Yellow crystals, $C_8H_{16}Cl_3O_2Y$, $M = 339.485$, triclinic, space group $P\bar{1}$, $a = 8.248(3)$ Å, $b = 8.408(3)$ Å, $c = 9.993(4)$ Å, $\alpha = 83.89(4)°$, $\beta = 69.73(3)°$, and $\gamma = 86.02(3)°$, $Z = 2$, $V = 638(5)$ $Å^3$, $D_c = 1.769(1)$ $g{\cdot}cm^{-3}$, $D_m = 1.750$ $g{\cdot}cm^{-3}$, $F(000) = 340$, $T = 300(1)$ K, $\mu = 5.07$ mm^{-1}.

Data Collection and Processing. Intensities were collected using a Kuma KM4 four-circle diffractometer in the $\omega{-}2\theta$ mode (with crystals of dimensions 0.7 × 0.5 × 0.5 mm^3 for **1** and 0.5 × 0.3 × 0.3 mm^3 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. Totals of 5182 ($4° < 2\theta < 56°$) and 2991 ($4° < 2\theta < 56°$) reflections were measured for **1** and **2**, respectively, from which 1210 and 1617 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 SHELX76.[16] The numbers of refined parameters were 127 for **1** and 197 for **2**. Neutral-atom scattering factors were taken from ref 17; real and imaginary components of anomalous dispersion were included for all non-H 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. Weighting schemes of the forms $w = 1/\sigma^2(F_o) + 0.000450F_o{}^2$ and $w = 1/\sigma^2(F_o) + 0.000527F_o{}^2$ were applied for **1** and **2**, respectively. Final R and R_w values are 0.034 and 0.041 for **1** and 0.049 and 0.061 for complex **2**. The R_{int} value for **2** is 0.047. For the last cycle of the refinement, the maximum values of the ratio Δ/σ were 0.081 for **1** and 0.047 for **2**. The final difference map showed a general background within −0.239 and 0.255 and within −0.677 and 0.939 for **1** and **2**, respectively. An absorption correction following the DIFABS[18] procedure was applied; minimum and maximum absorption corrections were 0.822 and 1.077 and 0.798 and 1.162, respectively. Final atomic coordinates and selected bond lengths, bond angles, and torsion angles are listed in Tables 1−4.

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Supplementary Material Available: Tables giving anisotropic thermal parameters, hydrogen atom parameters, bond lengths, bond angles, and torsion angles for **1** and **2** (10 pages). Ordering information is given on any current masthead page.

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