DALTON

New 2-tetrahydrofurfuryloxotitanium(IV) intermediates for the synthesis of olefin polymerization catalysts

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The complexes $[TiCl_3(tmen)\{\eta^1\text{-}OCH_2CH(CH_2)_3O\}]$ **1**, $[Ti_2(\mu\text{-}Cl)_2Cl_4\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}_2]$ **2** and $[TiCl_4(tmen)]$ **3** (tmen = $Me_2NCH_2CH_2NMe_2$) have been synthesized and structurally characterized by X-ray diffraction. The crystals of **1** consist of monomeric $[TiCl_3(tmen)\{\eta^1\text{-}OCH_2CH(CH_2)_3O\}]$ molecules. Three chloride, one oxygen and two nitrogen atoms form a distorted octahedron around the titanium atom. Compound **2** has a dimeric structure. Each titanium atom is surrounded by two bridging chloride atoms, two terminal chloride atoms and two oxygen atoms of the 2-tetrahydrofurfuryloxide ligand. The crystals of compound **3** consist of monomeric molecules in which four terminal chloride atoms and two nitrogen atoms from the chelate tmen ligand form a distorted octahedron around Ti. High catalytic activity was found for **1** and **2**.

Since alkoxides are potential molecular precursors of multi-component oxides, they are thus of interest for application in catalysis as well as in material sciences.[1a–d] Alkoxide derivatives have been postulated to act as catalysts in Ziegler–Natta polymerization[2a–d] or olefin metathesis[3] reactions, as well as in dinitrogen activiation,[4] but detailed characterization is lacking. The O-donor functions in bidentate alkoxide ligands are particularly advantageous, *e.g.* the vanadium derivative $[V(OCMe_2CH_2OMe)_3]$ has been one of the most volatile metal alkoxides known to date. To increase the volatility, the chiral alcohol *e.g.* $HOCMe_2CHMeOMe$ was employed.[1d] Using the racemate should reduce the melting point of the resulting metal complex and increase the volatility.

For example, we found that $TiCl_4$ or $TiCl_3$ reacts with chiral tetrahydrofurfuryl alcohol in tetrahydrofuran (thf) to yield a colourless $[TiCl_3(thf)\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}]$ and a blue $[TiCl_3(thf)\{\eta^2\text{-}HOCH_2CH(CH_2)_3O\}]$ compound, respectively.[5c] To extend this chemistry we have been attempting to synthesize a new species with free ether functions of 2-tetrahydrofurfuryloxo ligand, that is, ether oxygen not co-ordinated to the metal ('dangling ligand'). We expected that such a compound could be used as a suitable starting material for the preparation of homo- or hetero-polymetallic alkoxides and precursors of the modern high-activity polyolefin catalyst. Here we describe syntheses leading to the compounds $[TiCl_3(tmen)\{\eta^1\text{-}OCH_2CH(CH_2)_3O\}]$, $[Ti_2(\mu\text{-}Cl)_2Cl_4\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}_2]$ and $[TiCl_4(tmen)]$ (tmen = $Me_2NCH_2CH_2NMe_2$) and report the details of their crystal structures.

Results and Discussion

Synthesis and structure of $[TiCl_3(tmen)\{\eta^1\text{-}OCH_2CH(CH_2)_3O\}]$

As stated above, we were interested in determining whether a bidentate $\eta^2\text{-}OCH_2CH(CH_2)_3O$ ligand could easily be transformed into monodentate $\eta^1\text{-}OCH_2CH(CH_2)_3O$. We found that in the direct reaction of $[TiCl_3(thf)\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}]$ with tmen in a 1:1 molar ratio in CH_2Cl_2 an air-sensitive, bright yellow compound of composition $TiCl_3\cdot tmen\cdot 2$-tetrahydrofurfuryloxide is formed, equation (1), which is stable under dinitrogen.

$$[TiCl_3(thf)\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}] + tmen \xrightarrow{CH_2Cl_2} \underset{\mathbf{1}}{[TiCl_3(tmen)\{\eta^1\text{-}OCH_2CH(CH_2)_3O\}]} + thf \quad (1)$$

The new species **1** is diamagnetic. The IR spectrum shows stretching ν(Ti–Cl) and ν(Ti–O) modes at 240m, 315 (sh), 330vs, 351vs, 372 (sh), 393s and bands at 1060vs and 1103s cm^{-1} due to ν(C–O–C) vibrations characteristic of a non-co-ordinated ether oxygen atom. The crystalline compound is well soluble in hydrocarbons and tetrahydrofuran. Its composition and IR spectrum suggested it to be monomeric with a dangling 2-tetrahydrofurfuryloxide ligand. This was confirmed by a crystal structural study.

The crystalline compound is composed of discrete monomeric, six-co-ordinate molecules. Its structure is depicted in Fig. 1 and selected bond distances and angles are listed in Table 1. There are two independent complex molecules in the asymmetric unit. Each titanium atom is surrounded by three chloride atoms, two nitrogen atoms from the chelate tmen ligands and one alkoxo oxygen atom from 2-tetrahydrofurfuryloxide ligands and exhibits octahedral co-ordination. The titanium atoms and the chelate tmen ligands form a five-membered ring. The ether oxygen atoms in the 2-tetrahydrofurfuryloxide ligands remain non-co-ordinated. The octahedron around each titanium atom is somewhat distorted, especially the N(11)–Ti(1)–N(12) and N(21)–Ti(2)–N(22) angles, which are only 78.5(2) and 78.1(2)°, respectively. Hence the *cis* Cl–Ti–Cl, Cl–Ti–N, Cl–Ti–O and N–Ti–O angles are opened up [to 101.5(1)° for Cl(11)–Ti(1)–Cl(12)]. The nearest environments around the Ti(1) and Ti(2) atoms are almost identical (see Table 1), but the location of the tetrahydrofuran ring due to the $TiCl_3N_2O$ moiety is different for both molecules from an asymmetric unit. This can easily be seen when the torsion angles Ti(1)–O(11)–C(11)–C(12), Ti(2)–O(21)–C(21)–C(22), O(11)–C(11)–C(12)–C(13) and O(21)–C(21)–C(22)–C(23) which are −10.2(22), 91.7(8), 27.0(12) and 69.5(7)°, respectively, are compared. The Ti–Cl bond distances range from 2.278(2) to 2.378(2) Å and are a bit longer than those found in $TiCl_4O_2$ complexes.[5a,b] The terminal $Ti\text{–}O_{alkoxo}$ bond lengths of 1.728(3) and 1.744(3) Å are similar to those found in $[M\{Ti_2(OR)_9\}_2]$ (M = Ca or Ba)[6] where they range from 1.70(3) to 1.90(3) Å and $[Ti_4Mg_2(\mu\text{-}Cl)_2Cl_2(OEt)_{16}]$ complex [1.753(4)–1.770(5) Å].[7]

Synthesis and structure of $[Ti_2(\mu\text{-}Cl)_2Cl_4\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}_2]$

The addition of $TiCl_4$ to $[TiCl_3(thf)\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}]$ in a 1:2 molar ratio in dichloromethane results in the formation of the light yellow dimeric compound $[Ti_2(\mu\text{-}Cl)_2Cl_4\{\eta^2\text{-}$

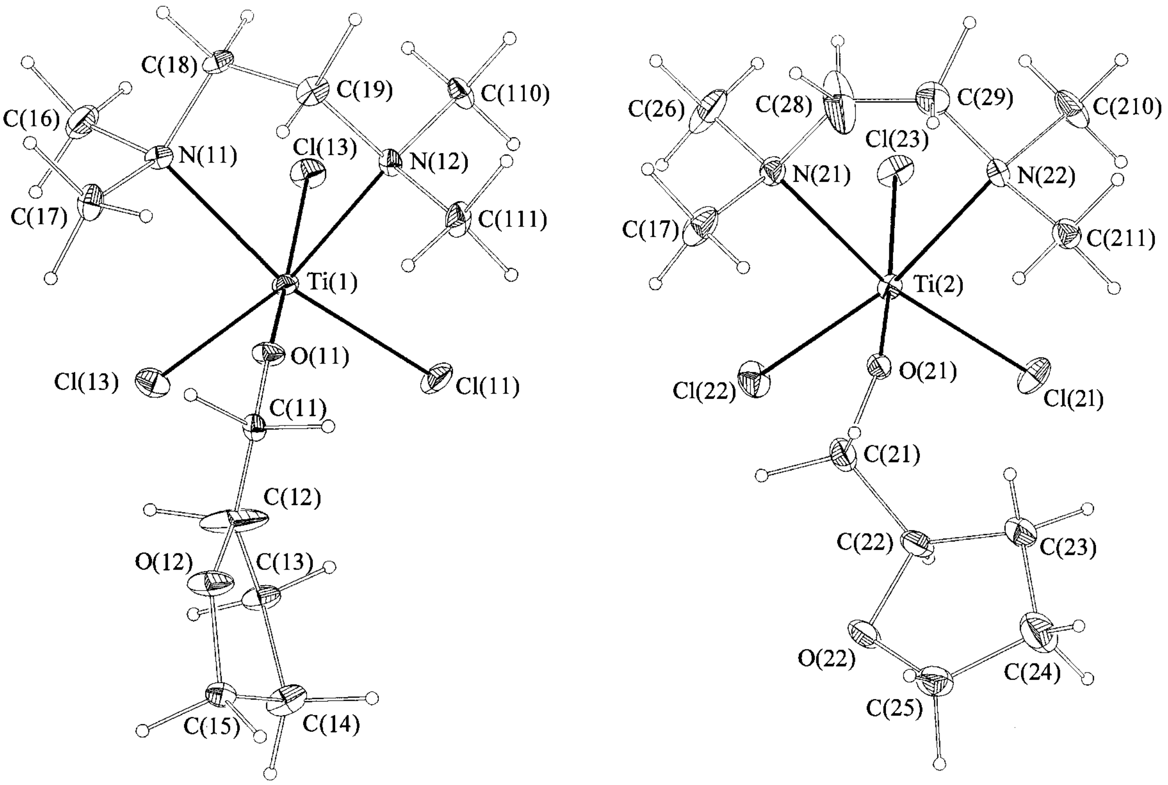

Fig. 1 Structure and numbering scheme of complex **1**

Table 1 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **1**

Ti(1)–N(11)	2.270(3)	Ti(1)–N(12)	2.300(3)
Ti(1)–Cl(11)	2.278(2)	Ti(1)–Cl(13)	2.378(2)
Ti(1)–Cl(12)	2.289(2)	Ti(1)–O(11)	1.728(3)
N(11)–C(16)	1.469(6)	N(12)–C(19)	1.471(5)
N(11)–C(17)	1.465(6)	N(12)–C(110)	1.470(5)
N(11)–C(18)	1.504(6)	N(12)–C(111)	1.473(5)
O(11)–C(11)	1.381(5)	O(12)–C(12)	1.413(6)
O(12)–C(15)	1.407(6)		
Cl(11)–Ti(1)–Cl(12)	101.5(1)	Cl(12)–Ti(1)–O(11)	93.3(2)
Cl(11)–Ti(1)–Cl(13)	88.6(1)	Cl(13)–Ti(1)–N(11)	84.8(1)
Cl(11)–Ti(1)–N(11)	167.1(2)	Cl(13)–Ti(1)–N(12)	89.2(1)
Cl(11)–Ti(1)–N(12)	90.3(1)	Cl(13)–Ti(1)–O(11)	174.1(2)
Cl(11)–Ti(1)–O(11)	94.9(2)	N(11)–Ti(1)–N(12)	78.5(2)
Cl(12)–Ti(1)–Cl(13)	90.7(1)	N(11)–Ti(1)–O(11)	90.8(2)
Cl(12)–Ti(1)–N(11)	89.7(1)	N(12)–Ti(1)–O(11)	85.9(2)
Cl(12)–Ti(1)–N(12)	168.1(1)		
Ti(2)–N(21)	2.266(4)	Ti(2)–N(22)	2.284(4)
Ti(2)–Cl(21)	2.304(2)	Ti(2)–Cl(23)	2.368(2)
Ti(2)–Cl(22)	2.288(2)	Ti(2)–O(21)	1.744(3)
N(21)–C(26)	1.421(8)	N(22)–C(29)	1.471(7)
N(21)–C(27)	1.459(7)	N(22)–C(210)	1.483(6)
N(21)–C(28)	1.485(8)	N(22)–C(211)	1.507(6)
O(21)–C(21)	1.416(6)	O(22)–C(22)	1.453(6)
O(22)–C(25)	1.397(7)		
Cl(21)–Ti(2)–Cl(22)	101.4(1)	Cl(22)–Ti(2)–O(21)	90.5(2)
Cl(21)–Ti(2)–Cl(23)	89.9(1)	Cl(23)–Ti(2)–N(21)	87.5(2)
Cl(21)–Ti(2)–N(21)	167.6(2)	Cl(23)–Ti(2)–N(22)	88.8(1)
Cl(21)–Ti(2)–N(22)	89.7(2)	Cl(23)–Ti(2)–O(21)	176.1(2)
Cl(21)–Ti(2)–O(21)	94.0(2)	N(21)–Ti(2)–N(22)	78.1(2)
Cl(22)–Ti(2)–Cl(23)	89.4(1)	N(21)–Ti(2)–O(21)	88.6(2)
Cl(22)–Ti(2)–N(21)	90.7(2)	N(22)–Ti(2)–O(21)	90.5(2)
Cl(22)–Ti(2)–N(22)	168.7(2)		

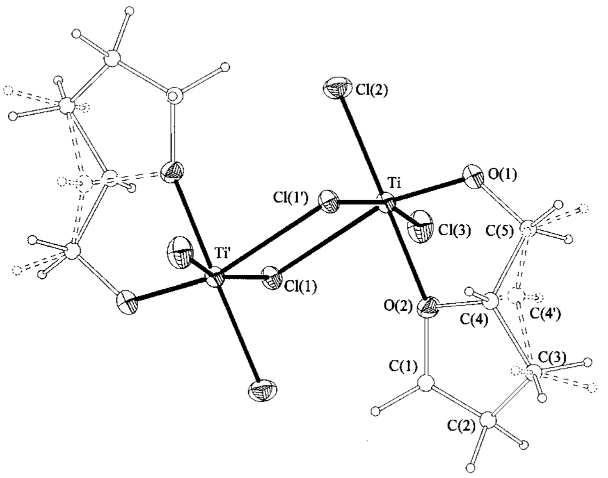

Fig. 2 Structure and numbering scheme of complex **2**

$$2[\mathrm{TiCl_3(thf)\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}}] + \mathrm{TiCl_4} \xrightarrow{\mathrm{CH_2Cl_2}} [\mathrm{Ti_2(\mu\text{-}Cl)_2Cl_4\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}_2}] + [\mathrm{TiCl_4(thf)_2}] \quad (2)$$

2

$OCH_2CH(CH_2)_3O\}_2]$ **2**. We expected that in this reaction (2) a dinuclear titanium species with a 2-tetrahydrofurfuryloxide ligand bridging two Ti atoms *via* alkoxo and ether oxygen atoms would be formed. Compound **2**, like **1**, is soluble in hydrocarbons and halogenated solvents and decomposes upon exposure either to air or moisture but is stable under N_2. It dissolves in thf immediately to give the compound $[TiCl_3(thf)\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}]$. The IR spectrum shows stretching ν(Ti–Cl) and ν(Ti–O) modes at 282m, 310m, 372vs, 401vs, 415 (sh), 431m and bands at 1010vs and 1030vs cm^{-1} due to ν(C–O–C) vibrations characteristic of a co-ordinated ether oxygen atom of the tetrahydrofuran ring.

Compound **2** was shown by X-ray diffraction studies to have a dimeric structure. An overall view of the $[Ti_2(\mu\text{-}Cl)_2Cl_4\text{-}\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}_2]$ molecule and numbering scheme are shown in Fig. 2. Principal bond distances and angles are given in Table 2. The titanium atoms are each surrounded by two

Table 2 Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex **2**

Ti–Cl(1)	2.472(1)	Ti–Cl(3)	2.255(2)
Ti–Cl(1′)	2.495(2)	Ti–O(1)	1.768(2)
Ti–Cl(2)	2.240(2)	Ti–O(2)	2.100(2)
Ti · · · Ti′	3.825(1)		
Cl(1)–Ti–Cl(1′)	79.3(1)	Cl(1′)–Ti–O(2)	83.9(1)
Cl(1)–Ti–Cl(2)	98.0(1)	Cl(2)–Ti–Cl(3)	96.1(1)
Cl(1)–Ti–Cl(3)	88.3(1)	Cl(2)–Ti–O(1)	100.5(1)
Cl(1)–Ti–O(1)	158.7(1)	Cl(2)–Ti–O(2)	173.8(1)
Cl(1)–Ti–O(2)	82.6(1)	Cl(3)–Ti–O(1)	100.2(1)
Cl(1′)–Ti–Cl(2)	90.1(1)	Cl(3)–Ti–O(2)	90.1(1)
Cl(1′)–Ti–Cl(3)	166.8(1)	O(1)–Ti–O(2)	77.9(1)
Cl(1′)–Ti–O(1)	90.1(1)	Ti–Cl(1)–Ti′	100.7(1)

Primed atoms are related to unprimed by: $1 - x, -y, 2 - z$.

Table 3 Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex **3**

Ti–N(1)	2.304(7)	Ti–N(2)	2.279(7)
Ti–Cl(1)	2.254(2)	Ti–Cl(3)	2.259(3)
Ti–Cl(2)	2.256(3)	Ti–Cl(4)	2.280(3)
N(1)–C(1)	1.446(14)	N(2)–C(2)	1.485(15)
N(1)–C(3)	1.513(12)	N(2)–C(5)	1.474(13)
N(1)–C(4)	1.47(2)	N(2)–C(6)	1.46(2)
C(1)–C(2)	1.30(2)		
Cl(1)–Ti–Cl(2)	101.5(2)	Cl(2)–Ti–N(2)	169.6(2)
Cl(1)–Ti–Cl(3)	92.5(2)	Cl(3)–Ti–Cl(4)	175.4(2)
Cl(1)–Ti–Cl(4)	91.3(2)	Cl(3)–Ti–N(1)	89.3(2)
Cl(1)–Ti–N(1)	167.3(2)	Cl(3)–Ti–N(2)	88.8(2)
Cl(1)–Ti–N(2)	88.9(2)	Cl(4)–Ti–N(1)	86.5(2)
Cl(2)–Ti–Cl(3)	91.7(2)	Cl(4)–Ti–N(2)	88.7(2)
Cl(2)–Ti–Cl(4)	90.1(2)	N(1)–Ti–N(2)	78.5(3)
Cl(2)–Ti–N(1)	91.1(2)		

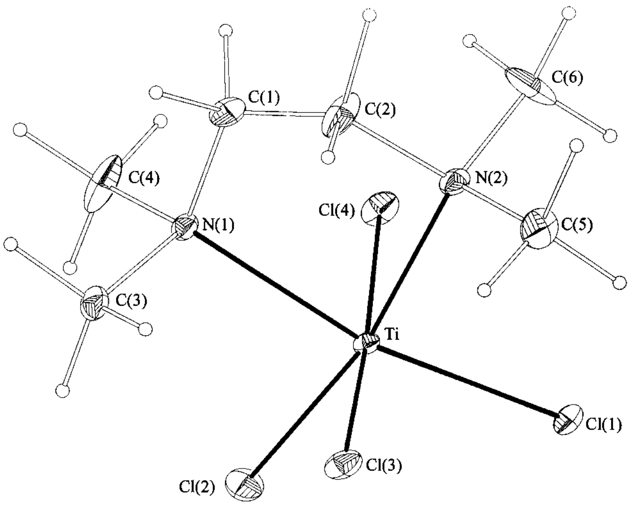

Fig. 3 Structure and numbering scheme of complex **3**

bridging chloride atoms, two terminal chloride atoms and two oxygen atoms of the 2-tetrahydrofurfuryloxide ligand which form a slightly distorted edge-sharing dioctahedron. The O(1) alkoxo oxygen atom is co-ordinated *trans* to the Cl(1) bridging atom while the ether O atoms are co-ordinated *cis* to both bridging chloride atoms. The $Ti-Cl_{bridging}$ distances are 2.472(1) and 2.495(2) Å. The Ti · · · Ti distance is 3.825(1) Å. The Ti–O(1) and Ti–O(2) bond distances are 1.768(2) and 2.100(2) Å, similar to those in **1**. The rhomboid of titanium atoms and bridging chlorides in **2** is planar, but this plane does not include the equatorial ligands.

Synthesis and structure of $[TiCl_4(tmen)]$ 3

The addition of $TiCl_4$ to $[TiCl_3(tmen)\{\eta^1\text{-}OCH_2CH(CH_2)_3O\}]$ **1** with a dangling 2-tetrahydrofurfuryloxide ligand in dichloromethane in 1 : 1 ratio gave a mixture of two compounds, equation (3). The light yellow solid was identified by elemental

Table 4 Polymerization[a] of ethylene with a $Ti–MgCl_2–AlEt_3$ catalyst

Titanium compound	Productivity[b]/kg polyethylene per g Ti per h
$[TiCl_3(thf)\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}]$	164
$[TiCl_3(thf)\{\eta^2\text{-}HOCH_2CH(CH_2)_3O\}]$	210
$[TiCl_3(tmen)\{\eta^1\text{-}OCH_2CH(CH_2)_3O\}]$	123
$[Ti_2(\mu\text{-}Cl)_2Cl_4\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}_2]$	172

[a] Polymerization conditions: $[Ti]_0 = 0.01$ mmol dm^{-3}, Al : Ti = 100 : 1, Mg : Ti = 10 : 1, $P_{ethylene} = 0.5$ MPa, in hexane. [b] Mass in kilograms of polymer formed per gram of titanium atom in 1 h.

$$[TiCl_3(tmen)\{\eta^1\text{-}OCH_2CH(CH_2)_3O\}] + TiCl_4 \xrightarrow{CH_2Cl_2} \mathbf{2} + \underset{\mathbf{3}}{[TiCl_4(tmen)]} \qquad (3)$$

analysis, IR spectroscopy and the Weissenberg photographs to be compound **2**. Cooling of the filtrate gave a yellow microcrystalline solid of composition $TiCl_4{\cdot}tmen$. This compound consists of discrete monomeric, six-co-ordinate molecules. Its structure is depicted in Fig. 3. Selected bond distances and angles are listed in Table 3. In the molecule the titanium atom exhibits octahedral co-ordination. It is surrounded by four chloride atoms and two nitrogen atoms from the chelate tetramethylethane-1,2-diamine ligand. The titanium atom and the chelate ligand form a five-membered ring. The octahedron around the titanium atom is distorted similarly as in **1**. The N(1)–Ti–N(2) angle is only 78.5(3)°. In the complex the Cl(1)–Ti–Cl(2) angle has opened up to 101.5(2)°. The remaining Cl–Ti–N angles are also different from the octahedral value. The Ti–N(1) and Ti–N(2) bond distances of 2.304(7) and 2.279(7) Å are similar to those found in $[TiCl_4(MeHNCH_2CH_2NMe_2)]$.[8] The Ti–Cl(4) bond length of 2.280(3) is longer than the remaining ones [average 2.256(3) Å] similarly as in $[TiCl_4(MeHNCH_2CH_2NMe_2)]$.[8]

Polymerization studies

The results of an ethylene polymerization test on the four related titanium-2-tetrahydrofurfuryloxide compounds are shown in Table 4. The catalyst was prepared by milling a hexane slurry of $MgCl_2$ and one of these compounds. Triethylaluminium was the cocatalyst. The highest activities were obtained with $[TiCl_3(thf)\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}]$ and $[Ti_2(\mu\text{-}Cl)_2Cl_4\{\eta^2\text{-}OCH_2CH(CH_2)_3O\}_2]$, 210 and 172 kg polyehtylene per g of Ti per h (Mg : Ti = 10, $[Ti]_0 = 0.01$ mmol dm^{-3} and [Al] = 5 mmol dm^{-3}), respectively. In contrast, 22.1 and 131.2 kg polyethylene per g of Ti per h were obtained under the same conditions when monomeric $[TiCl_3(thf)_3]$ and dimeric $[Ti_2(\mu\text{-}Cl)_2Cl_4(thf)_4]$[9] were used as procatalysts. Note that $TiCl_4–MgCl_2–AlEt_3$ is used as a commercial catalyst.

Conclusion

The results presented show that the bidentate $\eta^2\text{-}OCH_2CH(CH_2)_3O$ ligand co-ordinated to titanium(IV) could easily be transformed into dangling monodentate $\eta^1\text{-}OCH_2CH(CH_2)_3O$ ligand [equation (1)]. This transformation is very important for any study on the catalytic behaviour of metal alkoxides because the open site on the metal is potentially capable of binding activated molecules. The dangling ether oxygen atom, in **1**, does not react with the next $TiCl_4$ molecule. It follows that the titanium atom prefers to abstract the co-ordinated tmen molecule resulting in the formation of compounds **2** and **3** [equation (3)]. Also the co-ordinated thf molecule is removed by $TiCl_4$ from [$TiCl_3$(thf){η^2-$OCH_2CH(CH_2)_3O$}] and again the dimer **2** was obtained [equation (2)]. It follows that $TiCl_4$ prefers to abstract tmen or thf molecules from titanium rather than to form species with two Ti atoms bridged by alkoxo and ether oxygen atoms.

Preliminary results of the ethylene polymerization test on titanium–2-tetrahydrofurfuryloxo species show their high activity compared to the 21.2 or 131.2 kg of polyethylene per g Ti per h when [$TiCl_3(thf)_3$] or [$Ti_2(\mu\text{-}Cl)_2Cl_4(thf)_4$] was used, respectively, as procatalyst.[9] In our opinion the better incorporation of $AlEt_3$ with the complexes listed in Table 4 than with titanium–tetrahydrofuran compounds was responsible for their high catalytic activity in the ethylene polymerization process.

Experimental

All manipulations were carried out under dry dinitrogen following standard Schlenk techniques. All solvents were distilled under dinitrogen from the appropriate drying agents prior to use. The compounds $TiCl_4$, 2-tetrahydrofurfuryl alcohol and tmen were obtained from Aldrich Chemical Co. Infrared spectra were recorded on a Perkin-Elmer 180 instrument in Nujol mulls.

Syntheses

Trichloro(2-tetrahydrofurfuryloxo-*O*)(*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)titanium(IV) 1. To [$TiCl_3$(thf){η^2-$OCH_2CH(CH_2)_3O$}] (3.93 g, 12 mmol) in CH_2Cl_2 (100 cm^3) was added tmen (1.8 cm^3; 1.39 g, 12 mmol) and dropwise $TiCl_4$ (0.66 cm^3, 6 mmol). The mixture was stirred at room temperature for 2 h and the volume reduced *in vacuo* to 15 cm^3. After 2 weeks light yellow crystals were filtered off, washed with dichloromethane (3 × 5 cm^3) and dried *in vacuo*. Yield 1.5 g (34%) (Found: Cl, 28.55; Ti, 12.8. $C_{11}H_{25}Cl_3N_2O_2Ti$ requires Cl, 28.65; Ti, 12.9%). IR (Nujol, cm^{-1}): 240m, 315 (sh), 330vs, 351vs, 372 (sh), 393s, 448m, 472w, 575w, 588m, 617m, 673m, 801vs, 870m, 920s, 946vs, 980m, 992s, 1003s, 1060vs, 1103vs, 1190 (sh), 1161, 1173w and 1187w.

Di-μ-chloro-tetrachlorobis(2-tetrahydrofurfuryloxo-*O*,*O*′)dititanium(IV) 2. To [$TiCl_3$(thf){η^2-$OCH_2(CH_2)_4O$}] (3.93 g, 12 mmol) in CH_2Cl_2 (70 cm^3) was added dropwise $TiCl_4$ (0.66 cm^3, 6 mmol) and stirred. After 4 h a light yellow precipitate was filtered off and washed with dichloromethane (3 × 5 cm^3) and dried *in vacuo*. Yield 2.44 g (80%) (Found: Cl, 41.55; Ti, 18.65. $C_{10}H_{18}Cl_6O_4Ti_2$ requires Cl, 41.65; Ti, 18.75%). Crystals suitable for the structure determination were obtained by heating **1** (1.8 g) in CH_2Cl_2 (120 cm^3) under refluxed and then the solution was placed in a Dewar vessel for slow cooling. After 24 h the crystalline compound was filtered off. Yield 1.36 g. IR (Nujol, cm^{-1}): 282w, 310w, 372vs, 401vs, 415 (sh), 431m, 512m, 529m, 645s, 664m, 688w, 720w, 795s, 805s, 849m, 863m, 912s, 928s, 965s, 972s, 990vs, 1010vs, 1030vs, 1085w, 1125w, 1170w, 1218w, 1240w, 1285w and 1298w.

Tetrachloro(*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)titanium(IV) 3. To [$TiCl_3$(tmen){η^1-$OCH_2CH(CH_2)_3O$}] **1** (3.28 g, 10 mmol) in CH_2Cl_2 (60 cm^3) was added dropwise $TiCl_4$ (1.5 cm^3, 10 mmol) and stirred. Then, the species **2** was filtered off. Next the volume of the filtrate (after separation of **2**) was reduced to *ca.* 20 cm^3 and left to crystallize at 273 K. After 12 h yellow crystals were filtered off, washed with hexane (3 × 5 cm^3) and dried *in vacuo*. Yield 2.9 g (94.5%) (Found: Cl, 46.25; Ti, 15.75. $C_6H_{16}Cl_4N_2Ti$ requires Cl, 46.35; Ti, 15.7%). IR (Nujol mull): 262w, 295w, 365vs, 394 (sh), 448w, 488w, 518w, 583w, 715w, 766m, 793s, 919w, 942s, 970w, 982s, 993s, 1033m, 1065w, 1090w, 1122m, 1182w and 1270m.

Polymerization test

A slurry of $MgCl_2$ (30 mmol) in hexane was milled under argon in a glass mill (capacity 250 cm^3, with 20 balls of diameter 5–15 mm) at room temperature for 6 h. Then titanium compound (3 mmol) and hexane (50 cm^3) were added and the mixture was milled for 24 h. The sample of procatalyst suspension (containing 0.01% titanium) was activated with $AlEt_3$ (20 mmol) 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 stainless steel reactor (1 dm^3) equipped with a stirrer, in hexane at 0.6 MPa ethylene pressure. The polymerization was quenched with a 5% solution of HCl in methanol (150 cm^3) and the polymer was filtered off, washed with methanol and dried under vacuum.

Table 5 Crystal and structure refinement data for complexes **1–3**

	1	**2**	**3**
Empirical formula	$C_{11}H_{25}Cl_3N_2O_2Ti$	$C_{10}H_{18}Cl_6O_4Ti_2$	$C_6H_{16}Cl_4N_2Ti$
M	371.58	510.745	305.908
T/K	298(1)	300(1)	298(1)
Crystal system	Monoclinic	Monoclinic	Orthorombic
Space group	$C2/c$	$P2_1/c$	$Pc2_1n$
a/Å	25.704(4)	7.050(2)	7.436(2)
b/Å	8.676(2)	10.238(3)	11.822(3)
c/Å	30.565(6)	13.282(3)	14.713(5)
β/°	91.50(2)	95.59(2)	
U/Å^3	6814(3)	954(1)	1293(1)
Z	16	2	4
D_c/g cm^{-3}	1.449(1)	1.778(1)	1.571(1)
D_m/g cm^{-3}	1.437	1.761	1.579
μ/mm^{-1}	0.97	1.69	1.45
F(000)	3104	512	624
hkl Ranges	0–34, 0–11, −37 to 36	0–9, 0–13, −17 to 17	0–9, 0–14, 0–18
Unique reflections	2619	1513	804
Goodness of fit on F^2	1.063	1.056	1.075
Final $R1$[a]	0.0309	0.0305	0.0377
$wR2$[b]	0.0721	0.0780	0.0906

[a] $R1 = \Sigma(F_o - F_c)/\Sigma F_o$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

Crystallography

Intensities were collected using a Kuma KM4 four-circle diffractometer in the ω–2θ mode (with crystals of dimensions 0.4 × 0.4 × 0.3 for complex **1**, 0.4 × 0.5 × 0.4 for **2** and 0.4 × 0.4 × 0.3 mm for **3**) and Mo-Kα radiation with λ = 0.710 69 Å The crystals were cut from larger crystals. For all crystals the intensities of three standard reflections, monitored every 100 intensity scans, showed no evidence of crystal decay. 8992 ($4 < 2\theta < 56$), 2624 ($4 < 2\theta < 56$) and 1513 ($4 < 2\theta < 52°$) reflections were measured for **1**, **2** and **3**, respectively, from which 2651, 1608 and 805 reflections with $I > 3.0\sigma(I)$ were used for calculations. The structures were solved by the Patterson method and refined (based on F^2) by full-matrix least-squares calculations using SHELXL 93.[10] The number of refined parameters was 343 for **1**, 100 for **2** and 117 for **3**. Neutral atom scattering factors and anomalous dispersion terms used in the refinement were taken from ref. 11; 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. Absorption corrections following the DIFABS[12] procedure were applied for **1** and **2**: minimum and maximum absorption corrections were 0.938 and 1.020 for **1**, 0.929 and 1.090 for **2**. The residual electron densities on the Fourier-difference map found for **1** and **2** might be explained by the assumption that enantiomers of the chelating ligand occupy the same crystallographic position. For **2** we refined a model in which only the atoms C(4) and attached H atoms (H atoms on adjacent carbon atoms as well) of both enantiomers had different positions. The remaining atoms of the ligands were assumed to overlap.[5c] For **1** we refined the ordered model. There is also a small disorder of atoms C(2) and C(4) in **3**, which seem to occupy two positions, but also in this case the ordered model was refined. Weighting schemes of the form $w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 10.88P]$, $1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.91P]$ and $1/[\sigma^2(F_o^2) + (0.0397P)^2 + 2.01P]$, where P is defined as $(F_o^2 + 2F_c^2)/3$, were applied for **1**, **2** and **3**, respectively. For the last cycle of the refinement the maximum value of the ratio Δ/σ was below 0.005 Å for **1**–**3**. The final difference map showed a general background within −0.17 and 0.19 for **1**, −0.33 and 0.33 for **2**, −0.24 and 0.26 e Å^{-3} for **3**. The crystal data are summarized in Table 5.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote full literature citation and the reference number 186/317.

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References

1 (*a*) D. C. Bradley, R. C. Mehrotra and D. P. Gaur, *Metal Alkoxides*, Academic Press, New York, 1978; (*b*) D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317; (*c*) K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969; (*d*) W. A. Herrmann, N. W. Huber and O. Runte, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2187.

2 (*a*) E. Berger (Solvay & Cie), *Ger. Offen.*, 1974, 232 476; (*b*) C. E. Capshew (Philips Petroleum Co.), *Eur. Pat. Appl.*, 1980, 7425; (*c*) R. Fujio, M. Kojima, S. Anzai and A. Onishi, *Nippon Kaguku Kaishi*, 1972, 447; (*d*) R. C. Job (Shell Oil Company), *US Pat.*, 1989, 4 855 371.

3 H. Sinn and W. Kaminsky, *Adv. Orgamomet. Chem.*, 1980, **18**, 99.

4 M. E. Volpin, *J. Organomet. Chem.*, 1980, **200**, 319.

5 (*a*) P. Sobota, S. Szafert and T. Lis, *J. Organomet. Chem.*, 1993, **443**, 85; (*b*) P. Sobota, M. Wróblewska, S. Szafert and T. Głowiak, *J. Organomet. Chem.*, 1994, **481**, 57; (*c*) Z. Olejnik, T. Lis, J. Utko and P. Sobota, *Acta Crystallogr.*, 1996, **C52**, 847.

6 E. P. Turevskaya, V. G. Kessler, N. Ya. Turova, A. P. Pisarevsky, A. I. Yanovsky and Y. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 1994, 2303.

7 L. Malpezzi, U. Zucchini and T. Dall'Occo, *Inorg. Chim. Acta*, 1991, **180**, 245.

8 S. R. Drake, K. D. Sanderson, M. B. Hursthouse and K. M. A. Malik, *Polyhedron*, 1994, **13**, 181.

9 P. Sobota, J. Ejfler, S. Szafert, K. Szczegot and W. Sawka-Dobrowolska, *J. Chem. Soc., Dalton Trans.*, 1993, 2353.

10 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

11 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1992, vol. C, Tables 4.2.6.8 and 6.1.1.4, 1974.

12 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

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