New intermediates for the synthesis of alkene polymerization catalysts: the complex $[Mg_4\{\mu_3,\eta^2\text{-}OCH_2CH(CH_2)_3O\}_2\{\mu,\eta^2\text{-}OCH_2CH(CH_2)_3O\}_4Cl_2]$; crystal structure and properties

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The preparation and molecular structure of the title compound, obtained from the reaction of $Mg[OCH_2CH(CH_2)_3O]_2$ with $MgCl_2$, are reported; the compound exists as the centrosymmetric tetranuclear species with two different types of magnesium centres corresponding to octahedral MgO_6 and trigonal-bipyramidal MgO_4Cl coordination.

Metal alkoxides are valuable precursors for electronic and ceramic materials and potential candidates for chemical vapour deposition of metals and metal oxides.[1] Since alkoxides are potential molecular precursors of multicomponent oxides, they are of interest for application in catalysis and material science as well. Alkoxide derivatives have been postulated to act as catalysts in Ziegler–Natta polymerization[2] or alkene metathesis[3] reactions as well as in dinitrogen activation,[4] but detailed characterization is lacking.

Bimetallic complexes containing titanium, magnesium and electron-donor molecules, when combined with aluminium alkyls, show high catalytic activity in α-alkene polymerization.[5,6] A new approach has now been found, unique in that the crystalline alkoxo magnesium precursor is a molecule with a definite stoichiometry which forms crystalline particles of well defined shape, and that permits the preparation of crystalline species molecules which form procatalyst particles having not only excellent productivity and selectivity but also possessing excellent morphology. The polymer particles will have the shape of the procatalyst particles which have the shape of the magnesium precursor particles. One example of such a magnesium species has the formula $[Mg_4(OMe)_6(MeOH)_{10}]Cl_2$.[7] To extend this chemistry we have been attempting to synthesize a new magnesium species with the O-donor functions in bidentate alkoxo species such as the 2-tetrahydrofurfuroxo ligand. We have expected that such a compound would be used as a suitable starting material for the preparation of the modern high-activity polyalkene catalysts. Here we describe the synthesis of the $[Mg_4\{\mu_3,\eta^2\text{-}OCH_2CH(CH_2)_3O\}_2\{\mu,\eta^2\text{-}OCH_2CH(CH_2)_3O\}_4Cl_2]$ species and report the details of its X-ray crystal structure.

The direct reaction of magnesium turnings with 2-tetrahydrofurfuryl alcohol under reflux in toluene yields an air-sensitive compound of composition $Mg[OCH_2CH(CH_2)_3O]_2$, which can be stored under N_2 [eqn. (1)].

$$Mg + 2HOCH_2CH(CH_2)_3O \xrightarrow{toluene} \underset{\mathbf{1}}{Mg[OCH_2CH(CH_2)_3O]_2} + H_2 \quad (1)$$

Unexpectedly, after recrystallization of **1** from thf–CH_2Cl_2 (1 : 1) new colourless, cubic-shaped crystals were isolated and identified by elemental analysis as $Mg_4[OCH_2CH(CH_2)_3O]_6Cl_2$ **2**. The species is well soluble in halogenated solvents.

The structure of the complex consists of centrosymmetric tetranuclear molecules,† and an overall view and numbering scheme are shown in Fig. 1. In the compound a nearly regular Mg_4 rhombus is bridged by two μ_3-oxygen atoms O(5) and O(5a) of alkoxo groups, one above and one below the Mg_4 plane and in addition four μ-oxygen atoms bridge Mg–Mg edges. The $[Mg_4\{OCH_2CH(CH_2)_3O\}_6Cl_2]$ molecule contains two types of magnesium centres: the five-coordinated Mg(1) and Mg(1a) atoms and six-coordinated Mg(2) and Mg(2a) atoms. The Mg(1) atom has bipyramidal geometry with Cl(1)–Mg(1)–O(5) [174.0(1)°] representing the nearly linear group. The Mg(1)–Cl(1) bond distance of 2.363(2) Å is slightly shorter than the Mg–Cl [2.396(9) Å] distance in $[MgCl(thf)_5]^+$ cation.[8] The equatorial plane of the bipyramid is formed by two μ-O alkoxo oxygen atoms and one ether oxygen atom from the 2-tetrahydrofurfuroxo ligand. The bridging Mg(1)–μ-O bonds of 1.927(3) and 1.934(3) Å are shorter compared to the Mg(1)–μ_3-O bond length of 2.226(3) Å. The coordination sphere around Mg(2) is a slightly distorted octahedron formed by two μ_3-oxygen atoms, two μ-oxygen atoms and two ether oxygen atoms from the 2-tetrahydrofurfuroxo ligand (in *cis* position). The Mg(2)–O(ether) bond distances [2.158(3), 2.162(3) Å] are of the order of other Mg–O(ether) distances that have been observed in the octahedral structures of magnesium compounds.[9] However, the average Mg(2)–μ-O distances of 2.000(3) Å are slightly shorter than the average Mg(2)–μ_3-O distances of 2.066(3) Å.

To assist in understanding the transformation of $Mg[OCH_2CH(CH_2)_3O]_2$ into the alkoxo–chloride compound **2**

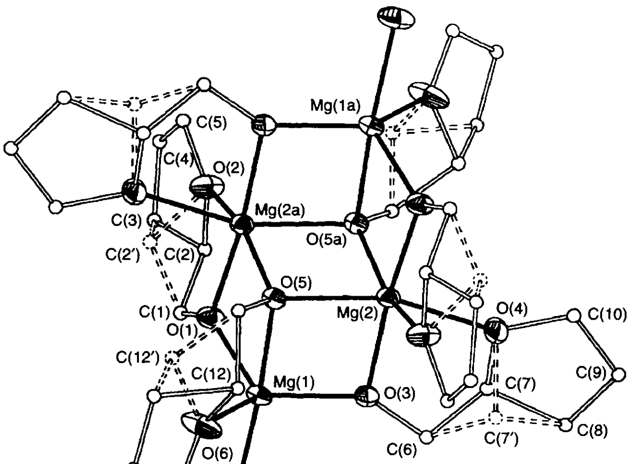

Fig. 1 The structure of **2** with atomic labelling (a labels identify atoms which are related by inversion; dashed labels identify disordered atoms). Hydrogen atoms were omitted for clarity. Important bond lengths (Å) and angles (°): Mg(1)–O(1) 1.927(3), Mg(1)–O(3) 1.934(3), Mg(1)–O(5) 2.226(3), Mg(1)–O(6) 2.064(3), Mg(1)–Cl(1) 2.363(2), Mg(1)–Mg(2) 3.103(2), Mg(1)–Mg(2a) 3.100(2), Mg(2)–O(3) 2.002(3), Mg(2)–O(4) 2.162(3), Mg(2)–O(5) 2.068(3), Mg(2)–O(5a) 2.064(3), Mg(2)–Mg(2a) 3.142(3), Mg(2a)–O(1) 1.998(3), Mg(2a)–O(2) 2.158(3); Cl(1)–Mg(1)–O(5) 174.0(1), O(1)–Mg(1)–O(3) 120.6(2), O(1)–Mg(1)–O(6) 113.7(2), O(3)–Mg(1)–O(6) 113.4(2).

during recrystallization, it was important to determine whether the impurities of metallic magnesium present in the species **1** can react with CH_2Cl_2. It is well known that CH_2Cl_2 does not react with metallic magnesium in ether solvent,[10] in contrast to CH_2Br_2 which creates di-Grignard compounds, *e.g.* $CH_2(MgBr)_2$ [eqn. (2)].[11]

$$CH_2Br_2 + Mg(Hg) \xrightarrow{Pr^i{}_2O} CH_2(MgBr)_2 \qquad (2)$$

The by-products are ethene, propene and cyclopropane.[12] We have observed the liberation of the same gaseous by-products during stirring under reflux of magnesium turnings with a saturated solution of $[MgCl_2(thf)_2]$ in CH_2Cl_2–thf (1 : 1). After several hours all magnesium was consumed and a white suspension of $[MgCl_2(thf)_2]$ was formed. The addition of a new portion of magnesium turnings and CH_2Cl_2–thf to the filtrate obtained after separation of $[MgCl_2(thf)_2]$ leads to the resumption of reaction. This procedure can be repeated many times and with the same result. Hence it follows that $[MgCl_2(thf)_2]$ and compound **1** are the promoters of the reaction between metallic magnesium and dichloromethane. How the magnesium species are incorporated with Mg and dichloromethane can only be answered by further studies. It is noteworthy that the direct reaction of $MgCl_2$ with $Mg[OCH_2CH(CH_2)_3O]_2$ in 1 : 3 molar ratio, yields tetranuclear compound **2** [eqn. (3)].

$$\begin{aligned}&MgCl_2 + 3Mg[OCH_2CH(CH_2)_3O]_2 \xrightarrow{CH_2Cl_2}\\&\quad [Mg_4\{\mu_3,\eta^2\text{-}OCH_2CH(CH_2)_3O\}_2\text{-}\\&\qquad\{\mu,\eta^2\text{-}OCH_2CH(CH_2)_3O\}_4Cl_2] \qquad (3)\\&\qquad\qquad \mathbf{2}\end{aligned}$$

Preliminary results of an ethylene polymerization test on **2**–$TiCl_4$–$AlEt_3$ gives *ca.* 170 kg polyethylene per g Ti h^{-1} (Mg : Ti = 10, $[Ti]_0 = 0.01$ mmol dm^{-3}, [Al] = 5 mmol dm^{-3}) while only 11.6 kg polyethylene per g Ti h^{-1} were obtained under the same conditions when $MgCl_2$–$TiCl_4$–$AlEt_3$ catalyst was used.[13]

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Footnote

† *Crystal data for* **2**: $C_{30}H_{54}Cl_2Mg_4O_{12}$: $M = 774.87$, triclinic, space group $P\bar{1}$, $a = 9.495(3)$, $b = 10.320(3)$, $c = 10.706(3)$ Å, $\alpha = 75.59(3)$, $\beta = 73.07(3)$, $\gamma = 89.97(3)°$, $U = 969.1(6)$ Å^3, $Z = 1$, $D_c = 1.328(1)$, $D_m = 1.307$, $\mu = 0.29$ mm^{-1}, $F(000) = 412$, $T = 300(1)$ K, Mo-Kα radiation ($\lambda = 0.71069$ Å). Preliminary data for the crystal were obtained from Weissenberg photographs. Intensities were collected using a Kuma KM4 four circle diffractometer in the ω–2θ mode with crystal of dimensions 0.7 × 0.7 × 0.8. Cell parameters were obtained from a least-squares fit of the setting angles of 35 reflections in the range $20 < 2\theta < 27°$. For the crystal the intensities of three standard reflections, monitored every 100 intensity scans, showed no evidence of crystal decay. 3705 ($4 < 2\theta < 52°$) reflections were measured from which 2169 independent reflections with $I > 3.0\sigma(I)$ were used for calculations. The structure was solved by the Patterson method and refined by full-matrix least-squares calculations on F^2 using SHELXL93.[14] The number of refined parameters was 247. Neutral atom scattering factor and anomalous dispersion terms used in the refinement were taken from ref. 15; 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. Refinement of the ordered model gave final $R_1 = 0.0631$. However, residual electron densities on the different Fourier map were found. It might be explained by the assumption that enantiomers of the chelating ligand occupy the same crystallographic position. We refined the model in which only the artoms C(2), C(7), C(12) 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; final $R_1 = 0.0483$ and $wR_2 = 0.1325$. A weighting scheme of the form $w = 1/\sigma(F_0{}^2) + (0.0716P)^2 + 0.75P$ was applied. For the last cycle of the refinement the maximum value of the ratio Δ/σ was < 0.005 Å. The final difference map showed a general background within −0.43 and 0.41 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/165.

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