DALTON
PERSPECTIVE

Incorporation of Ziegler–Natta catalyst components. Structures and reactivity of the intermediates

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Selected results of our last years research on Ziegler–Natta heterogeneous catalyst components are summarized to provide a perspective view of the area. Since the amount of information regarding the topic is enormous we have focused on alkoxy compounds that have become more and more interesting for the polymer industry. In this context single crystal X-ray crystallography is considered a very valuable and informative method. The presented summary may be useful in predicting trends for the development of new catalysts of this type.

Introduction

Although more than 50 years have passed since its "discovery" Ziegler–Natta (Z–N) catalysis remains one of the most important and profitable processes. Despite its long history it is also the fastest growing segment of the polymer industry.[1] Each year millions of tons of polyethylene and poly-α-olefins are produced. In the case of ethylene polymerization the process is uncomplicated in that the product type is not influenced by the manner in which the ethylene molecules add to the growing polymer chain and the resulting polyethylene does not exist in stereoisomeric forms. In this case polymer properties can be modified by addition of other olefins (copolymerization) and/or by termination of polymer chain growth at a specific stage. In the case of polymerization of propylene and other α-olefins the presence of the substituent R provides several types of product depending on the steric regularity with which units add to the growing polymer chain as shown in Scheme 1.[2]

Most commercial polypropylene polymers are crystalline. This results from stereoregular addition of propylene units in regular head-to-tail manner in contrast to atactic polypropylene in which the units add randomly. From this standpoint an important objective is to provide catalyst systems of sufficiently high selectivity toward isotactic products to obviate the necessity of extracting atactic polymer and residual catalyst components in a deashing step.

Several generations of Z–N catalysts have been developed.[3,4]

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Piotr Sobota

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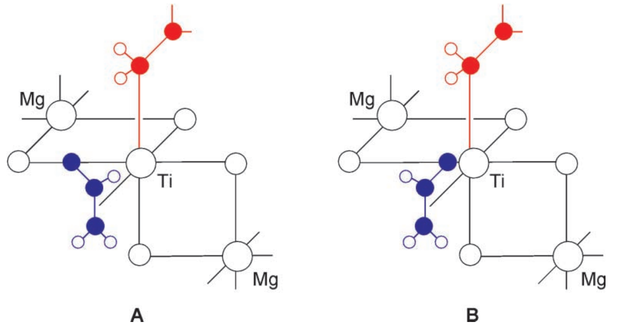


Scheme 1 The si (A) and re (B) coordination of α-olefin to the enantiomorphic metal site (red, growing polymer chain; blue, incoming α-olefin).

Each generation contributed a higher productivity of the process and quite often significant improvement of the stereospecifity of the α-olefin polymerization. The early trivalent titanium, chromium or vanadium heterogeneous catalysts were of low activity and the product contained significant amounts of catalyst residues.[3] High activity, heterogeneous, and stereoregular α-olefin polymerization catalysts can be produced from a solid species which typically contains titanium and magnesium moieties, an electron donor, and an organoaluminium compound. Other transition metals that are often used for procatalyst formation include zirconium, chromium, vanadium, and yttrium. The solid transition metal–magnesium containing constituent of such catalysts is herein referred to as the "procatalyst". The electron donor compound, whether used separately or with a procatalyst (as internal donor) or organoaluminium compound (as external donor), is referred to as the "selectivity control agent" (SCA). The organoaluminium compound, whether used separately or partially or totally complexed with an SCA, is referred to as the "cocatalyst".

The procatalysts mainly comprise MgCl$_2$ and TiX$_4$ (X = Cl or OR). Their properties are usually modified by a SCA. The cocatalyst usually is AlEt$_3$ or Al(^{i}Bu)$_3$. Each of these components influences the catalyst and polymer produced therefrom but the procatalyst seems to have the greatest impact. Therefore such a catalyst is referred to as a "supported coordination catalyst" or "supported coordination catalyst system".

Metallocene based high-activity homogeneous catalysts strongly reoriented research objectives towards well defined single site catalysts.[5,6] This resulted in the development of an enormous family of catalysts based not only on Group 4 metallocenes but also on half-sandwich amides (constrained geometry catalysts), Group 3 metal catalysts, and others that include metals across the Periodic Table.[7–9] However, these otherwise very convenient and highly active metallocene catalysts appear to bring polymer improvement at a much higher price than was originally predicted so their market penetration is still limited. Nevertheless some of them seem to reach the commercialization step. Nowadays metallocene catalysts supported on silica, alumina, magnesium dichloride or other supports are used.[10]

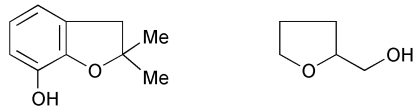
The mentioned difficulties with industrial applications of homogeneous catalysts mean that older but still very efficient heterogeneous catalysts remain of interest to the chemical industry. Thus novel titanium, zirconium and vanadium procatalysts have been obtained and investigated in our research group by reaction of Group IV and V metal chlorides or alkoxides with magnesium compounds. These compounds are viewed as potentially well defined magnesium supported heterogeneous catalysts for α-olefin polymerization.

Ligands

As mentioned before the most widely used magnesium procatalyst component is MgCl$_2$. Addition of a SCA which coordinates to the magnesium center (a) modifies the electronic properties of MgCl$_2$, (b) changes its molecular structure, and (c) enhances its otherwise poor solubility. The most commonly used SCA for ethylene polymerization is tetrahydrofuran.[11] For propylene polymerization aromatic esters such as ethyl benzoate, ethyl anisate, and diisobutyl phthalate are often used.[12] Others include ethyl acetate,[13] ethyl chloroacetate,[14] phosphorus oxychloride,[15] and silanes. All these ligands form a family of moderately weak Lewis bases and establish good leaving groups. These facts and other findings convinced us that alkoxy ligands could also very well play the role of SCA. Unusual interest of some company representatives that we have lately observed regarding alkoxy based procatalysts supports our strong belief that these ligands are very interesting from an industry perspective.[10b]

It is known that catalysts based on MgCl$_2$ and Mg(OR)$_2$ have similar activity and polymers derived therefrom have similar properties. Nonetheless the morphology of the alkoxy catalyst is much better in terms of particle shape and results in better polymer morphology (spherilene technology).[16] The morphology of the catalyst and resulting polymer is technologically crucial. For example build-up of small polymer particles can cause entrainment problems in the reactor, valves or transfer lines. It is also easier in case of alkoxy ligands to obtain a procatalyst with well defined stoichiometry.

In our research we mainly utilize commercially available 2,3-dihydro-2,2-dimethylbenzofuran-7-ol (dbbfo-H; **1a-H**) and tetrahydrofurfuryl alcohol (thffo-H; **1b-H**) as shown in Scheme 2. Deprotonation of these hydroxides affords bidentate O,O′ monoanions henceforth abbreviated as L^2.



1a-H 2,3-dihydro-2,2-dimethylbenzofuran-7-ol (dbbfo-H)

1b-H tetrahydrofurfuryl alcohol (thffo-H)

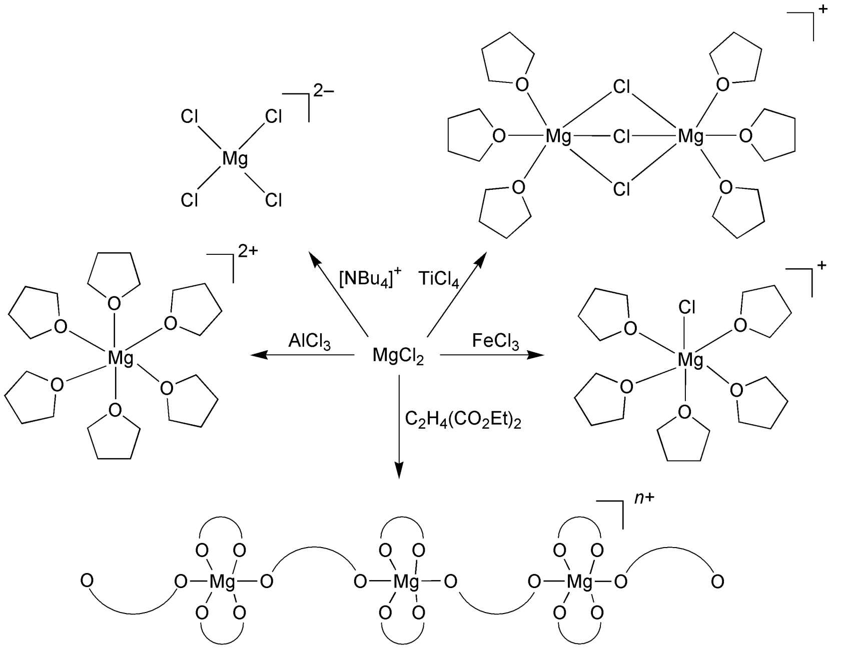
Scheme 2 Bidentate O,O′ alkoxo ligands.

Both ligands contain two donor atoms; one alkoxy and one ether oxygen atom, separated by two carbon atoms, that allow the ligands to act as chelating agents or be tethered between metal atoms in μ_3-η^2, μ-η^2, μ_3-η^1, or μ-η^1 modes to create multinuclear species. Some other coordination modes as well as coordination by neutral R–OH (when the reaction is performed in pure alcohol or an excess of alcohol is used) are possible, broadening the spectrum of possible motifs of polymetallic species. The weak donor properties of the L^2 ligands make their metal complexes labile and establish good leaving groups which facilitates grafting on the catalyst support. Lability makes these compounds very useful in sol–gel or vapor deposition techniques in material chemistry.

Magnesium alkoxides

The frequently dramatic and beneficial influence of species such as MgCl$_2$ on the catalyst activity of early-transition metal compounds is well recognized[4,17,18] but still poorly understood.[19,20] MgCl$_2$ as a catalyst component is especially attractive for studying the factors which favor polynuclear aggregation of magnesium species with TiX$_4$.[3] Hence, studies on the interaction among components of this inherently very complex MX$_{(3)4}$/Mg(OR)$_2$/AlR$_3$ (M = Ti, Zr or V; X = OR or Cl) catalyst system as well as on its interaction with ≡SiOH surface groups and/or SCA are very important and still a challenge.

Attempts to elucidate why MgCl$_2$ plays such an unusual role as a catalyst component failed because it was impossible to isolate compounds from the heterogeneous TiCl$_{(3)4}$/MgCl$_2$/AlR$_3$



Scheme 3 Reactions of $MgCl_2$.

reaction mixture. Despite the steady stream of new patents and publications, the role of $MgCl_2$ was considered as a support until 1984, when the formation of $[Mg_2(\mu\text{-}Cl)_3(thf)_6][TiCl_5(thf)]$ salt, in the reaction of magnesium dichloride with $TiCl_4$, was first announced.[21] This reaction shows that in polar solvents $MgCl_2$ is not a simple support but a Cl^- donor and a highly reactive species. Note that $[Mg_2(\mu\text{-}Cl)_3(thf)_6][TiCl_5(thf)]$ supported on SiO_2 together with an organometallic cocatalyst is used as a commercial ethylene polymerization catalyst.[10a,f] A few examples of $MgCl_2$ reactivity are shown in Scheme 3.

It is well documented that complexation of $MgCl_2$ by a SCA results in its polynuclear aggregation. The structure of $[Mg_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4(Et)_2(thf)_6]$ can serve as a good example.[22] Its structure is analogous to those of $MCl_2(thf)_{1.5}$ for M = Fe[23] or Co.[24] The metal species exist as centrosymmetric tetranuclear $[M_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4Cl_2(thf)_6]$ (M = Fe or Co) compounds with two different types of M(II) centers corresponding to six-coordinate octahedral MX_4O_2 and five-coordinate trigonal bipyramidal MX_4O chromophores. Identical behavior is expected when alkoxy ligands are used as the complexation agents.

Interaction of magnesium with "simple" alcohols like methanol is complicated. An X-ray study of crystals of magnesium methoxide obtained in the reaction of magnesium with MeOH allowed the formulation of the product as $Mg(OMe)_2{\cdot}3.5MeOH$. Its structure is built of residues of four types: neutral $[Mg_4(\mu_3\text{-}OMe)_4(OMe)_4(MeOH)_8]$ cubane, $[Mg_4(\mu_3\text{-}OMe)_4(OMe)_2(MeOH)_{10}]^{2+}$ cubane cations, $[(MeO)_2H]^-$ anions and eight crystallographically independent non-coordinated solvating methanol molecules.[25] Crystals of $Mg(OMe)_2{\cdot}3.5MeOH$ easily lose solvent at 293 K, supporting the statement about lability of alkoxy ligands. The structure of $Mg(OEt)_2$ is not known but its complexes with titanium tetrachloride give procatalysts with a very good crystallinity.[26] Although there are magnesium complexes with other "simple" alcohols, those in the patent literature mainly comprise methoxy and ethoxy compounds.

Reactions of **1a-H** and **1b-H** with di-*n*-butylmagnesium or magnesium turnings give complexes of $[Mg(L^2)_2]$ **2a**–**b** stoichiometry as white powders. Spectroscopic data for these compounds suggest a polynuclear character. X-Ray crystallographic analysis of **2a** indeed showed a tetranuclear $[Mg_4(\mu_3\text{-}\eta^2\text{-dbbfo})_2(\mu\text{-}\eta^2\text{-dbbfo})_4(\eta^1\text{-dbbfo})_2]$ compound with open dicubane geometry (Scheme 4 and Fig. 1).[27] An analogous structure has previously been observed involving 1-methoxy-2-propanol.[28]

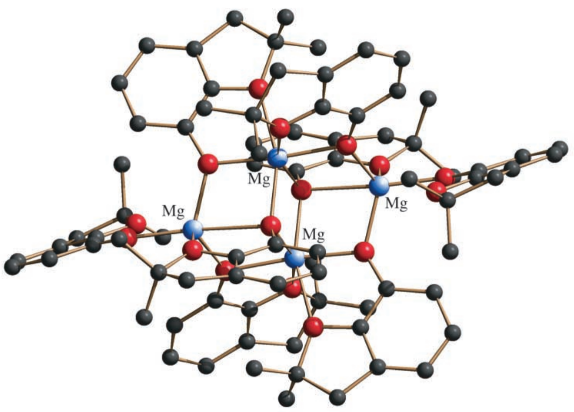
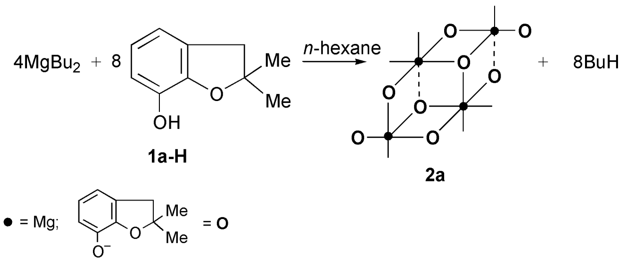


Fig. 1 A SCHAKAL[53] view of complex **2a**.



Scheme 4 Reaction of $MgBu_2$ with dbbfo-H.

The centrosymmetric molecule of **2a** possesses two five-coordinate magnesium atoms of trigonal bipyramidal geometry and two six-coordinate octahedral metal sites. This nearly regular Mg_4 rhombus is bridged by two μ_3- and four μ-oxygen atoms of six alkoxy groups to form an open dicubane. The presence of coordinatively unsaturated metal sites is the most interesting feature of these compounds. Two dbbfo ligands in **2a** are in μ_3-η^2 coordination mode. Four of them are in μ-η^2 and two are in η^1 fashion. As shown in Fig. 1 the equatorial plane of each bipyramid is formed by two μ-bridging alkoxy groups and one ether oxygen from a dbbfo ligand. Axial positions are filled by a μ_3-bridging alkoxy ligand and an η^1-dbbfo ligand. The coordination sphere around six-coordinate magnesium is a slightly distorted octahedron formed by two μ_3- and two μ-bridging alkoxy

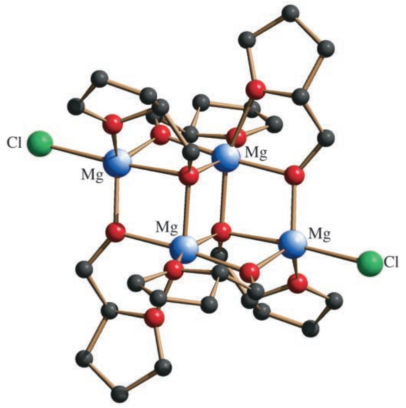


Fig. 2 A SCHAKAL view of complex **3**.

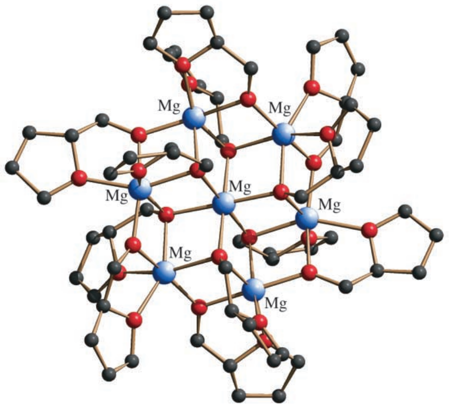


Fig. 3 A SCHAKAL view of the cation of complex **4**.

groups. Two remaining sites are occupied by two ether oxygens of two dangling dbbfo ligands (in *cis* position). The average bond lengths and bond distances are of the order of the corresponding magnesium–oxygen distances observed in other magnesium compounds.[29–31] It must be underlined that the open dicubane structure of **2a** presents a lot of similarities with the structure of the magnesium part of some of the catalyst theoretical models.[32] The (110) surface of $\mathrm{MgCl_2}$ can be described as an open polycubane structure. Exchange of Cl for bidentate ligands in this model enhances the space volume around the catalytic center which is as an important phenomenon in homogeneous systems. It should also be noted that the previously mentioned structures of magnesium alkoxides with "simple" alcohols usually form closed cubanes.

Reactivity of open dicubanes $[\mathrm{Mg_4(L^2)_8}]$

Complexes **2a** and **2b** are sensitive towards chlorinated hydrocarbons. $\mathrm{CH_2Cl_2}$ for example causes substitution of η^1-coordinated ligands by chlorine atoms to give in the case of **2b** the molecular complex $[\mathrm{Mg_4(\mu_3\text{-}\eta^2\text{-thffo})_2(\mu\text{-}\eta^2\text{-thffo})_4Cl_2}]$ **3** shown in Fig. 2.[29]

Compound **3** was also obtained when $\mathrm{MgCl_2}$ was treated with **2b**.[29] Based on the reaction stoichiometry and final yield we postulate that in this reaction at least two products are formed. The main product **3** precipitates while the accompanying ionic by-product stays in solution and can be trapped by addition of a suitable counter ion. $\mathrm{FeCl_2}$ fulfils that need and the polynuclear magnesium aggregate **4** can easily be isolated as shown in Fig. 3.[33] This magnesium compound with a $[\mathrm{Mg_7O_{24}}]^{2+}$ core is the largest structurally characterized magnesium alkoxide reported to date. Similar $[\mathrm{Zn_7X_{24}}]^{2+}$ (X = O or N) cores were found in the product obtained by crystallization of $\mathrm{ZnL_2}$ (L = pyridylmethanolate) from $\mathrm{CH_2Cl_2}$.[34]

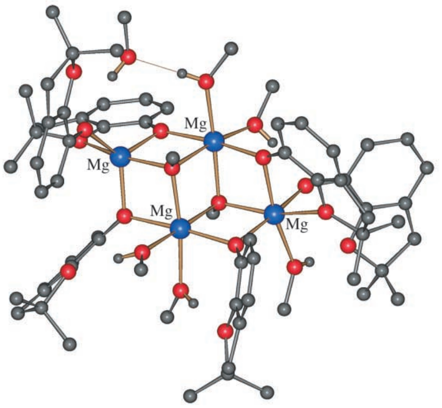


Fig. 4 A SCHAKAL view of complex **5**.

Although there is no indirect proof, compound **3** in methanol probably undergoes ionization and the $[\mathrm{Mg_4(\mu_3\text{-}\eta^2\text{-thffo})_2(\mu\text{-}\eta^2\text{-thffo})_4(MeOH)_{\mathit{x}}}]^{2+}$ cation is formed. This conclusion may be drawn from the fact that crystals of $[\mathrm{Mg_4(\mu_3\text{-}OMe)_4(OMe)_2(MeOH)_{10}}]\mathrm{Cl_2}$ with a similar cation were isolated as one of the products of the reaction of $\mathrm{Mg(OMe)_2{\cdot}3.5MeOH}$ with $\mathrm{MgCl_2}$.[35] Formation of **3** in thf is attributed to the stronger donor properties of chloride compared to those of thf which stays in the metal coordination sphere to form $[\mathrm{Mg_4(\mu_3\text{-}\eta^2\text{-thffo})_2(\mu\text{-}\eta^2\text{-thffo})_4Cl_2}]$ instead of ionic $[\mathrm{Mg_4(\mu_3\text{-}\eta^2\text{-thffo})_2(\mu\text{-}\eta^2\text{-thffo})_4(thf)_2}]\mathrm{Cl_2}$.

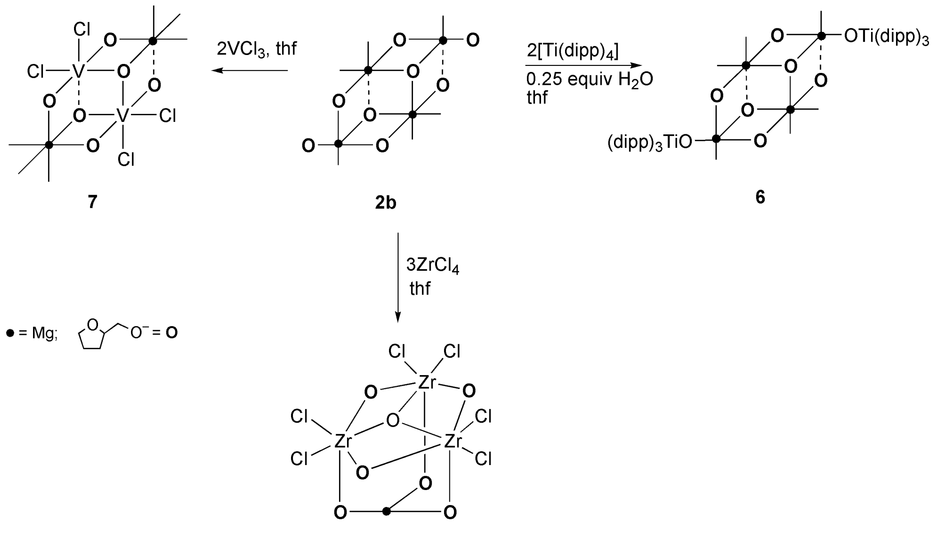
Compounds **2a** and **2b** with unsaturated metal sites are also interesting as regards their reaction with small molecules. Reaction of **2a** with MeOH gave a new colorless crystalline compound identified as $[\mathrm{Mg_4(\mu_3\text{-}OMe)_2(\mu\text{-}\eta^2\text{-dbbfo})_2(\mu\text{-}\eta\text{-dbbfo})_4(MeOH)_5}]\mathrm{{\cdot}MeOH{\cdot}thf}$ **5**. As shown in Fig. 4 the molecule contains one five-coordinate and three six-coordinate magnesium atoms. The inequivalence at the formerly identical five-coordinated magnesium centers arises from saturation of the coordination sphere of one of them by a MeOH molecule. It is clear from the structure that the uncoordinated MeOH molecule approaches the free coordination site of the other magnesium but it stays frozen at a distance resulting from numerous internal hydrogen bonds.[27]

$[\mathrm{Mg_4(L^2)_8}]$ based procatalysts

As an aid to explain the formation of catalytically active procatalysts we studied the interaction of **2a** and **2b** with $[\mathrm{Ti(dipp)_4}]$ (dipp = 2,6-diisopropylphenoxide),[27] $\mathrm{VCl_3}$[36] and $\mathrm{ZrCl_4}$.[37] Reactions were conducted in thf and gave complexes **6**–**8** as shown in Scheme 5. Compound **6**, which was obtained by controlled hydrolysis of the reaction product formed between **2b** and $[\mathrm{Ti(dipp)_4}]$, is shown in Fig. 5. Its molecular structure is similar to that of **3**. Both compounds possess a $[\mathrm{Mg_4(thffo)_6}]^{2+}$ core that originates from the starting magnesium compound. The only significant difference between them is that the two terminal Cl atoms that are bound to the five-coordinated magnesium centers in **3** are substituted by $[\mathrm{OTi(dipp)_3}]^-$ moieties in **6**.

The reactions of **2b** with vanadium trichloride and zirconium tetrachloride proceed according to a different course (Scheme 5). Violet $[\mathrm{V_2Mg_2(\mu_3\text{-}\eta^2\text{-thffo})_2(\mu\text{-}\eta^2\text{-thffo})_4Cl_4}]$ **7** was obtained in the reaction of **2b** with $\mathrm{VCl_3}$. As shown in Fig. 6 the centrosymmetric complex molecule also consists of a $\mathrm{M_4}$ rhombus in which two magnesium atoms were replaced by vanadium atoms. Each metal center is six-coordinate and the open dicubane structure is preserved.

As shown in Fig. 7 neutral $[\mathrm{Zr_3Mg(\mu_3\text{-}O)(\mu\text{-}\eta^2\text{-thffo})_6Cl_6}]$ **8** is a tetranuclear species. In the complex molecule three zirconium atoms form a nearly regular triangle that is held together by a μ_3-O ligand to give a motif of C_3 symmetry. Each zirconium is additionally surrounded by two terminal chlorine atoms, one



Scheme 5 Reactions of [Mg$_4$(thffo)$_8$] with [Ti(dipp)$_4$], VCl$_3$, and ZrCl$_4$.

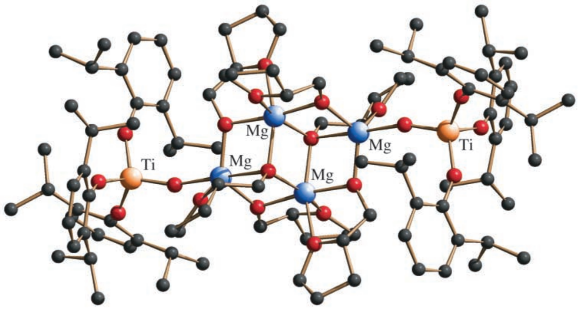


Fig. 5 A SCHAKAL view of complex **6**.

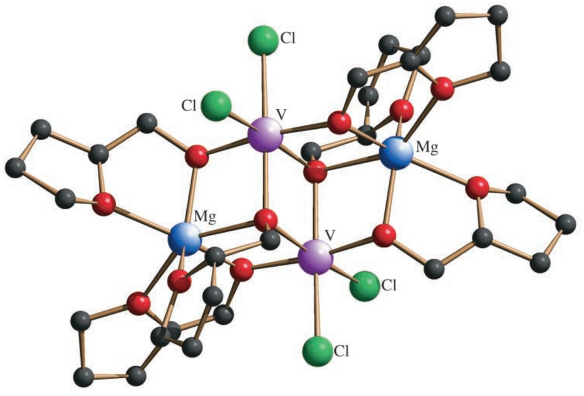


Fig. 6 A SCHAKAL view of complex **7**.

ether oxygen atom of a thffo ligand, and three bridging μ-O atoms of three thffo ligands. Six oxygen atoms of three tetrahydrofurfuroxy ligands form a slightly distorted octahedron around the magnesium center.

Formation of products containing a "lone" triply bridging μ_3-O atom that is encapsulated in an ensemble of three or more metal atoms is often observed during reactions of metal chlorides or alkoxides with alcohols as well as during electrochemical syntheses of metal alkoxides, regardless of the synthetic conditions.[38–40]

Formation of complexes **7** and **8** can be considered to proceed according to an ionic mechanism. Thus **7** is formed by entrapment of two $[VCl_2]^+$ moieties by two $[Mg(thffo)_3]^-$ to give the molecular solid. Similarly reaction of the trinuclear $[Zr_3(\mu_3\text{-}O)(\mu\text{-}\eta^2\text{-thffo})_3Cl_6]^+$ cation with a $[Mg(thffo)_3]^-$ moiety, which coordinates to the zirconium centers *via* μ-alkoxide oxygen atoms of the three thffo ligands, gives **8**.

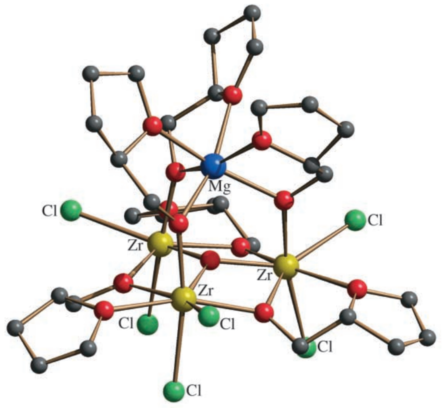
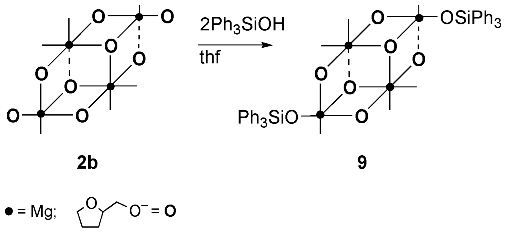


Fig. 7 A SCHAKAL view of complex **8**.

Reaction of magnesium open dicubanes with catalyst support

In order to reveal the interaction of silica surface OH groups with the magnesium catalyst component we studied the binding of Ph$_3$SiOH to the unsaturated magnesium centers in **2b**. The reaction course is similar to that for **6** and gives adduct **9** (Scheme 6 and Fig. 8).[41] Comparison of the structure **9** with



Scheme 6 Reaction of [Mg$_4$(thffo)$_8$] with Ph$_3$SiOH.

those of **3** and **6** shows a lot of similarities. Also here the $[Mg_4(thffo)_6]^{2+}$ core is present; the only difference is that both magnesium centers are substituted by $[OSiPh_3]^-$ groups and, what is interesting, remain five-coordinated.

Reaction of magnesium open dicubanes with cocatalyst

The reaction of **2b** with AlMe$_3$ results in the ultimate splitting of the tetranuclear magnesium core (Scheme 5) to give $[Al_3Mg(\mu_3\text{-}O)(\mu\text{-}\eta^2\text{-thffo})_3(Me)_6]\cdot C_6H_5CH_3$ **10**.[41] As shown in Scheme 7 and Fig. 9 the tetranuclear Al$_3$/Mg compound forms

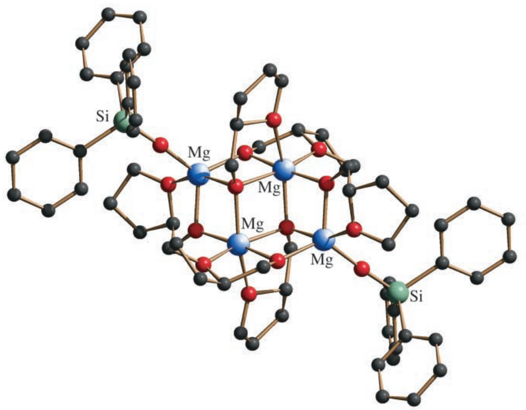


Fig. 8 A SCHAKAL view of complex **9**.

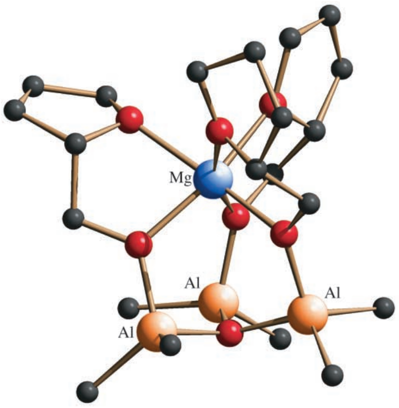
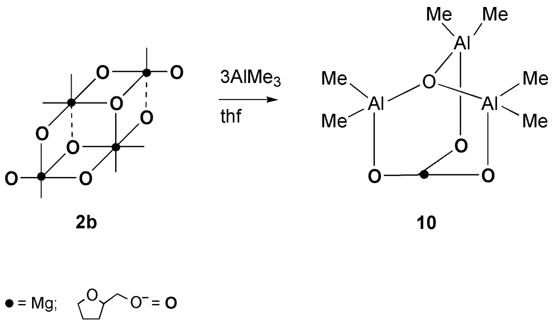


Fig. 9 A SCHAKAL view of complex **10**.



Scheme 7 Reactions of $[Mg_4(thffo)_8]$ with $AlMe_3$.

an assembly that is very similar to that of **8**. Three $AlMe_2$ moieties are held together by a μ_3-O oxygen atom to form a trinuclear $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ macrounit. The four-coordinated aluminium atom in **10** is surrounded by two methyl groups, one alkoxy μ_3-O atom and one alkoxy μ-O oxygen atom of a $[Mg(thffo)_3]^-$ moiety. The μ_3-O oxygen atom lies on a pseudo-3-fold axis and exhibits bond angles as expected for sp^2 hybridization $[116.42(9)°_{av}]$. Thus, the $Al_3(\mu_3\text{-}O)$ system is almost planar with the triply bridging oxygen being 0.35(1) Å out of the Al_3 plane. The Al–μ_3–O distances in **10** are similar to the corresponding bond lengths in $[Al_7O_6Me_{16}]^-$ and in $[\{(Me)_2Al(\mu_3\text{-}O)\text{-}Al(Me)_3\}_2]^{2-}$ anions.[42] The $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ cation could be considered as the undivisible part of methylaluminoxane (MAO) of general formula $[MeAlO]_n$. Some alkylaluminoxanes have been characterized crystallographically by Barron and co-workers,[43] who obtained them by partial hydrolysis of aluminium alkyls; thus, hydrolysis of $Al(^tBu)_3$ gave tetranuclear $[Al_4(\mu_3\text{-}O)_2(^tBu)_8]$.

Symmetry of procatalysts

It is widely accepted that the catalytic center responsible for isotactic polymerization of α-olefins is chiral. Its chirality can be derived from either chirality of the coordinated ligand or chirality of a metal site. Research activity on C_2-symmetric *ansa*-metallocenes has enormously accelerated since Brintzinger's development of C_2-symmetric *ansa*-zirconocene dichloride.[5] Those and other findings as well as conclusions derived therefrom directed our research into non-metallocene C_2-symmetry compounds that could act as active catalysts in isospecific polymerization. *cis*-$[TiCl_2\{C_2H_4(CO_2Et)_2\}_2][SbCl_6]_2$ was the first compound synthesized in our group that possessed a cation of C_2 symmetry.[44] We have also synthesized a series of chiral monometallic titanium alkoxides utilizing **2a** and **2b** and similar alcohols.[45]

It is very interesting to look at the earlier procatalysts from a stereochemical perspective. For instance when we consider the two magnesium parts in **7** to be chelating ligands then each vanadium atom with two such "magnesium ligands" and two terminal chlorines in *cis* position should be viewed as chiral. Nonetheless, since the molecule of **7** is centrosymmetric the complex must, unfortunately, be described as an unresolved *racemic* species. Interestingly we have synthesized a structurally analogous ethoxymagnesium–titanium compound $[Ti_2Mg_2(\mu_3\text{-}OEt)_2(\mu\text{-}OEt)_4(OEt)_6(EtOH)_4]$ in which the magnesium atoms are in chiral positions while the titanium atoms occupy non-chiral sites.[46]

Each zirconium atom in **8** also possesses two chlorine atoms in *cis* arrangement. Nonetheless each zirconium is seven-coordinated, which makes its nearest environment of C_1 symmetry.

Summary, conclusion, and outlook

As stated above, we were interested in determining the role of the reactive coordination site at the metal center in the Mg_4X_6 (X = Cl or OR) core. A series of magnesium open dicubanes was obtained in the reactions of dialkylmagnesium or magnesium turnings with bidentate O,O′ hydroxides. Crystallographic studies have shown that five- and six-coordinated metal sites are present in **2a**, **2b**, **3**, **6** and **9**. It has also been shown that five coordinate metal centers play a key role in complexation of incoming reagents and are very sensitive towards substitution. $[Ti(dipp)_4]$ and Ph_3SiOH are able to replace one of the μ-η^7 coordinated alkoxo ligands without splitting the dicubane framework and maintain coordinatively unsaturated magnesium centers. These magnesium centers can easily coordinate small molecules like MeOH.

The solid-state structures offer little assistance in the understanding of the reaction pathways involved in the formation of metal chiral centers. A plausible mechanism is shown in Scheme 8. We believe that the TiX_4 species blocks the reactive coordination site at the five-coordinate magnesium center in the Mg_4X_6 core, and compounds **11** and **12** are formed. These aggregates are insoluble and up to now it has been impossible to obtain them in a crystalline form. In **11** and **12** the titanium atom is bridge-bonded to the two five-coordinate magnesium atoms through two pairs of X (X = Cl or OR). Owing to the presence of these four bridging X atoms and two terminal X ligands in *cis* position, the geometry of coordination at the Ti atoms, in **11**, is chiral, and can be denoted as Δ or Λ according to IUPAC rules for chiral octahedral compounds.[47] As is apparent from Scheme 8, aggregate **11** is very similar to the Ti_2Cl_6 reliefs proposed earlier by Corradini and co-workers[2] as precursors of stereospecific active centers experimentally observed for the $TiCl_3/AlR_3$ and $TiCl_4/MgCl_2/AlR_3$ classes of catalysts.[11,48,49] Species **12** has a symmetry center, because the two terminal X atoms are in *trans* position and the titanium atom could be regarded as a non-stereospecific center. Up to now there is no crystallographic evidence for magnesium–titanium species of types **11** and **12**. However, for $MnCl_2$, which has similar properties to those of $MgCl_2$, the formation of species **13** is well

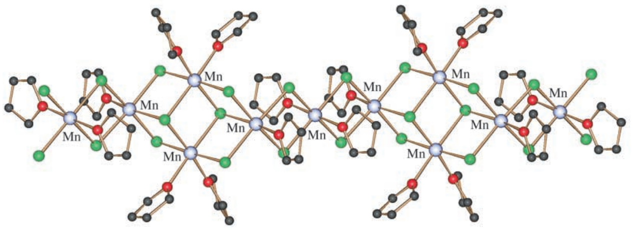
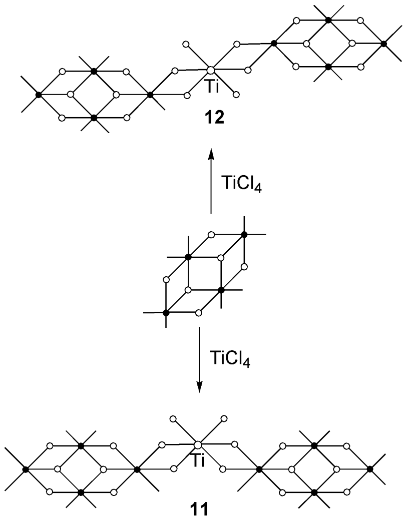


Fig. 10 A SCHAKAL view of complex **13**.



12

11

Scheme 8 Formation of chiral (**11**) and achiral (**12**) centers.

documented, *e.g.* $MnCl_2$ in the solid forms a polymer in which tetranuclear $[Mn_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4Cl_2(thf)_6]$ units are linked by μ-chloride bridges of $MnCl_2(thf)_2$ moieties as shown in Fig. 10.[50] The two thf molecules are in *trans* position.

We have for the first time demonstrated that magnesium alkoxy species could be grafted by ≡SiOH groups to form complex **6**. Moreover, in reaction of the $AlMe_3$ with the magnesium species the methylaluminoxane $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ macrounit is formed. This can be trapped by magnesium species as the molecular solid **10**.

The atom arrangement in the presented magnesium alkoxides seems also important in view of the fact that magnesium compounds with a Mg_4X_6 core are used as commercial catalyst components and are good additives boosting the activity of the catalytic mixture.[51] Our preliminary results in an ethylene polymerization test on $[Mg_4(\mu_3\text{-}\eta^2\text{-thffo})_2(\mu\text{-}\eta^2\text{-thffo})_4Cl_2]/TiCl_4/AlEt_3$ catalyst gave *ca.* 170 kg polyethylene per g Ti h^{-1} while only 11.6 kg were obtained under the same conditions when $MgCl_2/TiCl_4/AlEt_3$ catalyst was used.

As can be seen from the present Perspective our attempts to prepare new polynuclear procatalysts and understand the chemistry of these new complexes often led to unexpected reactions, which could be applied to syntheses of well defined heterogeneous olefin polymerization catalysts. Further experiments are being planned. In the next step we will "complicate" the system and aim at the synthesis of Si/Mg_4/Ti/Al species. Also transition metals other than titanium, vanadium and zirconium will be investigated. Recent discoveries on non-metallocene iron and cobalt olefin polymerization catalysts demonstrate that there is no limit in terms of metal site that can give a polymerization active center. We strongly believe that careful and rational ligand design can create enormous possibilities.[52]

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