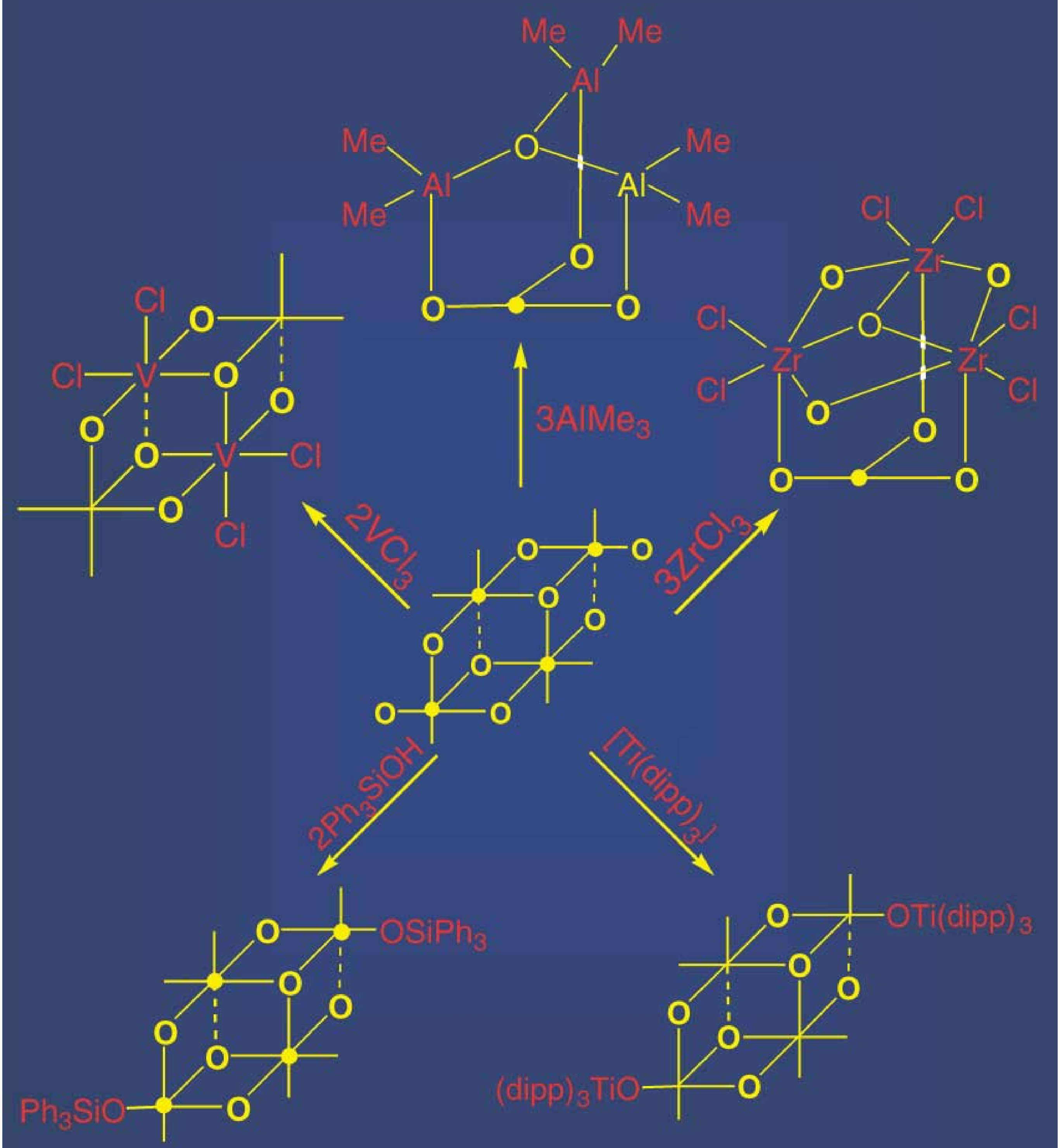
Ziegler–Natta Catalyst Intermediates



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Structure and Reactivity of Ziegler–Natta Catalyst Intermediates

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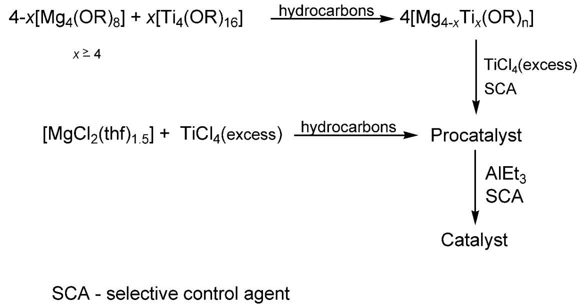
Abstract: This paper provides a survey of our recent research on chemistry that occurs among components of Ziegler–Natta catalysts. Since the amount of information regarding this topic is enormous we have focused on alkoxo compounds, which are attracting more and more attention in polymer industry. In this concept article we discuss recent studies on the inherently very complex catalyst system that involve isolation of various solid polynuclear metal-containing species, determination of their structures by X-ray crystallography, and relating their structures to the activity in polymerization. The presented research may be useful in predicting trends for the development of new single-site catalysts as well as new co-catalysts.

Keywords: alkoxides · alumoxanes · polymerization · structure elucidation · Ziegler–Natta catalysis

Introduction

Ziegler–Natta (Z-N) catalysis is consistently one of the most important and profitable petrochemical processes.[1] Over the years, the catalyst has evolved from simple $TiCl_3$ crystals into the nowadays used high-technology system based on the use of magnesium dichloride as a support for $TiCl_4$.[2] Although commercial implementation of homogeneous metallocene catalysts in polyolefin production[3] is often impractical, they can be heterogenized for efficient gas-phase or flow-through reaction by attaching them to a solid support.[4a] The Z-N catalysts are heterogeneous systems, with respect not only to the insolubility of the catalyst in the polymerizing medium, but also to its multisite nature, each of which has its own rate constants for monomer enchainment, stereoselectivity, co-monomer incorporation, and chain transfer.[4b] A few generations of Z-N catalysts have already been developed.[5] Each generation has contributed to higher productivity of the process and, quite often, to significant improvement of the stereospecifity of the α-olefin polymerization.[6] The result is catalysts that are difficult to study and understand, and that produce complex polymer mixtures with widely varying molecular weights and microstructures.[7]

High activity, heterogeneous, and stereoregular α-olefin polymerization catalysts can be produced from a solid species that typically contain titanium and magnesium moieties, a selective control agent (SCA), and an organoaluminum co-catalyst (Scheme 1). Other than titanium, transition metals that are often used for procatalyst formation include zirconium, chromium, and vanadium.[8] In this concept article we discuss our recent studies on the incorporation of various species in this inherently very complex $MX_x/MgX_2/AlR_3$ ($M = Ti, Zr, V$; $X = OR$ or Cl; $x = 3$ or 4) catalyst system; these involve isolation of various solid polynuclear metal-containing species, determination of their structures by X-ray crystallography and relating their structures to the activity in polymerization. Also interactions of alumoxane and silica supports with magnesium complexes have been investigated.



Scheme 1. Reaction scheme of heteregenous olefin polymerization catalyst formation.

Discussion

Magnesium components: As mentioned before the most widely used magnesium component is $MgCl_2$, which was considered as a support until 1984, when the formation of the salt $[Mg_2(\mu\text{-}Cl)_3(thf)_6][TiCl_5(thf)]$ in reaction of magnesium dichloride with $TiCl_4$ was first announced.[9a] This reaction shows that in tetrahydrofuran (THF) $MgCl_2$ is not a simple

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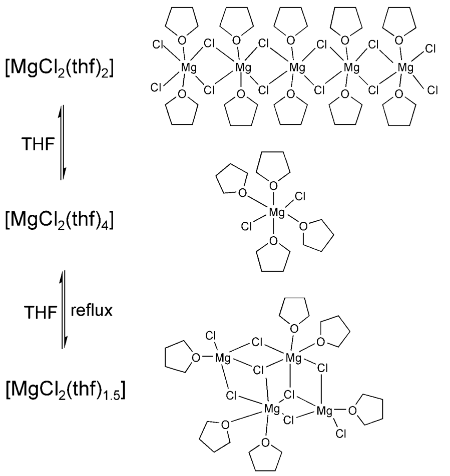
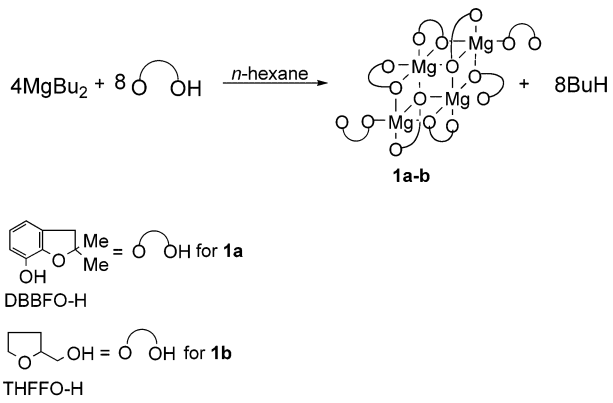
support but a Cl^- donor and is a highly reactive species. Note that the $[Mg_2(\mu\text{-}Cl)_3(thf)_6][TiCl_5(thf)]$ supported on SiO_2 together with organometallic co-catalyst is used as a commercial ethylene polymerization catalyst.[8a] Anhydrous $MgCl_2$ has been known in two crystal modifications: α-$MgCl_2$ and β-$MgCl_2$. The high-temperature α-$MgCl_2$ is produced by dehydration of $MgCl_2 \cdot 6H_2O$ in a flow of HCl at about 990 K followed by vacuum distillation.[10a] β-$MgCl_2$ is prepared by dehydration of $MgCl_2 \cdot 6H_2O$ in refluxing $SOCl_2$.[10b] Ball-milled $MgCl_2$ used as "support" could be regarded as a mixture of both forms.

For a deeper understanding of the influence of solvent/coordination ability on the reaction pathway and final product formation, we studied the $MgCl_2$ behavior in tetrahydrofuran. It was found that the crystalline $[MgCl_2(thf)_2]$ is a linear polymer[10c] and remains in equilibrium with $[MgCl_2(thf)_4]$ and $[MgCl_2(thf)_{1.5}]$[9b] (Scheme 2). Compounds $[MgCl_2(thf)_2]$ and $[MgCl_2(thf)_{1.5}]$ are used as ethylene and propylene catalyst components, respectively.[2, 5, 6]



Scheme 2. Reaction equilibrium of $MgCl_2$ with tetrahydrofuran.

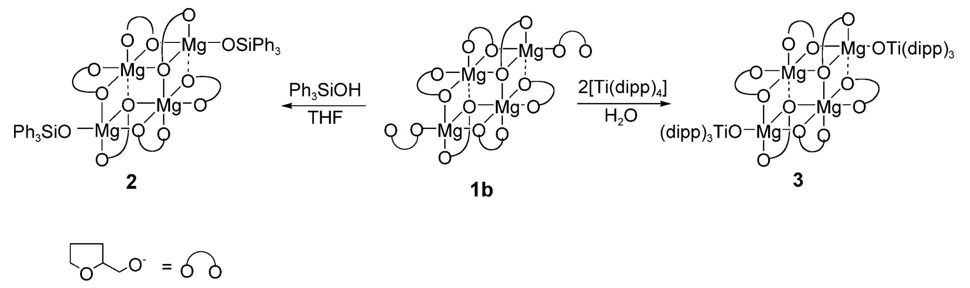
Magnesium alkoxides: It is already known that catalysts based on $MgCl_2$ and $Mg(OR)_2$ have comparable activity, and polymers derived from them have similar properties. Nonetheless, morphology of the alkoxo catalyst is much better in terms of particle shape.[11] It is also easier in the case of alkoxo ligands to obtain procatalyst in a crystalline form. Recently, we have been developing the magnesium chemistry of the chelating ligands 2,3-dihydro-2,2-dimethyl-7-benzofuran alcohol (DBBFO-H) and tetrahydrofurfuryl alcohol (THFFO-H) (Scheme 3). Deprotonation of these alcohols affords bidentate O,O′-monoanions, henceforth abbreviated as DBBFO and THFFO. With two oxygen donor atoms, ether and alkoxo, they can act not only as chelate ligands and occupy two coordination sites on the metal, but also they can act as a tether between metal atoms in μ_3,η^2, μ,η^2, μ_3,η^1, or η^1 modes to create multinuclear species.[12]



Scheme 3. Typical reaction of bidentate *O,O′*-alkoxy ligands with $MgBu_2$.

Reactions of DBBFO-H and THFFO-H with di-*n*-butyl magnesium or magnesium turnings give complexes of $[Mg_4(dbbfo)_8]$ (**1a**) and $[Mg_4(thffo)_8]$ (**1b**) stoichiometry. Crystal structure analysis of **1a** shows a tetranuclear molecule with an open dicubane geometry (Scheme 3). A molecule of **1a** possesses two five-coordinate magnesium atoms of trigonal biypiramid geometry and two six-coordinate octahedral metal sites.[12] The presence of coordinatively unsaturated metal sites is the most interesting feature of these compounds. It must be underlined that the open dicubane structure of **1a** is quite similar to the structure of the magnesium part of some of the theoretically deduced catalyst models.[13] In these models, the (110) surface of $MgCl_2$ 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; this an important phenomenon that occurs in the homogeneous systems. The X-ray study of crystals of magnesium methoxide obtained in the direct reaction of magnesium with MeOH allowed the formulation of the product as $[Mg(OMe)_2] \cdot 3.5\,MeOH$. Its structure consists of four tpyes of units: $[Mg_4(\mu_3\text{-}OMe)_4(OMe)_4(MeOH)_8]$ neutral cubane, $[Mg_4(\mu_3\text{-}OMe)_4(OMe)_2(MeOH)_{10}]^{2+}$ cubane ions, $[(MeO)_2H]^-$ ions, and eight crystallographically independent non-coordinated solvating methanol molecules.[14] The structure of $[Mg(OEt)_2]$ is unknown.

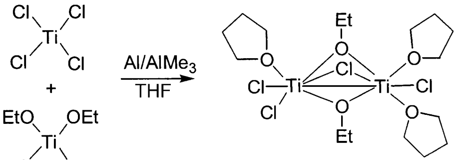
Reaction of magnesium open dicubanes with catalyst components: In Z-N methodologies, the SiO_2 surface is treated with MgX_2 (X = Cl or OR) followed by reaction with a titanium species. To reveal the interaction of the silica surface ≡Si-OH groups with the magnesium catalyst component we have studied the binding of Ph_3SiOH, used as a surface model, to the unsaturated magnesium centers in **1b**. The direct reaction of dicubane-like tetramer **1b** with Ph_3SiOH in toluene, gives $[Mg_4(thffo)_6(OSiPh_3)_2]$ (**2**).[15] We have found also that a similar compound $[Mg_4(thffo)_6\{OTi(dipp)_3\}_2]$ (**3**) could be obtained by controlled hydrolysis of the reaction product formed between **1b** and $[Ti(dipp)_4]$ (dipp = 2,6-diisopropylphenoxo group).[12] In the formation of **2** and **3**, two of the η^1-coordinated THFFO ligands of **1b** undergo substitution by $OSiPh_3$ and $OTi(dipp)_3$ without splitting the dicubane framework and maintaining coordinately unsaturated magnesium centers (Scheme 4). The $\{Mg_4(thffo)_6\}$ core in **2** and **3** is the same. The difference is that the two $OSiPh_3$ groups that bond to the five-coordinate magnesium atoms in **2** are replaced by two $OTi(dipp)_3$ groups in **3**.



dipp = 2,6 - diisopropylphenoxo group

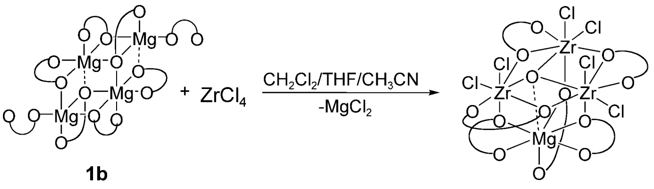
Scheme 4. Reactions of **1b** with [Ti(dipp)$_4$] and Ph$_3$SiOH.

The catalyst based on titanium species is very complex and nothing is known about its intermediates.[2, 5, 6] Red [Ti$_2$(μ-OEt)$_2$(μ-Cl)Cl$_3$(thf)$_3$] (**4**) was obtained in the reaction of an equimolar mixture of TiCl$_4$, Ti(OEt)$_4$, Al, and AlMe$_3$ in THF. The dimeric structure of **4** is composed of two TiCl(thf)$_2$ and TiCl$_2$(thf) moieties bridged by two μ-OEt and one μ-Cl ligands (Scheme 5). The short distance (2.599(1) Å) between "Ti^{III}" atoms, their diamagnetism, and ELF analysis indicate the presence of a Ti–Ti bond.[16] Reduction with only Al or AlMe$_3$ gave an oily product, the purification of which was demanding and eventually gave a "problematic" result. TiCl$_4$ cannot be efficiently reduced to TiCl$_3$ by AlMe$_3$ and that is why in the first step Al is used. Aluminum does not reduce Ti(OEt)$_4$, therefore one equivalent of AlMe$_3$ is needed. Addition of more that one equivalent of AlMe$_3$ leads to the formation of a species that contains a Ti–Me bond. Further studies are necessary to determine possible incorporation of **4** into catalytic cycles.

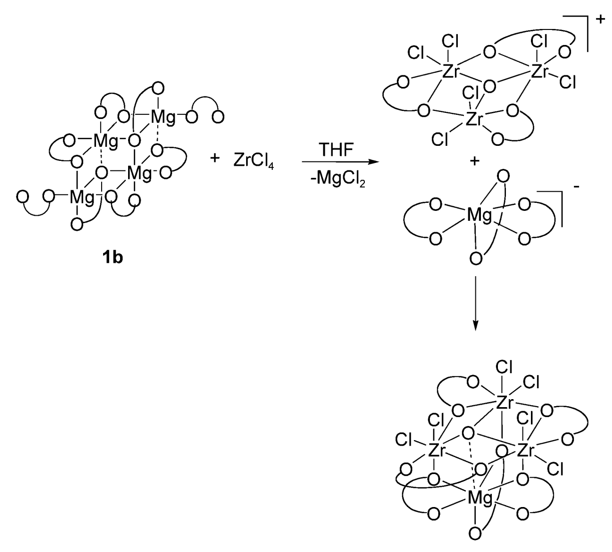


Scheme 5. Non-organometallic titanium(III)alkoxo-bridged dinuclear complexes.

In contrast to the titanium reactions, treatment of **1b** with ZrCl$_4$ leads to a different reaction course.[17] ZrCl$_4$ reacted with **1b** in a mixture of CH$_2$Cl$_2$, THF, and CH$_3$CN to give a thermally stable neutral heterobimetallic tetranuclear complex [Zr$_3$Mg(μ_3-O)(μ,η^2-thffo)$_6$Cl$_6$] (**5**, Scheme 6). In this complex molecule three zirconium atoms form a nearly regular triangle that is held together by a μ_3-O ligand to give motif of C_3 symmetry. Each zirconium is additionally surrounded by two terminal chlorine atoms, one ether oxygen atom of the THFFO ligand, and three bridging μ-O atoms of three THFFO ligands. Six oxygen atoms of three tetrahydrofurfuroxo ligands form a slightly distorted octahedron around a magnesium center. Formation of complex **5** can be considered to proceed by ionic mechanism. According to this, **5** is formed by entrapment of trinuclear [Zr$_3$(μ_3-O)(μ,η^2-thffo)$_3$Cl$_6$]$^+$ ions by one [Mg(thffo)$_3$]$^-$ ion to give [Zr$_3$Mg(μ_3-O)(μ,η^2-thffo)$_6$Cl$_6$] (**5**) (Scheme 7).[17] Next, we attempted to "replace" Mg^{2+} in **5** by AlMe$_3$. The precursor [Zr$_4$(μ_4-O)(μ-OMe)$_6$Cl$_8$(thf)$_4$] (**6**) was obtained through the direct reaction of ZrCl$_4$ with methanol. When **6** was allowed to react with AlMe$_3$ in THF [Zr$_3$Al(μ_4-O)(μ-OMe)$_6$Cl$_6$(Me)(thf)$_3$] (**7**) was isolated.[18] The significant difference between **6** and **7** is that one of the [ZrCl$_2$(thf)]$^{2+}$ moieties coordinated to a μ_4-O atom in **6** is substituted by an [Al-Me]$^{2+}$ unit in **7** (Scheme 8). Preliminary tests of catalytic properties of **7** for ethylene polymerization have indicated no activity. This result agrees with our presumptions due to lack of a Zr–CH$_3$ bond in **7**.

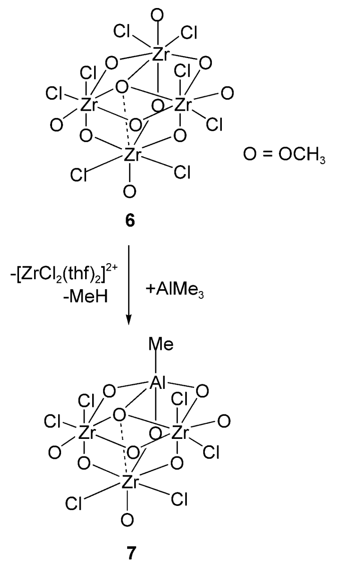


Scheme 6. Synthesis of **5**.



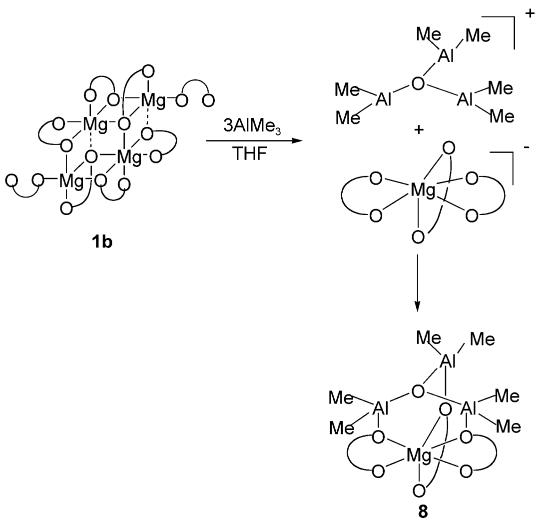
Scheme 7. Possible mechanism formation for **5**.

Reaction of magnesium open dicubanes with AlMe$_3$: We have shown that from the reaction of **1b** with AlMe$_3$ the methylalumoxane [Al$_3$(μ_3-O)(Me)$_6$]$^+$ moiety is formed; this was isolated and characterized as the compound [Al$_3$Mg(μ_3-O)(thffo)$_3$(Me)$_6$] (**8**).[15] The tetranuclear Al$_3$/Mg compound forms an assembly that is very similar to that of **7**. Three AlMe$_2$ moieties are held together by oxygen atom to form a

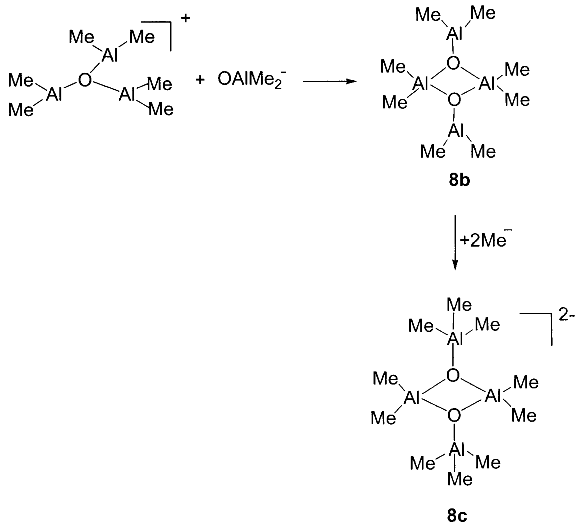


Scheme 8. Trapping of AlMe$_3$ with oxygen atom of the Zr$_3$(μ_3-O) unit.

trinuclear methylalumoxane [Al$_3$(μ_3-O)(Me)$_6$]$^+$ macrounit (Scheme 9). Formation of products containing a "lone" triply bridging μ_3-O atom that is encapsulated in ensembles of three or more metal atoms is often observed during reactions of alkoxides with alcohols.[19] The [Al$_3$(μ_3-O)(Me)$_6$]$^+$ ion can be considered as one among many unstable methylalumoxane intermediates trapped by [Mg(thffo)$_3$]$^-$ as a molecular solid. The compound illustrates nicely the delicate balance between packing efficiency, electronic requirements, and ionic pair interaction. The factor governing the stability of such intermediates is not yet well understood.[20] The problem has been overcome by comparison of [Al$_3$(μ_3-O)(Me)$_6$]$^+$ ion with the corresponding known tetranuclear compound [Al$_4$(μ_3-O)$_2$(*t*Bu)$_8$] (**8a**)[21] and [{(Me)$_2$Al(μ_3-O)Al(Me$_3$)}$_2$]$^{2-}$ ion.[22] We believe that the related compound [Al$_4$(μ_3-O)$_2$(Me)$_8$] (**8b**) could be formed from [Al$_3$(μ_3-O)(Me)$_6$]$^+$ ion by addition of an OAlMe$_2^-$ ion. As shown in Scheme 10 compound **8b** contains two four- and two three-coordinate aluminum atoms. The **8a** species with bulky *t*Bu groups is stable and could be isolated as solid. In contrast, methylation of **8b** results in the formation of the [{(Me)$_2$Al(μ_3-O)Al(Me$_3$)}$_2$]$^{2-}$ (**8c**) ion.

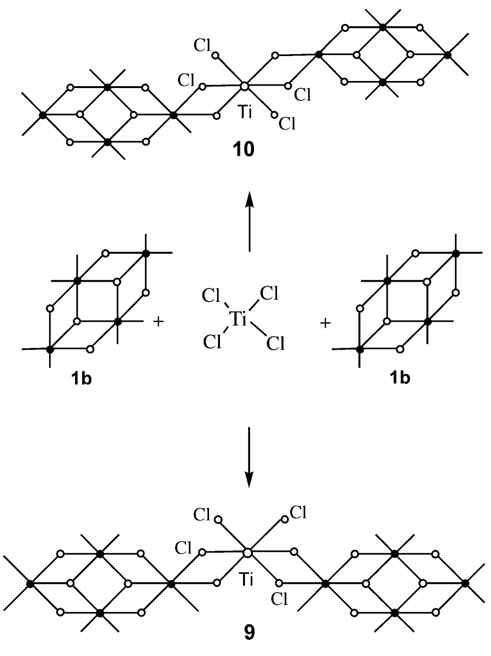


Scheme 9. Reaction of "dicubane-like" **1b** with AlMe$_3$.



Scheme 10. Reactivity of methylalumoxane [Al$_3$(μ_3-O)(Me)$_6$]$^+$ unit.

Chiral metal-site formation: It is widely accepted that catalytic center responsible for isotactic polymerization of α-olefin is chiral. Its chirality can be derived from either the chirality of a metal site or from the chirality of the ligand that is coordinated to a metal center. A plausible mechanism of the reactions involved in the formation of metal chiral centers is shown in Scheme 11. We believe that the TiCl$_4$ species block the reactive coordination sites at the five-coordinate magnesium center in the Mg$_4$Cl$_6$ core, and compounds **9** and **10** are



Scheme 11. Formation of chiral (**9**) and achiral (**10**) centers.

formed. In our model the titanium atom is bound by Cl bridges to the two five-coordinate magnesium atoms through two pairs of Cl atoms. Owing to the presence of these four bridging Cl atoms and two terminal Cl ligands in the *cis* position, the geometry of coordination at the Ti atoms in **9** is chiral. As is apparent from Scheme 11, aggregate **9** is very similar to the Ti_2Cl_6 pattern proposed earlier by Corradini[23] as precursors of stereospecifically active centers experimentally observed for the $TiCl_3/AlR_3$ and $TiCl_4/MgCl_2/AlR_3$ classes of catalysts.[4–6] Species **10** has a symmetry center, because the two terminal Cl atoms are *trans* to each other and the titanium atom could be regarded as a nonstereospecific center. These aggregates are insoluble, and up to now it has been impossible to obtain them in a crystalline form. However, for $MnCl_2$, which has similar properties to $MgCl_2$, the formation of species **10** is well documented, for example, solid $MnCl_2$ forms a polymer in which $[Mn_4Cl_6(thf)_6]$ units are linked by μ-chlorine bridges of $MnCl_2(thf)_2$ moieties similar to those in **10**.[24]

Conclusion and Outlook

As illustrated in the above examples, our attempts to prepare new polynuclear procatalysts and to understand the chemistry of their formation often led to findings of unexpected reactions, which could be applied to syntheses of well-defined heterogeneous olefin polymerization catalysts. Further experiments are being planned. We propose to investigate $[Al_3Mg(\mu_3\text{-}O)(thffo)_3(Me)_6]$ (**8**) as a metallocene and non-metallocene support and as a methylation agent. We have good in-house examples that species **8** works excellently with $[ZrCp_2Cl_2]$ or $[TiCl_2(L^2)]$, and compounds $[Al_3Mg_3(\mu_3\text{-}O)(thffo)_4(Me)_5Cl_4(thf)]$ (**11**) and $[TiMe_2(L^2)]$ (**12**) (L^2 = 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol)), respectively, are formed.[25] $MgCl_2$ formation is a driving force of these reactions. We believe that in situ formed $MgCl_2$ could be very important for isotactic propylene polymerization process. Currently, we speculate that Me^- group may be transferred form $[ZrCp_2Me_2]$ to coordinatively unsaturated aluminum atom in species **8a** and that the ion pair $[ZrCp_2Me]_2[\{(\text{-}Me)_2Al(\mu_3\text{-}O)Al(Me_3)\}_2]$ could be formed.[20]

Recent discoveries on non-metallocene iron and cobalt olefin polymerization catalysts prove that there is no limit in terms of the metal site that can give a polymerization active center.[26] We strongly believe that careful and rational ligand design can create enormous possibilities.

Acknowledgement

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