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Review

Metal-assembled compounds: precursors of polymerization catalysts and new materials

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Contents

Abstract

Selected results of our recent research on titanium, zirconium, hafnium and magnesium chloride and oxygen-based metal-assembled compounds are summarized from the perspective of these metals acting as catalysts for olefin polymerization. This paper discusses our studies on the isolation of various metal-assembled compounds, the determination of their structures by X-ray crystallography and the relationship of their polynuclear structures to their activity as polymerization catalysts as well as to the field of molecule-functional-based materials. As we demonstrate here, our attempts to prepare new metal-assembled pre-catalysts and to understand the chemistry of formation of these new complexes often led to unexpected reactions, which could be applied to syntheses of well-defined heterogeneous olefin polymerization catalysts.

Keywords: Alkoxides; Alumoxanes; New materials; Polymerization; Structure elucidation; Ziegler–Natta catalysis

1. Introduction

The last decades of research on olefin polymerization catalysis were dominated by metallocene complexes of early transition metals which were first introduced to olefin polymerization more than 40 years ago [1]. Such complexes activated by methylalumoxane (MAO) form highly active homogeneous catalysts which produce polymers with a narrow molecular weight distribution. Continuous search for novel catalysts resulted in the development of constrained-geometry catalysts [2] and a variety of non-metallocene complexes of metals across the periodic table [3]. An extraordinary amount of research has been directed toward the development of homogeneous, single-site polymerization catalysts [1,2]. These molecular compounds have the general formula LnMR, where Ln is an organic ligand set that remains bound to, and thus modifies the reactivity of the active metal center (M) during the entire chemical reaction; R is the polymer or initiating group. Before the recent discovery by Gibson and coworkers [4], Brookhart and coworkers [5] and Bennett [6] of the potent catalytic activity of electron-rich late metals which has

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revolutionized our way of thinking in this field, the paradigm requiring highly acidic metals for a functional catalyst has traditionally dominated the Ziegler–Natta (Z–N) catalysis scene. Heterogeneous catalysts typically have multiple active sites, each of which has its own rate constant for monomer enchainment, stereoselectivity, co-monomer incorporation, and chain transfer [7].

Alkoxo compounds have also attracted a lot of attention [8]. Due to their acid–base properties, they are important in many organic reactions such as oxidation of alcohols [9], allylation of aldehydes [10], Diels–Alder reaction [11], and many others [12]. They are especially important in enantioselective catalysis, one of the most important areas of synthetic organic chemistry [13]. Transition metal alkoxides have found widespread applications in many fields of technology [14], for example, in the sol–gel process to synthesize glasses, in ceramics and inorganic–organic materials [15], in metallo-organic chemical vapor deposition (MOCVD) [16], in the preparation of hydraulic liquids in oil exploration [17] as a crosslinker of polysaccharides, and in coatings of paper and textile [14]. Polyesters, coatings, and films are ubiquitous engineering materials. Although the vast majority of catalysts are designed for olefin polymerization, the extension of this area of catalysis for the polymerization of other monomers, such as lactones and epoxides, is already in progress. The most common metal-containing catalysts are metal alkoxides [18].

Ziegler–Natta catalysis is consistently one of the most important and profitable petrochemical processes [19]. Over the years, from simple $TiCl_3$ crystals, the catalyst has evolved into the currently used high-technology system based on the use of magnesium dichloride as a support for $TiCl_4$ [20]. The pro-catalysts mainly comprise MgX_2 and TiX_4 (X = Cl or OR). The electron donor compound, whether used separately or with pro-catalyst (as internal donor) or organoaluminum compound (as external donor) is referred to as “selectivity control agent” (SCA). The organoaluminum compound, whether used separately or partially or totally complexed with an SCA, is referred to as “co-catalyst”. Each of these components influences the catalyst and polymer produced therefrom but the pro-catalyst seems to have the greatest impact. Therefore, such catalyst is referred to as “supported coordination catalyst” or “supported coordination catalyst system”. This catalytic system is the most advanced method in industrial applications, guaranteeing very high yields and the highest stereochemical control of the polymers obtained [21]. Great interest is now focused on attempting to understand the structure of active sites [22]. The oxygen-based ligands support a very high level of catalytic activity. However, ligand abstraction and reduction of Ti(IV) to Ti(III) or V(III) to V(II) by co-catalyst constitute the main obstacle for the development of a competitive heterogeneous single site catalysts [23].

In this work, the behavior of some Mg and Ti, Zr and Hf complexes of different ligands systems based on Cl and O donor ligands will be reviewed.

2. Ligands

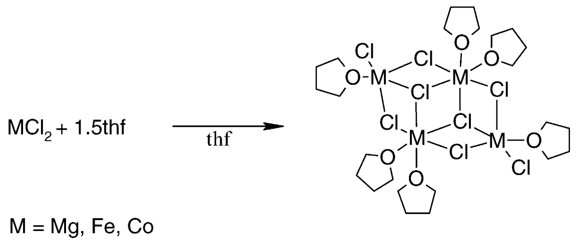
The starting point of our research in this field was a study of the commercially used $MX_4/MgX_2/AlR_3$ (M = Ti, Zr; X = Cl, OR) system. The aim was to understand the role of each catalyst component in sustaining the activity as well as those factors that control the catalyst stability. For this we synthesized a series of magnesium MgX_2 species bearing rather diversified substituents. The most widely used certainly are the magnesium halides and alkoxides.

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. The morphology of the catalyst and resulting polymer is technologically crucial. For example, the 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 pro-catalyst with well-defined stoichiometry.

As mentioned before, the most widely used magnesium pro-catalyst component is $MgCl_2$. The most commonly used SCA for ethylene polymerization is tetrahydrofuran [24]. The use of $MgCl_2$/EtOH adducts with a restricted range of composition yields, after inserting the $TiCl_4$, a most efficient and selective catalytic system for isotactic propylene polymerization. EtOH associates easily with $MgCl_2$ to form different adducts of complex architecture [25]. For propylene polymerization, aromatic esters such as ethyl benzoate, ethyl anisate, and diisobutyl phthalate are often used [26]. Others include ethyl acetate [27], ethyl chloroacetate [28], phosphorus oxychloride [29], and silanes. Addition of the above-mentioned 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. All these ligands form a family of moderately weak Lewis bases and establish good leaving groups. These facts and other observations convinced us that alkoxy ligands could also play the role of SCA. For this purpose, we synthesized a series of metal compounds bearing rather diversified ligands. In our research, we mainly utilize commercially available 2,3-dihydro-2,2-dimethylbenzofuran-7-ol (dbbfo-H), 1-methoxy-2-propanol (mpro-H) and tetrahydrofurfuryl alcohol (thffo-H). Among the several advantages offered by these ligands (large variety of substituents, electronic flexibility, etc.) the ability to form crystalline metal ion compounds suitable for X-ray diffraction studies, was particularly attractive.

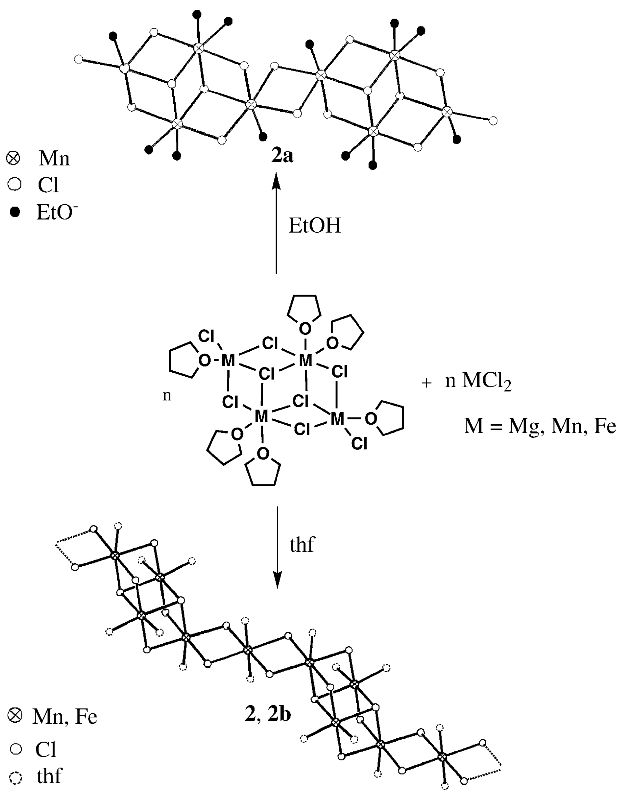
3. Chloride-based metal-assembled compounds

The frequently dramatic and sometimes beneficial influence of electropositive metal species such as MgX_2 (X = Cl,



Scheme 1. $[M_4(\mu_3\text{-Cl})_2(\mu\text{-Cl})_4(thf)_6]$ type compound with open dicubane-like structure [32–34].

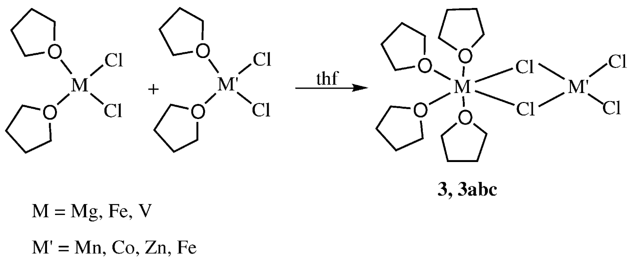
OR) on the polymerization activity of early-transition-metal compounds is widely recognized [30] but poorly understood [31]. $MgCl_2(thf)_{1.5}$, as a catalyst component, is especially attractive for studying the factors which favor the polynuclear aggregation of magnesium dichloride with $TiCl_4$. Until now, only the structures of $[M_4Cl_8(thf)_6]$ (M = Fe, Co and Mg) have been well documented [32–34]. The metal species exist as centrosymmetric tetranuclear $[M_4(\mu_3\text{-Cl})_2(\mu\text{-Cl})_4X_2(thf)_6]$ (X = Cl for M = Fe [32], Co [33], X = Et for M = Mg [34]) compounds with two different types of M(II) centers corresponding to six-coordinate octahedral MCl_4O_2 and five-coordinate trigonal bipyramidal MCl_4O chromophores (Scheme 1). The structure of $MgCl_2(thf)_{1.5}$ species is unknown, but is probably similar to that found for $[Mg_4(\mu_3\text{-Cl})_2(\mu_2\text{-Cl})_4Et_2(thf)_6]$ (**1**) [34].



Scheme 2. Reaction scheme for the preparation of metal-assembled polymeric $[\{Mn_5Cl_{10}(thf)_6\}_n]$ (**2**), $[Mn_4Cl_8(EtOH)_6]_n$ (**2a**), and $[\{Fe_5Cl_{10}(thf)_6\}_n]$ (**2b**), and compounds [35,36].

$MgCl_2(thf)_{1.5}$ has limited solubility and until now could not be obtained in crystalline state. With this in mind, we have been studying the reactivity of manganese $MnCl_2$ which has similar properties to $MgCl_2$. It was expected that these investigations would help in understanding the behavior of metal dichlorides toward the transition metals and furnish useful relationships between structure and activity. Anhydrous $MnCl_2$, when heated under reflux in tetrahydrofuran, yields a colorless compound of composition $MnCl_2(thf)_{1.6}$ (**2**) [35a]. An X-ray study revealed **2** to be the polymer $[\{Mn_5Cl_{10}(thf)_6\}_n]$ formed by the tetranuclear $[Mn_4(\mu_3\text{-Cl})_2(\mu_2\text{-Cl})_4Cl_2(thf)_6]$ building block linked by $MnCl_2(thf)_2$ moieties. As outlined in Scheme 2, the reaction of $MnCl_2$ with EtOH afforded a polymeric $[Mn_4Cl_8(EtOH)_6]_n$ (**2a**) species. The **2a** is built up of chains of $[Mn_4Cl_8(EtOH)_6]$ blocks linked by μ-Cl chlorine bridges [35b]. $[Fe_4Cl_8(thf)_6]$ (**2b**) as reported by Leigh and coworkers contains the same essential basic blocks as **2** and may be converted formally into polymeric $[\{Fe_5Cl_{10}(thf)_6\}_n]$ (**2b**) by replacing thf on the five coordinate iron atom in $[Fe_4Cl_8(thf)_6]$ by $FeCl_2(thf)$ or $CoCl_2(thf)$ moieties [36]. Subsequently, we isolated and completely characterized two more Mg/Mn and Mg/Fe complexes. The reaction between anhydrous $MgCl_2$ and $MnCl_2$ or $FeCl_2$ in refluxing thf produced $[MgMnCl_4(thf)_4]$ (**3**) and $[MgFeCl_4(thf)_4]$ (**3a**), respectively. An X-ray study revealed **3** and **3a** to be $[(thf)_4Mg(\mu\text{-Cl})_2MnCl_2]$ and $[(thf)_4Mg(\mu\text{-Cl})_2FeCl_2]$, respectively (Scheme 3). The magnesium atom in **3** is six-coordinate and the manganese atom four-coordinate, the octahedron and tetrahedron being linked by two chloride bridges.

The bimetallic molecular species **3** has an approximate two-fold rotational axis of symmetry passing through both metals, and the $MgMnCl_4O_4$ core has approximate C_{2v} molecular symmetry. There is a remarkable similarity in the molecular structures of **3**, to $[(thf)_4Mg(\mu\text{-Cl})_2FeCl_2]$ (**3a**) [36], $[(thf)_4Fe(\mu\text{-Cl})_2CoCl_2]$ (**3b**) [37a], and $[(thf)_4V(\mu\text{-Cl})_2ZnCl_2]$ (**3c**) [38]. Although the vanadium compound **3c** compared to **3** involves an inverted role for the transition metal and the electropositive metal, the similarity of structures even extends to very similar (±0.08(1) Å) metal–ligand bond lengths. Recrystallization of $[(thf)_4Fe(\mu\text{-Cl})_2CoCl_2]$ from $CHCl_3$/EtOH yielded $[\{(EtOH)_4Fe(\mu\text{-Cl})_2CoCl_2\}_n]$ (**3d**)



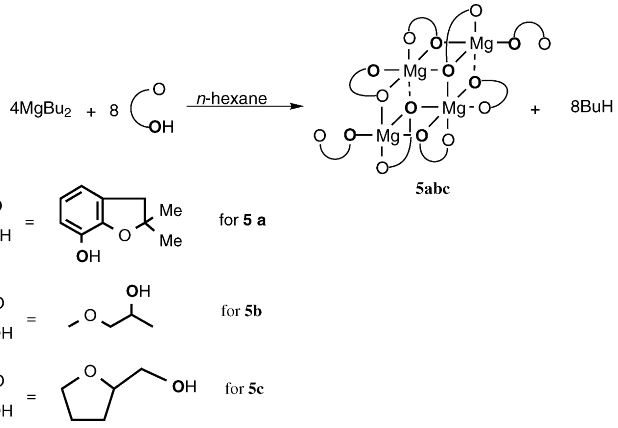
Scheme 3. Reaction scheme for the preparation of bimetallic molecular species **3** and **3abc** [36–38].

and its structure was determined crystallographically. Complex $[\{(EtOH)_4Fe(\mu\text{-}Cl)_2CoCl_2\}_n]$ is polymeric in the solid state. The Co atoms lie on crystallographic two-fold axes, and this generates infinite chains of alternating $CoCl_4$ and $Fe(C_2H_5OH)_4$ units linked by single Cl bridges [36]. By contrast, the salt $[Mg(H_2O)_2(thf)_4][Mg(H_2O)_4(thf)_2][MnCl_4]_2$ (**4**) was obtained by two routes, the first being accidental. Treatment of $MgCl_2$ with $MnCl_2$ in thf yields salt **4**. The origin of the water in **4** is probably wet $MnCl_2$ being used. Having established the structure of salt **4**, we sought a rational synthesis of this compound and found that it can be obtained in high yield by treatment of anhydrous $MgCl_2$ and $MnCl_2$ in thf with 3 equiv. of H_2O [35a]. The crystals of **4** are composed of centrosymmetric $[Mg(H_2O)_2(thf)_4]^{2+}$ and $[Mg(H_2O)_4(thf)_2]^{2+}$ cations and $[MnCl_4]^{2-}$ anions in a 1:1:2 ratio. In conclusion, we see (1) the great tendency of manganese, iron, cobalt, magnesium, and vanadium atoms to form tetranuclear species with M_4Cl_6 cores, (2) that manganese and iron [36] tend to form polymeric species **3d** while cobalt, and magnesium prefer the formation of tetranuclear $[M_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Cl_2(thf)_6]$ blocks, (3) that the magnesium atom shows a clear preference for six-coordination and manganese, iron, and zinc atoms prefer four-coordination, (4) that the higher solubility of the Mg or Mn halides leads to a coordination of $MCl_2(thf)_2$ at the five-coordinate metal center in the M_4Cl_6 core (Scheme 2), and (5) that the formation of ionic or molecular species in thf depends on the oxidation state of the metal M^{n+}.

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 reaction of magnesium dichloride with $TiCl_4$ was first announced [37b]. This reaction shows that in polar solvents $MgCl_2$ is not a simple support but a Cl^- donor and is a highly reactive species. Alternatively, dimeric cationic species such as $[V_2(\mu\text{-}Cl)_3(thf)_6]^+$ [38] and $[Fe_2(\mu\text{-}Cl)_3(thf)_6]^+$ [39] can also be isolated. 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 [37b].

4. Oxygen-based metal-assembled compounds

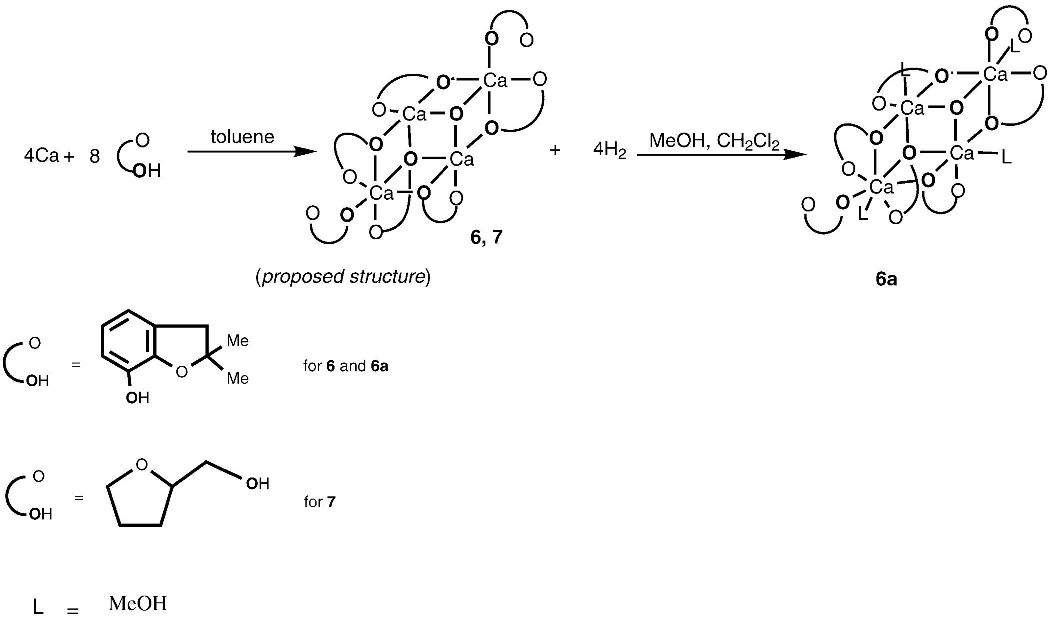
As outlined in Scheme 4, the protonolysis of the readily available precursor $MgBu_2$ (or Mg) with 2,3-dihydro-2,2-dimethyl-7-benzofuranol (ddbfo-H), 1-methoxy-2-propanol (mpro-H) or tetrahydrofurfuryl alcohol (thffo-H) in *n*-hexane yields **5abc** [40,41]. X-ray crystallographic analysis of **5a** and **5b** indeed showed a tetranuclear $[Mg_4(dbbfo)_8]$ [40] and $[Mg_4(mpro)_8]$ [41] compounds with open dicubane geometry. The centrosymmetric molecules of **5a** and **5b** possess two five-coordinate magnesium atoms of trigonal bipyramidal geometry and two six-coordinate octahedral metal sites. Interaction of metallic magnesium with “simple” alcohols like methanol and ethanol 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 up of residues of four types: neutral $[Mg_4(OMe)_8]$ cubane, $[Mg_4(OMe)_6(MeOH)_2]^{2+}$ cubane cations, $[(MeO)_2H]^-$ anions and eight crystallographically independent non-coordinated solvating methanol molecules [42]. 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. Although there are magnesium complexes with other “simple” alcohols, those in the patent literature mainly comprise methoxy and ethoxy compounds.



Scheme 4. Synthesis of **5abc**.

In comparison to magnesium, calcium is significantly larger and its coordination chemistry is notably different and much less developed than that of magnesium. Preparation of alkoxides $[Ca_4(ddbfo)_8]$ (**6**) and $[Ca_4(thffo)_8]$ (**7**) paralleled the route developed for the synthesis of **5abc** [40,41]. As shown in Scheme 5, direct reaction of Ca with tetrahydrofurfuryl alcohol (thffo-H) or 2,3-dihydro-2,2-dimethyl-7-benzofuran alcohol (ddbfo-H) in toluene afforded **6** or **7** as an analytically pure white powder [43a]. Crystallization of **6** from MeOH gave molecular adduct **6a**.

In the solid state, complexes **6** and **7** are most presumably tetrameric species and form open dicubane blocks similar to their magnesium analogs **5abc** [40,41]. This conclusion was drawn from analysis of the crystal structure of **6a**. As shown in Scheme 5, four Ca atoms form a nearly regular rhombus [43a]. Interestingly, discrete centrosymmetric molecule of **6a** contains two hexacoordinated and two heptacoordinated calcium atoms. The internal two Ca atoms have distorted octahedral geometry. The coordination spheres around external two calcium atoms are distorted pentagonal bipyramids. It seems obvious from the positions of MeOH molecules in **6a** that in **6** these sites remain unoccupied. Then, we can suspect that two pentacoordinated and two hexacoordinated Ca atoms are present in **6** and **7**. Interestingly, the

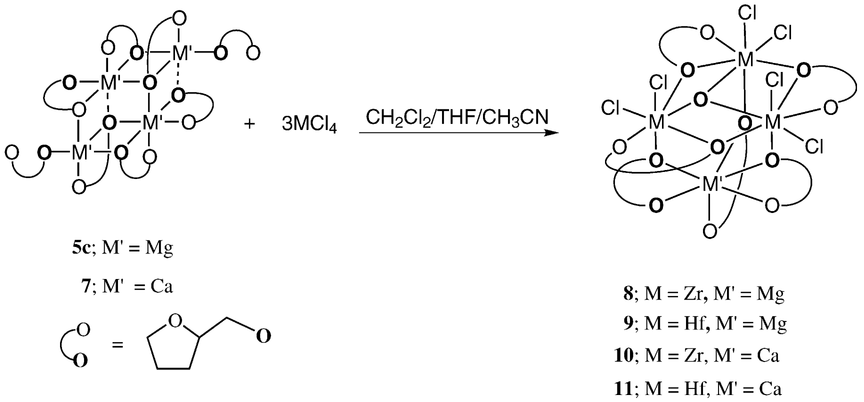


Scheme 5. Synthesis of **6**, **6a** and **7**.

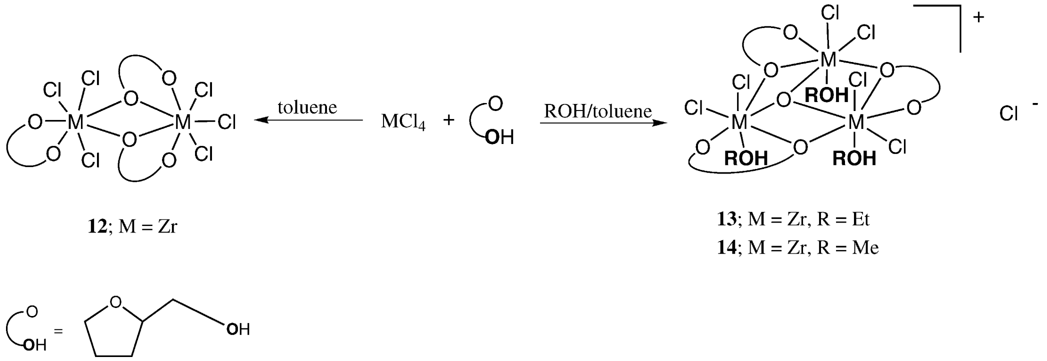
pentacoordinated centers in **6** and **7** are probably located “inside” calcium centers. These initial results are both extremely promising with regard to the potential utility of well-defined calcium coordination complexes for the ROP of lactide and illuminating with respect to the differences in the coordination chemistry of the elements Ca and Mg [18,44].

4.1. Metal alkoxo complexes with an $M_3(\mu_3\text{-}O)$ core

For several purposes, we sought an easy and high-yield method for preparation of mixed metal polynuclear alkoxides of Zr and Hf. Structural information from such compounds is interesting, as it can reveal steps in Z–N catalyst formation, as indicated in the introduction. Thus, MCl_4 (M = Zr or Hf) were treated with **5c** at a slightly elevated temperature in a mixture of CH_2Cl_2, thf, and CH_3CN (Scheme 6). The presence of CH_2Cl_2 in the solvent mixture is highly desirable since the insolubility of $MgCl_2$, which forms as a side-product of the reaction, in CH_2Cl_2 allows its precipitation and easy separation from the final product. Workups gave neutral heterobimetallic tetranuclear complexes $[M_3M'(\mu_x\text{-O})(\mu,\eta^2\text{-thffo})_6(Cl)_6]$ (M/M′/x: **8**, Zr/Mg/3; **9**, Hf/Mg/3; **10**, Zr/Ca/4; **11**, Hf/Ca/4) as white powders [43a]. These were stable for months as solids under dinitrogen and were characterized by IR and ^{1}H NMR spectroscopy, and X-ray diffraction studies. As can be concluded from the reaction pathway (Scheme 6), a small excess of **5c** and **7** is necessary to reach optimum yield of the final products. This is due to decomposition of some ligands (even under strict anaerobic conditions) to produce the residual bridging oxo atom. Such a phenomenon has abundant literature precedence [8]. Indeed when 3 equiv. of MCl_4 react with 4 equiv. of $[Mg_4(\text{thffo})_8]$



Scheme 6. Metal-assembled complexes **8**–**11** [43a].



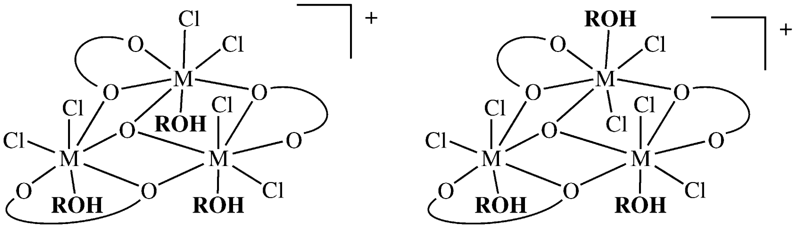
12; M = Zr

13; M = Zr, R = Et
14; M = Zr, R = Me

Scheme 7. The influence of solvent polarity on final product formation.

yields maximized. Nevertheless, reactions were tried at different molar ratios (ranging from 1:1 to 1:2) to continuously give analogous compounds based on ^{1}H NMR and X-ray measurements of the unit cells. Complexes **8** and **9** are isostructural [43a] (Scheme 6). Both include three seven-coordinated zirconium or hafnium atoms, each surrounded by two mutually *cis*-terminal chlorine atoms, three bridging oxo atoms from thffo$^-$ ligands, and one oxygen atom from a substituted tetrahydrofuran ring. The coordination sphere of each transition metal in **8–11** is completed by a triply bridging oxo atom which holds the M$_3$ triangle together. In these species, three magnesium sites are occupied by the oxygen atoms of substituted tetrahydrofuran rings. The remaining three sites are occupied by alkoxo atoms of three thffo$^-$ ligands that also constitute three bridges between magnesium and transition metal atoms. Next, we attempted to "replace" Mg^{2+}, in **8**, by AlMe$_3$. The precursor [Zr$_4$(μ$_4$-O)(μ-OMe)$_6$Cl$_8$(thf)$_4$] (**8a**) was obtained in direct reaction of ZrCl$_4$ with methanol. When **8a** reacted with AlMe$_3$ in thf, [Zr$_3$Al(μ$_4$-O)(μ-OMe)$_6$Cl$_6$(Me)(thf)$_3$] (**8b**) was isolated [43b]. The significant difference between **8a** and **8b** is that one of the [ZrCl$_2$(thf)]$^{2+}$ moieties coordinated to the μ$_4$-O oxygen atom in **8a**, is substituted by an [Al-Me]$^{2+}$ unit in **8b**. Preliminary tests of the catalytic properties of **8b** for ethylene polymerization have indicated no activity. This result agrees with our presumptions due to lack of a Zr–CH$_3$ bond in **8b**.We attempted to reveal the formation mechanism of **8–11** by accessing homometallic complexes that were possible precursors of **8–11** [43a]. A family of compounds was synthesized by combining ZrCl$_4$ or HfCl$_4$ with thffo-H in non-coordinating (toluene) and coordinating (EtOH or MeOH) solvents at low temperature (Scheme 7). The molecular structure of **12** (Scheme 7) shows a neutral dimeric species with zirconium atoms that have slightly different coordination spheres. Although both metals have analogous Cl$_3$O$_4$ pentagonal–bipyramid arrangements, one coordinates two bridging oxo ligands and two substituted tetrahydrofuran rings while the other coordinates one molecule of tetrahydrofurfuryl alcohol, apart from two bridging alkoxo atoms. The consequences of changing the solvent from toluene to ROH is quite surprising. Clearly solvent coordination in the final product composition is important. An X-ray diffraction study of **13** and **14** showed the complexes to be ionic species with a bulky monocation comprising three Zr atoms and Cl$^-$ as a counter ion. Three metal atoms in **13** and **14** are coordinated similarly to those in **8–11**. They also form M$_3$ triangles that are held together by μ$_3$-O oxo atom which originates from alcohol decomposition [43a]. These homopolymetallic species **13** and **14** are geometrically very interesting. They all exhibit C$_3$ symmetry, thanks to the *syn*-position of the three ROH molecules (or alternatively Cl atoms). Another possible isomer with two ROH molecules *syn* and one *anti* is shown in Scheme 8. Although the repulsion of the ROH molecules should be lower for such an isomer we saw no sign of its formation.

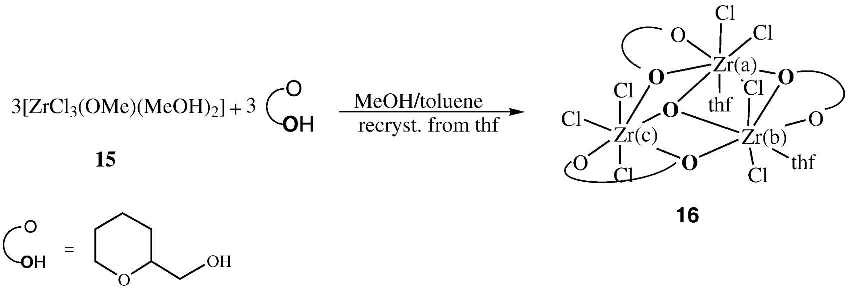
For a deeper understanding of the influence of solvent polarity/coordination ability on the reaction pathway and



syn, syn, syn

anti, syn, syn

Scheme 8. Possible isomers of cations in **13** and **14** [43a].



Scheme 9. Synthesis of **16** [43a].

final product formation, we also studied the reaction of $[ZrCl_3(OMe)(MeOH)_2]$ (**15**) with tetrahydropyran-2-methanol (thp-H). Compound **15** was obtained in a direct reaction of $ZrCl_4$ with methanol. This high-yield synthesis, which was easy to perform, gave product which was possibly oligo- or polymeric and which was observed to be a very good starting material for the syntheses of zirconium alkoxo species by ligand exchange [43a]. After its reaction with thp-H in a toluene/MeOH mixture at room temperature, workup involving thf recrystallization afforded a neutral, analytically pure sample of $[Zr_3(\mu_3\text{-O})(\mu,\eta^2\text{-thp})_3(thf)_2Cl_7]$ (**16**).The molecular structure of **16** (Scheme 9) consists of discrete trinuclear molecules that comprise a μ_3-O bridged M_3 triangle similar to **8–11**, **13** and **14**. Each thp^- ligand coordinates with central atoms through the oxygen atom of the heterocycle and the μ_2-bridging alkoxo oxygen atom. Analogously to those in **8–11**, **13** and **14,** each Zr atom is seven-coordinate but interestingly each of these complexes possesses a different ligand arrangement. Zr(a) is surrounded by the μ_3 oxo atom, one oxygen from the ligand heterocycle, two μ_2-bridging alkoxo oxygens, two terminal, mutually *trans*, chlorine atoms, and one thf molecule. Zr(b) differs from Zr(a) in the orientation of the two terminal chlorine atoms, these being in a mutually *cis*-orientation. In turn, Zr(c) lacks a thf molecule, which is replaced by the additional terminal Cl atom. Thus, **16** in the solid state has lost the C_3 symmetry that is typical for the compounds mentioned earlier.

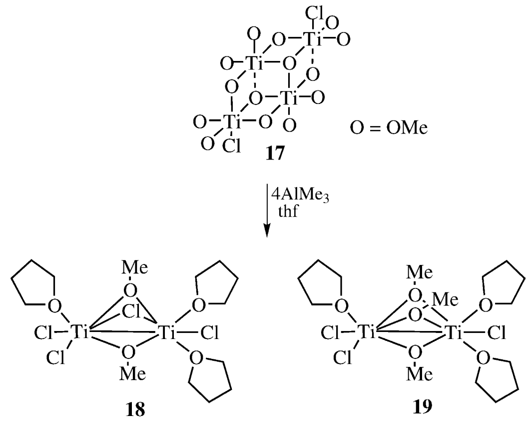
4.2. Titanium alkoxo-bridged dinuclear complexes

The titanium system catalyst is much more complex than the zirconium system, and almost nothing is known about its intermediates [45]. In contrast to the zirconium compound **8a**, treatment of $TiCl_4$ with methanol give a thermally stable neutral tetranuclear molecule with a cubane geometry $[Ti_4(OMe)_{14}Cl_2]$ [46] (**17**). Treatment of **17** with an excess of $AlMe_3$ (4 equiv., toluene/thf, −30 °C; Scheme 10) gave a co-crystallite $[Ti_2(\mu\text{-OMe})_2(\mu\text{-Cl})Cl_3(thf)_3]\cdot[Ti_2(\mu\text{-OMe})_3Cl_3(thf)_3]$ (**18**·**19**) in a 1:1 ratio. Similar to **18**, $[Ti_2(\mu\text{-OEt})_2(\mu\text{-Cl})Cl_3(thf)_3]$ (**20**) was obtained in the reaction of an equimolar mixture of $TiCl_4$, $Ti(OEt)_4$, Al, and $AlMe_3$.

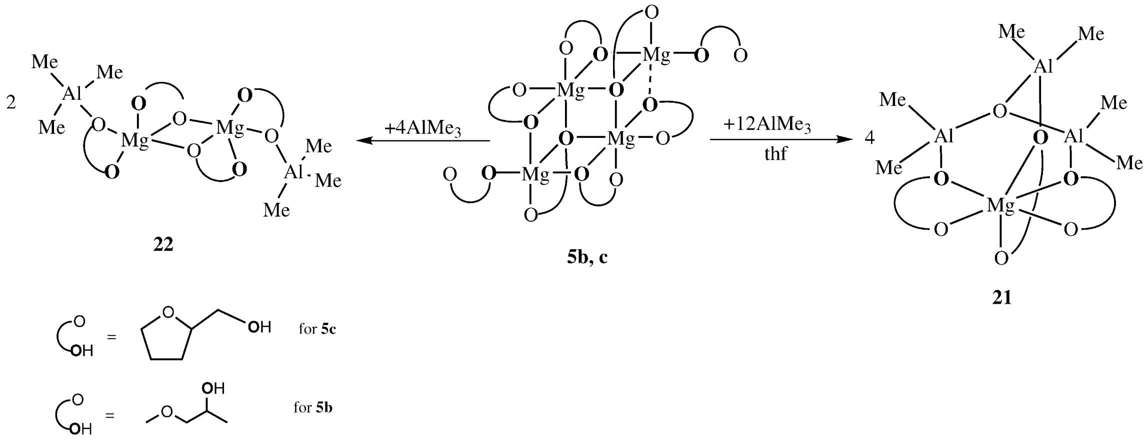
Addition of more than 1 equiv. of $AlMe_3$ leads most probably to the formation of species containing a Ti–Me bond and reduce the yield of **20**. Reduction with only Al or $AlMe_3$ gave an oily product, purification of which was demanding and eventually gave a "problematic" result. Species **18–20** dissolved in thf undergo slow decomposition to blue crystalline $[TiCl_3(thf)_3]$ based on X-ray measurements of unit cell parameters. The structure of the co-crystallite **18**·**19** is composed of two chemically independent $[Ti_2(\mu\text{-OMe})_2(\mu\text{-Cl})Cl_3(thf)_3]$ and $[Ti_2(\mu\text{-OMe})_3Cl_3(thf)_3]$ molecules which are statistically distributed in the crystal [47]. The only significant difference between $[Ti_2(\mu\text{-OMe})_2(\mu\text{-Cl})Cl_3(thf)_3]$ and $[Ti_2(\mu\text{-OEt})_2(\mu\text{-Cl})Cl_3(thf)_3]$ is that two μ-OMe moieties in **18** are substituted by two μ-OEt groups in **20**. The very short Ti · · · Ti distance [2.543(1) Å in **18**·**19** and 2.599(1) Å in **20**] accompanied by diamagnetism of both species might indicate the presence of a Ti–Ti single bond. However, the metal–metal distance is not a good bond criterion, especially in systems where the bridging constraints are substantial [48].

4.3. Reactivity of the Mg_4X_8 building blocks

High-activity, stereoregular olefin polymerization catalysts can be produced from an organoaluminum co-catalyst and titanium-magnesium pro-catalyst precursor containing



Scheme 10. Reaction scheme of the preparation of **18** and **19** [47].

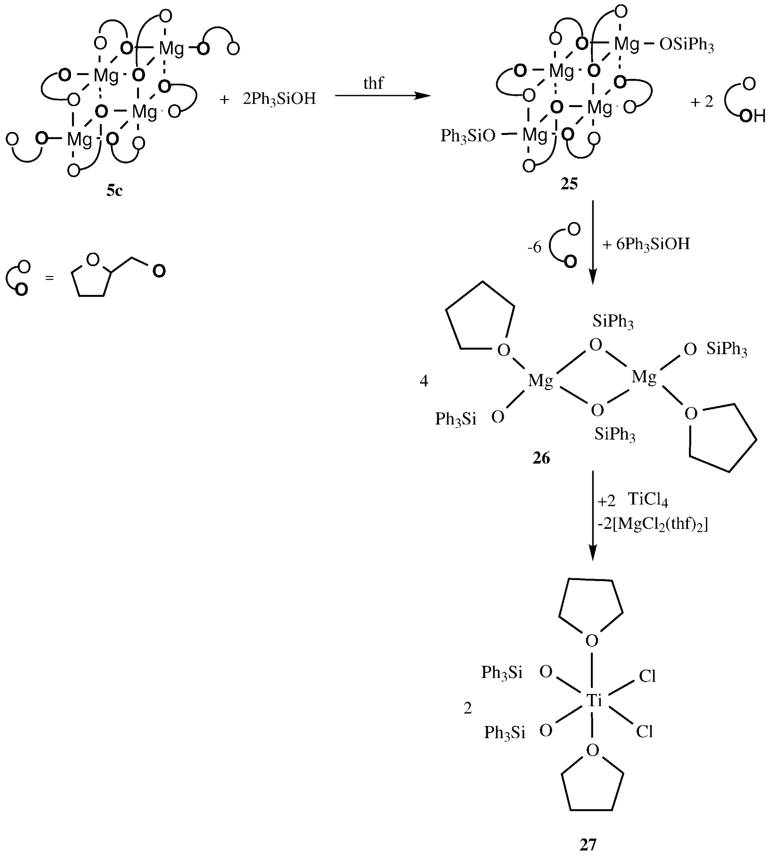


Scheme 11. Reaction scheme of the preparation of **21** and **22** [49,53].

alkoxide groups. Hence, studies on the interaction between each of the catalyst components and the ≡SiOH surface groups are very important. Very recently, we have found that in the reaction of **5c** with $AlMe_3$, the methylalumoxane $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ moiety is formed; this was isolated and characterized as the compound $[Al_3Mg(\mu_3\text{-}O)(thfo)_3(Me)_6]$ (**21**) [49]. In this case, the dicubane-like magnesium block **5c** splits and reacts with $AlMe_3$ to form crystals of **21** which are extremely sensitive toward moisture. The X-ray crystal structure of **21** was determined as shown in Scheme 11. The four-coordinate aluminum atom in **21** is surrounded by two methyl groups and one μ_3-O oxo and one μ-O alkoxo oxygen atom of the $[Mg(thffo)_3]^-$ moiety. Three $AlMe_2$ moieties are held together by μ_3-O oxygen atoms to form a trinuclear $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ macro unit. The coordination sphere of the magnesium atom in **21** is formed by six oxygen atoms: three ether and three bridging μ-O alkoxo atoms of the thffo ligands. The μ-O oxygen atom lies on a pseudo-three-fold axis and exhibits bond angles as expected for sp^2 hybridization.

The factor governing stability of the methylalumoxane $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ intermediates is not yet well understood [50]. Insight into the problem has been gained by comparison of $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ cation with the corresponding known tetranuclear $[Al_4(\mu_3\text{-}O)_2(^tBu)_8]$ compound [51] and $[\{(Me)_2Al(\mu_3\text{-}O)Al(Me_3)\}_2]^{2-}$ anion [52]. We believe that the compound $[Al_4(\mu_3\text{-}O)_2(Me)_8]$ relevant to $[Al_4(\mu_3\text{-}O)_2(^tBu)_8]$ could be formed from $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ cation by addition of the $OAlMe^{2-}$ anion. The $[Al_4(\mu_3\text{-}O)_2(^tBu)_8]$ species with bulky ^tBu groups is stable and could be isolated as a solid. In contrast, methylation of $[Al_4(\mu_3\text{-}O)_2(Me)_8]$ results in the formation of the $[\{(Me)_2Al(\mu_3\text{-}O)Al(Me_3)\}_2]^{2-}$ anion.To identify further intermediates and reactions steps that lead to the formation of the active co-catalyst species we found that the reaction of **5b** with $AlMe_3$ proceeds differently from that for **5c**. $AlMe_3$ reacted with **5b** to give a thermally stable neutral heterobimetallic complex $[Mg_2(mpro)_4(AlMe_3)_2]$ (**22**) [53]. Compound **22** was shown by X-ray diffraction study to have a centrosymmetric tetranulear chain structure as presented in Scheme 11. Complex **22** comprises two five-coordinate magnesium atoms and two four-coordinate aluminum centers. The alkoxide oxygen atoms of the chelating 1-methoxy-2-propoxide ligands bridge all of the metal atoms. Two of the alkoxide oxygen atoms bridge two magnesium atoms, and each of the two remaining ones bridge to $AlMe_3$ unit. The central Mg_2O_2 four-membered ring in **22** is planar with the ligands adopting a *trans*-orientation. The formation of a magnesium complex **22** containing $AlMe_3$ units coordinated to μ-alkoxide oxygen atom is unusual. This is reminiscent of the hydrolysis of $AlMe_3$, which makes the methylalumoxane (MAO) polymerization co-catalyst, and is believed to contain both $AlMe_3$ and AlMex(O) units [54]. The presence of magnesium atoms in **21** and **22** is an additional advantage of these compounds. The driving force for reaction between MCl_4 (M = Ti, Zr, Hf) and **22** should be the formation of $MgCl_2$ providing in return alkyl functions.

As stated earlier, we were interested in determining the role of the reactive coordination site at the five-coordinate metal center in the Mg_4X_8 (X = Cl, OR) building blocks. This study has shown that a series of tetranuclear compounds with Mg_4X_8 units exists and can be readily formed under the appropriate conditions. Complexes **5abc** are sensitive towards chlorinated hydrocarbons. CH_2Cl_2, for example, causes substitution of η^1-coordinated ligands by chlorine atoms to give in case of **5c** molecular complex $[Mg_4(thffo)_6Cl_2]$ (**23**). Compound **23** was also obtained when $MgCl_2$ reacted with **5c** [55]. Although there is no indirect proof, compound **23** in methanol probably undergoes ionization and the $[Mg_4(thffo)_6(MeOH)_x]^{2+}$ cation is formed. This conclusion may be drawn from the fact that crystals of $[Mg_4(OMe)_6(MeOH)_{10}]Cl_2$ with similar cation were isolated as one of the products of the reaction of $Mg(OMe)_2{\cdot}3.5MeOH$ with $MgCl_2$ [56]. Formation of **23** in thf is attributed to stronger than thf, donor properties of chlorine which stays in the metal coordination sphere to form $[Mg_4(thffo)_6Cl_2]$ instead of ionic $[Mg_4(thffo)_6(thf)_2]Cl_2$. The reaction of **5a** with CH_3OH gave crystals of new **24a**. The solid-state



Scheme 12. Reaction mechanism showing the substitution of thffo group in **5c** by Ph_3SiO group and formation of **25** and **27**.

structure of the complex **24** consists of the tetranuclear open dicubane $[Mg_4(\mu_3\text{-}OMe)_2(ddbfo)_6(CH_3OH)_5]$ [40]. The molecule contains one five-coordinate Mg atoms and three six-coordinate Mg atoms. The inequivalence between magnesium atoms arises from the six-coordinate environment of the third magnesium atom which additionally contains the methanol oxygen atom.

In Ziegler–Natta methodologies, the SiO_2 surface is reacted with MgX_2 (X = Cl or OR), followed by reaction with a titanium species. In order to reveal the interaction of the silica surface ≡Si–OH groups with the magnesium $[Mg_4(thffo)_8]$ (**5c**) catalyst component, we have studied the binding of Ph_3SiOH used as a “surface” model to the unsaturated magnesium centers in **5c**. The direct reaction of the dicubane-like tetramer $[Mg_4(thffo)_8]$ with Ph_3SiOH in a 1:2 molar ratio in toluene gives the air-sensitive compound $[Mg_4(thffo)_6(OSiPh_3)_2]$ [49] (**25**). A view of the structure of **25** is shown in Scheme 12. The $Mg_4(thffo)_6$ core in **25** is similar to that of $[Mg_4(thffo)_6Cl_2]$ (**23**). The difference is that the two $OSiPh_3$ groups bound to the five-coordinated magnesium atoms in **25** are replaced by two Cl atoms in **23**. The reaction of **25** with 6 equiv. Ph_3SiOH in tetrahydrofuran (thf) gives the new air-sensitive compound $[Mg_2(OSiPh_3)_4(thf)_2]$ (**26**) [57]. A crystal structure determination of **26** showed it to be a centrosymmetric dimer $[Mg_2(\mu\text{-}OSiPh_3)_2(OSiPh_3)_2(thf)_2]$. As an aid to explain the formation of the catalytically active surface centers, we are studying the binding of titanium species by magnesium centers in **26**. The addition of $TiCl_4$ to **25** in thf results in the formation of $[TiCl_2(OSiPh_3)_2(thf)_2]$ (**27**). It follows that coordinated by “surface” ≡SiO–Mg magnesium atom is extracted by titanium atom to yield a new reactive species **27**. Straightforward chloride replacement reaction by use of Li^tBu modified the arrangement around the titanium center in **27**. In the ^1H NMR spectrum, integration of the *tert*-butyl protons provides good evidence for $Ti–^tBu$ coordination at the new titanium center [57].

We have found also that a similar compound $[Mg_4(thffo)_6\{OTi(dipp)_3\}_2]$ (**28**) could be obtained by controlled hydrolysis of the reaction product formed between **5c** and $[Ti(dipp)_4]$ (dipp = 2,6-diisopropylphenoxo group) [40]. The complex **5c** was converted into the $[V_2Mg_2(thffo)_4Cl_4]$ (**29**) via simple treatment with VCl_3. The centrosymmetric complex molecule **29** also consists of 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 [58]. We were interested in determining whether the compound **5c** would also react with MCl_2 (M = Fe, Mn, Co). The reaction of $[FeCl_2(thf)_{1.5}]$ with 3 equiv. of **5c** in thf gave crystals of $[Mg_7(thffo)_{12}][FeCl_4]$ (**30**). The crystal lattice of **30** consists of centrosymmetric cations $[Mg_7(thffo)_{12}]^{2+}$ as well as $[FeCl_4]^{2-}$ anions in a

1:1 molar ratio. The $[Mg_7(thffo)_{12}]^{2+}$ cation is composed of 7 magnesium atoms and 12 thffo ligands [59].

5. Metal-assembled compounds as a new materials

In the last decade, has been made significant progress in the field of molecule-based functional materials, especially for bulk magnetic materials [60] and highly conducting materials [61]. For molecule-based magnetic materials, multi-dimensional lattices, which allow the magnetic arrangement of individual magnetic spins in the long-range order, are well designed by choosing adequate molecular blocks (and/or metal ions) and bridging ligands to form sublattices and counter ions to fill the voids among multi-dimensional lattices. The fabrication of molecule-based highly conducting materials was promoted by the development of organic charge-transfer molecules with tetrathiafulvalene (TTF) derivatives [61]. Thus, an effective strategy for fabricating such materials is to combine magnetic multi-dimensional lattices and organic conducting columns or layers [62].Recently, Miyasaka et al. succeeded in synthesizing a new hybrid system $(BEDT\text{-}TTF)_2[Mn_2Cl_5(EtOH)]$ (**31**) [63]. An assembled compound **31** consists of two structural lattices of one-dimensional $[Mn_2Cl_5(EtOH)]^-$ (1-D) chains and bis(ethylenedithio) tetrathiafulvalene $(BEDT\text{-}TTF)^+$ conducting layers in a 1:1 ratio. The 1-D chain is described as $[Mn_2Cl_5(EtOH)]^-$ in which two Mn(II) and four Cl ions form a ladder-like chain with Kagomé (cuboidal) sublattices, and the remaining Cl^- ion and an EtOH cap the edge-positioned Mn(II) ions of the chains. The $(BEDT\text{-}TTF)^+$ molecules are packed between the $[Mn_2Cl_5(EtOH)]^-$ chains. Note that $[\{Mn_5Cl_{10}(thf)_6\}_n]$ (**2a**) [35] formed by tetranuclear $[Mn_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Cl_2(thf)_6]$ building block linked by $MnCl_2(thf)_2$ moieties contains a double-cuboidal fragment in the chain (Scheme 2), similar to the Kagomé-like (cuboidal) sublattice of **31** [63]. We strongly believe that careful and rational strategy for syntheses of a new hybrid materials containing magnetic 1-D lattices and conducting layers can create enormous possibilities.

6. Results of ethylene polymerization

We examined the catalytic behavior of the series of Ti, Zr and Hf complexes with functionalized ligands using methylalumoxane MAO as the co-catalyst [64]. The results are collected in Table 1. The activities of these complexes are moderate. Ethylene–octene copolymerization using MAO as co-catalyst with the complexes presented in Table 1, were carried out at 140 °C.The activities of these catalytic systems were found to be one order of magnitude lower in comparison to the $[Cp^*\text{-}SiMe_2\text{-}N^tBu]TiCl_2$/MAO catalyst system under identical conditions. The polymer produced with those catalysts (entries 2–6) posses broad polydispersity (M_w/M_n values 30.3–54.5) and molecular weight M_n ca. 35400–78500, characteristic of a Z–N polymerization catalyst. These facts strongly indicate that during the process of catalyst formation the ligands have been abstracted from transition metal atoms and many active sites are formed [23,64]. The tendency of the thffo ligands towards dissociation from the metal centers after addition of MAO forced us to use the 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) ($edbp\text{-}H_2$) ligand [65]. By selecting the $edbp\text{-}H_2$ ligand, which contains phenols with *tert*-butyl “tails”, we expected to obtain compounds with markedly improved solubility in hydrocarbons, and an increased likelihood of compound stability in the presence of the aluminum co-catalyst [64]. The catalyst $[Ti(edbp)Cl_2]$/MAO (entry 7) which has an edbp ligand strongly bonded to the metal atom, furnished a narrower molecular weight dispersion of this polymer ($M_w/M_n = 6.23$) in comparison to the polymers produced with catalyst entries 2–6. The polymer densities of the ethylene–octene copolymers (entries 2–6) were found to be in excess of 0.93 g/mL indicating that octene was not being incorporated into the propagating polymer. The exception is for entry 1 of Table 1 where the polymer was determined to have a density of 0.89 g/mL indicating a significant amount of 1-octene incorporation resulting in a clearly elastomeric polymer sample upon drying.

Table 1
Results of ethylene–octene copolymerization/MAO[a]

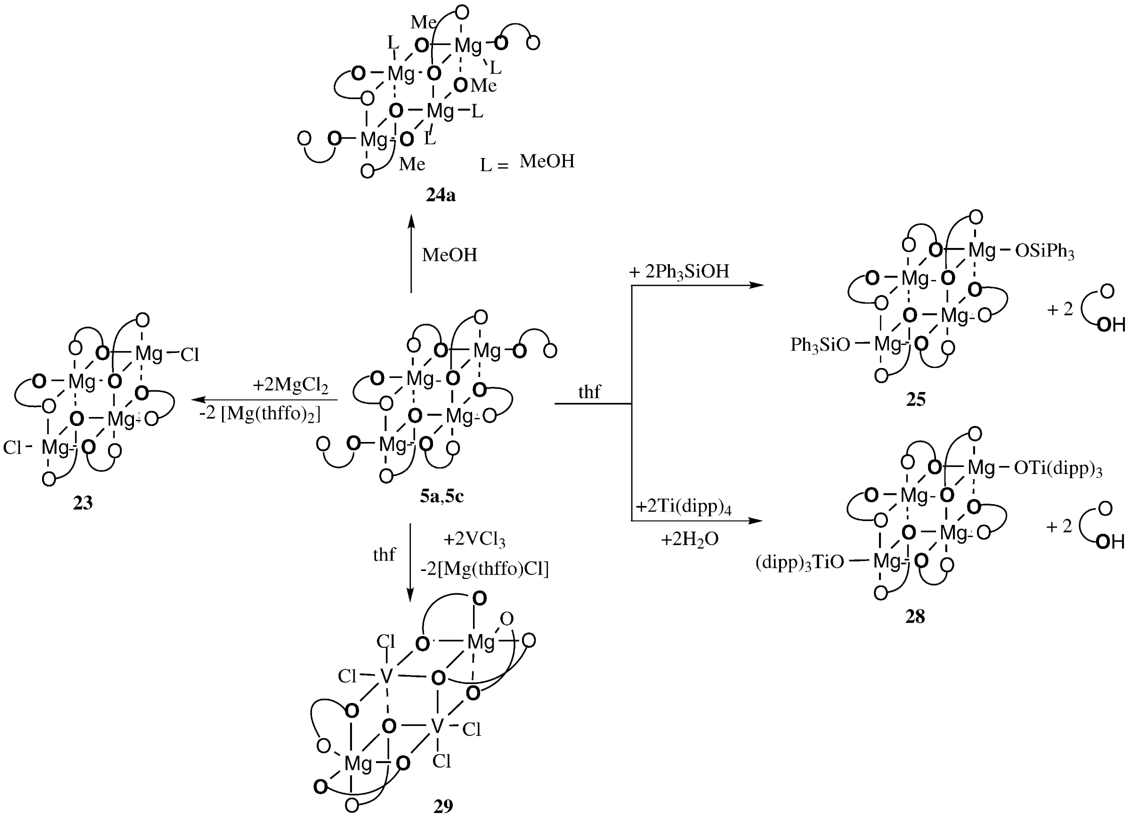
Entry	Complex	Efficiency (kg P/g Ti)	M_w[b]	PDI[b]
1	$[Cp^*\text{-}SiMe_2\text{-}N^tBu]TiCl_2$	443.8	90000	5.54
2	$[Zr_3Mg(\mu_3\text{-}O)(thffo)_6Cl_6]$	18.5	38400	54.5
3	$[Hf_3Mg(\mu_3\text{-}O)(thffo)_6Cl_6]$	0.7	–	–
4	$[Zr_3(\mu_3\text{-}O)(thffo)_3(EtOH)_3]Cl$	27.1	69200	30.3
5	$[Hf_3(\mu_3\text{-}O)(thffo)_3(EtOH)_3]Cl$	2.2	35400	45.1
6	$[Ti_4(OMe)_{14}Cl_2]$	27.5	78500	42.0
7	$[Ti(edbp)Cl_2]$	15.2	169000	2.28

[a] Conditions: MMAO-12/complex = 1000; temperature = 140 °C.

[b] Determined by GPC using polystyrene/polyethylene universal calibration.

7. Summary and conclusions

As stated earlier, we were interested in determining the role of the reactive coordination site at the five-coordinate metal center in the M_4X_8 (X = Cl, OR) blocks. The solid-state structures of these species offer little assistance in the understanding of the reaction pathways involved in the formation of **5**, **23**–**25** and **28**. A plausible mechanism for formation of **24** is shown in Scheme 13. The substitution of two ddbfo ligands in **5a** by two methoxide groups leads to the formation of the centrosymmetric $[Mg_4(\mu_3\text{-}OMe)_2(ddbfo)_6(CH_3OH)_4]$ (**24**) complex which has a Mg_4O_6 core similar to that of **5a** and is



Scheme 13. Reactivity of magnesium building blocks **5a** and **5c**.

probably an intermediate in the formation of the species [$Mg_4(\mu_3\text{-OMe})_2(ddbfo)_6(CH_3OH)_5$] (**24a**). Thus, two unsaturated five-coordinate metal sites in **5a** offer free coordination centers for incoming methanol molecules. However, only one CH_3OH is coordinated by the Mg atom, and complex **24a** is generated. It follows that compound **24a** is the least soluble species and precipitates preferentially, thus driving the equilibrium to its final position. We have demonstrated that the magnesium [$Mg_4(thffo)_8$] (**5c**) catalyst components can be trapped by $AlMe_3$, Ph_3SiOH, [$Ti(dipp)_4$] and VCl_3 species (Scheme 13) to form metal-assembled **23**, **25**, **28** and **29** compounds, respectively.

Schemes 6–10 summarize highly optimized routes to homo- and heterometallic polynuclear alkoxo complexes of Zr and Hf. Incorporation of an alkaline earth metal in **7–11** provides additional information about the possible nature of the interaction between pre-catalyst metal centers and the $MgCl_2$ or $Mg(OR)_2$ catalyst support. It is also clear from the data presented that solvent polarity plays a pivotal role in the final product formation. Small differences in the reaction conditions drive the reaction toward the formation of neutral or ionic species, as shown in the syntheses of **12–14**. It is interesting (and important) to note that the formation of the μ_3-oxo-bridged M_3 subunit is very common. This structure seems extremely stable [66]. We believe that this stability constitutes a major reason why the activity of such compounds in olefin polymerization is lower than that of titanium alkoxo species, which (for simple systems, for example, those containing $Ti(OEt)_4$) prefer motifs other than $M_3(\mu_3\text{-O})$ [47,67]. Further investigation of **7–11** showed that even with very strong alkylating agents the structure of the M_3 triangle (including the terminal chlorine atoms) remained untouched, proving the high stability of the trinuclear core [43b]. This stability prevents any metallic center in such a pre-catalyst from being activated (for example, by removal of a chlorine atom) to become a polymerization center.

We have discovered a surprising new class of alkoxo-bridged “Ti(III)” stable species **18–20** that can be accessed by direct syntheses (Scheme 10). It could it is possible that chloride ligands in these compounds in solution undergo substitution by an excess of $AlMe_3$ to give [$Ti_2(\mu\text{-OMe})_2(\mu\text{-Cl})(thf)_3(Me)_3$] which is relevant to [$Ti_2(\mu\text{-OMe})_2(O^tBu)_2(Me)_4$] [68] but up to now has not been isolated in pure form. It can be expected that these compounds will find application in several branches of chemistry such as olefin polymerization, sol–gel chemistry [69], and many others [8]. Further studies are needed to determine possible incorporation of **18–20** into catalytic cycles.

Magnesium compounds Mg_4X_8 are good additives boosting the activity of the catalytic mixture. For example, the preliminary results of an ethylene polymerization test on [$Mg_4(thffo)_6Cl_2$]/$TiCl_4$/$AlEt_3$ catalyst gives ca. 170 kg of polyethylene/g of Ti h^{-1} [55] while only 11.6 kg of polyethylene/g of Ti h^{-1} was obtained under the same conditions when the $MgCl_2/TiCl_4/AlEt_3$ catalyst was used [70].

As can be seen from the present review our attempts to prepare new metal-assembled pro-catalysts and to understand the chemistry of formation of these new complexes often led to observations of 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 consequently "complicate" the system and aim at the synthesis of $Si/Mg_4/Ti/Al$ species. Also other than titanium, vanadium and zirconium transition metals will be investigated. Recent discoveries on non-metallocene iron and cobalt olefin polymerization catalysts prove 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 [3–5].

Acknowledgements

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