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Structural Characterization of a Methylaluminoxane (MAO)–Magnesium Dichloride Cluster: Model of MAO Grafted onto a $MgCl_2$ Support

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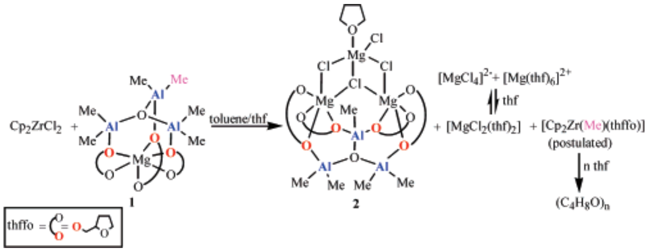
The study outlines our initial results that contribute to a better understanding of MAO/$MgCl_2$ (MAO = methylaluminoxane) incorporation in the Cp_2ZrCl_2/MAO/$MgCl_2$ catalytic system, which is currently of global industial use. We show here that the[$Al_3(\mu_3$-O)$(Me)_5]^{2+}$ moiety can be trapped by the tetrapodal [$Mg_3Cl_4(thffo)_4(THF)]^{2-}$ macrounit to form a cluster [$Al_3Mg_3(\mu_3$-O)$(thffo)_4(Me)_5Cl_4(THF)$] (thffo = 2-tetrahydrofurfuroxide). From this perspective, this macrounit might be considered as a part of the $MgCl_2$ support surface, which fulfills the requirement of a $Al_3(\mu_3$-O) core.

Ziegler–Natta catalysis is consistently one of the most important and profitable petrochemical processes.[1] Over the years, the catalyst, from simple crystalline $TiCl_3$, has evolved into the high-technology system incorporating SiO_2 or $MgCl_2$ as a support for $TiCl_4$.[2] Magnesium dichloride as a carrier for the single-site metallocene catalysts has been studied far less extensively than silica.[3] A comprehensive contribution to this topic is provided by Chen and Marks.[3b] $MgCl_2$-supported metallocene reacted with methylaluminoxane (MAO) forms a catalyst that exhibits activity two times higher in ethylene polymerization than silica-supported analogues.[4] Hence, studies on the interaction between each of the catalyst components and the $MgCl_2$ surface are of great importance.

Recently, we have found that in a reaction of [$Mg_4(thffo)_8$] (thffo = 2-tetrahydrofurfuroxide) with $AlMe_3$ the [$Al_3(\mu_3$-O)$(Me)_6]^+$ moiety is formed. This can be trapped by a tripodal [$Mg(thffo)_3]^-$ unit to form molecular solid [$Al_3Mg(\mu_3$-O)$(thffo)_3(Me)_6$] (**1**).[5] The present paper is our contribution to the understanding of the nature of the MAO/$MgCl_2$ adduct that, until now, has not been resolved and which takes an active part in the metallocene catalytic system. Here we describe our initial studies on the reaction of Cp_2ZrCl_2 with **1**.

Scheme 1. Formation of Cluster **2**



The precursor **1** and 1 equiv of Cp_2ZrCl_2 were combined at room temperature as shown in Scheme 1. After 1 h, the solution became cloudy and a precipitate of [$MgCl_2(THF)_2$] settled. No gas evolution was observed. Workup gave neutral air-sensitive crystalline [$Al_3Mg_3(\mu_3$-O)$(thffo)_4Cl_4(Me)_5(THF)$] (**2**) in 10% isolated yield and a colorless rubberlike side product. The product **2** is reasonably stable as a solid and can be stored under a dinitrogen atmosphere. It gave satisfactory microanalysis.

The ^1H NMR spectrum of the side product shows signals characteristic for a THF polymer and resonances of a Cp ring typical for metallocene species. It is known that THF

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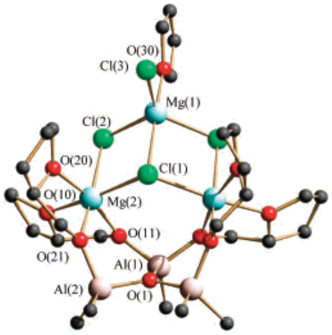


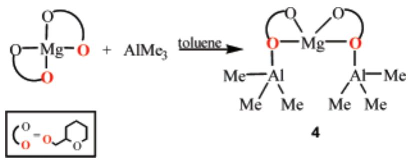
Figure 1. View of **2**. H atoms are not shown. Selected interatomic distances [Å]: Mg(1)−O(30), 2.070(4); Mg(1)−Cl(3), 2.375(2); Mg(1)−Cl(2), 2.397(2); Mg(1)−Cl(1), 2.610(2); Mg(2)−O(21), 2.030(3); Mg(2)−O(11), 2.039(2); Mg(2)−O(20), 2.067(3); Mg(2)−O(10), 2.071(3); Mg(2)−Cl(1), 2.519(2); Mg(2)−Cl(2), 2.538(2); Mg(2)−C(15), 2.847(3); Mg(2)−C(25), 2.868(4); Al(1)−O(11), 1.792(2); Al(1)−O(1), 1.793(3); Al(1)−C(3), 1.971(4); Al(2)−O(21), 1.817(2); Al(2)−O(1), 1.821(2); Al(2)−C(2), 1.977(4); Al(2)−C(1), 2.013(3). Symmetry transformations used to generate equivalent atoms: $x, -y + {}^{1}/_{2}, z$.

can undergo ring-opening polymerization after coordination to a metal site.[6] The zirconium species has not been isolated yet in pure form. The ^{27}Al NMR spectrum of **2** in C_6D_6 shows resonances at 158 and 181 ppm. These are typical for chlorinated methylaluminum species such as Me_2AlCl and $[Me_2AlCl]_2$[7] that suggest decomposition of **2** in solution.

The X-ray crystal structure of **2** was determined,[8] and the overall view is shown in Figure 1. The $Al_3(\mu_3\text{-}O)$ cores in **1** and **2** are similar. The significant difference is that one of the methyl groups of the $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ moiety in **1** is replaced by an alkoxo O atom of the thffo ligand in **2**, providing in return alkyl functions (see Scheme 1). The $[Mg_3Cl_4(thffo)_4(THF)]^{2-}$ macrounit in **2** contains two types of magnesium centers: two Mg atoms are six-coordinated surrounded by four μ-$O_{alkoxide}$, μ-Cl, and μ_3-Cl atoms, and one is five-coordinated surrounded by two μ-Cl, one μ_3-Cl, one terminal Cl, and an O of the coordinated THF molecule.

For a deeper understanding of the reaction pathway for the formation of cluster **2**, we studied the interaction of magnesium alkoxides with $AlMe_3$. The reaction of $[Mg_4(thffo)_8]$ with 2 equiv of $AlMe_3$ in toluene afforded an air-sensitive $[Mg(thffo)_2(AlMe_3)_2]$ (**3**), but it could be neither crystallized nor obtained in analytically pure form. Nevertheless, its spectroscopic data clearly show the analogy with related species $[Mg(thpm)_2(AlMe_3)_2]$ (**4**) (thpm = tetrahydropyran-2-methoxide). Compound **4** was obtained in crystalline form and identified by elemental analysis, spectroscopic data, and X-ray diffraction study. Unfortunately, the structure of **4** was not determined completely in view of low-quality crystals. Nonetheless, the structure is clearly visible and can be discussed. An overall view of the molecule is presented in Scheme 2.

Scheme 2. Preparation of **4**



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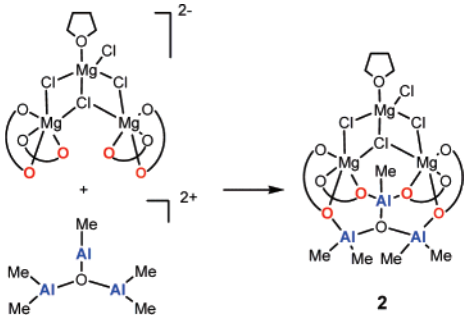
Scheme 3. $[Al_3(\mu_3\text{-}O)(Me)_5]^{2+}$ Moiety Trapped by the Tetrapodal $[Mg_3Cl_4(thffo)_4(THF)]^{2-}$ Macrounit



2

The monomeric complex **4** contains a four-coordinated Mg atom surrounded by four O atoms of two bidentate thpm ligands and two $AlMe_3$ molecules attached to the alkoxo O atoms of the $Mg(thpm)_2$ unit to give the molecular solid $[Mg(thpm)_2(AlMe_3)_2]$ (Scheme 2). According to this, it is also possible that the $[Al_3(\mu_3\text{-}O)(Me)_5]^{2+}$ moiety was trapped by the tetrapodal $[Mg_3Cl_4(thffo)_4(THF)]^{2-}$ macrounit during the formation of **2** (Scheme 3). Preliminary tests of the catalytic properties of **2** for ethylene polymerization have shown no activity.

Some alkylaluminoxanes have been characterized crystallographically by Barron and co-workers, who obtained them by partial hydrolysis of aluminum alkyls.[9] Thus, hydrolysis of $Al(^tBu)_3$ gave tetranuclear $[Al_4(\mu_3\text{-}O)_2(^tBu)_8]$, together with $[Al_8(\mu_3\text{-}O)_8(^tBu)_8]$.

In summary, our study contributes to a novel approach to the better understanding of the MAO/$MgCl_2$ adduct, which exploits the properties of $MgCl_2$ and is currently of global industrial use.[3a] The solid-state structures offer little assistance in the understanding of the reaction pathways involved in the formation of **2**. We believe that in the first step Cp_2ZrCl_2 reacts with **1**, terminating the cluster structure. The driving force for this reaction is the formation of $MgCl_2$. The substitution of two Cl's, in Cp_2ZrCl_2, perhaps by Me and thffo groups leads first to the formation of highly active zirconium metallocene intermediate, which catalyzes immediately the polymerization of THF. The $MgCl_2$ side product in solution undergoes ionization[10] and suffers agglomeration with $Mg(thffo)_2$ (rising from **1**) to form

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[8] Crystal data: $C_{29}H_{59}Al_3Cl_4Mg_3O_{10}$, fw = 863.43, monoclinic, $P2_1/m$ (No. 11), $T = 100(2)$ K, $a = 9.434(5)$ Å, $b = 16.963(5)$ Å, $c = 13.990(5)$ Å, $\beta = 104.903(5)°$, $V = 2163.5(15)$ Å^3, $Z = 2$, $D_{calc} = 1.334$ g·cm^{-3}, μ(Mo Kα) = 0.424 cm^{-1}, final R1 = 0.0577 ($I > 2.00\sigma(I)$), $R = 0.0727$ (all data) wR2 = 0.1576 (all data), GOF = 1.046.

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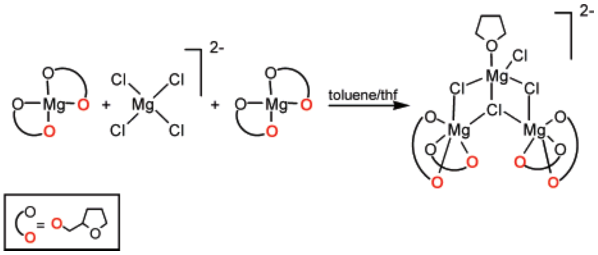
Scheme 4. Reaction Scheme Proposed for $[Mg_3Cl_4(thffo)_4(THF)]^{2-}$ Macrounit Formation



$[Mg_3Cl_4(thffo)_4(THF)]^{2-}$ (Scheme 4). From this perspective, this macrounit might be considered as a tetrapodal part of the $MgCl_2$ support surface, which fulfills the requirement of a $Al_3(\mu_3\text{-}O)$ core (Scheme 3). Further studies are needed to explain the mechanism of alkylaluminum species formation as a result of the decomposition of **2** in hydrocarbons.

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Supporting Information Available: Text and tables giving experimental and crystallographic details. Crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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