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Mysterious MAO

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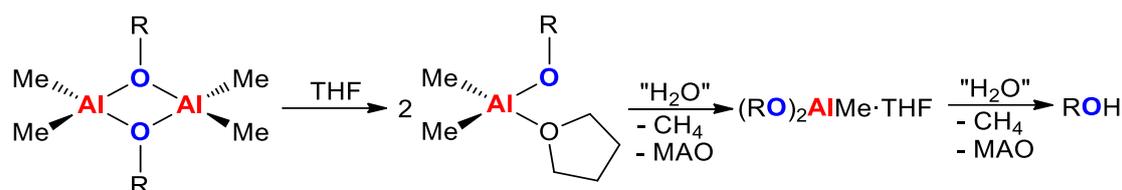
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Summary

Since its discovery in the early eighties, methylalumoxane (MAO) has grown from an academic serendipity to an industrial commodity. Today it is produced on a large scale and widely used as a cocatalyst for various olefin oligomerization and polymerization processes. Despite years of investigation, not much is known about the exact nature of MAO. What has been shown is that multiple species are in dynamic equilibrium with each other and the ever present unreacted trimethylaluminum (Me_3Al). This already complex mixture varies with time, temperature, and age. Furthermore, its stability is dependent on the storage conditions. It is well-known that upon standing at room temperature for several weeks, an insoluble gel is formed. All these properties give rise to a dynamic system that is notoriously hard to study. Over the years, numerous research groups have investigated MAO using an array of different techniques but no concrete structural insights have been gained. Expanding on these previous studies, we have investigated MAO and modified its structure in order to gain a better understanding of its configuration and working principles. As the dynamic behavior of MAO also hampers reproducibility in polymerization catalysis, we are also interested in the development of more stable well-defined cocatalysts.

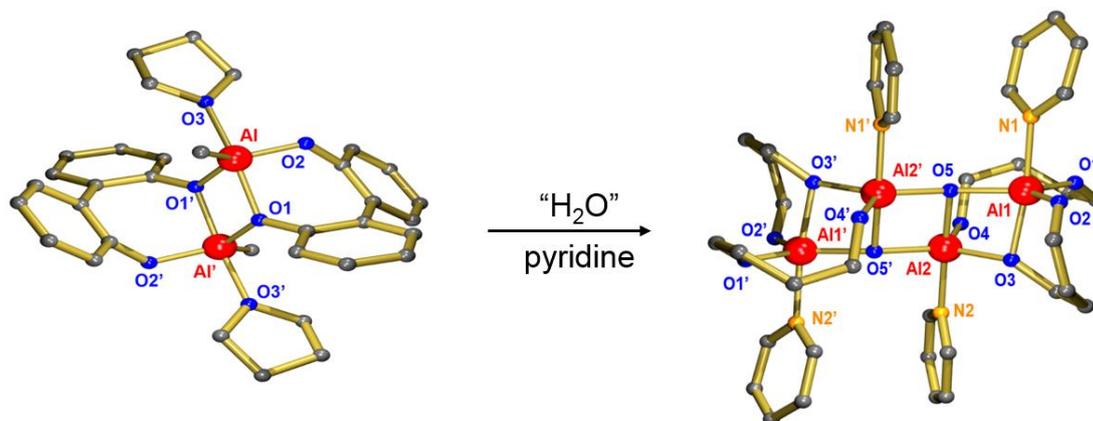
Chapter Two starts off with the first transmission electron microscopy (TEM) study into the large MAO particles (most likely gel precursors). By using an adapted cryo-TEM setup, it was possible to obtain images of the highly air- and moisture-sensitive MAO without complete decomposition. The observed particles were found to consist of highly regular fractal aggregates and most likely represent the gel formed in MAO solutions or a precursor thereof. The primary particles are connected in a pearl chain like fashion. The size of the spheres building the chain increases with age. Comparing these results to similar ones reported for partially combusted particles, such as diesel soot or aerosols, a growing mechanism based on particle sintering can be proposed. A repetition of this process could explain the dramatic change in structure, average molecular weight, and activity of MAO over time.

Chapter Three describes modified MAO derivatives based on the substitution of O^{2-} for RO^- . It was found that the reaction of a sterically demanding alcohol or diol with Me_3Al leads to isolatable and well-defined complexes. The synthesis and characterization of a series of bulky 2,6-disubstituted $(\text{ROAlMe}_2)_2$ complexes is reported. They react cleanly with alcohols to form the alkoxy bridged $[\text{ROAl}(\text{Me})(\mu\text{-OtBu})_2(\text{Me})\text{AlOR}]$. Their reactivity towards water is less straightforward and a coordinating solvent is needed to obtain well-defined structures. It was found that upon hydrolysis, only the $(\text{RO})_2\text{AlMe}$ -solvent complex is obtained (Scheme 1). Further hydrolysis leads to the quantitative formation of CH_4 , the corresponding alcohol, and an undefined $(\text{ROAlO})_n$ species.



Scheme 1. Stepwise hydrolysis of $(\text{ROAlMe}_2)_2$ in THF to eventually form ROH.

Similarly, diols can be used to create well-defined alumoxane clusters. Depending on the Al:diol ratio chosen, different species have been reported in the literature. Using bulky substituted diphenols, we set out to synthesize a monomeric non-solvent stabilized $(\text{RO})_2\text{AlMe}$ complex containing a Lewis acidic three-coordinate Al center. Despite several diol modifications, it was not possible to obtain such complexes and only their respective $[(\text{RO})_2\text{AlMe}\cdot\text{solvent}]_2$ derivatives were always observed. As the synthesis of such monomeric complexes was not possible, the reactivity of non-substituted diols, such as 2,2'-biphenol (BP), was investigated instead. Reaction of the BP- H_2 with Me_3Al in a coordinating solvent selectively led to the formation of $[(\text{BP})\text{AlMe}\cdot\text{solvent}]_2$. In the presence of a strong Lewis base, such as pyridine, this complex reacted with water in a controllable manner to give the ladder-like alumoxane $(\text{BPAl}\cdot\text{pyridine})_4(\mu\text{-O})_2$ (Scheme 2). This complex consists of four Al centers, four BP ligands, two O^{2-} moieties, and four stabilizing pyridine ligands and is a rare example of a well-defined alumoxane ladder structure formed upon direct hydrolysis.



Scheme 2. Hydrolysis of $(\text{BPAlMe}\cdot\text{THF})_2$ in pyridine to give $(\text{BPAl}\cdot\text{pyridine})_4(\mu\text{-O})_2$.

Chapter Four describes an investigation into the potential of *aza*-MAO, $(\text{RAINR}')_n$, and other amine based Al complexes as cocatalysts. The replacement of the O^{2-} in MAO for a RN^{2-} fragment allows for steric and electronic control of the resulting complex through the organic R moiety. These $(\text{RAINR}')_n$ complexes can be obtained in a straightforward manner and have a varying cluster size depending on the size of the R and R' substituents. The obtained clusters are structurally identical to their $(\text{tBuAlO})_n$ analogues but were found to be unreactive towards Lewis bases and Cp^*ZrMe_2 .

To increase the reactivity, amine complexes with a masked three-coordinate Al center were synthesized. Inclusion of a soft Lewis basic site in the ligand, such as a P atom or an aromatic ring, allowed for stabilization of the otherwise highly reactive three-coordinate Al center (Figure 1).

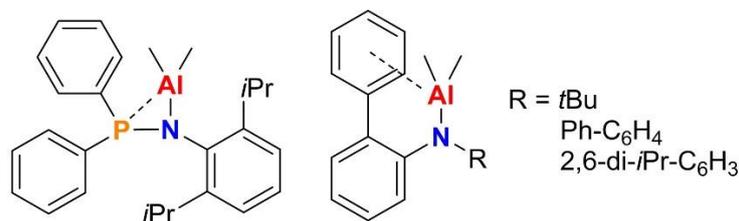
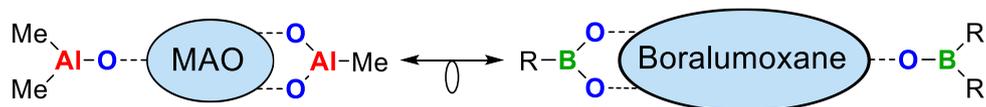


Figure 1. Internally stabilized masked three-coordinate Al alkyl complexes.

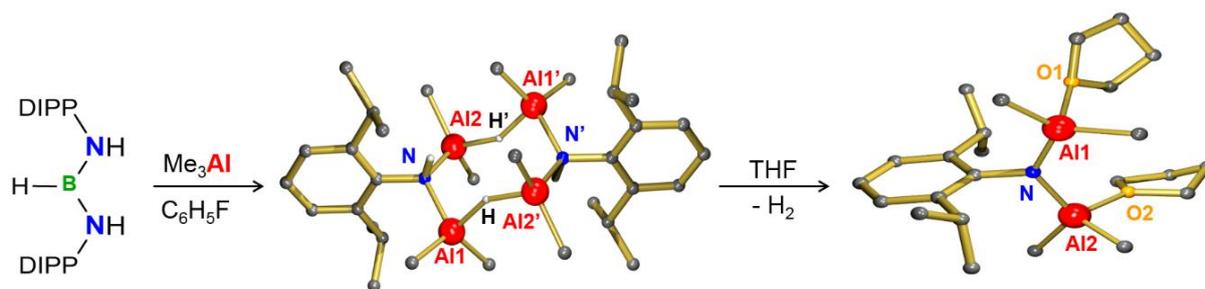
Despite the accessible Lewis acidic Al center and easy coordination of Lewis bases such as pyridine and THF, none of the above mentioned complexes showed significant reactivity towards zirconocene based polymerization catalysts. They do, however, form reactive Frustrated Lewis Pairs and readily activate a range of small molecules and unactivated alkenes.

The addition of boron containing compounds to MAO has been reported. The idea is that B/Al MAO clusters might show improved stability and activation properties. Keeping this idea in mind, Chapter Five describes the use of boronic acids and boronic acids to isolobally replace “OAlMe₂” and “O₂AlMe” units in MAO for “OBR₂” and “O₂BR” moieties (Scheme 3). Similar isolobal O²⁻ for RN²⁻ substitution also allows for the usage of bora-amidates instead of boronic acids.



Scheme 3. Isolobal replacement of Al for B moieties resulting in boralumoxanes.

The R groups of bora-amidates, (NRH)₂BR', provides an extra steric handle that should allow for straightforward control over the reaction products. It was found, however, that due to the facile ligand exchange, the anticipated R'B(NR)₂AlMe complexes did not form. Reaction of (DIPPNH)₂BH with Me₃Al gave under no circumstance the desired HB(NDIPP)₂AlMe but instead the ligand exchange products Me₃B, Me₂AlH, and Me₂AlN(H)DIPP were obtained. The latter two species can combine to form the isolatable [DIPPNH(AlMe₂)(AlMe₂H)]₂ complex (Scheme 4). The complex is temperature stable but in the presence of THF the dimer is cleaved and the acidic NH group and the hydridic proton react together to form H₂ and DIPPN(AlMe₂·THF)₂ (Scheme 4).



Scheme 4. Formation of $[\text{DIPP}(\text{NH}(\text{AlMe}_2)(\text{AlMe}_2\text{H}))_2]$ and its reaction with THF to give $\text{DIPP}(\text{NH}(\text{AlMe}_2\cdot\text{THF})_2)$.

Using aryl boronic acids, $\text{ArB}(\text{OH})_2$, ligand exchange is limited and well-defined boralumoxanes can be obtained. It was found that both, the boronic acid aryl and Al-alkyl substituents used, influence the stability of the resulting complex. The introduction of different aryl groups such, as anthracene, C_6F_5 , mesityl and *p*-tolyl gave products with a range of different structures. Depending on the B:Al ratio and the solvent used, a variety of well-defined complexes could be obtained and characterized using the anthracene derivative, $\text{AntB}(\text{OH})_2$ (Figure 2).

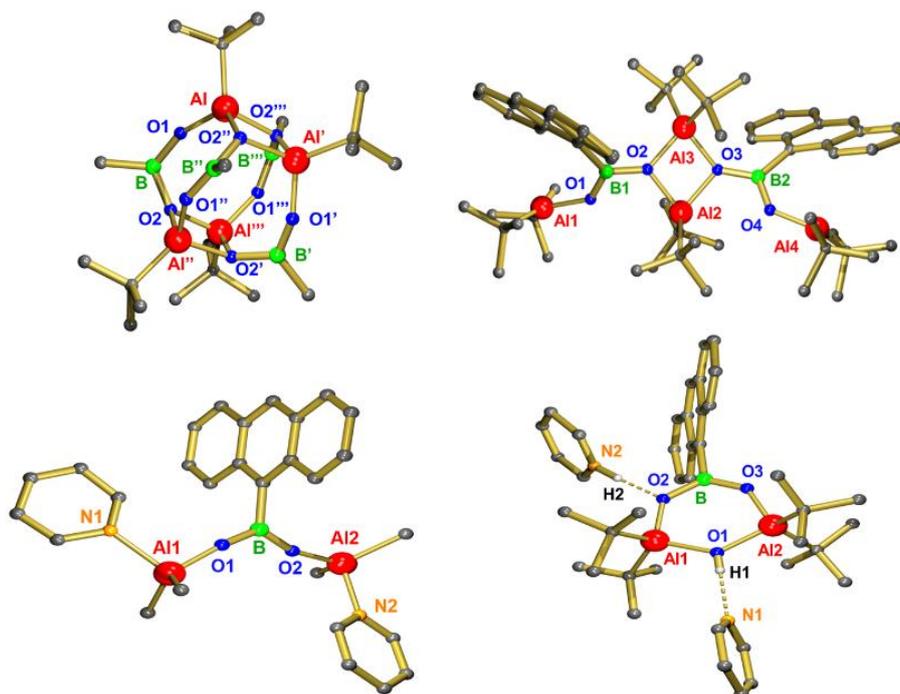


Figure 2. Selected well-defined anthracene based boralumoxanes.

These complexes, particularly $(\text{AntBO}_2\text{AltBu})_4$ and $(\text{AntBO}_2)_2(\text{AltBu}_2)_4$, are able to abstract Me groups from zirconocene catalysts and allow for isolation of the formed cation anion pairs that could be structurally characterized (Figure 3). Both boralumoxane precursors were used in polymerization with Cp_2ZrMe_2 and initial results show activities up to 3 kg PE/mol_{Zr}/h/bar.

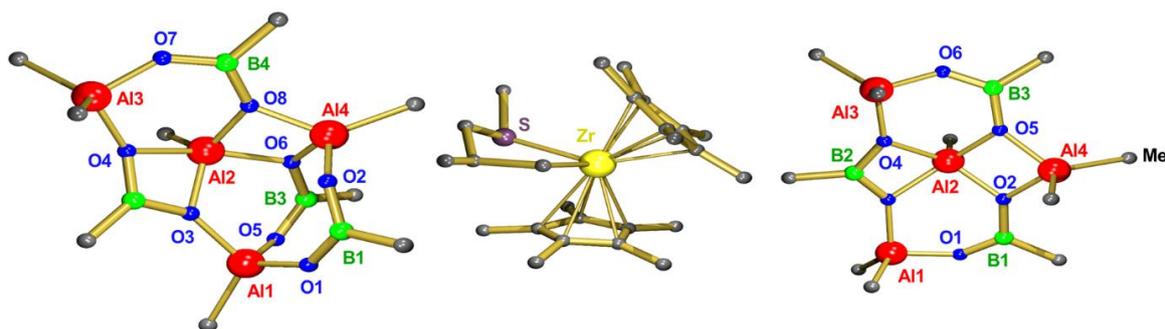


Figure 3. X-ray structure of $[\text{MetBu}_4\text{Al}_4\text{Ant}_4\text{B}_4\text{O}_8]^-$ and $[\text{MetBu}_6\text{Al}_4\text{Ant}_3\text{B}_3\text{O}_6]^-$ formed after reaction of $(\text{AntBO}_2\text{Al}t\text{Bu})_4$ and $(\text{AntBO}_2)_2(\text{Al}t\text{Bu}_2)_4$ with $\text{Cp}^*_2\text{ZrMe}_2$ (one Zr cation shown for illustration and only part of *t*Bu and Ant shown for clarity). The $\text{Cp}^*_2\text{ZrMe}^+$ was trapped by allyl methyl sulfide.

All together the work presented in this thesis shows that new insights into the structure and functioning of MAO can be obtained by modifying its core. A variety of substitutions can be made to obtain well-defined alumoxanes that function as model compounds for MAO. By studying these complexes, a better understanding of MAO can be obtained and potential new cocatalysts can be developed.