Organometallics **2001,** 20, 4466−4468

# *Correspondence*

## Reactivity and Acidity of Alkylaluminoxanes

**Erling Rytter,**[*,†,‡] **Jon Andreas Støvneng,**[‡]
**Jan Lasse Eilertsen,**[‡] **and Martin Ystenes**[§]
*Statoil Research Centre, N-7005 Trondheim, Norway, and Department of Chemical Engineering and Department of Chemistry, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway*

Received May 8, 2001

*Sir:* It is the discovery of methylaluminoxane (MAO) as an activator for metallocene catalysts for olefin polymerization that has stimulated a considerable effort in unveiling the cocatalyst structure and function in the catalyst activation process.[1] Recently, we have proposed models of MAO that were based on molecular modeling, in situ FTIR spectroscopy, titration with dimethylaluminum chloride, and cocatalytic activity during polymerization of ethene with $(Cp^{*})_2ZrCl_2$ and $(Cp)_2ZrMe_2$.[2] The main discoveries were as follows.

(1) MAO, as received from catalyst vendors, or correspondingly dried samples with an Me/Al ratio close to 1.5,[3] does not react with trimethylaluminum (TMA) in the temperature range from ambient to 80 °C.[6]

(2) MAO contains 15−20% of the methyl groups as bridges between aluminum atoms.

(3) These methyl groups are taking part in the activation of zirconocene catalysts.

According to our DFT calculations, the methyl groups are situated in low-strain rings of the −O−Al−O−Al−Me−Al− type, which open readily at the methyl bridge to reveal the latent Lewis acidic aluminum, participating in activation of the catalyst.

In a recent work by Watanabi et al.,[7] it was demonstrated that the alkylaluminoxane $^{t}Bu_6Al_6O_6$ (**I**) reacts with an equimolar amount of TMA, yielding $Me_3{}^{t}Bu_6Al_7O_6$ (**II**). The reaction can be visualized by opening up one of the Al−O bonds of the butylaluminoxane (BuAO) cage, coordinating the aluminum atom of TMA to the vacant coordination site created on the oxygen atom, and forming a bridging methyl bond between the electronically unsaturated aluminum atoms of TMA and BuAO. In addition, some methyl−*tert*-butyl exchange is assumed. The resulting structural features, particularly the methyl bridge, comply well with our proposed model for MAO.[2]

Most alkylaluminoxanes, and the related halo compounds, follow strict coordination rules for neutral to acidic compositions with four-coordinated aluminum centers, completing the valence shell octet, and three-coordinated oxygen atoms.[8] Lewis acidic, three-coordinated aluminum essentially is formed by dissociation at higher temperatures or if bulky ligands like $^{t}Bu$ and $^{i}Bu$ prevent the formation of −Al−Alk−Al− bonds that involve a five-coordinated carbon participating in three-center−two-electron bonding. The prevalence of the observed oxygen coordination, in a variety of shapes from planar to pyramidal, results in a free electron pair. To our knowledge, completing the tetrahedral oxygen coordination sphere, e.g. by attaching an electron acceptor such as monomeric TMA to the lone pair, has not been observed. On the low-coordination side, two-coordinated oxygen evidently is avoided, as exemplified by the formation of the dimeric form of $[^{t}Bu_4Al_2O]_2$ (**III**).[9]

Barron and co-workers characterized structurally the cage type compounds $[^{t}BuAlO]_n$, including **I**.[10] These BuAO's fulfill Smith's rule stating that such cages will be built up by six-membered rings and exactly six four-membered rings.[11] Naturally, the strain created by 90° angles associated with the four-membered rings makes these susceptible to bond cleavage and subsequent reactions,[12] as in the formation of **II** from **I**. To be able to examine this strain on a more quantitative basis, we have performed calculations based on density functional

---

[†] Statoil Research Centre.

[‡] Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU).

[§] Department of Chemistry, Norwegian University of Science and Technology (NTNU).

(1) See for example: (a) Kaminsky, W. *Catal. Today* **1994**, *20*, 257. (b) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(2) (a) Ystenes, M.; Eilertsen, J. L.; Liu, J.; Ott, M.; Rytter, E.; Støvneng, J. *J. Polym. Sci., A* **2000**, *38*, 3106. (b) Eilertsen, J. L.; Rytter, E.; Ystenes, M. *Vib. Spectrosc.* **2000**, *24*, 257. (c) Eilertsen, J. L.; Rytter, E.; Ystenes, M. In *Proceedings of the International Symposium on Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer: Berlin, 1999; p 136. (d) Eilertsen, J. L. Ph.D. Thesis, NTNU, Trondheim, Norway, 2000; ISBN 82-7984-139-3. (e) Rytter, E.; Ystenes, M.; Eilertsen, J. L.; Ott, M.; Støvneng, J. A.; Liu, J. In *Organometallic Catalysts and Olefin Polymerization*; Blom, R., Follestad, A., Rytter, E., Tilset, M., Ystenes, M., Eds.; Springer: Berlin, 2001; p 23.

(3) We have analyzed the Me/Al ratio both by determining methyl according to the volumetric method used by Sinn and co-workers[4] and the NMR method described by Imhoff and co-workers.[5] We obtained an Me/Al value for our samples of "dried" commercial type MAO between 1.50 and 1.55, close to the nominal value of 1.5 often stated, clearly below the "as received" samples of ca. 1.7 and significantly above the samples studied by Barron and co-workers (see ref 7 and references therein). The analyses of the MAO samples are discussed in refs 2a and 2b.

(4) Sinn, H. *Macromol. Symp.* **1995**, *97*, 27.

(5) Imhoff, D. W.; Simeral, L. S.; Samngokoys, S. Z.; Peel, J. H. *Organometallics* **1998**, *17*, 1941.

(6) By the term "react" we mean a reaction in the thermodynamic sense. In other words, from this term we exclude methyl exchanges and other dynamic rearrangements, such as TMA exchange.

(7) Watanabi, M.; McMahon, C. N.; Harlan, C. J.; Barron, A. R. *Organometallics* **2001**, *20*, 460.

(8) Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1997**, *543*, 1.

(9) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.

(10) Harlan, C. J.; Mason, M. R.; Barron, A. R. *Organometallics* **1994**, *13*, 2967.

(11) Hitchcock, P. B.; Smith, J. D.; Thomas, K. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1433.

(12) (a) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465. (b) Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 2213.

10.1021/om010379d CCC: $20.00
Publication on Web 10/03/2001

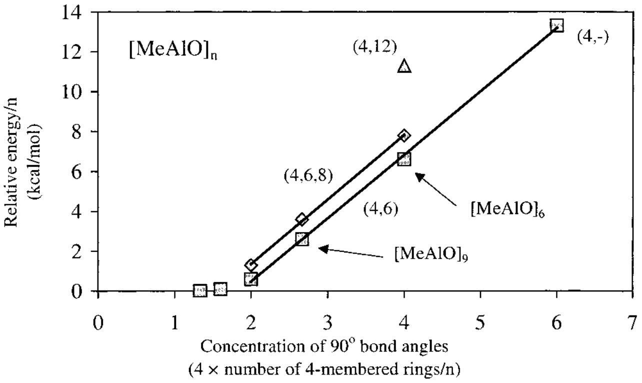

**Figure 1.** Relative energies per MeAlO unit of $[MeAlO]_n$ cage structures with $n$ between 4 and 18, plotted as a function of the concentration of 90° bond angles: (squares) cages with six-membered rings and six four-membered rings; (diamonds) cages with six-membered rings, two eight-membered rings, and eight four-membered rings; (triangle) cage ("drum") with two 12-membered rings and 12 four-membered rings. The straight lines are linear fits to the diamonds and four of the squares, respectively. Figures in parentheses denote the number of atoms in the rings as specified above. See ref 2a for detailed molecular models. Symmetric low-energy structures with distributed four-membered rings are selected when there are several options.

theory. Details on the computational method have been described earlier.[2] In Figure 1 we have plotted relative energies for some of the MAO cages $[MeAlO]_n$. The straight lines obtained clearly indicate that there is a specific energy destabilization associated with the four-membered rings that is diluted for larger complexes. From the slopes, we can even calculate the destabilization value to 3.2 kcal/(mol of 90° angles), corresponding to 13 kcal/(mol of four-membered rings). Further, it is clear that introducing larger rings also destabilizes the structures, as do three six-membered rings at a corner. (This simple model can be refined further in terms of the distribution of angles at each corner of the cages,[13] but the increased complexity tends to mask the main point.)

For $[MeAlO]_n$ cages with $n = 4$, 6, or 9, symmetric structures can be obtained with adjacent four-membered rings. Thus, one, two, or three TMA monomers can be introduced by opening up the common Al−O bond(s) of these pairs of four-membered rings, creating new six-membered rings of the type −Al−O−Al−Me−Al−O−. Below, we show an example of the calculated energies involved in these reactions (see Figure 2):

$$\underset{\textbf{IV}}{Me_6Al_6O_6 + {}^1/_2Me_6Al_2 = Me_9Al_7O_6} \qquad \Delta E = -6.5\ \text{kcal/mol}$$

$$\underset{\textbf{V}}{Me_9Al_7O_6 + {}^1/_2Me_6Al_2 = Me_{12}Al_8O_6} \qquad \Delta E = -\ 7.4\ \text{kcal/mol}$$

In other words, even breaking the comparatively stable double methyl bonds in dimeric TMA is energetically favorable, and it is gratifying that the energy gain

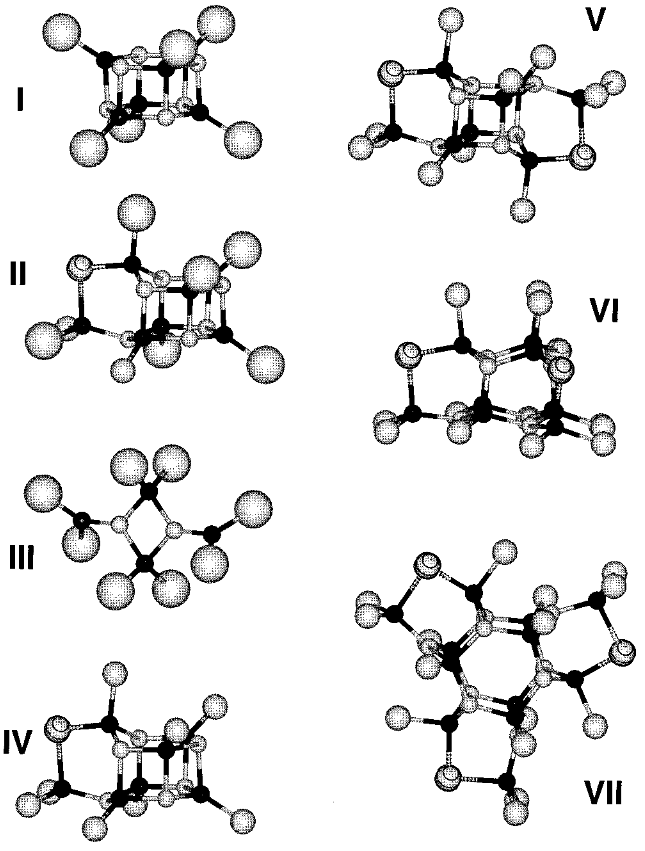

**Figure 2.** AlkAO cage structures. The structures with −Al−Me−Al− bridge(s) are obtained from $[^tBuAlO]_6$ or its methyl analogue after incorporation of one (**II** and **IV**), two (**V**), and three (**VI**) TMA monomers, by opening up Al−O bond(s) between adjacent four-membered rings. Legend: (black) Al; (gray, small) O; (gray, intermediate) Me; (gray/striped, intermediate) Me bridge; (gray, large) $^t$Bu.

is roughly the same for both steps. Adding three TMA monomers (or rather $^3/_2$ TMA dimers) to alternating four-membered rings of the starting structure $Me_6Al_6O_6$, thus obtaining $Me_{15}Al_9O_6$ (**VI**) with only six-membered rings, is endothermic by 8.6 kcal/mol due to steric repulsion between methyl groups. When **V**, or the larger cage $Me_{18}Al_{12}O_9$ (**VII**),[2] is reached, there is no obvious reason to expect a further reaction with TMA, as no reactive four-membered rings are left. This is the point made in our previous work,[2] which actually also was verified by quantitative in situ FTIR measurements. Unfortunately, Barron and co-workers missed this point in their latest contribution, as they state that their results contrast with ours, which they in fact do not, as the aluminoxane starting structures are different.[7] We rather prefer to work on MAO samples close to the commercial type composition, i.e., with an Me/Al ratio of approximately 1.5. Note that the structures **V** and **VII** fulfill this requirement exactly, whereas **VI** has Me/Al = 1.67 and **II**, equivalent to **IV**, has an Alk/Al ratio as low as 1.29. As the basic cage **I**, which has an Alk/Al ratio of 1, is the starting model for the latter structures **II** and **IV**, it is no wonder that the reactivities toward TMA differ.

A similar issue concerns the proposed "*latent Lewis acidity*", related to the strain present in the cages[10,12] and defined as the ability of an electron-precise molecule to undergo heterolytic bond cleavage to generate a Lewis

---

[13] Zurek, E.; Woo, T. K.; Firman, T. K.; Ziegler, T. *Inorg. Chem.* **2001**, *40*, 361.

acidic site. It was proposed that the cocatalytic activity of alkylaluminoxanes is a consequence of this latent Lewis acidity. First, we wish to emphasize that this acidity definition appears to be unfortunate and misleading, as heterolytic cleavage of an −Al−O− bond yields not only a Lewis acidic aluminum atom but also a highly basic oxygen atom. In fact, it is the bond between this basic oxygen and the electronically unsaturated aluminum atom of an incoming TMA monomer that is the main driving force for the reactions described above. In our earlier work, it was confirmed that two-coordinated oxygen is energetically highly unfavorable for aluminoxanes, whereas a reduction from four- to three-coordinated aluminum does not have such a significant effect. The subsequent formation of a methyl bridge between two aluminum atoms, however, represents a latent Lewis acidic site, now transferred from TMA to the extended MAO (or rather AlkAO) cage.

This methyl bridge is actually a prerequisite for activating the catalyst by MAO, as it can open and pick up a chloride or methide ligand from the catalyst.[2] The size of the cocatalyst molecules and their ability to distribute and “hide” the negative charge probably are important features distinguishing MAO from other alkylaluminum compounds. Therefore, it is not surprising that **II** can act as an activator for metallocenes. Details of this mechanism will be described elsewhere. Note also that normal practice with MAO is to operate with some excess of TMA. Therefore, significant amounts of stressed, reactive four-membered rings can hardly be left in the system. Trying to remove TMA beyond the Me/Al ratio of 1.5 results in a MAO that becomes insoluble in the solvents normally applied for catalyst impregnation and polymerization tests, presumably due to a more polar nature and the possibility of agglomeration. Such systems therefore are impractical for industrial use.

As we have rationalized the catalyst activation in terms of acidic aluminum atoms (or equivalent methyl bridges) on the cocatalyst, we propose that a better measure of Lewis acidity for MAO type activators simply is given by

$$\text{net number of Lewis acidic sites (NNLAS)} = n_{\text{Al(3)}} - n_{\text{O(2)}} + n_{\text{b}} \; (+n_{\text{O(4)}})$$

$$\text{NNLAS} = n_{\text{Al}} - n_{\text{O}}$$

counting the amount of three-coordinated acidic aluminum atoms, subtracting basic two-coordinated oxygen atoms, and adding methyl bridges and four-coordinated oxygens, if present. The last two coordination types represent a weak coordination to the acidic aluminum atoms and, therefore, the latent Lewis acidity. (If the bridges are chlorine atoms, we still may count them as acidic, but these three-center bonds seem to be too strong to participate in metallocene activation.) These equations yield a net acidity NNLAS = 0 for structure **I**, NNLAS = 1 for **II** and **IV**, and NNLAS = 2 for structure **V**. Important factors for catalyst activation are likely to be both NNLAS and the acidic strength and, for Alk/Al ≪ 1.5, the strain in four-membered rings.

We appreciate the preparative work and structural characterization of Barron and co-workers that have been invaluable for understanding the fundamentals of alkyl aluminoxane chemistry. Further, we look forward to additional structural characterization of well-defined compounds which are more relevant for MAO used as a cocatalyst, i.e., with Me/Al ≅ 1.5. At present, our comprehension of the activation mechanism for metallocene catalysts differs fundamentally from theirs. AlkAlO structures with low Alk/Al ratios contain four-membered rings, which strains are released upon addition of TMA. For commercial type MAO, there is a surplus of TMA and presumably MAO structures with less configurational strain, but with latent Lewis acidic sites of the −Al−Me−Al− type that participate in activation of metallocene catalysts.

OM010379D