APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 394–397
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.679

Organoboron water, part I: Synthesis and multinuclear magnetic resonance studies on the structure of tetramethyldialuminoxane

Kinga Kacprzak and Janusz Serwatowski*

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Received 6 December 2003; Revised 19 January 2004; Accepted 23 April 2004

The structure of tetramethyldialuminoxane was studied. The low-temperature ^{1}H and ^{13}C NMR spectra suggest that the methyl groups bridge the aluminum atoms in the dialuminoxane trimer. A new method of synthesis of methylaluminoxanes and tetramethyldialuminoxanes in the reaction of tetraethyldiboroxane (organoboron water) with trimethylaluminum (1 : 1 and 1 : 2 respectively) was applied to synthesize the investigated system. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: methylaluminoxane (MAO); tetramethyldialuminoxane; tetraethyldiboroxane

INTRODUCTION

Since the last review of Pasynkiewicz,[1] only a few studies regarding to synthesis, structure and chemical properties of alkylaluminoxanes and tetraalkyldialuminoxanes have appeared in the literature. Actually, only Barron and co-workers have published some chemistry of these compounds: the structural characterization of the corresponding *tert*-butyl derivatives[2,3] and a new method for the determination of the trialkylaluminum content in aluminoxanes;[4] in addition they described the reactions of trimethylaluminum (Me_3Al) with *tert*-butylaluminoxanes[5] and the formation of methylaluminoxane (MAO) in the decomposition reaction of dimethylaluminum alkoxyderivatives.[6] Other studies regarded mostly the chemistry of MAOs, and in particular an approach to their structural elucidation. Also, the application of MAO as a cocatalyst in polymerization has been widely studied. Diffusion measurements of MAO in toluene by ^{1}H NMR spin-lattice relaxation time described by Hansen *et al*.[7] showed that the internal structure of MAO changes with concentration. *In situ* FTIR spectroscopy during addition of Me_3Al to so called 'true' MAO (where Me/Al ratio is 1.5), reported by Ystenes and co-workers,[8] showed no formation of MAO–Me_3Al compounds, whereas others assumed the formation of this type of complex.[5,9,10] ^{1}H and ^{27}Al NMR spectroscopic measurements of MAOs synthesized in pentane or toluene exhibited species containing 4- or 5-coordinated aluminum atoms respectively.[11] All these approaches to explain the structure of MAO are of great interest in relation to their application in homogeneous polymerization of olefins. It is well known that MAOs are the most effective cocatalyst with metallocene catalysts in the polymerization process.[12–15] However, all the studies on the structure of MAOs and tetraalkyldialuminoxanes applied only one method of synthesis of these compounds: the hydrolysis of the corresponding trialkylaluminum. As water is a very aggressive reagent in the reactions with trialkylaluminums (especially with Me_3Al) it is possible that the reaction is not selective, even when proceeding at low temperatures and in low concentrations. The aluminoxanes obtained have different association degrees and actually are the mixtures of different species.[16] In addition, one has to distinguish between aluminoxanes of general formula $(RAlO)_n$ and dialuminoxanes of the formula $(R_4Al_2O)_n$, which also is not always exactly specified. Compounds of the formula $(RAlO)_n$ (with R/Al molar ratio of 1 : 1) are obtained in the reaction of R_3Al with H_2O in 1 : 1 molar ratio; and compounds of the formula $(R_4Al_2O)_n$ (with R/Al molar ratio of 2 : 1) are obtained in a 2 : 1 molar ratio. Both types of reaction can be easily controlled by the evolution of alkane. If the amount of alkane evolved is correct (e.g. 2 mol of methane per 1 mol of Me_3Al in the 1 : 1 reaction of Me_3Al with water) then it is impossible to obtain a product with Me/Al >1 (e.g. 1.5), which is widely reported. Furthermore, the existence of 'free'

*Correspondence to: Janusz Serwatowski, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland.
E-mail: serwat@ch.pw.edu.pl
Contract/grant sponsor: Aldrich Chem Co.
Contract/grant sponsor: State Committee for Scientific Research.

or complexed Me_3Al in $(MeAlO)_n$, often called 'residual' Me_3Al, after the quantitative 1:1 reaction with water is also hard to explain, unless one assumes that so called MAO is not $(MeAlO)_n$ (where each aluminum atom is bonded to one methyl group) but rather a mixture of Al_2O_3, $(MeAlO)_n$ and Me_3Al existing in equilibrium:

$$(MeAlO)_3 \rightleftharpoons Al_2O_3 + Me_3Al \quad (1)$$

This could be in agreement with the known observations that MAO cannot be always quantitatively dissolved in Me_3Al (Al_2O_3 is insoluble in Me_3Al), and also that Me_3Al as a 'free' compound can be determined in MAO by NMR spectroscopy.[4,9]

We have found the simple method of synthesis of aluminoxanes and dialuminoxanes in which so called 'organoboron water' (tetraethyldiboroxane, Et_4B_2O) is used instead of water in the reactions with trialkylaluminum. We have applied this method successfully in the synthesis of tetraethyldialuminoxane,[17] the structure of which we have reported earlier.[18] This study describes the synthesis and an approach to the structural elucidation of tetramethyldialuminoxane $(Me_4Al_2O)_3$. This work is the next step in the very relevant matter concerning the structure elucidation of MAOs.

EXPERIMENTAL

Reaction of Me_3Al with tetraethyldiboroxane

To 4.00 g (56.0 mmol) of Me_3Al in 10 ml of toluene cooled to −78 °C was added 4.31 g (28.0 mmol) of Et_4B_2O dropwise. The mixture was stirred for 1 h at −78 °C and then slowly heated to room temperature. ^1H NMR (toluene-d_8) δ 1.10 (m, 6H), 0.92 (q, 4H), 0.65 (s, 3H), −0.38 (s, 12H); ^{13}C NMR (toluene-d_8) δ 19.93, 8.84, 8.18, −7.38; ^{11}B NMR (toluene-d_8) δ 86.1; ^{17}O NMR (toluene-d_8) δ 59.8; ^{27}Al NMR (toluene-d_8) δ 153.0.

Reaction of Me_3Al with MAO

To 4.00 g (68.9 mmol) of MAO[19] suspended in 6.92 g of toluene was added 0.49 g (68.9 mmol) of Me_3Al dropwise. The mixture was stirred and heated at reflux for 3 h. The clear solution obtained (11.40 g) was cooled to room temperature.

Analysis. Methyl groups (gasometric): theoretical, 46.1%; found, 43.9%. Al: theoretical, 41.5%; found, 39.1%. Me/Al: theoretical, 2; found, 1.76.

Cryoscopic molecular weight determination in benzene: theoretical, 390 (for trimer); found, 366.6. ^1H NMR (toluene-d_8) δ −0.36; ^{13}C NMR (toluene-d_8) δ −7.44; ^{17}O NMR (toluene-d_8) δ 59.8; ^{27}Al NMR (toluene-d_8) δ 153.0.

RESULTS AND DISCUSSION

$(Me_4Al_2O)_3$ was synthesized in the reaction of Me_3Al with Et_4B_2O either in a 2:1 molar ratio respectively or in a 1:1 molar ratio, followed by the reaction of the 1:1 reaction product with the second mole of Me_3Al.

Method 1. The toluene solution of Me_3Al was treated at −78 °C by Et_4B_2O (2:1 respectively):

$$Et_4B_2O + 2Me_3Al \xrightarrow[-78\,^\circ C]{\text{toluene}} 2Et_2BMe + \tfrac{1}{3}(Me_4Al_2O)_3 \quad (2)$$

The reaction mixture was heated slowly to room temperature and subjected to multinuclear magnetic resonance spectroscopic measurements.

The ^{27}Al and ^{17}O NMR spectra of the reaction mixture performed at room temperature each showed only one signal (153 ppm and 59.6 ppm respectively). The ^{11}B NMR spectrum of the mixture also showed only one signal, at 86.1 ppm. No signals of Et_4B_2O ($\delta^{17}O = 223$ ppm and $\delta^{11}B = 53$ ppm) were detected in the corresponding spectra. This means that Et_4B_2O reacted quantitatively to transfer its oxygen atom from boron atoms to aluminum atoms, and that methylation of boron atoms occurred to form Et_2BMe ($\delta^{11}B = 86.1$ ppm). The most likely reaction course is represented in Equation (2). The $(Me_4Al_2O)_3$ formed existed in a mixture with methyldiethylboron in the toluene solution.

To confirm this suggestion, and also to explain the structure of $(Me_4Al_2O)_3$ obtained, the high-room- and low-temperature ^1H and ^{13}C NMR measurements of the reaction mixture were preformed. The results are collected in Table 1.

The room- and high-temperature ^1H and ^{13}C NMR spectra each showed only one signal of methyl groups (protons or carbon atoms respectively) bonded to aluminum atoms, whereas the low-temperature spectra exhibited the splitting of one signal to three signals and four signals for the ^1H and ^{13}C NMR spectra respectively. The ^1H and ^{13}C NMR signals of methyl and ethyl groups (proton or carbon atoms respectively) bonded to boron occurred at lower field and did not overlap the Me−Al signals. We interpret these results in terms of formation of bridging methyl groups in the dialuminoxane molecule.

This structure is similar to that suggested earlier for tetraethyldialuminoxane.[18] In structure **I** (Fig. 1), each aluminum atom has a coordination number of 4 and each oxygen atom has a coordination number of 3. These

Table 1. ^1H and ^{13}C (500 MHz) NMR results at variable temperatures. Toluene-d_8 as a solvent. Only Me−Al resonances are presented

Temperature/°C	δ^1H/ppm	$\delta^{13}C$/ppm
80	−0.39	−7.39
25	−0.38	−7.38
−80	0.03	−5.60
	−0.45	−6.94
	−0.56	−8.38
		−9.55

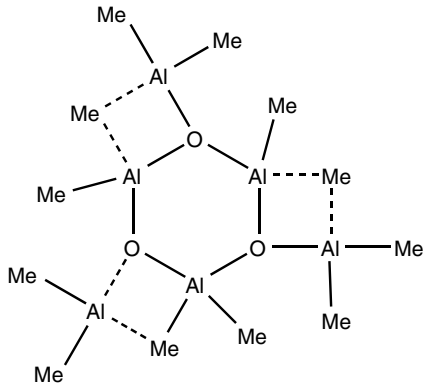

Figure 1. Structure of **I**.

coordination numbers correspond well with the ^{27}Al and ^{17}O NMR results obtained, which additionally confirm a symmetric, most likely cyclic, trimeric structure of the compound. In structure **I** one could expect two different ^{27}Al NMR for two different aluminum atoms. However, both aluminum atoms are four coordinated and the NMR signals of such aluminum atoms are very broad. It is possible that the signal which we observe at 153 ppm ($h_{1/2} = 80$ Hz) consists of the overlapped signals of two similar aluminum atoms. The proper assignment of ^{13}C resonances is difficult. One can expect that the signal at the highest field (−5.60 ppm) belongs to the carbon atom of the bridging methyl group and the three remaining signals (−6.94, −8.38 and −9.55 ppm) belong to the carbon atoms of the terminal methyl groups. We believe that the signal at −6.94 ppm belongs to the carbon atoms of the methyl groups bonded to the aluminum atoms in the Al_3O_3 ring. The remaining two signals belong to the carbon atoms of the methyl groups combined with the three exocyclic aluminum atoms. More difficult to interpret is the low-temperature ^{1}H NMR spectrum. Here, we have three signals: the singlet at 0.03 ppm, which we attribute to the protons of the bridging methyl groups; the multiplet at −0.45 ppm, which probably belongs to the protons of the methyl groups bonded to aluminum atoms in the Al_3O_3 ring; and the singlet at −0.56 ppm, which we attribute to the protons of the methyl groups combined with the three exocyclic aluminum atoms. The integration of these three signals is 1 : 1 : 2 respectively. We do not know why the signal at −0.45 ppm is a multiplet. It is possible that the rotation of the methyl group bonded to the aluminum atoms in the Al_3O_3 ring is slightly hindered at the low temperature. Moreover, the signal at −0.56 ppm is the signal of two overlapped singlets of protons of exocyclic Me groups, which accidentally occur at a similar chemical shift. That is why we see only three proton signals, whereas one could expect four. ^{13}C NMR spectroscopy is more sensitive in this case, and shows four signals. With the low-temperature ^{13}C NMR spectrum we have shown for the first time four different methyl groups in the $(Me_4Al_2O)_3$ molecule and we have confirmed our old suggestion of the existence of bridging alkyl groups in tetraalkyldialuminoxanes.[18]

The $(Me_4Al_2O)_3$ obtained by method 1 existed in this form only in the reaction mixture. Attempts to isolate it by distillation off the toluene and the boron by-products caused a decomposition of dialuminoxane.

Method 2. $(MeAlO)_n$ obtained according to[19] was suspended in toluene and treated with Me_3Al at reflux:

$$MeAlO + Me_3Al \xrightarrow[reflux]{\text{toluene}} \frac{1}{3}(Me_4Al_2O)_3 \qquad (3)$$

During this reaction the solid $(MeAlO)_n$ was dissolved slowly to form a clear solution. The ^{27}Al and ^{17}O room-temperature NMR spectra, as well as the variable-temperature ^{1}H and ^{13}C NMR spectra, of this solution were measured to show that in this reaction $(Me_4Al_2O)_3$ was formed. The ^{27}Al and ^{17}O NMR spectra each exhibited only one NMR resonance (δ^{27}Al = 153 ppm and δ^{17}O = 59.8 ppm). Room-temperature ^{1}H and ^{13}C NMR spectra each showed only one signal (at −0.36 ppm and −7.44 ppm respectively) attributable to the protons and carbon atoms of $(Me_4Al_2O)_3$ methyl groups, and no signals of Me_3Al (−0.59 ppm) or MAO (0.14 ppm) were detected in the spectra. The variable-temperature ^{1}H and ^{13}C NMR results are collected in Table 2.

As earlier (cf. Table 1), room- and high-temperature ^{1}H and ^{13}C NMR spectra each showed only one signal, whereas the low-temperature spectra exhibited the corresponding splitting of the signal. The behavior of the $(Me_4Al_2O)_3$ molecule obtained via method 2 in the NMR measurements is exactly the same as for the dialuminoxane molecule obtained via method 1. The small differences in chemical shifts could be caused by the different composition of the corresponding solutions (in method 1 the boron compounds were present in the solution).

The results obtained confirm that $(Me_4Al_2O)_3$ synthesized in the reaction in Equation (3) is a symmetric cyclic molecule, as was the one obtained in the reaction in Equation (2). This time, having the $(Me_4Al_2O)_3$ molecule as the sole compound in the toluene solution we have been able to perform a cryoscopic molecular weight determination of the system (Table 3). This showed that the molecule existed as a trimer in benzene–toluene solution.

Table 2. ^{1}H and ^{13}C (500 MHz) NMR results at variable temperatures. Toluene-d_8 as a solvent

Temperature/°C	δ^1H/ppm	δ^{13}C/ppm
80	−0.38	−7.36
25	−0.36	−7.44
−80	0.01	−5.50
	−0.43	−6.82
	−0.56	−8.11
		−9.32

Table 3. Cryoscopic molecular weight determination of $(Me_4Al_2O)_3$ in benzene–toluene solution

Time (h)	1	3	10	24
MW	349.7	358.8	366.6	366.7
n	2.69	2.76	2.82	2.82

Multinuclear magnetic resonance and cryoscopic studies on the structure of $(Me_4Al_2O)_3$ obtained in both methods proved finally the trimeric, cyclic structure of the compound with oxygen and carbon bridges. It is possible that structures of this type have only tetraalkyldialuminoxanes with smaller alkyl groups, such as Me or Et.[18] Bulkier groups, such as ^{i}Bu[20] or ^{t}Bu[2], do not occur in the bridge, causing the existence of structures with 3- and 4-coordinated aluminum atoms in the dialuminoxane molecule. $(Me_4Al_2O)_3$ exists only in solution, independent of the method used for the synthesis. Our approaches to isolate this compound via distillation failed because of decomposition. However, the formation in method 2 of $(Me_4Al_2O)_3$, which has the defined structure **I**, confirms indirectly that the starting material (MAO) cannot be a random mixture of the type $Me_3Al/(MeAlO)_n/Al_2O_3$ but also should have a defined structure. Our MAO, obtained using Et_4B_2O in the reaction with Me_3Al, probably has each aluminum atom combined with one methyl group, exists as a defined, small oligomer,[19] and can be easily transformed into $(Me_4Al_2O)_3$ by reaction with Me_3Al. Such MAO can be obtained only in the reaction which excludes water as a reagent with Me_3Al. Commercial MAO, widely reported as having an Me/Al molar ratio of 1.5, is actually a mixture of $(MeAlO)_3$ and $(Me_4Al_2O)_3$. That is why bridging methyl groups in such '1.5 true MAO' were observed.[8,21]

As Et_4B_2O has reacted with Me_3Al similarly to water to form $(MeAlO)_3$ and $(Me_4Al_2O)_3$ we have called this compound 'organoboron water' (Et_2B moiety in Et_4B_2O corresponds to the hydrogen atom in H_2O). Other reactions of Et_4B_2O with organic compounds confirm this property of Et_4B_2O.[17]

Acknowledgements

This work was supported by Aldrich Chem Co., Milwaukee, WI, USA, by continuous donation of chemicals and equipment. We thank also the State Committee for Scientific Research for financial support.

REFERENCES

1. Pasynkiewicz S. *Polyhedron* 1990; 429.
2. Mason MR, Smith JM, Bott SG, Barron AR. *J. Am. Chem. Soc.* 1993; **115**: 4971.
3. Harlan CJ, Mason MR, Barron AR. *Organometallics* 1994; **13**: 2957.
4. Barron AR. *Organometallics* 1995; **14**: 3581.
5. Watanabi M, McMahon CN, Harlan CJ, Barron AR. *Organometallics* 2001; **20**: 460.
6. Obrey SJ, Bott SH, Barron AR. *Organometallics* 2001; **20**: 5162.
7. Hansen EW, Blom R, Kvernberg PO. *Macromol. Chem. Phys.* 2001; **202**: 2880.
8. Eilertsen JS, Rytter E, Ystenes M. *Vib. Spectrosc.* 2000; **24**: 257.
9. Imhoff DW, Simeral LS, Sangokoya SA, Peel JH. *Organometallics* 1998; **17**: 1941.
10. Zurek E, Ziegler T. *Inorg. Chem.* 2001; **40**: 3279.
11. Korneev NN, Khranova IM, Polonsky AW, Ivanova NI, Kisin AW, Kolesov WS. *Izv. Akad. Nauk Ser. Khim.* 1993; **8**: 1453.
12. Chen XH, McCarthy SP, Gross RA. *Macromolecules* 1997; **30**: 3470.
13. Kaminsky W. *J. Chem. Soc. Dalton Trans.* 1998; 1413.
14. Abe N, Hanava H, Maruoka K, Sasaki M, Miyashita M. *Tetrahedron Lett.* 1999; **40**: 5369.
15. Wang Q, Weng JH, Fan ZQ, Feng LX. *Eur. Polym. J.* 2000; **36**: 1265.
16. Zurek E, Woo TK, Firman TK, Ziegler T. *Inorg. Chem.* 2001; **40**: 361.
17. Serwatowski J. *Synthesis and Some Chemical Reactions of Tetraalkyldiboroxanes*. Wydawnictwa Politechniki Warszawskiej: Warszawa, 1989.
18. Bolesławski M, Pasynkiewicz S, Kunicki A, Serwatowski J. *J. Organometal. Chem.* 1976; **116**: 285.
19. Kacprzak K, Serwatowski J. *Appl. Organometal. Chem.* 2004; **8**: 394.
20. Bolesławski M, Serwatowski J. *J. Organometal. Chem.* 1983; **254**: 159.
21. Rytter E, Stovneng JA, Eilertsen JL, Ystenes M. *Organometallics* 2001; **20**: 4466.