Formation and Unexpected Catalytic Reactivity of Organoaluminum Boryloxides

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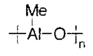
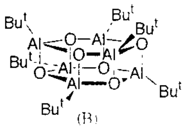
Aluminoxanes $[\mathrm{RAlO}]_n$ have been shown to play a special role in the activation of α-olefin polymerization precatalysts.[1] Within the general family of aluminoxanes, the most commonly utilized derivative is methylaluminoxane (MAO, **A**) which is often described as a mixture of linear and cyclic oligomers, and cage structures.[2] Studies by Barron and co-workers have revealed that sterically hindered alkylaluminoxanes, such as $(\mathrm{Bu^tAlO})_n$, exist as hexameric cages (**B**) and that their Lewis acidity arises by cleavage of one of the framework aluminum−oxygen bonds.[3] More recently, these researchers have also shown that the $[\mathrm{Bu^tAl}]$ units of $(\mathrm{Bu^tAlO})_6$ may be replaced by [MeAl] groups upon treatment with $\mathrm{Me_3Al}$ to give hybrid *tert*-butyl-methylaluminoxanes and even hexameric $(\mathrm{MeAlO})_6$.[4]



(A)



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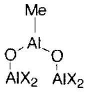
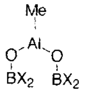


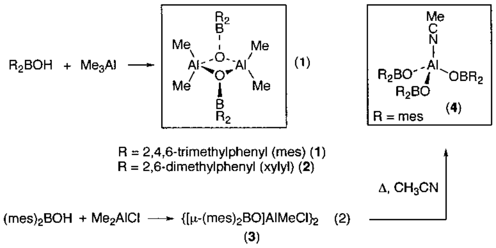
(C)



(D)

With a view to obtaining a greater understanding of MAO, we became interested in modeling the incipient highly Lewis acidic sites that give rise to their exceptional reactivity. In their simplest form, these sites may be viewed as consisting of an aluminum methyl moiety bonded to two highly electron withdrawing $(\mathrm{OAlX_2})$ units (**C**) which, in coordination chemistry terms, can be regarded as quasi-alkoxide ligands. It is also likely that species of this type form during the early stages of MAO formation by the hydrolytic route. For example, Roesky and co-workers have shown that hydrolysis of the sterically hindered model compound $\mathrm{mes_3Al}$ (mes = 2,4,6-trimethylphenyl) in thf affords $[\mathrm{mes_2AlOH}]_2$ as a thf adduct.[5] However, due to the lack of controlled routes to $\mathrm{HOAlX_2}$ species, and thereby to $-\mathrm{OAlX_2}$ ligands, we decided to model these groups using boryloxide units of the type $(-\mathrm{OBX_2})$ (**D**) whose metal derivatives may be readily synthesized via the more amenable borinic acids $(\mathrm{HOBR_2})$. The R substituents may be utilized to modulate the steric and electronic environment around the aluminum center as well as the solubility of the resultant boryloxide products. These boron-containing ligands are also expected to be more electron-withdrawing than their aluminum counterparts due to the higher electronegativity of boron [2.04] relative to aluminum [1.62] (Pauling scale). Known complexes of aluminum containing $(-\mathrm{OBR_2})$ ligands are limited to a few examples.[4−8] Here, we describe reactions of $\mathrm{Me_2AlX}$ (X = Me, Cl) with the borinic acids $\mathrm{HOBR_2}$ (where R = mesityl or 2,6-dimethylphenyl) to give novel organoboryloxide aluminum products. An unexpected outcome of these studies was the finding that $\mathrm{Al{-}OBR_2}$ species are capable of *catalyzing* the formation of boroxine $(\mathrm{RBO})_3$, a trimeric boron relative of the hexanuclear aluminoxanes which may be viewed as being composed of two stacked $(\mathrm{RAlO})_3$ rings.

Scheme 1



Treatment of $(\mathrm{mes})_2\mathrm{BOH}$ with excess $\mathrm{Me_3Al}$ (5 equiv) in refluxing toluene for 12 h, followed by recrystallization from acetonitrile, afforded a white crystalline compound, whose characterizing data are consistent with the mono-boryloxide aluminum species **1** (Scheme 1). The 2,6-dimethylphenyl derivative **2** can be prepared by an analogous procedure. Crystals of **1** suitable for an X-ray structure determination were grown from a saturated acetonitrile solution at room temperature;[9] the structure is shown in Figure 1. The molecule has crystallographic inversion symmetry about the center of the $\mathrm{Al_2O_2}$ ring which is planar and has transannular O···O and Al···Al separations of 2.44 and 2.86 Å, respectively, and Al−O−Al angles of 98.98(10)°. The Al−O−Al bridge is symmetric with Al−O distances of 1.876(2) [Al−O] and 1.879(2) Å [Al−O′], values that lie within the range normally observed for oxygen-bridged ring systems.

The reaction of $(\mathrm{mes})_2\mathrm{BOH}$ with excess $\mathrm{Me_2AlCl}$ under analogous conditions affords the closely related dimeric mono-boryloxide product **3** (Scheme 1). Upon reflux in acetonitrile, **3** reacts to give the tris(boryloxide)aluminum product $(\mathrm{R_2BO})_3\mathrm{Al}(\mathrm{NCMe})$ (**4**). The X-ray structure of **4**[9] is shown in Figure 2. The

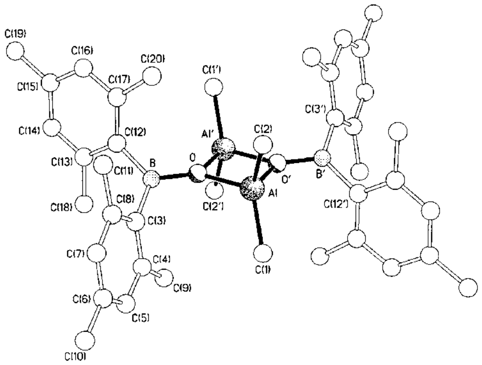


Figure 1. The molecular structure of **1**.

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(1) See: Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413 and references therein.

(2) See: (a) Pasynkiewicz, S. *Macromol. Symp.* **1995**, *97*, 1. (b) Barron, A. R. *Macromol. Symp.* **1995**, *97*, 15.

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(9) See Supporting Information for crystal data.

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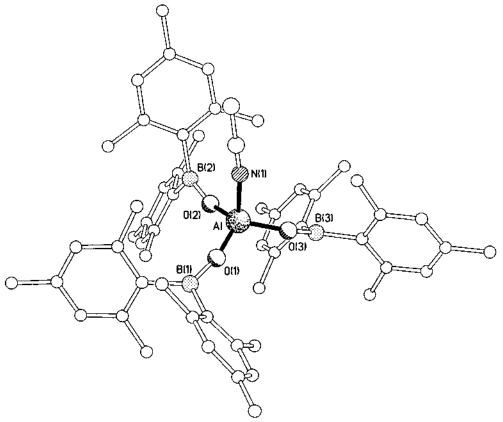

Figure 2. The molecular structure of **4**.

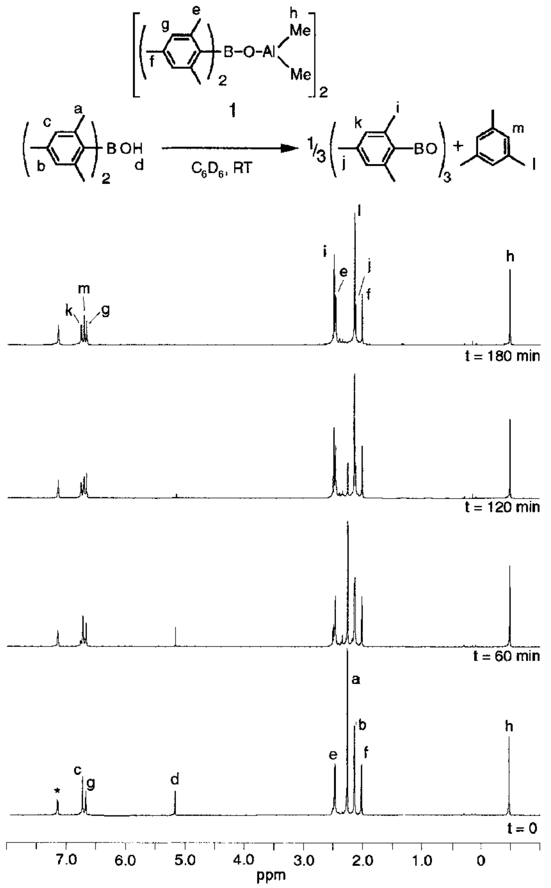

Figure 3. ^{1}H NMR spectra ($t = 0-180$ min) showing the conversion of (mes)$_2$BOH to [mesBO]$_3$ catalyzed by **1** (* resonance due to the residual protio impurity in C_6D_6).

geometry at aluminum is distorted tetrahedral with three coordination sites being occupied by boryloxide ligands and the fourth occupied by a strongly bound MeCN ligand [Al–N(1) 1.954(2) Å]. All three O–Al–N angles are noticeably contracted [ranging between 102.2(1) and 103.8(1)°] indicating a tendency toward trigonal pyramidal geometry with the acetonitrile ligand occupying the apical site. The Al–O distances range between 1.693(2) and 1.708(2) Å and the associated O–B bond lengths between 1.322(3) and 1.350(3) Å. Two Al–O–B units have essentially the same geometry, but the third, which has significantly longer Al–O and shorter O–B distances, also has an Al–O–B angle that shows the largest departure from linearity [144.2(2)°, cf. 163.9(2)° and 158.8(2)°].

An obvious potential alternative route to bis(boryloxide) and tris(boryloxide) species is via treatment of Me_3Al with 2 equiv of (Mes)$_2$BOH and excess (Mes)$_2$BOH, respectively. However, these reactions, rather than affording the higher aluminum boroxide species, gave copious quantities of the white crystalline cyclic boroxine, (MesBO)$_3$, along with concomitant formation of mesitylene (by NMR). Analysis of the residue showed that, in each case, only one methyl of Me_3Al is substituted to give **1** in addition to the boroxine ring. A series of control experiments were performed: under identical experimental conditions but in the absence of Me_3Al or (**1**), (Mes)$_2$BOH does not afford (MesBO)$_3$. Even after prolonged (24 h) reflux in toluene, (Mes)$_2$BOH may be recovered unchanged. Contrastingly, upon addition of a catalytic amount of Me_3Al (5 mol %) to a solution of (Mes)$_2$BOH, quantitative conversion to (MesBO)$_3$ occurs within 12 h at 60 °C, confirming the catalytic role of organoaluminum species in the formation of the boroxine. Historically, boroxines have been synthesized by a number of different routes, the most common being dehydration of boronic acids of the type RB(OH)$_2$ at 110 °C in the solid state[10,11] or in refluxing toluene.[12] To our knowledge, boroxines have not previously been accessed via borinic acid precursors.

To probe the catalytic role of the organoaluminum species, a series of NMR experiments were carried out in which the conversion of (Mes)$_2$BOH to (MesBO)$_3$ was monitored at room temperature in the presence of **1**. The ^{1}H NMR spectra recorded over 180 min are shown in Figure 3. At $t = 0$ (spectrum a), resonances attributable to (Mes)$_2$BOH and **1** only are observable. Spectra b–d show the progressive loss of (Mes)$_2$BOH and the appearance of signals assignable to mesitylene and (MesBO)$_3$. Significantly, no methane is formed. The intensities of the resonances attributable to **1** remain constant throughout the course of the reaction, which is first order in borinic acid (rate constant 10 mol^{-1} s^{-1} (293 K)). The reaction of (Mes)$_2$BOH with **2** afforded (MesBO)$_3$ exclusively; no mixed mesityl/2,6-dimethylphenyl boroxines were observed, and there was no exchange of the boryloxide ligands of **2**. Monitoring this reaction over the temperature range 293–333 K afforded the activation parameters: $\Delta H^\ddagger$ 89.1 kJ mol^{-1}; $\Delta S^\ddagger$ 145 J mol^{-1} K^{-1}; $\Delta G^\ddagger$ (293 K) 46.7 kJ mol^{-1}. The turnover frequency (TOF) at 298 K is dependent upon the aluminum and boryl substituents, the chloroaluminum catalyst **3** (TOF = 8.0 h^{-1}) giving a more active catalyst than **1** (TOF = 1.8 h^{-1}) or the 2,6-dimethylphenylboron catalyst **2** (TOF = 1.3 h^{-1}).

The detailed mechanism by which **1**–**3** catalyzes the conversion of borinic acids R_2BOH into boroxines (RBO)$_3$ remains to be established, and we refrain here from speculation. The elimination of mesitylene solely from the borinic acid highlights a pathway that contrasts with that observed in other systems where the elimination usually involves a methyl from the aluminum center to generate methane. The catalyzed formation of boroxines (RBO)$_3$ by boryloxide–aluminum species highlights the possibility that the formation of species such as [RAlO]$_n$ by hydrolysis of alkyl precursors may be autocatalyzed by intermediates formed during the hydrolytic procedure.

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Note Added in Proof. Subsequent to acceptance of this work for publication, a related study by Serwatowski and co-workers has been published: *Inorg. Chem.* **2000**, *39*, 5763.

Supporting Information Available: Synthetic procedures for **1**–**4** and kinetic data. Three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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