Structural characterization of a cationic zirconocene olefin polymerization catalyst with its methylated boralumoxane counterion

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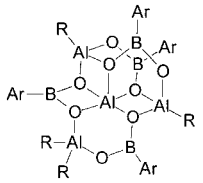
Structural Characterization of a Cationic Zirconocene Olefin Polymerization Catalyst with its Methylated Boralumoxane Counterion**

Bodo Richter, Auke Meetsma, Bart Hessen,* and Jan H. Teuben

The discovery by Sinn and Kaminsky that methyl alumoxane (MAO) can act as an efficient activator for metallocene olefin polymerization catalysts[1] has triggered tremendous developments in single-site olefin polymerization catalysis.[2] Presently, more than twenty years after the initial discovery, the actual nature of MAO and its mechanism of catalyst activation are still under debate.[3] Model studies on *tert*-butyl alumoxanes led Barron et al. to formulate the hypothesis that these alumoxanes consist of oligomeric $(RAlO)_n$ clusters, containing 4-coordinate Al in strained fused 4-membered Al_2O_2 rings that can exhibit "latent Lewis acidity" by ring opening, allowing Al to abstract an alkyl anion from the transition metal dialkyl catalyst precursor.[4, 5] The direct (structural, spectroscopic) study of these processes and their products is hampered by the apparent equilibrium nature of the alkyl transfer reaction, with the equilibrium constant strongly favoring the starting materials when well-defined alumoxanes with sterically demanding alkyl groups are used. Crystal structure determinations of the products resulting from the reaction of $[t\mathrm{BuAlO}]_6$ with MeLi[5] and with RNH_2[6] gave support for the proposed activation mechanism, but as yet the products of the activation of metallocene single-site olefin polymerization catalysts by alumoxane activators have eluded full characterization.

Recently we reported the synthesis and structural characterization of a well-defined boralumoxane species, $[t\mathrm{Bu}_4\mathrm{Al}_4\mathrm{Ar}_4\mathrm{B}_4\mathrm{O}_8]$ (**1**, Ar = 2,6-diisopropylphenyl), and showed that this compound is able to activate $[Cp_2ZrMe_2]$ for catalytic ethene polymerization.[7] Although **1** is topologically quite



1 (R = *t*Bu, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$)

different from the *t*Bu-alumoxane species isolated by Barron et al., containing 3-coordinate B and 4- and 5-coordinate Al, it shares with these compounds the presence of a strained 4-membered Al_2O_2-ring assembly (edge sharing with a $BAlO_2$

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ring) that could be instrumental in the activation process. Here we present an investigation into the latent Lewis-acidic behavior of this well-defined boralumoxane, involving studies of the reactivity of **1** with Lewis bases (pyridines) and with a zirconocene dialkyl complex. The results of this study include the first structural characterization of a salt containing a zirconocene alkyl cation and a methylated boralumoxane counterion.

The Lewis-acidic behavior of **1** was first probed by studying its reactivity with the hard Lewis bases pyridine and 2,6-dimethylpyridine. Experiments on NMR tube scale revealed a rapid reaction of **1** upon addition of one equivalent of pyridine, but with 2,6-dimethylpyridine no reaction was observed. This indicates that the reactivity of **1** with Lewis bases can be restricted by steric factors. Reaction of **1** with pyridine in pentane on a preparative scale allowed isolation of a microcrystalline product with composition $[t\mathrm{Bu}_4\mathrm{Al}_4\mathrm{Ar}_4\mathrm{B}_4\mathrm{O}_8(\mathrm{C}_5\mathrm{H}_5\mathrm{N})]$ (**2**) in 59% yield. A crystal structure determination[8] of $\mathbf{2}\cdot(\mathrm{C}_6\mathrm{H}_6)$, obtained by crystallization from benzene, showed a cluster (Figure 1) with basic structural features

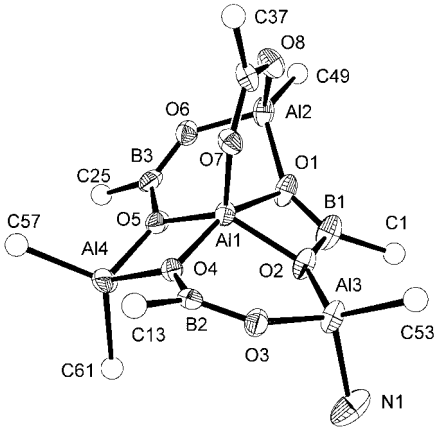
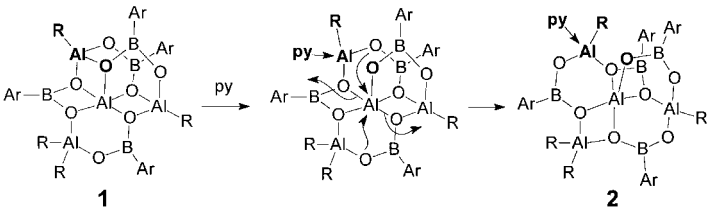


Figure 1. Molecular structure of **2**. All carbon and hydrogen atoms omitted, except for the *ipso* carbons of the groups directly bound to Al (*t*Bu) or B (2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$). Selected bond lengths [Å] and angles [°]: Al3-N1 1.961(4), Al3-C53 1.967(4), Al3-O2 1.826(3), Al3-O3 1.722(3), Al1-O1 2.004(3), Al1-O2 1.916(3), Al1-O4 1.862(3), Al1-O5 1.852(3), Al1-O7 1.709(3); O1-Al1-O2 69.53(11), O4-Al1-O5 81.93(11), O4-Al4-O5 80.95(11), O1-B1-O2 108.0(3).

similar to those of **1**, including a central 5-coordinate Al atom and interconnected 6-membered and 4-membered Al/B-O rings, but without the strained $\mathrm{Al}_2\mathrm{O}_2/\mathrm{BAlO}_2$ edge-sharing ring assembly. The pyridine molecule is coordinated to one of the two *t*BuAl moieties. It is possible that this structure arises from initial attack of pyridine on the *t*BuAl group in the strained ring, followed by a rearrangement of the oxygen atoms around the 5-coordinate Al core, as shown in Scheme 1. These intramolecular rearrangements are likely to be facile in the boralumoxane framework, as was shown by the rapid fluxionality of **1**, resulting in solution NMR spectra consistent with an average C_2 symmetry for this compound.[7] The formation of **2** from **1** and pyridine thus appears to be in line with the expected reactivity of **1** based on the concept of latent Lewis acidity. The ^{1}H NMR spectrum of **2** is complex, but



Scheme 1. Plausible mechanism for the reaction of **1** with pyridine to give **2**.

clearly shows the resonances of the coordinated pyridine, as well as four separate resonances for the Al*t*Bu groups, indicating an asymmetric structure.

Adding one equivalent of $[\mathrm{Cp}^*_2\mathrm{ZrMe}_2]$ ($\mathrm{Cp}^* = \eta^5\text{-}\mathrm{C}_5\mathrm{Me}_5$) to a solution of **1** in $\mathrm{C}_6\mathrm{D}_6$ in an NMR tube at ambient temperature results in a ^{1}H NMR spectrum that is essentially a superposition of the spectra of the starting materials. This suggests that with this zirconocene the reaction of the boralumoxane is either very sluggish, or invisible due to a highly unfavorable equilibrium constant for a possible reversible methyl transfer. In order to trap the $[\mathrm{Cp}^*_2\mathrm{ZrMe}]^+$ cation that would result from such a methyl transfer reaction, we added an excess of allyl methyl thioether to the solution containing **1** and $[\mathrm{Cp}^*_2\mathrm{ZrMe}_2]$. Allyl methyl thioether does not react with **1** itself, but is known to give stoichiometric insertion of the olefin into the Zr–Me bond of $[\mathrm{Cp}^*_2\mathrm{ZrMe}]^+$, resulting in the cationic chelate complex $[\mathrm{Cp}^*_2\mathrm{ZrCH}_2\mathrm{CH}(\mathrm{Me})\mathrm{CH}_2\mathrm{SMe}]^+$ (its OEt analogue was structurally characterized previously in our group[9]). The result of this reaction was a gradual precipitation over several hours of a red oily material and the disappearance of the NMR resonances associated with **1** and $[\mathrm{Cp}^*_2\mathrm{ZrMe}_2]$.

Performing the reaction on a preparative scale in a toluene/pentane mixture resulted in the formation of red-orange crystalline material. A crystal structure determination[8] showed this to be the salt $[\mathrm{Cp}^*_2\mathrm{ZrCH}_2\mathrm{CH}(\mathrm{Me})\mathrm{CH}_2\mathrm{SMe}][\mathrm{Me}t\mathrm{Bu}_4\mathrm{Al}_4\mathrm{Ar}_4\mathrm{B}_4\mathrm{O}_8]$ (**3**), cocrystallized with 1.5 equivalents of toluene per formula unit. The material was obtained in 89% yield. In Figure 2 top, cation and anion are shown schematically, revealing the position of the methyl group that has been transferred from the zirconocene, and in Figure 2 bottom, the core structure of the anion in **3** is shown. As with the pyridine reaction product **2**, the newly introduced group is attached to one of the *t*BuAl moieties, and again the strained $\mathrm{Al}_2\mathrm{O}_2/\mathrm{BAlO}_2$ edge-sharing ring assembly has been opened. The main difference with the structure of **2** is that the rearrangement after ring opening leads to a different arrangement around the central Al atom, but again this structure is readily derived from the presumed initial product of the ring opening (Scheme 2).

Performing the reaction in $\mathrm{C}_6\mathrm{D}_5\mathrm{Br}$ and following it with ^{1}H NMR spectroscopy showed the gradual formation of the known cation $[\mathrm{Cp}^*_2\mathrm{ZrCH}_2\mathrm{CH}(\mathrm{Me})\mathrm{CH}_2\mathrm{SMe}]^+$, and in addition a complicated set of resonances for the methylated boralumoxane anion appeared. Initially, a resonance appeared at $\delta = -0.58$ ppm, which is likely to be associated with the methyl group that is transferred to Al. In the course of time (hours) this species transformed into a product with the AlMe resonance at $\delta = -0.40$ ppm, whereas the resonances of

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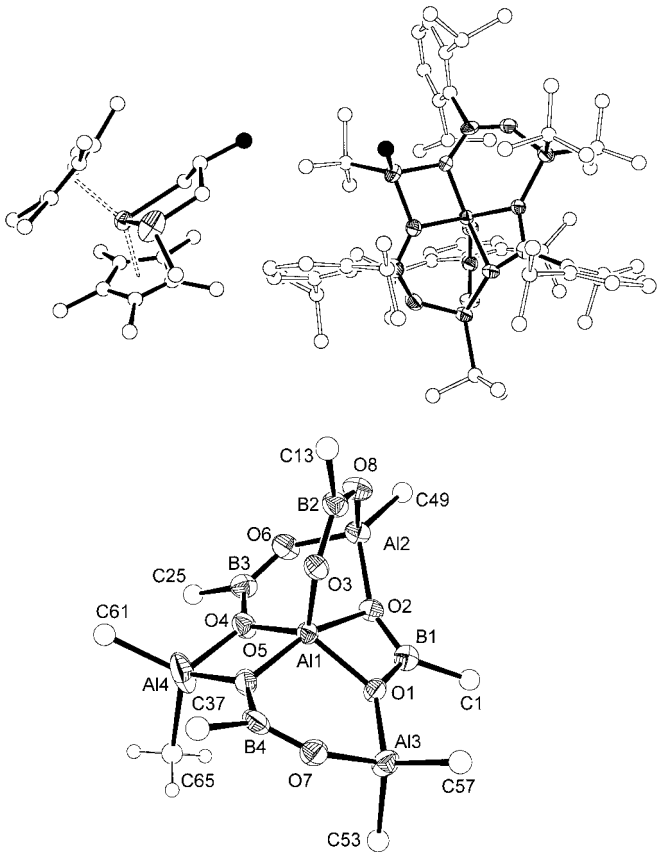
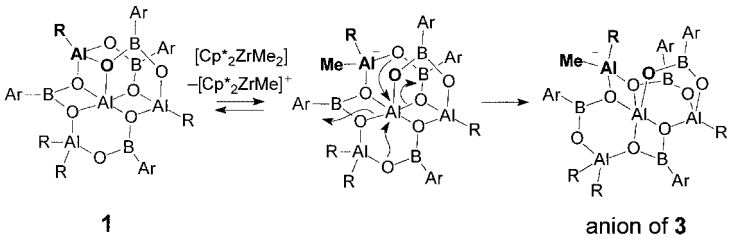


Figure 2. Molecular structure of **3**. Top left: Cation; top right: anion. Carbon atoms represented as spheres, shaded spheres representing the carbon atoms corresponding to the methyl groups that were originally bound to Zr in $[Cp^*_2ZrMe_2]$. Bottom: core of the anion. All carbon and hydrogen atoms omitted, except for the *ipso* carbons of the groups directly bound to Al (*t*Bu) or B (2,6-$iPr_2C_6H_3$), and for the methyl group transferred to Al4, for which the hydrogen atoms are also shown. Selected bond lengths [Å] and angles [°]: Al4-C65 2.091(9), Al4-C61 1.889(9), Al4-O4 1.867(4), Al4-O5 1.849(4), Al1-O1 1.883(3), Al1-O2 2.018(3), Al1-O3 1.717(3), Al1-O4 1.849(4), Al1-O5 1.856(3); O1-Al1-O2 65.52(13), O4-Al1-O5 81.37(15), O4-Al4-O5 81.08(16), O1-B1-O2 107.4(4).



Scheme 2. Plausible mechanism for the reaction of **1** with $[Cp^*_2ZrMe_2]$ and allyl methyl thioether to give **3**.

the cation remained unchanged. This suggests that the methylated boralumoxane anion is converted from a kinetically controlled to a thermodynamically controlled product. For both isomers, four separate resonances for the Al*t*Bu groups are observed, indicating asymmetric structures. Dissolving a portion of crystalline **3** (obtained from the reaction in toluene/pentane as described above) in C_6D_5Br initially showed a dominant AlMe ^{1}H NMR resonance at $\delta = -0.58$ ppm and subsequently a gradual dominance of the species with the resonance at $\delta = -0.40$ ppm. This suggests that the crystal structure of **3** most likely represents the structure of the kinetically controlled product.

The present study conclusively shows that the strained $Al_2O_2/BAlO_2$ edge-sharing ring assembly in the boralumoxane **1** is the feature responsible for the reactivity of this compound towards Lewis bases as well as zirconocene dimethyl complexes. Zirconocene dialkyl compounds are activated by alkyl transfer to the boralumoxane, and the resulting cationic species can insert olefins into the Zr– bond, as was seen by characterization of the product of the methyl allyl thioether insertion. These results give strong support for the concept of latent Lewis acidity formulated by Barron et al. for the mechanism of activation of zirconocene-based olefin polymerization catalysts by alumoxane activators. The observation of this reactivity with boralumoxane **1**, which is topologically quite different from the $[t\text{BuAlO}]_n$ alumoxanes, suggests that there may be a wider scope for metallacyclic activators for single-site olefin polymerization catalysts. It may be noted that the reaction between transition metal dialkyl compounds and alumoxane species stabilized with sterically demanding groups can be rather slow (for $[Cp^*_2ZrMe_2]$ and **1** in the order of hours at ambient temperature), making it more difficult to estimate the true activating potential of these species from polymerization experiments started by simple mixing of the metal dialkyl compound and the activator.

Experimental Section

2: Pyridine (26.5 μL, 0.328 mmol) was added to a suspension of **1** (0.378 g, 0.328 mmol) in 5 mL of *n*-pentane. Subsequently toluene (3 mL) was added, and the mixture was briefly warmed to 40 °C. After allowing the mixture to cool to ambient temperature, the supernatant was decanted and the precipitate was rinsed with 5 mL of *n*-hexane. Drying in vacuo yielded **2** (0.240 g, 59 %). Selected NMR data: ^{1}H NMR (500 MHz, [D$_6$]benzene, 25 °C): $\delta = 7.52$ (d, $J = 5.0$ Hz, 2 H, py *o*-H), 6.79 (t, $J = 7.7$ Hz, 1 H, py *p*-H), 6.40 (m, 2 H, py *m*-H), 1.26, 0.96, 0.83, 0.57 (s, 9 H each, *t*Bu) ppm. ^{11}B NMR (160 MHz, [D$_6$]benzene, 25 °C): $\delta = 30.0$ ($W_{1/2} = 2640$ Hz) ppm. ^{27}Al (130 MHz, [D$_6$]benzene, 25 °C): $\delta = 120$ (very br, $W_{1/2} > 50$ kHz), 41.9 ($W_{1/2} = 5900$ Hz) ppm. C,H,N analysis (%): calcd for $C_{69}H_{109}NO_8B_4Al_4$ (1231.8): C 67.28, H 8.92, N 1.14; found C 67.22, H 8.88, N 1.07.

3: A solution of $[Cp^*_2ZrMe_2]$ (0.134 g, 0.343 mmol) in 2 mL of toluene was added to a suspension of **1** (0.368 g, 0.319 mmol) in 3 mL of *n*-pentane. Subsequently allyl methyl thioether (0.2 mL) was added, and the mixture was allowed to stand overnight at ambient temperature. The supernatant was decanted from the red-orange crystalline material, which was rinsed with two portions of *n*-hexane (3 mL each). Drying in vacuo yielded **3**·$(C_7H_8)_{1.5}$ (0.505 g, 0.285 mmol, 89 %). Selected NMR data: ^{1}H NMR (500 MHz, [D$_5$]bromobenzene, 25 °C): cationic part: $\delta = 2.3$ (br m, 1 H, C*H*Me), 2.26 (ddd, $J = 10.8$, 4.3, 3.3 Hz, 1 H, SC*H*H), 2.14 (dd, $J = 10.7$, 12.6 Hz, 1 H, SCH*H*), 1.94 (dd, $J = 12.9$, 12.3, 1 H, ZrC*H*H), 1.67 (s, 3 H, SMe), 1.60, 1.57 (s, 15 H each, Cp*), 0.79 (d, $J = 6.3$ Hz, 3 H, CH*Me*), –1.12 (ddd, $J = 12.9$, 6.7, 3.4 Hz, 1 H, ZrCH*H*) ppm. anionic part, thermodynamic product: $\delta = 1.25$, 1.14, 1.09, 0.41 (s, 9 H each, *t*Bu), –0.40 (s, 3 H, AlMe) ppm. ^{11}B NMR (160 MHz, [D$_2$]dichloromethane, 25 °C): $\delta = 28.6$ ($W_{1/2} = 1900$ Hz) ppm. ^{27}Al NMR (130 MHz, [D$_2$]dichloromethane, 25 °C): $\delta = 124$ (very br, $W_{1/2} = 35$ kHz), 42.5 ($W_{1/2} = 3600$ Hz) ppm. C,H analysis (%): calcd for $C_{90}H_{148}O_8SB_4Al_4Zr(C_7H_8)_{1.5}$ (1770.8): C 68.49, H 9.02; found C 68.31, H 8.97.

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[8] Crystallographic structure determinations were performed on a Bruker SMART Apex CCD diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved with Patterson methods and extended by direct methods applied to difference structure factors. Crystallographic data for **2**: $C_{69}H_{109}Al_4B_4NO_8 \cdot (C_6H_6)$, $M_r = 1309.91$, monoclinic, space group $P2_1/n$, $a = 13.8868(6)$, $b = 25.188(1)$, $c = 23.346(1)$ Å, $\beta = 106.805(1)^\circ$, $V = 7817.2(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.113$ g cm^{-3}, $\mu = 1.1$ cm^{-1}, $T = 110$ K. A final refinement on F^2 converged at $wR(F^2) = 0.1789$ for 13782 reflections and $R(F) = 0.0733$ for 7505 reflections with $F_o \geq 4\sigma(F_o)$ and 857 parameters. Crystallographic data for **3**: $[C_{25}H_{41}SZr][C_{65}H_{107}Al_4B_4O_8] \cdot (C_7H_8)_{1.5}$, $M_r = 1770.83$, monoclinic, space group $P2_1/c$, $a = 20.6291(8)$, $b = 20.3125(8)$, $c = 26.301(1)$ Å, $\beta = 110.155(1)^\circ$, $V = 10346.0(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.137$ g cm^{-3}, $\mu = 2.11$ cm^{-1}, $T = 110$ K. A final refinement on F^2 converged at $wR(F^2) = 0.2289$ for 18278 reflections and $R(F) = 0.0808$ for 11143 reflections with $F_o \geq 4\sigma(F_o)$ and 1145 parameters and 16 restraints. One of the toluene molecules in the lattice shows extensive orientational disorder, resulting in unrealistic displacement parameters when allowed to vary anisotropically. The other toluene molecule is disordered over an inversion center, and was described as a single molecule with 0.5 occupancy with geometrical restraints. CCDC-177577 (**2**) and CCDC-177576 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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BuMgN*i*Pr$_2$: A New Base for Stoichiometric, Position-Selective Deprotonation of Cyclopropane Carboxamides and Other Weak CH Acids**

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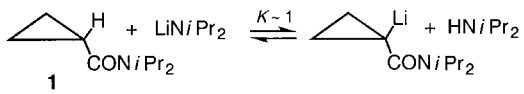
Organolithium (RLi) and -magnesium (R_2Mg) compounds are kinetically poor bases for proton removal from weak carbon acids. If an amine like *N*,*N*,*N*′,*N*′-tetramethylethylendiamine (TMEDA) is added, the barrier is sometimes lowered, but the nucleophility of the organometallic compound remains a problem. This can be ameliorated by using metal amides like lithium diisopropylamide (LDA) and bis(diisopropylamido)magnesium (DA_2Mg). These poor nucleophiles are still kinetically effective bases for deprotonation of weakly acidic CH groups ($pK_a \approx 30 - 35$).[1] However, as the pK_a of the liberated amine and that of the CH acid (e.g. **1**) are similar, such deprotonations are nowhere near stoichiometric (e.g. Scheme 1[2]). This is unsatisfactory.



1

Scheme 1. The equilibrium reaction of LDA with amide **1**.

We now introduce alkylmagnesium amides, here specifically BuMgN*i*Pr$_2$, denoted hereafter as BuMgDA, as an effective solution to this problem.[3] We prepare BuMgDA simply by adding 1.0 equivalent of anhydrous diisopropylamine (DAH) to commercial[4] dibutylmagnesium in heptane (ca. 1.0 M) at room temperature and then stirring the solution for five minutes at 50 °C. BuMgDA[3b] in heptane is quite reactive. Replacing heptane, all or in part, with THF (after the base has been formed) increases this usefully. Unlike Bu_2Mg and many organolithium bases, BuMgDA is stable even in refluxing THF for many hours. BuMgDA, like DA_2Mg, deprotonates/metalates amide-activated[5] cyclopropyl-CH (α, β, or beyond) and cubyl-CH (*ortho*),[6] but the BuMgDA deprotonations are driven to completion by irreversible formation of butane.

It is instructive to compare the metalation of the cyclopropylcarboxamide **2** using Bu_2Mg solutions in heptane treated first with 0, 0.5, or 1.0 equivalent of DAH. Bu_2Mg itself reacted only slowly;[7] mostly starting material was recovered. In the other two cases, when at least some BuMgDA[3b] was present, the overall deprotonation/metalation/carboxylation proceeded in high yield, but the final

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