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Synthesis and structural characterisation of a boralumoxane capable of activating a zirconocene ethene polymerisation catalyst†‡

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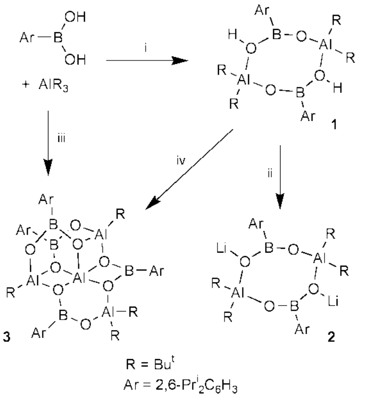
The reaction of Bu^t_3Al with $ArB(OH)_2$ (Ar = 2,6-diisopropylphenyl) leads, *via* the intermediate $[Bu^t_2Al(O)BAr(OH)]_2$ 1, to the crystallographically characterised boralumoxane $Al(Bu^t_2Al)(Bu^tAl)_2(O_2BAr)_4$ 3 which is able to activate Cp_2ZrMe_2 to effect catalytic ethene polymerisation.

The discovery of methylalumoxane (MAO) and its use as a cocatalyst for zirconocene-based olefin polymerisation catalysts[1] has spurred an explosive development of 'single-site' olefin polymerisation catalysts.[2] Despite its widespread use as a cocatalyst for these systems, the actual nature of MAO and the species responsible for its activating ability has still not been unequivocally established. Work by Barron and coworkers on *tert*-butylalumoxane model systems,[3] and various theoretical studies[4] have shown that this property is likely to stem from oligomeric $(MeAlO)_n$ clusters containing four-coordinate Al, that exhibit 'latent' Lewis acidity through ring-opening of strained Al_2O_2 four-membered rings. In several patents it was shown that boronic acids $RB(OH)_2$, boronic esters or boroxines $(RBO)_3$ can act as promotors, enhancing the activating properties of MAO.[5] Boralumoxane materials obtained from reactions of aluminium alkyls with boronic acids or boroxines have been shown to be active as cocatalysts in olefin polymerisation, but these are generally poorly defined species.[6] Very recently, reactions of borinic acids R_2BOH with aluminium trialkyls have yielded some well-defined complexes, but there have been no reports of their properties as cocatalysts.[7] Here we describe the synthesis and structural characterisation of the first well-defined boralumoxane with overall composition $[(RAlO)(R'BO)]_n$, and show that this species is capable of activating zirconocene dimethyl to effect catalytic ethene polymerisation.

In studying the reactivity between trialkylaluminium compounds and boronic acids $RB(OH)_2$ we have focused on Al and B compounds bearing sterically demanding ligands, in order to enhance the possibility of obtaining well-defined species. The reaction of $AlBu^t_3$ with an equimolar amount of the arylboronic acid $ArB(OH)_2$ (Ar = 2,6-diisopropylphenyl) in *n*-pentane solvent at 0 °C initially yielded the species $[Bu^t_2Al(O)BAr(OH)]_2$ **1**, obtained as an analytically pure solid in 83% yield (Scheme 1). The presence of isolated hydroxy groups was established by IR spectroscopy (ν_{OH} 3591 cm^{-1}) and ^1H NMR (OH δ 4.73).[8] It proved difficult to obtain **1** as single crystals suitable for X-ray structure determination. Its formulation as a dimer was supported by its reaction with Bu^nLi followed by the crystallisation of the Li salt $[Bu^t_2Al(O)BAr(OLi)]_2$ **2**, obtained as a benzene solvate. A structure determination§ of $\mathbf{2}\cdot 2C_6H_6$ (Fig. 1) revealed an eight-membered $Al_2B_2O_4$ ring core. Two oxygen atoms on opposite positions on the ring bear Li atoms, that are further stabilised by the proximity of benzene molecules present in the crystal lattice (Li–$C_{benzene}$ distances range over 2.80–3.05 Å). The Al–O–B angle around the unsubstituted oxygen atom O(1) is relatively obtuse, 168.3(2)°, compared to the Al–O(2)–B angle of 128.1(1)°, and the Al(1)–O(1) distance of 1.744(2) Å is clearly shorter than Al(1)–O(2) of 1.821(2) Å. Based on this structure it seems reasonable to formulate **1** as the cyclic species $[Bu^t_2Al(\mu\text{-}O)BAr(\mu\text{-}OH)]_2$.



Scheme 1 *Reagents and conditions*: i, *n*-pentane, 0 °C, 1 h; ii, Bu^nLi, 20 °C, benzene; iii, toluene, 50 °C, recryst. from benzene; iv, hexane, reflux, 2 h.

Allowing a highly concentrated (0.38 M) solution of **1** in benzene-d_6 to stand at ambient temperature and monitoring the sample by ^1H NMR spectroscopy showed that isobutane is evolved gradually, and that various (as yet unidentified) transient species are formed. Eventually, all resonances attributable to hydroxy groups disappear, and a colourless crystalline compound is deposited. This product **3** could be obtained on a preparative scale (Scheme 1), either from **1** by refluxing in hexane for 2 h (48% isolated yield), or from a mixture of

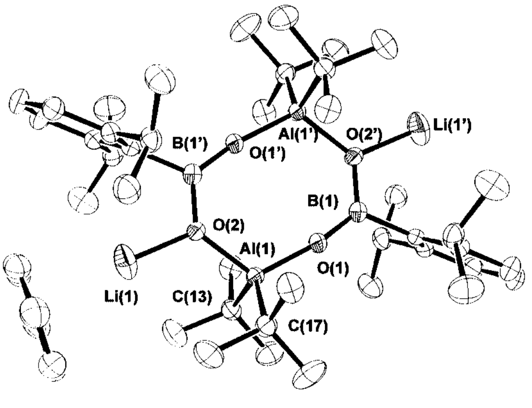


Fig. 1 Molecular structure of **2** (hydrogen atoms omitted for clarity). Selected interatomic distances (Å) and angles (°): Al(1)–O(1) 1.744(2), Al(1)–O(2) 1.821(2), Al(1)–C(13) 1.998(3), Al(1)–C(17) 2.003(2), B(1)–O(1) 1.319(3), B(1)–O(2) 1.380(3), O(2)–Li(1) 1.841(5); O(1)–Al(1)–O(2) 116.20(8), C(13)–Al(1)–C(17) 119.6(1), O(1)–B(1)–O(2) 123.7(2), Al(1)–O(1)–B(1) 168.3(2), Al(1)–O(2)-B(1′) 128.1(1).

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† Electronic supplementary information (ESI) available: experimental, spectroscopic and polymerisation details. See http://www.rsc.org/suppdata/cc/b1/b103670j/

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$ArB(OH)_2$ and Bu^t_3Al by warming in toluene at 50 °C followed by crystallization from benzene (79% isolated yield of its benzene solvate). Compound **3** was identified, by a crystal structure determination of its benzene solvate,§ as $Al(Bu^t_2Al)(Bu^tAl)_2(O_2BAr)_4$ (Fig. 2). The overall composition of the compound corresponds to a tetramer of '$Bu^tAlOBArO$', but it is clear that the remaining *tert*-butyl groups are not evenly distributed over the four Al atoms. The central Al atom bears no alkyl substituent, and is bound to five oxygen atoms. The other three Al atoms are four-coordinate, and all B-atoms are three-coordinate. The structure of **3** may be described as consisting of three six- and three four-membered Al/B–O rings that share the central Al atom. One of the most notable features in the structure is that there are two edge-sharing four-membered rings, containing Al(1)O(2/7)Al(3) and Al(1)O(1/2)B(1), respectively. This arrangement is highly strained, as seen *e.g.* from the angles O(2)–Al(3)–O(7) 83.03(6)°, O(2)–Al(1)–O(7) 81.48(6)° and O(1)–Al(1)–O(2) 71.90(6)°, and may result in 'latent' Lewis acidic behaviour. The longest Al–O distances to four-coordinate Al in the structure are Al(2)–O(1), 1.940(1) Å, a bond to the relatively electron-rich Bu^t_2Al-group, and Al(3)–O(7), 1.890(2) Å, a bond to the Bu^tAl group in the edge-sharing four-membered ring assembly. In solution, the structure of **3** appears to be highly fluxional, showing at ambient temperature only two resonances for the Bu^t groups in the ^1H NMR spectrum. This fluxionality is likely to be due to rapid decomplexation/complexation of O(1) and O(6) to the central Al(1) atom. This results in an average C_2-symmetry of the complex, with the C_2 axis passing through Al(1) and bisecting the O(7)–Al(1)–O(4) angle.

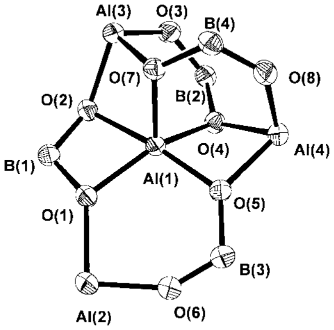

Fig. 2 Molecular structure of **3** (carbon and hydrogen atoms omitted for clarity; each B atom bears one 2,6-diisopropylphenyl group, Al(2) bears two Bu^t groups, Al(3) and Al(4) one Bu^t group each). Selected interatomic distances (Å) and angles (°): Al(1)–O(1) 1.869(1), Al(1)–O(2) 1.924(1), Al(1)–O(4) 1.867(1), Al(1)–O(5) 1.823(1), Al(1)–O(7) 1.851(1), Al(2)–O(1) 1.940(1), Al(2)–O(6) 1.761(2), Al(3)–O(2) 1.827(1), Al(3)–O(3) 1.747(2), Al(3)–O(7) 1.890(2), Al(4)–O(4) 1.873(1), Al(4)–O(5) 1.856(1), Al(4)–O(8) 1.759(1); O(1)–Al(1)–O(2) 71.86(6), O(1)–Al(1)–O(5) 104.00(7), O(4)–Al(1)–O(5) 81.54(6), O(2)–Al(1)–O(4) 97.24(6), O(2)–Al(1)–O(7) 81.48(6), O(1)–B(1)–O(2) 105.8(2), O(1)–Al(2)–O(6) 94.56(7), O(2)–Al(3)–O(7) 83.03(6).

Compounds **1** and **3** were each combined with an equimolar amount of the zirconocene dialkyl Cp_2ZrMe_2 **4** in toluene solvent and exposed to ethene (5 bar), in order to determine whether these species can act as activators for single-site olefin polymerisation catalysts. The combination of **1** and **4** (in an Al : Zr ratio of 2 : 1) did not result in ethene polymerisation activity. In contrast, the combination of **3** and **4** (in an Al : Zr ratio of 4 : 1) readily polymerised ethene to polyethene (M_w = 16600, M_w/M_n = 1.9) with a productivity of 2.59 kg mol^{-1} h^{-1} bar^{-1} (toluene, 5 bar ethene, 23 °C, 30 min run time).

In conclusion, we have shown that the reaction of the boronic acid $ArB(OH)_2$ (Ar = 2,6-diisopropylphenyl) with Bu^t_3Al results in stepwise formation of a well-defined boralumoxane species, $Al(Bu^t_2Al)(Bu^tAl)_2(O_2BAr)_4$ **3**, that is able to act as an activator for zirconocene alkyl olefin polymerisation catalysts. Although **3** contains structural units similar to those in the alumoxanes $[Bu^tAlO]_n$ obtained by Barron and coworkers[3] (six- and four-membered $[(Al/B)O]_n$ rings), it is topologically quite different from these due to three-coordinate B acting as structural element (compared to four-coordinate Al in the alumoxanes). It has in common with these species the presence of edge-sharing four-membered rings, and it is therefore possible that its activating properties are also due to the 'latent' Lewis acidic behaviour of these moieties, as proposed by Barron for the alumoxanes. Further research into the structural and reactivity features of these and related boralumoxanes is expected to shed more light on the nature and activating behaviour of alumoxane-based activators.

Notes and references

§ *Crystallographic data*: for $\mathbf{2}\cdot 2C_6H_6$: $(C_{20}H_{35}AlBLiO_2)_2\cdot 2C_6H_6$, M = 860.64, monoclinic, space group $P2_1/n$, a = 11.773(1), b = 14.868(1), c = 15.097(2) Å, β = 90.863(6)°, U = 2642.3(5) Å^3, T = 180 K, Z = 2, D_c = 1.082 g cm^{-3}, μ = 0.95 cm^{-1}, Enraf-Nonius CAD4-F diffractometer, λ(Mo-Kα) = 0.71073 Å, 6058 unique reflections, final residuals $wR(F^2)$ = 0.1207, $R(F)$ = 0.0571 for 3501 reflections with $F_o \geqslant 4\sigma(F_o)$ and 444 parameters.

For $\mathbf{3}\cdot 2.5C_6H_6$: $C_{64}H_{104}Al_4B_4O_8\cdot 2.5C_6H_6$, M = 1344.96, triclinic, space group $P\bar{1}$, a = 14.0027(5), b = 14.2483(5), c = 22.7478(9) Å, α = 79.888(1), β = 86.886(1), γ = 65.389(1)°, U = 4061.2(3) Å^3, T = 200 K, Z = 2, D_c = 1.100 g cm^{-3}, μ = 1.08 cm^{-1}, Bruker SMART APEX CCD diffractometer, λ(Mo-Kα) = 0.71073 Å, 20435 unique reflections, final residuals $wR(F^2)$ = 0.1689, $R(F)$ = 0.0582 for 13923 reflections with $F_o \geqslant 4\sigma(F_o)$ and 912 parameters. CCDC reference numbers 163150 and 163151. See http://www.rsc.org/suppdata/cc/b1/b103670j/ for crystallographic data in CIF or other electronic format.

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8 NMR data for **1**: ^1H NMR (500 MHz, C_6D_6, 298 K) δ 7.22 (t, $^3J_{HH}$ 7.5 Hz, 1 H, *p*-H), 7.05 (d, $^3J_{HH}$ 7.5 Hz, 2 H, *m*-H), 4.73 (s, 1 H, OH), 3.24 (sept, $^3J_{HH}$ 7.0 Hz, 2 H, $C\mathit{H}Me_2$), 1.38 (br, 6 H, $CH\mathit{Me}_2$), 1.28 (br, 6 H, $CH\mathit{Me}_2$), 1.11 (s, 18 H, CMe_3). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 298 K) δ 151.2 (*o*-ArC), 130.6 (*p*-ArCH), 123.3 (*m*-ArCH), 35.8 ($\mathit{C}HMe_2$), 30.0 ($C\mathit{Me}_3$), 26.8 (br, $CH\mathit{Me}_2$) 25.0 (br, $CH\mathit{Me}_2$). ^{11}B NMR (160 MHz, C_6D_6, 298 K) δ 21.5 ($W_{1/2}$ = 1495 Hz). ^{27}Al NMR (130 MHz, C_6D_6, 298 K) δ 128.6 ($W_{1/2}$ = 18.9 kHz).

9 NMR data for **3**: ^1H NMR (500 MHz, toluene-d_8, 298 K) δ 7.26 (t, $^3J_{HH}$ 8.0 Hz, 2 H, *p*-H), 7.13 (m, 6 H, *p*- and *m*-H), 7.02 (d, 4 H, *m*-H), 3.31 (sept, $^3J_{HH}$ 6.5 Hz, 2 H, $C\mathit{H}Me_2$), 3.27 (sept, $^3J_{HH}$ 6.5 Hz, 2 H, $C\mathit{H}Me_2$), 3.23 (br, 4 H, $C\mathit{H}Me_2$), 1.49 (br, 12 H, $CH\mathit{Me}_2$), 1.40 (br, 24 H, $CH\mathit{Me}_2$), 1.33 (br, 12 H, $CH\mathit{Me}_2$), 1.16 (s, 18 H, CMe_3), 0.56 (s, 18 H, CMe_3). ^{13}C NMR (75 MHz, toluene-d_8, 298 K) δ 153.4 (*o*-ArC), 153.0 (*o*-ArC), 131.4 (*p*-ArCH), 130.9 (*p*-ArCH), 123.1 (*m*-ArCH), 123.0 (*m*-ArCH), 36.2 (br, $\mathit{C}HMe_2$), 35.9 ($\mathit{C}HMe_2$), 35.8 ($\mathit{C}HMe_2$), 30.5 ($C\mathit{Me}_3$), 29.3 ($CH\mathit{Me}_3$), 26.4 (br, $CH\mathit{Me}_2$), 25.7 ($CH\mathit{Me}_2$). ^{11}B NMR (160 MHz, toluene-d_8, 298 K) δ 31.9 ($W_{1/2}$ = 2957 Hz). ^{27}Al NMR (130 MHz, toluene-d_8, 353 K) δ 123.3 ($W_{1/2}$ = 34.5 kHz), 50.3 ($W_{1/2}$ = 3550 Hz).