Al and Ga Compounds

Tetranuclear Homo- and Heteroalumoxanes Containing Reactive Functional Groups: Syntheses and X-ray Crystal Structures of $[\{[LAl(Me)](\mu\text{-}O)(MH_2)\}_2]$**

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There is considerable interest in organoaluminum compounds containing Al–O bonds. This is primarily due to the discovery of methylalumoxane (MAO) as an extremely potent cocata-

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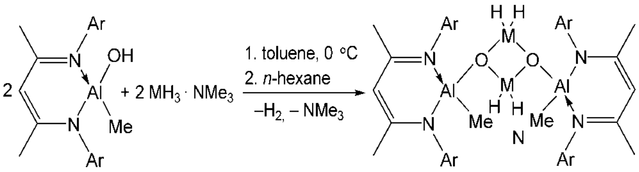
lyst in the polymerization of ethylene and propylene by Group 4 metallocenes.[1] There have been several attempts to prepare discrete molecular organoalumoxanes with well defined structures because the active site structure in MAO is not known. These efforts focussed on the controlled hydrolysis of aluminumtrialkyls or -triaryls where the substituent groups on aluminum are sterically encumbered.[2] Although several interesting compounds have been isolated by the above approach and structurally characterized, none of these was as effective as MAO as a cocatalyst. The second problem of using controlled hydrolysis as a synthetic tool is the lack of predictability of the reaction in being able to assess the nature of the product. The task of assembling compounds with Ga–O–Ga bonds is similarly fraught with synthetic challenges although some trinuclear[3] and a tetranuclear[4] derivatives are known. To assemble soluble lipophilic organoalumoxanes in a predictable and rational manner a change in the synthetic approach is required. Thus, instead of taking the Al–C or Al–H bonds as the starting point for making Al–O–Al bonds it would be more convenient to use organoaluminum hydroxides containing Al–O linkages as the precursors. The recent isolation of a discrete aluminum dihydroxide $[LAl(OH)_2]$,[5] prompted us to look for a suitable synthon that would allow a rational and facile assembly of structural units of alumoxanes as well as heteroalumoxanes. A second goal was to retain reactive groups on the metal centers in such compounds. This arrangement would allow a stepwise synthesis of cage structures. Herein, we describe the synthesis and structural characterization of $[\{[LAl(Me)](\mu\text{-}O)(AlH_2)\}_2]$ (**2**) and $[\{[LAl(Me)](\mu\text{-}O)(GaH_2)\}_2]$ (**3**; L = HC{(CMe)(2,6-$i\text{Pr}_2C_6H_3N$)}$_2$). The synthesis of **2** and **3** were possible by preparing an unprecedented terminal aluminum monohydroxide [LAlMe(OH)] (**1**).[6] Compounds **2** and **3** are the first examples of a tetranuclear alumoxane[7] and a gallium congener, respectively. Apart from being examples of simple building blocks (Al_2O_2 and Ga_2O_2) these compounds also contain a pair of reactive MH_2 (M = Al, Ga) groups in the central core and Al–Me groups as the terminal end groups, which should allow their rapid elaboration.

The reaction of [LAl(OH)Me] with a stoichiometric amount of $MH_3{\cdot}NMe_3$ (M = Al, Ga) in toluene at 0 °C results in a vigorous evolution of hydrogen and the formation of **2** and **3** in good yields (Scheme 1). Thus, this synthetic method represents a viable and rational route for the preparation of novel compounds. While compound **2** is the first example of an alumoxane with an Al_4O_2 moiety which also carries reactive hydride groups on the aluminum centers, compound **3** is the first example of a Al-O-Ga unit bearing reactive hydride groups.

Compounds **2** and **3** have been unambiguously characterized by means of spectroscopic, spectrometric, and crystallographic techniques. Both **2** and **3** are colorless crystalline solids and are thermally quite stable. They decompose with melting at 260 and 234 °C, respectively. The EI mass spectrum of **2** revealed that the most intense peak appears at m/z 1007 and corresponds to the loss of one hydrogen atom from the molecular ion. Similarly a peak at m/z 1079 in **3** is due to $[M^+-CH_3]$. The IR spectrum of **2** shows a sharp doublet (1833 and 1850 cm^{-1}) corresponding to the symmetric and antisymmetric stretch of the AlH_2 fragment. The corresponding stretching modes for **3** appear at 1901 and 1929 cm^{-1}. The ^{1}H NMR resonance signals for **2** and **3** are broad at room temperature. However, a variable temperature ^{1}H NMR spectroscopy study revealed that the room-temperature spectra of **2** and **3** are simplified by a dynamic process and upon cooling the broad signals become sharp and eventually resolve into different resonances for the two halves of the molecules as expected based on the solid-state structures for **2** and **3**. For **2** (−60 °C) and **3** (−70 °C) two sharp singlets were observed for the methyl groups which are located on the terminal aluminum atoms. This observation suggests that the local environment around the two aluminum centers is slightly different at least at lower temperatures. This feature is also reflected in the hydride resonances of the central $Al_2O_2H_4$ and $Ga_2O_2H_4$ units. Although the exact nature of the dynamic process involved has not been clearly established it is possible that this may be due to the restricted rotation of Al–O–Al(Ga) bond at lower temperatures.



Scheme 1. Preparation of the tetranuclear alumoxane **2** (M = Al) and the gallium congener **3** (M = Ga); Ar = 2,6-$i\text{Pr}_2C_6H_3$.

Single crystals of **2** and **3** suitable for X-ray structural analysis were obtained from their n-hexane solutions (Figure 1 and Figure 2). Both the compounds crystallize with a molecule of n-hexane, compound **2** in the monoclinic space group $P2_1/c$ and **3** in $P2_1/m$.[11]

The X-ray crystal structure of **2** reveals that it is a dimer of the $[LAl(Me)OAl(H)_2]$ unit. The structure contains two terminal LAlMe units that are linked to a central $\{(H)_2AlO\}_2$ core. The terminal aluminum centers are part of the six-membered C_3N_2Al rings. Each aluminum center of the central $\{(H)_2AlO\}_2$ four-membered ring contains two reactive hydride groups. These are located above and below the plane of the Al_2O_2 ring. The two methyl groups on the terminal Al atoms are *cis* with respect to each other. The central four-membered ring is nearly planar. The terminal six-membered rings are displaced in an approximately perpendicular manner with respect to the central $\{(H)_2AlO\}_2$ ring. The metric parameters observed in **2** are not unusual. Thus, the Al–O bonds in the Al_2O_2 ring (1.824(14)–1.842(14), av 1.833 Å) are longer than the terminal Al–O bonds (1.748(14) Å and 1.772(13) Å, av 1.760 Å) and are similar to those found in aluminum alkoxides for example $[\{(t\text{Bu})_2(Me)COAlH_2\}_2]$ (Al–O 1.841 Å)[8] and $[\{t\text{BuOAlH}_2\}_2]$ (Al–O 1.815 Å).[9] The average O-Al-O and Al-O-Al angles in the Al_2O_2 ring are 86.10 and 93.43°, respectively, while the average exocyclic Al-O-Al angles are 122.02 and 144.08°.

The molecular structure of **3** is analogous to that of **2**. Thus, compound **3** also exists as a dimer and contains reactive hydride groups on the central gallium atoms of the planar Ga_2O_2 ring. The terminal C_3N_2Al rings are arranged in an

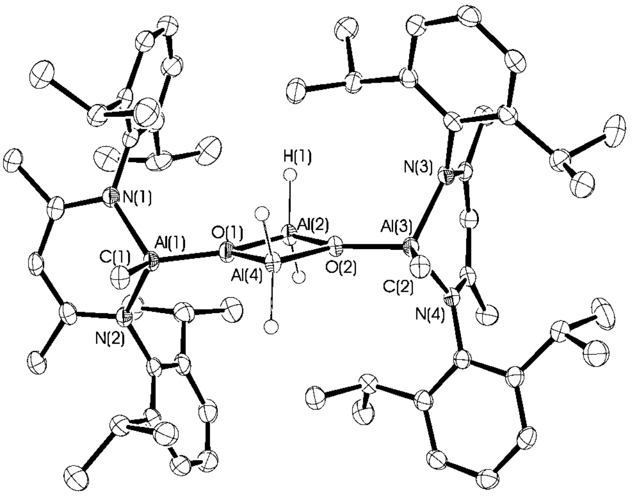


Figure 1. Molecular structure of **2**. The hydrogen atoms of the C–H bonds and hexane molecule are omitted for clarity. Selected interatomic distances [Å] and bond angles [°]: Al(1)-O(1) 1.748(14), Al(2)-O(1) 1.838(14), Al(2)-O(2) 1.828(14), Al(4)-O(2) 1.824(14), Al(4)-O(1) 1.842(14), Al(2)···Al(4) 2.679, Al(3)-O(2) 1.772(13), Al(1)-N(1) 1.913(16), Al(1)-C(1) 1.965(2); Al(1)-O(1)-Al(2) 145.44(8), Al(1)-O(1)-Al(4) 121.13(8), O(1)-Al(2)-O(2) 86.10(6), Al(2)-O(2)-Al(4) 94.36(6), Al(3)-O(2)-Al(2) 142.73(8), Al(3)-O(2)-Al(4) 122.91(8), N(1)-Al(1)-N(2) 96.51(7), N(1)-Al(1)-O(1) 113.52(7).

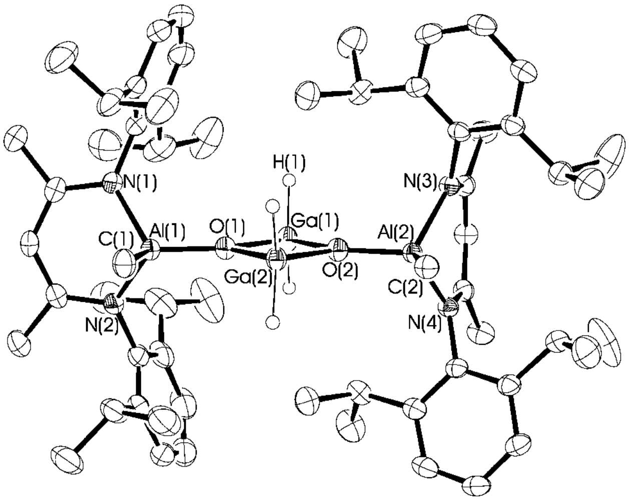


Figure 2. Molecular structure of **3**. The hydrogen atoms of the C–H bonds and hexane molecule are omitted for clarity. Selected interatomic distances [Å] and bond angles [°]: Al(1)-O(1) 1.733(2), Ga(1)-O(1) 1.933(2), Ga(1)-O(2) 1.924(2), Ga(2)-O(2) 1.917(2), Ga(2)-O(1) 1.939(2), Ga(1)-H(1) 1.516, Ga(1)···Ga(2) 2.849(7), Al(2)-O(2) 1.755(2), Al(1)-N(1) 1.920(19), Al(1)-C(1) 1.967(4); Al(1)-O(1)-Ga(1) 145.00(14), Al(1)-O(1)-Ga(2) 120.25(13), O(1)-Ga(1)-O(2) 84.73(9), Ga(1)-O(2)-Ga(2) 95.78(9), Ga(1)-O(2)-Al(2) 141.57(13), Ga(2)-O(2)-Al(2) 122.65(12), N(1)-Al(1)-N(2) 96.19(12), N(1)-Al(1)-O(1) 114.44(8).

approximately perpendicular manner with respect to the central Ga_2O_2 ring. Also, the methyl groups on the terminal aluminum centers are *cis* with respect to each other. The average O-Ga-O and Ga-O-Ga angles within the Ga_2O_2 ring are 84.73 and 95.27°, respectively. This may be compared with those observed in [{*t*BuOGaH$_2$}$_2$] (101.4°).[9] The slightly wider angle in the latter is perhaps due to the bulky *t*Bu group that elongates the O···O diagonal in the four-membered ring. The average exocyclic Al-O-Ga angles in **3** are 121.44 and 143.28°. The average terminal Al–O bond in **3** (1.744 Å) is similar to that found in **2**. The Ga–O bond within the Ga_2O_2 ring (1.917(2)–1.939(2) Å, av 1.928 Å) are similar to those found in gallium alkoxides for example [{*t*BuOGaH$_2$}$_2$] (Ga–O 1.908 Å)[9] and in [{$Me_2NCH_2CH_2OGaH_2$}$_2$] (Ga–O 1.911 Å).[10]

In conclusion we have demonstrated a new synthetic strategy for the preparation of an alumoxane and a corresponding gallium derivative. This procedure utilizes the reaction of an Al–OH motif and is a change in the standard synthetic protocols which rely on the use of Al–C or Al–H motifs. The resulting compounds [{[LAl(Me)](μ-O)(AlH_2)}$_2$] and[{[LAl(Me)](μ-O)(GaH_2)}$_2$] are novel tetranuclear building blocks. The reactive hydride and methyl groups present on the central and terminal metal atoms in these compounds should allow a further elaboration of these tetranuclear structures.

Experimental Section

All manipulations were performed under a dry and oxygen-free atmosphere (N_2 or Ar) using Schlenk line and glove box techniques.

2: [LAl(Me)OH] (0.95 g, 2.00 mmol) dissolved in toluene (20 mL) was added dropwise at 0 °C to a stirred (1.0 M) solution of $AlH_3 \cdot NMe_3$ (2.10 mL, 2.10 mmol) in toluene (15 mL). The solution was allowed to warm to room temperature and stirred for 15 h. After removal of all the volatiles the residue was extracted with *n*-hexane (40 mL). Partial removal of the solvent and storage of the remaining solution at room temperature for 2 days afforded colorless crystals of **2**. Yield (0.75 g, 74 % with respect to **1**). M.p. 258–260 °C (decomp); elemental analysis (%) calcd for $C_{60}H_{92}Al_4N_4O_2$ (1008.65): C 71.40, H 9.19, N 5.55; found: C 71.75, H 9.55, N 5.14; EI-MS: *m/z* (%): 1007 (92) [M^+–H], 993 (72) [M^+–Me], 979 (60) [M^+–Al–2H], 965 (100) [M^+–Al–Me–3H], 951 (20) [M^+–2Al–3H]; IR (Nujol): $\tilde{\nu}$ = 1850, 1833, 1552, 1527, 1318, 1260, 1177, 1101, 1055, 1023, 936, 874, 803, 726, 724, 656, 634 cm^{-1}, ^1H NMR (500 MHz, C_7D_8, −60 °C): δ = 7.26–6.89 (m; Ar), 4.80 (s, 1H; γ-CH), 4.79 (s, 1H; γ-CH), 3.93 (br, 4H; AlH_2), 3.54 (sept, $^3J_{H,H}$ = 6.3 Hz, 2H; C*H*Me$_2$), 3.40 (sept, $^3J_{H,H}$ = 6.5 Hz, 2H; C*H*Me$_2$), 3.27 (sept, $^3J_{H,H}$ = 6.5 Hz, 2H; C*H*Me$_2$), 2.97 (sept, $^3J_{H,H}$ = 6.5 Hz, 2H; C*H*Me$_2$), 1.70–1.66 (m, 12H; CH*Me*$_2$), 1.46 (s, 6H; C*Me*), 1.39 (s, 6H; C*Me*), 1.34 (d, $^3J_{H,H}$ = 6.3 Hz, 6H; CH*Me*$_2$), 1.20 (m, 12H; CH*Me*$_2$), 1.14 (d, $^3J_{H,H}$ = 6.2 Hz, 6H; CH*Me*$_2$), 1.04 (d, $^3J_{H,H}$ = 6.4 Hz, 6H; CH*Me*$_2$), 0.92 (d, $^3J_{H,H}$ = 6.4 Hz, 6H; CH*Me*$_2$), 0.07 (s, 3H; Al*Me*), −0.81 ppm (s, 3H; Al*Me*); ^1H NMR (500 MHz, C_7D_8, 100 °C): δ = 7.16–6.96 (m; Ar), 5.02 (s, 2H; γ-CH), 3.65 (br, 4H; AlH_2), 3.40 (sept, $^3J_{H,H}$ = 6.7 Hz, 4H; C*H*Me$_2$), 3.14 (br, 4H; C*H*Me$_2$), 1.60 (s, 12H; C*Me*), 1.38–1.31 (br, 24H; C*H*Me$_2$ and C*Me*), 1.10 (m, 24H; CH*Me*$_2$), −0.56 ppm (s, 6H; Al*Me*).

3: The preparation of **3** was carried out by using a similar procedure as that for **2**. The quantities of the reactants used were [LAl(Me)OH] (1.43 g, 3.00 mmol), $GaH_3 \cdot NMe_3$ (0.40 g, 3.00 mmol). Yield (1.30 g, 79 % with respect to **1**). M.p. 234 °C (decomp); elemental analysis (%) calcd for $C_{60}H_{92}Al_2Ga_2N_4O_2$ (1094.81): C 65.82, H 8.47, N 5.12; found: C 65.67, H 8.33, N 5.29; EI-MS: *m/z* (%): 1094 (24) [M^+], 1079 (100) [M^+–Me], 1052 (16) [M^+–Al–Me], 1022 (20) [M^+–Ga–2H], 1007 (20) [M^+–Me–Ga–2H]; IR (Nujol): $\tilde{\nu}$ = 1929, 1901, 1585, 1551, 1521, 1315, 1293, 1256, 1183, 1176, 1107, 1098, 938, 874, 797, 770, 755, 737, 709, 659, 642, 616, 531, 507 cm^{-1}; ^1H NMR (500 MHz, C_7D_8, −70 °C): δ = 7.22–6.88 (m, Ar), 5.20 (s, 2H; GaH_2), 5.05 (s, 2H; GaH_2), 4.70 (s, 1H; γ-CH), 4.63 (s, 1H; γ-CH), 3.77 (m, 2H; C*H*Me$_2$), 3.45 (m, 2H; C*H*Me$_2$), 3.32 (m, 2H; C*H*Me$_2$), 2.96 (m, 2H; C*H*Me$_2$), 1.68 (d, $^3J_{H,H} = 17.3$ Hz, 12H; CH*Me*$_2$), 1.49 (d, $^3J_{H,H} = 5.8$ Hz, 12H; CH*Me*$_2$), 1.40 (s, 12H; C*Me*), 1.14 (dd, $^3J_{H,H} = 17.3$ Hz, 18H; CH*Me*$_2$), 0.92 (d, $^3J_{H,H} = 6.0$ Hz, 6H; CH*Me*$_2$), 0.04 (s, 3H; Al*Me*), −0.95 ppm (s, 3H; Al*Me*); ^{1}H NMR (500 MHz, C_7D_8, 70 °C): $\delta = 7.17$–6.96 (m; Ar), 4.91 {s, 6H (2H, γ-CH and 4H, GaH$_2$)}, 3.48 (br, 4H; C*H*Me$_2$), 3.15 (br, 4H; C*H*Me$_2$), 1.56 (s, 12H; C*Me*), 1.43 (br, 12H; CHMe$_2$), 1.32 (br, 12H; CH*Me*$_2$), 1.17 (d, $^3J_{H,H} = 6.5$ Hz, 12H; CH*Me*$_2$), 1.10 (d, $^3J_{H,H} = 8.7$ Hz, 12H; CH*Me*$_2$), −0.65 ppm (s, 6H; Al*Me*).

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[11] Crystallographic data for compound **2**·C_6H_{14} ($C_{66}H_{106}Al_4N_4O_2$): $M_r = 1095.47$, monoclinic, $P2_1/c$, $a = 20.420(2)$, $b = 17.760(10)$, $c = 18.850(10)$ Å, $\beta = 103.210(14)°$, $V = 6655.2(8)$ Å^3, $Z = 4$, crystal size $= 0.2 \times 0.1 \times 0.2$ mm^3, $\rho_{calcd} = 1.093$ Mg m^{-3}, $2.22 \leq 2\theta \leq 58.93°$, $T = 103(2)$ K, $\lambda = 1.54178$ Å, $\mu = 0.973$ mm^{-1}, $F(000) = 2392$, 61271 reflections collected, 9543 were independent and were used in the structure refinement of 786, $R1 = 0.0403$ ($I > 2\sigma(I)$), $wR2 = 0.1162$ (all data), min./max. residual electron density 0.411/−0.310 e Å^{-3}. Crystallographic data for compound **3**·C_6H_{14} ($C_{66}H_{106}Al_2Ga_2N_4O_2$): $M_r = 1180.95$, monoclinic, $P2_1/m$, $a = 9.4431(13)$, $b = 17.889(2)$, $c = 20.491(5)$ Å, $\beta = 103.117(14)°$, $V = 3371.1(10)$ Å^3, $Z = 2$, crystal size $= 0.3 \times 0.2 \times 0.2$ mm^3, $\rho_{calcd} = 1.163$ Mg m^{-3}, $3.06 \leq 2\theta \leq 49.60°$, $T = 133(2)$ K, $\lambda = 0.71073$ Å, $\mu = 0.868$ mm^{-1}, $F(000) = 1268$, 20878 reflections collected, 5960 were independent and were used in the structure refinement of 388, $R1 = 0.0362$ ($I > 2\sigma(I)$), $wR2 = 0.09995$ (all data), min./max. residual electron density 0.719/−0.536 e Å^{-3}. CCDC-236234 (**3**) and CCDC-236235 (**2**) contain the supplementary crystallographic data. 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). The structures were solved by direct methods using SHELXS-97 and refined against F^2 on all data by full-matrix least squares; G. M. Sheldrick programs for crystal structure refinement, Universität Göttingen, Göttingen (Germany), **1997**. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model.