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Trinuclear Alumoxanes with an Acyclic Al-O-Al-O-Al Core and Studies of Their Reactivity

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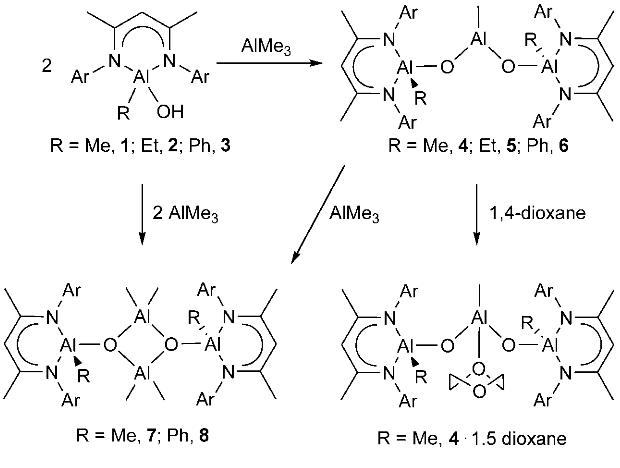
Dedicated to Professor Wolfgang Kaim on the occasion of his 60th birthday

Considerable interest in the field of organometallic oxides has developed owing to the remarkable properties of methylalumoxane (MAO) as activator for metallocene catalysts in olefin polymerization.[1,2] Full details of the structure of MAO are currently still elusive. Numerous efforts have been made to synthesize characterizable alumoxanes of general composition $\{RAlO\}_n$, in attempts to elucidate their role in polymerization reactions.[3] Due to the oxophilicity of aluminum, these alumoxanes tend to readily undergo association by forming oligomers with cyclic or cage structures. The first structurally characterized alkylalumoxane $\{(t\mathrm{Bu})_2\mathrm{Al\text{-}O\text{-}Al}(t\mathrm{Bu})_2\}$ was a monomeric binuclear species with a linear Al-O-Al arrangement and only available when the vacant sites of aluminum were occupied by coordinate pyridine molecules.[4] Later related analogues were obtained with the support of sterically encumbered ligands.[5] However, the trinuclear alumoxane with an open-chain structure is so far rare. The only example is the $[\mathrm{Mes^*(Et)Al\text{-}O\text{-}Al(Mes^*)\text{-}O\text{-}Al(Et)_2}]$ ($\mathrm{Mes^* = Me_3C_6H_2}$), which dimerizes to a ladder-like hexanuclear structure as a result of forming O→Al donor–acceptor bonds.[1,6] The recent successful isolation of well-defined, soluble, heterobi- and heterotrimetallic oxides in our laboratory[7] was the motivation for preparing trinuclear alumoxanes with an acyclic Al-O-Al-O-Al arrangement, by taking advantage of the OH functionality of organoaluminum hydroxide [LAlR(OH)] (R = Me, **1**; Et, **2**; Ph, **3**; L = CH[C(Me)N(Ar)]$_2$, Ar = 2,6-$i\mathrm{Pr_2C_6H_3}$).[8] Herein, we report on the preparation and characterization of the open-chain trinuclear alumoxanes $[\{\mathrm{LAlR}(\mu\text{-O})\}_2\mathrm{AlMe}]$ (R = Me, **4**; Et, **5**; Ph, **6**), and the reactions of **4** and **6** with trimethylaluminum to form alumoxanes $[\{\mathrm{LAlR}(\mu\text{-OAlMe_2})\}_2]$ (R = Me, **7**; Ph, **8**) containing the $\mathrm{Al_4O_2}$ core.

Reaction of two equivalents of [LAlMeOH] (**1**) with one equivalent of $\mathrm{AlMe_3}$ proceeded in toluene under mild conditions to give an opaque solution. After removal of all the volatiles under vacuum, the residue was extracted with toluene to afford a colorless crystalline solid $[\{\mathrm{LAlMe}(\mu\text{-O})\}_2\mathrm{AlMe}]$ (**4**, Scheme 1) in moderate yield.



Scheme 1. Preparation of compounds **4**–**8** (Ar = 2,6-$i\mathrm{Pr_2C_6H_3}$)

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The absence of the OH stretching frequency of **4** was confirmed by IR spectroscopy, while the most intense peak (m/z 977) in the mass spectrum is assignable to a monomeric fragment $[M^{+}{-}\mathrm{Me}]$ with the correct isotopic pattern. The ^{1}H NMR spectrum of **4** exhibits two singlets ($\delta=-0.76$, -0.51 ppm) in a ratio of 2:1 at high field, corresponding to the methyl groups of AlMe and $(\mu\text{-O})_2$AlMe, respectively. In the ^{13}C NMR spectrum, the chemical shifts for the three Al bound methyl groups are identical ($\delta=-12.2$ ppm). Other resonances can be easily assigned to the backbone of the ligand. The ^{27}Al NMR shows two overlapping broad resonances centered at $\delta=69.57$ ppm. The NMR spectra (including NOE experiments) are in full agreement with the assumed acyclic structure in solution. The solid-state compound **4** is sensitive to air, but is thermally rather stable with a surprisingly high melting point of 287 °C. The single-crystal X-ray analysis of **4** exhibits the monomeric composition,[9] although further refinement was hindered as a result of statistical disorder occurring at the $\{\mathrm{AlMe}(\mu\text{-O})\}_2\mathrm{AlMe}$ unit. In analogous reactions discrete molecular alumoxanes $[\{\mathrm{LAlEt}(\mu\text{-O})\}_2\mathrm{AlMe}]$ (**5**) and $[\{\mathrm{LAlPh}(\mu\text{-O})\}_2\mathrm{AlMe}]$ (**6**) were smoothly obtained by using ethyl- and phenyl-substituted organoaluminum hydroxide precursors, **2** and **3**, respectively. Both **5** and **6** have been characterized by elemental analysis, spectroscopic methods and X-ray studies.

Compound **5** crystallizes in the orthorhombic space group $Pna2_1$. The X-ray crystal structure of **5** contains two four-coordinate and one three-coordinate Al center (Figure 1). To the best of our knowledge **5** represents the first example of a trinuclear alumoxane with a stable acyclic Al-O-Al-O-Al core. The atoms in the $\{\mathrm{AlEt}(\mu\text{-O})\}_2\mathrm{AlMe}$ unit are essentially coplanar, and the bridging oxygen atoms deviate only marginally from the Al_3 plane (e.g., O(1) 0.025, O(2) 0.027 Å). In comparison, a related trimeric alumoxane $[(\mathrm{LAl})_2(\mathrm{MeAl})(\mu\text{-O})_3]$, which also bears two four-coordinate Al and one three-coordinate Al, forms a highly puckered six-membered $(\mathrm{AlO})_3$ ring.[10] The Al(3)−O bond lengths (1.6647, 1.666 Å) of **5** are shorter than those observed in $[(\mathrm{LAl})_2(\mathrm{MeAl})(\mu\text{-O})_3]$ (1.708 Å)[10] and $[(t\mathrm{Bu})_2\mathrm{Al}\text{-O-Al-}(t\mathrm{Bu})_2(\mathrm{py})_2]$ (1.711 Å; py = pyridine),[4] but longer than those (1.648(7) Å) found in the homoleptic aluminum aryloxide $[\mathrm{Al(OAr^{*})_3}]$.[11] Moreover, they fall in the range of the predicted Shannon–Prewitt radii (1.65–1.68 Å) in terms of three-coordinate Al and two-coordinate O.[12] The O-Al(Me)-O angle (123.26°) of **5** is larger than that in $[(\mathrm{LAl})_2(\mathrm{MeAl})(\mu\text{-O})_3]$ (115.53°)[10] and those in the monosubstituted organoalumoxane $[(\mathrm{Mes^{*}AlO})_4]$ (117.92, 119.85°).[6] We assume that the short Al(3)−O bond length is mainly due to the ionic contribution rather than to the Al−O π bonding,[13] with the result that the bond angles are more easily distorted due to the higher non-directed ionic bond character.[13a] The Al(3)-O-Al angles are 141.76 and 151.32°. In a broader sense, compound **5** can be considered as consisting of a trapped MeAlO species, the monomer of MAO,[14] with a strong ionic Al−O bond.

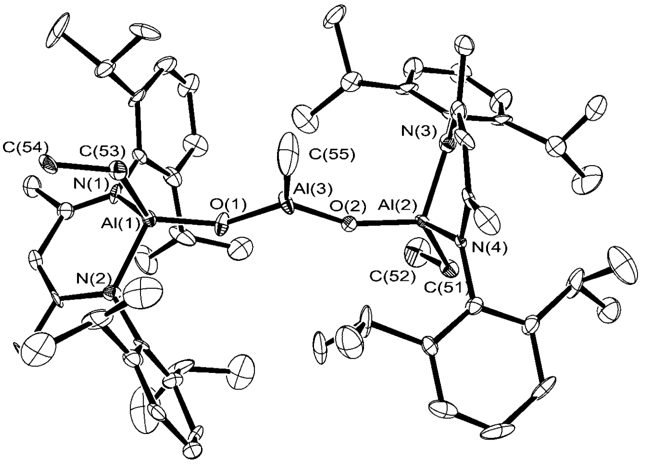


Figure 1. Molecular structure of **5**·0.8 toluene. Thermal ellipsoids are drawn at the 30 % probability level, and the hydrogen atoms of the L ligand are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)−O(1) 1.6920(18), Al(1)−N(1) 1.927(5), Al(1)−N(2) 1.898(5), Al(1)−C(53) 1.962(3), Al(2)−O(2) 1.7045(18), Al(2)−N(3) 1.904(6), Al(2)−N(4) 1.915(5), Al(3)−O(2) 1.6647(18), Al(3)−O(1) 1.666(2), Al(3)−C(55) 1.930(4); N(2)-Al(1)-N(1) 96.60(10), N(3)-Al(2)-N(4) 95.57(11), O(1)-Al(3)-O(2) 123.26(10), O(2)-Al(3)-C(55) 118.30(14), O(1)-Al(3)-C(55) 118.27(14), Al(3)-O(1)-Al(1) 141.76(12), Al(3)-O(2)-Al(2) 151.32(12).

$[\{\mathrm{LAlPh}(\mu\text{-O})\}_2\mathrm{AlMe}]$ (**6**, Figure S1 in the Supporting Information) crystallizes in the monoclinic space group $C2/c$, and shows again a monomeric structure. The phenyl groups on Al are arranged in a *trans* conformation to each other, similar to those found in the ethyl analogue (**5**). In contrast, these two phenyl groups tilt from the Al_3 plane by about 71°, owing to the steric hindrance of the substituents. The Al(3)−O bond separation of **6** (1.6682 Å) is a little longer, but comparable to those in **5**. The angle for O-Al(3)-O is 120.83° and furnishes the methyl-substituted Al in a nearly perfect three-coordinate trigonal plane, as evidenced by the angle sum around Al(3) (359.99°).

The structures of **5** and **6** suggest that the less hindered three-coordinate Al could act as a Lewis acid site, while the two-coordinate O atoms still have "an open environment"[6] and hence represent potential Lewis base sites. This feature highly resembles the cage-opened product of $[\{(t\mathrm{Bu})\mathrm{Al}(\mu_3\text{-O})\}_6]$ upon breaking one of its Al−O bonds along the vertical edge of the cage.[3d] It is therefore possible to study the reactivity of the Al-O-Al-O-Al chain towards different species. When **4** was treated with 1,4-dioxane, the acyclic conformation was stabilized by a coordinate donor solvent molecule at the Al site (**4a**·1.5 dioxane, Scheme 1), as revealed by X-ray single-crystal structural characterization of $[\{\mathrm{LAlMe}(\mu\text{-O})\}_2\mathrm{AlMe(dioxane)}]$ (Figure S2 in the Supporting Information). In contrast, the Al-O-Al-O-Al chain is also reactive to some Lewis acids. The reaction of **4** and **6** with each of two equivalents of $\mathrm{AlMe_3}$ only consumed one equivalent and consequently resulted in the methyl transfer products $[\{\mathrm{LAlR}(\mu\text{-OAlMe}_2)\}_2]$ (R = Me, **7**; Ph **8**) in modest yield. Both compounds crystallize in the triclinic space group $P\bar{1}$. In the asymmetric unit, two crystallographically independent molecules are found with minor differences in their dimensions. As shown in Figure 2, compound **7** is a

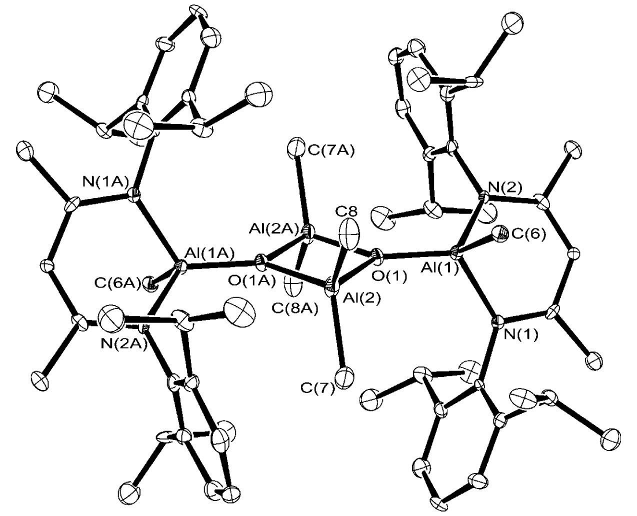
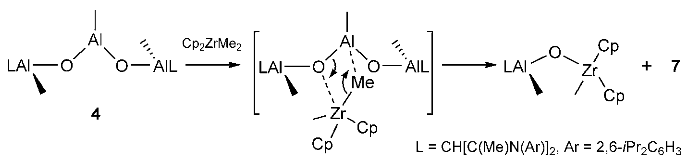


Figure 2. Molecular structure of **7**. Thermal ellipsoids are drawn at the 30 % probability level, and the hydrogen atoms of the L ligand are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–O(1) 1.745(3), Al(1)–N(2) 1.902(3), Al(1)–N(1) 1.929(3), Al(1)–C(6) 1.961(4), Al(2)–O(1 A) 1.830(3), Al(2)–O(1) 1.863(3), Al(2)–C(7) 1.946(4), Al(2)–C(8) 1.963(4); N(2)-Al(1)-N(1) 96.48(14), O(1)-Al(2)-O(1A) 87.98(13), Al(1)-O(1)-Al(2A) 143.97(17), Al(2)-O(1)-Al(2A) 92.02(13).

dimer of composition $[\{LAlMe(\mu\text{-}O)AlMe_2\}_2]$ and consists of a $(Me_2AlO)_2$ four-membered ring that is supported by two terminal (LAlMe) subunits. The Al–O bonds in the $(AlO)_2$ ring (av 1.8493 Å) are shorter than the average distance (1.865 Å) for the ring Al–O bonds in $[((tBu)_2Al\{\mu\text{-}OAl(tBu)_2\})_2]$[4] and a little longer than that in a coordination polymer containing dimeric $[\{Me_2Al(\mu\text{-}O)AlMe_2\}_2]$ alumoxane units (av 1.8295 Å).[15] It is interesting to note that compound **7** is a methyl-substituted analogue of the tetranuclear alumoxane $[\{LAlMe(\mu\text{-}OAlH_2)\}_2]$ that carries two hydrogen atoms on each aluminum atom in the ring.[16] Compound $[\{LAlMe(\mu\text{-}OAlH_2)\}_2]$ features a *cis* arrangement of two methyl groups on the terminal Al atoms,[16] while their equivalent in **7** is *trans* with respect to each other. The structural features of $[\{LAlPh(\mu\text{-}OAlMe_2)\}_2]$ (**8**, Figure S3 in the Supporting Information) are highly analogous to those of **7**. The ring Al–O bonds (av 1.8553 Å) in **8** are slightly longer compared to those in **7**. An alternative route allowed the access to compounds **7** and **8** by the reaction of [LAlR(OH)] with stoichiometric amounts of $AlMe_3$ in toluene (Scheme 1).

Furthermore, we were interested in whether the methyl-transfer reaction between the Al-O-Al-O-Al chain and $[Cp_2ZrMe_2]$ could occur to form a complex with catalytic activity for the ethylene polymerization, as was shown for the alumoxane cage $[\{(tBu)Al(\mu_3\text{-}O)\}_6]$.[3d] The in situ NMR tube reaction of an equimolar mixture of **4** and $[Cp_2ZrMe_2]$ in C_6D_6 at ambient temperature demonstrated the weak presence of $\{Cp_2ZrMe\}$ fragment in terms of the new singlets at $\delta = 5.40$ and 0.19 ppm corresponding to Cp ligands and the zirconium methyl group, respectively. However, only a trace of polyethylene was produced by this mixture in toluene solution during the polymerization experiment. Reflux in toluene for 10 h of an equivalent amount of **4** and $[Cp_2ZrMe_2]$ promoted the shift of complexation equilibrium towards the methyl-transfer product, and finally it turned out to be the heterobimetallic oxide $[LAlMe(\mu\text{-}O)ZrMeCp_2]$,[8a] with concomitant formation of the dimeric $[\{LAlMe(\mu\text{-}O)AlMe_2\}_2]$ (**7**). The reaction of **4** could adopt the following course as illustrated in Scheme 2. In the first step complexation of $[Cp_2ZrMe_2]$ with the Lewis acidic site of **4** to form $[\{LAlMe(\mu\text{-}O)\}_2Al(Me){\leftarrow}Me\text{-}Zr(Me)Cp_2]$ occurred. Following this, an attachment of Zr to the adjacent oxygen took place forming a donor–acceptor complex. At this point a methyl-transfer occurs, and finally the cleavage of the O–Al bond of the (Zr)O–Al(Me_2) moiety proceeds due to the strong steric repulsion of the Cp and L ligands.



Scheme 2. Proposed mechanism for the reaction of **4** with Cp_2ZrMe_2.

Nevertheless, no intermediate could be unambiguously detected by NMR analysis that shows the Al(μ-Me)Zr linkage or $(AlZrO_2)$ four-membered ring. The acyclic Al-O-Al-O-Al chain of **4** lends its reaction with $[Cp_2ZrMe_2]$ a unique pattern when compared with that of the cage alumoxane $[\{(tBu)Al(\mu_3\text{-}O)\}_6]$[3d] or MAO. Compounds **4**–**6** are also found to be reactive with water to give the respective monohydroxide precursors [LAlR(OH)] (**1**–**3**).

In conclusion, we report on the synthesis of stable alumoxanes **4**–**6**, which represent a new type of trinuclear alumoxanes containing an acyclic Al-O-Al-O-Al core showing ambivalent reactivity at both Lewis acidic and basic sites. Treatment of **4** and **6** with $AlMe_3$ resulted in tetranuclear alumoxanes **7** and **8**, respectively, bearing a $(Me_2AlO)_2$ four-membered ring. The novel trinuclear alumoxanes **4**–**6** are promising precursors for further studies assembling higher tetranuclear homo- or heteroalumoxanes.

Acknowledgements

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Keywords: aluminum · alumoxanes · hydroxides · Lewis acids · oxides

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[9] a) Cell parameters for **4** ($C_{61}H_{91}Al_3N_4O_2$): $M_r = 993.32$; $a = 12.7989(7)$, $b = 15.6593(7)$, $c = 15.8784(10)$ Å; $\alpha = 90$, $\beta = 106.258(6)$; $\gamma = 90°$; $V = 3055.1(3)$ Å^3; $Z = 2$; space group *Pn* (monoclinic)—the quality of the crystals could not be improved by repeated recrystallizations from toluene; b) CCDC-777395 (**4**·1.5 dioxane), CCDC-776495 (**5**·0.8 toluene), CCDC-776496 (**6**), CCDC-776497 (**7**), and CCDC-776498 (**8**·toluene) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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