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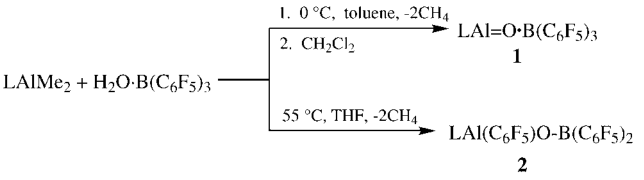
Formation and Characterization of the First Monoalumoxane, LAlO·B(C_6F_5)$_3$[**]

Dante Neculai, Herbert W. Roesky,[*]
Ana Mirela Neculai, Jörg Magull, Bernhard Walfort,
and Dietmar Stalke

Dedicated to Professor Heribert Offermanns
on the occasion of his 65th birthday

It has been shown that alumoxanes of the general formula (RAlO)$_n$ for $n > 1$ can be obtained by the controlled reaction of organoaluminum compounds with either water or water contained in hydrated salts or (Me_2SiO)$_3$.[1] Although the simplest member of the series, namely (RAlO), was predicted to be obtainable based on the analogy with aluminum imides,[2] its formation and characterization has remained elusive, presumably because it implies the presence of an Al–O double bond, which is likely to be very unstable even though π interactions between Al and O atoms have been invoked by several groups.[3] However, compounds with such bonds may be either sterically (by using bulky ligands bonded to the aluminum) or electronically (by using Lewis acids) stabilized. Our approach for the stabilization was to use $H_2O{\cdot}B(C_6F_5)_3$, which has been shown to act as a strong Brønsted acid,[4] and whose ability to protonate M–R bonds has been verified.[5] Furthermore if a monoalumoxane is formed, $B(C_6F_5)_3$ may hinder the aggregation owing to its strong Lewis acid character.[6]

Indeed, the reaction of $LAlMe_2$ (where L is a monoanionic β-diketiminato ligand, Scheme 1)[7] and $H_2O{\cdot}B(C_6F_5)_3$ in toluene gave $LAlO{\cdot}B(C_6F_5)_3$ (**1**), which was filtered off at room temperature and crystallized from dichloromethane (−26 °C). In contrast, when the same reagents were allowed to react in THF at 55 °C for 2 h, after the solvent had been removed, an oily product was formed which crystallized as an isomer of **1**, formulated as $LAl(C_6F_5)OB(C_6F_5)_2$ (**2**; Scheme 1).



where L = $Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$

Scheme 1. Synthesis of compounds **1** and **2**.

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[*] Prof. Dr. H. W. Roesky, D. Neculai, A. M. Neculai, Prof. Dr. J. Magull
Institut für Anorganische Chemie
Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
Fax: (+49) 551-393-373
E-mail: hroesky@gwdg.de

Dr. B. Walfort, Prof. Dr. D. Stalke
Institut für Anorganische Chemie
Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)

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Both complexes were characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray structural analysis.[8] However, contrary to the ^{1}H NMR spectra of **1** and **2** in solution, which are consistent with the equivalency of the dangling arms of the ligand, the solid-state structures of **1** and **2** reveal that only one arm of the ligand is coordinated to the Al atom (see Figure 1 and 2). One possible explanation for this equivalency is a rapid interconversion in solution.

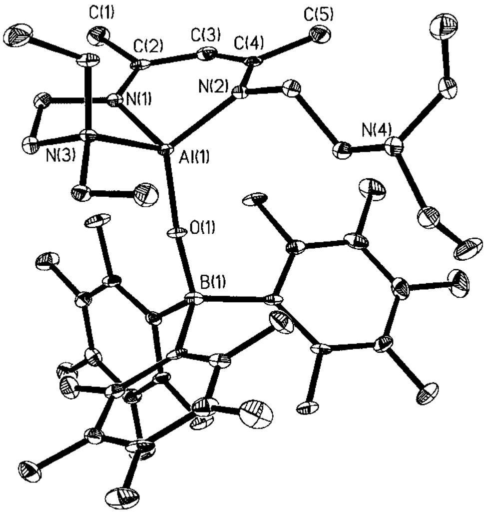
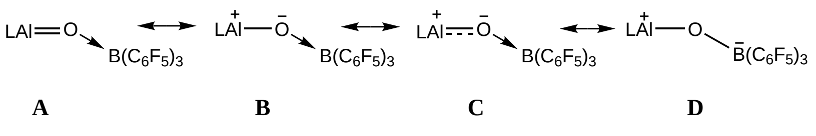


Figure 1. Structure of **1** (50% thermal ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Al(1)-N(1) 1.853(2), Al(1)-N(2) 1.857(4), Al(1)-N(3) 1.988(4), N(2)-C(4) 1.356(3), C(3)-C(2) 1.401(3), C(4)-C(3) 1.402(0), N(1)-C(2) 1.334(4), Al(1)-O(1) 1.659(3), B(1)-O(1) 1.444(3); Al(1)-O(1)-B(1) 163.76(2), N(2)-C(4)-C(3) 123.45(2), N(2)-Al(1)-N(1) 96.69(1), C(4)-C(3)-C(2) 126.79(2), N(1)-Al(1)-N(3) 86.50(1), C(3)-C(2)-N(1) 119.68(2), Al(1)-N(2)-C(4) 118.02(2), C(2)-N(1)-Al(1) 123.44(2).

The Al–O bond length in **1** is 1.659(3) Å, which is, to the best of our knowledge, the shortest Al–O bond reported for a tetracoordinate Al atom (Figure 1); an Al–O distance of 1.6877(4) Å was reported for a tricoordinate Al atom.[3] This short bond can be explained by considering the resonance structures given in Scheme 2. Resonance forms **A** and **C** can be considered with regard to the shortness of the Al–O bond, and imply a certain double-bond character. These resonance structures can also be taken into account to explain the B–O bond length (1.444(3) Å), which is intermediate between the coordinative B–O bond in $H_2O{\cdot}B(C_6F_5)_3$ (1.597(2) Å)[4d] and a B–O covalent bond (1.311(2) Å for **2**). Even so the $B(C_6F_5)_3$ group stabilizes the monoalumoxane by dispersing the negative charge from oxygen (**B**, **C**, and **D**; Scheme 2). The β-diketiminato ligand must also be taken into consideration because it reduces the positive charge on the Al center by acting as a Lewis base.[7] In addition these resonance structures support the irreversible isomerization of **1** to **2**.



Scheme 2. Proposed resonance structures for **1**.

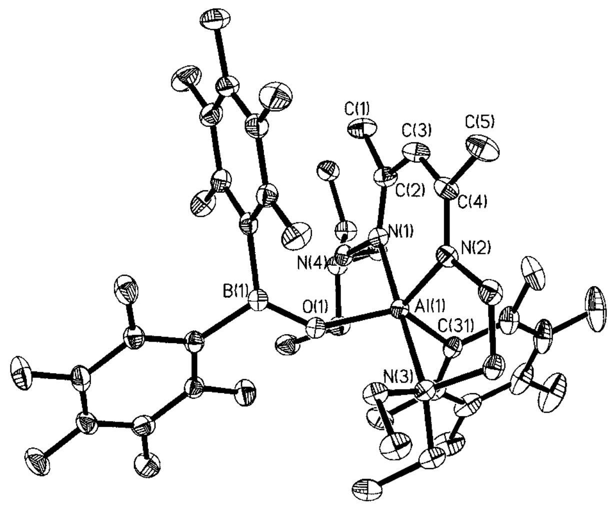


Figure 2. Structure of **2** (30% thermal ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Al(1)-O(1) 1.780(2), O(1)-B(1) 1.311(2), Al(1)-N(1) 1.964(2), Al(1)-N(2) 1.890(2), Al(1)-N(3) 2.195(2), N(1)-C(2) 1.322(2), N(2)-C(3) 1.346(3), C(2)-C(3) 1.384(3), C(3)-C(4) 1.409(3), Al(1)-C(31) 2.043(2); Al(1)-O(1)-B(1) 141.69(13), C(3)-C(2)-N(1) 122.50(17), N(2)-Al(1)-N(1) 94.11(7), Al(1)-N(1)-C(2) 125.19(13), Al(1)-N(2)-C(4) 125.62(13), N(2)-Al(1)-N(3) 82.48(6), N(2)-C(4)-C(3) 123.68(17), C(31)-Al(1)-O 123.43(7), C(2)-C(3)-C(4) 127.43(18).

For complex **2**, the Al–O and B–O bond lengths of 1.780(2) and 1.311(2) Å (Figure 2), respectively, are in the range of those in previously reported compounds.[1,6c]

In both complexes the Al atom is a member of two nonplanar, five- and six-membered heterocycles. The Al–N bond lengths for **1** (av 1.855 Å) are somewhat shorter than those previously reported for similar compounds (av 1.90 Å).[9] In **2** the Al–N distances have normal values (av 1.925 Å).[9,10] A similar trend is observed for the coordinative Al–N bond lengths; the Al–N(3) bond length in **1** (1.988(4)) is shorter than the Al–N(3) bond length in **2** (2.195(29), however they are in the range found for previously reported similar compounds.[11] The β-diketiminato C–N and C–C ring distances of both compounds have values (av 1.34 and 1.40 Å) corresponding to a delocalized π-electron system.[9] In the light of the different Al–O bond order for the complexes **1** and **2** (seen from the different bond lengths), deviation of the Al-O-B angles from 163.76(2) (**1**) to 141.69(13) (**2**) is expected.

In conclusion, we have provided evidence for the existence of the monomeric member of the $(RAlO)_n$ series. Nevertheless it has to be stated that the nature of the Al–O bond in complex **1** is still under debate; additional insights from future calculations may make things clearer. $H_2O{\cdot}B(C_6F_5)_3$ has been shown to be an excellent reagent for the synthesis of the first monoalumoxane, and its further application towards the synthesis and stabilization of other unusual compounds with multiple M–O bonds is in progress.

Experimental Section

All operations involving air- and moisture-sensitive compounds were performed by using standard Schlenk line and dry box techniques under a purified nitrogen atmosphere. $H_2O{\cdot}B(C_6F_5)_3$ was prepared according to the procedure described in reference [4a]. Toluene, THF, hexane, and CH_2Cl_2 were dried from appropriate drying agents, Na/K alloy (toluene, THF, hexane), CaH_2 (CH_2Cl_2), and distilled under nitrogen prior to use. C_6D_6 and $[D_8]$THF were dried over Na/K alloy and degassed. ^{1}H, ^{13}C, ^{19}F, ^{11}B, and ^{27}Al NMR spectra were recorded at ambient temperature on a Bruker AM 200. Chemical shifts are reported in δ units downfield from TMS (^{1}H, ^{13}C), C_6F_6 (^{19}F), $Et_2O{\cdot}BF_3$ (^{11}B), $AlCl_3$ (^{27}Al), with the solvent as the reference signal. Elemental analyses were carried out at the Analytical Laboratory of the Institute of Inorganic Chemistry of the University of Göttingen. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected.

$LAlMe_2$: Dry hexane (50 mL) was added to LH (1.553 g, 5.24 mmol; for L see Scheme 1) in a 100 mL Schlenk flask. The mixture was cooled to −78 °C and a solution of $AlMe_3$ (7.38 mL, 5.3 mmol of a 1.42 M solution in hexane) was added dropwise. The mixture was stirred for 2 h at −78 °C, and then stirred overnight at room temperature until the methane evolution had ceased. The solvent was removed and the yellowish oil obtained (1.832 g; 99 %) was used without any further purification. Elemental analysis (%) calcd for $C_{17}H_{41}AlN_4$: C 64.73, H 11.72, N 15.89; found: C 64.50, H 11.80, N 16.30; ^{1}H NMR (200 MHz, TMS; C_6D_6): $\delta = 4.45$ (s, 1 H; CH), 3.26 (m, 4 H; $NC\mathit{H}_2CH_2NEt_2$), 2.41 (m, 12 H; $C\mathit{H}_2N(C\mathit{H}_2CH_3)_2$), 1.72 (s, 6 H; $CHCC\mathit{H}_3$), 0.91 (t, $J = 7.07$ Hz, 12 H; $CH_2C\mathit{H}_3$,), −0.47 ppm (s, 6 H; $Al(CH_3)_2$); ^{13}C NMR (125.75 MHz, TMS, C_6D_6): $\delta = 167.91$ ($\mathit{C}CH\mathit{C}$), 96.938 (CH), 54.20 ($CN\mathit{C}H_2$), 47.90 ($NCH_2\mathit{C}H_2$), 46.69 ($N\mathit{C}H_2CH_3$), 20.84 ($CHC\mathit{C}H_3$), 12.58 ($NCH_2\mathit{C}H_3$), −8.73 ppm ($Al\mathit{C}H_3$); ^{27}Al NMR (65 MHz, $AlCl_3$ in D_2O, C_6D_6): $\delta = 150.36$ ppm.

$LAlO{\cdot}B(C_6F_5)_3$ (**1**): A solution of $LAlMe_2$ (0.217 g, 0.61 mmol) in toluene (15 mL) was allowed to react with $H_2O{\cdot}B(C_6F_5)_3$ (0.326 g, 0.61 mmol) in toluene (10 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C, and then stirred overnight at room temperature until the methane evolution had ceased. The suspension was filtered and the precipitate was redissolved in CH_2Cl_2 (10 mL). Colorless crystals were obtained by cooling the CH_2Cl_2 solution at −26 °C. Then the crystals were filtered off. Yield 0.317 g (60 %); m.p. 156 °C; elemental analysis (%) calcd for **1**, $C_{35}H_{35}AlBF_{15}N_4O$: C 49.43, H 4.15, N 6.59; found: C 49.81, H 4.33, N 6.63; ^{1}H NMR (200 MHz, TMS; $C_6D_6/[D_8]$THF): $\delta = 4.82$ (s, 1 H; CH), 3.11 (t, $J = 6.85$ Hz, 4 H; $NC\mathit{H}_2CH_2NEt_2$), 2.41 (m, $J = 7.19$ Hz, 12 H; $C\mathit{H}_2N(C\mathit{H}_2CH_3)_2$), 1.76 (s, 6 H; $CHCC\mathit{H}_3$), 0.78 ppm (t, $J = 7.1$ Hz, 12 H; $CH_2C\mathit{H}_3$); ^{13}C NMR (125.75 MHz, TMS, C_6D_6): $\delta = 171.82$ ($\mathit{C}CH\mathit{C}$), 98.32 ($\mathit{C}H$),54.31 ($CN\mathit{C}H_2$), 51.78 ($NCH_2\mathit{C}H_2$), 45.58 ($N\mathit{C}H_2CH_3$), 20.95 ($CHC\mathit{C}H_3$), 10.17 ppm ($NCH_2\mathit{C}H_3$); ^{19}F NMR (188 MHz, ext. C_6F_6, $C_6D_6/[D_8]$THF) $\delta = -134.5$ (m, 6 F; *ortho*), −163.7 (t, 3 F; *para*), −166.5 ppm (m, 6 F; *meta*); ^{11}B NMR (80 MHz, ext. $Et_2O{\cdot}BF_3$, $C_6D_6/[D_8]$THF): $\delta = -4.83$ ppm.

$LAl(C_6F_5)OB(C_6F_5)_2$ (**2**): A solution of $LAlMe_2$ (0.25 g, 0.71 mmol) in THF (15 mL) was allowed to react in a solution of $H_2O{\cdot}B(C_6F_5)_3$ (0.375 g, 0.71 mmol) in THF (10 mL) at 55 °C for 2 h. The solvent was removed and the oily product was left to crystallize at room temperature. The crystals formed were washed with cold hexane. Yield 0.44 g (73 %); m.p. 85–87 °C; elemental analysis (%) calcd for **2**, $C_{35}H_{35}AlBF_{15}N_4O$: C 49.43, H 4.15, N 6.59; found: C 49.75, H 4.27, N 6.46; ^{1}H NMR (200 MHz, TMS; C_6D_6): $\delta = 4.28$ (s, 1 H; $C\mathit{H}$), 3.22 (m, 2 H, $NC\mathit{H}_2CH_2N(CH_2)_2$), 2.95 (m, 2 H, $NC\mathit{H}_2CH_2NEt_2$), 2.19 (q, $J = 7.53$ Hz, 8 H; $C\mathit{H}_2CH_3$), 1.85 (m, 2 H; $NCH_2C\mathit{H}_2NEt_2$), 1.51 (s, 6 H; $CHCC\mathit{H}_3$), 0.70 ppm (t, 12 H; $CH_2C\mathit{H}_3$); ^{13}C NMR (125.75 MHz, TMS, C_6D_6): $\delta = 168.61$ ($\mathit{C}CH\mathit{C}$), 97.29 ($\mathit{C}H$), 50.51 ($CN\mathit{C}H_2$), 45.48 ($NCH_2\mathit{C}H_2$), 45.28 ($N\mathit{C}H_2CH_3$), 21.57 ($CHC\mathit{C}H_3$), 9.62 ppm ($NCH_2\mathit{C}H_3$); ^{19}F NMR (188 MHz, ext. C_6F_6, C_6D_6): $\delta = -118.09$ (m 2 F; AlC_6F_5 *ortho*), −133.2 (m, 4 F; BC_6F_5 *ortho*), −152.5 (t, 2 F; BC_6F_5 *para*), −155.3 (t, 1 F; AlC_6F_5 *para*), −159.7 (m, 2 F; AlC_6F_5 *meta*), −161.5 ppm (m, 4 F; AlC_6F_5 *meta*); ^{11}B NMR (80 MHz, ext. $Et_2O{\cdot}BF_3$, C_6D_6): $\delta = 36.83$ ppm.

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[8] Unfortunately, ^{27}Al NMR spectra for **1** and **2** could not be recorded. The ^{13}C resonances of the C atoms from C_6F_5 groups from both complexes could not be assigned. a) Crystal data for **1**, $C_{35}H_{35}AlBF_{15}N_4O$, $M_r = 850.46$, $T = 130(2)$ K, monoclinic, space group $P2(1)/n$; $a = 10.618(3)$, $b = 17.108(4)$, $c = 20.457(6)$ Å, $\beta = 100.402(6)°$, $V = 3655.0(18)$ Å^3, $Z = 4$, $\rho_{cald} = 1.546\ g\,cm^{-3}$, $\mu = 0.169\ mm^{-1}$, $R = 0.0614$ for 8646 independent reflections ($R_1 = 0.0823$ for all 28476 data), GOF = 0.977. The data were collected from shock-cooled crystals on a Bruker Smart-Apex diffractometer (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) equipped with a low-temperature device at 130(2) K. a) D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171; b) T. Kottke, R. J. Lagow, D. Stalke, *J. Appl. Crystallogr.* **1996**, *29*, 465; c) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615. For the refinement of the data of compound **1**, which crystallized as a non meroedric twin, two separate matrices of the two domains were determined. Every domain was integrated on its own. The structure solution was performed by direct methods by using the data of the first domain. A new hklf5 file with the reflections of both domains was then written. The reflections are divided into five overlapping ranges, and the data was refined well with 10 scaling factors (one for each range and domain). b) Crystal data for **2**, $C_{35}H_{35}AlBF_{15}N_4O$, $M_r = 850.46$, $T = 133(2)$ K, monoclinic, space group $P2(1)/n$; $a = 9.8994(6)$, $b = 21.4678(17)$, $c = 18.1143(12)$ Å, $\beta = 104.315(5)°$, $V = 3730.09(4)$ Å^3, $Z = 4$, $\rho_{cald} = 1.514\ g\,cm^{-3}$, $\mu = 0.166\ mm^{-1}$ $R = 0.0388$ for 5121 reflections with $I > 2\sigma(I)$ ($R_1 = 0.0492$ for all 28476 data), GOF = 1.021. Data for crystal structure of **2** were collected on a Stoe Image Plate IPDS II-System. Both structures were solved by direct methods (SHELXS-97) (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467) and refined by full-matrix least-squares methods against F^2 (SHELXL-97), (G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen (Germany), **1997**). CCDC-187737 (**1**) and 187738 (**2**) 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 CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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