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Communication

Synthesis and Structural Characterization of a Terminal Hydroxide Containing Alumoxane via Hydrolysis of Aluminum Hydrides

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A novel terminal hydroxide containing dinuclear alumoxane LAl-(OH)OAlL(OCH=N-*t*Bu) (**3**; L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) was prepared by treatment of aluminum dihydride LAlH$_2$ (**1**) and *tert*-butyl isocyanate in the presence of trace amounts of water and alternatively from **1** and LAlH(OCH=N-*t*Bu) (**2**) with water. Compound **2** was obtained from the reaction of **1** and *tert*-butyl isocyanate.

The investigation by Sinn and Kaminsky in 1980, that methylalumoxane (MAO) is a highly active cocatalyst in ethylene and propylene polymerization by group 4 metal-locenes,[1] has promoted the studies on the structural determination of alumoxanes to exemplify their role in the polymerization reactions. Alumoxanes, containing the Al−O−Al unit, are generally prepared by the controlled hydrolysis of aluminum alkyls or organoaluminum hydrides with water or reactive oxygen-containing species.[2−6] In numerous studies several low aggregated alumoxanes containing bridging OH groups have been prepared.[7] However,

the synthesis and isolation of aluminum compounds with terminal hydroxides are rarely known. Only recently we reported on the synthesis of the first terminal aluminum dihydroxide LAl(OH)$_2$[8a] and (LAlOH)$_2$O[8b] by the reaction of LAlI$_2$ with KOH containing water and KH in a liquid ammonia/toluene two-phase system. Parkin and co-workers published an example where a dimethylaluminum trispyra-zolylborate was hydrolyzed to give the corresponding dihydroxide characterized by elemental analyses and IR and NMR spectra.[8c] To the best of our knowledge, organoalumoxane hydroxides synthesized from aluminum hydrides and water are not known, and the hydrolysis of dihydride LAlH$_2$ (**1**) gives an intractable material.[8a] Herein, we report the synthesis of the first alumoxane hydroxide LAl(OH)OAlL(OCH=N-*t*Bu) (**3**) (L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) by the reaction of aluminum dihydride LAlH$_2$ (**1**)[9] and *tert*-butyl isocyanate in the presence of trace amounts of water and from **1** and LAlH(OCH=N-*t*Bu) (**2**) with water, respectively.

The reaction of excess LAlH$_2$ (**1**) with *tert*-butyl isocyanate in refluxing toluene followed by removal of the solvent resulted in a mixture of products **1** and **2**, and there is no interaction between **1** and **2** from the NMR spectrum. This mixture was dissolved in pentane, and the resulting filtrate reacted with water when it was stored at 0 °C to obtain **3** as colorless crystals in low yield (Scheme 1, eq 1).[10a] Compound **3** is soluble in most common organic solvents such as pentane, hexane, toluene, etc. The presence of the Al−OH bond is confirmed by IR and ^{1}H NMR (δ_H −0.30 in C$_6$D$_6$). The resonance is similar to that reported for the compound (Mes$_3$Ga·OHLi)·3THF (δ_H −0.56 in THF-*d*$_8$).[11] In order to elucidate the formation of **3**, we have carried out a reaction between **1** and *tert*-butyl isocyanate in a 1:1 ratio. In this case we have isolated a nucleophilic addition product LAlH-
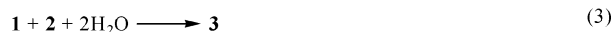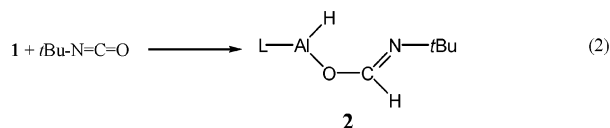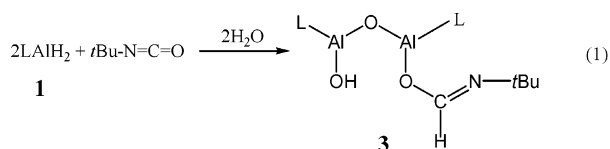
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(1) (a) Sinn, H.; Kaminsky, W.; Vollmer, H.-J.; Woldt, R. *Angew. Chem.* **1980**, *92*, 396−398; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390−392. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99−149.
(2) (a) Ishida, S. I. *J. Polym. Sci.* **1962**, *62*, 1−14. (b) Storr, A.; Jones, K.; Laubengayer, A. W. *J. Am. Chem. Soc.* **1968**, *90*, 3173−3177.
(3) (a) Ziegler, K.; Krupp, F.; Weyer, K.; Larbig, W. *Liebigs Ann. Chem.* **1960**, *629*, 251−256. (b) Ueyama, N.; Araki, T.; Tani, H. *Inorg. Chem.* **1973**, *12*, 2218−2225. (c) Atwood, J. L.; Hrncir, D. C.; Priester, R. D.; Rogers, R. D. *Organometallics* **1983**, *2*, 985−989.
(4) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 8387−8388.
(5) (a) Zheng, W.; Mösch-Zanetti, N. C.; Roesky, H. W.; Noltemeyer, M.; Hewitt, M.; Schmidt, H.-G.; Schneider, T. R. *Angew. Chem.* **2000**, *112*, 4446−4448; *Angew. Chem., Int. Ed.* **2000**, *39*, 4276−4278. (b) Zheng, W.; Roesky, H. W.; Noltemeyer, M. *Organometallics* **2001**, *20*, 1033−1035.
(6) Roesky, H. W.; Walawalkar, M. G.; Murugavel, R. *Acc. Chem. Res.* **2001**, *34*, 201−211.
(7) (a) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971−4984. (b) Harlan, C. J.; Mason, M. R.; Barron, A. R. *Organometallics* **1994**, *13*, 2957−2969.

(8) (a) Bai, G.; Peng, Y.; Roesky, H. W.; Li, J.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem.* **2003**, *115*, 1164−1167; *Angew. Chem., Int. Ed.* **2003**, *42*, 1132−1135. (b) Bai, G.; Roesky, H. W.; Li, J.; Schmidt, H.-G.; Noltemeyer, M. accepted by *Angew. Chem.* (c) Looney, A.; Parkin, G. *Polyhedron* **1990**, *9*, 265−276.
(9) Cui, C.; Roesky, H. W.; Hao, H.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem.* **2000**, *112*, 1885−1887; *Angew. Chem., Int. Ed.* **2000**, *39*, 1815−1817.

Scheme 1[a]

$$2LAlH_2 + tBu-N=C=O \xrightarrow{2H_2O}$$

(1)

1

3

$$1 + tBu-N=C=O \longrightarrow$$

(2)

2

$$1 + 2 + 2H_2O \longrightarrow 3$$

(3)

L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$

[a] L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$.

(OCH=N-tBu) (**2**, Scheme 1, eq 2).[12] The analytical and spectroscopic data correspond to the formula of **2**. The band at 1868 cm^{-1} in the IR spectrum of **2** indicates the presence of an Al−H bond.[5b] The most intense peak in the EI mass spectrum of **2** appeared at m/z 544[M$^+$ − H], and the peak at m/z 545 (38%) was assigned to the molecular ion [M$^+$]. Compound **1** can also react with 2 equiv of $tert$-butyl isocyanate. Treatment of a mixture of **1** and **2** (1:1 molar ratio) with 2 equiv of water in THF also led to **3** (Scheme 1, eq 3),[10b] and an excess of water will result in the decomposition of **3**. Compound **2** can react cleanly with 1 equiv of
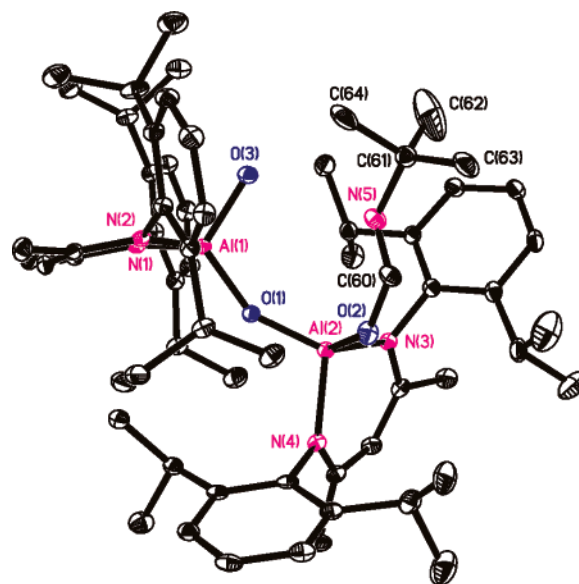
(10) Synthesis of **3**. (a) Method 1: The procedure is the same as that for the preparation of **2**, except that the ratio of the reagents is 1:2, and the resulting concentrated pentane solution reacted with water when it was stored at 0 °C to obtain **3** in 18% yield. (b) Method 2: A solution of H$_2$O (0.07 mL, 3.9 mmol) in THF (70 mL) was added dropwise to a solution of **1** (0.87 g, 1.95 mmol) and **2** (1.06 g, 1.95 mmol) in THF (20 mL) at −30 °C. The resulting solution was warmed slowly to room temperature and stirred for an additional 12 h. All volatiles were removed under reduced pressure. The residue was extracted with pentane (8 mL). After filtration the solution was concentrated and kept at 0 °C. Colorless crystals were obtained. Yield: 0.40 g, 20%. Mp: 185 °C (dec). EI-MS: m/z (%) 1021 (40) [M$^+$], 604 (100) [M$^+$ − L]. ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ 7.81 (s, 1H, CH=N), 7.25−7.00 (m, 12H, Ar−H), 4.91 (s, 1H, γ-H), 4.86 (s, 1H, γ-H), 1.57 (s, 3H, Me), 1.54 (s, 3H, Me), 1.50 (s, 3H, Me), 1.45 (s, 3H, Me), 3.73 (sept, 2H, CHMe$_2$), 3.57 (sept, 1H, CHMe$_2$), 3.46 (sept, 1H, CHMe$_2$), 3.24 (sept, 2H, CHMe$_2$), 3.12 (sept, 2H, CHMe$_2$), 1.41 (d, 6H, $^3J_{H-H}$ = 6.7 Hz, CHMe_2), 1.35 (d, 12H, $^3J_{H-H}$ = 6.8 Hz, CHMe_2), 1.20 (d, 3H, $^3J_{H-H}$ = 6.9 Hz, CHMe_2), 1.14 (d, 15H, $^3J_{H-H}$ = 6.9 Hz, CHMe_2), 1.09 (s, 6H, tBu), 0.87 (s, 3H, tBu), 0.82 (d, 6H, $^3J_{H-H}$ = 6.6 Hz, CHMe_2), 0.73 (d, 6H, $^3J_{H-H}$ = 6.7 Hz, CHMe_2), −0.30 (s, 1H, OH). IR (Nujol mull, cm^{-1}): 3458 (br, $\tilde{v}$OH). Calcd for C$_{68}$H$_{104}$Al$_2$N$_5$O$_3$ (1093.52): C, 74.69; H, 9.59; N, 6.40. Found: C, 73.81; H, 9.58; N, 6.31.

(11) Storre, J.; Klemp, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Fleischer, R.; Stalke, D. *J. Am. Chem. Soc.* **1997**, *119*, 7505−7513.

(12) Synthesis of **2**: $tert$-Butyl isocyanate (0.14 mL, 1.2 mmol) was added by syringe to LAlH$_2$ (0.55 g, 1.25 mmol) in toluene (20 mL). The solution was refluxed for 1 h. After removal of all the volatiles the residue was recrystallized from pentane. The resulting solution was concentrated to ca. 5 mL and kept at 0 °C to afford colorless crystals. Yield: 68% (0.44 g). Mp: 141−143 °C. EI-MS: m/z (%) 545 (38) [M$^+$], 544 (100) [M$^+$ − H]. ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ 7.54 (s, 1H, CH=N), 7.12−7.15 (m, 6H, Ar−H), 5.09 (s, 1H, γ-H), 3.41 (sept, 4H, CHMe$_2$), 1.55 (s, 6H, Me), 1.38 (d, 6H, $^3J_{H-H}$ = 6.8 Hz, CHMe_2), 1.28 (d, 6H, $^3J_{H-H}$ = 6.7 Hz, CHMe_2), 1.18 (d, 6H, $^3J_{H-H}$ = 6.8 Hz, CHMe_2), 1.12 (d, 6H, $^3J_{H-H}$ = 6.9 Hz, CHMe_2), 1.07 (s, 9H, tBu). IR (Nujol mull, cm^{-1}): 1868 ($\tilde{v}_{Al-H}$). Calcd for C$_{34}$H$_{52}$-AlN$_3$O (545.78): C, 74.82; H, 9.60; N, 7.70. Found: C, 75.03; H, 9.51; N, 7.83.

Figure 1. The crystal structure of **3**. The hydrogen atoms of the C−H bonds are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al(1)−O(1) 1.699(2), Al(1)−O(3) 1.727(2), Al(1)−N(2) 1.926(2), Al(2)−O(1) 1.706(2), Al(2)−O(2) 1.739(2), O(3)···N(5) 3.175(5); O(1)−Al(1)−O(3) 112.35(9), O(1)−Al(1)−N(2) 119.83(9), O(1)−Al(1)−N(1) 111.34(9), O(3)−Al(1)−N(1) 109.57(10), N(2)−Al(1)−N(1) 94.95, O(1)−Al(2)−O(2) 114.38(9), O(2)−Al(2)−N(3) 106.18(10), Al(1)−O(1)−Al(2) 147.85(10).

water, and **3** can be prepared from **2** without adding compound **1** from the reaction between **2** and water in a 2:3 molar ratio. We believe that the coordination of the OCH=N-tBu group and the bulky L ligand to the Al center is essential for stabilizing the L−Al bond and the terminal OH group of **3**.

Compound **3** crystallizes in the monoclinic space group $P2_1/c$ with one molecule of pentane.[19] As shown in Figure 1, **3** contains a bent Al−(μ-O)−Al unit with two tetrahedral distorted Al centers. Al(1) is surrounded by one terminal OH group, one bridging oxygen atom, and two nitrogen atoms of the L ligand. The coordination sphere of Al(2) is completed by two nitrogen atoms of the L ligand, one bridging oxygen atom, and one oxygen atom of the $tert$-butyl isocyanate moiety. The Al(1)−OH bond length (1.727-(2) Å) is comparable to those in LAl(OH)$_2$ (1.6947(15) and 1.7107(16) Å),[8a] and significantly shorter than those of the Al−(μ-OH) and Al−(μ_3-OH) bonds in [(tBu)$_2$Al(μ-OH)]$_3$ (1.848 Å)[7a] and [Al$_5$(tBu)$_5$(μ_3-O)$_2$(μ_3-OH)$_2$(μ-OH)$_2$(μ-O$_2$-CPh)$_2$] (Al−(μ-OH) 1.820(3) to 1.828(3) Å; Al−(μ_3-OH) 1.914(5) to 2.086(4) Å).[13] The Al−(μ-O) bond length of **3** (1.703 Å) is similar to those exhibited by the compounds [(tBu)$_2$Al(py)$_2$]$_2$(μ-O) (1.710 Å)[7a] and [{(tBu)$_2$Al(NH(Me)-CH$_2$CH$_2$NMe$_2$)}$_2$(μ-O)] (1.690(7) and 1.714(7) Å).[14] The Al-(2)−O(2) bond length (1.739(2) Å) is slightly longer than those of Al−OH and Al−(μ-O) in **3**. The Al−N bond length (from 1.912(2) to 1.931(2) Å, av 1.925 Å) is within the range of those previously observed (LAlMe$_2$ av 1.922 Å).[15]

(13) Koide, Y.; Barron, A. R. *Organometallics* **1995**, *14*, 4026−4029.
(14) McMahon, C. N.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1998**, 3703−3704.
(15) Qian, B.; Ward, D. L.; Smith, M. R., III. *Organometallics* **1998**, *17*, 3070−3076.

A broad band at 3458 cm^{-1} was observed in the IR spectrum of **3**, assigned to the OH stretch.[8a] Therefore we believe that there is an intra- or intermolecular hydrogen bond in the solid state structure of **3**. However, we cannot find the proton position in the X-ray structural analysis of **3**. Theoretical calculation, based on the DFT method RI-BP86/SV(P)[16] within Turbomole,[17] was carried out in order to verify the existence of the H atom and investigate its character. The four CH(Me)$_2$ groups which are far away from O(3) were replaced by H during the calculation in order to reduce the computer time. The full geometry optimization was carried out for compound **3** both with and without the H atom. The calculation proved the existence of the H atom in compound **3**: with H in the optimized geometry the distance of O(3)···N(5) is 2.93 Å, and this value is close to that (3.175(5) Å) in the X-ray structure, while without H the optimized O(3)···N(5) distance is 5.87 Å. Also the structure of compound **3** with the H atom is much more similar to that of the X-ray structure (mean deviation for all Al bonds, 0.02 Å; bond angles, 3.3°) than without H (mean deviation for all Al bond lengths, 0.05 Å; bond angles, 5.7°).

The calculated result shows that there is a strong O—H···N hydrogen bond[18] between the OH group and the N atom of the O—CH=N-*t*Bu moiety (H—O 1.00 Å, H···N 1.93 Å, O—H···N 172.6°, H—O—Al 110.1°) in agreement with the

(16) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824.
(17) Ahlrichs, R.; Bär, M.; Baron, H.-P.; Bauernschmitt, R.; Böcker, S.; Deglmann, P.; Ehrig, M.; Eichkorn, K.; Elliott, S.; Furche, F.; Haase, F.; Häser, M.; Horn, H.; Hättig, C.; Huber, C.; Huniar, U.; Katannek, M.; Köhn, A.; Kölmel, C.; Kollwitz, M.; May, K.; Ochsenfeld, C.; Öhm, H.; Schäfer, A.; Schneider, U.; Sie, M. *TURBOMOLE 5.5*; University of Karlsruhe: Karlsruhe, Germany, 2002.
(18) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principle of Structure and Reactivity*, 4th ed.; Harper Collins: 1993; p 301, Table 8.4.
(19) Crystal data for **3**·pentane: C$_{68}$H$_{104}$Al$_2$N$_5$O$_3$, M_r = 1093.52, monoclinic, space group $P2_1/c$, a = 14.128(3) Å, b = 21.500(4) Å, c = 22.083(4) Å, α = 90°, β = 98.01(3)°, γ = 90°, V = 6642(2) Å^3, Z = 4, ρ_{calcd} = 1.093 Mg m^{-3}, $F(000)$ = 2388, λ = 0.71073 Å, T = 133(2) K, μ = 0.090 mm^{-1}; crystal dimensions 0.25 × 0.23 × 0.15 mm, 1.74° < θ < 24.87°; of 39741 reflections collected, 11408 were independent (R(int) = 0.1377). The R values are $R1$ = 0.0484 and $wR2$ = 0.0935 ($I > 2\sigma(I)$); max/min residual electron density: 0.254/−0.250 e Å^{-3}. The OH group and the *tert*-butyl isocyanate unit are disordered (nearly 50:50%). All non-hydrogen atoms were refined anisotropically except the pentane molecule. All hydrogen atoms were included at geometrically calculated positions and refined using a riding model.
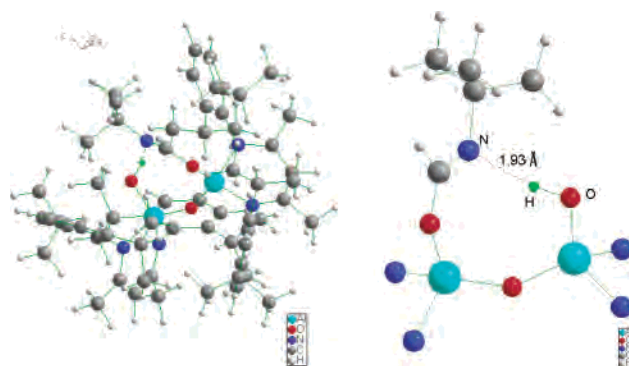
Figure 2. The intramolecular hydrogen bond in compound **3**. The position of the H atom (green) was obtained by RIBP86/SV(P) geometry optimization. Left: The position of H(O) in the whole molecule. Right: The local region of the intramolecular hydrogen bond.

IR spectrum of **3**. Furthermore, as shown in Figure 2, the formation of the intramolecular O—H···N hydrogen bond leads to good shielding of the OH group from the bulky *t*Bu group, and the O—CH=N-*t*Bu moiety will be far away from O(3) if the H atom is not present (as mentioned above in this case r(O(3)···N(5)) = 5.87 Å). This shielding together with the bulky L ligand on the Al atom protects the OH group from attack by another Lewis acidic Al center. Obviously that is the reason why the binuclear terminal hydroxide containing **3** does not aggregate to larger clusters.

In summary, we describe a new method for the synthesis of alumoxane hydroxide by the direct hydrolysis of aluminum hydrides with water. The intramolecular hydrogen bond and the bulky L ligand on the Al atom stabilize the reactive terminal OH group in **3**. **3** should react with other less bulky organometallic compounds in solution, which provides the possibility for the synthesis of aluminum containing homo- or heteroorganometallic compounds and their application for the polymerization of olefins.

Supporting Information Available: The X-ray crystallographic data in CIF format for **3**·pentane. This material is available free of charge via the Internet at http://pubs.acs.org.

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