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Communications

Hydrolytic Synthesis of an Alumoxane Hydride Bearing Terminal Pyrazolato Ligands[†]

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Summary: The novel alumoxane hydride $[(\mu\text{-}\eta^1:\eta^1\text{-}3,5\text{-}tBu_2pz)_2(\eta^1\text{-}3,5\text{-}tBu_2pz)_2(\mu_3\text{-}O)(\mu\text{-}Al)_3H_3]\cdot 2THF$ *(**2**; 3,5-*$tBu_2pz = 3,5$*-tert-butylpyrazolato) is formed when aluminum dihydride* $[(\mu\text{-}\eta^1:\eta^1\text{-}3,5\text{-}tBu_2pz)(\mu\text{-}Al)H_2]_2$ *(**1**) is reacted with 1 equiv of water. The core of compound **2** consists of two tetra- and one hexacoordinated Al atoms with short Al−O bonds. The two central* N_2Al_2O *ring systems share a common Al−O edge with a hexacoordinated Al atom, and two of the pyrazolato ligands bind in an* η^1 *and* $\mu\text{-}\eta^1:\eta^1$ *arrangement.*

The controlled hydrolysis of organoaluminum compounds with water results in the formation of alumoxanes of the general formulas $(RAlO)_n$ and $(R_2AlOAlR_2)_n$.[1,2] Since Sinn and Kaminsky found in 1980 that methylalumoxane (MAO) is a highly active cocatalyst in ethylene and propylene polymerization by group 4 metallocenes (e.g., Cp_2ZrMe_2),[3] important stimulus was given to the structural determination of alumoxanes to clarify their role in these polymerization reactions. Although the role of MAO seems to be understood,[4] the structure of the catalytically active species of methylalumoxane remains unknown. Recently, several lower aggregated alumoxanes $[tBuAlO]_n$ ($n = 6-9$) as well as aluminum hydroxides (oxide hydroxides) were prepared by the reaction of R_3Al (R = *t*Bu, Me, Mes, Ph) with water or anhydrous lithium hydroxide.[5,6] On the other hand, it has been shown that aluminum hydride compounds can be used as precursors for the synthesis of organoalumoxane with the formula $(RAlO)_4$ ($R = 2,4,6\text{-}tBu_3C_6H_2$) and organoalumoxane hydride with the formula $\{[(\mu\text{-}\eta^1:\eta^1\text{-}3,5\text{-}tBu_2pz)(\mu\text{-}Al)H]_2O\}_2$ ($tBu_2pz = 3,5$-di-*tert*-butylpyrazolato) by employing the oxygen-trans-

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[†] Dedicated to Professor Tris Chivers on the occasion of his 60th birthday.

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(1) Alkylalumoxanes generally are species containing an oxygen bridge between two metal atoms, Al−O−Al. Oligomeric aluminum alkoxides (hydroxide) bridged by an alkoxy (hydroxide) group, Al−O(R)−Al (Al−O(H)−Al), and compounds containing no organic group generally are not included in this classification; see: Pasynkiewicz, S. *Polyhedron* **1990**, *9*, 429.

(2) Alkylalumoxanes usually are prepared by hydrolysis of organoaluminum compounds using water[2a] or hydrated metal salts[2b] or by the reaction with species containing reactive oxygen such as CO_2, $RCONR_2$, $MeCO_2H$, and Me_2SO:[2c] (a) Ishida, S. I. *J. Polym. Sci.* **1962**, *62*, 1. (b) Razuvaev, G. A.; Sangalov, Yu. A.; Ne'lkenbaum, Yu. Ya.; Minsker, K. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 2547; *Chem. Abstr.* **1976**, *84*, 59627x. Collins, S.; Gauthier, W. J.; Holden, D. A.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Organometallics* **1991**, *10*, 2061. (c) Ziegler, K.; Krupp, F.; Weyer, K.; Larbig, W. *Liebigs Ann. Chem.* **1960**, *629*, 251. Zakharkin, L. J.; Khorlina, I. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1959**, 2146.

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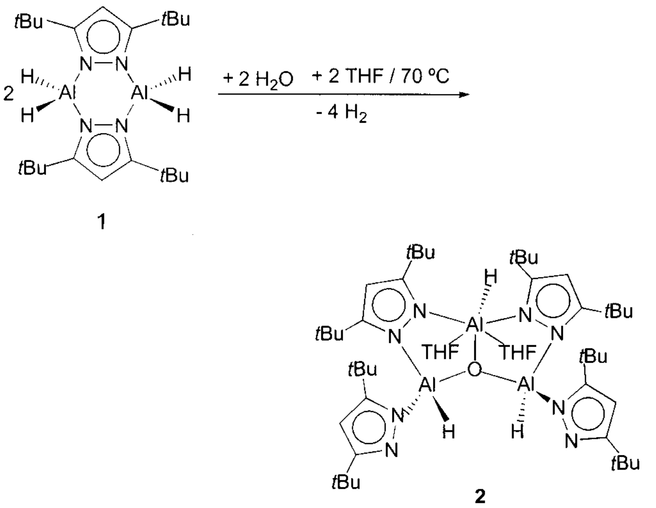
Scheme 1. Synthesis of Compound 2



fer species $[Me_2SiO]_3$[7] and dioxane.[8] However, reactions of organoaluminum hydrides with water to synthesize organoalumoxane or organoalumoxane hydride have not been reported. In this paper the synthesis of the alumoxane hydride $[(\mu\text{-}\eta^1{:}\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz})_2(\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz})_2(\mu_3\text{-O})(\mu\text{-Al})_3\mathrm{H_3}]\cdot 2\mathrm{THF}$ (**2**) by the reaction of the aluminum dihydride $[(\mu\text{-}\eta^1{:}\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz})(\mu\text{-Al})\mathrm{H_2}]_2$ (**1**)[9] with 1 equiv of water is described.

To a stirred solution of compound **1** in dry THF (or dioxane) at 70 °C, 1 equiv of water in THF (or dioxane) was added slowly to yield **2** (Scheme 1).[11] The X-ray crystal analysis of **2** reveals an arrangement involving three aluminum atoms and four ligands (Figure 1).[12] The composition in the gas phase is supported by the MS (EI) spectrum ($(M - H)^+$, m/z 815). In compound **2**, the presence of remaining Al−H bonds was confirmed by ^{1}H NMR spectroscopy (δ 4.2 (br), THF-d_8) and by the IR spectrum ($\nu_{\mathrm{Al-H}}$ 1872 and 1896 cm^{-1}).[13] The three Al atoms of the Al_3O core form a regular triangle (Al(1)−O(1) = 1.774(3) Å, Al(2)−O(1) = 1.861(6) Å). The Al atoms use two μ-η^1:η^1 pyrazolato ligands to generate two chairlike five-membered Al_2N_2O rings. An interesting finding is that the oxygen atoms of two THF molecules bind to the Al(2) atom to form a 6-fold coordination sphere. Moreover, the surprising feature of **2** is that two pyrazolato ligands, which generally form stable complexes with aluminum in an η^1:η^1 and, very recently, an η^2 mode,[8,14] are terminally coordinated to two of the aluminum centers. This coordination pattern is uncommon for the known pyrazolato complexes.[15] Only a few transition-metal complexes (M = Ir, Ta, Ni, Cr) with terminal η^1-pyrazolato ligands have appeared recently in the literature.[16] In **2**, the 6-fold coordination

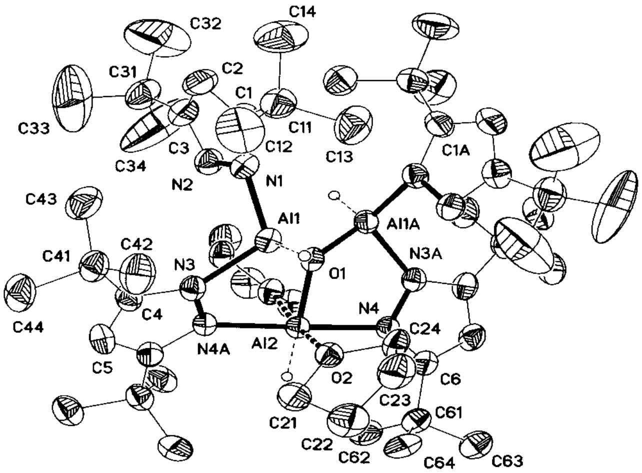


Figure 1. Perspective view and atom-labeling scheme of compound **2**, showing the numbering scheme and thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Al(1)−O(1) = 1.774(2), Al(2)−O(1) = 1.861(6), Al(2)−O(2) = 2.023(4), Al(1)−N(1) = 1.860(5), Al(1)−N(3) = 1.930(5), Al(2)−N(4) = 2.050(4); Al(1)−O(1)−Al(2) = 115.56(16), O(1)−Al(1)−N(1) = 110.7(2), O(1)−Al(1)−N(3) = 96.3(2), N(2)−N(1)−Al(1) = 106.78(3), O(1)−Al(2)−N(4) = 89.12(14), O(1)−Al(2)−O(2) = 85.96(13), Al(1)−N(3)−C(4) = 137.2(4), Al(1)−N(1)−C(1) = 142.9(4).

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[9] To a stirred solution of H[tBu$_2$pz][10a] (0.36 g, 2.0 mmol) in toluene (50 mL) was slowly added $AlH_3\cdot NMe_3$[10b] (4.0 mL of a 0.80 M solution in C_6H_6, 3.2 mmol) in excess with evolution of H_2 at 50 °C. The mixture was stirred for 3 h at 50 °C and for 15 h at room temperature. The solvent was removed and the crude product dried under reduced pressure for at least 6 h to afford **1** as a pure white powder (0.38 g, 91%). Alternatively, the crude product was recrystallized in toluene at −26 °C (0.31 g, 76%). Mp: 194−196 °C. ^{1}H NMR (C_6D_6): δ 1.44 (s, 36 H, tBu), 6.14, (s, 2 H, CH), 5.4 (very br ($W_{1/2}$ = 144 Hz), 4 H, Al−H). ^{13}C NMR (C_6D_6): δ 30.75 (s, CH$_3$), 32.79 (s, CMe$_3$), 104.11 (s, CH), 167.26 (s, C-tBu). MS (EI; m/z (%)): 415 ($(M - H)^+$, 100). IR (Nujol mull; cm^{-1}): Al−H 1869, 1920. Anal. Calcd for $C_{22}H_{42}Al_2N_4$: C, 63.37; H, 10.16; Al, 12.95; N, 13.44. Found: C, 63.11; H, 10.08; Al, 12.77; N, 13.40.

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[11] Method 1: To a stirred solution of **1** (2.08 g, 5.0 mmol) in dioxane (50 mL), was slowly added water (0.090 mL, 5.0 mmol) in dioxane (100 mL) (over 5 h) with evolution of H_2 at 70 °C. The solution was filtered through Celite. The filtrate was reduced (to 15 mL), and **2** was recrystallized at room temperature to yield colorless crystals (0.84 g, 41%). Mp: 188 °C. ^{1}H NMR (THF-d_8): δ (η^1:η^1) 1.24 (s, 36 H, C(6)-tBu), 5.88 (s, 2 H, C(5)H); δ (η^1) 1.34 (s, 18 H, C(1)-tBu), 1.5 (br ($W_{1/2}$ = 33 Hz), 18 H, C(3)-tBu), 6.09 (s, 2 H, C(2)H), 4.5 (very br ($W_{1/2}$ = 90 Hz), 3 H, Al−H). ^{13}C NMR (THF-d_8): δ (η^1:η^1) 31.53 (s, C(62)), 32.63 (s, C(61)), 99.42 (s, C(5)H), 162.67 (s, C(6)); δ (η^1) 31.46 (s, C(12)), 33.01 (s, C(11)), 31.1 (br, C(32)), 31.2 (br, C(31)), 103.64 (s, C(2)H), 164.38 (s, C(1)), 167.32 (br, C(3)). MS (EI; m/z (%)): 815 ($(M - H)^+$, 100), 759 ($(M - AlMe_2)^+$, 35). IR (Nujol mull, cm^{-1}): Al−H, 1872, 1896 cm^{-1}. Anal. Calcd for $C_{44}H_{79}Al_3N_8O$: C, 64.71; H, 9.68; N, 6.86. Found: C, 64.21; H, 9.54; N, 6.78. Method 2: The procedure is the same as in method 1, except that THF was used as a solvent and **2** is recrystallized at −26 °C (1.30 g, 54%). Single crystals suitable for X-ray diffraction analysis were obtained from THF at −26 °C.

[12] Crystal data for **2**:[18] $C_{68}H_{127}Al_3N_8O_7$ (includes six THF molecules), M_r = 1249.72, monoclinic, space group $C2/c$, a = 15.312(10) Å, b = 26.90(4) Å, c = 19.779(6) Å, α = 90°, β = 109.53(2)°, γ = 90°, V = 7680(12) Å^3, Z = 4, ρ_{calcd} = 1.081 Mg m^{-3}, F(000) = 2744, μ(Mo Kα) = 0.101 mm^{-1}. The total number of reflections measured was 5871 in the range 7.22 ≤ 2θ ≤ 45.16°, of which 5035 were unique. Final R indices: R1 = 0.0850 ($I > 2\sigma(I)$) and wR2 = 0.2575 (all data), maximum/minimum residual electron density 450/−291 e nm^{-3}.

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sphere around the Al(2) atom differs sharply from other characterized alumoxanes in which coordination numbers of 3, 4,[5a,b,7] and 5[8] were found. The Al−O bond lengths of the Al_3O core range from 1.774(3) Å (Al(1)−O(1)) to 1.861(6) Å (Al(2)−O(1)) (Figure 1), and these values are shorter than the sum of the respective covalent radii.[17] However, the Al(2)−O(2) bond length (2.023(4) Å) is much longer than that of Al(1)−O(1), indicating that bonding between Al(2) and the O atom from THF is not as strong as in Al(1)−O(1), due to the 6-fold coordination site. The Al(1)−N(1) bond length (1.860(5) Å) is considerably shorter than those of Al(1)−N(3) (1.930(5) Å) and Al(2)−N(4) (2.050(4) Å), probably due to the higher electronic density of the N atoms on the terminal ligands.

The ^{1}H NMR spectrum of **2** in THF-d_8 showed that each type of the pyrazolato ligands gives rise to an independent set of signals (δ 1.24, 5.88 ppm and δ 1.34, 1.5 (br, $W_{1/2} = 33$ Hz), 6.07 ppm, at 25 °C), implying that the two types of groups are not rapidly exchanging on the NMR time scale at this temperature. Furthermore, the two different chemical shifts of *t*Bu groups on the η^1-pyrazolato ligands (δ 1.34, 1.5 ppm) and one broad signal indicated that the exchange between Al(1)−N(1) and Al(1)−N(2) as well as the rotation around the Al(1)−N(1) axis are both hindered. These features are in sharp contrast to the transition-metal complexes with terminal pyrazolato ligands (e.g., Ta complex), in which such characteristics were not observed, even at −80 °C.[16b] The experimental investigations of the reaction of **2** (at +70 °C) showed that quite small amounts of a white unidentified insoluble solid as well as H_2 were formed. It is noteworthy to mention that the yield of product **2** is much lower, along with more insoluble byproducts when the hydrolysis is conducted at room temperature or −78 °C. The mechanism of this process is currently unknown, but it probably involves initial intermediate containing Al−OH species.

In summary, this paper demonstrates that precursor **1** can be used to generate alumoxane hydride **2** by hydrolysis. In addition, the structure of **2** illustrates for the first time that pyrazolato ligands also prefer to bind terminally to aluminum(III) centers, besides the known η^1:η^1 or η^2 modes. Although some arguments in favor of this terminal arrangement have been proposed that this feature is probably caused by the steric or electronic factors of the structures,[16b] we cannot yet confirm which factor plays a central role in determining the overall structure. However, as in the case of compound **2**, it seems that the adopted terminal arrangement is likely due to the sterically bulky *t*Bu groups of the ligands rather than to electronic factors.

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Supporting Information Available: Text giving experimental details of the syntheses and tables of final atomic coordinates, bond distances and angles, and anisotropic thermal parameters for the structural analyses of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The electronic contributions of short Al−O bond lengths have recently attracted interest. However, observation of the shortening has brought about controversy, since several explanations for this feature are possible: see ref 8 and references therein.

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