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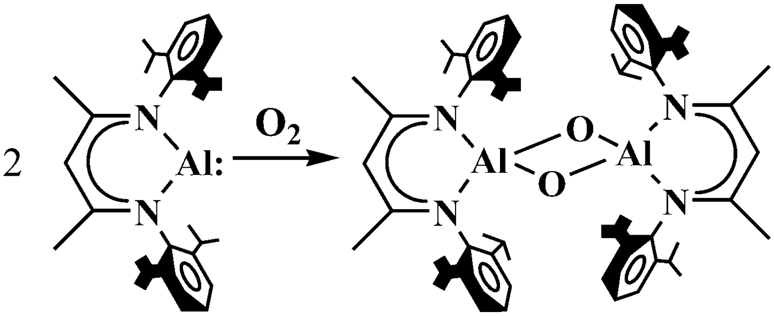

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The Selective Preparation of an Aluminum Oxide and Its Isomeric C−H-Activated Hydroxide

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Alumoxane can be used as the active catalyst in the polymerization of epoxides,[1a−c] aldehydes,[1d,e] and olefins[1f] and, therefore, attracts much attention to chemists. In 1980, methylalumoxane (MAO, $[\mathrm{MeAlO}]_n$) was found to be a highly active cocatalyst for group 4 metallocenes, catalyzing ethylene and propylene polymerization.[2] This has been of remarkable industrial importance. In general, alumoxanes of formula $[\mathrm{RAlO}]_n$ or $[\mathrm{R_2AlOAlR_2}]_n$ can be synthesized by the controlled hydrolysis of organoaluminum compounds using water, or water contained in hydrated metal salts,[3] or alternatively by their reaction with oxygen-containing species.[4] This is well documented with the structural characterization of such alumoxanes prepared in recent years, although the related reaction process is complex.[3,4e,f] Meanwhile, it has been shown that the hydrolysis of those organoaluminum compounds often leads to the generation of Al−OH-containing species.[3]

It is known that alkylaluminum(III) compounds reacting with O_2 normally undergo insertion reaction into the Al−alkyl bond and result in aluminum alkoxides[5] or alkylperoxides.[6] In contrast, the reaction of low-valent aluminum compounds with O_2, which could directly yield alumoxanes, has not been investigated so far. Herein, we report on the reaction of aluminum(I) monomer LAl (L = $\mathrm{HC[(CMe)(NAr)]_2}$, Ar = 2,6-$i\mathrm{Pr_2C_6H_3}$)[7] with molecular oxygen and the isolation of an aluminum oxide $[\mathrm{LAlO}]_2$ (**1**). Further hydrolysis of **1** to an aluminum oxide hydroxide **2** and the reaction of LAl with $\mathrm{N_3Ar''}$ in the presence of a small amount of water to a C−H-activated aluminum hydroxide **4**, an isomer of **1**, are also described (Scheme 1).

A toluene solution of LAl in an atmosphere of O_2 under stirring in the temperature range of −78 °C to room temperature changed slowly the color from red to orange, to yellow, and finally to almost colorless. At ca. −15 °C, **1** separated from the solution as a crystalline solid. The formation of **1** involves the O_2 oxidation of two central Al atoms. This might proceed through a $\mathrm{LAl}(\eta^2\text{-}O_2)$ intermediate, which is not stable and reacts further with another molecule of LAl. Comparable examples are reported for the reaction of copper(I) with O_2[8] and the matrix experiment of AlX and O_2.[9] Recently, the reaction of LAl with a large bulky azide $\mathrm{N_3Ar'}$ has shown two types of intramolecular addition to an Al═N multiple bond species.[10] The reproducible reaction of LAl with $\mathrm{N_3Ar''}$ containing a small amount of H_2O leads to the respective isolation of **3**, **4**, and $\mathrm{H_2NAr''}$ (**5**) and indicates the partial hydrolysis of a C−H-activated product (**3** to **4**) at low temperature. The Al−N bond imposed by the bulky Ar″ in **3** might preferentially react with H_2O to form **4**, an isomer of **1**. **3** and **5** are characterized by spectral analysis (Supporting Information), and **3** is further confirmed by X-ray measurement (Supporting Information).

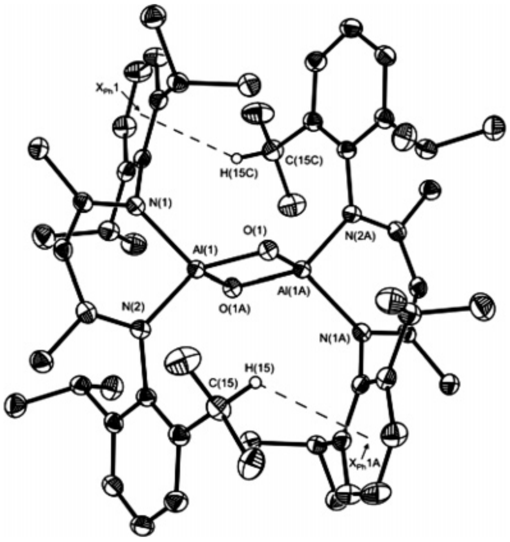
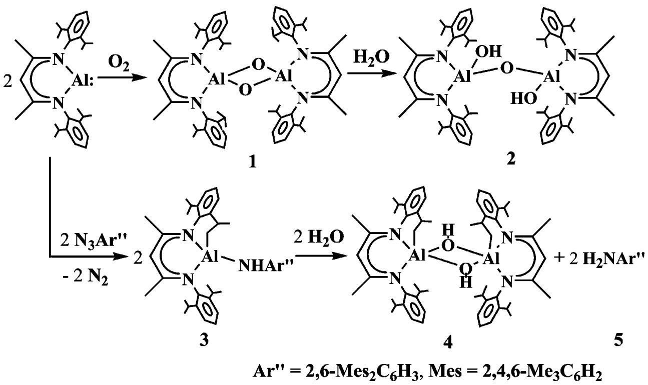


Figure 1. Molecular structure of **1** (50% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Al(1)−O(1) 1.760(1), Al(1)−O(1A) 1.763(1), Al(1)···Al(1A) 2.472(1), C(15)H(15)(56%)···X_{Ph}(1A) 2.71, C(15C)H(15C)(44%)···X_{Ph}(1) 3.02, O(1)−Al(1)−O(1A) 90.86(5), Al(1)−O(1)−Al(1A) 89.14(5).

Scheme 1



Ar'' = 2,6-$\mathrm{Mes_2C_6H_3}$, Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$

Compound **1** was obtained in high yield (80%). It melts at 314−315 °C, and the isotope-distributed peaks in the EI MS spectrum (*m*/*z* 920.4, 30%) are assigned to the molecular ion [M^+]. **1** is soluble in hot aromatic solvents (toluene and benzene), whereas its solubility is poor at room temperature. Compound **4** was isolated as colorless crystals, which melted in the range of 333−335 °C. **1** and **4** both have been characterized by spectroscopy, as well as by X-ray crystallography.

The structural analysis of **1** (Supporting Information) reveals a dimer with crystallographic centro-symmetry (Figure 1). The central $\mathrm{Al_2}(\mu\text{-O})_2$ core is formed in a nearly perfect square (Al−O: 1.760(1), 1.763(1) Å; O−Al−O: 90.89(1)°; Al−O−Al: 89.11(1)°). The Al−O bond lengths are a little longer than those observed in compounds with four-coordinate μ-oxo-aluminum

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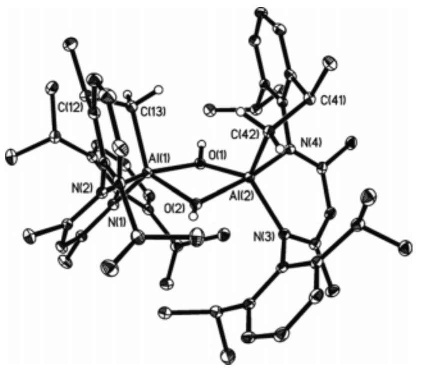

Figure 2. Molecular structure of **4** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Al(1)−O(1) 1.910(1), Al(1)−O(2) 1.850(1), Al(1)−C(13) 1.986(2), C(13)−C(12) 1.549(2), Al(2)−O(1) 1.852(1), Al(2)−O(2) 1.905(1), Al(2)−C(42) 1.989(2), C(42)−C(41) 1.554(3), Al(1)···Al(2) 2.950(1), O(1)−Al(1)−O(2) 73.84(6), Al(1)−O(2)−Al(2) 103.54(6), O(2)−Al(2)−O(1) 73.92(6), Al(2)−O(1)−Al(1) 103.25(6).

(1.659−1.753 Å).[11] However, they are much shorter than the predicted one (1.96 Å).[12] This may be largely due to ionic contribution to the Al−O bond.[13] The short Al−O bonds in $Al_2(\mu\text{-}O)_2$ result in short Al···Al contacts (2.472(1) Å) and subsequent steric crowding of the Ar substituents from the two oriented L. Similar structural features are discussed for compounds L_2M (M = Mg, Ca, Sr, Ba)[15a] and suggested for $[LGaO]_2$.[15b] This structural character is further recognized in solution by NMR spectroscopic analysis. The *i*Pr groups at Ar of L give rise to four separated septets and eight doublets, indicating different steric environments of two Ar groups of the LAl moiety. Moreover, one septet and one doublet of those appear at higher field (δ 2.63 and 0.22 ppm) in comparison to the resonance range (δ 4.14−3.06, 1.58−0.72 ppm) of similar compounds.[11e,14] This suggests that the corresponding methine (CH) and methyl (CH_3) protons of *i*Pr are shielded due to the ring current effect within the aryl groups caused by steric crowding.[16] The $^{13}C\{^1H\}$ NMR data also exhibit the methine carbon resonance at high field (δ 71.4 ppm). This property may result in a not energetically favorable approach to **1** by using $[LAlCl(\mu\text{-}O)]_2$ as a precursor (Supporting Information).

The X-ray structural analysis of **4** (Supporting Information) shows the same composition similar to that of **1** but with five-coordinate Al and an $Al_2(\mu\text{-}OH)_2$ nonplanar core instead (Δ = 0.1009 Å, Figure 2). The bond lengths of Al−C (1.988(2) Å (av.)) and $C_{activated}$−C (1.552(2) Å (av.)) exhibit normal single bond character; however, the related parameters of $Al_2(\mu\text{-}OH)_2$ (Al−O: 1.879(1) Å (av.); O−Al−O: 73.88(6)° (av.); Al−O−Al: 103.40(1)° (av.)) compare differently with that of the $Al_2(\mu\text{-}O)_2$ in **1**. These data indicate a less crowded structure of **4** than that of **1**. The NMR (Al−CH_2: δ −1.69 (t), −0.35 (dd) ppm; Al-μ-OH: 0.29 (s) ppm) and IR spectral data (Al-μ-OH: ν 3400 (br) cm^{-1}) confirm the notable functionalities of **4**.

The reaction of **1** with stoichiometric amounts of water was accomplished, affording a known compound **2**.[11e] This is in agreement with the analysis of the NMR tube sample of **1**, which was kept at room temperature for 1 month; the resonances of *i*Pr at high field (one septet and one doublet) disappeared, while the data can be identified as **2**, including a small amount of free LH. Obviously, the conversion of **1** with H_2O to **2** indicates a ring opening of the $Al_2(\mu\text{-}O)_2$ and the formation of terminal Al−OH and implied a process of less crowding.

Although **1** does not contain three-coordinate Al centers, which are proposed to have strong Lewis acidity and are vital for catalytic activity, the notable structural character of **1** prompted us to test its cocatalytic property for the dimethylzirconocene polymerization of ethylene in toluene solution at either 25 or 80 °C. However, no activity was observed. Moreover, no reaction occurred between **1** and Cp_2ZrMe_2.

In summary, we have prepared an aluminum oxide $[LAlO]_2$ (**1**) by reaction of LAl with O_2. **1** has a stronger steric crowding than that of its isomer **4** obtained from the hydrolysis of the bulky aluminum amide **3**. An attempt to convert **1** to **4** by high temperature treatment, whether in toluene solution or in its solid state, was not successful. The preparation of isomers **1** and **4** is possible using selective routes.

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Supporting Information Available: The Experimental Section including the detailed synthetic procedures, analytical, spectral, and crystallographic characterization data (PDF). The molecular structure of **4**. CIF data for **1**, **3** (0.12 toluene, 0.05 *n*-hexane), and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Colclough, R. O. *J. Polym. Sci.* **1959**, *34*, 171. (b) Vandenberg, E. J. *J. Polym. Sci.* **1960**, *47*, 486. (c) Colclough, R. O.; Gee, G.; Jagger, A. H. *J. Polym. Sci.* **1960**, *48*, 270. (d) Ishida, S. I. *J. Polym. Sci.* **1962**, *62*, 1. (e) Saegusa, T.; Fujii, Y.; Fujii, H.; Furukawa, J. *Makromol. Chem.* **1962**, *55*, 232. (f) Longiave, C.; Castelli, R. *J. Polym. Sci.* **1963**, *4C*, 387.
(2) (a) Sinn, H.; Kaminsky, W.; Vollmer, H. J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.
(3) (a) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971. (b) Harlan, C. J.; Mason, M. R.; Barron, A. R. *Organometallics* **1994**, *13*, 2957.
(4) (a) Ziegler, K.; Krupp, F.; Weyer, K.; Larbig, W. *Liebigs Ann. Chem.* **1960**, *629*, 251. (b) Zakharkin, L. J.; Khorlina, I. M. *Izv. Akad, Nauk SSSR, Ser. Khim.* **1959**, 2146. (c) Harney, D. W.; Meisters, A.; Mole, T. *Aust. J. Chem.* **1974**, *27*, 1639. (d) Boleslawski, M.; Pasynkiewicz, S. *J. Organomet. Chem.* **1972**, *43*, 81. (e) Uhl, W.; Koch, M.; Hiller, W.; Heckel, M. *Angew. Chem., Int. Ed.* **1995**, *34*, 989. (f) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 8387.
(5) (a) Ziegler, K. *Angew. Chem.* **1956**, *68*, 721. (b) Davies, A. G.; Roberts, B. P. *J. Chem. Soc. B* **1968**, 1074. (c) Lewiński, J.; Zachara, J.; Goś, P.; Grabska, E.; Kopeć, T.; Madura, I.; Marciniak, W.; Prowotorow, I. *Chem. Eur. J.* **2000**, *6*, 3215.
(6) Lewiński, J.; Zachara, J.; Grabska, E. *J. Am. Chem. Soc.* **1996**, *118*, 6794.
(7) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4274.
(8) (a) Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 2108. (b) Lewis, E. A.; Tolman, W. B. *Chem. Rev.* **2004**, *104*, 1047.
(9) (a) Bahlo, J.; Himmel, H.-J.; Schnöckel, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 4696. (b) Bahlo, J.; Himmel, H.-J.; Schnöckel, H. *Inorg. Chem.* **2002**, *41*, 2678.
(10) Zhu, H.; Chai, J.; Chandrasekhar, V.; Roesky, H. W.; Magull, J.; Vidovic, D.; Schmidt, H.-G.; Noltemeyer, M.; Power, P. P.; Merrill, W. A. *J. Am. Chem. Soc.* **2004**, *126*, 9472.
(11) (a) McMahon, C. N.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1998**, 3703. (b) Uhl, W.; Koch, M.; Pohl, S.; Saak, W.; Hiller, W.; Heckel, M. *Z. Naturforsch.* **1995**, *50b*, 635. (c) Neculai, D.; Roesky, H. W.; Neculai, A. M.; Magull, J.; Walfort, B.; Stalke, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4294. (d) Kuhn, N.; Fuchs, S.; Niquet, E.; Richter, M.; Steimann, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 717. (e) Bai, G.; Roesky, H. W.; Li, J.; Noltemeyer, M.; Schmidt, H.-G. *Angew. Chem., Int. Ed.* **2003**, *42*, 5502.
(12) Based on a radius of 1.3 Å for Al and 0.66 Å for O: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 221.
(13) Petrie, M. A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8704.
(14) Zhu, H.; Chai, J.; He, C.; Bai, G.; Roesky, H. W.; Jancik, V.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **2005**, *24*, 380.
(15) (a) Harder, S. *Organometallics* **2002**, *21*, 3782. (b) Hardman, N. J.; Power, P. P. *Inorg. Chem.* **2001**, *40*, 2474.
(16) Haigh, C. W.; Mallion, R. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1980**, *13*, 303.

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