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Reaction of $LAlH_2$ with *tert*-Butyl Hydrogenperoxide under C–H Bond Activation and Substitution Leads to the Formation of a Pentacoordinated *tert*-Butylperoxo Aluminum Compound

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The reaction between β-diketiminato-stabilized aluminum dihydride $LAlH_2$ and ^{t}BuOOH leads to the formation of a pentacoordinated *tert*-butylperoxo aluminum compound.

Organoperoxy aluminum compounds are formed as intermediates in the oxidation of organometallic compounds.[1,2] The alkylperoxy aluminum compounds are highly unstable because of the high reactivity of the R−O−O−Al group, and in general, aluminum alkoxides are obtained.[3] There are a few reports of organic peroxides being allowed to react directly with aluminum alkyls to prepare alkylperoxo aluminum compounds, but the products were not structurally characterized. A monomeric aluminum peroxide $ROOAl(OEt)_2$ (R = cumyl, ^{t}Bu) was reported by Anisimov et al. from the reaction of ROOH (R = cumyl, ^{t}Bu) and diethoxyaluminum chloride in the presence of ammonia.[4] A dimeric $PhC(Me)_2OOAl(OEt)_2$ was obtained by Razuvaev et al. from diethoxyaluminum chloride with the sodium salt of cumyl hydrogenperoxide.[5] Davies and Hall also reported on the synthesis of tris(decahydro-9-naphthylperoxy)aluminum from decahydro-9-naphthyl hydrogenperoxide and aluminum *tert*-butoxide, which decomposed after the removal of solvent.[3] In addition to the direct treatment of aluminum alkyls with organic peroxides, attempts have been made to synthesize alkylperoxy aluminum compounds by investigating the interaction of dioxygen and aluminum alkyls. A complex mixture of aluminum alkoxides was obtained when aluminum alkyls were treated with dioxygen.[1]

Recently, autoxidation reactions on $Ga(^{t}Bu)_3$ and $In(^{t}Bu)_3$ resulted in the isolation of *tert*-butylperoxo gallium[6] and indium[7] compounds. A similar reaction on $Al(^{t}Bu)_3$ gave $[(^{t}Bu)_2Al(\mu\text{-}O^{t}Bu)]_2$.[8] These reactions proceed by the interaction of molecular dioxygen and three-coordinated metal alkyls. In 1996, Lewiński et al. isolated and characterized a terminal *tert*-butylperoxo aluminum compound $(^{t}BuOO)(^{t}BuO)Al(\mu\text{-}O^{t}Bu)_2Al(mesal)_2$ by the oxidation of the four-coordinated aluminum center of a di-*tert*-butylaluminum compound $(^{t}Bu)_2Al(mesal)$ (mesal = methyl salicylate).[9,10] Its formation was described to proceed via an intermediate pentacoordinated aluminum center.[11]

The objective of the present work is to emphasize the direct application of organic peroxides in the synthesis of alkylperoxy aluminum compounds, and thus, we report the reaction of $LAlH_2$ (**1**) [L = $HC\{(2,6\text{-}i\text{-}Pr_2C_6H_3N)(CMe)\}_2$] with *tert*-butyl hydrogenperoxide in the synthesis of the pentacoordinated *tert*-butylperoxo aluminum compound **2**.

To a solution of $LAlH_2$[12] in diethyl ether (30 mL) was added dropwise 2 equiv of ^{t}BuOOH (5−6 M solution in decane) at −78 °C. The ^{t}BuOOH solution in decane contains approximately 4% water. After the addition, the reaction mixture was slowly warmed to room temperature and stirred overnight at this temperature. During the reaction, the color

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[†] Dedicated to Professor Konrad Seppelt on the occasion of his 60th birthday.

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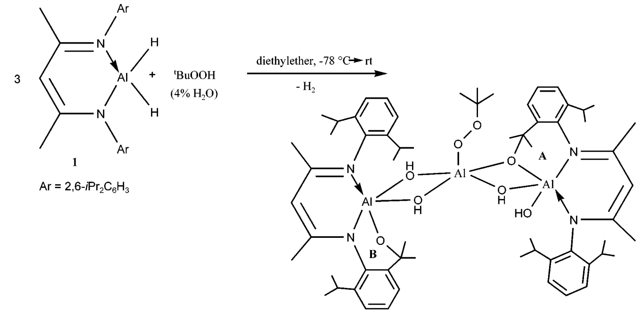
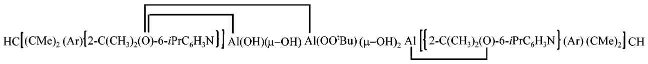
Scheme 1. Synthesis of Pentacoordinated *tert*-Butylperoxo Aluminum Compound



2



$$HC[(CMe)_2(Ar)\{2\text{-}C(CH_3)_2(O)\text{-}6\text{-}\mathit{i}PrC_6H_3N\}]\,Al(OH)(\mu\text{–}OH)\,Al(OO^tBu)(\mu\text{–}OH)_2\,Al[\{2\text{-}C(CH_3)_2(O)\text{-}6\text{-}\mathit{i}PrC_6H_3N\}(Ar)(CMe)_2]CH$$

2

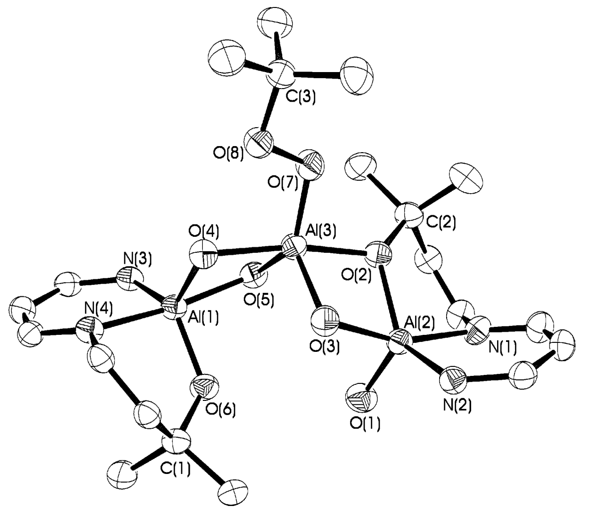


Figure 1. Molecular structure of **2**. Only the core of the molecule is shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Al(1)−O(4) 1.826(2), Al(1)−O(5) 1.894(2), Al(1)−O(6) 1.757(2), Al(1)−N(3) 1.934(2), Al(1)−Al(3) 2.873(1), Al(2)−O(1) 1.732(2), Al(2)−O(2) 1.891(2), Al(2)−O(3) 1.888(2), Al(2)−Al(3) 2.871(1), Al(3)−O(4) 1.871(2), Al(3)−O(5) 1.836(2), Al(3)−O(2) 1.874(2), Al(3)−O(3) 1.803(2), Al(3)−O(7) 1.764(2), O(7)−O(8) 1.487(3), C(1)−O(6) 1.434(3), C(2)−O(2) 1.463(3), Al(1)−O(4)−Al(3) 101.97(11), Al(1)−O(6)−C(53) 126.07(17), O(4)−Al(1)−O(5) 75.69(9), Al(1)−Al(3)−Al(2) 109.42(4), Al(2)−O(2)−Al(3) 99.40(9), Al(3)−O(2)−C(24) 130.64(16), Al(3)−O(7)−O(8) 112.07(14), O(7)−O(8)−C(3) 106.97(18), O(3)−Al(3)−O(5) 106.82(10), O(3)−Al(3)−O(2) 78.79(19).

of the solution changed to light yellow, and this color was sustained during the course of the reaction. The volume of the solution was reduced to 15 mL, and the solution was then stored at 0 °C. The expected four-coordinate aluminum di-*tert*-butylperoxide, LAl(OO^{t}Bu)$_2$ was not formed; instead, colorless crystals of **2** were obtained after 1 week (Scheme 1). The reaction pathway involved in the formation of **2** is not clear, but we assume that the intermediate *tert*-butyl aluminumperoxide, which is probably formed in the reaction medium, activates the C−H bond of the isopropyl group resulting in the C−O−Al formation. During the course of the reaction, two C*H* protons (out of a total of 8 CH protons) of the isopropyl groups of the β-diketiminato ligand are activated, leading to the formation of two six-membered heterocyclic rings **A** and **B**. Each ring contains one Al−O bond.

Compound **2** is stable in the solution. Complete characterization of **2** after its isolation from the mother liquor was not possible because of its decomposition under formation of the β-diketimine ligand. The identity of the latter compound was confirmed by spectral analysis.

The molecular structure of **2** in the solid state was determined by X-ray crystal structural analysis. An ORTEP plot of **2** is shown in Figure 1. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with a diethyl ether molecule in the asymmetric unit. **2** has two four-membered Al_2O_2 rings connected by a β-diketiminato ligand at the aluminum centers Al(1) and Al(2). Each aluminum atom is five-coordinate. The aluminum atom Al(3) present at the center of the molecule has a distorted trigonal bipyramidal geometry, in which three oxygen atoms occupy the basal sites with bond angles of O(3)−Al(3)−O(5) 106.82(10)°, O(7)−Al(3)−O(3) 120.3(11)°, O(7)−Al(3)−O(5) 132.85(10)°. It is bound to a *tert*-butylperoxide group with an Al(3)−O(7) bond length of 1.764(2) Å. The O(7)−O(8) bond length of 1.487(3) Å is slightly longer than that of the peroxo bond distance of (^{t}BuOO)(^{t}BuO)Al(μ-O^{t}Bu)$_2$Al(mesal)$_2$[9] and those of transition metal peroxides.[13] In addition, the bond angles of Al(3)−O(7)−O(8) and O(7)−O(8)−C(59) [112.07(14)° and 106.97(18)°, respectively] deviate slightly from the alkylperoxo bond angles of (^{t}BuOO)(^{t}BuO)Al(μ-O^{t}Bu)$_2$Al(mesal)$_2$.[9] Al(3) lies above the plane of Al(1) and Al(2) with an Al(1)−Al(3)−Al(2) bond angle of 109.42(4)°. The average Al−Al distance is 2.872 Å. Al(3) is connected to Al(1) through two bridging hydroxyl groups [O(4)H and O(5)H], whereas Al(2) and Al(3) are bridged by an oxo [O(2)] and a hydroxyl group [O(3)H]. The bridging Al−OH bond has an average bond length of 1.864 Å.

Al(1) and Al(2) atoms, which are flanked by β-diketiminato ligands, have a distorted trigonal bipyramidal geometry. Al(2) has a terminal hydroxyl group with an Al(2)−O(1) bond length of 1.732(2) Å, and it is similar to the reported terminal aluminum hydroxide.[14−16] The two six-membered rings **A** and **B** have similar bond parameters and are highly puckered. The rings lie almost perpendicular to the plane of the β-diketiminato ligand. The carbon atom adjacent to the oxygen atom in **A** and **B** has two methyl groups. One methyl group in each ring is projected over the plane of the β-diketiminato ligand, whereas the second methyl group is projected away. Oxygen atom O(2) present in **A** has a coordination number of three, which results in the elongation of the Al(2)−O(2) bond, whereas oxygen atom O(6) in **B**

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has a coordination number of two. The Al(2)−O(2) bond [1.891(2) Å] present in the four- and six-membered ring (**A**) is longer than the Al(1)−O(6) bond length [1.751(2) Å] of ring **B**.

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Supporting Information Available: X-ray structural information and experimental data of **2**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC-249830 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax (international) +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk].

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