

C–H-Activated Aluminum Hydroxide via Molecular Oxygen

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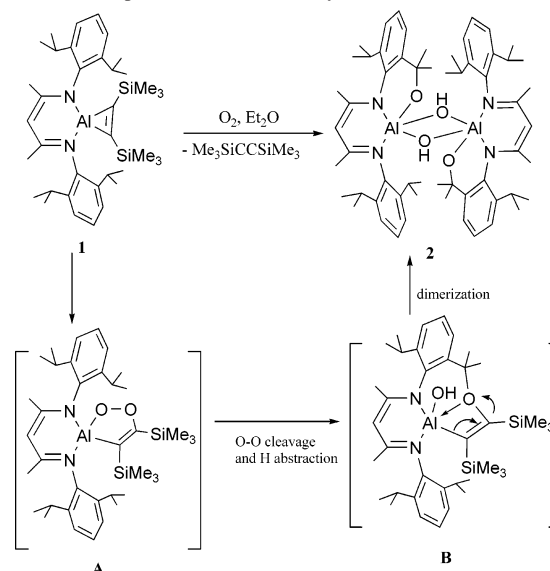
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The reaction of $\text{LAl}[\eta^2\text{-}(\text{C}_2(\text{SiMe}_3)_2)]$ (**1**; $\text{L} = \text{HC}[(\text{CMe})(\text{NDipp})]_2$, $\text{Dipp} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) with dioxygen leads to the elimination of bis(trimethylsilyl)acetylene and the formation of the corresponding aluminum monohydroxide via the oxidation of one of the CHMe_2 groups on the Dipp ring.

Dioxygen activation with well-defined organometallic complexes is very important for the understanding of its activation and transfer mechanism.¹ The interaction of dioxygen with heavier group 13 elemental alkyls has been investigated for decades.² The earlier studies showed that controlled oxidation of aluminum alkyls with molecular oxygen normally leads to the formation of aluminum alkoxides, which were presumably formed via alkyl peroxide intermediates, followed by oxygen atom transfer.² In 1996, Lewiński and co-workers reported a fully characterized aluminum alkyl peroxide and provided the first experimental evidence for the previous assumption.^{3a} Very recently, the mechanism for dioxygen activation with several types of four-coordinate aluminum alkyls has been explored.^{3b} It has been shown that these higher-coordinate aluminum alkyls can also be readily oxidized via alkyl peroxide intermediates. However, very little is known about the insertion of molecular oxygen into an aluminum–alkenyl linkage. Herein we report on the reaction of $\text{LAl}[\eta^2\text{-}(\text{C}_2(\text{SiMe}_3)_2)]$ (**1**; $\text{L} =$

Scheme 1. Proposed Reaction Pathway for the C–H Activation



$\text{HC}[(\text{CMe})(\text{NDipp})]_2$, $\text{Dipp} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$)^{4a} with molecular oxygen to yield an aluminum hydroxide and eliminate bis(trimethylsilyl)acetylene via an intramolecular C–H activation. The previous studies on the reactivity of **1** showed that it could activate a range of unsaturated small organic molecules, affording several novel types of aluminum heterocycles.⁴

When a red-black solution of **1** was exposed to dry dioxygen in diethyl ether at $-78\text{ }^\circ\text{C}$, the immediate color change of the solution to light yellow was observed. Compound **2** was isolated in modest yield after a standard workup (Scheme 1).⁵ The reaction proceeds similarly in toluene, and the activation of the methyl group of toluene was not observed, indicating that the C–H activation has a certain geometric requirement. To confirm side products, the reaction was carried out in toluene-*d*₈; both ¹H and ¹³C NMR spectra indicate the formation of **2** and free bis(trimethylsilyl)acetylene along with a small amount of impurities.

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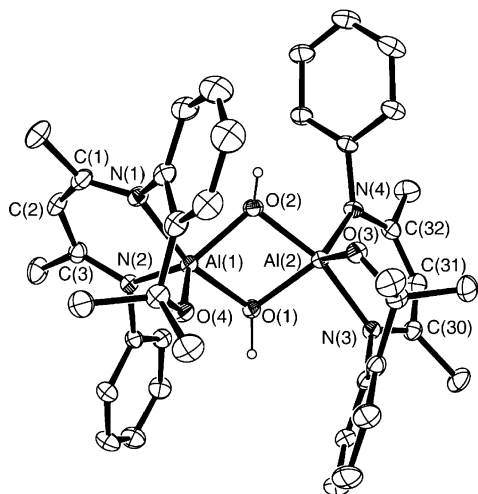


Figure 1. Thermal ellipsoid drawing of **2** (30% probability). Hydrogen atoms and CHMe₂ groups on Dipp rings except those oxidized have been omitted. Selected bond distances (Å) and angles (deg): Al(1)–O(1) 1.868(2), Al(1)–O(2) 1.860(2), Al(1)–O(4) 1.740(2), Al(2)–O(1) 1.868(2), Al(2)–O(2) 1.868(2), Al(2)–O(3) 1.741(2), O(1)–Al(1)–O(2) 75.09(10), O(1)–Al(2)–O(2) 75.04(9), Al(1)–O(1)–Al(2) 102.35(10), Al(1)–O(2)–Al(2) 102.44(10).

Compound **2** is stable both in solution and in the solid state under an inert atmosphere and is allowed to be characterized by ¹H and ¹³C NMR and IR spectroscopies, elemental analysis, and X-ray single-crystal analysis. The NMR spectra are informative; the spectral patterns are consistent with the structure of **2**. The IR spectrum displayed the broad absorption centered at 3450 cm⁻¹, attributed to the bridging OH vibration.⁶ The structure of **2** was finally confirmed by X-ray single-crystal analysis.

Single crystals of **2** were obtained from diethyl ether at 5 °C; the structure is shown in Figure 1. The complex has a dimeric structure, with the two aluminum atoms connected by the bridging hydroxyl groups.⁷ Each aluminum atom

adopts a distorted bipyrimidal geometry, with one oxygen atom of the bridging hydroxyl groups and one of the nitrogen atoms on the ligand backbone occupying the axial positions [O(1) and N(1); O(2) and N(2)]. The central Al₂O₂ ring is slightly folded (mean deviation from the plane = 0.1367 Å). The Al–O(bridging) distances (1.860–1.868 Å) are in the known range for the aluminum compounds containing bridging hydroxyl groups.^{6b} The C–O bond lengths [1.424(4) and 1.402(5) Å] are consistent with a C–O single bond, and the Al–O(alkyl) bond lengths [1.741(2) and 1.740(2) Å] indicate an Al–O(R) (R = alkyls) single bond.^{6,8}

A similar C–H oxidation has been previously observed in the reaction of LAIH₂ with *tert*-butyl hydroperoxide containing small amounts of water.⁹ However, the reaction products could not be fully characterized by spectroscopic methods because of its decomposition in solution. In addition, the existence of multiple reactants did not allow us to deduce a reasonable mechanism for the activation. Although we have not obtained the direct evidences for the reaction pathway because the reaction is too fast even at low temperatures to allow the detection of any intermediate, we reasoned that the formation of **2** may involve the initial insertion of dioxygen into one of the Al–C bonds to yield the postulated peroxide intermediate **A** in Scheme 1, which undergoes O–O bond cleavage, followed by abstraction of the α-hydrogen atom from one of the CHMe₂ groups to form **B** as an AlNCCCOCC eight-membered ring, which subsequently eliminates the alkyne to form a stable six-membered AlNCCCO ring; alternatively, because of the high oxophilicity of the aluminum cations, **A** could directly eliminate C₂(SiMe₃)₂ to form the aluminum dioxygen intermediate LAI(η²-O₂), which then undergoes O–O bond cleavage followed by C–H oxidation. For transition-metal peroxide complexes, in many cases, they are postulated to undergo either homolytic or heterolytic O–O bond cleavage to give reactive metal oxo species facilitated by oxidation of the metal centers.¹⁰ Herein the oxidation of Al³⁺ is not possible; O–O bond cleavage may take place with the oxidation of the C–H bond of a CHMe₂ group in the Dipp ring instead of the aluminum center; the selective oxidation of the α-carbon atom of the CHMe₂ group suggests the homolytic cleavage of the O–O bond. This kind of O–O bond cleavage has recently been reported for a d⁰ titanocene *tert*-butyl peroxide.^{10b} The reaction of **1** may be compared to that of LAI with dioxygen, in which a dimeric aluminum oxide

(5) A solution of **1** (0.31 g, 0.5 mmol) in diethyl ether was exposed to dry oxygen at -78 °C. The immediate color change from red black to light yellow was observed. The excess of dioxygen was removed at this temperature, and the mixture was allowed to warm to room temperature. The volatiles were removed to afford a pale-yellow solid, which was washed with *n*-hexane to give analytically pure **2** as a white solid (45%). Mp: 128 °C (dec). ¹H NMR (CDCl₃): δ -0.03 (d, 6H, CHMe₂), 0.06 (s, 6H, OCM₂), 0.85 (s, 2H, OH), 0.92 (d, 6H, CHMe₂), 0.94 (d, 6H, CHMe₂), 1.04 (s, 6H, OCM₂), 1.13 (d, 6H, CHMe₂), 1.28 (m, 12H, CHMe₂), 1.39 (s, 6H, Me), 1.70 (s, 6H, Me), 2.41 (sept, 2H, CHMe₂), 3.34 (sept, 2H, CHMe₂), 3.50 (sept, 2H, CHMe₂), 4.75 (s, 2H, γ-CH), 6.91 (m, 2H, ArH), 6.98 (m, 4H, ArH), 7.08 (m, 6H, ArH). ¹³C NMR (CDCl₃): δ 22.18, 23.25, 23.92, 25.17, 25.23, 25.59, 25.84, 26.08, 26.40, 26.77, 27.32 (β-Me, OCM₂, CHMe₂), 29.71, 30.90, 31.66 (CHMe₂), 70.81 (OCMe₂), 95.67 (γ-C), 122.06, 123.76, 124.53, 124.58, 124.97, 126.20, 141.01, 141.78, 144.44, 145.33, 145.72, 147.63 (ArC), 166.74, 167.83 (β-CN). IR: ν/cm⁻¹ 3450 (br, AlOH). Anal. Calcd for C₅₈H₈₂Al₂N₄O₄: C, 73.08; H, 8.67; N, 5.87. Found: C, 73.21; H, 8.95; N, 5.48.

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(7) Crystal data for 2·0.75Et₂O: C₆₁H_{89.50}Al₂N₄O_{4.75}, *M* = 1008.83, triclinic, space group *P*1̄, *a* = 13.1549(15) Å, *b* = 13.4828(15) Å, *c* = 17.764(2) Å, α = 77.282(2)°, β = 87.337(2)°, γ = 86.216(2)°, *V* = 3065.1(6) Å³, *Z* = 2, *D*_c = 1.093 g·cm⁻³, *F*(000) = 1095, 17 445 reflections measured (12 362 unique). *R*1 [*I* > 2σ(*I*)] = 0.0626, *wR*2 (all data) = 0.2153, GOF = 1.027 for 730 parameters and 74 restraints. The X-ray data were collected on a Siemens Smart-CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) at 294(2)

K. The structure was solved by direct methods (SHELXS-97)¹¹ and refined by full-matrix least squares on *F*². All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).¹²

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(LAIO)₂ was solely isolated presumably via the LAl(η^2 -O₂) intermediate.^{6b} In the latter case, it is very likely that the reaction involving the transfer of one of the oxygen atoms from LAl(η^2 -O₂) to another molecule of LAl to form (LAIO)₂ may be faster than that of dioxygen with LAl.

In summary, **1** is highly reactive toward dioxygen because of the strained AlC₂ framework despite the four-coordinate aluminum center. The formation of **2** may involve an aluminum peroxide intermediate, which undergoes O–O bond cleavage accompanied by the intramolecular oxidation of an α -C–H bond in one of the CHMe₂ groups and the elimination of bis(trimethylsilyl)acetylene. This reaction

demonstrates that **1** could be used as an alternative LAl source, however, with the formation of a different product. Further investigation of **1** with other chalcogens is currently underway.

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Supporting Information Available: X-ray structural data for **2** (CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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