# A Cyclopropenylaluminum Derivative from Hydrolysis and Alcoholysis of an Aluminacyclobutenone

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*Summary: Hydrolysis and alcoholysis of the cyclic aluminum acyl* $LAl[C(O)C(SiMe_3)C(SiMe_3)]$ *(**1**;* $L = HC[(CMe)(NAr)]_2$, $Ar = 2,6\text{-}iPr_2C_6H_3$*) resulted in the formation of the cyclopropenylaluminum derivative* $LAl\{[C_3(SiMe_3)_2]C(O)C(SiMe_3)C(SiMe_3)\}$ *(**2**) with the elimination of aluminum hydroxides LAlOH(OR) (R = H, Et, tBu).*

In recent years, strained rings that incorporate heavier main-group elements have been intensely investigated, owing to their unusual chemical and physical properties.[1] It has been shown that $AlC_2$ ring compounds are highly reactive and display diverse reaction patterns because of the ring strain and relatively weak Al−C bonds.[2] Despite the fact that several $AlC_2$ ring compounds have been studied, the chemistry of $AlC_3$ ring systems has received less attention. Recently, we reported on the first synthesis of the cyclic aluminum acyl complex $LAl[C(O)C(SiMe_3)C(SiMe_3)]$ (**1**) by a CO insertion reaction with $LAl[\eta^2\text{-}(Me_3SiC_2SiMe_3)]$ ($L = HC[(CMe)(NAr)]_2$, $Ar = 2,6\text{-}i\text{Pr}_2C_6H_3$).[3] This $AlC_3$ ring species contains two different Al−C bonds, and their relative reactivities are of fundamental interest. On the other hand, well-defined aluminum acyl compounds are very rare[4] and the nature of Al−C(O) bonds has been essentially unexplored. It has been reported that compound **1** is readily oxidized by molecular oxygen at low temperature, resulting in the selective insertion of one oxygen atom into the Al−C(O) bond.[3] Herein we report on the unexpected formation of the first cyclopropenylaluminum complex via hydrolysis and alcoholysis of **1**.

We recently demonstrated a high-yield route for the preparation of an aluminum hydroxide by controlled hydrolysis of $LAl[\eta^2\text{-}(Me_3SiC_2SiMe_3)]$.[5] The selective cleavage of the Al−C bond in the small-ring system prompted us to investigate the relative reactivity of the two different Al−C bonds of **1** toward $H_2O$. Thus, hydrolysis of **1** was conducted in toluene at low temperature.[6] The $^1H$ NMR spectrum of the crude product indicates almost quantitative formation of two products in a 1:1 ratio (Scheme 1). Compound **2** was obtained as orange crystals in modest yield by crystallization of the crude product from *n*-hexane, and colorless crystals of **3** could be isolated in low yield (ca. 20%) by repeated crystallization of the remaining solid from *n*-hexane. Compound **2** has been fully characterized by $^1H$ and $^{13}C$ NMR, UV−vis, and IR spectroscopy, by elemental analysis, and by X-ray single-crystal analysis.[6,7] The formation of **3** was confirmed by $^1H$ and $^{13}C$ NMR and IR spectroscopy and X-ray structural analysis. **3** was previously prepared by hydrolysis of $LAlI_2$ in a two-phase ammonia/toluene system or in the presence of an N-heterocyclic carbene and has been fully characterized.[8]

The $^1H$ NMR spectrum of **2** displays three singlets for the $SiMe_3$ groups, and the total integration is doubled compared to that of **1**, indicating the transfer of the $C_2(SiMe_3)_2$ moiety from one molecule of **1** to the other. The $^{13}C$ NMR spectrum of **2** shows the resonances for the carbonyl group at δ 212.6 ppm and for the olefinic carbons in the cyclopropene subunit at δ

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(6) To a solution of $LAl[C(O)C(SiMe_3)C(SiMe_3)]$ (0.13 g, 0.20 mmol) in *n*-hexane (10 mL) was added a solution of water (1.8 μL, 0.10 mmol) in toluene (2 mL) at −78 °C. The mixture was warmed to room temperature. All volatiles were removed under vacuum, and the remaining solid was crystallized from *n*-hexane at −20 °C to yield **2** as yellow crystals (0.05 g, 59%). Anal. Calcd for $C_{47}H_{77}AlN_2OSi_4$ (825.45): C, 68.39; H, 9.32; N, 3.39. Found: C, 68.31; H, 8.95; N, 3.37. $^1H$ NMR ($C_6D_6$): δ −0.02 (s, 18H, Si*Me*$_3$), 0.51, 0.52 (s, 2 × 9H, Si*Me*$_3$), 1.00 (d, 6H, *J* = 6.80 Hz, CH*Me*$_2$), 1.17 (d, 12H, *J* = 6.80 Hz, CH*Me*$_2$), 1.21 (d, 6H, *J* = 6.80 Hz, 6H, CH*Me*$_2$), 1.31 (s, 6H, *Me*), 2.97, 3.09 (sept, 2 × 2H, *J* = 6.80 Hz, C*H*Me$_2$), 5.07 (s, 1H, γ-C*H*), 7.01−7.09 (m, 6H, Ar *H*). $^{13}C$ NMR ($C_6D_6$): δ 0.79, 3.85, 4.64 (Si*Me*$_3$), 24.30, 24.69, 25.21, 26.00, 26.57 (CH*Me*$_2$, *Me*), 27.90, 28.69 (*C*HMe$_2$), 102.36 (γ-*C*H), 102.47 (Al−*C* in the $C_3$ ring), 123.57 (Al−C(SiMe$_3$)−*C*(SiMe$_3$)),124.98, 125.77, 134.20, 141.93, 143.63, 145.18 (Ar *C*), 171.81 (*C*═N), 183.23 (Al−C*C*$_2$(SiMe$_3$)$_2$), 196.60 (br, Al−*C*(SiMe$_3$)), 212.57 (*C*O). IR: $\nu$/cm$^{-1}$ 1715 (m, C═C), 1611 (s, CO), 1536 (s, C═C). UV−vis (hexanes): $\lambda_{max}$/nm 345 (shoulder). $LAl(OH)_2$ was obtained by repeated crystallization of the remaining solid from *n*-hexane. The spectroscopic data are the same as those reported.[8] Reactions of **1** with EtOH and *t*BuOH were conducted similarly. Compound **2** was isolated by crystallization from *n*-hexane in ca. 50% yield for both of the reactions. Hydroxyaluminum alkoxides **4** and **5** can not be isolated in pure form by repeated crystallization. The NMR spectra of **4** and **5** containing small amount of **2** indicate their formation. Selected $^1H$ NMR ($C_6D_6$) data for **5**: δ 0.53 (s, 1H, OH), 0.83 (s, 9H, *t*Bu), 1.06, 1.16, 1.35, 1.45 (d, 4 × 6H, *J* = 6.80 Hz, CH*Me*$_2$), 1.55 (s, 6H, Me), 3.36, 3.47 (sept, 2 × 2H, *J* = 7.20 Hz, C*H*Me$_2$), 4.84 (s, 1H, γ-C*H*). IR: $\nu$/cm$^{-1}$ 3744 (OH).

(7) Crystallographic data for **2**: Mo Kα ($\lambda$ = 0.710 73 Å) radiation at 113(2) K, monoclinic, space group $P1_21/n_1$, $a = 11.1041(7)$ Å, $b = 38.623(2)$ Å, $c = 12.8542(8)$ Å, $\beta = 115.449(2)°$, $Z = 4$, GOF = 1.061, R1 = 0.0481, wR2 = 0.1095 for 11 848 reflections ($I > 2\sigma(I)$); R1 = 0.0583, wR2 = 0.1157 for all data. CCDC-620154 contains the supplementary crystallographic data for this paper.

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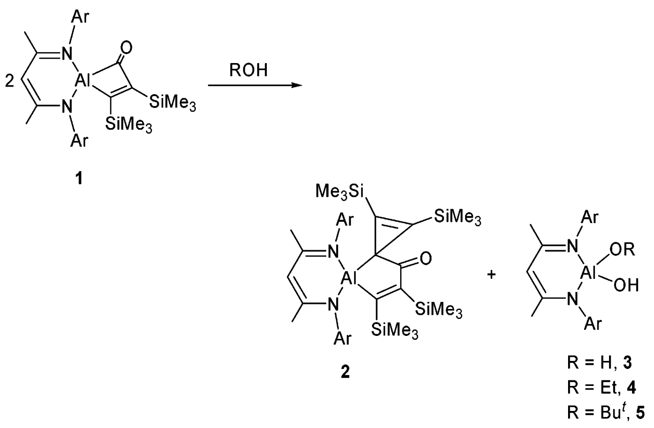
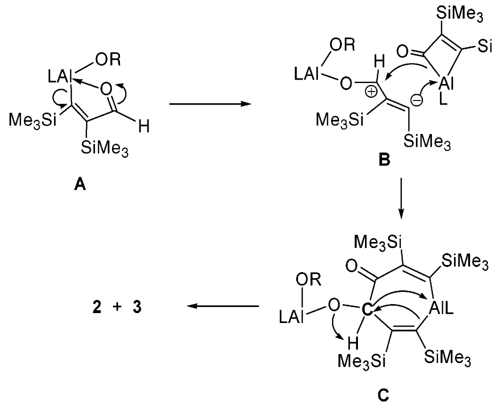
10.1021/om070028k CCC: $37.00

**Scheme 1**



Ar = 2,6-$i$Pr$_2$C$_6$H$_3$, R = H, Et, Bu$^t$

**Scheme 2. Proposed Mechanism**



183.2 ppm. The IR spectrum of **2** shows a strong band at 1611 cm$^{-1}$ due to the carbonyl group and a band at 1715 cm$^{-1}$ attributed to the C═C stretching vibration in the cyclopropene ring.[9] The molecular structure of **2** was finally confirmed by X-ray single-crystal analysis.

Single crystals of **2** suitable for X-ray analysis were obtained from $n$-hexane at −5 °C. The molecular structure of **2** is shown in Figure 1, together with selected bond parameters. The structure reveals one carbon expansion of the AlC$_3$ ring of **1** and the formation of an unusual spirocyclic species, in which a cyclopropene and an AlC$_4$ ring are fused by a carbon atom. The Al−C33 bond length (1.9615(16) Å) is consistent with an Al−C single bond,[2c] indicating that the cyclopropene unit is bonded to the aluminum atom in an $\eta^1$ fashion. The C30−C31 (1.376(2) Å) bond length in the AlC$_4$ ring is longer by 0.074 Å than that of C34−C35 (1.302(2) Å) in the C$_3$ ring because of the electron delocalization in the unsaturated carbonyl group of the five-membered ring as well as the ring strain in the cyclopropenyl subunit,[2c,10] but both lengths are in the range for a C−C double bond. The C33−C34 and C33−C35 bond lengths are identical (1.570(2) Å) and are in line with C−C single bonds. The internal angles of the C33−C34−C35 ring are 48.95(9), 65.52(11), and 65.52(11)°, indicating a cyclopropene structure.[2f] The C32−O1 bond length (1.2328(18) Å) is only slightly longer than that found in LAl[OC(O)C(SiMe$_3$)C(SiMe$_3$)] (1.218(2) Å).[3b]

The generation of LAl(OH)$_2$ suggests that the initial step may involve the hydrolytic cleavage one of the Al−C bonds. We reason that alcoholysis of **1** may lead to a similar reaction with the elimination of hydroxyaluminum alkoxides. Indeed, the reaction of **1** with ethanol and *tert*-butyl alcohol afforded **2** and the corresponding aluminum alkoxides LAl(OH)(OR) (R = Et (**4**), $t$Bu (**5**)). Pure **2** could be obtained by crystallization from $n$-hexane. Attempts to isolate the side products LAl(OH)(OR) were not successful, since they always contain small amounts of **2** after repeated crystallization. However, the NMR spectra of the mixtures indicate their formation.[6] The reaction of **1** with $t$BuOH in C$_6$D$_6$, monitored by the $^1$H NMR spectra, disclosed that only $^1/_2$ equiv of $t$BuOH was consumed instantaneously to yield **2** and **5**, irrespective of the amount of $t$BuOH employed. This finding indicates that the first step of the reaction yielded a much more reactive intermediate toward **1** than H$_2$O and alcohols. It is proposed that the initial hydrolytic or alcoholytic cleavage of the Al−C(O) bond took place to give the unstable species LAl(OR)[(SiMe$_3$)CC(SiMe$_3$)CH(O)] (**A**; Scheme 2), in which the oxygen atom of the carbonyl group may attack the aluminum center, resulting in the cleavage of the Al−C bond to yield the highly reactive intermediate **B.** The C$_3$ fragment of **B** then immediately inserted into the Al−C(O) bond of **1** to give **C**. The central carbon atom (in boldface type) in **C** may be deprotonated by the alkoxyl group of the central carbon atom to generate the carbanion, which then attacks the aluminum center to form a stable five-membered aluminum cycle followed by **C**−O bond breaking and C−C coupling to generate **2** and the aluminum hydroxide.

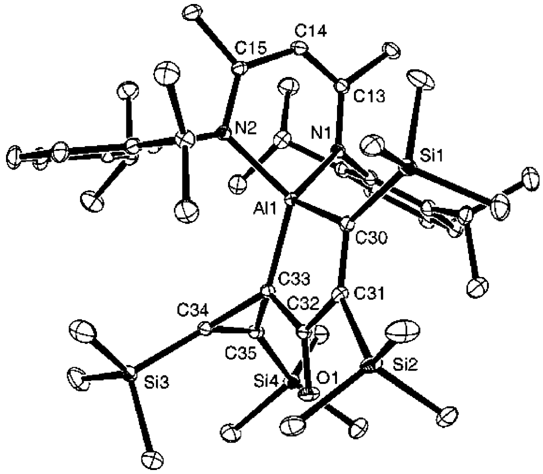


**Figure 1.** Ortep drawing of **2** (30% probability). Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg): Al1−N1 = 1.9217(14), Al1−N2 = 1.9228(13), Al1−C30 = 2.0237(16), Al1−C33 = 1.9615(16), C30−C31 = 1.376(2), C31−C32 = 1.513(2), C32−O1 = 1.2328(18), C32−C33 = 1.502(2), C33−C34 = 1.570(2), C33−C35 = 1.570(2), C34−C35 = 1.301(2); N1−Al1−N2 = 95.74(6), C30−Al1−C33 = 91.92(6), Al1−C30−C31 = 107.63(11), Al1−C33−C32 = 104.07(10), C31−C32−C33 = 118.42, C34−C33−C35 = 48.95(9), C33−C34−C35 = 65.52(11), C33−C35−C34 = 65.53(11), O1−C32−C31 = 118.42(13), O1−C32−C33 = 122.60(14).

In summary, the four-membered-ring aluminum acyl compound **1** underwent interesting hydrolysis and alcoholysis reactions to afford the first cyclopropenyl aluminum species **2**, with the elimination of aluminum hydroxides. The existence of the two different functional groups in the strained AlC$_3$ ring of **1** may be responsible for the unique reactivity and have rich chemistry to be explored. Further studies of **1** with various reagents, especially carbonyls, alkyl halides, and Lewis acids, are currently in progress.

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**Supporting Information Available:** CIF file giving X-ray data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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