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-i-Pr$_2$C$_6$H$_3$) 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[η^2-(Me$_3$SiC$_2$SiMe$_3$)] (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$).[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-[η^2-(Me$_3$SiC$_2$SiMe$_3$)].[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 ^{1}H 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 ^{1}H 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 ^{1}H 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 ^{1}H 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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(1) For reviews, see: (a) Sekiguchi, A.; Lee, V. Y. *Chem. Rev*. **2003**, *103*, 1429. (b) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Satge, J. *Coord. Chem. Rev.* **1994**, *130*, 427. (c) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828. (d) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902.

(2) (a) Zhu, H.; Oswald, R. B.; Fan, H.; Roesky, H. W.; Ma, Q.; Yang, Z.; Schmidt, H.-G.; Noltemeyer, M.; Starke, K.; Hosmane, N. S. *J. Am. Chem. Soc.* **2006**, *128*, 5100. (b) Zhu, H.; Chai, J.; Fan, H.; Roesky, H. W.; He, C.; Jancik, V.; Schmidt, H.-G.; Noltemeyer, M.; Merrill, W. A.; Power, P. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 5090. (c) Cui, C.; Köpke, S.; Herbst-Irmer, R.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Wrackmeyer, B. *J. Am. Chem. Soc*. **2001**, *123*, 9091. (d) Uhl, W.; Spies, T.; Koch, R.; Saak, W. *Organometallics* **1999**, *18*, 4598. (e) Li, X.; Song, H.; Duan, L.; Cui, C.; Roesky, H. W. *Inorg. Chem*. **2006**, *45*, 1912. (f) Zhu, H.; Chai, J.; Ma, Q.; Jancik, V.; Roesky, H. W.; Fan, H.; Herbst-Irmer, R. *J. Am. Chem. Soc*. **2004**, *126*, 10194.

(3) Li, X.; Ni, C.; Song, H.; Cui, C. *Chem. Commun*. **2006**, 1763.

(4) Mason, M. R.; Song, B.; Kirschbaum, K. *J. Am. Chem. Soc.* **2004**, *126*, 11812.

(5) Li, X.; Duan, L.; Song, H.; Ni, C.; Cui, C. *Organometallics* **2006**, *25*, 5665.

(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. ^{1}H 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: ν/cm^{-1} 1715 (m, C═C), 1611 (s, CO), 1536 (s, C═C). UV−vis (hexanes): λ_{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 ^{1}H 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: ν/cm^{-1} 3744 (OH).

(7) Crystallographic data for **2**: Mo Kα (λ = 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, β = 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.

(8) (a) Zhu, H.; Chai, J.; He, C.; Bai, G.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **2005**, *24*, 380. (b) Bai, G.; Peng, Y.; Roesky, H. W.; Li, J.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed*. **2003**, *42*, 1132.

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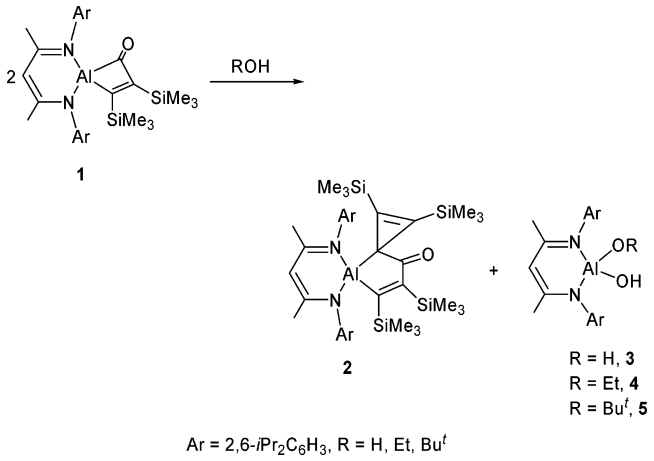
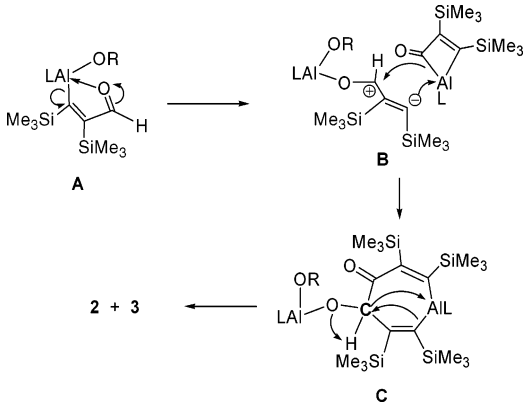
Scheme 1



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 η^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

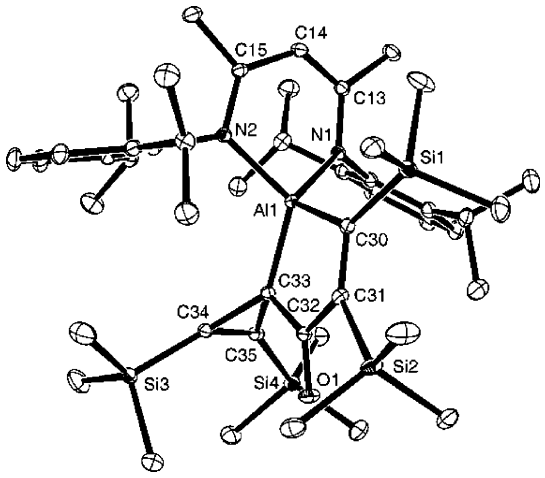


Figure 1. Ortep drawing of **2** (30% probability). Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg): Al1−N1 = 1.9217(14), Al1−N2 = 1.9228(13), Al1−C30 = 2.0237(16), Al1−C33 = 1.9615(16), C30−C31 = 1.376(2), C31−C32 = 1.513(2), C32−O1 = 1.2328(18), C32−C33 = 1.502(2), C33−C34 = 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).

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_6D_6, monitored by the ^1H 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_2O 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.

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.

(9) Wiberg, K. B.; Dempsey, R. C.; Wendoloski, J. J. *J. Phys. Chem.* **1984**, *88*, 5596.
(10) Carter, F. L.; Frampton, V. L. *Chem. Rev.* **1964**, *64*, 497.

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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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