Notes

Facile Generation of Aluminum 1,2-Dihydropyridyl and Hydroxyl Derivatives from an Aluminum Cyclopropene Analogue

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*Summary: Reaction of LAl(η^2-$Me_3SiC_2SiMe_3$) (**1**; L = HC[(CMe)(NDipp)]$_2$, Dipp = 2,6-iPr$_2$C$_6$H$_3$) with pyridine afforded the (1,2-dihydropyridyl)aluminum species LAl[$C_2(SiMe_3)_2CHN(C_4H_4)$] (**2**), having an AlC_3N five-membered ring, as a major product via insertion into one of the Al−C bonds, while hydrolysis of **1** at low temperature resulted in ring cleavage to yield the monomeric aluminum alkenyl hydroxide LAl(OH)[C(SiMe$_3$)CH(SiMe$_3$)] (**3**). The molecular structures of **2** and **3** were determined by X-ray single-crystal analysis.*

Introduction

Simple 1,2-dihydropyridines are electron-rich diene components, which can undergo Diels−Alder reactions and reactions characteristic of enamines.[1] The most convenient preparation of such species is the direct addition of alkyllithium and Grignard reagents to pyridine or N-substituted electrophilic pyridinium salts.[1] Lithium aluminum hydride (LAH) in pyridine also is known to reduce ketones selectively in the presence of ester and carboxyl groups. It has been proposed, on the basis of NMR investigations, that several isomers of lithium tetrakis(dihydropyridyl)aluminate containing 1,2- and 1,4-dihydropyridyl ligands which formed initially are active species for the reduction reactions.[2] Recently the thermodynamically stable (1,4-dihydropyridyl)aluminates and the corresponding neutral species have been isolated and structurally characterized by X-ray single-crystal analysis.[3] However, it is well-known that aluminum alkyls do not undergo insertion reactions with simple pyridine derivatives under normal conditions but form adducts such as Py·AlR$_3$.[4] Recent studies of the reactivity of the AlC$_2$ strained-ring compound LAl[η^2-($Me_3SiC_2SiMe_3$)] (**1**; L = HC[(CMe)(NDipp)]$_2$, Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$)[5a] have shown that it displayed diverse reactivity toward a number of functional groups, such as ketones, nitriles, isonitriles, organic azides, and small molecules such as O$_2$, CO, and CO$_2$.[5] These reactions either afforded insertion products or involved an initial insertion followed by subsequent transformations. The high reactivity of **1** combined with its tendency to form stable five-membered aluminum heterocycles by insertion into C═X (X = O, N) bonds suggested that **1** could be a promising candidate to generate 1,2-dihydropridyl subunits, provided that **1** could insert into the C═N bond of aromatic pyridines. Herein we report the facile generation of dihydropyridylaluminum heterocycles by the reaction of **1** with pyridine, along with the hydrolytic reaction of **1** to yield an aluminum alkenyl hydroxide.

Results and Discussion

Reaction of **1** with 1 equiv of pyridine from −78 °C to room temperature followed by removal of volatiles under vacuum afforded an orange solid. The ^{1}H NMR spectrum of the crude product showed that it contains two species, the ratio of which was estimated to be ca. 10:1 according to the integration of the SiMe$_3$ resonances (Scheme 1). Orange crystals of **2** were obtained by crystallization from diethyl ether. They were characterized by ^{1}H and ^{13}C NMR and IR spectroscopy and by X-ray single-crystal analysis. The ^{1}H and ^{13}C NMR spectra of **2** exhibit characteristic resonances for a 1,2-dihydropyridyl unit. The IR spectrum displays relatively strong absorption bands centered at 1637 and 1602 cm^{-1}, which were assigned to the stretching frequencies of the diene group. The molecular array has been further verified by an X-ray single-crystal structural analysis. Unfortunately, we were unable to isolate the minor product in pure form, because its solubility was quite similar to that of the major product. It is postulated that the minor product could be the 1,4-addition product, since the proton NMR spectrum of the crude product mixture also showed weak separated resonances at δ 4.31, 5.09, 5.75, and 6.52 ppm in the dihydropyridine unit region[1a] and two singlets at δ 0.29 and 0.48 ppm for the two SiMe$_3$ groups, while the other resonances for the compound overlapped with those of the major product. The high selectivity to undergo a pyridine 1,2-insertion reaction is attributed to the AlC$_2$ three-membered-ring structure of **1**, as this type of insertion leads to the formation of the more stable AlC$_3$N five-membered ring in compound **2**. Proton NMR studies on **2** in C$_6$D$_6$ indicated that it did not decompose or isomerize over 4 h at 75 °C. This behavior is in contrast to the

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(1) For reviews, see: (a) Eisner, U.; Kuthan, J. *Chem. Rev.* **1972**, *72*, 1. (b) Stout, D. M.; Meyers, A. I. *Chem. Rev.* **1982**, *82*, 223. (c) Kuthan, J.; Kurfürst, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 191. (d)

(2) (a) Lansbury, P. T.; Rogozinski, J. R.; Coblentz, F. L. *J. Org. Chem.* **1961**, *26*, 2277. (b) Lansbury, P. T.; Peterson, J. O. *J. Am. Chem. Soc.* **1963**, *85*, 2236. (c) Tanner, D. D.; Yang, C.-M. *J. Org. Chem.* **1993**, *58*, 1840.

(3) Hensen, K.; Lemke, A,; Stumpf, T.; Bolte, M.; Fleischer, H.; Pulham, C. R.; Gould, R. O.; Harris, S. *Inorg. Chem.* **1999**, *38*, 4700.

(4) Lichtenberger, D. L.; Hogan, R. H.; Healy, M. D.; Barron, A. R. *Organometallics* **1991**, *10*, 609.

(5) (a) Cui, C.; Köpke, S.; Herbst-Irmer, R.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Wrackmeyer, B. *J. Am. Chem. Soc.* **2001**, *123*, 9091. (b) Zhu, H.; Chai, J.; Ma, Q.; Jancilk, V.; Roesky, H. W.; Fan, H.; Herbst-Irmer, R. *J. Am. Chem. Soc.* **2004**, *126*, 10194. (c) Li, X.; Song, H.; Duan, L.; Cui, C.; Roesky, H. W. *Inorg. Chem.* **2006**, *45*, 1912. (d) Li, X.; Ni, C.; Song, H.; Cui, C. *Chem. Commun.* **2006**, 1763.

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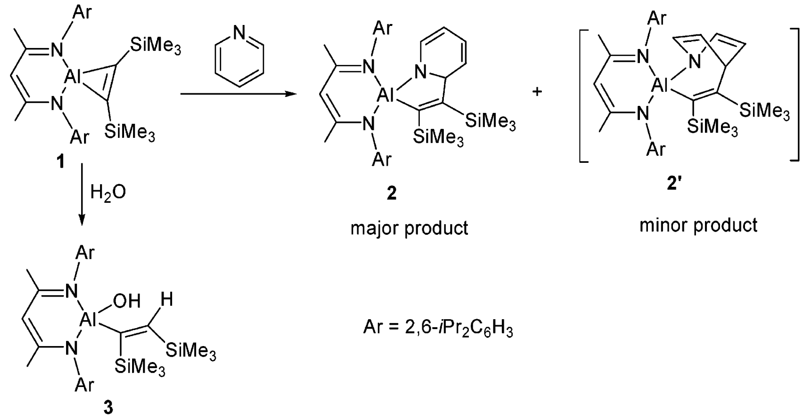
Scheme 1. Synthesis of 2 and 3



hydroalumination of pyridine, in which dynamic isomerization from 1,2- to 1,4-pyridinyl has been reported to occur.[4]

Single crystals of **2** suitable for an X-ray diffraction analysis were obtained from diethyl ether at −20 °C. The structure of **2** is shown in Figure 1, together with selected bond parameters. The structure reveals the presence of the AlC_3N five-membered ring, formed via pyridine addition to one of the Al−C bonds. The C30−C31 (1.348(9) Å), C31−C32 (1.429(10) Å), and C32−C33 (1.313(9) Å) bond lengths indicate the C30−C31−C32−C33 diene moiety. The N3−C30 (1.376(7) Å) bond length is shorter than that of N3−C34 (1.470(8) Å) because of the partial overlap of the lone-pair electron on the nitrogen atom with the diene π electrons. The dihydropyridyl ring is not planar, and the internal angles range from 109.5(5) to 123.9(6)°. These structural features correlate well with those of 1,2-dihydropyridine derivatives.[6] C34−C35 (1.527(8) Å) and C35−C36 (1.365(8) Å) are typical of C−C single and double bonds, respectively.

Reaction of **1** with water in diethyl ether proceeded instantly at −78 °C to give pale yellow crystals of **3** in high yield after crystallization from diethyl ether (Scheme 1). In contrast, controlled hydrolysis of $LAlR_2$ and $LAlH_2$ leads to ligand cleavage. Several ligand L supported aluminum hydroxides are known, but they are generated from the corresponding aluminum halides in the presence of NHC carbenes or in ammonia and from hydrolysis of the aluminum amide and oxide.[7] None were prepared by the direct hydrolytic cleavage of an Al−C bond. The selective cleavage of the Al−C bond in **1** may result from ring strain reactivity. The ^{1}H NMR spectrum of **3** displays a broad singlet at δ 0.42 ppm, attributed to the resonance of the hydroxyl proton. The IR spectrum shows the characteristic OH absorption centered at 3731 cm^{-1}. The structure was finally confirmed by an X-ray single-crystal analysis, which is shown in Figure 2. The Al1−O1 (1.7036(15) Å) bond length is very close to those found in $LAl(OH)_2$ (1.7107(16) and 1.6947(15) Å).[7a] The Al−C bond length (1.9845(19) Å) is in the reported range for a Al−C single bond.[5a] The C30−C31 bond length (1.353(3) Å) is consistent with a C−C double bond.[5a]

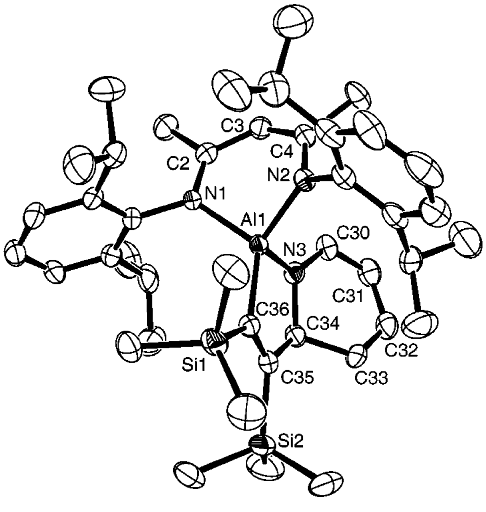


Figure 1. Ortep drawing of **2** (30% probability). One of the two independent molecules in the unit cell and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1−N1 = 1.916(5), Al1−N2 = 1.913(5), Al1−N3 = 1.838(4), Al1−C36 = 1.974(6), N3−C30 = 1.376(7), N3−C34 = 1.470(8), C30−C31 = 1.348(9), C31−C32 = 1.429(10), C32−C33 = 1.313(9), C33−C34 = 1.536(8), C34−C35 = 1.527(8), C35−C36 = 1.365(8); N1−Al1−N2 = 96.5(2), N3−Al1−C36 = 92.0(2), Al1−N3−C30 = 132.1(4), Al1−N3−C34 = 110.7(3), N3−C30−C31 = 123.9(6), N3−C34−C33 = 109.5(5), C30−N3−C34 = 115.7(5), C30−C31−C32 = 116.8(6), C31−C32−C33 = 121.9(6), C32−C33−C34 = 118.4(6).

Compound **3** is thermally stable and could be stored under an inert atmosphere for a long time. The OH group does not seem to dissociate in the presence of pyridine or to interact with a strong Lewis acid, $B(C_6F_5)_3$, according to ^{1}H NMR studies.

In summary, reaction of **1** with pyridine resulted in the insertion of pyridine into one of the Al−C bonds with high

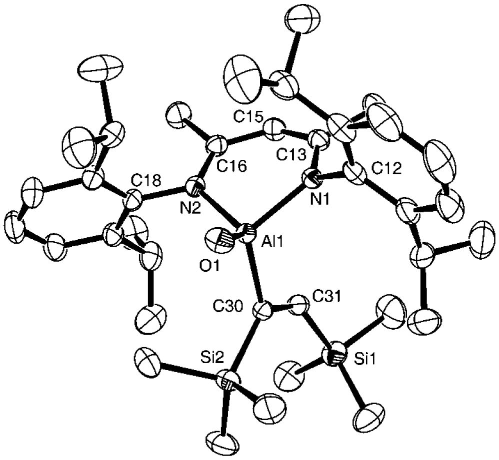


Figure 2. Ortep drawing of **3** (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1−N1 = 1.9075(16), Al1−N2 = 1.9249(17), Al1−O1 = 1.7036(15), Al1−C30 = 1.9845(19), C30−C31 = 1.353(3); N1−Al1−N2 = 96.27(7), N1−Al1−O1 = 108.17(7), N1−Al1−C30 = 114.48(8), N2−Al1−O1 = 113.03(7), N2−Al1−C30 = 110.51(8), O1−Al1−C30 = 113.25(8).

region selectivity. The formed (1,2-dihydropyridyl)aluminum compound is thermally stable, and its isomerization to the 1,4-dihydropyridyl subunit was not observed. Hydrolysis of **1** resulted in selective cleavage of one of the Al−C bonds and yielded an aluminum alkenyl hydroxide. These results indicate that the ring strain results not only in the high reactivity of **1** but also in the high selectivity in the two reactions. Because of the dihydropyridyl unit in **2** and OH group in **3**, both compounds could be used for further transformations.

Experimental Section

All experiments were carried out under an argon atmosphere using Schlenk line and glovebox techniques. The solvents were dried over activated molecular sieves and then refluxed over sodium and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMD-400 NMR spectrometer. IR spectra were recorded on a Bio-Rad FTS 6000 spectrometer. Compound **1** was prepared according to literature methods.[5a]

LAl[$C_2(SiMe_3)_2CHN(C_4H_4)$] (2). To a solution of **1** (1.28 g, 2.0 mmol) in *n*-hexane at −78 °C was added neat pyridine (0.16 g, 2 mmol). The mixture was warmed slowly. A gradual color change from black-red to orange was observed over 30 min. The mixture was stirred for an additional 2 h at room temperature. The solution was concentrated (to ca. 10 mL) and stored at −20 °C for 1 week to give orange crystals of **2** (0.59 g, 41%). Mp: 137−139 °C. ^{1}H NMR (C_6D_6): δ −0.24, 0.38 (s, 9H + 9H, SiMe$_3$), 1.02 (d, 3H, J = 6.40 Hz, CH*Me*$_2$), 1.11 (d, 3H, J = 6.80 Hz, CH*Me*$_2$), 1.12 (d, 6H, J = 6.80 Hz, CH*Me*$_2$), 1.19 (d, 6H, J = 6.00 Hz, CH*Me*$_2$), 1.29 (d, 3H, J = 6.40 Hz, CH*Me*$_2$), 1.31 (d, 3H, J = 6.80 Hz, CH*Me*$_2$), 1.44 (s, 3H, CMe), 1.57 (s, 3H, CMe), 3.04, 3.20, 3.37, 3.83 (sept, 1H + 1H + 1H + 1H, J = 6.80 Hz, C*H*Me$_2$), 4.87 (s br, 1H, NC*H*), 4.99 (s, 1H, γ-CH), 5.19 (d, 1H, C*H*), 5.45 (t, 1H, C*H*), 6.24 (t, 1H, C*H*), 6.95−7.11 (m, 7H, Ar *H* + C*H*). ^{13}C NMR (C_6D_6): δ 2.01, 2.44 (Si*Me*$_3$), 23.54, 24.54, 24.76, 24.88, 25.12, 25.34, 25.63, 26.03 (*Me* and CH*Me*$_2$), 28.05, 28.54, 28.64, 28.94 (*C*HMe$_2$), 68.40 (N*C*HCSi), 100.48, 100.63 (*C*H and γ-*C*H), 100.82 (*C*H), 124.38, 124.53, 125.00, 125.24, 127.21, 127.54, 140.36, 141.30, 142.03, 142.45, 143.90, 145.25, 145.60 (Ar *C* and *C*H), 170.87, 172.09 (N*C*Me), 179.72 (N*C*CH). UV−vis (hexanes): λ_{max}/nm (ϵ/mol^{-1} L cm^{-1}) 351.4 (20 700). IR: ν/cm^{-1} 3404, 3058, 2960, 2926, 2868, 1638, 1601, 1548, 1463, 1440, 1382, 1315, 1258, 1094, 1018, 935, 875, 835, 801, 758, 633, 486, 453. Anal. Calcd for $C_{42}H_{64}AlN_3Si_2$ (693.45): C, 72.67; H, 9.29; N, 6.05. Found: C, 72.60; H, 9.60; N, 5.45.

LAl(OH)[C(SiMe$_3$)CH(SiMe$_3$)] (3). To a solution of **1** (0.31 g, 0.5 mmol) in diethyl ether (20 mL) at −78 °C was added a solution of water in diethyl ether (1 mL, 0.5 M, 0.5 mmol). The black-red solution immediately turned to pale yellow. The mixture was warmed to room temperature and stirred for 30 min. The resulting yellow solution was concentrated (to ca. 5 mL) under vacuum and stored at −30 °C overnight to give colorless crystals of **3** (0.25 g, 79%). Mp: 172 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −0.37 (s, 9H, Si*Me*$_3$), −0.20 (s, 9H, Si*Me*$_3$), 0.42 (s, 1H, O*H*), 1.04 (d, 6H, J = 6.40 Hz, CH*Me*$_2$), 1.08 (m, 12H, CH*Me*$_2$), 1.19 (d, 6H, J = 6.80 Hz, CH*Me*$_2$), 1.78 (s, 6H, β-C*Me*), 3.04 (sept, 2H, J = 6.80 Hz, C*H*Me$_2$), 3.38 (sept, 2H, J = 6.80 Hz, C*H*Me$_2$), 5.24 (s, 1H, γ-C*H*), 7.0−7.24 (m, 6H, Ar *H*), 7.27 (s br, 1H, C*H*SiMe$_3$). ^{13}C NMR (CDCl$_3$): δ 1.22, 2.10 (SiMe$_3$), 24.14 (β-*Me*), 24.87, 25.05 (CH*Me*$_2$), 28.23 (*C*HMe$_2$), 98.66 (γ-*C*), 109.8 (C=*C*HSiMe$_3$), 124.3, 124.6, 126.9, 141.4, 143.6, 144.6 (Ar *C*), 152.0 (Al−*C*), 169.6, 170.5 (N*C*). IR (cm^{-1}): 3731 (OH), 3057, 2964, 2869, 2760, 2610, 2475, 2360, 1932, 1867, 1803, 1702, 1662, 1585, 1548, 1524, 1463, 1439, 1392, 1317, 1252, 1174, 1055, 1018, 937, 860, 833, 800, 761, 735, 685, 668, 596, 534. Anal. Calcd for $C_{37}H_{61}AlN_2OSi_2$ (633.05): C, 70.20; H, 9.71; N, 4.43. Found: C, 70.05; H, 10.19; N, 4.32.

X-ray Structural Determination. Data were collected at 294(2) K on a Bruker Smart-Apex II diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. All structures were solved by direct methods (SHELXS-97)[8] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined by a riding model (SHELXL-97).[9] Crystallographic data for **2**: $C_{42}H_{64}AlN_3Si_2$, M_r = 694.12, orange plate, 0.30 × 0.26 × 20 mm, monoclinic, space group *Pn*, a = 12.67554(17) Å, b = 21.369(3) Å, c = 16.374(2) Å, β = 99.367(2)°, V = 4369.2(10) Å,^{3} Z = 4, D_c = 1.055 g cm^{-3}, F(000) = 1512, 24 627 reflections measured (12 113 unique). R1 = 0.0642 ($I > 2\sigma(I)$), wR2 = 0.1929 (all data), GOF = 1.007 for 896 parameters and 26 restraints. Crystallographic data for **3**: $C_{37}H_{62}AlN_2OSi_2$, M_r = 634.05, colorless plate, 0.52 × 0.46 × 0.26 mm, monoclinic, space group $P2_1/n$, a = 11.326(4) Å, b = 19.690(7) Å, c = 18.246(6) Å, β = 102.217(4)°, V = 3977(2) Å,^{3} Z = 4, D_c = 1.059 g cm^{-3}, F(000) = 1388, 16 271 reflections measured (11 213 unique). R1 = 0.0454 ($I > 2\sigma(I)$), wR2 = 0.1355 (all data), GOF = 1.031 for 404 parameters and 3 restraints.

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Supporting Information Available: CIF files for the structures of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) (a) Krow, G. R.; Raghavachari, R.; Siatkowski, R.; Chodosh, D. F. *J. Org. Chem.* **1986**, *51*, 1916. (b) Brunner, B.; Stogaitis, N.; Lauteus, M. *Org. Lett.* **2006**, *8*, 3473.

(7) (a) Bai, G.; Peng, Y.; Roesky, H. W.; Li, J.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1132. (b) Zhu, H.; Chai, J.; He, C.; Bai, G.; Roesky, H. W.; Jancik, V.; Schmidt, H.−G.; Noltemeyer, M. *Organometallics* **2005**, *24*, 380. (c) Zhu, H.; Chai, J.; Jancik, V.; Roesky, H. W.; Merrill, W. A.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 10170. (d) Bai, G.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2005**, *127*, 3449.

(8) Sheldrick, G. M. *SHELXS-90/96*, Program for Structure Solution. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(9) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen, Göttingen, Germany, 1997.