Synthesis and Characterization of Derivatives of a Chelating Aluminum Dichloride Complex Containing a 3,5-Di-*tert*-butylpyrazolato Unit

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Dedicated to Professor Richard L. Wells

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The chelating aluminum complex [{3,5-N-*t*Bu_2pz-N′–CH=C($SiMe_3$)}AlR_1R_2] [$R^1 = R^2$ = Me (**2**); $R^1 = R^2$ = H (**3**); $R^1 = R^2$ = I (**4**)] was prepared in modest yield from an organoaluminum dichloride precursor [{3,5-N-*t*Bu_2pz-N′–CH=C($SiMe_3$)}$AlCl_2$] (**1**). Compounds **2** and **3** were obtained from the reaction of **1** with MeLi in Et_2O or with $LiAlH_4$ in THF, respectively. Reaction of **2** or **3** with I_2 in toluene gave **4**. In addition, the reaction of **1** with two equivalents of water yielded the hydrolyzed product H[3,5-N-*t*Bu_2pz-N′–CH=C($SiMe_3$)] (**5**). All compounds were characterized by elemental analysis, NMR spectroscopy, and mass spectrometry. The X-ray structure analysis shows that complex **2** exhibits one fused five-membered AlC_2N_2 ring and one pyrazolato ring system.

Introduction

Organoaluminum compounds have been explored widely owing to their importance in a variety of applications.[1] The chemistry of sterically hindered neutral derivatives of organoaluminum halides, hydrides and alkyls is especially important as they are key starting materials for a variety of compounds with unusual bonding and oxidation states, as well as unique structures.[2] Recent progress in aluminum chemistry has shown that aluminum halides with a bulky ligand may be used as precursors for synthesizing low-valent Al^I species.[3] Additionally, the reaction of aluminum alkyls with extremely strong Lewis acids such as $B(C_6F_5)_3$ leads to the formation of low-coordinate cationic compounds that are potential catalysts for olefin polymerization.[4] Furthermore, organoaluminum hydrides have been shown to be ideal starting materials for preparing various unusual compounds that were difficult to synthesize by other routes.[5,6] Obviously, the sterically demanding ligands play a crucial role during the formation of these compounds. In the course of the reaction of aluminum pyrazolato compounds and trimethylsilylacetylene, an unusual compound [{3,5-N-*t*Bu_2pz-N′−CH=C($SiMe_3$)}$AlCl_2$] (**1**) was formed. It has been shown that the Al−Cl bonds in **1** are readily cleaved and can be substituted by other functional groups.[7] Apparently, the chelating [3,5-N-*t*Bu_2pz-N′−CH=C($SiMe_3$)]$^-$ ligand in compound **1** is more sterically demanding than the simple 3,5-di-*tert*-butylpyrazole. Due to the interest in precursors of sterically demanding aluminum halides, alkyls and hydrides, reactions using **1** as a starting material have been examined.

Results and Discussion

A solution of **1** and two equivalents of MeLi in Et_2O was stirred at −78 °C for 3 h and then at ambient temperature for 15 h to give [{3,5-N-*t*Bu_2pz-N′−CH=C($SiMe_3$)}$AlMe_2$] (**2**) in fair yield (ca. 70%; Scheme 1).[8] Compound **2** is extremely soluble in *n*-hexane and it can be purified in two steps. First, the resulting residue was sublimed at 0.01 mbar and 100 °C and then recrystallized from *n*-hexane at −26 °C to afford colorless crystals. The mass spectrum (EI) shows **2** to be monomeric {m/z (%) = 334 (10) [M^+], 319 (100) [$M^+ - Me$]}. The ^1H NMR spectrum shows a set of resonances for the chelating moiety {δ = 0.37 [Si(C*H*$_3$)$_3$], 1.00 [C(3)−C(C*H*$_3$)$_3$], 1.28 [C(1)−C(C*H*$_3$)$_3$], 5.86 [C(2)*H*], 7.63 [=C(4)*H*]} and one signal for the protons of the Al−Me groups at $\delta = -0.15$, clearly indicating the formation of **2**. However, the ^{27}Al NMR resonance is too broad to be distinguished.

The crystallographic data of **2** are listed in Table 1. It crystallizes in the monoclinic crystal system, space group *C*2/*c* (Figure 1). The similar cell parameters of [{3,5-N-*t*Bu_2pz-N′−CH=C($SiMe_3$)}$AlMe_2$] (**2**) and [{3,5-N-*t*Bu_2pz-N′−CH=C($SiMe_3$)}$AlCl_2$] (**1**) indicate a structural relationship between these two compounds.[7] As in

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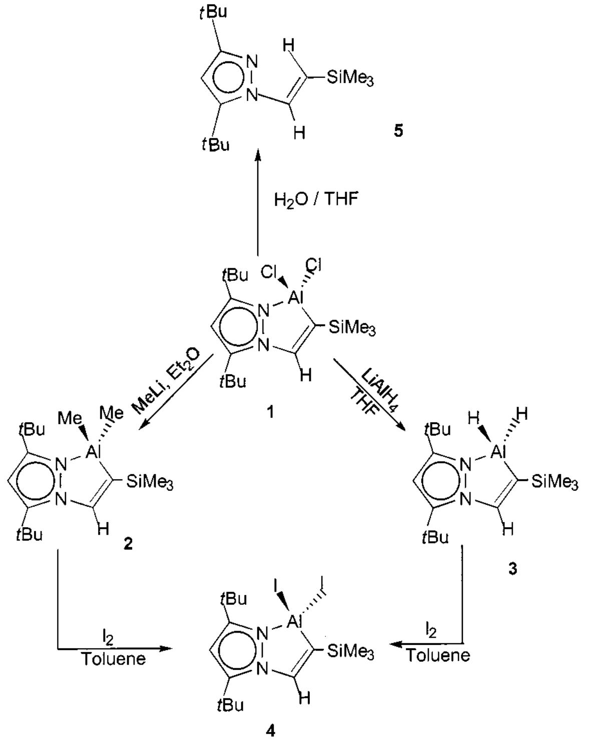

Scheme 1. Synthesis of compounds **2−5**

compound **1**, the geometry at the aluminum atom is a distorted tetrahedron [N1−Al1−C5 = 84.90(9)° and C21−Al1−C22 = 115.24(11)°] due to the strain imposed by the chelate ring. The fused five-membered AlC_2N_2 ring and the pyrazolato moiety are approximately coplanar. The C=C bond length of the inserted trimethylsilylacetylene molecule is significantly increased [C4−C5 = 1.328(3) Å] but is slightly shorter than the C=C double bonds of the σ complex of $AlCl_3$ with tetramethylcyclobutadiene [1.387(3) Å][9] and 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene [1.367(3) Å].[10] The terminal Al(1)−C bond lengths [1.971(2) Å] are similar to those in $[(\eta^1,\eta^1\text{-3,5-}t\mathrm{Bu_2pz})(\mu\text{-}\mathrm{AlMe_2})]_2$ [Al−C = 1.962(2) Å].[11]

Treatment of **1** with 2.1 equivalents of $LiAlH_4$ in THF at −30 °C yielded $[\{3,5\text{-N-}t\mathrm{Bu_2pz\text{-}N'{-}CH{=}C(SiMe_3)}\}\text{-}\mathrm{AlH_2}]\cdot(\mathrm{THF})_2$ [**3**·$(THF)_2$] as a white solid (Scheme 1) that is only slightly soluble in common organic solvents, except THF. Compound **3**·$(THF)_2$ is sensitive to oxygen and water. The mass spectrum (EI) suggests that **3**·$(THF)_2$ is a monomer {m/z (%) = 306 (100) [M^+]}, probably because of the sterically demanding chelating ligand $[3,5\text{-N-}t\mathrm{Bu_2pz\text{-}N'{-}CH{=}C(SiMe_3)}]^-$. The THF molecules of **3**·$(THF)_2$ can be removed by heating at 50 °C under high vacuum for 15 hours to give **3** {δ = 0.14, 1.410, 1.415, 3.80 (br.), 6.21 and 7.60 in [D_8]THF}. The ^1H NMR spectrum ([D_8]THF) reveals a set of resonances for the chelating moiety and a broad Al−H signal (δ = 3.80, $W_{1/2}$ = 85 Hz). The ^{27}Al NMR spectrum shows one signal at δ = 106.4, implying a coordination number of four at the Al atom. The two resonances of the protons of the nonequivalent *t*Bu groups are close to each other (δ = 1.410 and 1.415). The IR spectrum exhibits two strong bands in the expected range for Al−H stretching bands (1780 and 1812 cm^{-1}) implying terminal Al−H bonds in the solid state.[12] However, whether the THF molecules in **3**·$(THF)_2$ coordinate directly to the aluminum center or are incorporated in the crystal lattice is currently unknown.

Table 1. Crystallographic data for **2**

	2
Empirical formula	$C_{18}H_{35}AlN_2Si$
Molecular weight	334.55
Temperature (K)	200(2)
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	*C*2/*c*
Unit cell dimensions	a = 29.890(24) Å b = 9.478(10) Å c = 18.256(20) Å α = 90° β = 122.44(3)° γ = 90°
Volume	4364.7(75) $Å^3$
Z	8
Density (calculated)	1.018 Mg/m^3
Absorption coefficient	0.148 mm^{-1}
F(000)	1472
Crystal size	1.0 × 1.0 × 0.2 mm^3
θ range for data collection	3.77 to 25.02 °
Index ranges	$-35 \leq h \leq 35$ $-11 \leq k \leq 11$ $-21 \leq l \leq 21$
Reflections collected	7698
Independent reflections	3849 [*R*(int) = 0.0251]
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	3845/0/210
Goodness-of-fit on F^2	1.032
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0457, wR_2 = 0.1241
R indices (all data)	R_1 = 0.0515, wR_2 = 0.1327
Largest different peak and hole [e·$Å^{-3}$]	0.532 and −0.376

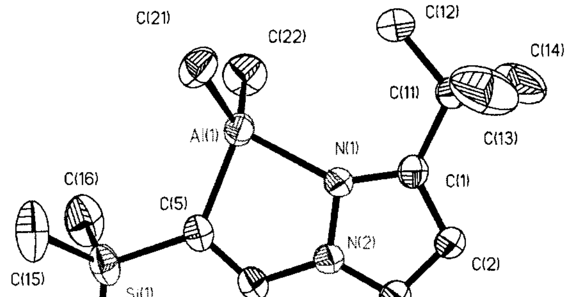

Figure 1. Perspective view of compound **2**, showing the numbering scheme and the thermal ellipsoids at the 50% probability level: Al(1)−C(5) 1.993(3), Al(1)−C(21) 1.971(2), Al(1)−C(22) 1.971(3), Al(1)−N(1) 2.016(3), C(4)−C(5) 1.328(3) Å; C(5)−Al(1)−N(1) 84.90(9)°, C(21)−Al(1)−C(22) 115.24(11)°

The reaction of **2** with two equivalents of I_2 in toluene afforded the compound [{3,5-N-*t*Bu$_2$pz-N′−CH=C(SiMe$_3$)}AlI$_2$] (**4**) after refluxing for 24 h (Scheme 1).[13] Compound **4** is readily soluble in toluene but only slightly soluble in *n*-hexane and can be readily purified by crystallization from toluene at −26 °C to give small pale crystals. The mass spectrum is in good agreement with the formulation of **4** as a monomer {*m*/*z* (%) = 558 (4) [M$^+$], 553 (15) [M$^+$ − Me], 431 (100) [M$^+$ − I]}. The ^{1}H NMR spectrum shows one set of resonances for the chelating moiety [3,5-N-*t*Bu$_2$pz-N′−CH=C(SiMe$_3$)]$^-$ (δ = 0.42, 082, 1.43, 5.81 and 7.36 in C_6D_6), indicating the formation of **4**. Alternatively, **4** can also be prepared by the reaction of **3** and two equivalents of I_2 under mild conditions (room temp.). The reaction of **3** with I_2 gives higher yields than that with **2**.[14] It is essential that the THF molecules in the precursor **3**·(THF)$_2$ are removed prior to the reaction of **3** with I_2 as otherwise the product is difficult to separate from the oily residue.

The reaction of [{3,5-N-*t*Bu$_2$pz-N′−CH=C(SiMe$_3$)}-AlCl$_2$] (**1**) with two equivalents of water in THF led to the formation of the free ligand [3,5-N-*t*Bu$_2$pz-N′−CH=CH(SiMe$_3$)] (**5**) (Scheme 1), which could be purified by sublimation at 90 °C under high vacuum (0.01 mbar). Compound **5** is soluble in both aliphatic and aromatic solvents at ambient temperature. The mass spectrum (EI) {*m*/*z* (%) = 278 (20) [M$^+$], 263 (100) [M$^+$ − Me]} and elemental analysis are in accordance with a monomeric formula for **5**. The ^{1}H NMR spectrum in C_6D_6 shows two doublets at δ = 6.77 and 7.48 (^2J = 16.3 Hz) for the two hydrogen atoms of the inserted TMS(H$_a$)C=(H$_b$) group. No proton resonance was observed in the range δ = 10−12 [the resonance of an N$_{(pyrazole)}$−H proton is usually found between δ = 10 and12 in C_6D_6],[15] confirming that the added H$_a$ atom is found in a terminal position at the TMS(H$_a$)C= group. Unfortunately, no lithium salt of **5** could be isolated from our attempts to deprotonate **5** with *t*BuLi at −78 °C or at ambient temperature. The reason why compound **5** is resistant to deprotonation is as yet unclear.

Conclusion

In summary, this paper reports the preparation of three aluminum complexes **2−4**, with an unusual chelating ligand containing a bulky 3,5-di-*tert*-butylpyrazolato unit, and the formation of ligand **5**, all from the readily accessible aluminum dichloride complex **1**. We have also shown that the Al−Cl bonds of **1** can be easily substituted partly[7] or completely by various basic substituents under different conditions, while the metallaheterocycle in these compounds seems to be rather stable. We are interested in a variety of aluminum complexes that have unique binding modes due to their potential applications as catalysts.[2] Compounds **1−4** are therefore ideal starting materials for further studies.

Experimental Section

General: All reactions were performed using standard Schlenk and dry box techniques. Solvents were appropriately dried and distilled under dinitrogen prior to use. All NMR spectra were obtained in 5-mm tubes with dry degassed [D$_6$]benzene as solvent (except for **3**, which was measured in [D$_8$]THF), referenced to external SiMe$_4$. Elemental analyses were performed by the Analytisch-Chemisches Laboratorium des Instituts für Anorganische Chemie, Göttingen.

Compound **1** was prepared according to the published method.[7]

Synthesis of [{3,5-N-*t*Bu$_2$pz-N′−CH=C(SiMe$_3$)}AlMe$_2$] (2): MeLi (4 mL, 4 mmol) in Et$_2$O (20 mL) was added slowly at −78 °C to a suspension of **1** (0.74 g, 2.0 mmol) in Et$_2$O (40 mL). The solution was allowed to warm to room temperature and then stirred for 15 h. The solvent was removed and the resulting residue sublimed at 100 °C under high vacuum (0.01 mbar) to give a white powder mainly consisting of **2**. Pure **2** was obtained by recrystallization from *n*-hexane at −26 °C (ca. 0.46 g, 70%). Crystals suitable for X-ray diffraction analysis were obtained from *n*-hexane at 4 °C. M.p. 157 °C. ^{1}H NMR (200.130 MHz, C_6D_6): δ = −0.15 (s, 6 H, Al−C*H*$_3$), 0.37 [s, 9 H, Si(C*H*$_3$)$_3$], 1.00 [s, 9 H, C(3)−C(C*H*$_3$)$_3$], 1.28 [s, 9 H, C(1)−C(C*H*$_3$)$_3$], 5.86 [s, 1 H, C(2)*H*], 7.63 [s, 1 H, =C(4)*H*]. ^{13}C NMR (125.758 MHz, C_6D_6): δ = −7.1 [br, Al-*C*(5)=], −0.9 (Al−CH$_3$), −0.01 [Si−*C*(16)], 29.7 [*C*(12,13,14)], 30.6 [*C*(11)], 31.4 [*C*(32,33,34)], 32.6 [*C*(31)], 103.2 [*C*(4)], 132.7 [*C*(2)], 150.7 [*C*(1)], 161.9 [*C*(3)]. MS (EI): *m*/*z* (%) = 334 (10) [M$^+$], 319 (100) [M$^+$ − Me]. $C_{18}H_{35}AlN_2Si$ (334.55): calcd. C 64.62, H 10.54, N 8.37; found C 64.3, H 10.1, N 8.2.

Synthesis of [{3,5-N-*t*Bu$_2$pz-N′−CH=C(SiMe$_3$)}AlH$_2$] (3): A solution of **1** (0.74 g, 2.0 mmol) in THF (20 mL) was added slowly at −30 °C to a suspension of LiAlH$_4$ (0.16 g, 4.2 mmol) in THF (30 mL). The suspension was stirred for an additional 15 h at room temperature and then filtered through celite. The solution was concentrated to ca. 8 mL and **3**·(THF)$_2$ crystallized as a white crystalline solid at −26 °C. After the removal of THF molecules of **3**·(THF)$_2$ at 50 °C under high vacuum for 15 h, **3** was obtained as a white powder (0.35 g, 57%). M.p.: 134 °C. ^{1}H NMR (200.130 MHz, [D$_8$]THF): δ = 0.14 [s, 9 H, Si−(C*H*$_3$)$_3$], 1.410 [s, 9 H, C(3)−C(C*H*$_3$)$_3$], 1.415 [s, 9 H, C(1)−C(C*H*$_3$)$_3$], 3.80 (br, s, 2 H, Al−*H*), 6.21 [s, 1 H, C(2)*H*], 7.60 [s, 1 H, =C(4)*H*]. ^{13}C NMR (125.758 MHz, [D$_8$]THF): δ = −0.01 [Si−*C*(16)], 29.9 [*C*(12,13,14)], 30.2 [*C*(11)], 32.4 [*C*(32,33,34)], 32.8 [*C*(31)], 104.2 [*C*(4)], 135.1 [*C*(2)], 143.6 (br, Al−*C*=), 152.0 [*C*(1)], 162.3 [*C*(3)]. ^{27}Al NMR (65.170 MHz, [D$_8$]THF): δ = 106.4. ^{29}Si NMR (99.362 MHz, [D$_8$]THF): δ = −6.2. MS (EI): *m*/*z* (%) = 306 (100) [M$^+$], 291 (70) [M$^+$ − Me]. IR (KBr, nujol mull): ν_{Al-H} = 1780 (ms), 1812 (ms) cm^{-1}. $C_{16}H_{31}AlN_2Si$ (306.50): calcd. C 62.70, H 10.19, N 9.14; found C 61.8, H 9.9, N 9.0

Synthesis of [{3,5-N-*t*Bu$_2$pz-N′−CH=C(SiMe$_3$)}AlI$_2$] (4). Method 1: A solution of I_2 (1.00 g, 4.0 mmol) in toluene (40 mL) was added slowly at room temperature to a solution of **2** (0.66 g, 2.0 mmol) in toluene (20 mL). The solution was stirred for 15 h at room temperature and then refluxed for 12 h. The solution was filtered through celite and then concentrated to ca. 10 mL to give small colorless crystals at −26 °C (0.82 g, 73%).
Method 2: A solution of I_2 (1.00 g, 4.0 mmol) in toluene (40 mL) was added slowly to a suspension of **3** (0.61 g, 2.0 mmol) in toluene (20 mL) and then stirred for 12 h at room temperature until the brown color disappeared. The solution was filtered through celite and the filtrate was concentrated to about 10 mL. Compound **4** crystallized as a pale solid at −26 °C (0.49 g, 43%). M.p.: 192 °C.

^{1}H NMR (200.130 MHz, C_6D_6): δ = 0.42 [s, 9 H, Si(CH_3)$_3$], 0.82 [s, 9 H, C(3)−C(CH_3)$_3$], 1.43 [s, 9 H, C(1)−C(CH_3)$_3$], 5.81 [s, 1 H, C(2)*H*], 7.36 [s, 1 H, =C(4)*H*]. ^{13}C NMR (125.758 MHz, C_6D_6): δ = 0.09 [Si−*C*(16)], 29.4 [*C*(12,13,14)], 31.39 [C(11)], 31.44 [*C*(32,33,34)], 33.3 [C(31)], 105.0 [*C*(4)], ca. 128 (br, Al−C=, overlapped by C_6D_6 signals), 134.7 [*C*(2)], 153.5 [*C*(1)], 165.3 [*C*(3)]. ^{29}Si NMR (99.362 MHz, C_6D_6): δ = −6.4. MS (EI): *m*/*z* (%) = 558 (4) [M$^+$], 543 (15) [M$^+$ − Me] , 431 (100) [M$^+$ − I]. $C_{16}H_{29}AlI_2N_2Si$ (558.29): calcd. C 34.42, H 5.24, N 5.02; found C 33.8, H 5.1, N 5.2.

Synthesis of [{3,5-N-*t*Bu$_2$pz-N′−CH=C(SiMe$_3$)}H] (5): 0.036 mL of a solution of water (2.0 mmol) in THF (10 mL) was added slowly to a solution of compound **1** (0.75 g, 2.0 mmol) in THF (30 mL) at room temperature. After stirring for 15 h at room temperature, the solvent was removed in vacuo. The resulting residue was sublimed at 90 °C under high vacuum (0.01 mbar) to afford the colorless solid **5** (0.39 g, 70%). M.p.: 173 °C. ^{1}H NMR (200.130 MHz, C_6D_6): δ = 0.12 [s, 9 H, Si(CH_3)$_3$], 1.17 [s, 9 H, C(3)−C(CH_3)$_3$], 1.44 [s, 9 H, C(1)−C(CH_3)$_3$], 6.01 [s, 1 H, C(2)*H*], 6.77 [d, $^2J_{H,H}$ = 16.3 Hz, 1 H, C(5)*H*], 7.48 [d, $^2J_{H,H}$ = 16.3 Hz, 1 H, =C(4)*H*]. ^{13}C NMR (125.758 MHz, C_6D_6): δ = −1.3 [Si−*C*(16)], 30.0 [*C*(12,13,14)], 30.3 [*C*(11)], 30.9 [*C*(32,33,34)], 33.1 [*C*(31)], 101.2 [*C*(4)], 111.2 [*C*(5)], 135.7 [*C*(2)], 150.8 [*C*(1)], 161.4 [*C*(3)]. MS (EI): *m*/*z* (%) = 278 (20) [M$^+$], 263 (100) [M$^+$ − Me]. $C_{16}H_{30}N_2Si$ (278.51): calcd. C 69.00, H 10.86, N 10.06; found C 70.4, H 11.0, N 10.3.

X-ray Crystallography: Crystals of **2** (*M* = 334.55) were grown from a concentrated *n*-hexane solution cooled to 4 °C. **2** crystallized in the monoclinic crystal system with space group *C*2/*c*. Relevant details and data are summarized in Table 1. The crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether.[16] Diffraction data were collected on a Stoe−Siemens four-circle diffractometer coupled to a Siemens CCD area detector at 200(2) K, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS-96[17] and refined against F^2 on all data by full-matrix least-squares with SHELXS-97.[18] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the model at their geometrically calculated positions and refined using a riding model. CCDC-170473 (**2**) 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, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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