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An Unusual Monomeric Alkenyl-Substituted Pyrazolato Aluminum Dichloride and Its Derivatives with Both Terminal and η^2-Pyrazolato Ligands[†]

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The facile formation of the unusual monomeric alkenyl-substituted pyrazolato aluminum dichloride [(3,5-^{t}Bu$_2$-*N*-CH=C(SiMe$_3$)-pz)AlCl$_2$] (**2**; 3,5-^{t}Bu$_2$pz = 3,5-di-*tert*-butylpyrazolato) was achieved in high yield by reacting dimeric pyrazolato aluminum dichloride [η^1-η^1-3,5-^{t}Bu$_2$pz(μ-Al)Cl$_2$]$_2$ (**1**) with 2 equiv of trimethylsilylethine. The addition of 1 and 2 equiv of K[3,5-^{t}Bu$_2$pz] to **2**, respectively, resulted in the formation of two novel complexes, [(3,5-^{t}Bu$_2$-*N*-CH=C(SiMe$_3$)-pz)AlCl(3,5-^{t}Bu$_2$pz)] (**3**) and [(3,5-^{t}Bu$_2$-*N*-CH=C(SiMe$_3$)-pz)Al(η^1-3,5-^{t}Bu$_2$-pz)(η^2-3,5-^{t}Bu$_2$pz)] (**4**), for which crystallographic data are presented. The coordination of the pyrazolato ligand in **3** represents an extreme example of a "slipped" η^2-coordination.

Introduction

Pyrazolato ligands have been widely employed in coordination chemistry,[1] and they are enjoying a renaissance due to the discovery of η^2- and η^5-coordination modes with transition, main group, and lanthanoide metals.[2] Recently, the syntheses of several new aluminum compounds with pyrazolato ligands have been reported.[3] Only two examples of η^1- and η^2-coordination with aluminum have been observed: the homoleptic [(η^2-3,5-^{t}Bu$_2$pz)$_3$Al][2b] and the terminally coordinated alumoxanehydride.[3d] Other Al−pyrazolato compounds show exclusively bridged η^1-η^1-coordination.[3a−c] In the course of our investigations on the reactivity of the pyrazolato aluminum dihydride [(3,5-^{t}Bu$_2$pz(μ-Al)H$_2$]$_2$[3d] toward ethine reagents, a formal insertion of trimethysilylethine into an aluminum nitrogen bond was observed, resulting in a bulky alkenyl-substituted pyrazolato ligand, [(3,5-^{t}Bu$_2$pz-*N*-CH=C(SiMe$_3$))Al(C≡CSiMe$_3$)$_2$].[3a] This reaction may be viewed as a [2 + 3]-cycloaddition with the aluminum pyrazolato species functioning as the dipolar component. This type of reaction may be of general significance in the preparation of heterocyclic compounds, and it has attracted interest in aluminum-catalyzed enantioselective versions.[4] In our group we are interested in whether such cycloadditions occur in a general way and if these complexes may be used for broader applications. In this paper, we report the preparation of [(3,5-^{t}Bu$_2$pz-*N*-CH=C(SiMe$_3$))-AlCl$_2$] (**2**) from [η^1-η^1-3,5-^{t}Bu$_2$pz(μ-Al)Cl$_2$]$_2$ (**1**)[3c] and HC≡CSiMe$_3$ and its reactivity toward K[3,5-^{t}Bu$_2$pz], forming η^1- and η^2-coordinated aluminum pyrazolato species.

Experimental Section

General Procedures. All manipulations were performed on a high-vacuum line or in a glovebox under a purified N$_2$ atmosphere. Solvents were distilled from Na/benzophenone ketyl prior to use. Chemicals were purchased from Aldrich and used as received. 3,5-Di-*tert*-butylpyrazole[5] and 3,5-di-*tert*-butylpyrazolato potassium[6] were prepared as described in the literature. HC≡CSiMe$_3$ was dried over molecular sieves prior to use. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Bruker AM 200 and Bruker AM 250 spectrometers were used to record ^{1}H (200 MHz), ^{13}C (100.6 MHz), and ^{27}Al NMR (104.245 MHz) spectra. The chemical shifts were externally referenced to SiMe$_4$ (^{1}H, ^{13}C) and AlCl$_3$ (^{27}Al), respectively. EI (700 eV) mass spectra were measured on Finnigan MAT 8230 or Varian MAT CH5 instruments. Melting points were measured in sealed glass tubes and were not corrected.

Preparation of [(3,5-^{t}Bu$_2$-*N*-CH=C(SiMe$_3$)-pz)AlCl$_2$] (2). To the solution of **1** (5.54 g, 10.0 mmol)[3c] in toluene (50 mL)

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[†] Dedicated to Professor Walter Kaminsky on the occasion of his 60th birthday.

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was added slowly $HC\equiv CSiMe_3$ (3.2 mL, 22.5 mmol) with a syringe at room temperature. The solution was refluxed for 2 h and then the solvent removed. The resulting residue was washed with cold *n*-pentane (−20 °C, 2 × 5.0 mL) to give **2** as a pure white powder (7.18 g, 96%). Mp: 196 °C. ^{1}H NMR (C_6D_6): δ 0.35 (s, 9 H, $SiMe_3$), 0.84 (s, 9 H, C(3)-^{t}Bu), 1.35 (s, 9 H, C(1)-^{t}Bu), 5.78 (s, 1 H, C(2)H), 7.48 (s, 1 H, =C(4)H). ^{13}C NMR (125 MHz, C_6D_6): δ −0.43 (s, Si-*C*), 29.52 (s, *C*12), 31.44 (s, *C*31), 30.61 (s, *C*32), 33.08 (s, *C*11), 104.76 (s, *C*4), 135.78 (s, *C*2), 138.06 (br, Al-*C*(5)=), 153.05 (s, *C*1), 164.53 (s, *C*3). ^{29}Si NMR (99 MHz, C_6D_6): δ −6.40 (s). MS (EI) *m*/*z* (%): 374 (M^+, 15), 359 (($M^+ - 15$), 100). Anal. Calcd for $C_{16}H_{29}AlCl_2N_2Si$ (M_r = 375.38): C, 51.20; H, 7.73; N, 7.47. Found: C, 50.65; H, 7.58; N 7.32. Single crystals suitable for X-ray diffraction analysis were obtained from *n*-hexane at 4 °C.

Synthesis of [(3,5-^{t}Bu$_2$-*N*-CH=C(SiMe$_3$)-pz)AlCl(3,5-^{t}Bu$_2$pz)] (3). After the suspension of **2** (0.75 g, 2.0 mmol) and K[3,5-^{t}Bu$_2$pz] (0.44 g, 2.0 mmol)[6] in toluene (40 mL) was stirred for 15 h, the solvent was removed. The resulting residue was extracted with *n*-hexane (3 × 10 mL). The solvent was reduced to 10 mL, and **3** crystallized at room temperature (0.96 g, 93%). Mp: 189−190 °C. ^{1}H NMR (C_6D_6): δ 0.25 (s, 9 H, $SiMe_3$), 0.84 (s, 9 H, C(3)-^{t}Bu), 1.04 (s, 9 H, C(1)-^{t}Bu), 1.39 (s, 18 H, C(6,8)-^{t}Bu); 5.85 (s, 1 H, C(2)H), 6.10 (s, 1 H, C(7)H), 7.62 (s, 1 H, C(4)H). ^{13}C NMR (C_6D_6): δ −0.48 (s, Si-*C*), 29.68 (s, *C*(12)), 30.08 (s, *C*(62,82)), 31.07 (s, *C*(32,33,34)), 31.42 (s, *C*(31)), 32.23 (s, *C*(61,81)), 32.70 (s, *C*(11)), 100.65 (s, *C*(7)), 103.49 (s, *C*(4)), 134.06 (s, *C*2), 140.51 (br, Al-*C*=), 151.43 (s, *C*(1)), 161.50 (s, *C*(6)), 162.19 (s, *C*(3)). ^{29}Si NMR (C_6D_6): δ −6.30 (s). MS (EI) *m*/*z* (%): 518 (M^+, 100), 503 (($M^+ - 15$), 35). Anal. Calcd for $C_{27}H_{48}AlClN_4Si$ (M_r = 519.21): C, 62.55; H, 9.27; N, 10.81. Found: C, 62.00; H, 9.41; N, 10.60. Single crystals suitable for X-ray diffraction analysis were obtained from *n*-hexane at room temperature.

Synthesis of [(3,5-^{t}Bu$_2$-*N*-CH=C(SiMe$_3$)-pz)Al(η^1-3,5-^{t}Bu$_2$pz)(η^2-3,5-^{t}Bu$_2$pz)] (4). In a procedure similar to the synthesis of **3**, **2** (0.75 g, 2.0 mmol) and 2 equiv of K[3,5-^{t}Bu$_2$-pz] (0.88 g, 4.0 mmol) were reacted in toluene (40 mL), and then **4** was cystallized from ca. 15 mL of *n*-hexane to give colorless crystals at 4 °C (1.10 g, 83%). Mp: 187 °C. ^{1}H NMR (C_6D_6): δ 0.15 (s, 9 H, $SiMe_3$), 1.10 (s, 9 H, C(3)-^{t}Bu), 1.12 (s, 9 H, C(1)-^{t}Bu), 1.37 (s, 36 H, C(6,8,9,11)-^{t}Bu); 5.88 (s, 1 H, C(2)H), 6.17 (s, 2 H, C(7,10)H), 7.74 (s, 1 H, =C(4)H). ^{13}C NMR (C_6D_6): δ 0.06 (s, Si-*C*), 29.73 (s, *C*(12)), 30.31 (s, *C*(62, 82, 92, 112)), 31.32 (s, *C*(32)), 31.33 (s, *C*(31)), 32.26 (s, *C*(61, 81, 91, 111)), 32.64 (s, C(1)*C*), 100.31 (s, *C*(7, 10)), 103.57 (s, *C*(4)), 135.40 (s, *C*(2)), 142.00 (br, Al-*C*=), 150.21 (s, *C*(1)), 161.18 (s, *C*(6, 8, 9, 11)), 161.92 (s, *C*(3)). ^{29}Si NMR (C_6D_6, 99 MHz): δ -4.94 (s). MS (EI) *m*/*z* (%): 662 (M^+, 35), 483 (($M^+ -$ ^{t}Bu$_2$pz), 100). Anal. Calcd for $C_{38}H_{67}AlN_6Si$ (M_r = 663.05): C, 68.89; H, 10.77; N, 12.59. Found: C, 68.50; H, 10.17; N, 12.05. Single crystals suitable for X-ray diffraction analysis are obtained from *n*-hexane at room temperature.

Results and Discussion

Treatment of **1** with 2.2 equiv of $HC\equiv CSiMe_3$ in refluxing toluene for 2 h gave smoothly the product **2** in virtually quantitative yield (>90%) (Scheme 1).[7] Drying commercially available $HC\equiv CSiMe_3$ over molecular sieves for at least 2 days prior to use is crucial, otherwise hydrolysis of the product occurs. For the synthesis of large amounts of **2** (over 20 mmol) it is advisable to monitor the reaction by ^{1}H NMR spectroscopy. If **1** is not consumed completely, the reaction should be continued under the addition of more $HC\equiv CSiMe_3$ since the separation of the product from the starting material is difficult.

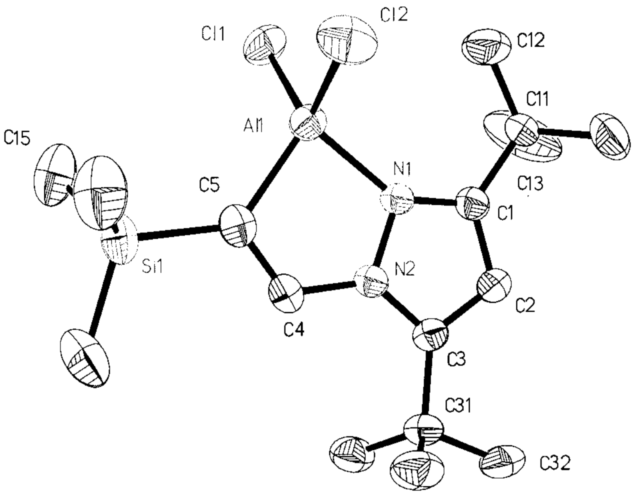
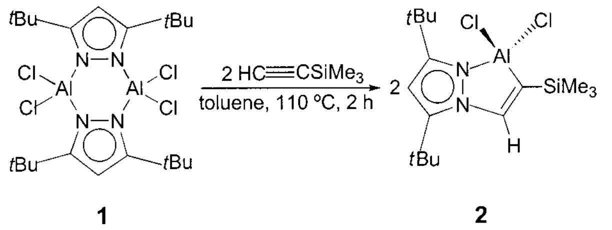


Figure 1. Perspective view and atom-labeling scheme of compound **2**, showing the numbering scheme and the thermal ellipsoids at the 50% probability level.

Scheme 1. Synthesis of Complex 2



The ^{1}H NMR spectrum of **2** shows two resonances for the ^{t}Bu groups (0.84 and 1.35 ppm, C_6D_6), evidencing the asymmetric environment of the 3,5-^{t}Bu$_2$pz ring. The proton resonances of the inserted $HC\equiv CSiMe_3$ molecule (7.48 ppm for H−C≡ and 0.35 ppm for $SiMe_3$) experience a significant downfield shift in comparison to the free ethine (2.06 and 0.094 ppm). The resonance of the ^{27}Al NMR spectrum seems too broad to be observed.

The X-ray crystal structural analysis[8] reveals a mononuclear aluminum complex with a metal atom coordinated by the [3,5-^{t}Bu$_2$-*N*-CH=C(SiMe$_3$)-pz] chelating group and two Cl atoms (Figure 1). The crystallographic data and selected bond lengths and angles of **2** are listed in Tables 1 and 2. The geometry of the aluminum atom is distorted tetrahedral (N1−Al1−C5 88.03(9)° and Cl1−Al1−Cl2 109.87(4)°) due to the constraint imposed by the chelate ring. The two fused five-membered AlN_2C_2 and pyrazolato rings are approximately coplanar. The C≡C bond length of the inserted trimethylsilylethine molecule is significantly increased (C4−C5, 1.323(4) Å) but is slightly shorter than those of the C=C double bonds of the σ-complex of $AlCl_3$ with tetramethylcyclobutadiene (**5**) (1.387(3) Å)[9] and the 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene (**6**) (1.367(3) Å),[10] respectively. The Al(1)−C(5) bond length (1.954(2) Å) is slightly shorter

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[7] We also found that compound **2** is formed in low yield (about 30%) when [(3,5-^{t}Bu$_2$pz-*N*-CHC(SiMe$_3$))Al(C≡CSiMe$_3$)$_2$]^{3a} was treated with CuCl in a mixture of THF and toluene at 50 °C.

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Table 1. Summary of Crystallographic Data for Complexes 2, 3, and 4

	2	3	4
formula	$C_{16}H_{29}AlCl_2N_2Si$	$C_{27}H_{48}AlClN_4Si$	$C_{38}H_{67}AlN_6Si$
fw	375.38	519.21	663.05
temp (K)	200(2)	203(2)	200(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*P*2$_1$/*n*	*P*2$_1$/*c*
unit cell dimensions			
a (Å)	29.678(7)	10.2032(12)	19.888(5)
b (Å)	9.381(3)	21.065(6)	11.5236(18)
c (Å)	18.093(5)	15.849(3)	18.789(3)
α (*deg*)	90	90	90
β (deg)	121.564(8)	105.961(12)	98.828 (19)
γ (deg)	90	90	90
V (Å^{-3})	4292(2)	3275.2(11)	4255.1(14)
Z	8	4	4
d(cacld) (Mg/m^3)	1.162	1.053	1.035
abs coeff (mm^{-1})	0.398	0.200	0.107
F(000)	1600	1128	1456
cryst size (mm)	1.00 × 0.90 × 0.60	0.70 × 0.50 × 0.30	0.90 × 0.40 × 0.30
θ range (deg)	3.75 to 25.06	3.57 to 25.03	3.52 to 25.03
limiting indices	$-35 \leq h \leq 35$	$-12 \leq h \leq 12$	$-5 \leq h \leq 23$
	$-11 \leq k \leq 11$	$-6 \leq k \leq 25$	$-13 \leq k \leq 2$
	$-21 \leq l \leq 21$	$-18 \leq l \leq 18$	$-22 \leq l \leq 22$
no. of reflns collected	8080	7790	7510
no. of indep reflns	3785	5764	7496
	($R_{int} = 0.0807$)	($R_{int} = 0.0643$)	($R_{int} = 0.1458$)
no. of data/restraints/params	3785/0/208	5764/0/322	7496/0/437
GOF/F^2	1.033	1.035	1.050
R indices	$R_1 = 0.0524$	$R_1 = 0.0593$	$R_1 = 0.0642$
[$I > 2\sigma(I)$]	$wR_2 = 0.1359$	$wR_2 = 0.1458$	$wR_2 = 0.1440$
R indices	$R_1 = 0.0574$	$R_1 = 0.0728$	$R_1 = 0.0989$
(all data)	$wR_2 = 0.1427$	$wR_2 = 0.1573$	$wR_2 = 0.1708$
largest diff peak/hole (e Å^{-3})	0.403/−0.542	0.772/−0.324	0.480/−0.358

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Compound 2

Al(1)−C(5)	1.954(2)	Cl(1)−Al(1)−Cl(2)	109.87(4)
Al(1)−N(1)	1.960(2)	C(5)−Al(1)−N(1)	88.03(9)
Al(1)−Cl(1)	2.1347(10)	Al(1)−N(1)−N(2)	107.60(13)
C(4)−C(5)	1.323(3)	Al(1)−C(5)−C(4)	107.72(16)
C(4)−N(2)	1.439(3)	C(5)−C(4)−N(2)	120.5(2)
N(1)−N(2)	1.385(2)	C(4)−C(5)−Si(1)	121.09(18)
C(5)−Si(1)	1.861(2)	Si(1)−C(5)−Al(1)	131.18(13)
C(1)−C(2)	1.3940(3)	C(5)−Al(1)−Cl(1)	116.07(7)

than those in **5** (Al−C 1.979(5) Å)[9] and **6** (Al−C 1.990 (av) Å).[10]

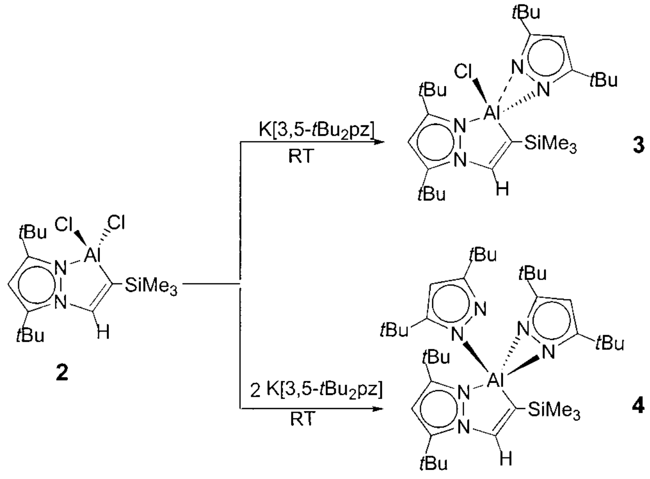
From the formation of **2**, it may be assumed that compound **1** dissociates prior to the reaction with ethine. It seems more likely that in the dissociated species the three-coordinate aluminum is the more reactive site.

The synthesis of η^2-coordinated aluminum species was one of our primary goals. The high yield and the convenient solubility features of **2** (highly soluble in most common organic solvents) triggered the use as an excellent starting material. Therefore, the reactions of **2** with 1 and 2 equiv of K[3,5-^{t}Bu$_2$pz] were investigated (Scheme 2).

The conversion of **2** with 1 equiv of K[3,5-^{t}Bu$_2$pz] in toluene afforded [(3,5-^{t}Bu$_2$-*N*-CH═C(SiMe$_3$)-pz)AlCl(3,5-^{t}Bu$_2$pz)] (**3**) (Scheme 2). The elimination of KCl occurred smoothly, and **3** was readily purified by crystallization from *n*-hexane.

At room temperature the ^{1}H NMR spectrum shows only one resonance for the ^{t}Bu groups (1.40 ppm, C_6D_6) of the ^{t}Bu$_2$pz ligand, implying a dynamic process in solution. The resonances for the alkenyl-substituted pyrazolato ligand appeared at 1.03 and 1.21 ppm for the ^{t}Bu groups and at 0.25 ppm for the SiMe$_3$ group. To investigate the behavior in solution, variable-temperature ^{1}H NMR spectra in toluene-d_8 were carried out.

Scheme 2. Syntheses of Compounds 3 and 4



At 273 K the spectrum shows three resonances in the ratio 1:1:2 for ^{t}Bu groups, indicating a fast rotation of the ^{t}Bu$_2$pz ligand (Figure 2). At 203 K the (C/D) resonances coalesce, and below that temperature the exchange is slow, evidenced by two new shoulders (1.73 and 1.37 ppm). However, it is difficult to decide which resonance (C or D) in Figure 2 corresponds to which of the ^{t}Bu groups of the ^{t}Bu$_2$pz ligand.

X-ray diffraction analysis[8] of **3** reveals a monomeric molecule coordinated by one chelating [3,5-^{t}Bu$_2$-*N*-CH═C(SiMe$_3$)-pz] moiety, one ^{t}Bu$_2$pz ligand, and one Cl atom (Figure 3). The crystallographic data and selected bond lengths and angles of **3** are listed in Tables 1 and 3. The distance to N(4) (1.838(2) Å) is within the expected range of aluminum nitrogen bonds, whereas the one to N(3) (2.312(3) Å) is too long for an η^2-coordination in comparison to [(η^2-3,5-^{t}Bu$_2$pz)$_3$Al] (Al−N bond distances

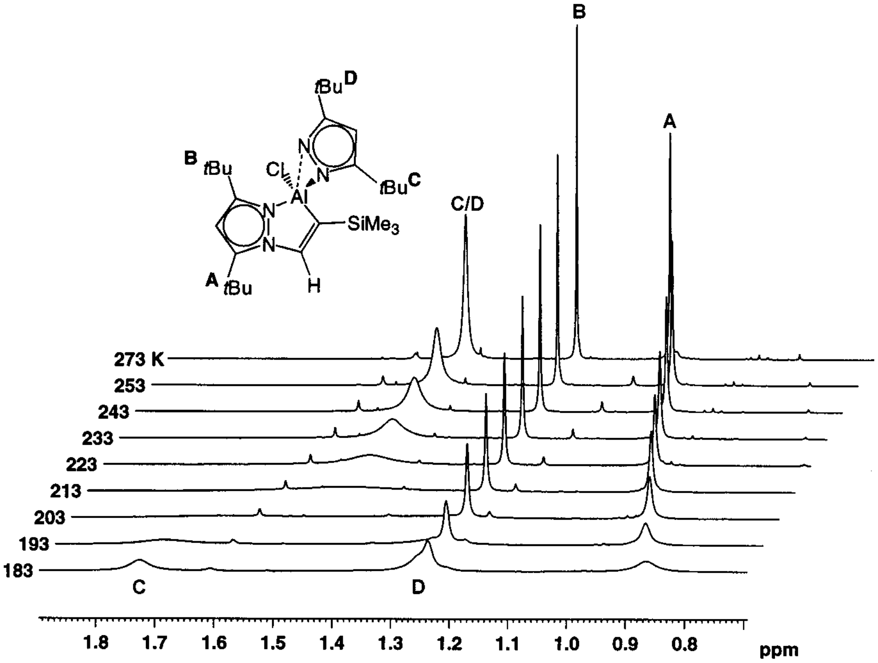


Figure 2. Variable-temperature ^{1}H NMR spectra of compound **3**.

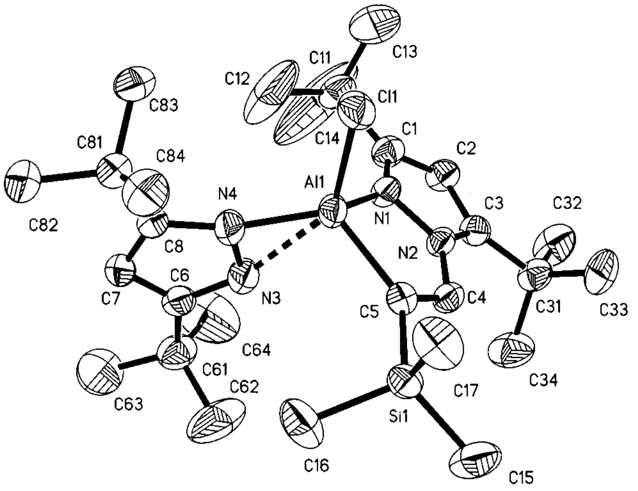


Figure 3. Perspective view and atom-labeling scheme of compound **3**, showing the numbering scheme and the thermal ellipsoids at the 50% probability level.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Compound 3

Al(1)−N(4)	1.838(2)	N(4)−Al(1)−C(5)	119.52(11)
Al(1)−N(1)	1.956(2)	N(1)−Al(1)−C(5)	87.99(10)
Al(1)−C(5)	1.961(3)	N(4)−Al(1)−Cl(1)	110.11(9)
Al(1)−Cl(1)	2.1531(11)	N(1)−Al(1)−Cl(1)	105.87(8)
Al(1)−N(3)	2.312(3)	C(5)−Al(1)−Cl(1)	113.27(9)
N(1)−N(2)	1.376(3)	N(4)−Al(1)−N(3)	36.75(10)
C(4)−C(5)	1.320(4)	C(8)−N(4)−Al(1)	159.4(2)
N(4)−Al(1)−N(1)	117.91(11)	C(6)−N(3)−Al(1)	159.6(2)

1.903(2) and 1.911(2) Å),[2b] but significantly shorter than that to N(2) (Al(1)−N(2) 2.708(2) Å).[11] Nevertheless, N(3) is definitely tilted toward the metal. This is an interesting feature for aluminum compounds with pyrazolato ligands, which generally form stable complexes with aluminum in a μ-η^1-η^1 fashion.[3] Besides the mentioned [(η^2-3,5-^{t}Bu$_2$pz)$_3$Al] complex,[2b] only one other coordination mode has been observed (a terminal η^1-pyrazolato alumoxane hydride[3d]). Moreover, the aluminum atom resides slightly out of the pyrazolato plane (Al(1)−N(4)−C(8) 159.4(2)°, Al(1)−N(3)−C(6) 159.6(2)°). This twisted structure most likely stems from crowding effects of the chelating moiety.

Table 4. Selected Bond Lengths [Å] and Angles [deg] for Compound 4

Al(1)−N(5)	1.889(2)	N(5)−Al(1)−N(4)	105.84(11)
Al(1)−N(4)	1.899(2)	N(5)−Al(1)−C(5)	118.38(12)
Al(1)−C(5)	1.970(3)	N(4)−Al(1)−C(5)	112.69(12)
Al(1)−N(3)	1.999(3)	N(5)−Al(1)−N(3)	140.38(11)
Al(1)−N(1)	1.999(2)	N(4)−Al(1)−N(3)	41.62(10)
Al(1)−N(2)	2.751(3)	Al(1)−N(3)−C(6)	172.8(2)
Al(1)−N(6)	2.655(2)	Al(1)−N(4)−C(8)	176.7(2)
C(4)−C(5)	1.331(4)	C(5)−Al(1)−N(1)	86.59(11)

The addition of 2 equiv of K[3,5-^{t}Bu$_2$pz] to **2** in toluene gave [(3,5-^{t}Bu$_2$-*N*-CH=C(SiMe$_3$)-pz)Al(η^1-3,5-^{t}Bu$_2$pz)(η^2-3,5-^{t}Bu$_2$pz)] (**4**) (Scheme 2). Compound **4** is purified by crystallization from *n*-hexane.

Analogous to **3**, at room temperature the ^{1}H NMR spectrum of **4** displays, next to the resonances for the chelating moiety (1.10 and 1.12 ppm, C$_6$D$_6$), only one sharp resonance for the ^{t}Bu groups of two coordinated ^{t}Bu$_2$pz ligands (1.37 ppm, C$_6$D$_6$), implying a dynamic process in solution. However, variable-temperature ^{1}H NMR spectroscopy does not elucidate this process in toluene-*d*$_8$, since the exchange seems to be still fast on the NMR time scale even at 183 K.

To understand the bonding, X-ray diffraction analysis of **4** was carried out on a crystal obtained from *n*-hexane. The crystallographic data and selected bond lengths and angles are listed in Tables 1 and 4. Compound **4** crystallizes as a monomer, in which the aluminum center is five-coordinated by one chelating [3,5-^{t}Bu$_2$-*N*-CH=C(SiMe$_3$)-pz] moiety and two ^{t}Bu$_2$pz ligands (Fig-

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[11] Such feature, termed slipped-η^2 coodination, has been only observed in two other element pyrazolato compounds (Ta and Tl); see: (a) Guzei, I. A.; Yap, G. P. A.; Winter, C. H. *Inorg. Chem.* **1997**, *36*, 1738. (b) Deacon, G. B.; Delbridge, E. E.; Forsyth, C. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2000**, 745.

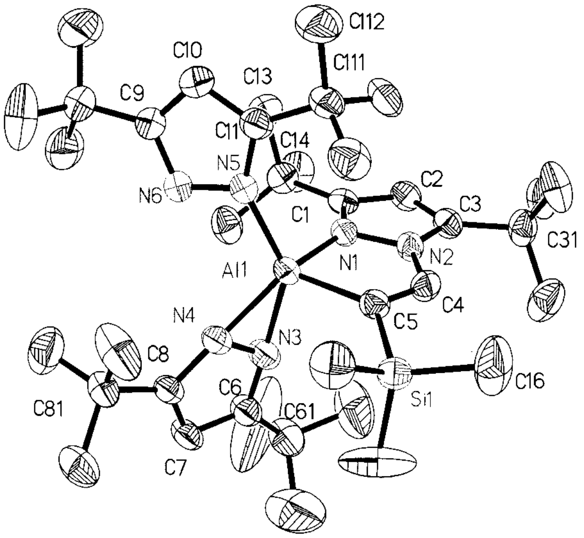

Figure 4. Perspective view and atom-labeling scheme of compound **4**, showing the numbering scheme and the thermal ellipsoids at the 50% probability level.

ure 4). Their Al−N bond distances are Al(1)−N(3) 1.999(3), Al(1)−N(4) 1.899(2), Al(1)−N(5) 1.889(2), and Al(1)−N(6) 2.655(2) Å, clearly exhibiting an η^1- as well as an η^2-coordination of two ligands, respectively. The bond lengths of the η^2-coordinated ligand are slightly shorter than those in [(η^2-3,5-^{t}Bu$_2$pz)$_3$Al],[2b] which is presumably due to the lower coordination number at aluminum (e.g., Al(1)−N(4) 1.838 Å in **3**).

Summary and Conclusions

This paper describes an unusual reaction forming an alkenyl-substituted monomeric aluminum dichloride **2**. However, in attempts to prepare analogous complexes using other substituted ethine HC≡CR (R = alkyl, aryl) no reaction occurred. The Al−Cl bonds in **2** seem to be readily cleaved by metathesis reaction. Compound **3** (**4**) contains a rare slipped η^2-coordinated (a real η^2-coordinated in **4**) pyrazolato ligand. Complex **2** is particularly interesting as a precursor for the synthesis of a series of related aluminum complexes due to its convenient synthetic route in high yield. Further investigations of **2** are in progress.

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Supporting Information Available: Text giving experimental details of the syntheses and tables of final atomic coordinates, bond distances and angles, and anisotropic thermal parameters for the structural analyses of **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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