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Syntheses and Characterization of μ,η^1,η^1-3,5-Di-*tert*-butylpyrazolato Derivatives of Aluminum†

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The 3,5-di-*tert*-butylpyrazolato (3,5-tBu$_2$pz) derivatives of aluminum $[(\eta^1,\eta^1\text{-3,5-}t\mathrm{Bu_2pz})(\mu\text{-Al})R_1R_2]_2$ ($R_1 = R_2$ = Me **1**; $R_1 = R_2$ = Et, **2**; $R_1 = R_2$ = Cl, **3**; $R_1 = R_2$ = I, **4**; $[(\eta^2\text{-3,5-}t\mathrm{Bu_2pz})_3\mathrm{Al}]$, **5**; $[\mathrm{Al_2}(\eta^1,\eta^1\text{-3,5-}t\mathrm{Bu_2pz})_2(\mu\text{-E})(\mathrm{C{\equiv}CPh})_2]$ (E = S (**6**), Se (**7**), Te (**8**)) have been prepared in good yield. Compounds **1** and **2** were obtained by the reactions of H[3,5-tBu$_2$pz] with Me_3Al and Et_3Al, respectively. Reaction of $[(\eta^1,\eta^1\text{-3,5-}t\mathrm{Bu_2pz})(\mu\text{-Al})\mathrm{H_2}]_2$ with the pyrazole H[3,5-tBu$_2$pz] gave $[(\eta^2\text{-3,5-}t\mathrm{Bu_2pz})_3\mathrm{Al}]$ (**5**). The reaction of $[(\eta^1,\eta^1\text{-3,5-}t\mathrm{Bu_2pz})(\mu\text{-Al})R_2]_2$ (R = H, Me) and I_2 yielded **4**, while the reaction of 1 equiv of K[3,5-tBu$_2$pz] and $AlCl_3$ afforded **3**. In addition, the reaction of $[\mathrm{Al_2}(\eta^1,\eta^1\text{-3,5-}t\mathrm{Bu_2pz})_2(\mu\text{-E})\mathrm{H_2}]$ and HC≡CPh gave **6**, **7**, and **8**. All compounds have been characterized by elemental analysis, NMR, and mass spectroscopy. The molecular structure analyses of compounds **1**, **3**, **6**, and **7** by X-ray crystallography showed that complexes **1** and **3** are dimeric with two η^1,η^1-pyrazolato groups in twisted conformation while **6** and **7** with two η^1,η^1-pyrazolato groups display a boat conformation.

Introduction

Recently, we started developing the chemistry of aluminum complexes with bulky pyrazolato ligands.[1] It is known that pyrazolato ligands have been widely employed in complexes of transition metals and exhibit either η^1-bonding to a single metal ion or form an η^1,η^1-bridge between two metal centers.[2] Moreover, it was observed that the pyrazolato ligand coordinates in an η^2- as well as in an η^5-fashion to the metal center.[3] However, examples of crystallographically characterized μ,η^1,η^1-pyrazolato complexes of aluminum are still limited.[4] Only few related 3,5-di-*tert*-butylpyrazolato aluminum derivatives have been investigated and structurally characterized.[1,5] Herein, we report the syntheses and chemistry of 3,5-di-*tert*-butylpyrazolato aluminum complexes **1**−**8** and the single-crystal structures of **1**, **3**, **6**, and **7**.

Results and Discussion

Alkyl derivatives of aluminum with a pyrazolato ligand were previously prepared by reacting benzene solutions of the appropriate aluminum compound with a stoichiometric amount of pyrazole at room temperature.[4a]

In a modified synthesis, compounds **1** and **2** were prepared by the reaction of Me_3Al, or Et_3Al, and 3,5-di-*tert*-butylpyrazole H[3,5-tBu$_2$pz] in hexane to give in good yields compound $[(\eta^1,\eta^1\text{-3,5-}t\mathrm{Bu_2pz})(\mu\text{-Al})R_2]_2$ (R = Me, **1**; R = Et, **2**):[5a]

$$2\mathrm{H}[3,5\text{-}t\mathrm{Bu_2pz}] + 2\mathrm{R_3Al} \rightarrow [\eta^1,\eta^1\text{-3,5-}t\mathrm{Bu_2pz}(\mu\text{-Al})\mathrm{R_2}]_2 + 2\mathrm{RH} \quad (\mathrm{R} = \mathrm{Me}\ (\mathbf{1}),\ \mathrm{Et}\ (\mathbf{2})) \tag{1}$$

In both cases alkane elimination occurred at room temperature. Compounds **1** and **2** are purified by recrystallization from *n*-hexane. **1** can be also purified by sublimation in vacuo.

Crystals suitable for X-ray diffraction studies were obtained from *n*-hexane at −26 °C. The crystallographic data and selected bond lengths and angles are listed in Tables 1 and 2. Compound **1** crystallizes in the orthorhombic crystal system, space group

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† Dedicated to Professor François Mathey on the occasion of his 60th birthday.

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(4) Sample studies of compounds $[(\eta^1,\eta^1\text{-pz})(\mu\text{-Al})R_1R_2]_2$ ($R_1 = R_2$ = Me, Et; R_1 = Me, Et, R_2 = Cl],[4a] $[\eta^1\text{-HB(3,5-Me_2pz)_3AlMe_2}]$, $[\eta^1\text{-HB(3-}t\mathrm{Bupz})_3\mathrm{AlMe_2}]$, $[\eta^1\text{-H}_2\mathrm{B(3\text{-}}t\mathrm{Bupz})_2\mathrm{AlMe_2}]$,[4b] $\{\eta^1\text{-H(3-}t\mathrm{Bupz})\text{-B(3-}t\mathrm{Bupz})_2\}\mathrm{AlEt_2}$, $\{\eta^1\text{-H(3-}t\mathrm{Bupz})\mathrm{B(3\text{-}}t\mathrm{Bupz})(5\text{-}t\mathrm{Bupz}\}\mathrm{AlEt_2}$,[4c] $[\{\eta^1\text{-HB(3-}t\mathrm{BupzH})_3\}\mathrm{Cl}][\mathrm{AlCl_4}]$,[4d] and $[\{\eta^1\text{-HB(3-Phpz)_2(5-Phpz)}\}_2\mathrm{Al}][\mathrm{AlCl_4}]$.[4e] (a) Arduini, A.; Storr, A. *J. Chem. Soc., Dalton Trans.* **1974**, 503. (b) Looney, A.; Parkin, G. *Polyhedron* **1990**, *9*, 265. (c) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C. *Inorg. Chem*. **1996**, *35*, 445. (d) Looney, A.; Parkin, G.; Rheingold, A. L. *Inorg. Chem.* **1991**, *30*, 3099. (e) Darensbourg, D. J.; Maynard, E. L.; Holtcamp, M. W.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1996**, *35*, 2682. (f) Chang, C.-C.; Her, T.-Y.; Hsieh, F.-Y.; Yang, C.-Y.; Chiang, M.-Y.; Lee, G.-H.; Wang, Y.; Peng, S.-M. *J. Chin. Chem. Soc*. **1994**, *41*, 783. (g) Lewinski, J.; Zachara, J.; Gos, P.; Grabska, E.; Kopec, T.; Madura, I.; Marciniak, W.; Prowotorow, I. *Chem.*−*Eur. J.* **2000**, *6*, 3215.

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Table 1. Summary of Crystallographic Data for Complexes **1**, **3**, **6**, and **7**

	1	**3**	**6**	**7**
formula	$C_{26}H_{50}Al_2N_4$	$C_{22}H_{38}Al_2Cl_4N_4$	$C_{52}H_{64}Al_2N_4S$ incl toluene	$C_{52}H_{64}Al_2N_4Se$ incl toluene
fw	472.66	554.32	831.09	877.99
temp (K)	203(2)	203(2)	203(2)	203(2)
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	*pbcn*	*pbcn*	$P2_1/c$	$P2_1/c$
a (Å)	9.3230(10)	13.171(3)	18.260(3)	18.291(3)
b (Å)	20.403(3)	17.706(4)	15.835(7)	15.891(6)
c (Å)	16.186(3)	12.870(2)	18.652(4)	18.594(3)
α (deg)	90	90	90	90
β (deg)	90	90	115.590(12)	115.261(11)
γ (deg)	90	90	90	90
V (Å^{-3})	3078.9(8)	3001.3(11)	4864(2)	4888(2)
Z	4	4	4	4
d(calcd) (Mg/m^3)	1.020	1.227	1.135	1.193
abs coeff (mm^{-1})	0.113	0.470	0.140	0.842
F(000)	1040	1168	1784	1856
cryst size (mm)	0.60 × 0.60 × 0.50	0.90 × 0.60 × 0.30	0.50 × 0.40 × 0.30	0.70 × 0.20 × 0.20
θ range (deg)	3.71 to 25.04	3.52 to 25.05	3.53 to 25.03	3.53 to 25.05
limiting	$-10 \le h \le 11$, $-24 \le k \le 24$, $-19 \le l \le 19$	$-15 \le h \le 15$, $-21 \le k \le 10$, $-15 \le l \le 15$	$-21 \le h \le 21$, $-12 \le k \le 18$, $-19 \le l \le 22$	$-21 \le h \le 21$, $-18 \le k \le 18$, $-22 \le l \le 22$
no. reflns collected	5656	4438	9561	12 675
no. indep reflns	2718 ($R_{int} = 0.0184$)	2655 ($R_{int} = 0.0564$)	8530 ($R_{int} = 0.0528$)	8620 ($R_{int} = 0.0553$)
no. data/restraints/params	2714/0/154	2651/0/152	8491/0/546	8583/15/546
GOF on F^2	1.053	1.052	1.075	1.089
R indices [$I > 2\sigma(I)$]	R1 = 0.0384, wR2 = 0.1027	R1 = 0.0427, wR2 = 0.1061	R1 = 0.0563, wR2 = 0.1148	R1 = 0.0511, wR2 = 0.0992
R indices (all data)	R1 = 0.0469, wR2 = 0.1130	R1 = 0.0559, wR2 = 0.1242	R1 = 0.0791, wR2 = 0.1415	R1 = 0.0813, wR2 = 0.1221
largest diff peak/hole (e Å^{-3})	0.211/−0.192	0.319/−0.343	0.800/−0.816	0.824/−0.750

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Compounds **1** and **3**

1		**3**	
Al(1)−N(1))	1.9638(13)	Al(1)−N(1)	1.904(2)
Al(1)−C(6)	1.962(2)	Al(1)−Cl(1)	2.1181(9)
C(5)−Al(1)−N(1)	114.67(7)	N(1A)−Al(1)−Cl(1A)	114.36(6)
C(5)−Al(1)−N(2)	102.09(7)	Cl(1A)−Al(1)−Cl(1)	112.22(6)
C(6)−Al(1)−C(5)	121.80(9)	N(2A)−Al(2)−Cl(2A)	112.52(6)
C(6)−Al(1)−N(1)	102.17(7)	N(1A)−Al(1)−N(1)	104.86(12)
C(6)−Al(1)−N(2)	114.56(7)	N(1)−Al(1)−Cl(1)	114.36(6)
N(1)−Al(1)−N(2)	99.77(6)	N(2A)−Al(2)−N(2)	105.02(12)

Pbcn. X-ray diffraction analysis of **1** shows a dimeric molecule with a six-membered Al_2N_4 ring and four terminal methyl groups (Figure 1), comparable to that observed in the pyrazolato derivative $[(\eta^1,\eta^1\text{-pz})(\mu\text{-Al})Me_2]_2$.[4f] Two *tert*-butylpyrazolato groups serve as bridges between the two aluminum atoms, and the six-membered Al_2N_4 ring consists of four nitrogen atoms from two *tert*-butylpyrazolato groups and two aluminum atoms. Surprisingly, the Al_2N_4 ring features a twisted conformation, which is in sharp contrast to the related $[(\eta^1,\eta^1\text{-pz})(\mu\text{-Al})Me_2]_2$ compound that takes up a boat conformation. This structural difference might be due to the bulky *tert*-butyl groups. Both the Al−N and Al−C bond lengths (e.g., Al(1)−N(1), 1.9638(13) Å, and Al(1)−C(6), 1.962(2) Å) as well as the N−Al−N angle (e.g., N(1)−Al(1)−N(2), 99.77(6)°) are in the expected range and are comparable to the related bond lengths and angle in $[(\eta^1,\eta^1\text{-pz})(\mu\text{-Al})Me_2]_2$ (Al(1)−N(1), 1.923(1) Å; Al(1)−C(8), 1.939 Å; N(1)−Al(1)−N(3), 99.3°).[4f] The C(5)−Al(1)−C(6) angle is 121.80(9)°, which is somewhat larger than the corresponding one in $[(\eta^1,\eta^1\text{-pz})(\mu\text{-Al})Me_2]_2$ (C(8)−Al(1)−C(10), 118.8(1)°). Most likely, this stems from the difference in their conformations.

The addition of an equivalent amount of aluminum trichloride to K[3,5-tBu$_2$pz] [9] in toluene at room temperature gave $[(\eta^1,\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})Cl_2]_2$, **3**. Single crystals suitable for X-ray diffraction studies were obtained from *n*-hexane at −26 °C. Figure 2 shows a perspective view of compound **3**, along with the atom-labeling scheme. The crystallographic data and selected bond lengths and angles are listed in Tables 1 and 2. Compound **3** crystallizes in the orthorhombic crystal system, space group *Pbcn*. The very similar cell parameters of $[(\eta^1,\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})Cl_2]_2$, **3**, and $[(\eta^1,\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})Me_2]_2$, **1**, indicate structural similarities between these two compounds (Figures 1 and 2). Both compounds have a six-membered ring with pyrazolato groups as bridging ligands. Like in compound **1**, the six-membered ring takes up a twisted conformation due to steric effects. In compound **3**, the Al(1)−N(1) bond length (1.904(2) Å) is slightly shorter than that in compound **1** (Al(1)−N(1), 1.9638(13)) Å) owing to the higher electron-withdrawing properties of the chlorine atoms. In **3**, the N(1A)−Al(1)−N(1) angle (104.86(12)°) is somewhat larger than that in compound **1** (N(1)−Al(1)−N(2), 99.77(6)°).

Organoaluminumiodide compounds are usually prepared by the reaction of the related organomethylaluminum compounds and iodine in toluene.[6] However, to increase the rate of cleavage at the Al−C bonds, unfavorable reaction conditions such as long-term stirring and refluxing are often adopted. Alternatively, we found that the reaction of the organoaluminum dihydride $[(\eta^1,\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})H_2]_2)$[1c] and I_2 at room temperature in toluene proceeds smoothly, yielding **4** under elimination of HI in high yield:

$$[(\eta^1,\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})H_2]_2 + 4I_2 \rightarrow \underset{\mathbf{4}}{[(\eta^1\text{-}\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})I_2]_2} + 4HI \quad (2)$$

Apparently, this route is a new way to prepare organoaluminum iodide compounds and has not been reported in the literature

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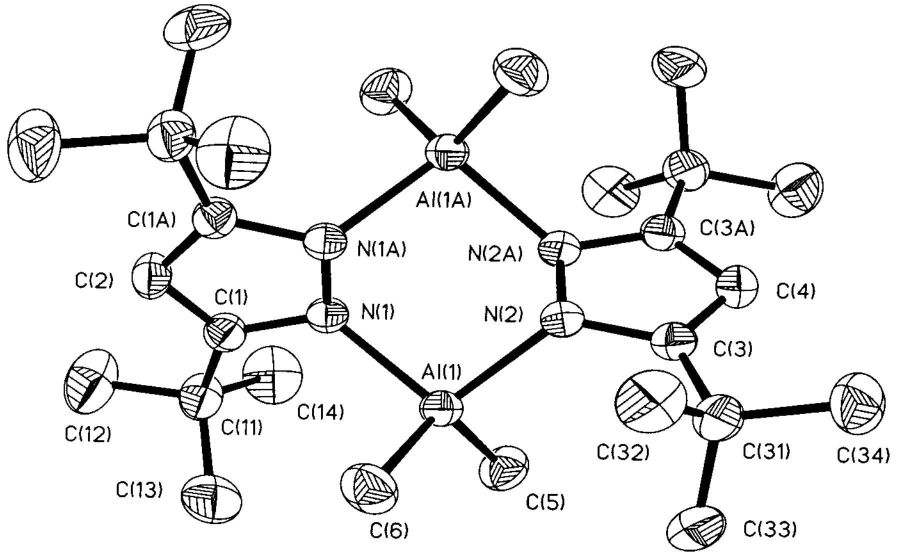


Figure 1. Perspective view of the complex $[(\eta^1,\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz})(\mu\text{-Al})\mathrm{Me_2}]_2$ (**1**), showing the numbering scheme and the thermal ellipsoids at the 50% probability level.

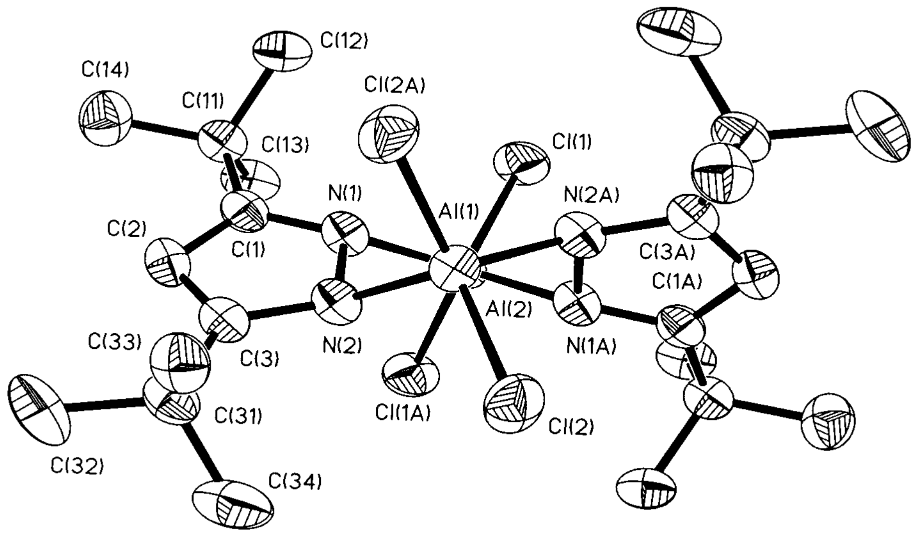


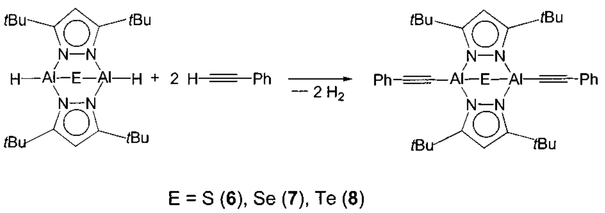
Figure 2. Perspective view of the complex $[(\eta^1,\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz})(\mu\text{-Al})\mathrm{Cl_2}]_2$ (**3**), showing the numbering scheme and the thermal ellipsoids at the 50% probability level.

before. ^{1}H NMR and mass spectroscopy as well as elemental analysis data are all consistent with the formation of **4**.

Compound $[(\eta^2\text{-}3,5\text{-}t\mathrm{Bu_2pz})_3\mathrm{Al}]$, **5**, has recently been synthesized from the reaction of $\mathrm{AlCl_3}$ and 3 equiv of K[3,5-$t\mathrm{Bu_2pz}$].[5b] Alternatively, we found that **5** can be prepared in nearly quantitative yield by treatment of $[(\eta^1,\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz})(\mu\text{-Al})\mathrm{H_2}]_2$[1c] with 4 equiv of H[3,5-$t\mathrm{Bu_2pz}$], proceeding smoothly at room temperature in toluene under elimination of hydrogen. The physical data of compound **5** are identical to those reported in the literature.[5b]

Recently, we described the preparation of the first structurally characterized aluminum complexes with terminal acetylide groups[1a] and especially the reaction of aluminumhydride with congeners of oxygen affording the related aluminum chalcogenide hydrides.[1b] We were interested in whether the remaining hydride on each aluminum atom in these compounds is still reactive for substitution. Because of our interest in aluminum complexes with terminal acetylide groups, we started to investigate the synthesis of $[\mathrm{Al_2}(\eta^1,\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz})_2(\mu\text{-E})(\mathrm{C{\equiv}CPh})_2]$ (E = S, Se, Te).

An excess of phenylacetylene reacted with $[\mathrm{Al_2}(\eta^1,\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz})_2(\mu\text{-E})\mathrm{H_2}]$ (E = S, Se, Te)[1b] in toluene to give $[\mathrm{Al_2}(\eta^1,\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz})_2(\mu\text{-E})(\mathrm{C{\equiv}CPh})_2]$ (**6**−**8**) in good yields:



(3)

Compounds **6**−**8** were characterized by ^{1}H and ^{13}C NMR and EI mass spectroscopy as well as elemental analysis. Suitable single crystals of compounds **6** and **7** for X-ray diffraction were obtained by crystallization from toluene at room temperature. The crystal structures of compounds **6** and **7** are shown in Figures 3 and 4. The crystallographic data and selected bond lengths and angles are given in Tables 1 and 3. Compounds **6** and **7** are isostructural and crystallize in the monoclinic system, space group $P2_1/c$. Both compounds take up a boat-shaped six-

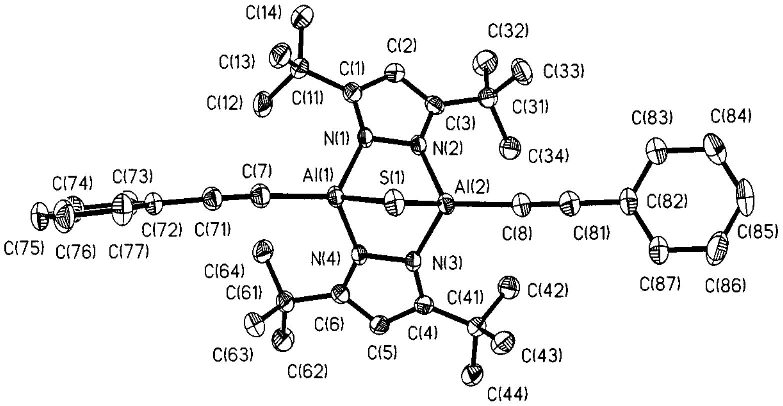


Figure 3. Perspective view of the complex $[Al_2(\eta^1,\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-S})(C{\equiv}CPh)_2]$ (**6**), showing the numbering scheme and the thermal ellipsoids at the 50% probability level.

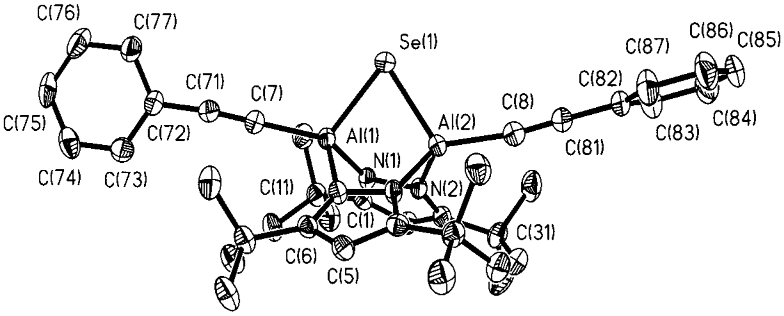


Figure 4. Perspective view of the complex $[Al_2(\eta^1,\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-Se})(C{\equiv}CPh)_2]$ (**7**), showing the numbering scheme and the thermal ellipsoids at the 50% probability level.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Componds **6** and **7**

6		7	
S(1)−Al(1)	2.1977(11)	Se(1)−Al(1)	2.3293(11)
Al(1)−C(7)	1.911(3)	Al(1)−C(7)	1.905(4)
Al(1)−N(1)	1.938(2)	Al(1)−N(1)	1.938(3)
Al(1)−N(4)	1.963(2)	Al(1)−N(4)	1.958(3)
Al(1)−Al(2)	2.8086(13)	Al(1)−Al(2)	2.843(2)
C(7)−C(71)	1.204(4)	C(7)−C(71)	1.209(5)
C(8)−C(81)	1.206(4)	C(8)−C(81)	1.204(5)
C(71)−C(72)	1.443(4)	C(71)−C(72)	1.437(5)
C(72)−C(77)	1.384(4)	C(72)−C(77)	1.402(5)
Al(2)−S(1)−Al(1)	79.46(4)	Al(2)−Se(1)−Al(1)	75.28(4)
C(7)−Al(1)−N(1)	118.15(11)	C(7)−Al(1)−N(1)	118.2(2)
C(7)−Al(1)−N(4)	115.49(11)	C(7)−Al(1)−N(4)	115.44(14)
N(1)−Al(1)−N(4)	98.65(10)	N(1)−Al(1)−N(4)	98.38(13)
C(7)−Al(1)−S(1)	119.80	C(7)−Al(1)−Se(1)	118.84(12)
N(1)−Al(1)−S(1)	100.18(7)	N(1)−Al(1)−Se(1)	100.81(9)
N(4)−Al(1)−S(1)	101.01(7)	N(4)−Al(1)−Se(1)	101.81(9)
C(7)−Al(1)−Al(2)	169.75(10)	C(7)−Al(1)−Al(2)	170.82(12)

membered ring geometry due to the constraint of the chalcogenide bridge (S for **6**, Se for **7**) between two Al atoms. The interesting features are that the two phenyl groups on both sides of the molecule take up a vertical position relative to each other and the phenylacetylene groups arrange terminally, comparable to that in $[(\eta^1,\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-Al})(C{\equiv}CPh)_2]_2$.[1a] The Al−C−C angle is 174.3(3)°, showing a nearly linear geometry of the acetylide ligand. The Al−C bond lengths (Al(1)−C(7), 1.911(3) Å in **6** and 1.905(4) Å in **7**) are comparable to those in $[(\eta^1,\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})(C{\equiv}CPh)_2]_2$ (Al(1)−C(21), 1.913(3) Å; Al(1)−C(11), 1.929 Å).[1a] The Al−E bond lengths (**6**, Al(1)−S(1) 2.1977(11) Å; **7**, Al(1)−Se(1) 2.3293(11) Å) are slightly shorter than those in $[Al_2(\eta^1,\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-E})H_2]$ (Al(1)−S(1), 2.2080(4) Å (E = S); Al(1)−Se(1), 2.3449(10) Å (E = Se)).[1b] The angles of Al−E−Al (Al(1)−S(1)−Al(2), 79.46(4)° in **6**; Al(1)−Se(1)−Al(2), 75.28(4)° in **7**) are close to those in $[Al_2(\eta^1,\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-E})H_2]$ compounds (Al(1)−S(1)−Al(2), 79.58(2)° (E = S); Al(1)−Se(1)−Al(2), 75.78(3)° (E = Se)).

Conclusions and Remarks

This paper describes the syntheses and characterization of novel η^1,η^1-3,5-di-*tert*-butylpyrazolato derivatives of aluminum. On the whole, our results point out the versatility of the 3,5-di-*tert*-butylpyrazolato ligand in aluminum chemistry. Presently we are investigating the application of these compounds for various transformations, and the results will be published elsewhere.

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. $H_3Al{\cdot}NMe_3$,[7] 3,5-di-*tert*-pyrazole,[8] and 3,5-di-*tert*-pyrazolatopotassium[9] were prepared as described in the literature. 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 (250.130 MHz), ^{13}C (100.600 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). FI−IR spectra were measured on a Bio-Rad FTS-7 instrument as Nujol mulls between KBr plates in the range 4000−400 cm^{-1} (abbreviations: vs, very strong; s, strong; m, medium). EI (700 eV) mass spectra were measured on

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Finnigan MAT 8230 and Varian MAT CH5 instruments. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of [(η^1,η^1-3,5-*t*Bu$_2$pz)(μ-Al)Me$_2$]$_2$, 1. Me$_3$Al (1.50 mL, 2.0 mmol) was slowly added by syringe to a stirred solution of H[3,5-*t*Bu$_2$pz] (0.36 g, 2.0 mmol) in *n*-hexane (40 mL) under evolution of CH$_4$ at room temperature. After the mixture was stirred for 4 h, the solvent was reduced (about 10 mL) and **1** crystallized at −26 °C (0.40 g, 85%). Alternatively the mixture was stirred for 4 h, the solvent removed, and the residue sublimed at 120 °C under reduced pressure (0.01 mbar) (0.43 g, 91%). Mp: 173 °C. ^{1}H NMR (C$_6$D$_6$): δ −0.55 (s, 12 H, Al−CH$_3$), 1.37 (s, 36 H, *t*Bu), 6.23 (s, 2 H, CH). ^{13}C NMR (C$_6$D$_6$): δ −6.62 (br, Al-*C*), 30.94 (s, *C*H$_3$), 32.70 (s, *C*Me$_3$), 107.3 (s, *C*H), 171.93 (s, *C*−*t*Bu). EI-MS *m/e* (%): 457 ((M − 15)$^+$, 100). Anal. Calcd for C$_{26}$H$_{50}$Al$_2$N$_4$: C, 66.10; H, 10.59; N, 11.86. Found: C, 65.79; H, 10.40; N 11.56.

Synthesis of [(η^1,η^1-3,5-*t*Bu$_2$pz)(μ-Al)Et$_2$]$_2$, 2. The method of preparation is analogous to that of **1**. **2** was isolated by crystallization from cold hexane (0.41 g, 78%). Mp: 127 °C. ^{1}H NMR (C$_6$D$_6$): δ 0.15 (t, 8 H, CH$_2$), 0.95 (m, 12 H, CH$_3$), 1.40 (s, 36 H, *t*Bu), 6.30 (s, 2 H, CH). ^{13}C NMR (C$_6$D$_6$): δ 3.85 (s, Al−*C*H$_2$−), 8.77 (s, Al−CH$_2$−*C*H$_3$), 30.99 (s, *C*H$_3$), 32.87 (s, *C*Me$_3$), 108.02 (s, *C*H), 172.06 (s, *C*−*t*Bu). EI-MS *m/e* (%): 499 ((M − Et)$^+$, 100). Anal. Calcd for C$_{30}$H$_{58}$Al$_2$N$_4$: C, 68.10; H, 10.97; N, 10.59. Found: C, 68.05; H, 11.06; N, 10.36.

Synthesis of [(η^1,η^1-3,5-*t*Bu$_2$pz)(μ-Al)Cl$_2$]$_2$, 3. A suspension of AlCl$_3$ (0.27 g, 2.0 mmol) and K[3,5-*t*Bu$_2$pz] (0.44 g, 2.0 mmol) in toluene (40 mL) was stirred for 15 h at room temperature, and the solvent was removed under reduced pressure (0.01 mbar). The resulting residue was extracted with *n*-hexane, and **3** crystallized at −26 °C (0.35 g, 63%). Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from *n*-hexane. Mp: 175 °C. ^{1}H NMR (C$_6$D$_6$): δ 1.43 (s, 36 H, *t*Bu), 6.33 (s, 2 H, CH). ^{13}C NMR (C$_6$D$_6$): δ 30.65 (s, *C*H$_3$), 33.34 (s, *C*Me$_3$), 110.81 (s, *C*H), 176.99 (s, *C*−*t*Bu). EI-MS *m/e* (%): 554 (M$^+$, 100), 539 ((M − 15)$^+$, 50). Anal. Calcd for C$_{22}$H$_{38}$Al$_2$Cl$_4$N$_4$: C, 47.65; H, 6.86; Cl, 25.63; N, 10.11. Found: C, 47.78; H, 6.97; Cl, 26.24; N, 9.96.

Synthesis of [(η^1,η^1-3,5-*t*Bu$_2$pz)(μ-Al)I$_2$]$_2$, 4. In method 1, a solution of I$_2$ (1.02 g, 4.0 mmol) in toluene (30 mL) was slowly added to a solution of **1** (0.47 g, 1.0 mmol) in toluene (15 mL). The mixture was stirred for 15 h and then refluxed for an additional 24 h. After filtration over celite the solution was concentrated to 5 mL and **4** crystallized at −26 °C (0.65 g, 71%).

In method 2, a solution of I$_2$ (1.02 g, 4.0 mmol) in toluene (30 mL) was slowly added to a solution of [(η^1-3,5-*t*Bu$_2$pz)(μ-Al)H$_2$]$_2$[1c] (0.42 g, 1.0 mmol) in toluene (20 mL). The mixture was stirred for 3 h at room temperature. The solvent was removed, the resulting brown residue extracted with *n*-hexane (3 × 10 mL), and **4** crystallized at −26 °C to afford colorless crystals (0.77 g, 84%). Mp: 256−257 °C. ^{1}H NMR (C$_6$D$_6$): δ 1.51 (s, 36 H, *t*Bu), 6.42 (s, 2 H, *C*H). ^{13}C NMR (C$_6$D$_6$): δ 31.46 (s, *C*H$_3$), 33.81 (s, *C*Me$_3$), 114.27 (s, *C*H), 179.03 (s, *C*−*t*Bu). ^{27}Al NMR (C$_6$D$_6$): δ 62.27. EI-MS *m/e* (%): 905 ((M$^+$ − 15), 3), 793 ((M − I)$^+$, 100). Anal. Calcd for C$_{22}$H$_{38}$Al$_2$I$_4$N$_4$: C, 28.70; H, 4.13; N, 6.09. Found: C, 29.16; H, 4.28; N, 6.10.

Synthesis of [(η^2-3,5-*t*Bu$_2$pz)$_3$Al], 5. [(η^1,η^1-3,5-*t*Bu$_2$pz)(μ-Al)H$_2$]$_2$ (0.42 g, 1.0 mmol) and H[3,5-*t*Bu$_2$pz] (0.72 g, 4.0 mmol) were dissolved in toluene (50 mL), and the solution was stirred at room temperature for 15 h until the elimination of H$_2$ ceased. The solvent was removed under reduced pressure (0.01 mbar). The residue was extracted with *n*-hexane (4 × 10 mL), and **5** crystallized at −26 °C (1.05 g, 93%). The analytical data were identical to those reported in the literature.[5b]

Synthesis of [Al$_2$(η^1,η^1-3,5-*t*Bupz)$_2$(μ-S)(C≡CPh)$_2$], 6. An excess of phenylacetylene (0.67 mL, 6.0 mmol) was slowly added to a solution of [Al$_2$(η^1,η^1-3,5-*t*Bupz)$_2$(μ-S)H$_2$] (0.89 g, 2.0 mmol)[1b] in toluene (40 mL) using a syringe, and solution was stirred overnight at 50 °C. The solution was allowed to cool to room temperature, and the solvent was removed under reduced pressure (0.01 mbar). The residue was washed with cold pentane (2 × 8 mL) to give a pure white solid of **6** (0.83 g, 64%). Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from toluene at room temperature. Mp: 149−151 °C. ^{1}H NMR (CDCl$_3$): δ 1.58 (s, 36 H, *t*Bu), 5.97 (s, 2 H, CH), 7.32−7.50 (m, 10 H, Ph). ^{13}C NMR (CDCl$_3$): δ 31.47 (s, *C*H$_3$), 32.40(s, *C*Me$_3$), 102.93 (s, *C*H), 165.58 (s, *C*−*t*Bu), 109.20 (br, Al−*C*), 112.00 (s, *C*Ph), 123.99, 128.40, 131.58, 131.80 (4s, Ph). EI-MS *m/e* (%): 646 (M$^+$, 100). IR (Nujol mull): 2140(vs), 1595(m), 1519(vs), 1488(vs), 1465(vs) 1365 (vs), 1320(s), 1251(vs), 1217(vs), 1049(vs), 1028(vs), 819(vs), 761(vs), 614(vs), 527(vs), 408(vs) cm^{-1}. Anal. Calcd for C$_{38}$H$_{48}$Al$_2$N$_4$S: C, 70.59; H, 7.43; N, 8.67. Found: C, 69.87; H, 7.46; N, 8.66.

Synthesis of [Al$_2$(η^1,η^1-3,5-*t*Bu$_2$pz)$_2$(μ-Se)(C≡CPh)$_2$], 7. An excess of phenylacetylene (0.67 mL, 6.0 mmol) was slowly added to a solution of [Al$_2$(η^1,η^1-3,5-*t*Bu$_2$pz)$_2$(μ-Se)H$_2$][1b] (1.39 g, 2.0 mmol) in toluene (40 mL) using a syringe, and the solution was stirred at 60 °C for 2 h. The solvent was removed under reduced pressure (0.01 mbar) and the resulting residue washed with cold pentane (2 × 8 mL) to afford a white solid of **7** (0.85 g, 61%). Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from toluene at room temperature. Mp: 172 °C. ^{1}H NMR (CDCl$_3$): δ 1.58 (s, 36 H, *t*Bu), 5.98 (s, 2 H, CH), 7.30−7.50 (m, 10 H, Ph). ^{13}C NMR (CDCl$_3$): δ 31.47 (s, *C*H$_3$), 32.46 (s, *C*Me$_3$), 103.25 (s, *C*H), 101.50 (br, Al−*C*), 112.41 (s, *C*Ph), 165.57(s, *C*−*t*Bu), 124.01, 128.27, 128.38, 131.52 (4s, Ph). EI-MS *m/e* (%): 694 (M$^+$, 30), 613 (M$^+$ − H$_2$Se, 100). IR (Nujol mull): 2137(s), 1518(m), 1261(m), 1207(m), 814(m), 610(m), 497(m) cm^{-1}. Anal. Calcd for C$_{38}$H$_{48}$Al$_2$N$_4$Se: C, 65.71; H, 6.92; N, 8.07. Found: C, 66.27; H, 6.68; N, 8.08.

Synthesis of [Al$_2$(η^1,η^1-3,5-*t*Bu$_2$pz)$_2$(μ-Te)(C≡CPh)$_2$], 8. An excess of phenylacetylene (0.35 mL, 3.0 mmol) was slowly added to a solution of [Al$_2$(η^1,η^1-3,5-*t*Bu$_2$pz)$_2$(μ-Te)H$_2$] (0.54 g, 1.0 mmol)[1b] in toluene (50 mL) using a syringe, and the solution was stirred overnight at room temperature. The solvent was removed under reduced pressure (0.01 mbar). Finally, the residue was washed with cold pentane (2 × 8 mL), and **8** was recrystallized from toluene at room temperature (0.43 g, 57.8%). Mp: 216 °C (dec). ^{1}H NMR (CDCl$_3$): δ 1.59 (s, 36 H, *t*Bu), 6.00(s, 2 H, CH), 7.30−7.50 (m, 10 H, Ph). ^{13}C NMR (CDCl$_3$): δ 31.49 (s, *C*H$_3$), 32.59 (s, *C*Me$_3$), 103.92 (s, *C*H), 102.8 (br, Al−*C*), 113.00 (s, *C*Ph), 165.43 (s, *C*−*t*Bu), 124.11, 128.19, 128.32, 131.40 (4s, Ph). EI-MS *m/e* (%): 744 (M$^+$, 100). IR (Nujol mull): 2135(vs), 1517(vs), 1487(s), 1365(s), 1215(s), 1065(s), 1027(vs), 818(vs), 759(s), 609(s), 492(s), 429(s) cm^{-1}. Anal. Calcd for C$_{38}$H$_{48}$Al$_2$N$_4$Te: C, 61.29; H, 6.45, N, 7.53. Found: C, 62.32; H, 6.54; N, 7.95.

X-ray Structure Determinations and Refinements for Compounds 1, 3, 6, and 7. Data for crystal structures of compounds **1**, **3**, **6**, and **7** were collected on a Stoe-Siemens four-circle diffractometer using Mo Kα radiation (λ = 0.710 73 Å). All structures were solved by direct methods (SHELXS-96)[10] and refined against F^2 using SHELXL-97.[11] All heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with $U_{\rm iso}$ tied to the $U_{\rm iso}$ of the parent atoms. A summary of cell parameters, data collection, and structure solution is given in Table 1.

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Supporting Information Available: Tables giving full data collection parameters and further details of refinement, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, hydrogen coordinates, and isotropic thermal parameters for **1**, **3**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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