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[11] To corroborate the identity of trimer **8b**, a small sample of **7a** was withdrawn and subjected to the following conditions. Treatment of **7a** with piperidine, followed by acidic treatment afforded crude trimer **8b**, which was purified by gel permeation chromatography (HW-40, 1% acetic acid). Trimer **8b** was characterized by ^{1}H and ^{13}C NMR spectroscopy, ESI mass spectrometry, and capillary electrophoresis.

The First Structurally Characterized Aluminum Compounds with Terminal Acetylide Groups**

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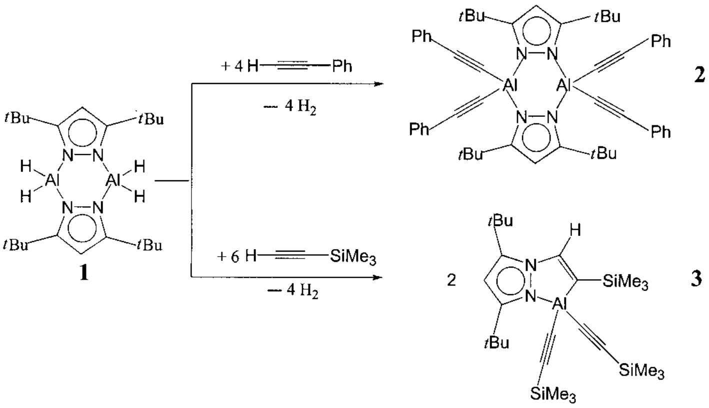
Herbert W. Roesky,* Manuel Hewitt, Fanica Cimpoesu,
Thomas R. Schneider, Andreas Stasch, and Jörg Prust

Aluminum compounds containing acetylide groups have been known since 1960.[1] All the published aluminum acetylides feature a dimeric structure with a bridging acetylide ligand between two aluminum centers[2] or between one aluminum atom and one early transition metal atom.[3] Since the addition of aluminum acetylides to unsaturated hydrocarbons is of interest in organic synthesis,[4] it is surprising that only few structurally characterized aluminum acetylides have been reported.[2, 3] Therefore, we set out to synthesize such complexes starting from an aluminum dihydride precursor with bulky pyrazolato ligands.[5] Herein, we present the preparation and molecular structures of **2** and **3** (see Scheme 1), which to the best of our knowledge, represent the first structurally characterized terminal acetylide complexes of aluminum.

The starting material for **2** and **3**, the aluminum dihydride **1**, is synthesized from H[*t*Bu$_2$pz] (*t*Bu$_2$pz = 3,5-di-*tert*-butylpyrazolate)[6] and AlH$_3$ · NMe$_3$[7] in high yield.[8]

Compound **2** is prepared from **1** and an excess of HC≡CPh (Scheme 1). The X-ray structure analysis of **2** shows a dimeric species with some interesting features (Figure 1).[9] Most surprisingly, the six-membered Al$_2$N$_4$ ring is in a twisted conformation. This is in sharp contrast to other bridged bispyrazolate compounds.[5c] Another interesting finding is the marked deviation of the two Al−C≡C backbones from linearity (Al1-C11-C12 160.2(3)° vs. Al1-C21-C22 178.3(3)°; the C11−C12 and C21−C22 bond lengths are 1.211(4) and 1.218(4) Å, respectively). Whereas some small angles in M−C≡C units in transition metal complexes have been



Scheme 1.

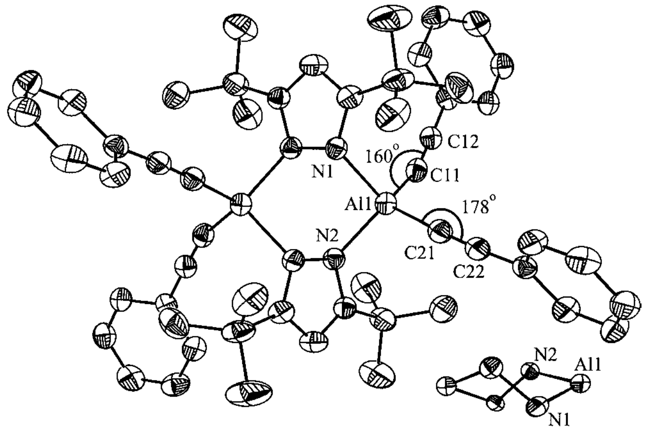


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: Al1-C11 1.929, Al1-C21 1.913(3), C11-C12 1.211(4), C21-C22 1.218(4); C12-C11-Al1 160.2(3), C22-C21-Al1 178.3(3), C21-Al1-C11 116.99(12), N2-Al1-N1 102.88(10). Bottom right: the twisted core of **2**.

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[**] This work was supported by the Deutsche Forschungsgemeinschaft. N.C.M.-Z. thanks the Schweizerischer Nationalfonds for a fellowship.

reported,[10] only two examples[11] are known in main group chemistry (160.5° for M = Bi[11a] and 166.4° for M = Ge[11b]).

Ab initio calculations were carried out to gain a better understanding of the geometry of **2**.[12] We considered an idealized molecule with D_{2h} symmetry[12a] and subsequently analyzed the forces causing its distortion.[12b] We were able to identify four instability coordinates of the reference backbone[12c] with A_u, B_{1u}, B_{2g}, and B_{3g} symmetries.[12d] These correspond to vibrations with computed imaginary frequency and are manifestations of the pseudo-Jahn–Teller effect.[12b] The experimentally found geometry may be described as a superposition of 93.2 % A_u and 6.8 % B_{1u}. The contributions of B_{2g} and B_{3g} are negligible. The distortion of A_u type is in good agreement with the results of the X-ray structure determination.

The analysis of the different contributions to the vibronic curvature of the A_u nuclear coordinate $K_v(A_u)$ gives an insight into the intimate stereochemical mechanism.[12e] The driving force seems to be the strong reluctance of Al atoms for π bonding, thereby converting these contributions to a higher σ character. Two possible $\pi \rightarrow \sigma^*$ electron promotions associated with this effect are shown in Figure 2. The depicted unoccupied states of the σ type contain aluminum atomic orbitals (AOs), while the π significant states are located on the ligands. The vibronic energy gain accompanying such excitations[12f] determines the above-mentioned distortion. Therefore, the observed bending and twisted character in **2** seems to be caused by inner features of the pyrazolato ligands rather than by the electronic structure of the acetylide ligands themselves.

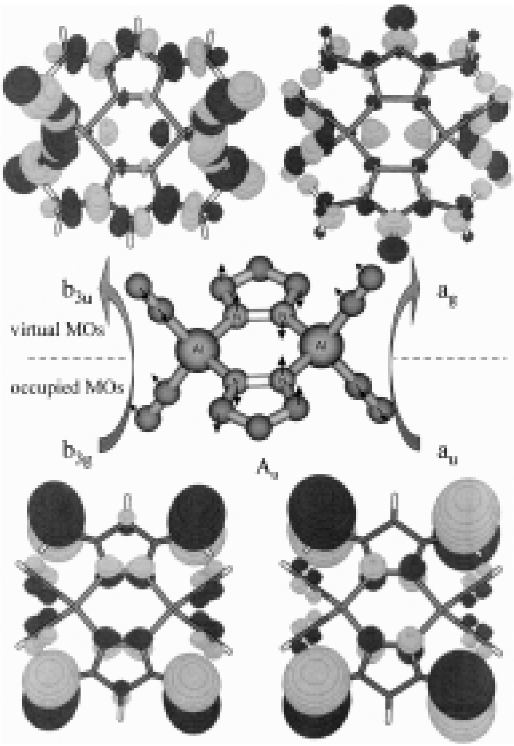

Figure 2. Two pairs of the transformed orbitals are shown, which are vibronically coupled through the normal coordinate of the A_u distortion. The notion of transformed orbitals refers to the states whose coupling leads to transition densities that concentrate the electron density flow associated with the distortion in a maximal way.[12f] The represented excitations, $a_u \rightarrow a_g$ and $b_{3g} \rightarrow b_{3u}$, are matching 25% of the vibronic curvature.

Reaction of **1** with an excess of HC≡CSiMe$_3$ affords compound **3** (Scheme 1). The X-ray structure analysis of **3** reveals a mononuclear aluminum compound with an aluminum atom coordinated by the [tBu$_2$-N-CH=C(SiMe$_3$)-pz] chelating unit and two C≡CSiMe$_3$ groups (Figure 3).[9] The chelating unit consists of a pyrazolato ligand which has formally added to a C≡C bond, thereby forming a five-membered metallacycle with the aluminum center. The two fused five-membered rings, AlN$_2$C$_2$ and pyrazolate, are close to coplanar. The C≡C bond length of the inserted acetylene molecule is significantly elongated (C43–C44 1.337(4) vs. C63–C64 1.219(4) Å) indicating double-bond character. The geometry of the aluminum atom is distorted tetrahedral (N1-Al1-C43 87.31(10)° and C54-Al1-C64 113.42(12)°) due to the constraint imposed by the chelate ring. The angles of the Al–C≡C bonds (178.2(2)° and 175.5(2)°) are in the normal range of other known aluminum acetylides.[2a, 3b]

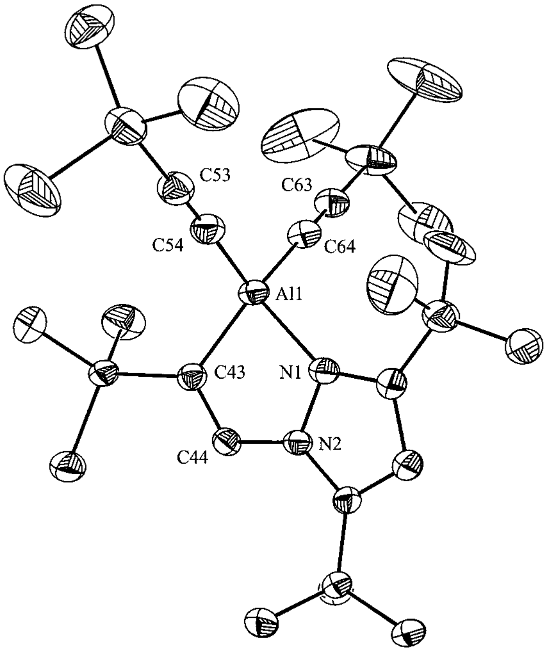

Figure 3. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: C44-C43 1.337(4), C53-C54 1.223(4); C54-Al1-C64 113.42(12), N1-Al1-C43 87.31(10), C53-C54-Al1 178.2(2).

The chelating unit in **3** is unusual and its formation shows that this should be a promising new ligand for other metal ions.

Experimental Section

2: HC≡CPh (1.8 mL, 16 mmol) was added in excess to a solution of **1** (0.83 g, 2.0 mmol) of in toluene (50 mL). The mixture was stirred for 5 h (50 °C) and then for 2 h at room temperature. After the solvent was removed, the residue was washed with cold pentane (3 × 7 mL) to yield **2** (0.96 g, 59 %). Single crystals suitable for X-ray diffraction analysis were obtained from toluene/hexane (5:1) at −26 °C. M.p. 212 °C. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ = 1.72 (s, 18 H; tBu), 6.44 (s, 1 H; CH), 6.91–7.40 (m, 10 H; Ph); ^{13}C NMR (125 MHz, C$_6$D$_6$): δ = 31.46 (s; Me), 33.38 (s; CMe$_3$), 102.9 (br; Al-C), 108.42 (s; CH), 174.54 (s; C-tBu), 108.31 (s; C-Ph) 125.35, 127.78, 128.31, 132.04 (s; Ph); MS(EI): m/z (%): 816 ([M^+] 100); IR: $\tilde{\nu}$ = 2143, 2129, 1596, 756, 691 cm^{-1}; elemental analysis (C H N) is correct for $C_{54}H_{58}Al_2N_4$.

3: $HC{\equiv}CSiMe_3$ (2.0 mL, 14 mmol) was added in excess to a solution of **1** (0.83 g, 2.0 mmol) in toluene (50 mL). The mixture was stirred under reflux for 1.5 h and then for 2 h at room temperature. The solvent was removed and **3** was isolated in hexane as white crystals at −26 °C (1.0 g, 51 %). Single crystals suitable for X-ray diffraction analysis were obtained from THF at −26 °C. M.p. 133 °C. ^{1}H NMR (200 MHz, C_6D_6): $\delta = 0.13$ (s, 18H; $\equiv CSiMe_3$), 0.44 (s, 9H; $SiMe_3$), 0.81 (s, 9H; C3-tBu), 1.56 (s, 9H; C1-tBu), 5.79 (s, 1H; C2-H), 7.42 (s, 1H; C44-H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = -0.08$ (s; Si1-Me$_3$), 0.29 (s; Si2(3)-Me$_3$), 32.91 (s; C10), 31.34 (s; C30), 30.79 (s; C31(32,33)), 29.52 (s; C11(12,13)), 103.80 (s; C44), 116.35 (s; Si2-C≡), 125.40 (br; Al-C≡), 141.80 (br; Al-C=), 134.62 (s; C2), 152.00 (s; C1), 163.08 (s; C3); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -21.51$ (s; Si2(3)), −5.74 (s; Si1); IR: $\tilde{\nu}$ = 3041, 2075, 1941, 1079, 955, 857, 618 cm^{-1}; MS(EI): m/z(%): 498 ([M^+], 20), 441 ([$M^+ - AlMe_2$], 100); elemental analysis (C H N) is correct for $C_{26}H_{47}AlN_2Si_3$.

Received: May 4, 2000 [Z 15078]

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[9] X-ray structure determination: The data were collected on a Stoe–Siemens–Huber four-circle instrument (−140 °C) for **2** and **3**, with graphite-monochromated Mo$_{K\alpha}$ radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined against F^2 on all data by full-matrix least-squares with SHELXS-97.[13] **2**: $C_{54}H_{58}Al_2N_4$, M_r = 817, monoclinic, space group $C2/c$, a = 22.079(4), b = 9.541(2), c = 23.734(5) Å, β = 96.60(3)°, V = 4966.20(17) Å^3, Z = 4, ρ_{calcd} = 1.093 Mg m^{-3}, crystal size: 0.6 × 0.4 × 0.2 mm^3, F(000) = 1744, μ(Mo$_{K\alpha}$) = 0.096 mm^{-1}. The total number of reflections measured was 3145 in the range $4.66 \leq 2\theta \leq 43.46°$, of which 2924 were unique, 2309 with $F > 4\sigma(F)$, 277 parameters. Final R indices: R_1 = 0.0487 ($I > 2\sigma(I)$) and wR_2 = 0.1125 (all data). Residual electron density, max./min. 253/−238 e nm^{-3}. **3**: $C_{26}H_{47}AlN_2Si_3 \cdot C_4H_8O$, M_r = 571, monoclinic, space group $P2_1/n$, a = 12.261(3), b = 16.424(3), c = 20.151(4) Å, β = 103.02(3)°, V = 3954(1) Å^3, Z = 4, ρ_{calcd} = 0.959 Mg m^{-3}, crystal size: 0.5 × 0.5 × 0.15 mm^3, F(000) = 1248, μ(Mo$_{K\alpha}$) = 0.163 mm^{-1}. The total number of reflections measured was 6909 in the range $4.34 \leq 2\theta \leq 49.46°$, of which 6650 were unique. 5289 with $F > 4\sigma(F)$, 277 parameters. Final R indices: R_1 = 0.0530 ($I > 2\sigma(I)$) and wR_2 = 0.1351 (all data). Residual electron density, max./min. 312/−326 e nm^{-3}. The THF molecule was modeled as threefold disordered. Owing to this disorder, the oxygen atom of THF could not be localized and was modeled as a CH$_2$ group. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-143738 (**2**) and CCDC-143739 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Ruthenium-Catalyzed Enyne Metathesis of Acetylenic Boronates: A Concise Route for the Construction of Cyclic 1,3-Dienylboronic Esters

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Since its inception in the late 1980s, the ring-closing metathesis (RCM) reaction of dienes has inspired a plethora of exciting studies.[1] In comparison, the enyne ring-closing metathesis reaction is less well documented. Most reports on this topic are confined to the assembly of compounds containing an unsubstituted or an alkyl-substituted 1,3-dienyl

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