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

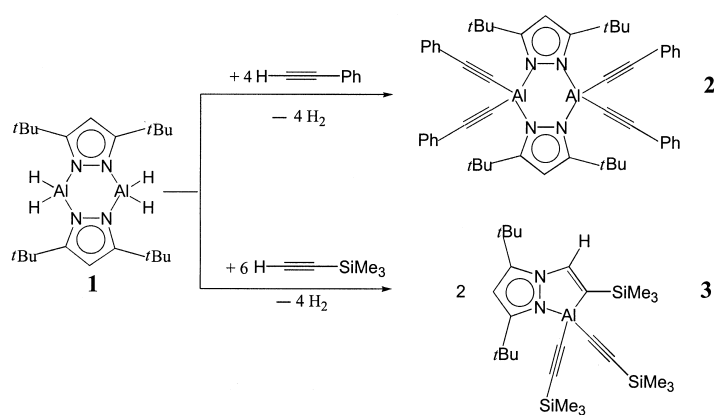
Wenjun Zheng, Nadia C. Mösch-Zanetti, Herbert W. Roesky,* Manuel Hewitt, Fanica Cimpoesu, Thomas R. Schneider, Andreas Stasch, and Jörg Prust

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 $\text{H}[\text{tBu}_2\text{pz}]$ (tBu_2pz = 3,5-di-*tert*-butylpyrazolate)^[6] and $\text{AlH}_3 \cdot \text{NMe}_3$ ^[7] in high yield.^[8]

Compound **2** is prepared from **1** and an excess of $\text{HC}\equiv\text{CPh}$ (Scheme 1). The X-ray structure analysis of **2** shows a dimeric species with some interesting features (Figure 1).^[9] Most



Scheme 1.

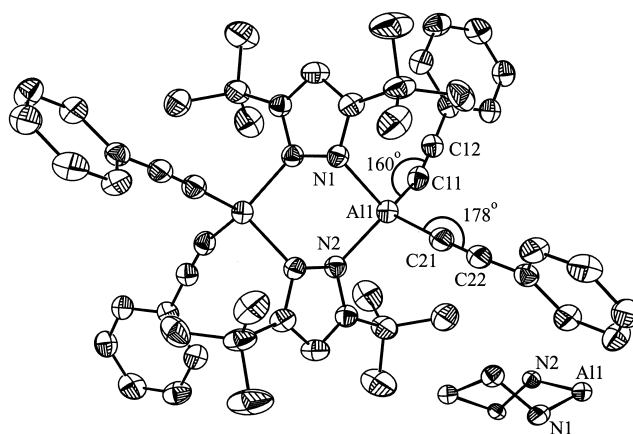


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: Al1–C11 1.929, Al1–C21 1.913(3), C11–C12 1.211(4), C21–C22 1.218(4); C12–C11–Al1 160.2(3), C22–C21–Al1 178.3(3), C21–Al1–C11 116.99(12), N2–Al1–N1 102.88(10). Bottom right: the twisted core of **2**.

surprisingly, the six-membered Al_2N_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 $\text{Al}-\text{C}\equiv\text{C}$ backbones from linearity ($\text{Al1}-\text{C11}-\text{C12}$ $160.2(3)^\circ$ vs. $\text{Al1}-\text{C21}-\text{C22}$ $178.3(3)^\circ$; the $\text{C11}-\text{C12}$ and $\text{C21}-\text{C22}$ bond lengths are 1.211(4) and 1.218(4) Å, respectively). Whereas some small angles in $\text{M}-\text{C}\equiv\text{C}$ units in transition metal complexes have been

[*] Prof. Dr. H. W. Roesky, Dipl.-Chem. W. Zheng, Dr. N. C. Mösch-Zanetti, M. Hewitt, Dr. F. Cimpoesu, Dr. T. R. Schneider, Dipl.-Chem. A. Stasch, Dipl.-Chem. J. Prust, Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, 37077 Göttingen (Germany), Fax: (+49) 551-39-3373, E-mail: hroesky@gwdg.de

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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.

Reaction of **1** with an excess of $\text{HC}\equiv\text{CSiMe}_3$ affords compound **3** (Scheme 1). The X-ray structure analysis of **3** reveals a mononuclear aluminum compound with an aluminum atom coordinated by the [*t*Bu₂-*N*-CH=C(SiMe₃)-pz] chelating unit and two $\text{C}\equiv\text{CSiMe}_3$ groups (Figure 3).^[9] The chelating unit consists of a pyrazolato ligand which has

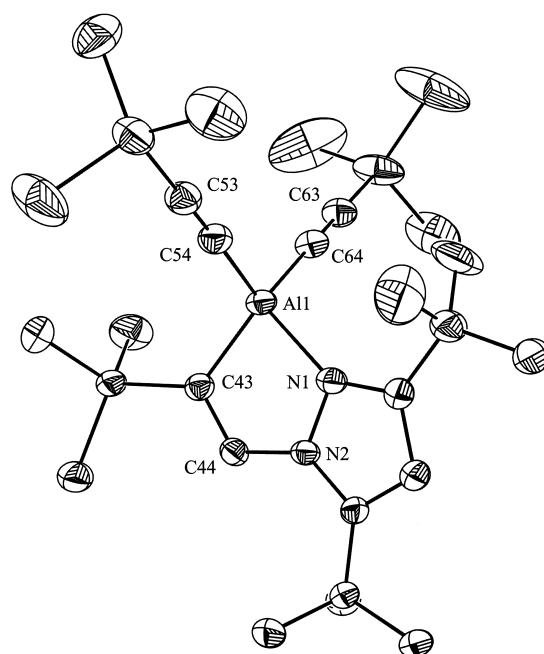


Figure 3. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: C44–C43 1.337(4), C53–C54 1.223(4); C54–Al1–C64 113.42(12), N1–Al1–C43 87.31(10), C53–C54–Al1 178.2(2).

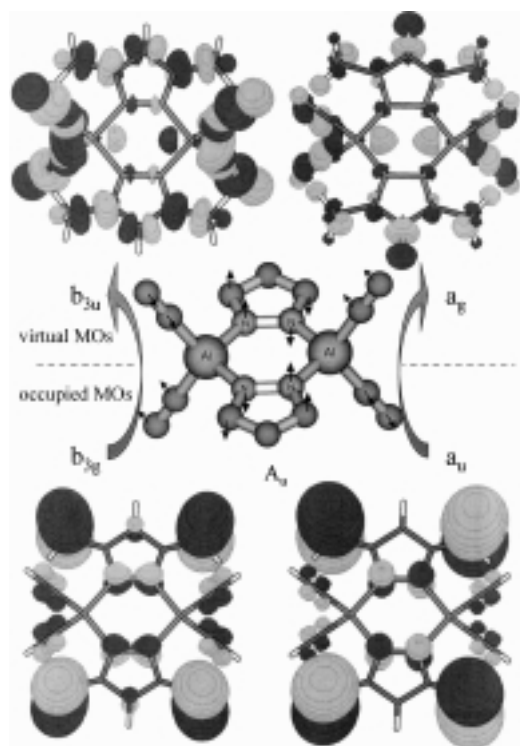


Figure 2. Two pairs of the transformed orbitals are shown, which are vibronically coupled through the normal coordinate of the A_u distortion. The notion of transformed orbitals refers to the states whose coupling leads to transition densities that concentrate the electron density flow associated with 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.

formally added to a $\text{C}\equiv\text{C}$ bond, thereby forming a five-membered metallacycle with the aluminum center. The two fused five-membered rings, AlN_2C_2 and pyrazolate, are close to coplanar. The $\text{C}\equiv\text{C}$ 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 $\text{Al}-\text{C}\equiv\text{C}$ bonds (178.2(2)° and 175.5(2)°) are in the normal range of other known aluminum acetylides.^[2a, 3b]

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: $\text{HC}\equiv\text{CPh}$ (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. ¹H NMR (200 MHz, C_6D_6): δ = 1.72 (s, 18H; *t*Bu), 6.44 (s, 1H; CH), 6.91–7.40 (m, 10H; Ph); ¹³C NMR (125 MHz, C_6D_6): δ = 31.46 (s; Me), 33.38 (s; CMe_3), 102.9 (br; Al–C), 108.42 (s; CH), 174.54 (s; C-*t*Bu), 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 $\text{C}_{34}\text{H}_{58}\text{Al}_2\text{N}_4$.

3: $\text{HC}\equiv\text{CSiMe}_3$ (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 . ^1H NMR (200 MHz, C_6D_6): δ = 0.13 (s, 18H; $\equiv\text{CSiMe}_3$), 0.44 (s, 9H; SiMe_3), 0.81 (s, 9H; C3-*t*Bu), 1.56 (s, 9H; C1-*t*Bu), 5.79 (s, 1H; C2-H), 7.42 (s, 1H; C44-H); ^{13}C NMR (125 MHz, C_6D_6): δ = -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 $\equiv$), 125.40 (br; Al-C $\equiv$), 141.80 (br; Al-C $\equiv$), 134.62 (s; C2), 152.00 (s; C1), 163.08 (s; C3); ^{29}Si NMR (99 MHz, C_6D_6): δ = -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 ($[M^+ - \text{AlMe}_2]$, 100); elemental analysis (C H N) is correct for $\text{C}_{26}\text{H}_{47}\text{AlN}_2\text{Si}_3$.

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total number of reflections measured was 6909 in the range $4.34 \leq 2\theta \leq 49.46^\circ$, 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. $312/-326 \text{ e nm}^{-3}$. 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 CB2 1EZ, 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

Johanne Renaud,* Claus-Dieter Graf, and Lukas Oberer

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

[*] Dr. J. Renaud, Dr. C.-D. Graf, L. Oberer^[†]
Novartis Pharma AG
K-136.3.25
4002 Basle (Switzerland)
Fax: (+41) 61-696-6071
E-mail: johanne.renaud@pharma.novartis.com

[†] NMR analyses.

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