orange flat needles, yield 52% based on V. The hydrolysis of pyrazinamide results in a higher final pH (≈6) in the synthesis of **3** than in **1** and **2** (≈4).

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[21] Single-crystal data were collected at 223 K for **1** (293 K for **2**,**3**) on a Siemens Smart-CCD diffractometer. Crystal data for **1**: tetragonal, space group $I4$, $a = b = 17.6831(7)$, $c = 12.4616(7)$ Å, $V = 3896.6(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.250$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 31.28$ cm^{-1}. For **2**: tetragonal, space group $I4$, $a = b = 17.671(1)$, $c = 12.268(1)$ Å, $V = 3831.0(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.287$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 34.16$ cm^{-1}. For **3**: monoclinic, space group Cc, $a = 12.4122(11)$, $b = 24.958(2)$, $c = 24.949(2)$ Å, $\beta = 90.102(2)^\circ$, $V = 7728.6(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.195$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 29.26$ cm^{-1}. $\lambda = 0.71073$ Å, graphite monochromator, crystal dimensions: **1**, 0.3 × 0.03 × 0.03 mm; **2**, 0.3 × 0.02 × 0.02 mm; **3**, 0.35 × 0.10 × 0.02 mm; unique reflections: **1**, 4455 ($R_{int} = 0.0485$); **2**, 3930 ($R_{int} = 0.1032$); **3**, 13544 ($R_{int} = 0.0548$). Empirical absorption corrections and extinction corrections are applied. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares by using the SHELXTL program. All non-hydrogen atoms except the oxygen atoms (Ow) of lattice water were refined anisotropically. The disordered Ow and H atoms were refined isotropically. The H atoms attached to Ow of the lattice and coordinated water molecules or the ammonium nitrogen atom were not located. Absolute structure parameter: 0.03(2) for **1**, 0.07(3) for **2**, and 0.56(3) for **3**. $(\Delta\rho)_{max,min}$: **1**, 1.157, −0.523 e Å^{-3}; **2**, 1.075, −0.675 e Å^{-3}; **3**, 1.461, −0.663 e Å^{-3}. Final R indices ($I > 2\sigma(I)$) ($R1$, $wR2$): **1**, 0.0424, 0.0833; **2**, 0.0678, 0.1111; **3**, 0.0517, 0.1171. GOF: **1**, 1.082; **2**, 1.055; **3**, 0.993. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147014 (**1**), CCDC-147015 (**2**), and CCDC-147016 (**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).

[22] Elemental analysis: **1**: Calculated for $C_{20}H_{12}Co_4N_8O_{25}V_6 \cdot 1.6\,H_2O$ (%): C 17.99, H 1.14, N 8.39, Co 17.67, V 22.91; found: C 18.50, H 1.14, N 8.41, Co 17.26, V 21.33; **2**: Calculated for $C_{20}H_{12}Ni_4N_8O_{25}V_6 \cdot 1.6\,H_2O$ (%): C 18.00, H 1.14, N 8.40, Ni 17.61, V 22.93; found: C 17.91, H 1.27, N 8.47, Ni 17.73, V 22.41; **3**: Calculated for $C_{40}H_{36}Co_8N_{18}O_{48}V_{10} \cdot 3\,H_2O$ (%): C 18.80, H 1.57, N 9.87, Co 18.47, V 19.95; found: C 18.66, H 1.63, N 9.80, Co 19.33, V 19.87.

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[HC{(CMe)(NAr)}$_2$]Al[(NSiMe$_3$)$_2$N$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$): The First Five-Membered AlN$_4$ Ring System**

Chunming Cui, Herbert W. Roesky,*
Hans-Georg Schmidt, and Mathias Noltemeyer

Dedicated to Professor Pierre Braunstein

Main group heterocycles have attracted much attention from the pharmaceutical, agrochemical, and material science communities.[1] Among the varieties of ring systems, tetrazoles are of current interest. The discovery of the antiallergic, antibiotic activities and the important roles in biological systems of tetrazoles has stimulated extensive research on their chemistry in recent years.[2] In contrast, very little is

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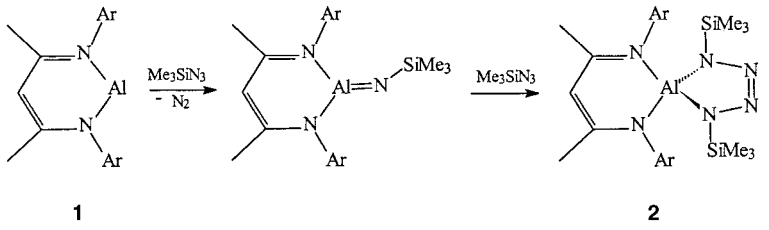
known about the other main group element analogues of tetrazoles. To the best of our knowledge only a few heavier Group 14 elements containing MN_4 (M = Si, Ge, Sn) cyclic compounds have been reported.[3] Similarly, for Group 13 elements, with the exception of boron,[4] metalloid-containing MN_4 (Al, Ga, In, Tl) cyclic tetrazoles are hitherto unknown. Structurally authenticated heterocycles of this type are limited to only a handful of carbon-containing CN_4 rings.[2]

In the course of our study on the chemistry of bulky β-diketoiminate aluminum compounds, we prepared the first stable monomeric Al^I compound $[HC\{(CMe)(NAr)\}_2]Al$ (**1**) (Ar = 2,6-*i*$Pr_2C_6H_3$).[5] Being interested in Al–N binary systems, we began to explore the reactivity of this compound towards a few azides. Herein we report on the reaction of **1** with Me_3SiN_3 and the first example of a structurally characterized Group 13 element containing tetrazole MN_4 ring system $[HC\{(CMe)(NAr)\}_2]Al[(NSiMe_3)_2N_2]$ (**2**).

The aluminum-containing tetrazole heterocycle **2** was synthesized by the reaction of the monomeric Al^I compound **1** with two equivalents of Me_3SiN_3 from low to room temperature (Scheme 1). The reaction of $[\{Cp^*Al\}_4]$ ($Cp^* = C_5Me_5$) with various organic azides has been reported to yield four-membered Al_2N_2 ring systems at elevated temperatures.[6] The higher reactivity of **1** compared to $[\{Cp^*Al\}_4]$ toward the azide may be attributed to the monomeric nature of **1** even at low temperature. The formation of the cyclic aluminum-containing tetrazole **2** is particularly interesting since it has been reported that the heavier Group 14 elements containing cyclic tetrazoles are prepared by a [2+3] cyclo-



Scheme 1. Synthesis of **2**. Ar = 2,6-*i*$Pr_2C_6H_3$.

addition of the $R_2M{=}NR'$ (M = Si, Sn; R, R′ = organic group) unit with organic azides.[3] Similarly we therefore assume that the reaction of **1** with Me_3SiN_3 proceeds via the $[HC\{(CMe)(NAr)\}_2]Al{=}NSiMe_3$ intermediate, although stable compounds containing an Al=N unit have not yet been reported (Scheme 1). It is noted that even when one equivalent of Me_3SiN_3 was employed, the only isolated product is **2** and the unreacted **1** could be detected, indicating that the $[HC\{(CMe)(NAr)\}_2]Al{=}NSiMe_3$ intermediate is highly reactive. No dimerization of $[HC\{(CMe)(NAr)\}_2]Al{=}NSiMe_3$ was observed, presumably due to the bulky chelating β-diketoiminate ligand preventing association.

Compound **2** was characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, EI mass spectrometry, and elemental analysis. The EI mass spectrum shows a molecular ion which is consistent with the formulation of **2**. The NMR spectra all give two distinct singlets for the $SiMe_3$ groups, indicating the two groups in different environments. This is also reflected in the ^1H NMR pattern of the β-diketoiminate ligand, in which two sets of signals for γ-CH and four doublets for C*H*Me_2 groups are observed. In order to confirm the bonding in the AlN_4 ring system, an X-ray single-crystal analysis was undertaken using yellow crystals of **2** obtained from toluene at −30 °C (Figure 1). Compound **2** crystallizes in the monoclinic system, space group $P2_1/n$.[7] The aluminum atom is coordinated by

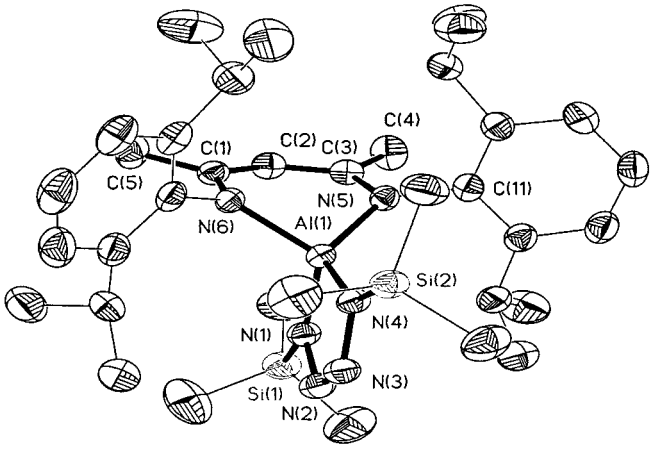


Figure 1. Molecular structure of **2** in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Al(1)-N(1) 185.1(2), Al(1)-N(4) 181.52(15), Al(1)-N(5) 189.6(2), Al(1)-N(6) 189.97(14), N(1)-N(2) 141.4(2), N(2)-N(3) 126.3(2), N(3)-N(4) 141.4(2), Si(1)-N(1) 174.9(2); N(1)-Al(1)-N(4) 87.15(7), N(5)-Al(1)-N(6) 96.50(6), N(1)-Al(1)-N(5) 117.01(7), N(4)-Al(1)-N(6) 117.70(7), N(2)-N(1)-Al(1) 109.10(11), N(2)-N(1)-Si(1) 108.20(11), Si(1)-N(1)-Al(1) 142.66(9), N(3)-N(2)-N(1) 116.68(15), N(2)-N(3)-N(4) 116.44(14).

four nitrogen atoms and connects two fused rings with a distorted tetrahedral arrangement. The Al(1)–N(5) (189.6(2) pm) and Al(1)–N(6) (189.97(14) pm) distances fall within the range of those in β-diketoiminate aluminum derivatives.[8] The Al(1)–N(4) distance (181.52(15) pm) is shorter (ca 3.6 pm) than that of Al(1)–N(1) (185.1(2) pm), which is in line with the NMR spectral data for the $SiMe_3$ groups, indicating the solid-state structure of **2** is maintained in solution. Similar short Al–N bond lengths have been found only in three-coordinate aluminum amide complexes[9] and a few four-coordinate aluminum amide dihalides.[10] However they are unusual for a very crowded molecule such as **2**. The shortening of the Al–N bond length and the N(1)-Al(1)-N(4) angle (87.15(7)°) are an indication of the increased ionic interactions between the Al center and the N_4 unit. The N(2)–N(3) bond length (126.3(2) pm) is consistent with a N=N double bond. The N(1)–N(2) and N(3)–N(4) (141.4(2) pm) bond lengths are slightly shorter than a N–N single bond (ca 150 pm).

Interestingly, the AlN_4 five-membered ring is essentially planar and the geometries at N(1) and N(4) are both trigonal planar (sums of angles 360.0° and 359.7°, respectively). This planar arrangement of the AlN_4 ring may be comparable to Group 13 element diazabutadiene complexes which feature planar C_2N_2M (M = B, Ga) five-membered rings. In the latter case, a 6 π-electron system for the C_2N_2M ring is suggested to explain the bonding situation of the diazabutadiene derivatives.[11]

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In summary, we have prepared and structurally characterized a five-membered AlN_4 ring compound. Evidently, compound **2** represents the first structurally characterized Group 13 element MN_4 system, although various binary M–N (M = Group 13 element) rings are known which show unique structural features.[12] The synthesis of **2** under mild conditions indicates that **1** is very reactive toward organic azides. Stimulated by this result, we are investigating the reaction of **1** with more bulky organic azides in an effort to prepare stable compounds containing Al=N double-bond systems.

Experimental Section

All manipulations were carried out under an argon atmosphere by using Schlenk line techniques.

2: Neat Me_3SiN_3 (0.23 g, 2 mmol) was added to a solution of **1** (0.44 g, 1 mmol) in toluene (20 mL) at −78 °C leading to an immediate color change from red to orange-yellow. The mixture was allowed to warm to room temperature, and stirred for 1 h. The yellow solution was concentrated (ca. 5 mL) and stored at −30 °C overnight to give yellow crystals of **2** (0.37 g, 58 %). M.p. 130 °C (decomp); ^{1}H NMR (C_6D_6): $\delta = 7.08$ (m, 6H; Ph), 5.04 (s, 1H; γ-CH), 3.48 (sept, 2H, $J = 6.8$ Hz; C*H*Me$_2$), 3.02 (sept, 2H, $J = 6.8$ Hz; C*H*Me$_2$), 1.52 (s, 6H; Me), 1.30 (d, 6H; CH*Me*$_2$), 1.20 (d, 6H; CH*Me*$_2$), 1.14 (d, 6H; CH*Me*$_2$), 1.02 (d, 6H; CH*Me*$_2$), 0.48 (s, 9H; $SiMe_3$), −0.14 (s, 9H; $SiMe_3$); ^{13}C NMR (C_6D_6): $\delta = 172.49$ (CN), 145.78, 142.68, 140.11, 125.67, 124.28 (Ph), 101.08 (γ-C), 28.91, 28.83, 25.22, 25.20 (CHMe$_2$), 24.07 (Me), 1.64, 0.62 ($SiMe_3$); ^{29}Si NMR (C_6D_6): $\delta = 4.89$, 3.08 ($SiMe_3$); EI-MS: *m*/*z* (%): 646 (20, [M^+]), 631 (100, [M^+ − Me]).

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[7] The data were collected on a Stoe-Siemens four-circle diffractometer using $Mo_{K\alpha}$ ($\lambda = 71.073$ pm) radiation. The structure was solved by direct methods (SHELXS-96)[13] and refined against F^2 using SHELXL-97.[14] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the refinement in geometrically ideal positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149345. 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). Crystallographic data for **2**: $C_{35}H_{59}AlN_6Si_2$, $M_r = 647.04$, monoclinic, $P2_1/n$, $T = 200(2)$ K, $a = 1245.71(11)$, $b = 2203.7(6)$, $c = 1413.6(2)$ pm, $\beta = 91.358(11)^\circ$, $V = 3.8793(12)$ nm^3, $Z = 4$, $\rho_{calcd} = 1.108$ g cm^{-3}; crystal size: $0.70 \times 0.60 \times 0.20$ mm, $7.02 \le 2\theta \le 50.1^\circ$; of the 10122 reflections collected, 6843 were independent and were used for the structure refinement of 413 parameters. The *R* values are $R1 = 0.0436$, $wR2 = 0.1110$ ($I > 2\sigma(I)$) and $R1 = 0.0511$, $wR2 = 0.1201$ (all data); min./max. residual electron density: 320/−256 e nm^{-3}.

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Synthesis of Stable Organo(bis-silanetriols): X-Ray Powder Structure of 1,4-Bis(trihydroxysilyl)benzene**

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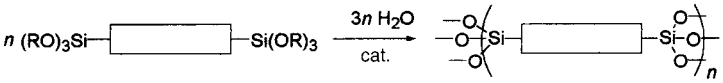
In the course of our work concerning nanostructured hybrid organic–inorganic materials,[1] we have been interested in finding an alternative route to the commonly used hydrolytic polycondensation (the sol–gel process).[2] This general method permits access to materials through a procedure that is very convenient from a practical point of view (Scheme 1). Moreover it allows easy processing of the compounds obtained during the sol step. However, the mechanism is highly complex since the polysubstitutions and polycondensations are concurrent with other reactions, and many points of this process are not well understood.[3] For these reasons we have examined the possibility of preparing and isolating stable silanetriols that contain at least two $Si(OH)_3$ groups in the



Scheme 1. The hydrolytic polycondensation process. The rectangle represents the bridging organo group.

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