A Polyhedral Aluminum Compound with an $Al_4C_4N_4$ Framework**

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Dedicated to Professor Philipp Gütlich

Recently the oligomeric and polyhedral compounds of aluminum containing Al–N and Al–C cores have attracted considerable interest following the preparation of a few three-coordinate iminoalanes[1] and the determination of the structures of carbaalanes.[2] Heteroatom-containing organoaluminum cage compounds[3] are potential precursors for various applications such as catalysts, reagents, and for chemical vapor deposition,[3a, 4, 5] as well as being of theoretical importance.[6] Although the formation of iminoalanes and carbaalanes is now almost understood,[1–3] compounds containing an $Al_nC_nN_n$ framework ($n > 2$) are still unknown.[7] We figured that such species should exhibit some interesting features. Herein we report the structure of the polyhedron **1** and the synthesis of the bridging compound with bulky pyrazolato ligands **2** ($t\mathrm{Bu_2pz}$ = 3,5-di-*tert*-butylpyrazolato).

$[\{(\mu_3\text{-AlH})(\mu_3\text{-CH}_2\text{N}t\text{Bu})\}_4]$ **1**

$[(\mu\text{-AlH})_2(\mu\text{-CH}_2\text{N}t\text{Bu})(\eta^1\text{-}\eta^1\text{-}t\text{Bu}_2\text{pz})_2]$ **2**

Treatment of $H_3Al \cdot NMe_3$[8] with one equivalent of CN*t*Bu in refluxing toluene smoothly gives **1** in 75% yield. Compound **1** is well soluble in toluene and readily crystallizes.

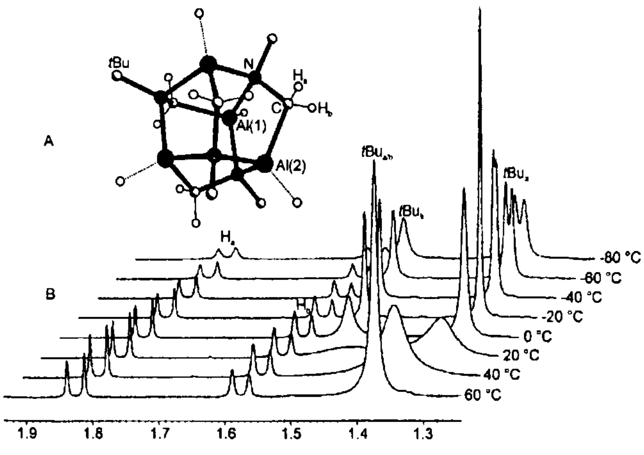

Figure 1. A) Molecular structure of **1** (*t*Bu groups are represented by C atoms). Selected bond lengths [Å] and angles [°]: Al(1)-N(1) 1.968(2), Al(1)-N(2) 1.9693(19), Al(1)-C(4) 1.992(2), N(1)-C(1) 1.529(3); N(1)-Al(1)-N(2) 104.44(8), N(1)-Al(1)-C(4) 107.09(9), N(2)-Al(1)-C(4) 98.60(9), C(1)-N(1)-Al(1) 105.42(13), C(1)-N(1)-Al(2) 106.33(13), Al(1)-N(1)-Al(2) 102.49(8), N(1)-C(1)-Al(3) 109.95(14), N(2)-C(2)-Al(2) 110.07(14). B) Variable-temperature ^{1}H NMR spectra of **1** in [D$_8$]toluene.

The X-ray structure analysis of **1** reveals a remarkable $Al_4C_4N_4$ cage configuration in which the C atoms adopt *exo* positions and thus may be formally viewed as inserting into four Al–N bonds of an Al_4N_4 cube (Figure 1 A).[9] It is surprising that a significant difference in the arrangement of the atoms within the cage skeleton of **1** is found in comparison with those of other known aluminum compounds with a 12-membered core ($(AlE)_6$, E = N,[3d–g] O,[10a] S,[10b] P,[10c] As[10d]) which exclusively adopt the form of a hexagonal-prismatic array. The core of **1** consists of six faces formed by two boat-shaped six-membered $Al_2C_2N_2$ rings and four puckered five-membered Al_2CN_2 rings. The two six-membered heterocycles are positioned crosswise to each other, and the four five-membered rings are arranged between the two. Each atom of the core participates in two different types of ring systems, and the geometries of both Al and N atoms are slightly distorted tetrahedral. Four Al atoms have a common center to which the distance of each Al atom is 1.95(1) Å. The Al–C bond lengths (1.979(2) to 1.992(2) Å) are all within the expected range in comparison with the carbaalanes (Al–C 1.948(3)–2.212(2) Å),[2] whereas the Al–N bond lengths (1.966(2) to 1.978(2) Å) are slightly longer than those in iminoalanes with the 12-membered Al_6N_6 core structure (e.g. Al–N 1.898(3)–1.955(3) Å in $(\mathrm{HAlN}i\mathrm{Pr})_6$).[3e] The molecular symmetry is quite close to S_4. No critical intermolecular contacts were observed since the closest Al···Al distance (e.g. Al(1)···Al(2)) is more than 3.073 Å.

The mass spectrometry data and elemental analysis data are in complete agreement with the formula of **1**. The ^{27}Al NMR spectrum shows only one resonance ($\delta = 148.5$), which indicates four-coordinate Al atoms.[11] However, the ^{1}H NMR (C_6D_6, RT) spectrum displays a quite broad resonance ($\delta = 1.4$, $W_{1/2} = 60$ Hz, 36 H) and two sets of doublets ($\delta = 1.61$ and 1.85, $^2J = 12.65$ Hz, 8 H; ratio 1:1). The resonances of the ^{13}C NMR spectrum are too broad to be distinguished. Broad resonances in the ^{1}H and ^{13}C NMR spectra suggest that **1** is involved in dynamic processes in solution at room temperature.[12] Preliminary information regarding these processes was elucidated from the variable-temperature ^{1}H NMR spectrum in [D$_8$]toluene (Figure 1 B). At 60 °C the spectrum clearly shows one sharp resonance at $\delta = 1.37$ (36 H) indicating fast rotation of the *t*Bu groups. This signal (*t*Bu$_{a/b}$) coalesces at about 10 °C, and below this temperature the exchange is slow as demonstrated by the two new shoulders ($\delta = 1.33$ (*t*Bu$_a$) and 1.50 (*t*Bu$_b$), ratio 2:1 (−20 °C)). Surprisingly, the *t*Bu$_a$ signal further splits into two sharp singlets below −40 °C (the ratio is close to 1:1). In any case the integration of the resonances (H_a:H_b:*t*Bu$_b$:*t*Bu$_a$) are strictly in the ratio of 1:1:3:6. Such dynamic behavior is unprecedented and it is currently not clear whether three sharp resonances (3:3:3) of the *t*Bu$_{a/b}$ group below −40 °C really correspond to the three frozen non-

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equivalent methyl groups or indicate a dissociation of the molecules in solution. However, the two sets of coupled resonances may be tentatively assigned to the two unequal hydrogen atoms (H_aH_b) of the core of **1** due to steric effects. The IR spectrum shows two strong bands in the range of Al–H stretching frequencies (1831 and 1858 cm^{-1}), which implies terminal Al–H bonds in the solid state.[13]

Further insight into the molecular structure of **1** is gained by ab initio calculations[14] on the model compound $[\{(\mu_3\text{-AlH})(\mu_3\text{-CH}_2\text{NMe})\}_4]$ (**1a**)[15] with molecular symmetry S_4.

A suggestion of the bonding situation in **1** (**1a**) is offered by the representation of the Laplacian of the electronic density.[16] The negative zones (dark areas in Figure 2) display the tendencies for charge accumulation, for example in the terminal hydrides and the σ skeleton of the embedded CH_2NMe fragments. The positive Laplacian shows the depletion of the electron density around the positively charged aluminum atoms.

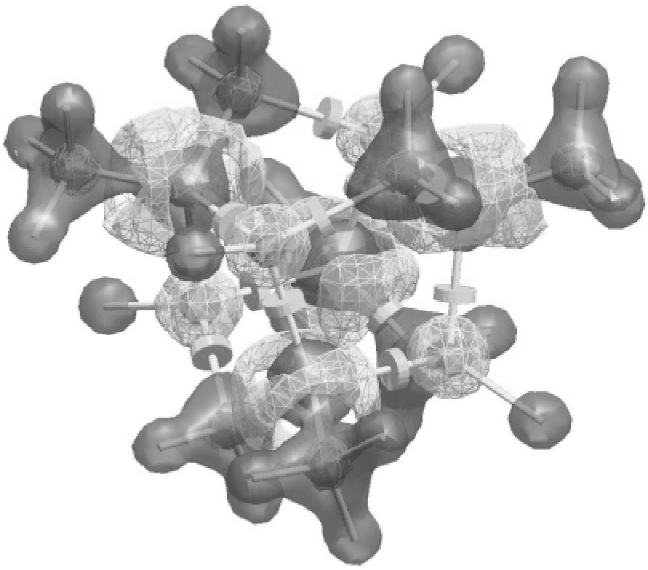

Figure 2. The isosurfaces (at the 0.2 e$Å^{-3}$ value) for the Laplacian of the electron density in $[\{(\mu_3\text{-AlH})(\mu_3\text{-CH}_2\text{NMe})\}_4]$ (**1a**). The dark solid surface corresponds to density accumulation (negative Laplacian) and illustrates the lone pairs at C and N. The zones with depletion of electron density (e.g. metal centers) are depicted with the light-colored mesh. The positions of the (3, −1) bond critical points are highlighted with circular sectors.

The Al–N and Al–C contacts reveal accumulated charge on N and C with the lone pairs of nonmetals directed toward the metal atom. The Laplacian analysis shows that the CH_2NMe fragments can be regarded as μ_3-coordinating ligands. The (3, −1) bond critical points are placed closer to the electropositive partner, as is clearly seen for the Al–C and Al–N bonds. Moreover the analysis reveals the (3, +1) critical points (cycle) on all the faces of the cluster and a (3, +3) critical point in the center of gravity. This is specific for a closed cage. The small ellipticities of the Hessian eigenvalues of the Al–C, Al–N, and C–N (3, −1) critical points show the σ nature of the bonds.

The coordination-type of the bonding is evident from the results of natural bond orbital (NBO) analysis,[17] which shows that in both types of Al–N bonds the content of nitrogen AOs is ~92%, which corresponds to a ligand-field regime. The Al–C bonds contain 85% nonmetal character. The composition of the NBOs of the Al–N bonds shows sp^3-like hybrids in the bonding with s character ranging from 22 to 25% (the content of d orbitals is low ~1.5%). The Al–C bonds reveal 32.8% s and 67.2% p participation for the carbon AOs. However, the apparent sp^2 character of carbon does not correspond to the π bonding. The lower p content in the natural hybrids of the C atom is only the counterpart of higher p character in the C–N bond (79.3%).

The dynamic NMR experiment detected changes in the resonance for the *t*Bu groups with temperature. This phenomenon can be assigned to the promotion of rotational disorder around the C–N bond of the terminal fragments. The differentiation of protons probably takes place by through-space dipolar interactions of the corresponding *t*Bu and CH_2 groups.

Reaction of the dimeric aluminum dihydride $[\{(\eta^1\text{-}\eta^1\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})\text{H}_2\}_2]$[18a] and CN*t*Bu at room temperature leads to the formation of **2** in 91% yield. However, a further reaction of **2** using an excess of CN*t*Bu was not observed at room temperature.

The ^1H NMR spectrum of **2** displays three different sharp resonances for the *t*Bu groups ($\delta = 1.39$, 1.46, and 1.52, ratio 2:1:2) indicating the asymmetric nature of the molecule. However, the resonance in the ^{27}Al NMR spectrum appears too broad to be observed. The X-ray structure analysis of **2** reveals a structure with two Al_2CN_3 rings and one Al_2N_4 heterocycle (Figure 3).[9] To our surprise the Al(1)–N(5) bond length (1.778(2) Å) is significantly shorter than those in comparable iminoalanes with four-coordinate aluminum atoms (1.898(3) – 1.955(3) Å)[3e] and even shorter than those in compounds with three-coordinate aluminum atoms (Al–N 1.804(av) – 1.824 Å),[1] whereas the other Al–N bond lengths

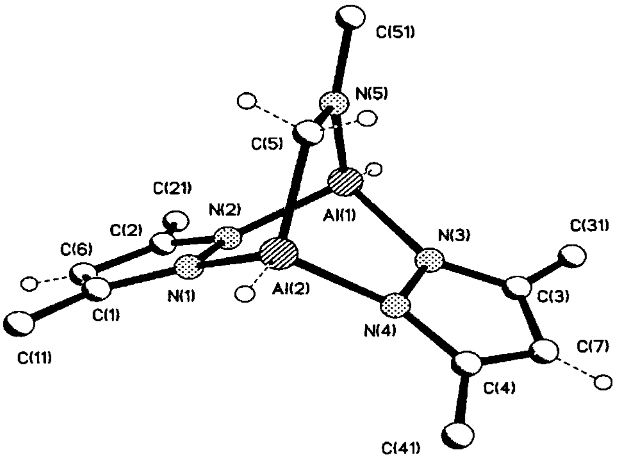

Figure 3. Molecular structure of **2** (C(11, 21, 31, 41, 51) represent *t*Bu groups). Selected bond lengths [Å] and angles [°]: Al(1)-N(5) 1.778(2), Al(1)-N(2) 1.9698(18), Al(2)-N(4) 1.9335(18); N(2)-Al(1)-N(3) 99.38(8), N(1)-Al(2)-N(4) 99.87(8), Al(2)-C(5)-N(5) 118.43(15), Al(1)-N(5)-C(5) 110.59(14), N(1)-Al(2)-C(5) 102.54(9), N(2)-Al(1)-N(5) 106.73(9).

of **2** fall in the expected range (1.9265(19) – 1.9698(18) Å). The Al(2)–C(5) distance (1.966(2) Å) is in accordance with those in $[\{(\eta^1\text{-}\eta^1\text{-}t\mathrm{Bu_2pz})(\mu\text{-Al})\mathrm{Me_2}\}_2]$ (Al–C 1.962(2) Å).[18b]

In summary, we have reported the preparation of the polyhedron aluminum compound **1** and the dinuclear aluminum species **2** by hydroalumination of CN*t*Bu. The $\mathrm{Al_4C_4N_4}$ core of **1** is unique and thus can be considered as a fused carbaaminoalane. The exact mechanism for the formation of **1** and **2** is unknown, but probably an initial donor – acceptor intermediate is involved, in which the isocyanide carbon coordinates to the aluminum center followed by hydrogen migration from aluminum to carbon to yield the $\mathrm{CH_2}$ moiety.[7]

Experimental Section

1: CN*t*Bu (1.4 mL, 12.4 mmol) was added at room temperature by syringe to a solution of $\mathrm{H_3Al \cdot NMe_3}$[8] (15.0 mL, 0.8 M solution in toluene, 12.0 mmol) in toluene (30 mL). The solution was refluxed for 0.5 h and then the solvent from the resulting red solution was removed under reduced pressure. The resulting residue was dried for 3 h in vacuo and then dissolved in warm toluene (10 mL) to afford colorless crystals within 2 h at −26 °C (1.02 g, 75 %). M.p. 261 °C; ^{1}H NMR ($\mathrm{C_6D_6}$, 500 MHz): $\delta = 1.4$ (br ($W_{1/2} = 60$ Hz), 36 H; *t*Bu), 1.61 (d, $^2J(\mathrm{H_a,H_b}) = 12.65$ Hz, 4 H; Al-CH$_\mathrm{b}$), 1.85 (d, $^2J(\mathrm{H_b,H_a}) = 12.65$ Hz, 4 H; Al-CH$_\mathrm{a}$), 4.3 (v br ($W_{1/2} = 550$ Hz), 4 H; Al-H); ^{13}C NMR ([D$_8$]toluene, 125 MHz, 90 °C): $\delta = 27.6$ (s, *C*H$_3$), 33.0 (br Al–*C*), 57.5 (s, N–*C*(CH$_3$)$_3$); ^{27}Al NMR($\mathrm{C_6D_6}$, 65 MHz): $\delta = 148.5$(s); IR (Nujol mull): $\tilde{\nu}_{\mathrm{Al-H}} = 1831, 1858$ cm^{-1}; MS(EI): *m/z* (%): 451 ([$M^+ - 1$], 1), 395 ([$M^+ - t$Bu], 100); elemental analysis (%) calcd for $\mathrm{C_{20}H_{48}Al_4N_4}$: C 53.09, H 10.62, N 12.39; found: C 52.86, H 10.54, N 11.92. Single crystals suitable for X-ray diffraction analysis were obtained from toluene at room temperature. The thermogravimetric analysis of **1** shows a complete conversion into AlN in the temperature range of 350 to 400 °C.

2: CN*t*Bu (0.24 mL, 2.1 mmol) was added at room temperature by syringe to a suspension of $[\{(\eta^1\text{-}\eta^1\text{-}t\mathrm{Bu_2pz})(\mu\text{-Al})\mathrm{H_2}\}_2]$[18a](0.83 g, 2.0 mmol) in hexane (50 mL). After the mixture had been stirred for 3 h, the solvent of the clear solution was removed under reduced pressure to afford **2** (0.91 g, 91 %) as a pure white solid. M.p. 176 °C; ^{1}H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta = 1.39$ (s, 18 H; C(11,41)CH$_3$), 1.46 (s, 9 H; C(51)CH$_3$), 1.52 (s, 18 H; C(21,31)CH$_3$), 6.08 (s, 2 H; C(6,7)H), 2.30 (s, 2 H; NC–H); ^{13}C NMR ($\mathrm{C_6D_6}$, 125 MHz): $\delta = 28.5$ (br Al–*C*(5)), 30.5 (s, C(51)*C*), 31.1 (s, C(2,3)C–*C*H$_3$), 31.0 (s, C(1,4)C–*C*H$_3$), 32.6(s, C(2,3)*C*), 32.3(s, C(1,4)*C*), 53.2 (*C*(51)), 102.0(s, *C*(6,7)), 163.8(s, *C*(1,4)), 165.2 (s, *C*(2,3)); IR (Nujol mull): $\tilde{\nu}_{\mathrm{Al-H}} = 1887, 1918$ cm^{-1}; MS(EI): *m/z* (%): 498 ([$M^+ - 1$], 10), 442 ([$M^+ - t$Bu], 100); elemental analysis (%) calcd for $\mathrm{C_{27}H_{51}Al_2N_5}$: C 51.20, H 7.73, N 7.47; found: C 50.51, H 7.58, N 7.23. Single crystals suitable for X-ray diffraction analysis were obtained from Et$_2$O at −26 °C.

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Anion-Templated Syntheses of Rhombohedral Silver–Alkynyl Cage Compounds

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The interest in metal alkynyl complexes stems not only from their range of organometallic transformations, but also from their flexible structural features.[1] The linear and rigid arrangement of atoms in these compounds makes them attractive building blocks for a wide range of complex architectures.[2, 3] The alkynyl moiety has a flexible coordination environment, being able to form metal–alkynyl σ and π bonds.[4] Alkynyl complexes of the coinage metals are of particular interest since these metals can display additional noncovalent (metallophilic) M⋯M interactions,[5] which provide an extra degree of complexity. These metallophilic interactions are well-established for gold(I) complexes,[6] but have not been as widely studied for silver(I)[7] and copper(I).[8]

Alkynyl complexes of the coinage metals tend to form polymeric materials.[9] A potential route to oligomeric species (e.g., macrocyclic and cage-type structures) rather than polymeric products could involve the use of templating agents.[10] Most templating agents are cationic or neutral, but recently increasing interest has focused on templating anions.[11, 12]

The synthesis and novel structure of the gold(I) catenane [{[Au(C≡C*t*Bu)]$_6$}$_2$][13] stimulated us to carry out similar studies with silver(I). Here we report the remarkable anion-templated syntheses of silver–alkynyl cage-type compounds with general formula [Ag$_{14}$(C≡C*t*Bu)$_{12}$X]Y (X = Cl, Br; Y = OH, BF$_4$).

When a solution of AgBF$_4$ in THF is treated with a mixture of *t*BuC≡CH and NEt$_3$ in THF, a white precipitate is obtained. On the basis of IR spectroscopy, FAB$^+$ mass spectrometry, and elemental analyses, this solid was formulated as polymeric [Ag(C≡C*t*Bu)]$_n$ (**1**).[14] To establish the structure of **1**, attempts were made to recrystallize it. Although a wide variety of common solvents (THF, acetone, chloroform, dichloromethane, ethanol, methanol, toluene, hexane) were tried, **1** was found to dissolve only in chloroform. Addition of diethyl ether to this solution gave a white precipitate **2**, and the fact that this could then be redissolved, not only in chloroform, but also in other solvents such as acetone, ethanol, and THF (in which **1** is insoluble), suggested that a chemical modification had occurred. Crystals of this compound were obtained by slow evaporation of an ethanolic solution.

A single-crystal X-ray analysis[15, 16] showed **2** to be the novel silver cage compound [Ag$_{14}$(C≡C*t*Bu)$_{12}$Cl]OH (Figure 1). The cage comprises fourteen silver atoms and twelve *tert*-butylethynyl ligands, and has a chloride anion at its center. The silver atoms are arranged so as to form a near-regular rhombic dodecahedron having crystallographic S_6 symmetry and molecular O_h symmetry, with Ag⋯Ag distances for the "edges" in the range of 2.953(2)–2.986(2) Å. These distances are comparable to those observed, for example, in the silver double salts reported by Mak et al. and attributed to argentophilic Ag⋯Ag interactions.[17] The cage contains three crystallographically unique silver centers (labeled 1, 2, and 3 in Figure 1); six of these (of type 2) can be envisaged as forming an octahedron (with the anion position at its center) which interpenetrates a cubic array made up of silver atoms of types 1 and 3 such that each silver atom of the "cube" caps a trigonal face of the octahedron. The silver atoms of the

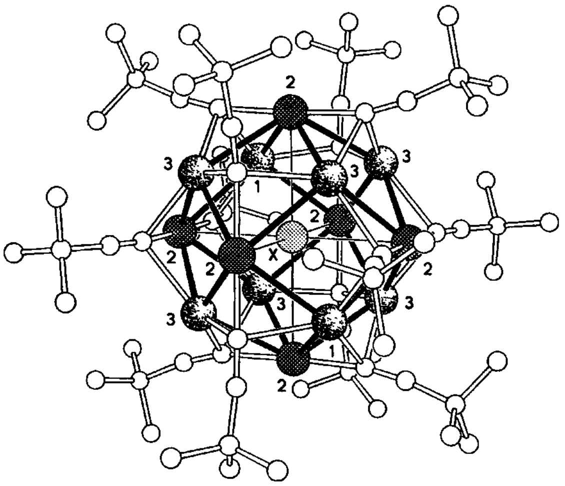

Figure 1. The structure of the silver cage complexes **2** (X = Cl) and **4** (X = Br), showing the rhombic dodecahedron of silver atoms (solid bonds) and the encapsulation of a halide anion at the center of an octahedron of type 2 silver atoms. Silver atoms of types 1 and 3 cap the faces of this octahedron and define a cubic array.

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