

Hydroalumination of Nitriles and Isonitriles

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Hydroalumination of $\text{H}_5\text{C}_6\text{-C}\equiv\text{N}$ with di(*tert*-butyl)aluminum hydride **1** or the corresponding diethyl compound **2** yielded the products $t\text{Bu}_2\text{Al-N}=\text{C}(\text{C}_6\text{H}_5)\text{H}$ **3** and $\text{Et}_2\text{Al-N}=\text{C}(\text{C}_6\text{H}_5)\text{H}$ **4**, respectively, both of which form dimers possessing Al_2N_2 heterocycles with two exocyclic $\text{C}=\text{N}$ double bonds. NMR spectroscopic data indicate the occurrence of *cis/trans* isomers in solutions of compound **4**. The dimerization of the imide *via* Al-N interactions was prevented by employing the hydride $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{AlH}$ **6** bearing the bulky bis(trimethylsilyl)methyl substituents. Its reaction with benzonitrile yielded the compound $\text{R}_2\text{Al-N}=\text{C}(\text{C}_6\text{H}_5)\text{H}(\text{N}\equiv\text{C-C}_6\text{H}_5)$ **7** [$\text{R} = \text{CH}(\text{SiMe}_3)_2$], in which the coordinative saturation of the aluminum atoms was achieved by adduct formation with one molecule of the starting nitrile. In these cases the $\text{C}\equiv\text{N}$ triple bond inserted completely into the Al-H bond of the hydride. In contrast, the reaction of *tert*-butyl isonitrile afforded the product $t\text{Bu}_2\text{Al-C}(\text{H})=\text{N-C}_6\text{H}_5$ **8** by the insertion of its terminal carbon atom into the Al-H bond. Hence, it has a geminal arrangement of the aluminum and hydrogen atoms. Dimerization of **8** yielded a six-membered heterocycle. Hydroalumination does not occur upon treatment of the hydride **1** with trimethylsilylnitrile. Instead, the Si-CN bond was cleaved, and the aluminum cyanide $(t\text{Bu}_2\text{Al-C}\equiv\text{N})_4$ **9** was isolated in a high yield.

Key words: Aluminum, Hydroalumination, Nitriles, Isonitriles

Introduction

The addition of Al-H bonds to $\text{C}=\text{C}$ double or $\text{C}\equiv\text{C}$ triple bonds (hydroalumination) is a well-known method for the reduction of unsaturated organic compounds [1]. Usually, the organoaluminum intermediates were not isolated, but hydrolyzed *in situ* by the treatment of the reaction mixture with an excess of water to finally isolate the corresponding hydrocarbons. Thus, information from literature concerning the true structures of these aluminum compounds is rather limited and in some cases misleading. In some recent investigations we were able to isolate and completely characterize the organoaluminum products of the reactions between dialkylaluminum hydrides and organic alkynes [2]. Crystal structure determinations reveal the selective *cis*-addition of the Al-H bonds, and vinylaluminum compounds could be isolated in high yields. Aluminum alkynides afforded novel products containing clusters formed by aluminum and carbon atoms

(carbaalanes) upon hydroalumination and release of trialkylaluminum derivatives [3, 4].

Hydroalumination of heteronuclear double or triple bonds was reported to a lesser extent. Nitriles reacted with di(isobutyl)aluminum hydride by the formation of imines $[i\text{Bu}_2\text{Al-N}=\text{C}(\text{H})\text{R}]_2$, which form dimers possessing Al_2N_2 heterocycles [5, 6]. Organoelement dihydrides of aluminum and gallium are stable with very bulky substituents only [7]. Double hydroalumination was reported to occur upon treatment of those dihydrides with nitrile or isonitrile [8]. An adduct of aluminum trihydride, $\text{AlH}_3 \cdot \text{NMe}_3$, reacted with several nitriles to yield aluminum-nitrogen compounds which possess hexagonal-prismatic cages of alternating aluminum and nitrogen atoms [9]. A similar adduct gave hydrazine derivatives upon treatment with tetramethyl-2,3-diazabutadiene by the complete hydroalumination of both $\text{C}=\text{N}$ double bonds [10]. This reaction opens a novel route for the synthesis of aluminum hydrazides, which are of interest owing

to their capability to afford aluminum nitride on thermolysis. In contrast, organoaluminum or gallium hydrides usually gave the addition of the E-H bonds to one C=N bond of the diazabutadienes only to yield molecular backbones comprising a N-C single and a N-C double bond [11, 12]. In some cases, cleavage of the N-N bond occurred [12]. Here we report on our first attempts on the hydroalumination of organic nitriles or isonitriles by dialkylaluminum hydrides as part of a broader research activity, in which we hope to achieve double additions by an excess of the hydrides or condensation reactions by the release of trialkylaluminum. The last reaction may result in the formation of oligomeric or polymeric species similar to those obtained with aluminum alkynides before [3]. Furthermore, we hope to stabilize unusual bonding situations in monomeric products, for instance, by employing bulky substituents.

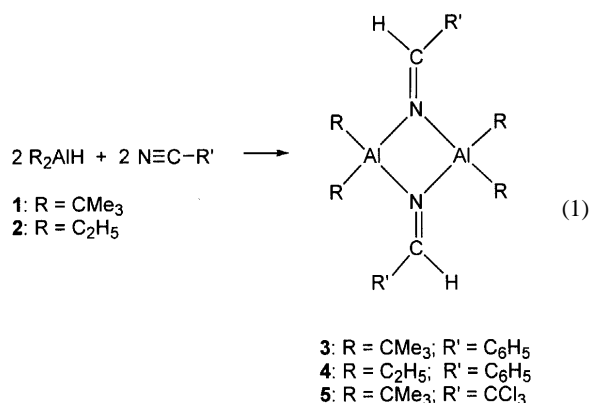
Preparative Results

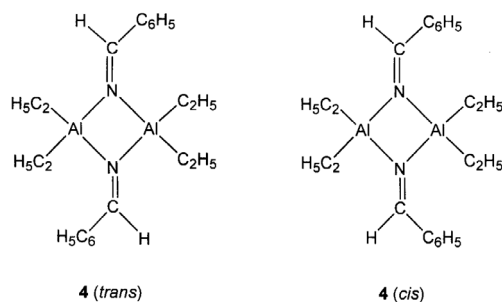
Reactions of dialkylaluminum hydrides with benzonitrile

Di(*tert*-butyl)aluminum hydride reacted with benzonitrile in *n*-pentane at room temperature to afford the expected product of hydroalumination, [*t*Bu₂Al-N=C(C₆H₅)H]₂ (**3**), of which yellow crystals were isolated in 85% yield (eq. (1)). The most characteristic result of the NMR spectroscopic characterization is the strong low-field shift of the resonance of the single proton which is attached to the carbon atom of the C=N double bond ($\delta = 9.13$). Compound **3** is thermally quite stable and melts at 220 °C without decomposition.

While **3** was formed in a rather selective reaction, the treatment of benzonitrile with diethylaluminum hy-

dride gave a mixture of products. Repeated recrystallization yielded a crystalline product (**4**), which, however, revealed two resonances of protons attached to C=N bonds ($\delta = 8.84$ and 8.82) in an integration ratio of 1.0 to 0.44. While only one quartet was observed for the methylene protons of the ethyl groups attached to aluminum, three triplets of methyl protons were detected at $\delta = 1.42$, 1.32 and 1.23. The first and third resonances possess equal intensities (integration ratio 0.22 to 1.0 to 0.22). Warming to 360 K gave a simpler spectrum with only one singlet at $\delta = 8.90$ and a broad resonance of the methyl protons at $\delta = 1.25$. The integration ratio is in accordance with the expected formula of the hydroalumination product, [Et₂Al-N=C(C₆H₅)H]₂ **4** (eq. (1)). The ¹H NMR data verify a dynamic equilibrium in solution, which may be caused by the occurrence of *cis/trans* isomers (Scheme 1). Similar findings were reported for some dimeric aluminum or gallium hydrazides, for instance, possessing four-membered Al₂N₂ or Ga₂N₂ heterocycles and exocyclic N-N bonds [13]. The *trans*-isomer was detected in the solid state by crystal structure determination (see below). It possesses a center of symmetry, and its ethyl groups are equivalent. Thus, the resonances of the main species observed in the ¹H NMR spectra can clearly be assigned to that particular isomer. The configuration of the *cis*-isomer results in two chemically different AlEt₂ groups, which is in accordance with the occurrence of two triplets of the methyl protons at room temperature. Fast exchange at elevated temperature resulted in a simpler spectrum showing only one average species. The difference of the chemical shifts of the methylene protons seems to be too small to result in a splitting of their resonance. The activation barrier for the exchange process was estimated to be about 75 kJ/mol [14]. The reaction of trichloroacetonitrile Cl₃C-C≡N with di(*tert*-butyl)aluminum hydride afforded a mixture of products. One resonance in the ¹H NMR spectrum at $\delta = 8.09$ may be assigned to an N=C-H group, it is, however, slightly outside the range usually observed. Beside one sharp resonance for *tert*-butyl groups, the main-intensity is covered by very broad signals. Thus, an unclear reaction course occurred, in which the desired product may be formed as a minor component. Few single crystals (compound **5**) precipitated in the NMR tube with toluene-D₈ as a solvent. However, all attempts to recrystallize the crude product from different solvents in a preparative scale failed.





Scheme 1.

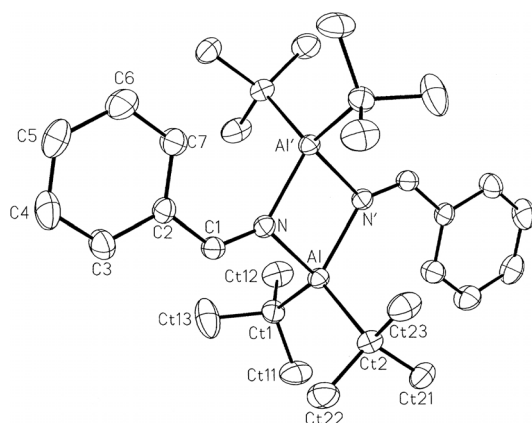


Fig. 1. Molecular structure of compound **3**. The ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°] for the related compounds **3** to **5**. **3**: Al1–N1 196.4(1), Al1–N1' 195.3(1), N1–C1 127.6(2), N1–Al1–N1' 82.73(4), Al1–N1–Al1' 97.27(4), Al1–N1–C1 124.69(8), Al1'–N1–C1 138.01(9), N1–C1–C2 128.8(1); N1' and Al1' generated by $-x + 1/2, -y + 1/2, -z$. **4**: Al1–N1 192.8(3), Al1–N1' 194.9(2), N1–C1 127.6(4), N1–Al1–N1' 84.2(1), Al1–N1–Al1' 95.8(1), Al1–N1–C1 138.4(2), Al1'–N1–C1 125.4(2), N1–C1–C2 127.9(3); N1' and Al1' generated by $-x + 1, -y, -z + 2$. **5**: Al1–N1 196.7(2), Al1–N1' 200.4(1), N1–C1 125.1(3), N1–Al1–N1' 81.34(8), Al1–N1–Al1' 98.66(9), Al1–N1–C1 138.3(2), Al1'–N1–C1 123.0(2), N1–C1–C2 127.5(2); N1' and Al1' generated by $-x + 2, -y, -z + 1$.

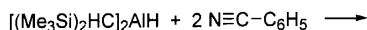
Crystal structure determinations were conducted with the three compounds described before (**3** to **5**). The molecular structure of **3** is depicted in Fig. 1; its legend summarizes the selected bond lengths and angles of all compounds. They adopt centrosymmetric structures and contain four-membered Al_2N_2 heterocycles with two exocyclic $\text{C}=\text{N}$ double bonds in their molecular cores. All structural parameters are close to standard values with a more or less significant dependency on the steric demand and electronic properties of the substituents [5, 6, 11, 12]. The Al–

N bonds in the rings (**3**: 195.9 pm; **4**: 193.9 pm; **5**: 198.6 pm) are longest for the trichloro derivative **5**, shortest for the less sterically crowded diethyl compound **4**. The transannular Al \cdots Al contacts are 293.9, 287.6, and 301.2 pm, respectively. A relatively short $\text{C}=\text{N}$ bond length of 125.1 pm compared to 127.6 pm for **3** and **4** was determined for the trichloroacetoneitrile derivative **5**. This difference may be caused by the particular electron withdrawing properties of the trichloromethyl group. The phenyl substituents attached to the $\text{C}=\text{N}$ groups of compounds **3** and **4** are almost ideally in plane with the Al_2N_2 heterocycles (angles between the normals of the planes 8.3 and 16.1°, respectively), which may be indicative for some π -interaction.

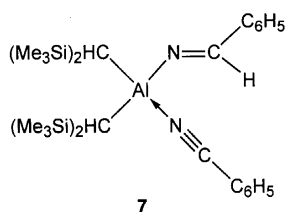
Reaction of $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Al-H}$ with benzonitrile

The employment of very bulky substituents such as the bis(trimethylsilyl)methyl group influences the reaction course of hydroalumination as was observed in our group several times before. Furthermore, the isolation of a monomeric product possessing a coordinatively unsaturated aluminum atom attached to a $\text{C}=\text{N}$ double bond may succeed as an interesting aspect of these experiments. The synthesis of the important starting dialkylaluminum hydride, $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{AlH}$ **6**, has been described by our group only recently [15], an improved procedure is given in the Experimental Section. Treatment of benzonitrile with equimolar quantities of **6** yielded a complex mixture of unknown products, and we did not succeed in isolating any constituent by recrystallization. In contrast, a single product (**7**) was obtained and isolated in almost quantitative yield, when we employed an excess of benzonitrile (molar ratio 1:2, eq. (2)). The integration ratio of the ^1H NMR spectrum showed that the product contains two phenyl groups per AlR_2 moiety, and the IR spectrum confirms the coordination of an intact benzonitrile molecule ($\nu_{\text{C}=\text{N}} = 2269 \text{ cm}^{-1}$). As was shown by crystal structure determination, an adduct had formed in which the expected product of hydroalumination, $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Al-N}=\text{C}(\text{C}_6\text{H}_5)\text{H}$, is stabilized by the coordination of a benzonitrile ligand. The formation of an adduct is also confirmed by the high-field shift of the inner $\text{AlC}(\text{H})\text{Si}_2$ protons, the resonance of which ($\delta = -0.79$) is in the characteristic range of bis(trimethylsilyl)methyl compounds possessing tetracoordinated aluminum atoms [16].

The molecular structure of **7** (Fig. 2) contains a central aluminum atom attached to two bulky alkyl



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(2)

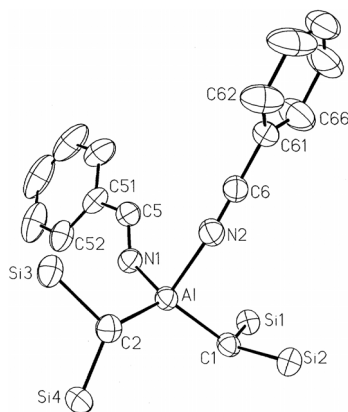


Fig. 2. Molecular structure of compound **7**. The ellipsoids are drawn at the 40% probability level; methyl groups of the SiMe_3 substituents and hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: Al–N1 182.3(2), Al–N2 201.6(2), N1–C5 125.3(3), N2–C6 114.0(3), C5–C51 148.5(3), C6–C61 142.9(3), Al–N1–C5 138.6(2), N1–C5–C51 124.5(2), Al–N2–C6 166.2(2), N2–C6–C61 179.1(3).

groups, an imino group *via* its nitrogen atom and a benzonitrile ligand in a distorted tetrahedral coordination sphere. Aluminum and hydrogen atoms of the starting hydride are on the same side of the $\text{C}=\text{N}$ double bonds (*cis*-addition), as often observed for the hydroalumination of $\text{C}\equiv\text{C}$ triple bonds before [2]. The Al–N bond lengths reflect the different bonding situations. A relatively long distance (201.6 pm) compared to that to the imino substituent (182.3 pm) was detected for the coordinative bonding to the intact benzonitrile ligand. The angle $\text{Al}-\text{N}\equiv\text{C}$ shows a small deviation from linearity (166.2°), while, as expected, the $\text{N}\equiv\text{C}-\text{C}$ group is linear (179.1°). An angle of 138.6° was detected for the aluminum-imino group $\text{Al}-\text{N}=\text{C}$. The C–N distances differ in accordance with the different bond orders and show values of 125.3 (C=N) and 114.0 pm ($\text{C}\equiv\text{N}$), both being slightly shorter than the standard values [17]. In this case, too, the phenyl group is almost ideally in plane with the $\text{C}=\text{N}$ double bond (angle

between the normals of the planes of the $\text{Al}-\text{N}=\text{C}$ and the phenyl groups 5.2°), which may indicate some π -interaction between both π -systems.

Reaction of di(*tert*-butyl)aluminum hydride with *tert*-butylisonitrile

The reaction between di(*tert*-butyl)aluminum hydride and *tert*-butylisonitrile succeeded at room temperature over a period of a few hours, and the colorless product **8** was isolated after recrystallization from *n*-hexane in 87% yield (eq. (3)). The spectroscopic findings are quite similar to those described before, but the resonance of the $\text{N}=\text{C}-\text{H}$ protons in the ^1H NMR spectrum is shifted to a lower field ($\delta = 9.76$) compared to those of the $\text{R}-\text{C}\equiv\text{N}$ products **3** and **4**. Compound **8** decomposes at 240 °C by gas evolution.

Compound **8**, $(\text{Me}_3\text{C})_2\text{Al}-\text{C}(\text{H})=\text{N}-\text{CMe}_3$, is formed by the insertion of the isonitrile carbon atom into the Al–H bond of the hydride. Dimers result from the intermolecular interaction between the β -nitrogen atoms and the coordinatively unsaturated aluminum atoms (Fig. 3). The six-membered $\text{Al}_2\text{N}_2\text{C}_2$ heterocycle in the molecular core of **8** is almost ideally planar with a

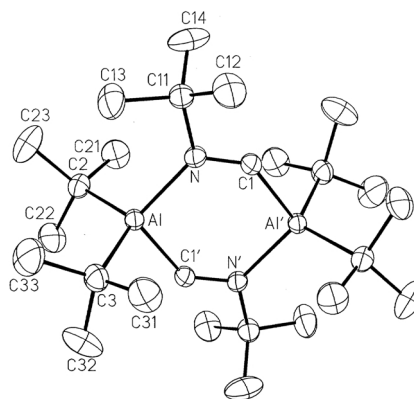
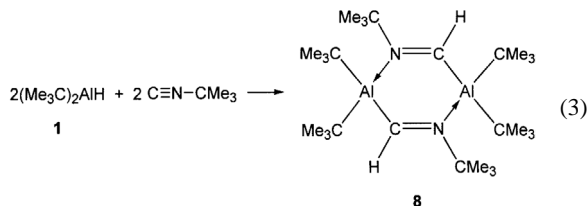


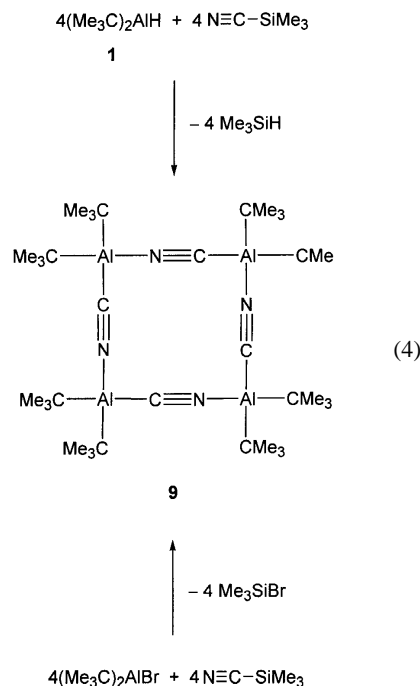
Fig. 3. Molecular structure of compound **8**. The ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: Al–N 197.8(2), Al–C1' 203.8(2), N–C1 128.5(2), Al–N–C1 116.7(1), N–Al–C1' 103.69(7), N–C1–Al1' 139.6(2), Al–N–C11 125.5(1), C1–N–C11 117.8(2); C1' and Al1' generated by $-x, -y, -z+1$.

maximum deviation of an atom from the average plane of 1.3 pm only. The Al-N distances (197.8 pm) correlate well with a donor interaction between the imino nitrogen and the aluminum atoms. The Al-C distances to the terminal *tert*-butyl groups and to the endocyclic carbon atoms are in a narrow range at about 203 pm and reflect standard values of Al-C single bonds involving tetracoordinated aluminum atoms. The C=N bond length is 128.5 pm, which is only slightly lengthened compared to compounds **3** and **4** and corresponds well to the standard value of C=N double bonds [17]. As expected, the nitrogen atoms attached to two carbon atoms (*tert*-butyl group and N=C double bond) and an aluminum atom have an ideally planar surrounding (sum of angles = 360°).

Reaction of di(*tert*-butyl)aluminum hydride with trimethylsilylcyanide

The reaction of trimethylsilylcyanide with di(*tert*-butyl)aluminum hydride (eq. (4)) did not yield a product of hydroalumination, which immediately became obvious from the missing of a resonance of N=C-H protons ($\delta > 8$) in the ^1H NMR spectrum of the crude product. The IR spectrum showed an absorption at 2211 cm^{-1} in the characteristic range of $\text{C}\equiv\text{N}$ triple bonds. The formation of di(*tert*-butyl)aluminum cyanide **9** was confirmed by crystal structure determination, which verifies a tetrameric formula unit with four cyano ligands bridging four aluminum atoms in the solid state. Compound **9** is only sparingly soluble in non-coordinating solvents. Thus, we were not able to determine the molar mass in solution or to detect the ^{13}C NMR resonances of the cyanido groups. **9** was also obtained in a high yield by the reaction of di(*tert*-butyl)aluminum bromide with trimethylsilyl cyanide (eq. (4)) under release of trimethylsilyl bromide. The synthesis of **9** starting with a dialkylaluminum hydride may open the facile access to similar heterocyclic compounds. In a preliminary further experiment we treated $\text{Me}_3\text{Si-N}_3$ with di(*tert*-butyl)aluminum hydride and obtained the corresponding dialkylaluminum azide. Further experiments are in progress [18].

The molecular structure of **9** (Fig. 4) comprises a tetrameric formula unit of the dialkylaluminum cyanide $(\text{Me}_3\text{C})_2\text{Al-CN}$. The structure may be described by a square of aluminum atoms which are connected by bridging cyano ligands to yield a twelve-membered, planar $\text{Al}_4\text{C}_4\text{N}_4$ heterocycle. The molecule is located on a center of symmetry, and the nitro-



gen and carbon atoms of the cyanide groups are statistically disordered as often observed before. Thus, each atomic position of the CN couples was refined by an occupation with half a carbon and half a nitrogen atom. The CN groups have an almost ideally linear surrounding with bond angles Al-N-C and Al-C-N of 177.3° on average. The $\text{C}\equiv\text{N}$ bond lengths (115.1 pm on average) correspond well to the standard value [17]. The Al-C/N distances in the ring are in the expected range at 199.4 pm. Dialkylaluminum or -gallium cyanides have been known since many decades [19], often they were characterized by IR spectroscopy and elemental analyses only. Crystal structure determinations are rare. Two compounds bearing the bulky bis(trimethylsilyl)methyl substituents attached to their central aluminum or gallium atoms, $(\text{R}_2\text{E-C}\equiv\text{N})_3$ [E = Al, Ga; R = $\text{CH}(\text{SiMe}_3)_2$], were described by our group [20,21]. In contrast to the tetrameric di(*tert*-butyl)aluminum compound **9**, these compounds adopt a trimeric structure in the solid state, which may be caused by the particular packing of the very bulky substituents and was observed for an azido derivative also [22]. In solution the aluminum compound seems to be dimeric, while owing to spectroscopic findings the gallium compound was reported to be a tetramer similar to the structure of **9** in the solid state. ^{13}C NMR data revealed an unsymmetrical struc-

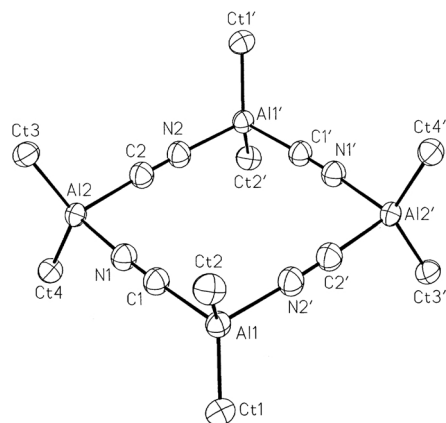


Fig. 4. Molecular structure of compound **9**. The ellipsoids are drawn at the 40% probability level; methyl groups are omitted. Selected bond lengths [pm] and angles [°]: Al1–C1/N2 199.2(2), Al1–N3'/C4' 199.6(2), Al2–N1/C2 199.5(2), Al2–C3/N4 199.4(2), C1/N2–N1/C2 115.2(2), C3/N4–N3/C4 114.9(2), Al1–C1/N2–N1/C2 177.6(1), C1/N2–N1/C2–Al2 176.1(1), Al2–C3/N4–N3/C4 177.5(1), C3/N4–N3/C4–Al1' 178.0(1), C1/N2–Al1–N3'/C4' 95.66(6), N1/C2–Al2–C3/N4 94.92(6); N3', C4' and Al1' generated by $-x+1, -y+1, -z+1$.

ture in that case [21] with one gallium atom attached to two carbon atoms and another one to two nitrogen atoms. The remaining two gallium atoms are coordinated by a carbon and a nitrogen atom each. Such an unsymmetrical structure was also derived from the IR spectra of tetrameric dialkylgallium cyanides bearing smaller substituents [21]. As mentioned before, the low solubility of **9** prevented the detection of ^{13}C NMR resonances of the CN groups and, hence, the clear assignment of the molecular symmetry and the orientation of the bridging CN ligands. A cyano group bridging two gallium atoms was further found in the anion $[\text{Me}_3\text{Ga}-\text{C}\equiv\text{N}-\text{GaMe}_3]^-$ with Cs^+ as a counterion [23].

Experimental Section

All procedures were carried out under purified argon in dried solvents (*n*-pentane and *n*-hexane over LiAlH_4). Commercially available (Aldrich) benzonitrile, *tert*-butylisonitrile and trimethylsilyl cyanide were employed without further purification. The oligomeric starting compounds Et_2AlH [24], $(\text{Me}_3\text{C})_2\text{AlH}$ [15, 25], and $(\text{Me}_3\text{C})_2\text{AlBr}$ [26] were obtained according to literature procedures.

$[(\text{Me}_3\text{C})_2\text{Al}-\text{N}=\text{C}(\text{C}_6\text{H}_5)\text{H}]_2$ (**3**)

A solution of $(\text{Me}_3\text{C})_2\text{AlH}$ **1** (0.69 g, 4.84 mmol) in 20 ml of *n*-pentane was added to a solution of benzonitrile (0.50 g, 4.84 mmol) in 20 ml of the same solvent at room temper-

ature. The color of the mixture changed to yellow. The solution was stirred for 3 h, concentrated to one third of its original volume and cooled to -15°C . Yield: 1.01 g (85% based on **1**); yellow crystals. M.p. (under argon, sealed capillary) 220°C . – IR (cm^{-1} ; paraffin; CsBr plates): 1695 w, 1620 vs, 1599 s, 1579 s ν C=N, ν CC; 1463 vs paraffin; 1411 w δ CH; 1379 s paraffin; 1309 m δ CH; 1206 m, 1175 w, 1080 w, 1002 m, 931 w ν CN, ν CC; 847 m, 810 m, 747 m δ CC; 618 vw, 584 m, 553 vs, 506 w, 482 m, 450 m, 404 w, 358 m ν AlC, ν AlN, phenyl. – ^1H NMR (400 MHz, C_6D_6): δ 1.28 (18 H, s, CMe_3), 7.07 (3 H, br., *meta*- and *para*-H of phenyl), 7.51 (2 H, pseudo-d, *ortho*-H of phenyl), 9.13 (1 H, s, N=C-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6): δ = 17.4 (AlC), 32.8 (CH_3), 129.1, 129.3, 133.3, and 136.4 (phenyl), 177.0 (C=N).

$[(\text{H}_5\text{C}_2)_2\text{Al}-\text{N}=\text{C}(\text{C}_6\text{H}_5)\text{H}]_2$ (**4**)

A solution of $(\text{H}_5\text{C}_2)_2\text{AlH}$ **2** (0.42 g, 4.84 mmol) in 20 ml of *n*-pentane was added to a solution of benzonitrile (0.50 g, 4.84 mmol) in 20 ml of the same solvent at room temperature. The color of the mixture changed to yellow. The solution was stirred for 3 h. The solvent was removed in vacuum, and the residue was thoroughly evacuated to 10^{-3} Torr for 14 h. A solid remained, which was recrystallized several times from *n*-pentane ($20/-50^\circ\text{C}$). Yield: 0.41 g (45% based on **2**); yellowish crystals. M.p. (under argon, sealed capillary) 65°C . – IR (cm^{-1} ; paraffin; CsBr plates): 1688 m, 1635 vs, 1601 s, 1581 s ν C=N, ν CC; 1460 vs paraffin; 1407 m δ CH; 1376 s paraffin; 1327 w, 1308 m, 1289 w δ CH; 1205 s, 1177 m, 1101 w, 1071 m, 1026 w, 985 s, 949 m, 915 m ν CN, ν CC; 843 s, 748 s, 715 vs, 688 s, 631 br., ν δ CC; 562 s, 477 m, 411 w ν AlC, ν AlN, phenyl. – ^1H NMR (400 MHz, C_6D_6 , 360 K): δ = 0.37 (4 H, q, $^3J_{\text{HH}}$ = 8 Hz, CH_2 of ethyl), 1.25 (6 H, br., s, CH_3 of ethyl), 7.20 (3 H, m, *meta*- and *para*-H of phenyl), 7.52 (2 H, m, *ortho*-H of phenyl), 8.90 (1 H, s, N=C-H). – ^1H NMR (400 MHz, C_6D_6 , 300 K): two isomers in the ratio 1 to 0.44; *trans*-form: δ = 0.46 (for both isomers, pseudo-q, Al- CH_2), 1.32 (6 H, t, $^3J_{\text{HH}}$ = 8 Hz, CH_3 of ethyl), 7.07 (for both isomers, m, *meta*- and *para*-H of phenyl), 7.48 (for both isomers, m, *ortho*-H of phenyl), 8.84 (1 H, s, N=C-H); *cis*-form (in addition to those resonances observed for both isomers): 1.23 and 1.42 (each 3 H, t, $^3J_{\text{HH}}$ = 8 Hz, CH_3 of ethyl), 8.82 (1 H, s, N=C-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 300 K): δ = 0.40 (br., AlC), 9.9 (CH_3) [9.8 and 10.0 of the *cis*-isomer], 129.03, 129.1, 132.63, 137.3 (phenyl) [128.96, 129.4, 132.60, and 137.2 of the *cis*-isomer], 174.9 (C=N) [175.3 of the *cis*-isomer].

$[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Al}-\text{H}$ (**6**)

A mixture of $\text{Al}[\text{CH}(\text{SiMe}_3)_2]_3$ [26] (8.47 g, 16.8 mmol) and $\text{AlH}_3 \cdot \text{NMe}_2\text{Et}$ (1.04 g, 10.1 mmol, excess) without a solvent was slowly (2 to 3 h) heated from room tem-

Table 1. Crystal data, data collection, and structure refinement.

	3	4	5	7	8	9
<i>Crystal data</i>						
Empirical formula	C ₃₀ H ₄₈ Al ₂ N ₂	C ₂₂ H ₃₂ Al ₂ N ₂	C ₂₇ H ₃₈ Al ₂ Cl ₆ N ₂	C ₂₈ H ₄₉ AlN ₂ Si ₄	C ₂₆ H ₅₆ Al ₂ N ₂	C ₃₆ H ₇₂ Al ₄ N ₄
M _r	490.66	378.46	657.25	553.03	450.69	668.90
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	C2/c; no. 15 [29]	P $\bar{1}$; no. 2 [29]	P2 ₁ /c; no. 14 [29]	P2 ₁ /c; no. 14 [29]	P2 ₁ /n; no. 14 [29]	P $\bar{1}$; no. 2 [29]
a [pm]	1985.9(2)	740.4(1)	993.1(2)	1393.2(3)	860.1(1)	893.49(7)
b [pm]	976.7(1)	818.1(1)	1538.1(3)	1449.2(3)	1163.6(1)	1198.72(9)
c [pm]	1623.5(2)	1041.5(2)	1219.0(2)	1781.5(4)	1475.8(2)	1269.52(9)
α [°]	90	105.01(2)	90	90	90	69.253(6)
β [°]	109.232(8)	109.27(2)	111.05(3)	98.66(3)	90.61(1)	71.743(6)
γ [°]	90	96.18(2)	90	90	90	85.403(6)
V [Å ³]	2973.2(6)	562.1(2)	1737.8(6)	3555.9(13)	1476.9(3)	1206.8(2)
ρ_{calc} [g cm ^{−3}]	1.096	1.118	1.256	1.033	1.013	0.920
Z	4	1	2	4	2	1
F(000)	1072	204	684	1200	504	368
μ (Mo-K α) [cm ^{−1}]	1.17	1.37	5.64	2.09	1.13	1.20
<i>Data collection</i>						
T [K]	193(2)	193(2)	193(2)	193(2)	193(2)	193(2)
Measured reflections	10620	5336	20669	28645	10468	17589
Unique reflections	2804	2031	3483	6870	2964	4814
	[R(int) = 0.0414]	[R(int) = 0.0401]	[R(int) = 0.0426]	[R(int) = 0.0588]	[R(int) = 0.0325]	[R(int) = 0.0465]
Reflections I > 2 σ (I)	2469	1532	2717	4303	2391	3986
<i>Refinement</i>						
Refined parameters	160	120	187	328	145	211
<i>Final R values</i>						
R1[I > 2 σ (I)] ^[a]	0.0335	0.0619	0.0426	0.0409	0.0550	0.0411
wR2 ^[b] (all data)	0.0981	0.1877	0.1278	0.1005	0.1616	0.1249
ρ_{fin} (max/min) [eÅ ^{−3}]	0.236/−0.173	0.650/−0.348	0.347/−0.236	0.159/−0.213	0.733/−0.379	0.206/−0.255

^[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; ^[b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

perature to 170 °C and further stirred at this temperature for 2 h. Elemental aluminum precipitated. The mixture was cooled to room temperature, and all volatile components were removed in vacuum. The residue was recrystallized from *n*-hexane (20/−50 °C). Yield: 4.96 g (57%, based on AlR₃), colorless crystals. Characterization: see reference [15].

[(Me₃Si)₂HC]₂Al-N=C(C₆H₅)H·N≡C-C₆H₅ (7)

A solution of benzonitrile (0.294 g, 2.85 mmol) in 20 ml of *n*-hexane was added to a cooled solution (−10 °C) of [(Me₃Si)₂HC]₂Al-H **6** (0.495 g, 1.43 mmol) in 20 ml of *n*-hexane. The color of the mixture changed to yellow. After 1 h at −10 °C the solution was warmed to room temperature and stirred for further 3 h. The solvent was removed in vacuum, and the residue was evacuated (10^{−3} Torr) for 14 h. The remaining solid was recrystallized from *n*-hexane (20/−50 °C). Yield: 0.72 g (91%). M.p. (under argon, sealed capillary) 75 °C. – IR (cm^{−1}; paraffin; CsBr plates): 2269 s ν C≡N; 1685 s, 1627 m, 1596 m, 1582 m, 1488 m ν C=N, ν CC; 1453 vs, 1377 s paraffin; 1299 w, 1287 w, 1245 vs δ CH; 1200 m, 1178 w, 1166 w, 1154 w, 1066 w ν CN, ν CC; 1009 vs δ CH(Si₂); 912 s, 850 vs, 780 vs, 755 vs ρ CH₃(Si);

672 s ν_{as} SiC; 637 w, 628 w, 610 w ν_{s} SiC, δ CC; 583 w, 554 m, 512 s, 475 w, 413 m, 320 m ν AlC, ν AlN, phenyl. – ¹H NMR (300 MHz, C₆D₆): δ = −0.79 (2 H, s, CHSi₂), 0.30 (36 H, s, SiMe₃), 6.52, 6.73, 7.04, 7.17, 7.86 (each m, phenyl), 9.73 (1 H, s, N=C-H). – ¹³C{¹H} NMR (75.5 MHz, C₆D₆, 300 K): δ = 0.82 (AlC), 4.6 (CH₃), 106.9 (C≡N), 120.6, 130.1, 132.8, 135.6, and 141.3 (phenyl), 160.7 (C=N).

[(Me₃C)₂Al-C(H)=N(CMe₃)]₂ (8)

A solution of (Me₃C)₂AlH **1** (0.344 g, 2.42 mmol) in 20 ml of *n*-hexane was treated with a solution of *tert*-butylisonitrile (0.201 g, 2.42 mmol) in 20 ml of the same solvent at room temperature. The solution was stirred for 4 h. The solvent was removed in vacuum, and the solid residue was recrystallized from *n*-hexane (20/−50 °C). Yield: 0.474 g (87%); colorless crystals. Dec.p. (under argon, sealed capillary) 240 °C (gas evolution). – IR (cm^{−1}; paraffin; CsBr plates): 1647 vw, 1553 m, 1539 m ν C=N; 1462 vs, 1380 vs paraffin; 1243 m, 1230 m δ CH; 1184 s, 1032 w, 1001 m, 957 w, 932 s, 875 m, 809 vs ν N, ν C; 771 , 724 w, 663 s δ CC; 574 s, 544 vs, 503 m, 467 s, 425 s, 404 s, 355 m ν AlC, ν AlN, phenyl. – ¹H NMR (400 MHz, C₆D₆): δ = 1.08 (18 H, s, N-CMe₃), 1.20 (36 H, s, Al-CMe₃),

9.76 (1 H, s, N=C-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6): δ = 16.6 (AlC), 29.6 (methyl of N-CMe₃), 32.8 (methyl of Al-CMe₃), 62.2 (N-C), 227.1 (C=N).

[(Me₃C)₂Al-C≡N]₄ (9)

a) Starting with (Me₃C)₂AlH: A solution of trimethylsilyl cyanide (0.331 g, 3.34 mmol) in 20 ml of *n*-hexane was added dropwise to a solution of (Me₃C)₂AlH **1** (0.475 g, 3.35 mmol) in 20 ml of the same solvent at room temperature. The yellow solution was stirred for 4 h. All volatiles were removed in vacuum, and the solid residue was recrystallized from *n*-hexane (20/–15 °C). Yield: 0.475 g (85%). *b) Starting with (Me₃C)₂AlBr:* (Me₃C)₂AlBr (0.559 g, 2.53 mmol) and trimethylsilyl cyanide (0.299 g, 3.02 mmol) were mixed at room temperature without a solvent. Slow gas evolution occurred. The mixture was stirred for 4 h, and all volatiles were removed in vacuum. The residue was recrystallized from *n*-hexane (20/–15 °C). Yield: 0.381 g (90%, based on R₂AlBr); colorless crystals, only sparingly soluble in non-coordinating solvents. M.p. (under argon, sealed capillary) 170 °C. – IR (cm^{–1}; paraffin; CsBr plates): 2211 vs ν C≡N; 1462 vs, 1377 s paraffin; 1362 s δ CH; 1217 w, 1195 w; 1003 s ν_{as} C₃C; 937 s ρ_3 ; 815 vs ν_{s} C₃C; 722 paraffin; 613 vs, 558 vs, 513 vs, 432 w, 396 s ν AlC, ν AlN. – ^1H NMR (400 MHz, D₈-toluene): δ = 1.09 (CMe₃). – A clearly resolved $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum could not be recorded.

Crystal structure determination

Single crystals were obtained by cooling of saturated solutions in different solvents (**3**: *n*-pentane, –15 °C; **4**: *n*-pentane, –50 °C; **5**: D₈-toluene, +6 °C; **7**: *n*-hexane, –50 °C; **8**: *n*-hexane, –50 °C; **9**: *n*-hexane, –15 °C). Data collections were performed on a STOE IPDS diffractometer employing graphite-monochromated Mo-K α radiation. The structures were solved by direct methods and refined by full matrix least-squares calculations based on F^2 [28]. The hydrogen atoms were calculated on ideal positions and refined by the riding model. Crystal data, data collection parameters, and details of the structure refinement are given in Table 1. The crystallographic data of all compounds (excluding structure factors) were deposited with the Cambridge Crystallographic Data Centre, CCDC-242635 (**3**), -242634 (**4**), -243078 (**5**), -242637 (**7**), -242636 (**8**), and -242638 (**9**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk). The molecules of **3**, **4**, **5**, **8**, and **9** are located on centers of symmetry. Compound **5** crystallizes with a disordered toluene-molecule; hydrogen atoms of the solvent molecule were not considered.

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