

A Methylene-Bridged Dialuminium Compound as a Chelating Lewis Acid: Complexation of Nitrite and Nitrate Anions by $R_2Al-CH_2-AlR_2$ [$R = CH(SiMe_3)_2$][☆]

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Sodium nitrite ($NaNO_2$) dissolves readily in THF, when the methylene-bridged dialuminium compound $R_2Al-CH_2-AlR_2$ [$R = CH(SiMe_3)_2$] **1** with two coordinatively unsaturated aluminium atoms is added. Compound **1** reacts as a chelating Lewis acid, and, as shown by a crystal structure determination of the $[Na\{[18]crown-6\}(Et_2O)]^+$ derivative **5c**, a compound (**5**) is formed, in which one oxygen atom and the nitrogen atom of the nitrite ion are each coordinated by one

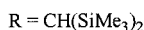
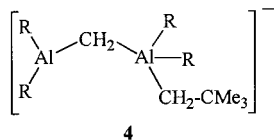
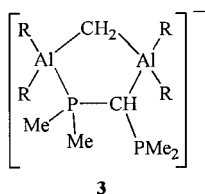
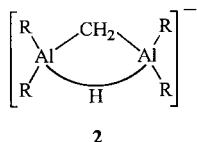
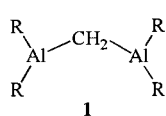
aluminium atom to form a five-membered Al_2CNO heterocycle. The second oxygen atom of the nitrite anion is not affected. Similarly, lithium nitrate ($LiNO_3$) reacts with **1** to yield a THF soluble product (**6a**). Single crystals were obtained of the $[Li(N,N',N''\text{-trimethyltriazinane})_2]^+$ derivative **6c**, whose structure shows each aluminium atom to be coordinated by one oxygen atom of the nitrate ion to give a six-membered Al_2CNO_2 heterocycle.

Chelating Lewis bases for the effective coordination of cations are extraordinarily important in all areas of chemistry as can be seen from thousands of known compounds. In contrast, chelating Lewis acids as anion receptors for the complexation and recognition of anions are investigated to a much lower extent, and by far the most of these ligands were obtained by the protonation of amino groups of macrocyclic or polycyclic compounds^[1]. Organoelement derivatives of the elements of the third main-group have a coordinatively unsaturated central atom and are therefore suitable as Lewis acids, but only few examples exist, which have more than one atom of those elements and could possibly be useful as a chelating ligand. Well documented and characterized^[2] compounds of this type are for instance 1,8-naphthlenediylbis(dimethylborane)^[3], $Cl_2Al-CH_2-AlCl_2$ ^[4], $Cl_2Al-CH_2CH_2-AlCl_2$ ^[5], $R_2Al-CH_2-AlR_2$ **1** [$R = CH(SiMe_3)_2$]^[6], $R(Cl)Al-CH_2-Al(Cl)R$ [$R = CH(SiMe_3)_2$]^[7], $Me_2(THF)AlOC_6H_4OAl(THF)Me_2$ ^[8], $Cl_2In-CH_2-InCl_2 \cdot 2\text{ TMEDA}$ ^[9], and $Hg(C_6H_4-InCl_2 \cdot THF)_2$ ^[10]. However, most of these compounds have up to now not been investigated concerning their ability to act as a chelating Lewis acid. Exceptions are the diborane compound with a single example of a hydrido bridge^[3] and the methylene bridged tetraalkyl dialuminium derivative **1**, which was recently synthesized by our group^[6]. Few chelate complexes of **1** have been isolated and characterized, in which heterocycles are formed by the coordination of both aluminium atoms to one hydride (**2**)^[11], hydroxide^[12], or

thiomethanolate anion^[13]. A remarkable five-membered ring (**3**) was obtained by the reaction of **1** with $LiCH(PMe_2)_2$, in which one Al atom is coordinated to the central carbanion and the other one to a phosphorus atom^[14]. A terminal coordination of a neopentyl group is observed by the reaction of **1** with neopentyllithium (**4**)^[15]. Much more interest deserve, however, the up to now unknown complexes with multidentate inorganic anions like nitrate, nitrite, azide, sulfate etc. in order to find specific anion receptors or in order to use a Lewis-acid like **1** as a phase transfer reagent to dissolve ionic compounds in organic solvents and to study their changed, possibly enhanced reactivity. We started now with systematic investigations into those reactions and wish to report here on the complexes of **1** with sodium nitrite and lithium nitrate. Carbon bridged dialuminium compounds have recently been used in organic syntheses to form for instance $C=C$ double bonds, but they usually were only used as reactive intermediates, and they were not isolated or well characterized^[16].

Reactions of the Methylene-Bridged Dialuminium Compound **1** with $NaNO_2$ and $LiNO_3$

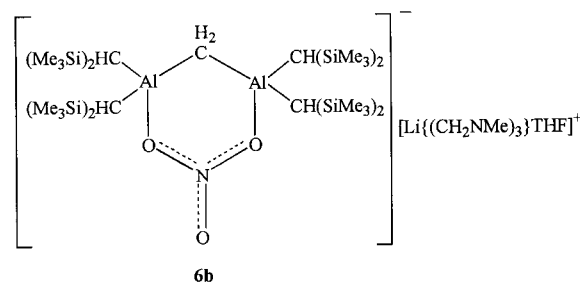
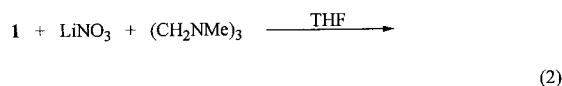
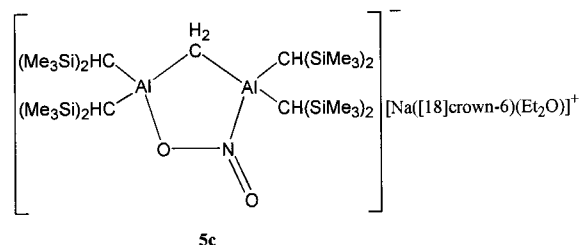
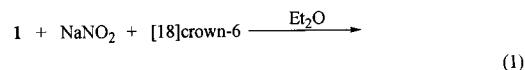
Both, sodium nitrite and lithium nitrate are insoluble even in a large excess of THF. But upon addition of one equivalent of the chelating Lewis-acid μ -methylene tetraalkyldialuminium $R_2Al-CH_2-AlR_2$ **1** the complete dissolution of the crystalline salts occurred within several hours by stirring



at room temperature. Yellow solutions were formed, from which the yellow addition products **5a** and **6a** were isolated after concentration and cooling to -50°C in a high yield. The crystals rapidly became amorphous upon drying in vacuo and had low melting points of 92°C and 135°C (**5a** and **6a**, respectively). The ^1H - and ^{13}C -NMR spectroscopic characterization gave some important changes in comparison to the neutral starting compound **1**, and all signals of groups bound to aluminium showed a significant shift to high field. In **1** the protons of the $\text{Al}-\text{CH}_2-\text{Al}$ group resonated at $\delta = -0.50$, and we observed the methine protons at $\delta = -0.22$ and the corresponding carbon atoms at $\delta = 13.2$; in **5a** and **6a** these resonances were shifted to $\delta(\text{Al}-\text{CH}_2\text{Al}) = -1.24$ and -1.27 , $\delta(\text{AlCHSi}_2) = -1.06$ and -1.05 , $\delta(\text{AlCHSi}_2) = 4.1$ and 4.3 , respectively. Such shifts to a higher field are very indicative of the enhancement of the coordination number at the aluminium atoms from three to four^{[11][12][13][14][15][17]}.

Both compounds were stable in THF solutions, but slow decomposition by the precipitation of NaNO_2 or LiNO_3 and the formation of **1** was observed in more nonpolar solvents like diethyl and diisopropyl ether or in mixtures of ether with toluene or pentane. Single crystals of the nitrate derivative **6a** with the counterion $[\text{Li}(\text{THF})_4]^+$ could not be obtained, while single crystals of **5a** showed a severe disorder of the $\text{Na}(\text{THF})_3$ cation, and the structure could not be refined satisfactorily. Therefore, we synthesized several derivatives of **5** and **6** by using different chelating Lewis-bases like the crown ether [18]crown-6, tetramethylethylenediamine (TMEDA), tetramethylpropylenediamine (TMPDA), pentamethyldiethylenetriamine (PMDETA), and N,N',N'' -trimethyltriazinane. Some of the isolated products are described in detail in the Experimental Section, the spectroscopic properties of their anions as well as their solubility in polar or nonpolar solvents differ only slightly from those of the THF adducts. But owing to the chelating coordination of the cations they show a significantly increased stability and can be stored in diethyl ether solution at room temperature without decomposition and precipitation of the corresponding salts. High quality single

crystals were obtained of compounds **5c** $\{[\text{Na}([18]\text{crown-6})(\text{Et}_2\text{O})]^+\}$ (Eq. 1) and **6c** $\{[\text{Li}(\text{triazinane})_2]^+\}$; the last one crystallized from a dilute solution of the mixed triazinane/THF adduct **6b** (Eq. 2) in diethyl ether in the presence of triazinane.



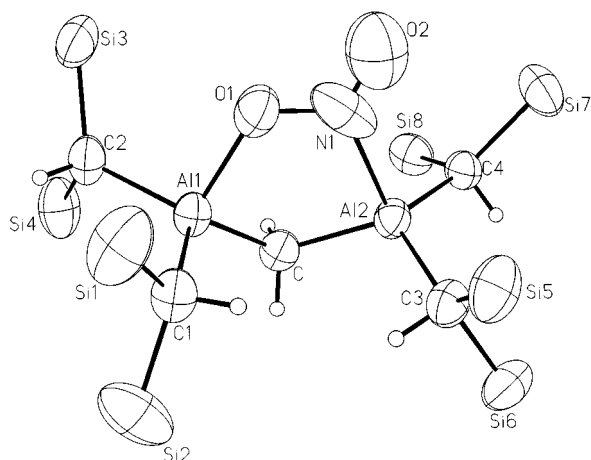
As shown in Eq. (1), the structure of the complex **5c** comprises the nitrite anion coordinated by one oxygen atom and the lone pair at the central nitrogen atom. This structure should result in two chemically different AlR_2 moieties, but at room temperature only one singlet was detected in the ^1H -NMR spectrum for both the methine and the SiMe_3 protons. However, a splitting into two resonances was observed upon cooling a sample of **5c** dissolved in $[\text{D}_{10}]\text{diethyl ether}$ to -70°C indicating a fast exchange process at elevated temperatures.

Crystal Structures of **5c** and **6c**

The molecular structures of the nitrito complex **5c** and the nitrate complex **6c** are depicted in Figures 1 and 2. To the best of our knowledge, it is the first time, that chelating Lewis-acids like compound **1** with coordinatively unsaturated atoms of the elements of group 13 are successfully used for the coordination of at least bidentate anions and that the coordination mode could be determined by crystal structure determinations. Both anions are coordinated in a chelating manner by both aluminium atoms of **1**. As expected, the nitrate anion in **6c** is bound by two oxygen atoms to form a six-membered $\text{Al}_2\text{CO}_2\text{N}$ heterocycle, while a five-membered Al_2CNO heterocycle is observed in **5c** with the nitrite anion coordinated via one oxygen and the central

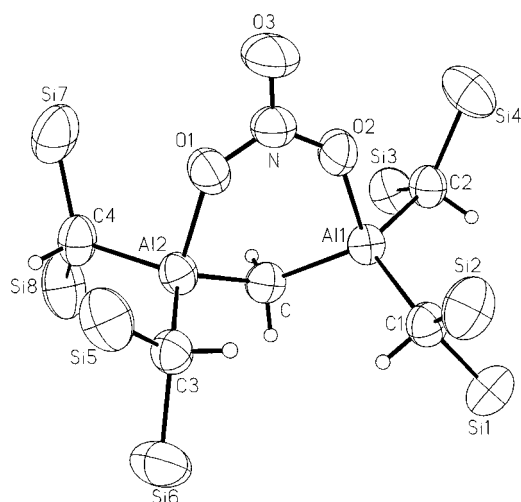
nitrogen atom. One oxygen atom of each anion is in a terminal position.

Figure 1. Molecular structure and numbering scheme of the anion of **5c**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity^[a]



^[a] Selected bond lengths [pm] and angles [°]: Al1–O1 196.0(3), Al2–N1 212.3(5), N1–O1 137.6(5), Al1–C 196.1(3), Al2–C 195.0(3), Al1–C1 202.7(3), Al1–C2 202.6(3), Al2–C3 199.9(3), Al2–C4 201.3(3), C–Al1–O1 96.8(1), Al1–O1–N1 114.4(2), O1–N1–Al2 119.2(2), N1–Al2–C 89.5(2), Al1–C–Al2 111.3(2).

Figure 2. Molecular structure and numbering scheme of the anion of **6c**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity^[a]



^[a] Selected bond lengths [pm] and angles [°]: Al1–O2 193.9(3), Al2–O1 195.7(3), N–O1 126.1(4), N–O2 125.2(4), N–O3 121.4(4), Al1–C 194.5(4), Al2–C 195.0(4), Al1–C1 201.4(3), Al1–C2 202.7(4), Al2–C3 203.8(4), Al2–C4 200.8(4), C–Al2–O1 99.8(2), Al2–O1–N 136.0(3), O1–N–O2 121.3(4), N–O2–Al1 135.9(3), O2–Al1–C 100.4(2), Al1–C–Al2 116.2(2).

The methylene bridged tetraalkyldialuminium moieties of both compounds are quite similar. The Al–C distances of the CH(SiMe₃)₂ substituents are 201.6 (**5c**) and 202.2 pm (**6c**) on average, and the smallest distances are observed to the aluminium atom bound to nitrogen. The bond lengths to the carbon atom of the methylene bridge are 195.6 (**5c**) and 194.8 pm (**6c**). As expected from the enhancement of the coordination number at the aluminium

atoms^{[11][12][13][14][15][17]}, all distances are lengthened compared with the starting compound **1**^[6], which had the corresponding values at 195.7 and 193.8 pm. The structure of **1** showed a strongly enlarged Al–C–Al angle (129.6°) caused by steric and electrostatic repulsion between the bulky substituents and the positively charged Al atoms^[6]. Owing to the formation of five and six membered heterocycles this angle is reduced in **5c** and **6c** to 111.3° and 116.2°, respectively.

The Al–O distance in the nitrito compound **5c** is slightly lengthened to 196.0 pm compared with complexes of trimethylaluminium with sulfate or nitrate anions (ca. 191 pm)^{[18][19]}. The Al–N1 distance is long (212.3 pm) with respect to some [bis(trimethylsilyl)methyl]aluminium compounds recently obtained in our group^[20], which may indicate only a weak coordinative interaction to the Al atom Al2. Unfortunately, the N–O distances N1–O1 137.6 pm and N1–O2 103.1 pm, which is in the range of the triple bond in NO⁺, are incorrect due to a disorder of the atoms N1 and O2. Both atoms could not be refined in split positions to give acceptable positions. The same disorder was observed for the THF adduct, which could not be completely refined due to the severe disorder of the cation. The distances should therefore not further be discussed in detail, but it seems clear, that strong differing distances are present with one value approaching a double bond and one approaching a single bond similar to the situation in nitrous acid HONO (N–O = 142 and 118 pm)^[21]. A similar coordination mode with bridging μ -NO₂-N,O groups has been observed before in several coordination compounds of the transition metals. As expected, the N–O distances of the bridging NO groups of these complexes are elongated compared to those of terminal N=O groups by up to 17 pm^[22]. The atoms of the nitrito group (N1, O1, O2) and the aluminium atom coordinated by nitrogen (Al2) lie almost ideally within a plane (sum of the angles 359.8 pm). The most acute angles in the five-membered central heterocycle are at the Al atoms with 96.8° at Al1 and 89.5° at Al2, the last one is coordinated by the nitrogen atom. The heterocycle adopts an envelope conformation with the four atoms Al1, Al2, O1, and N1 almost ideally within a plane and the bridging carbon atom 58 pm above the plane. The angle between the normals of the planes (Al1O1N1Al2 and Al1–CA12) is 31.7°.

In contrast to the strongly differing N–O distances of **5c**, a more delocalized electronic system is observed in the nitrate compound **6c** with three quite similar N–O distances. The N–O bond length to the terminal oxygen atom is 121.4 pm, which is only 4.5 pm shorter than the distance between nitrogen and the bridging oxygen atoms (125.7 pm on average). The longer distances are similar to the N–O bond lengths of the nitrate ions in many salt-like compounds, which are in the range of about 126 pm^[23]. Two metal atoms bridged by two different oxygen atoms of a nitrate group as in **6c** are for instance observed in some aquo Zn-, Cu-, or Ni nitrate complexes^[24]. The Al–O distances of **6c** are similar to **5c** (194.8 pm on average). The most acute angles of the six-membered heterocycle are

found at the aluminium atoms (100.1° on average), while the angles Al–O–N are much enlarged to 136° . As expected, the nitrogen atom is planar surrounded by three oxygen atoms (sum of the angles = 360.0°). The heterocycle has an envelope conformation similar to **5c** with the bridging carbon atom 59.2 pm above the plane spanned by the five atoms Al1, Al2, O1, O2, and N, which have a maximum deviation from this plane of only 2.5 pm (angle between the normals of the planes 34.9°).

No short bonding distances are observed between atoms of the complex anions and the corresponding cations in both compounds. The sodium atom in **5c** is coordinated by six oxygen atoms of the crown ether (Na–O = 248.7 to 271.8 pm) and one oxygen atom of an ether molecule (Na–O 247.0 pm) with a distorted coordination geometry. In **6c**, the Li atoms of the counterions [Li(triazinane) $_2$] $^+$ are located on a crystallographic inversion center; the Li atoms are coordinated by six nitrogen atoms with Li–N distances between 215.7 and 234.0 pm.

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Experimental Section

General: All procedures were carried out under purified argon in dried solvents (THF and diethyl ether over Na/benzophenone). Compound **1** was synthesized as described in ref.^[6], *N,N',N''*-trimethyltriazinane and pentamethyldiethylenetriamine (PMDETA) were distilled over Na (PMDETA under reduced pressure) and stored over molecular sieve, commercially available crown ether 18-crown-6 (Merck-Schuchardt), NaNO₂ (Aldrich), and LiNO₃ (Riedel-deHaen) were thoroughly evacuated at room temperature and used without further purification.

Synthesis of $[(\mu\text{-NO}_2\text{-N,O})\text{R}_2\text{AlCH}_2\text{AlR}_2]^- [\text{Na}(\text{THF})_3]^+$ (5a**):** A solution of 0.362 g (0.514 mmol) of **1** in 25 ml of THF is added to an excess (0.057 g, 0.826 mmol) of solid NaNO₂. The mixture is vigorously stirred for 22 h, and the solution adopts a pale yellow color. After filtration the solution is concentrated in vacuo at room temp. and cooled to -50°C . The product is isolated as yellow crystals, which rapidly become amorphous at room temperature and normal pressure. Yield: 0.404 g (79%). – M. p. (argon, sealed capillary): 92°C . – ^1H NMR ($[\text{D}_{10}]\text{Et}_2\text{O}$, 300 MHz): δ = 3.66 (m, 12 H, OCH₂ of THF), 1.82 (m, 12 H, CH₂CH₂ of THF), 0.09 (s, 72 H, SiMe₃), -1.06 (s, 4 H, AlCHSi₂), -1.24 (s, 2 H, AlCH₂Al). – ^{13}C NMR ($[\text{D}_{10}]\text{Et}_2\text{O}$, 75.5 MHz): δ = 68.4 (OCH₂ of THF), 26.2 (CH₂CH₂ of THF), 5.9 (SiMe₃), 5.0 (br., AlCH₂Al), 4.1 (AlCSi₂). – IR (CsBr, paraffin): ν = 1497 m cm⁻¹ νNO ; 1462 vs, 1377 s paraffin; 1339 w, 1316 w, 1244 vs δCH_3 ; 1192 m, 1159 m, 1049 vs, 1028 s νCC , νCO ; 1003 vs δCH ; 934 vs, 918 vs, 899 vs, 843 vs, 777 vs, 750 vs, 725 s $\rho\text{CH}_3(\text{Si})$; 698 s, 669 vs $\nu_{\text{as}}\text{SiC}$; 629 m, 613 w $\nu_{\text{s}}\text{SiC}$; 588 w, 561 s, 521 m, 503 w, 496 m, 448 w νAlC , νAlO ; 386 vw, 366 vw δSiC . – UV/vis (diethyl ether) (ϵ): 240 (1750), 290 (sh, 700), 370 nm (sh, 90). – C₄₁H₁₀₂Al₂NNaO₅Si₈ (990.90): calcd. Al 5.4, Na 2.3; found Al 5.4, Na 2.2.

Synthesis of $[(\mu\text{-NO}_2\text{-N,O})\text{R}_2\text{AlCH}_2\text{AlR}_2]^- [\text{Na}(\text{PMDETA})_2]^+$ (5b**):** An excess of solid NaNO₂ (0.070 g, 1.01 mmol) is treated with a solution of 0.513 g (0.727 mmol) of **1** in 50 ml of diethyl ether. 2 ml of PMDETA is added to the suspension, and the mixture is vigorously stirred for 18 h. The solution adopts a pale yellow color. After filtration the solution is concentrated in vacuo at room temp. to about 4 ml and cooled to -50°C . The product is isolated as

yellow crystals, which become amorphous at room temperature. Yield: 0.588 g (72%). – M. p. (argon, sealed capillary): 140°C . – ^1H NMR ($[\text{D}_{10}]\text{Et}_2\text{O}$, 300 MHz): δ = 2.48 and 2.38 (each: pseudo-t, 8 H, NCH₂ of PMDETA), 2.26 (s, 6 H, N-Me of PMDETA), 2.22 (s, 24 H, NMe₂ of PMDETA), 0.10 (s, 72 H, SiMe₃), -1.05 (s, 4 H, AlCHSi₂), -1.23 (s, 2 H, AlCH₂Al). – ^{13}C NMR ($[\text{D}_{10}]\text{Et}_2\text{O}$, 75.5 MHz): δ = 58.6 and 56.7 (NCH₂ of PMDETA), 46.4 (NMe₂ of PMDETA), 43.7 (NMe of PMDETA), 6.0 (SiMe₃), 4.9 (br., AlCH₂Al), 4.3 (AlCSi₂). – IR (CsBr, paraffin): ν = 1497 m cm⁻¹ νNO ; 1464 vs, 1377 s, 1366 s, 1355 m paraffin; 1341 vw, 1308 s, 1291 s, 1252 vs, 1242 vs, 1225 vs δCH_3 ; 1161 s, 1150 s, 1127 m, 1111 s, 1096 m, 1065 m, 1026 vs νCC , νCN ; 1007 vs δCH ; 930 vs, 901 vs, 843 vs, 777 vs, 750 vs, 727 s $\rho\text{CH}_3(\text{Si})$; 667 vs $\nu_{\text{as}}\text{SiC}$; 629 m, 615 w $\nu_{\text{s}}\text{SiC}$; 590 w, 559 s, 517 m, 503 m, 496 m, 465 w, 449 w, 424 vw νAlC , νAlO ; 380 w, 353 vw δSiC . – UV/vis (diethyl ether) (ϵ): 240 (2050), 270 nm (sh, br., 1230). C₄₇H₁₂₄Al₂NaN₇O₂Si₈ (1210.84): calcd. Al 4.8, Na 2.0; found Al 4.8, Na 2.0.

Synthesis of $[(\mu\text{-NO}_2\text{-N,O})\text{R}_2\text{AlCH}_2\text{AlR}_2]^- [\text{Na}([18]\text{crown-6})(\text{Et}_2\text{O})]^+$ (5c**):** An excess of solid NaNO₂ (0.061 g, 0.884 mmol) is treated with a solution of 0.507 g (0.719 mmol) of **1** and 0.252 g (0.953 mmol) [18]crown-6 in 50 ml of diethyl ether. The mixture is vigorously stirred for 18 h, and the solution adopts a pale yellow color. After filtration the solution is concentrated in vacuo at room temp. and cooled to -50°C . The product is isolated as yellow crystals, which become amorphous upon thorough drying in vacuo and include about 0.4 molecules of diethyl ether in each formula unit. Yield: 0.455 g (59%). – M. p. (argon, sealed capillary): 163°C . – ^1H NMR ($[\text{D}_{10}]\text{Et}_2\text{O}$, 300 MHz): δ = 3.69 (s, 24 H, [18]crown-6), 3.39 (q, 1.6 H, OCH₂ of Et₂O), 1.12 (t, 2.4 H, CH₃ of Et₂O), 0.11 (s, 72 H, SiMe₃), -1.04 (s, 4 H, AlCHSi₂), -1.23 (s, 2 H, AlCH₂Al). – ^1H NMR ($[\text{D}_{10}]\text{Et}_2\text{O}$, 500 MHz, 203 K): δ = 3.65 (s, 24 H, [18]crown-6), 3.38 (q, 1.6 H, OCH₂ of Et₂O), 1.15 (t, 2.4 H, CH₃ of Et₂O), 0.15 and 0.06 (each: s, 36 H, SiMe₃), -1.0 and -1.1 (each: br., 2 H, AlCHSi₂), AlCH₂Al not detected. – ^{13}C NMR ($[\text{D}_{10}]\text{Et}_2\text{O}$, 75.5 MHz): δ = 69.8 ([18]crown-6), 6.0 (SiMe₃), 5.0 (br., AlCH₂Al), 4.2 (AlCSi₂). – IR (CsBr, paraffin): ν = 1501 m cm⁻¹ νNO ; 1462 vs, 1377 s, 1354 m paraffin; 1321 vw, 1296 m, 1244 vs δCH_3 ; 1157 m, 1111 s, 1100 s, 1026 m νCC , νCO ; 1005 s δCH ; 953 sh, 932 s, 899 s, 845 vs, 777 s, 750 s, 725 m $\rho\text{CH}_3(\text{Si})$; 669 s $\nu_{\text{as}}\text{SiC}$; 629 w, 610 w $\nu_{\text{s}}\text{SiC}$; 588 w, 561 m, 517 w, 505 w, 498 w, 463 vw, 449 vw νAlC , νAlO ; 388 vw, 359 vw δSiC . – UV/vis (diethyl ether) (ϵ): 230 (2530), 280 (sh, 870), 360 nm (90). C₄₁H₁₀₂Al₂NaNO₈Si₈·0.4 C₄H₁₀O (1068.55): calcd. Al 5.1, Na 2.2; found Al 5.1, Na 2.0.

Synthesis of $[(\mu\text{-NO}_3\text{-O,O'})\text{R}_2\text{AlCH}_2\text{AlR}_2]^- [\text{Li}(\text{THF})_4]^+$ (6a**):** Solid LiNO₃ (0.038 g, 0.554 mmol) is treated with a solution of an equimolar amount of 0.391 g (0.554 mmol) of **1** in 50 ml of THF. The mixture is vigorously stirred for 12 h. The yellow solution is concentrated to about 1 ml, and the product crystallizes as yellowish crystals upon cooling to -50°C . Yield: 0.490 g (83%). – M. p. (argon, sealed capillary): 135°C . – ^1H NMR ($[\text{D}_{10}]\text{diethyl ether}$, 300 MHz): δ = 3.64 (m, 16 H, OCH₂ of THF), 1.79 (m, 16 H, CH₂CH₂ of THF), 0.10 (s, 72 H, SiMe₃), -1.05 (s, 4 H, AlCHSi₂), -1.27 (s, 2 H, AlCH₂Al). – ^{13}C NMR ($[\text{D}_{10}]\text{diethyl ether}$, 75.5 MHz): δ = 68.2 (OCH₂ of THF), 26.3 (CH₂CH₂ of THF), 5.7 (SiMe₃), 5.0 (br., AlCH₂Al), 4.3 (AlCSi₂). – IR (CsBr, paraffin): ν = 1501 s cm⁻¹ νNO ; 1462 vs, 1377 vs paraffin; 1344 m, 1281 vs, 1248 vs δCH_3 ; 1179 w, 1067 s, 1044 vs νCC , νCO ; 1007 s δCH ; 930 vs, 912 s, 845 vs, 777 vs, 750 s, 725 s $\rho\text{CH}_3(\text{Si})$; 667 s $\nu_{\text{as}}\text{SiC}$; 629 m, 611 w $\nu_{\text{s}}\text{SiC}$; 583 w, 556 s, 521 m, 505 m, 465 vw, 452 w, 421 w νAlC , νAlO , νLiO ; 372 vw, 334 vw, 316 vw δSiC . – UV/vis (THF) (ϵ): 225 (2470), 260 nm (sh, br., 990). C₄₅H₁₁₀Al₂LiNO₇Si₈ (1062.96): calcd. Al 5.1, Li 0.6; found Al 5.1, Li 0.6.

Table 1. Crystal data, data collection parameters, and structure refinement for **5c** and **6c**^[a] (crystal data of **5a** and **5d** [Na(TMPDA)₂] included)

	5a	5c	5d	6c
Formula	C ₄₁ H ₁₀₂ NO ₅ NaAl ₂ Si ₈	C ₄₅ H ₁₁₂ NO ₉ NaAl ₂ Si ₈	C ₄₃ H ₁₁₄ N ₅ O ₂ NaAl ₂ Si ₈	C ₄₁ H ₁₀₈ LiN ₇ O ₃ Al ₂ Si ₈
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	<i>P</i> 2(1)/ <i>n</i> ; No. 14 ^[25]	<i>P</i> 2(1)/ <i>n</i> ; No. 14 ^[25]	<i>P</i> 2(1)/ <i>n</i> ; No. 14 ^[25]	<i>P</i> 1; No. 2 ^[25]
<i>Z</i>	4	4	4	2
Temperature [K]	297(1)	300(2)	297(1)	293(2)
<i>d</i> _{calc.} [g/cm ³]	0.842	1.041	0.975	0.994
<i>a</i> [pm]	1816.2(2)	1496.0(1)	1989.6(3)	1404.5(2)
<i>b</i> [pm]	1837.1(2)	2766.5(3)	1507.0(3)	1437.6(2)
<i>c</i> [pm]	2385.9(3)	1716.0(1)	2393.1(5)	1935.3(2)
<i>α</i> [°]	90	90	90	78.97(2)
<i>β</i> [°]	100.98(2)	90.594(7)	100.78(3)	85.54(2)
<i>γ</i> [°]	90	90	90	64.09(1)
<i>V</i> [10 ^{−30} m ³]	7815(1)	7102(1)	7049(2)	3449.8(8)
<i>μ</i> [mm ^{−1}]		0.223		0.215
Crystal size [mm]	0.65 × 0.65 × 0.04	0.67 × 0.70 × 0.33	1.06 × 0.72 × 0.61	0.65 × 0.53 × 0.53
Diffractionmeter	AED-2	Stoe-IPDS	AED-2	AED-2
Radiation	Mo- <i>K</i> _α ; graphite monochromator			
2 θ range [°]		3.8 ≤ 2 θ ≤ 48.2		3.2 ≤ 2 θ ≤ 46
Index ranges		−15 ≤ <i>h</i> ≤ 17 −31 ≤ <i>k</i> ≤ 31 −19 ≤ <i>l</i> ≤ 17		−15 ≤ <i>h</i> ≤ 15 −15 ≤ <i>k</i> ≤ 15 0 ≤ <i>l</i> ≤ 21
Independent reflections		10572		9621
Reflections <i>F</i> > 4 σ (<i>F</i>)		5380		5823
Parameters		621		630
<i>R</i> = $\Sigma F_o - F_c /\Sigma F_o $ [<i>F</i> > 4 σ (<i>F</i>)]		0.0531		0.0873
<i>wR</i> ² = $\{\Sigma w(F_o ^2 - F_c ^2)^2 / \Sigma w(F_o^2)\}^{1/2}$ (all data)		0.0795		0.1068
Max./min. residual electron density [10 ³⁰ e/m ³]		0.480/−0.280		0.295/−0.208

[a] Programmes SHELXL-93; SHELXTL^[26]; solutions by direct methods, full matrix refinement with all independent structure factors.

Synthesis of [(μ-NO₃-O, O')R₂AlCH₂AlR₂][−][Li{(CH₂NMe)₃}-THF]⁺ (6b**):** Solid LiNO₃ (0.048 g, 0.696 mmol) is treated with a solution of an equimolar amount of 0.490 g (0.694 mmol) of **1** and 2 ml of trimethyltriazinane in 45 ml THF. The mixture is vigorously stirred for 24 h. The yellow solution is evaporated, the residue is treated with 5 ml of diethyl ether, and THF is added dropwise until a clear solution is obtained. Product **6b** crystallizes as yellow crystals upon cooling to −50 °C, which contain one molecule of THF and one molecule of trimethyltriazinane in each formula unit. The product (**6c**) with two trimethyltriazinane molecules coordinated to lithium, which was used for the crystal structure determination, was obtained on slow cooling of a dilute solution of **6b** in diethyl ether by the addition of a small amount of trimethyltriazinane. Yield of **6b**: 0.465 g (69%). – M. p. (argon, sealed capillary): 99 °C. – ¹H NMR ([D₈]THF, 300 MHz): δ = 3.62 (m, 4 H, OCH₂ of THF), 3.10 (br., 6 H, NCH₂ of triazinane), 2.20 (s, 9 H, Me of triazinane), 1.78 (m, 4 H, CH₂CH₂ of THF), 0.10 (s, 72 H, SiMe₃), −1.06 (s, 4 H, AlCHSi₂), −1.28 (s, 2 H, AlCH₂Al). – ¹³C NMR ([D₈]THF, 75.5 MHz): δ = 78.3 (NCN of triazinane), 40.5 (Me of triazinane), 5.8 (SiMe₃), 5.1 (br., AlCH₂Al), 4.4 (AlCSi₂). – IR (CsBr, paraffin): ν = 1503 m cm^{−1} νNO; 1466 vs, 1377 s paraffin; 1346 w, 1289 m, 1274 m, 1244 s δCH₃; 1159 m, 1119 s, 1051 vs vCC, vCO, vCN; 1015 s δCH; 916 s, 843 vs, 777 s, 737 m, 725 m pCH₃(Si); 671 s ν_{as}SiC; 631 m, 611 w ν_sSiC; 579 m, 554 m, 519 s, 506 m, 465 m, 452 w, 419 w νAlC, νAlO; 395 w, 372 w, 339 w, 316 w δSiC. – UV/vis (THF) (ε): 240 (1710), 260 nm (sh, br., 1320). – C₃₉H₁₀₁Al₂LiN₄O₄Si₈ (975.84): calcd. Al 5.5, Li 0.7; found Al 5.6, Li 0.7.

Crystal Structure Determinations: Single crystals of compound **5c** were obtained by recrystallization from diethyl ether, the crystals of compound **6c** were grown by recrystallization of **6b** from a dilute

solution in ether in the presence of a small quantity of triazinane. Crystal data and structure refinement parameters are given in Table 1^[27]. One of the [Li(triazinane)₂]⁺ cations shows a disorder with a partial overlap of the atoms of the triazinane molecules. Crystal data of **5a** and of **5**[Na(TMPDA)₂] (**5d**) (TMPDA = tetramethylpropylenediamine) are also given in Table 1; both structures could not be satisfactorily refined due to the severe disorder of the cations. **5d** was obtained on the same route as compound **5b**, but was not isolated in a high yield.

★ Dedicated to Prof. Dr. Heinrich Nöth on the occasion of his 70th birthday.

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