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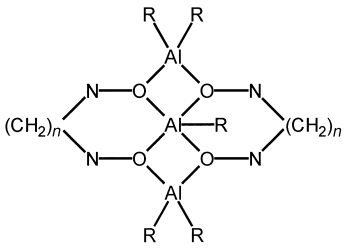
The Highly Flexible Bis(hydroxylamine) Ligand $[ON(Me)]_2CH_2^{2-}$ and Its Different Behavior in the Chemistry of Aluminum and Gallium**

Christian Lustig and Norbert W. Mitzel*

The coordinative flexibility of diolate substituents could be markedly improved if they contained additional donor atoms, preferably in close proximity to the primary donor sites. Such systems are accessible as anions of OH functional bis(hydroxylamines), that is as diolates that contain additional N-heteroatoms in geminal position relative to the metal to be bound. Such diolate ligands with improved flexibility should offer a diverse range of applications, because diolates and other difunctional ligands, in particular those of the salen type, are currently employed in a number of investigations in organoaluminum chemistry.[1] Interest in this area is directed towards the preparation of bimetallic complexes[2] and aluminum cations, which are exceedingly strong Lewis acids and capable of catalyzing reactions such as oxirane oligomerization,[3] where other Lewis acids fail to work. Fundamental investigations have recently produced a number of trinuclear aluminum diolate complexes of the type shown in Scheme 1.[4]

Herein we present the chemistry of the so far neglected tetrafunctional ligand system $[ON(Me)]_2CH_2^{2-}$ with organoaluminum and -gallium compounds. Until now this ligand has only been applied in the coordination chemistry of the nonmetal boron,[5] but not a single metal complex is known. $[HON(Me)]_2CH_2$ is available in high yields using a condensation reaction of *N*-methylhydroxylamine hydrochloride and formaldehyde mediated by potassium carbonate.[6]



Scheme 1. Typical structure of trinuclear diolate complexes of aluminum (and analogously gallium) as obtained from the reaction of AlR_3 with diols. R = alkyl, halogen, H.

The bis(hydroxylamine) $[HON(Me)]_2CH_2$ can be deprotonated with *n*-butyllithium in nonpolar solvents. The resulting suspensions of $[LiON(Me)]_2CH_2$ react with dimethylaluminum and dimethylgallium chloride to afford the heteronorbornane systems $[Me_2MON(Me)]_2CH_2$ (M = Al (**1**), Ga (**2**)); hereby four chemical bonds, including two dative ones, are formed in an one-step reaction. This reaction is completely selective for **2**, but if dimethylaluminum chloride is employed, both products **1** and **3** (see Scheme 2) are possible; subtle changes in conditions switch the selectivity completely to one or the other product. In several runs of this reaction we obtained **3** more often than **1**, but to date we have not been able to establish the conditions under which the selectivity is reliably predictable.

The heteronorbornane systems **1** and **2** parallel our recent findings using the isoelectronic ligand system $[^-CH_2N(Me)]_2CH_2$, which also leads to the heteronorbornane cages $[Me_2MCH_2N(Me)]_2CH_2$.[7] The only organoaluminum hydroxylamide compound published to date is the trimeric $[Me_2AlONMe_2]_3$ compound; its interesting intramolecular Al···N contacts lead to the coordination numbers 4, 5, and 6 in the same molecule.[8]

In an attempt to find a simpler synthetic route to the compounds $[Me_2MON(Me)]_2CH_2$ we treated the OH-functional bis(hydroxylamine) $[HON(Me)]_2CH_2$ with trimethylaluminum and -gallium. In the case of trimethylgallium, the product of this reaction was identical to **2**. This is in contrast to the reaction products of $GaMe_3$ with diols, which are usually analogous to the trinuclear aluminum compounds shown in Scheme 1.[2] It is clearly the presence of the nitrogen atoms in geminal position to the gallium atom, which induce this different reaction mode. The reaction with trimethylaluminum afforded colorless crystals of **3a**, which contains four- and five-coordinate aluminum atoms (Scheme 2) as indicated by the two resonance signals in the ^{27}Al NMR spectrum. Crystal structure analyses revealed the two different reaction modes with these earth metal organyl compounds. Both reactions are not sensitive to the stoichiometric ratio of the reagents. Compound **2** is formed even under a stoichiometry of $[HON(Me)]_2CH_2$:$GaMe_3$ of 2:3, while **3** results also from $[HON(Me)]_2CH_2$:$AlMe_3$ mixtures in the ratio 1:2.

The gallium heteronorbornane **2** is aggregated into endless chains in the crystal lattice (Figure 1) through the formation of four-membered Ga_2O_2 rings resulting from two Ga···O contacts (2.332(4) and 2.348(4) Å), which are substantially longer than the Ga–O bond in the norbornane skeleton (1.928(4) Å). The Ga–N distances are 2.256(5) and 2.257(5) Å

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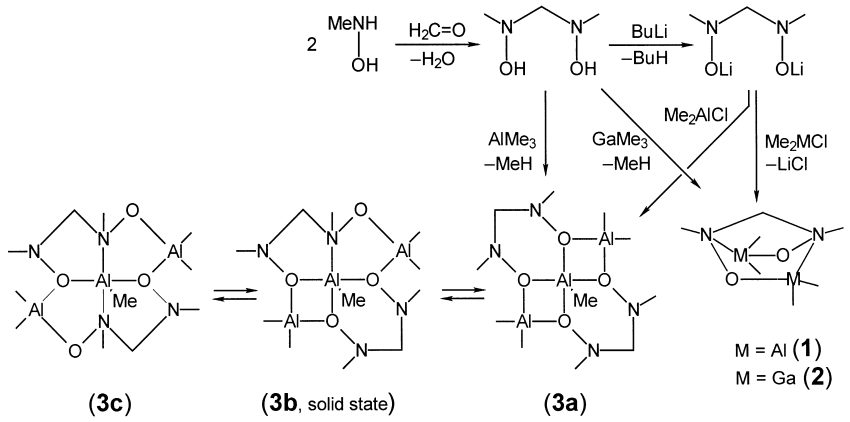

Scheme 2. Reactions of the bis(hydroxylamine) $[HON(Me)]_2CH_2$ with $AlMe_3$ and $GaMe_3$ and reactions of the dilithiated bis(hydroxylamine) $[LiON(Me)]_2CH_2$ with Me_2GaCl and Me_2AlCl. The latter reaction produces different products upon different reaction conditions. Also shown is the isomerism of the compounds **3a**–**c**.

and correspond to endocyclic N–Ga donor–acceptor bonds, whereby they are longer than those in Me_3Ga–NMe_3 (Ga–N 2.09(3)).[9] The NMR spectra of **2** are consistent with the interpretation of monomeric units in solution and show different resonance signals for the equatorial and axial methyl groups at the gallium centers. This behavior remains unchanged in the temperature range between -90 to $+90\,^{\circ}C$ in $[D_8]$toluene and is the same as that for **1**, for which we could not determine the solid-state structure.

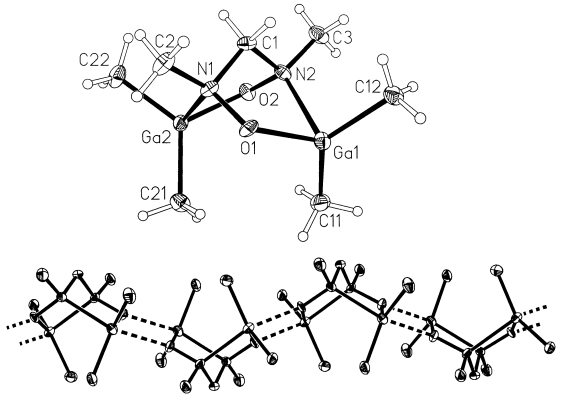

Figure 1. Crystal structure of the monomer of **2** (top) and a plot to illustrate the aggregation into endless chains (bottom). Selected intramolecular distances [Å] and angles [°]: Ga1-O1 1.929(4), Ga1-N2 2.257(5), Ga1-C11 1.940(6), Ga1-C12 1.967(6), O1-N1 1.433(6), N1-C1 1.465(7), N1-C2 1.450(7); Ga1-O1-N1 115.1(3), O1-Ga1-N2 79.2(2), O1-N1-C1 105.5(4), N1-C1-N2 105.0(4), O1-Ga1-C11 115.5(2), O1-Ga1-C12 116.8(2), C11-Ga1-C12 126.8(3), O1-N1-C2 108.1(4), C1-N1-C2 110.1(5). Intermolecular distances [Å] and angles [°]: Ga1-O1′ 2.348(4), Ga2-O2′ 2.332(4); Ga1-O1-Ga1′ 111.4(2), Ga2-O2-Ga2′ 110.8(2), O1-Ga1-O1′ 68.6(2), O2-Ga2-O2′ 69.2(2).

As already indicated in Scheme 2, the crystal structure of **3** (Figure 2) differs from that of the expected symmetrical isomer **3a** and represents the isomer **3b**. In contrast to the 1,3-propanediolates (Scheme 1), both independent molecules in the crystal structure of compound **3** comprise one six-membered, two five-membered, and one four-membered ring arranged about a central five-coordinate Al atom, which has a $AlCO_3N$ connectivity. The difference between the structures **3a** and **3b** is that the central Al atom forms a bond to one of the four nitrogen centers (which were three-coordinate in **3a**), while giving up the connectivity to the neighboring oxygen atom. This demonstrates that switching between two donor centers connected with one another is the reason for the enormous coordinative flexibility of $[ON(Me)]_2CH_2^{2-}$ ligands in comparison to 1,3-propanediolates and other difunctional ligands, which do not possess such donor centers geminal to the metal center.

However, in C_6D_6 solution at ambient temperature we observed NMR signals for ^1H, ^{13}C, and ^{27}Al, which are consistent with

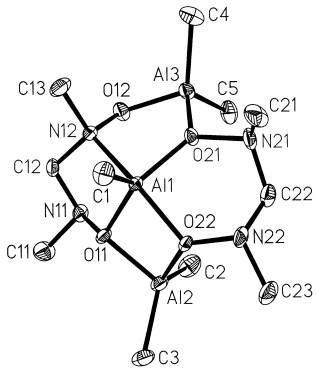

Figure 2. Crystal structure of one of the two independent molecules of **3b**. The other molecule is very similar in geometry but related to the one shown here by inversion symmetry. Selected distances [Å] and angles [°]: Al1-C1 1.945(5), Al1-O11 1.892(3), Al1-O21 1.841(3), Al1-O22 1.874(3), Al1-N12 2.080(3), Al2-O11 1.866(3), Al2-O21 1.856(3), Al3-O12 1.804(3), Al3-O21 1.844(3); C1-Al1-O11 117.6(2), C1-Al1-O21 114.2(2), C1-Al1-O22 108.0(2), C1-Al1-N12 104.1(2), O11-Al1-N12 81.6(1), N12-Al1-O21 84.2(1), O21-Al-O22 90.7(1), O22-Al1-O11 76.0(1), O11-Al2-O22 77.1(1), O12-Al2-O21 91.2(1).

a pseudo C_{2v} structure **3a** (given rotational symmetry of the central methyl group). The seeming difference between solution and solid-state structures are the result of the highly dynamic behavior of **3**, which we studied by ^1H NMR spectroscopy in $[D_8]$toluene in a temperature range between -80 and $+20\,^{\circ}C$ (Figure 3). At $-80\,^{\circ}C$ five signals for the Al-bound methyl groups occur and four for the N-bound ones, clearly indicating the isomer **3b** to be the only species dissolved. Upon warming the solution to $+20\,^{\circ}C$, the spectrum becomes simpler and only three signals for the Al-bound methyl groups and a broad one for the N-bound methyl groups can be observed. This would be consistent with isomer **3a**, but has to be rationalized by a rapid exchange between isomer **3b** and isomer **3a**, which means that averaged over time the five-coordinate aluminum atom interacts with all eight donor centers of the $C_2N_4O_4Al_2$ macrocycle.

The relative energies of the three isomers have been estimated by calculations at the B3LYP/6-31G(d) level of theory, which confirmed **3b** to be the ground state, but **3a** is only 4.5 kJ mol^{-1} higher in energy (the lowest energy con-

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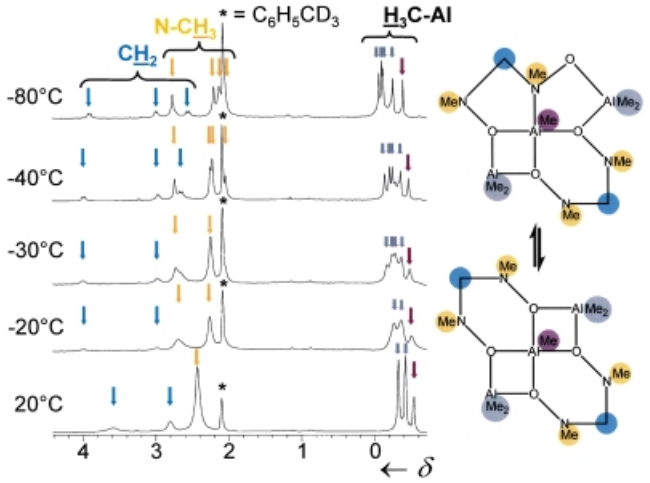

Figure 3. ^{1}H NMR spectra of a solution of **3** in [D$_8$]toluene recorded at temperatures between -80 and $+20\,^\circ$C.

former in each case). The isomer **3c** (Scheme 1), which can be considered as a third possibility, is predicted to be 94 kJ mol^{-1} higher in energy than **3b** and should thus not be observable in solution.

All this demonstrates the enormous flexibility of the $[ON(Me)]_2CH_2^{2-}$ ligand, which is able to adopt and stabilize different coordination modes of the five-coordinate Al atom in **3**; the two isomers **3a** and **3b** have very similar energies allowing the ease of their interconversion. Subtle energy differences are probably also responsible for the different reaction pathways of $[HON(Me)]_2CH_2$ with $AlMe_3$ and $GaMe_3$. The ligand $[ON(Me)]_2CH_2^{2-}$ can thus be expected to become a valuable extension of diolate chemistry, as it can adapt itself to the coordinative requirements of a metal atom to be stabilized, possibly even during a reaction involving this center.

Experimental Section

1: Dimethylaluminum chloride (12.0 mL, 1.0 M solution in hexane, 12 mmol) was slowly added to a suspension of the dilithiated bis(hydroxylamine) in diethyl ether prepared by deprotonation of the free hydroxylamine (0.64 g, 6.0 mmol) with *n*BuLi (7.5 mL of a 1.6 M solution in hexane) at 0 °C, stirred overnight at ambient temperature and filtered to remove lithium chloride. The solvent was removed under reduced pressure and a colorless solid (**1**) was obtained. Yield: 0.52 g (40 %); m.p. 127 °C; ^{1}H NMR (C_6D_6): $\delta = -0.67$ (s, 6H; $AlCH_3$), -0.34 (s, 6H; $AlCH_3$), 1.82 (s, 6H; NCH_3), 2.16 (s, 2H; NCH_2N); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = -10.5$ (s; $AlCH_3$), -9.0 (s; $AlCH_3$), 45.8 (s; NCH_3), 81.2 (s; NCH_2N); ^{27}Al NMR (C_6D_6): $\delta =$ 177.5; elemental analysis correct for $C_7H_{20}Al_2N_2O_2$. The Ga compound **2** can be synthesized in an analogous manner starting from dimethylgallium chloride.

2: The bis(hydroxylamine) $[HON(Me)]_2CH_2$ (0.53 g, 5 mmol) was dissolved in toluene (40 mL) and cooled to 0 °C. A solution of trimethylgallium (1.15 g, 10 mmol) in diethyl ether (15 mL) was added very slowly. During the addition a white solid precipitated. The suspension was stirred overnight, filtered, and stored at $-40\,^\circ$C, whereby **2** formed crystals. Both the crystalline material as well as the precipitate were analytically pure products. Yield: 1.32 g (87 %); m.p. 158 °C (decomp); sublimation point: 73 °C (0.1 mbar); ^{1}H NMR (C_6D_6): $\delta = -0.32$ (s, 6H; $GaCH_3$), 0.17 (s, 6H; $GaCH_3$), 2.25 (s, 6H; NCH_3), 2.63 (s, 2H; NCH_2N); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = -7.2$ (s; $GaCH_3$), -4.1 (s; $GaCH_3$), 43.1 (s; NCH_3), 84.1 (s; NCH_2N); MS (CI): *m*/*z* (%): 304 [M^+] (14), 289 [$M^+ -$ Me] (23); elemental analysis correct for $C_7H_{20}Ga_2N_2O_2$.

3: The bis(hydroxylamine) $[HON(Me)]_2CH_2$ (0.53 g, 5 mmol) was dissolved in diethyl ether (30 mL) and cooled to 0 °C. A solution of trimethylaluminum (10 mL, 1.0 M in hexane, 10 mmol) was slowly added to the solution. After addition, the reaction mixture was allowed to warm to room temperature and stirred overnight, filtered, concentrated to half its volume, and stored at $-78\,^\circ$C. After a week colorless crystals of **3** were formed. Yield: 0.78 g (43 %); m.p. 94 °C; ^{1}H NMR (C_6D_6): $\delta = -0.53$ (s, 3H; $AlCH_3$), -0.45 (s, 6H; $Al(CH_3)_2$), -0.35 (s, 6H; $Al(CH_3)_2$), 2.48 (s, 12H; NCH_3), 2.93 (br s, 2H; NCH_2N), 3.70 (br s, 2H; NCH_2N); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = -11.1$ (s; $AlCH_3$), -8.8 (s; $AlCH_3$), -8.5 (s; $AlCH_3$), 46.1 (s; NCH_3), 83.7 (s; NCH_2N); ^{27}Al NMR (C_6D_6): $\delta = 75$ (s, $\nu_{1/2} =$ 2700 Hz; $AlCH_3$), 149 (s, $\nu_{1/2} = 7500$ Hz; $Al(CH_3)_2$); MS(CI): *m*/*z* (%): 364 [M^+] (92), 349 [$M^+ -$ Me] (23); elemental analysis correct for $C_{11}H_{31}Al_3N_4O_4$.

X-ray crystal structure determinations: The data for **2** [**3**] were collected on a Nonius Turbo CAD4 [Nonius DIP 2020] diffractometer at 123(2) [153(2)] K with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined against F^2 by full-matrix least-squares with SHELXS 97.[10] **2** ($C_7H_{20}Ga_2N_2O_2$): $M_r = 303.69$, monoclinic, space group $P2_1/n$, $a = 7.388(2)$, $b = 10.040(4)$, $c = 16.161(4)$ Å, $\beta = 93.69(2)^\circ$, $V = 1196.3(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.686$ g cm^{-3}, $F(000) = 616$, $\mu(Mo_{K\alpha}) = 4.479$ mm^{-1}. A total of 2619 reflections were measured in the range $4.8 \le 2\theta \le 54.0^\circ$, of which 2563 were unique ($R_{int} = 0.093$). Final *R* indices: $R_1 = 0.0605$ ($I > 2\sigma(I)$), $wR_2 = 0.1705$ (all data); max./min. residual electron density 1.23/-1.18 e Å^{-3}. **3** ($C_{11}H_{31}Al_3N_4O_4$): $M_r = 364.34$, triclinic, space group $P\bar{1}$, $a = 9.0333(1)$, $b = 9.4842(2)$, $c = 25.5842(56)$ Å, $\alpha =$ 88.4744(15), $\beta = 83.3769(12)$, $\gamma = 70.4065(15)^\circ$, $V = 2051.0(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.180$ g cm^{-3}, $F(000) = 784$, $\mu(Mo_{K\alpha}) = 0.203$ mm^{-1}. A total of 98955 reflections were measured in the range $5.2 \le 2\theta \le 54.6^\circ$, of which 4867 were unique ($R_{int} = 0.044$), Intensity corrections were applied by the program SCALEPACK.[11] Final *R* indices: $R_1 = 0.0861$ ($I > 2\sigma(I)$), $wR_2 =$ 0.1839 (all data); max./min. residual electron density 0.56/-0.36 e Å^{-3}. 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-166900 (**2**) and CCDC-166901 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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