Partial Reduction of the N–O Functions of Partially Deprotonated Bis(hydroxylamine) Complexes

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Z. Naturforsch. **2009**, *64b,* 1208 – 1212;
received July 20, 2009

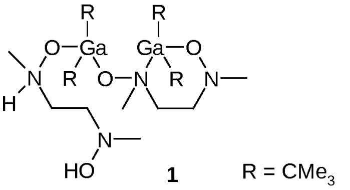
The reduction of a partially deprotonated bishydroxylamine complex $\{(^t\mathrm{Bu_2Ga})_2[\mathit{cyclo}\text{-}\mathrm{ON(Me)(CH_2)_2(Me)NO}][\mathrm{HON(Me)(CH_2)_2(Me)(H)NO}]\}$ with a reagent composed of titanium tetrachloride and methyllithium leads to the reduction of one of the N–O groups to an amine function affording the salt $\{(^t\mathrm{Bu_2Ga})[\mathit{cyclo}\text{-}\mathrm{ON(H)(Me)(CH_2)_2NHMe}]\}^+$ $\{t\mathrm{Bu_2GaCl_2}\}^-$. This has been characterised by ^{1}H and ^{13}C NMR spectroscopy, by elemental analysis and by single crystal X-ray diffraction, showing the neutral amine/hydroxylamine ligand to be present in its tautomeric aminoxide form. The molecules form hexameric cyclic aggregates by N–H$\cdots$Cl hydrogen bonds.

Key words: Gallium, Hydroxylamine, Aminoxide,
N,O-Ligands, Crystal Structure

Introduction

Hydroxylaminato anions of the type R_2NO^- are generally easily accessible by alkane elimination reactions from the metal alkyls and OH-functional hydroxylamine precursors [1]. They show a range of interesting ligand properties due to the presence of directly adjacent anionic oxygen and neutral nitrogen donor sites. In this respect they are related to hydrazides, $R_2N\text{-}(R)N^-$ [2] and alkylperoxides, ROO^- [3]. This common feature is the basis for a unique flexibility in changing between different coordination modes in their compounds with Lewis-acidic metal atoms.

Only recently we have shown that it is possible to prepare a compound with both, hydroxylamine N–OH and gallium alkyl functions, in the same molecule [4]. This unusual molecule contains the mutually reactive OH and gallium-alkyl functions simultaneously. Another interesting feature of this compound is that it comprises different bis-hydroxylamine units in the same aggregate, *viz.* a doubly deprotonated one and another one, which still bears its two protons. The latter itself contains an -N(Me)OH function and a tautomeric aminoxide function -NH(Me)-O, which is bonded to a gallium atom (Scheme 1).



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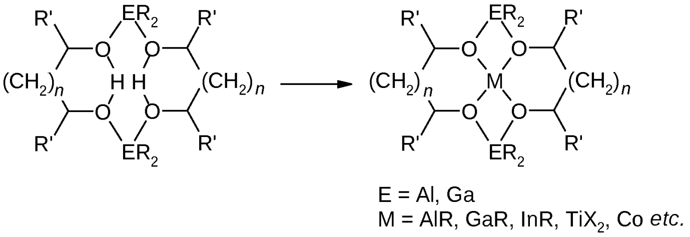
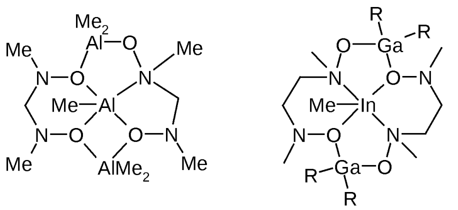
Scheme 1. The partially deprotonated bishydroxylaminato-di-*tert*-butylgallium compound **1**.

Related partly deprotonated systems [5] exist in the diolate chemistry of group 13 metals [6]. Such compounds have been used as reagents for the stepwise synthesis of compounds with a diolato/organometallic macrocyclic system surrounding a different central metal atom (Scheme 2). Trinuclear homometallic complexes of related constitution have been obtained by directly reacting the diols with reactive metal alkyls [6].

For the bishydroxylamines we have previously shown that it is possible to obtain – similar to the diolate chemistry – trinuclear complexes like $[(\mathrm{MeAl})\{(\mathrm{Me_2Al})_2[\mathrm{ON(Me)CH_2(Me)NO}]\}]$ with a central five-coordinate Al atom (Scheme 3). These compounds are extremely dynamic in solution due to the presence of adjacent N and O atoms and the resulting ease of 1,2-shift rearrangements [7]. We could also show that compound **1** may be used as a building block for the generation of heterobimetallic systems with such a flexible ligand periphery. With trimethylindium it reacts under formation of a related but heterotrinuclear complex $[(\mathrm{MeIn})\{(t\mathrm{Bu_2Ga})_2[\mathrm{ON(Me)(CH_2)_2(Me)NO}]\}]$ (Scheme 3) [8]. In contrast to the trinuclear Al compound, where the central MeAl unit prefers to be bonded to three oxygen atoms and one nitrogen atom, the indium atom in the latter compound is bonded to two oxygen and two nitrogen atoms of the outer macrocycle; this reflects the capability of the hydroxylamine ligands to adapt themselves to the electronic needs of the metal atoms they are bonded to.



Scheme 2. Heterobimetallic diolato complexes from partially deprotonated group 13 diolates.



Scheme 3. Homometallic and heterobimetallic bishydroxylaminato complexes.

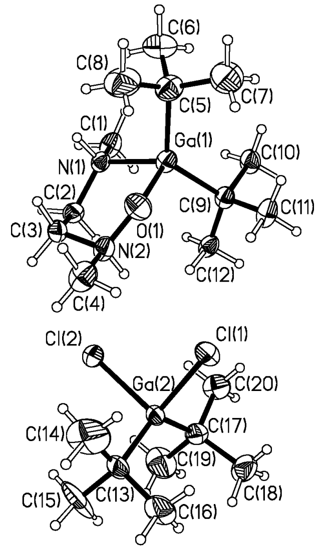


Fig. 1. Structure of the cation and the anion of **2** in the solid state. Selected bond lengths (Å) and angles (deg): Cation: Ga(1)–O(1) 1.889(3), Ga(1)–N(1) 2.049(4), O(1)–N(2) 1.357(5); Ga(1)–O(1)–N(2) 121.1(3), Ga(1)–N(1)–C(1) 115.3(3), Ga(1)–N(1)–C(2) 111.7(3), C(1)–N(1)–C(2) 111.2(4), O(1)–N(2)–C(3) 113.3(4), O(1)–N(2)–C(4) 105.9(4); anion: Ga(2)–Cl(1) 2.319(2), Ga(2)–Cl(2) 2.297(2), Ga(2)–C(13) 1.997(4), Ga(2)–C(17) 1.988(5); Cl(1)–Ga(2)–Cl(2) 97.03(5), C(13)–Ga(2)–(C17) 126.9(2), C(13)–Ga(2)–Cl(1) 107.2(2), C(13)–Ga(2)–Cl(2) 107.4(2).

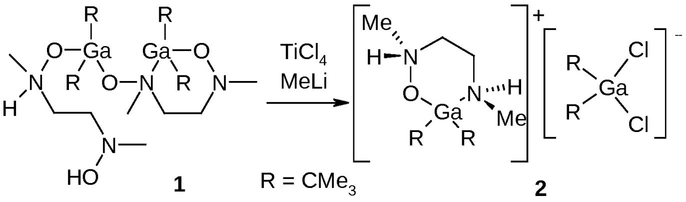
Discussion

We have now made an attempt to introduce a $TiMe_2$ unit into a $\{(t\mathrm{Bu}_2\mathrm{Ga})_2[\mathrm{ON(Me)(CH_2)_2(Me)NO}]\}$ macrocycle, with the aim to generate a heterobimetallic bis-hydroxylaminato complex analogous to the diolato compounds shown in Scheme 2. To achieve this, we reacted **1** with titanium tetrachloride and lithium methyl in a one-pot protocol (Scheme 4), because the introduction of titanium fragments with simultaneous methylation turned out to be a useful method for the introduction of Cp*TiMe units (reagent: Cp^*TiCl_3 + MeLi) in hydroxylamine complexes $[\mathrm{CpTiMe}(\{\mathrm{ON(Me)CH_2}\}_2)]$, which we reported recently [9].

However, instead of the expected titanium complex we obtained a reduction product of one of the hydroxylamine ligands in moderate yield of 48 %. Other products could not be identified. Product **2** contains a semi-deoxygenated bis-hydroxylamine, which at its non-reduced end is present in the tautomeric aminoxide form and serves as a neutral ligand to chelate a $t\mathrm{Bu}_2\mathrm{Ga}$ cation. This cation is complemented by a di-*tert*-butyldichlorogallate anion.

Compound **2** was characterised by elemental analysis, NMR spectroscopy and determination of its crystal structure by X-ray diffraction. The proton of the aminoxide unit of **2** causes a resonance at 9.54 ppm in the ^{1}H NMR spectrum, which is close to the value observed for **1** (9.77 ppm) [4]. Two broad resonances at 2.58 and 3.06 ppm belong to the ethylene unit and are shifted to lower field as compared to **1** (2.75–2.71 ppm) [4], for which they have been observed as non-resolved multiplets. The methyl groups at the two different nitrogen atoms give two singlets at 1.96 and 2.11 ppm, while the *tert*-butyl groups at the gallium atoms give a broad multiplet between 0.99 and 1.12 ppm. The ^{13}C NMR spectrum contains only one broad resonance at 60.5 ppm for the two methyl groups, while the other carbon atoms are found as well resolved signals: two sets of two signals for the two chemically distinct *tert*-butyl groups of the cation and one set for the anion (23.0, 25.8, 30.3, 30.4, 30.8 and 31.1 ppm).

Compound **2** (Fig. 1) crystallises in the hexagonal space group $R\bar{3}$ with 18 formula units per unit cell. The



Scheme 4. Partial reduction of one of the hydroxylamine ligands in **1** to an ethylene(amine)(hydroxylamine).

hydrogen atoms at N(1) and N(2) were refined isotropically. The structure contains highly disordered hexane solvent molecules (1/3 per formula), so the reflection data were treated with the SQUEEZE procedure of PLATON [10]. The interpretation of the ligand function as an aminoxide form follows from the N–O bond length of 1.357(5) Å. This is very short, shorter than the gallium-bound aminoxide unit in **1** at 1.405(2) Å [4] and even shorter than in Me_3N-O at 1.388 Å [11]. The Ga–O distance at 1.889(3) Å is shorter than the Ga–O distance to the aminoxide unit in **1** (1.953(2) Å), but intermediate between the endocyclic (1.876(2) Å) and exocyclic (1.973(2) Å) Ga–O distances to the anionic oxygen atoms in **1**. The Ga(1)–O(1)–N(2) angle in the ring found for **2** to be 121.1(3)° is substantially wider than the corresponding endocyclic one in **1**, but similar to the Ga–O–N angle belonging to the gallium-bound aminoxide unit in **2** (119.7(2)°).

The Ga(1)–N(1) bond length in **2** at 2.049(4) Å is shorter than for $[\mu\text{-}O(CH_2)_3N(H)Me]Ga^tBu_3$ at 2.093(2) Å [12], solid Me_3N–GaH_3 (2.081 Å) [13], gaseous Me_3N–$GaMe_3$ (2.09(5) Å) [14], and $(Me_2GaCH_2NMe_2)_2$ at 2.093(2) Å [15], which might be due to the cationic character of **2**. The two ring-bound methyl groups are in *trans*-configuration (equatorial-equatorial) of the chair-form metallacycle.

In the anion of **2** the small Cl–Ga–Cl angle of 97.0(1)° is comparable to the angle of 99.5° found in the anion of the bis[tetrakis(isopropanol)lithium] di-*tert*-butyl-dichloro-gallate salt $[Li(^iPrOH)_4][^tBu_2GaCl_2]$ [16]. It is closer to the Cl–Ga–Cl angle of the two bridging chlorine atoms in the dimer $(GaCl_3)_2$ (89.1(1)°) than to the exocyclic one 122.2(1)° [17].

Table 1. Structural parameters (Å, deg) of hydrogen bonds in **2**[a].

D–H	A	*d*(D–H)	*d*(H···A)	∠DHA	*d*(D···A)
N1–H1	Cl1′[a]	0.78(4)	2.57	146	3.25
N2–H2	Cl2	0.99(6)	2.48	130	3.21

[a] Symmetry code for Cl1′: $x-y+2/3, x+1/3, -z+1/3$.

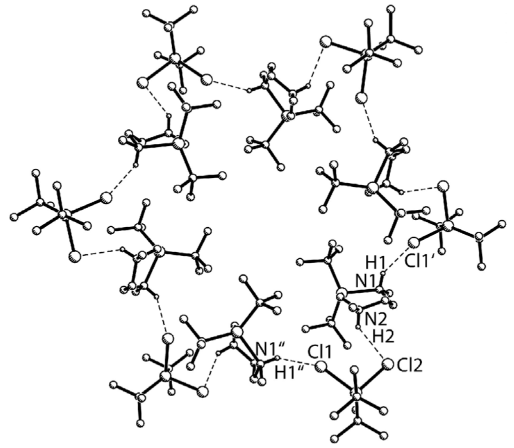


Fig. 2. Hydrogen-bonded hexameric ring aggregates of **2**.

Compound **2** shows an interesting pattern of hydrogen bonding (Fig. 2). Both N–H functions of the cation are linked to neighbouring chlorine atoms of two anions. In this way, six alternating cations and anions form a ring structure of S_6 symmetry. The H···Cl distances are 2.48 and 2.57 Å, which is perfectly in the range for weak N–H···Cl hydrogen bonding finding its mean of the distribution of known distances at 2.50 Å [18]. The volume of the void inside a hexamer was calculated [10] to be 73 Å^3. The volume of 585 Å^3 between the hexamers accommodates two hexane solvent molecules. The relatively small N–H···Cl angles of 146 and 130° are noteworthy (Table 1).

In essence, we have shown that the reagent $TiCl_4$/MeLi can be used to achieve a reduction of one of two N–OH functions of a bis(hydroxylamine) ligand in its gallium complex **1**. This represents a further possibility of the synthesis of compounds containing hydroxylamine and secondary amine units in the same molecule and may be advantageous in comparison to partial oxidation of a bis(amine). Desoxygenations with low-valent titanium compounds are well established procedures and were investigated in particular by McMurry [19]. The desoxygenation of aminoxides has already been described [20], but not that of hydroxylamines. In the present case it could also be the hydroxylamine-aminoxide tautomerism upon metal complexation, which makes this reduction possible.

Experimental Section

All operations were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and saturated with nitrogen by standard methods. NMR spectra were recorded on a Bruker AV 400 NMR spectrometer. Chemical shifts are reported in ppm with reference to the residual solvent signals. Elemental analyses were carried out on a VARIO E1 III CHNS instrument.

*[Cyclo-(^{t}Bu$_2$Ga)-O,N′-ONH(Me)CH$_2$CH$_2$-NH(Me)][^{t}Bu$_2$GaCl$_2$] (**2**)*

10 mL of a 0.1 M solution of $TiCl_4$ in *n*-hexane was dropped into a suspension of compound **1** (0.61 g, 1.0 mmol) in 10 mL *n*-hexane at −78 °C followed by 1.3 mL of a 1.5 M solution of MeLi in diethyl ether. The reaction mixture was stirred over night, while it reached slowly ambient temperature. The mixture was filtered through carefully dried celite in a sintered glass frit (porosity 4). The filtrate was reduced to one third of its volume under reduced pressure. Cooling it to −26 °C afforded the precipitation of colourless crystals after a few days. Yield: 1.23 g 2.5 mmol (48 %). – M_r = 542.96; found C 43.73, H 8.83, N 5.33 %; $C_{20}H_{48}Ga_2Cl_2N_2O$ requires C 44.24 H 8.91 N 5.16 % (vacuum-dried hexane-free sample). – ^{1}H NMR (200 MHz, C_6D_6): δ = 0.99 – 1.12 (m, 36 H, $C(CH_3)_3$), 1.96 (s, 3 H, NCH_3), 2.11 (s, 3 H, NCH_3), 2.58 (s, br, 2 H, NCH_3), 3.06 (s, br, 2 H, NCH_3), 9.54 (s, br, 1 H NH) (the amine NH proton was not found). – ^{13}C NMR (50 MHz, C_6D_6): δ = 23.0 ($C(CH_3)_3$), 25.8 ($C(CH_3)_3$), 30.3 ($C(CH_3)_3$), 30.4 ($C(CH_3)_3$), 30.8 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 49.9 (NCH_2), 51.7 (NCH_2), 60.5 (NCH_3).

Crystal structure determination

Diffraction data for **2** were collected with a Bruker APEX diffractometer equipped with a rotating anode at 153(2) K using monochromated MoK_α radiation (λ = 0.71073 Å). A crystal was selected and prepared under perfluoropolyether and mounted in a drop of this liquid onto the tip of a glass fibre on the goniometer head of the diffractometer. The structure was solved by Direct Methods and refined with the full-matrix least-squares procedures against F^2 (SHELXTL [21]). Formula $C_{22}H_{52.67}Cl_2Ga_2N_2O$ (reflection data were treated with the SQEEZE procedure of PLATON [10] to account for the contribution of highly disordered hexane molecules). M_r = 571.67, crystal size: 0.03 × 0.05 × 0.09 mm^3, crystal system: hexagonal, space group $R\bar{3}$, a = 29.9640(16), b = 29.9640(16), c = 18.1758(19) Å, V = 14132.7(2) Å^3, T = 153(2) K, Z = 18, ρ_{calc} = 1.209 g cm^{-3}, μ = 1.900 mm^{-1}. 38312 scattering intensities were collected, 5538 of which were independent, and 3818 met the "observed" criterion [$I \geq 2\sigma(I)$]. $R1$ = 0.0518, $wR2$ = 0.1056 for observed reflections, and $R1$ = 0.0866, $wR2$ = 0.1166 for all data. $\Delta\rho_{fin}$ = 0.62 / −0.38 e Å^{-3}.

CCDC 740794 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We are grateful to Deutsche Forschungsgemeinschaft for financial support. The authors thank Dr. Alexander Hepp (Münster) for recording NMR data and Tania Pape (Münster) for X-ray diffraction data collection.

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