Preparation and Structure of Cyclic Gallium(III) and Gallium(II) 2-Amino-ethyl-amides

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Gallium(III) and Gallium(II) Amides, Gallium Amino Complexes, Gallium Coordination

The reaction of \(N,N'-\text{di('butyl)-ethane-1,2-diamine with NaH}\) followed by anhydrous \(\text{GaCl}_3\) (molar ratios 1:2:1) gives mainly an insoluble bis(diamido)gallium chloride together with a low yield (28%) of a soluble monocyclic dichlorogallium-[2-(butylamino)-ethyl-(butyl)amide], \(\text{Cl}_2\text{Ga('BuNH-CH}_2\text{CH}_2\text{-N'Bu)}\) I, the structure of which has been determined. Metallation of the same diamine with \('\text{butyl}-\text{lithium and GaCl}_3\) (1:2:1) gave small quantities of the corresponding dinuclear, bicyclic gallium(II) compound 2, \([\text{('BuNH-CH}_2\text{CH}_2\text{-N'Bu)}\text{GaCl}_2]_2\) with a Ga-Ga single bond connecting the two units, as again shown by a single crystal X-ray diffraction analysis.

Introduction

In the course of our current investigations in the chemistry of low-valent and low-coordinate gallium we have become interested particularly in heterocycles with the metal atom in a bridge position between nitrogen atoms (A, B). The corresponding anions (C, D) are analogues of cyclic carbenes of the Wanzlick-Anduengo type which have been the subject of recent preparative and structural studies in several laboratories [1 - 5].

\[
\begin{array}{c}
\text{R} - \text{N} unpleasant - \text{N} unpleasant Ga \text{Cl} \\
\text{A} \\
\text{R} - \text{N} unpleasant - \text{N} unpleasant Ga \text{Cl} \\
\text{B} \\
\text{R} - \text{N} unpleasant - \text{N} unpleasant Ga \text{Cl} \\
\text{C} \\
\text{R} - \text{N} unpleasant - \text{N} unpleasant Ga \text{Cl} \\
\text{D}
\end{array}
\]

Results and Discussion

Our own synthetic and structural studies were successful with the unsaturated type of heterocyclic anions (C), which appears to be stabilized by the quasi-aromaticity of their 6 \(\pi\) electron system [6, 7]. The corresponding saturated anions (D) have not yet been prepared. A program was therefore initiated oriented at the synthesis of suitable precursors for these target molecules. The present paper is a report of our recent work in this area.

The literature has only a few entries of cyclic di-amides of gallium which were obtained following conventional methods of synthesis starting from gallium halides and alkali amides [8 - 11] or by dihydrgallation of diazabutadiens with \(\text{GaH}_3\) [12, 13].

Preparative Results

For the preparation of a monocyclic gallium(III) bis-amide \(N,N'-\text{di('butyl)-ethane-1,2-diamine with NaH}\) followed by anhydrous \(\text{GaCl}_3\) (molar ratios 1:2:1) was chosen as the difunctional component. The \('\text{butyl}-\text{substituted diamine was metallated using two equivalents of sodium hydride in tetrahydrofuran and the reaction mixture containing the metallation product subsequently reacted with equimolar quantities of gallium trichloride. After separation of insoluble precipitates a colourless crystalline product could be isolated from the clear solution. It was identified as dichlorogallium(III)-[2-(butylamino)-...
ethyl-(‘butyl)amide], 1 (28% yield). The analytical and spectroscopic data and the single crystal X-ray diffraction study showed consistently that the metallation of the diamine was incomplete. It appears that only the mono-deprotonated amine gives a soluble product, while insoluble material is produced from the bis-metallated amine.

\[
{\text{tBu-NH-CH}_2\text{CH}_2\text{-NH-tBu}} \quad (\text{1})
\]

According to mass spectrometry results compound 1 is a monomer in solution and in the gas phase. In THF-\text{d}_6 solution the two ‘butyl groups and the two methylene groups are inequivalent and give rise to separate \(^1\text{H}\) and \(^{13}\text{C}\) resonances (at 25 °C). A broad singlet signal is observed for an NH proton.

The insoluble products were not investigated any further because of severe problems with the separation from sodium chloride or its adducts. Treatment of 1 with NaH or with an amine base also lead only to insoluble products.

In an attempt to establish conditions where similar complications are not to be expected, the metallation of the ‘Bu-NH-CH\(_2\)CH\(_2\)-NH-tBu was carried out with two equivalents of ‘butyl-lithium in hydrocarbon solvents (pentane, hexane). The subsequent reaction with GaCl\(_3\) in tetrahydrofuran employing the same stoichiometry as with the NaH metallation gave yet another unexpected result: While the main products were insoluble and could not be further characterized, small amounts of a yellow soluble compound were isolated by extraction with hexane and identified as a dinuclear gallium(II) compound. This compound (2) is the reduced form of the monocyclic product 1 obtained in the NaH/GaCl\(_3\) reaction (above).

\[
2 \text{'Bu-NH-CH}_2\text{CH}_2\text{-NH-tBu} \quad (\text{2})
\]

The \(^1\text{H}\) NMR spectrum of solutions of 2 in benzene-\text{d}_6 has a broad singlet resonance of NH protons, a multiplet of the four ethane protons and two distinct singlet resonances of equal intensities of the methyl groups. The \(^{13}\text{C}\{^1\text{H}\}\) spectrum has two singlet resonances of equal intensity for methylene, methyl and quaternary carbon atoms. These results suggest that the ligand is present in its unsymmetrical, mono-protonated form \(\text{[tBu-NH-CH}_2\text{CH}_2\text{-NH-tBu]}^-\).
Fig. 2. Packing of the molecules in the crystal of compound 1 (CH-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: N1-H 0.766, Cl1--H 2.699, N1-C11 3.427; N1-H--Cl1 159.6.

Fig. 3. Molecular structure of compound 2 (ORTEP drawing with 50% probability ellipsoids; CH-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ga-N1 2.103(2), Ga-N2 1.876(2), Ga-Cl 2.296(1), Ga-Ga* 2.448(1); N1-Ga-N2 86.8(1), N1-Ga-Cl 93.0(1), N2-Ga-Cl 110.7(1), Cl-Ga-Ga* 112.6(1), N1-C1-C2-N2 -53.3.

The asymmetric unit contains only one half of the molecule, because the two halves are related by a twofold axis through the middle of the Ga-Ga bond (Fig. 3). The Ga-Ga* distance of 2.448(7) Å is consistent with a standard metal-metal single bond. The five-membered rings have a twist conformation, and the nitrogen atoms are non-equivalent with distances Ga-N1 2.103(2) and Ga-N2 1.876(2) Å and a significant difference in the sum of the valence angles [N1 343.4, N2 350.8°]. The presence of a hydrogen atom was verified for N1. It is engaged in hydrogen bonding with a neighbouring molecule in the lattice: N1-H1 0.93(4), Cl--H1 2.589 Å, N1-H--Cl1 149.5° (Fig. 4). The Ga-Cl bond length in 2 [2.296(1) Å] is very similar to those in compound 1 [2.214(1) and 2.172(1) Å]. It generally appears that the bonding in the two heterocycles of 2 is quite comparable to that in 1. The substitution of a chlorine atom in 1 by a gallium atom (in 2) causes very little changes in the molecular skeleton.

Experimental Part

All reactions were routinely carried out under dry nitrogen or argon either in Schlenk vessels or in a glove-box, respectively. Solvents were dried, degassed and saturated with nitrogen, and all glassware was oven-dried and filled with nitrogen/argon. Standard equipment was used throughout. All basic chemicals were commercially available.

* Dichlorogallium(III)-[2-(‘butylamino)-ethyl-(‘butyl)amide] (1)

\[ N,N’-Di-‘butyl-ethane-1,2-diamine (0.794 g, 4.61 mmol) is mixed with a suspension of NaH (0.22 g, 9.22 mmol) in tetrahydrofuran (10 ml) at -78 °C. The mixture is, after allowing it to warm up to 25 °C, stirred for 18 h. While repeatedly cooling the reaction vessel to -78 °C, a solution of anhydrous GaCl3 (0.82 g, 4.61 mmol) in tetrahydrofuran (10 ml) is added, and the mixture is stirred for additional 18 h at 25 °C. The colourless precipitate is removed by filtration and the volume of the
Table 1. Crystal data, data collection, and structure refinement for compounds 1 and 2.

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(filtrate reduced to one half in a vacuum. After a week colourless crystals are formed (0.41 g, 28% yield). NMR (THF-d\(_8\), 25 °C); \(^1\)H: \(\delta\) 1.19 (s, 9 H, C(CH\(_3\))\(_3\)), 1.40 (s, 9 H, C(CH\(_3\))\(_3\)), 2.69 - 3.17 (m, 4 H, CH\(_2\)), 4.76 (b, 1 H, NH); \(^13\)C\{\(^1\)H\}: \(\delta\) 26.6 (s, C(CH\(_3\))\(_3\)), 29.3 (s, C(CH\(_3\))\(_3\)), 42.1 (s, C-N), 44.2 (s, C-N), 51.8 (s, C-H\(_2\)), 55.9 (s, C-H\(_2\)). MS (Cl) \(m/e\) 311 [\((\text{C}_{10}\text{H}_{22}\text{N}_2)\text{HGaCl}_2\)]\(^+\), 276 [\((\text{C}_{10}\text{H}_{22}\text{N}_2)\text{HGaCl}\)]\(^+\), 241 [\((\text{C}_{10}\text{H}_{22}\text{N}_2)\text{HGa}\)]\(^+\). (Ga-Ga)-Bis\{(chlorogallium(II)-[2-(N,N-di-(butyl)ethane-1,2-diamine (2.29 g, 13.3 mmol) in hexane (10 ml) is treated with N,N-di-(butyl)-lithium (17.6 ml of a 15% pentane solution, 26.6 mmol) at 0 °C. After the mixture is allowed to warm to 25 °C and stirred for 18 h, the solvent is removed in a vacuum and the residue redissolved in tetrahydrofuran (10 ml). This solution is reacted with anhydrous GaCl\(_3\) (2.34 g, 13.3 mmol) dissolved in tetrahydrofuran (10 ml) at –78 °C and the resulting mixture is stirred for additional 48 h at 25 °C, followed by evaporation of all volatiles and extraction of the residue with hexane (20 ml). The volume of the resulting hexane filtrate is reduced to one half in a vacuum and in two weeks time a few yellow single crystals are formed (0.25 g, 1.5% yield). NMR (C\(_6\)D\(_6\), 25 °C); \(^1\)H: \(\delta\) 1.26 (s, 9 H, C(CH\(_3\))\(_3\)), 1.40 (s, 9 H, C(CH\(_3\))\(_3\)), 2.57 (b, 1 H, NH), 3.01 - 3.12 (m, 4 H, CH\(_2\)); \(^{13}\)C\{\(^1\)H\}: \(\delta\) 28.8 (s, C(CH\(_3\))\(_3\)), 30.8 (s, C(CH\(_3\))\(_3\)), 45.3 (s, C-N), 46.3 (s, C-N), 54.0 (s, C-H\(_2\)), 55.7 (s, C-H\(_2\)). MS (Cl) \(m/e\) 554 [\[(\text{C}_{10}\text{H}_{22}\text{N}_2)\text{HGaCl}_2\)]\(^+\), 518 [\[(\text{C}_{10}\text{H}_{22}\text{N}_2)\text{HGaCl}\]]\(^+\), 482 [\[(\text{C}_{10}\text{H}_{22}\text{N}_2)\text{HGa}\]]\(^+\). Elemental analysis (C\(_{20}\)H\(_{26}\)Cl\(_2\)Ga\(_2\)N\(_4\) + C\(_6\)H\(_{12}\)): calcd. C 48.9, H 9.4, N 8.80; found C 47.21, H 9.07, N 8.81.

Crystal structure determination

Specimens of suitable quality and size of compounds 1 and 2 were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 (1) and a Nonius CAD4 diffractometer (2), respectively, employing graphite-monochromated Mo-K\(\alpha\) radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares cal-
culations on $F^2$ (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were located and refined isotropically. The scattering contribution of a highly disordered solvent molecule in the crystals of compound 2 was taken into account by means of the program SQEZE which is part of the PLATON suite of programs: A. L. Spek, Acta Crystallogr. A46, C-34 (1990).

Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding Figure Captions. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre. The data are available on request on quoting CCDC No. 163152 (1) and 163153 (2).

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