Preparation and Structure of Lithium Bis[cis-ethene-1,2-di('butylamido)]gallate(III) Tetrahydrofuran

Eva S. Schmidt, Norbert W. Mitzel, and Hubert Schmidbaur
Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Reprint requests to Prof. Dr. H. Schmidbaur. E-mail: H.Schmidbaur@lrz.tum.de
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The dilithium diamide reagent obtained from N,N’-di('butyl)-1,4-diazabutadiene and two equivalents of lithium metal reacts with anhydrous gallium trichloride in tetrahydrofuran / hexane, followed by treatment with metallic potassium, to give the title compound in about 40% yield. Cyclic imides of gallium(III) and gallium(II) are by-products of this process. The structure of Li[(cis-C5H5(N’Bu)2]G] has been determined from single crystals containing one mole equivalent of tetrahydrofuran. The gallium atom is chelated by two diamide ligands. One of the five-membered chelate rings is planar while the second one is folded at its nitrogen atoms. The lithium atom is octahedrally-coordinated to the 1,4-diazabutene(2) unit of this ring and further to the oxygen atom of the solvent molecule.

During our recent investigations in the chemistry of low-valent and low-coordinate gallium [1-3] we have become interested 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-Arduengo type which have been the subject of careful studies in several laboratories [4-8]. Our own synthetic and structural work was successful with the unsaturated type of heterocyclic anions (C), which appear to be stabilized by the quasi-aromaticity of their 6π electron system [1].

One of our experiments oriented at the synthesis of compounds of this type lead to the unintended isolation of the intimate ion-pair of a lithium cation and an ate-complex anion which results from a redistribution of the ligands between the gallium and lithium atoms in the reaction mixture (I). The

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\begin{align*}
2 \text{t-Bu-NLi-CH=CH-NLi-tBu} & \rightarrow 2 \text{GaCl}_3 \\
& + 2 \text{K} / \text{THF} \\
& \rightarrow (\text{t-Bu-N-CH=CH-N-tBu})_2 \text{Ga}_2 \text{Cl}_2_2 \\
& (\text{t-Bu-N-CH=CH-N-tBu})_2 \text{Ga}_2 \\
\end{align*}
\]

(1)
remainder of the reaction products [2, 3, eq. (1)] have been described previously [1 - 3] and are not discussed here any further. Pertinent references were also quoted in earlier publications.

Treatment of N,N'-di-(butyl)-1,4-diazabutadiene with two equivalents of lithium metal in tetrahydrofuran affords the corresponding cis-ethene-1,2-di(butylamido) in almost quantitative conversion. The in situ reaction of this product with one equivalent of anhydrous gallium trichloride in hexane at 0 °C leads to a colour change to brown and to a yellow precipitate. Reduction of the filtrate by an equivalent quantity of potassium metal (in tetrahydrofuran / hexane) at 20 °C gives a reaction mixture, from which brown crystals can be isolated after filtration, concentration of the filtrate and cooling to −28 °C. Based on the gallium content, the yield is almost 40%.

The H1 NMR spectrum of solutions of the new complex 1 in benzene-d8 shows two singlet resonances at δ 1.46 and 6.02 ppm for the methyl protons and CH=CH, respectively (rel. intensity 9:1). The 13C {1H} spectrum has three resonances at δ = 32.15, 51.48 and 111.21 ppm for Me, Me3C and CH=CH carbon atoms. These spectra show that the two chelate rings are virtually equivalent in solution on the NMR time scale at ambient temperature. The mass spectrum (CI) has the cation [(Bu2N2C2)2Ga] as the parent peak at m/z = 407 (71Ga). The data of elemental analysis of the crystals are in agreement with the formula proposed on the basis of the crystal structure analysis including one tetrahydrofuran molecule per molecule of complex.

Crystals of 1 are triclinic, space group P̅1, with Z = 2 formula units in the unit cell (T = 183 K). The lattice contains individual ate complex molecules with no sub-vaW ver Waals intermolecular contacts. The complex has no crystallographically imposed symmetry, but approaches quite closely the symmetry requirements of a mirror plane passing through the Li and Ga atoms and containing the (almost) planar chelate ring N20-C20-C21-N21 (Fig. 1). The ring atoms of the tetrahydrofuran molecule are displaced significantly from the mirror plane.

The chelate ring (N20-C10=C11-N11)Ga has two equidistant Ga-N bonds [Ga-N20: 1.881(2) and Ga-N21: 1.889(2) Å], a short C20-C21 bond [1.346(3) Å] and two short C-N bonds [C20-N20: 1.401(2), C21-N21: 1.396(3) Å]. The configuration at the two nitrogen atoms is planar [sum of the va-
tances $\text{Li-C10} = \text{Li-C11} = 2.169(4)$ Å are very simi-
lar to the distances $\text{Li-N10}$ and $\text{Li-N11}$ [2.099(4) and
2.111(4) Å, respectively], suggesting that there is an $\eta^1$
bonding of the lithium atom to the chelate ring. In other
words, the lithium may be consid-
ered side-on coordinated to the
C=C double bond as drawn in Fig. 1. This multicenter interac-
tion with the 1,4-diaza-butadiene(2) appears to be energetically
favoured over the alternative coordination to e. g.
N10 and N20 as for the peripheral gallium atom in
complex 2 [2].

According to the NMR spectra complex 1 is flux-
ional in solution rendering the two chelate rings
NMR-equivalent. The activation barrier for a trans-
er of the lithium atom from one of the four equi-

everent coordination sites to the other appears to be
low. It is not unlikely that intermediate coordination
to the nitrogen atoms of two different chelate rings
plays a role in the energy profile of the process.

**Experimental Part**

All experiments were carried out in an argon-filled dry-
box and in carefully dried, oxygen-free solvents. Stan-
dard equipment was used throughout. The chemicals were
commercially available.

**Preparation**

Lithium metal (0.069 g, 10 mmol) is reacted with N,N'-
di-1-butyl-diazabutadiene (0.841 g, 5 mmol) in tetrahydro-
furan (15 ml) to give a solution of the dilithio-diamide.

A solution of anhydrous gallium trichloride (0.880 g,
5 mmol) in hexane (5 ml) is slowly added at 0 °C. With
stirring the mixture is allowed to warm to 20 °C. A light
yellow precipitate forms in a brown solution. The solution
is filtered immediately and transferred into a flask which
is stirred for 4 d. After filtration the filtrate is reduced to
half its volume in a vacuum. Brown crystals separate upon
cooling to -28 °C (0.95 g, 39% yield). NMR (C$_6$D$_6$, 25°C),

$^1$H: $\delta$ 1.46 (s, 18H, Me), 6.02 (s, 2H, C$_5$H$_2$); $^{13}$C: 32.15 (s,
Me), 51.48 (s, CN), 111.21 (s, C$_5$H$_2$); both spectra show
the resonances of tetrahydrofuran. MS (Cl): $m/z = 407$
[($^t$BuNCH)$_4$Ga]. $C_{32}H_{58}GaLiN_4O$ (485.32 g/mol): calcd.
C 59.40, H 9.97, N 11.55; found C 59.50, H 10.79, N
11.60.

**Crystal structure determination**

A suitable crystal of 1 was mounted onto a glass
fibre in inert perfluoropolyether. Data collection was
performed on a Nonius Turbo CAD4 diffractometer.

$C_{32}H_{54}GaLiN_4O$, $M_r = 485.32$, crystal system triclinic,

space group $P\bar{1}$, $Z = 2$, $a = 10.236(1), b = 10.250(1), c =
15.235(2)$ Å, $\alpha = 75.13(1), \beta = 94.79(1), \gamma = 64.304(8)$°,

$V = 1373.6(3)$ Å$^3$ at 183(2) K, $\mu = 1.022$ mm$^{-1}$. $\beta_{\text{max}} =
53.96°, 5947$ scattering intensities collected, 5947 inde-

dependent reflections ($R_{\text{int}} = 0.024$). No absorption

correction was applied. 436 parameters, $R_1 = 0.0334$ for
5413 scattering intensities with $F_0 > 4 \sigma(F_0)$ and $wR_2 =
0.1541$ for all data. Solution by direct methods and re-

finement of the structure were undertaken with the pro-
gram SHELXTL 5.01 [9]. Hydrogen atoms were refined

with isotropic thermal displacement parameters, all other
atoms anisotropically. Crystallographic data (excluding
structure factors) have been deposited with the Cam-
bridge Crystallographic Data Centre as supplementary
publication no. CCDC-164906. Copies of the data can
be obtained free of charge on application to CCDC,
12 Union Road, Cambridge CB2 1EZ, UK (e-mail: de-
posit@ccdc.cam.ac.uk).

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