A Gallium-Nitrogen Heteronorbornane with Bulky ^{t}Butyl Substituents

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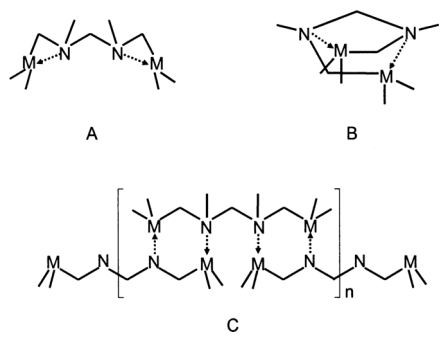
Selective formation of 3,3,6,6-tetra-^{t}butyl-1,4-dimethyl-3,6-digallium-1,4-diaza-norborane is achieved by the reaction of bis(lithiomethyl-methylamino)methane with di^{t}butylgallium chloride by simultaneous formation of two dative metal-carbon and two metal-nitrogen bonds accompanied by two ring closures. Despite the high steric demand of the ^{t}butyl groups, the norbornane-like structure is favoured over potential isomers containing three-membered rings and over polymeric aggregation. The compound was identified by elemental analysis, NMR spectroscopy (^{1}H, ^{13}C) and by determination of its crystal structure in which it is present as a monomer.

Key words: Gallium, Nitrogen, Heteronorbornane, Organometallic Compounds, Crystal Structure

Introduction

Nitrogen compounds of aluminum and gallium with small molecules are the subjects of recent interest owing to their potential as molecular precursors for III/V semiconductor materials [1a]. Investigations on both donor–acceptor adducts and metal amides have been intensely pursued [1b]. We have recently reported the first syntheses of compounds with saturated Al-C-N and Ga-C-N linkages [2], in which we reported our understandings on the fundamentals of systems with donor and acceptor centres in geminal positions. These investigations revealed various types of possible aggregation patterns, either intramolecular *via* formation of three-membered ring systems as in compounds containing *BCN* [3], *BNN* [4], *AlCN* [5] and *AlNN* [6], but also *SiON* [7], *GeON* [8] and *SnON* [9] units or intermolecular *via* formation of dimers with cyclohexane-like six-membered rings as in $[(H_2BCH_2SMe)_2]$ [10], $[Me_2Al(CH_2PMe_2)]_2$ and $[Al(CH_2PMe_2)_3]_2$ [11], $[(Me_3CCH_2)_2InCH_2PPh_2]_2$ [12], $[Me_2AlCH_2NMe_2]_2$ and $[Me_2GaCH_2NMe_2]_2$ [2a], $[Me_2AlCH_2N^iPr_2]_2$ and $[Me_2GaCH_2N^iPr_2]_2$ [2b], as well as the sulphur systems $[H_2BCH_2SMe]_2$ [13], $[Me_2ECH_2SMe]_2$ (E = Al, Ga, In) [14]. Compounds which contain two *ECN* functions joined by a common bridging unit were also studied. The compounds $[Me_2ECH_2N(Me)]_2CH_2$ (E = Al, Ga) [15] were found to be intramolecularly aggregated into heteronorbornane systems (Scheme 1 B). Three modes of aggregation of these systems are depicted in Scheme 1. These are two three-membered rings (A), six-membered rings in either polymeric arrays (C) or in the above mentioned norbornane-like structure (B). In another study, we found that increasing the steric requirement of the substituents at the Al atoms upon replacing methyl groups by the more bulky ^{t}butyl groups $[^tBu_2AlCH_2N(Me)]_2CH_2$ [16] did not change the norbornane-like aggregation.



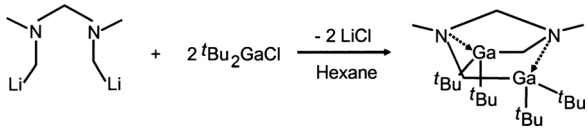
Scheme 1.

In this contribution we report the study of replacing methyl groups by ^{t}butyl groups on Ga atoms, and again found that the intramolecular metal-nitrogen heteronorbornane mode (B) persisted.

Results and Discussion

*Synthesis of [^{t}Bu$_2$GaCH$_2$N(Me)]$_2$CH$_2$ (**1**)*

The reaction of the dilithiated aminal [LiCH$_2$(Me)N]$_2$CH$_2$ [17] with two equivalents of di^{t}butylgallium chloride in hexane at −78 °C leads to the simultaneous formation of four chemical bonds and two ring closures, and gives 3,3,6,6-tetra-^{t}butyl-1,4-dimethyl-3,6-digalla-1,4-diaza-norborane, [^{t}Bu$_2$*Ga*CH$_2$*N*(Me)]$_2$CH$_2$ (**1**), as depicted in Scheme 2. This reaction proceeds uniformly and no signs of the presence of structures of type A and C were observed.



Scheme 2.

Compound **1** is sensitive to oxygen and moisture and was isolated as a colourless crystalline material upon cooling a hexane solution to −25 °C. It is well soluble in non-polar solvents such as pentane and hexane, and even better in toluene or ethers. It is thermally stable up to its melting point at 182 °C but cannot be sublimed in vacuum (10^{-2} Torr) before onsetting of melting. Compound **1** has been identified by elemental analyses, NMR spectroscopy of the nuclei ^{1}H and ^{13}C in C$_6$D$_6$ and single crystal X-ray crystallography. In the NMR spectra the typical patterns of norbornane units are observed: two sets of signals for the two non-equivalent geminal ^{t}butyl groups at the gallium atoms and the geminal hydrogen atoms of the methylene units connecting the Al and N atoms.

*Crystal structure of [^{t}Bu$_2$GaCH$_2$N(Me)]$_2$CH$_2$ (**1**)*

Compound **1** crystallizes in the polar trigonal crystal system with space group $P3_121$. The molecules in the crystal have C_2 symmetry with the C_2 axis passing through the aminal carbon atom, and are thus chiral. The investigated crystal was a racemic twin. As it is shown in Fig. 1, compound **1** adopts the same type of intramolecular aggregation as the corresponding aluminum-nitrogen heteronorbornane with di^{t}butyl substituents [^{t}Bu$_2$*Al*CH$_2$*N*(Me)]$_2$CH$_2$ [16] and their methyl analogous [Me$_2$ECH$_2$N(Me)]$_2$CH$_2$ (E = Al, Ga) [15], which bear methyl instead of ^{t}butyl groups at the metal atoms. It shows that ^{t}butyl substituents are not sterically bulky enough to change the aggregation mode of **1**.

Table 1. Selected bond lengths and angles of **1** [Å, °]. Symmetry transformation used to generate equivalent atoms: *y*, *x*, −*z*.

Ga-C3*	2.041(2)	C3*-Ga-N	82.8(1)
Ga-C15	2.043(3)	C15-Ga-N	109.9(1)
Ga-C11	2.044(3)	C11-Ga-N	110.1(1)
Ga-N	2.144(2)	C2-N-C4	109.1(2)
N-C2	1.476(3)	C2-N-C3	108.6(2)
N-C4	1.489(3)	C4-N-C3	111.5(2)
N-C3	1.510(3)	C2-N-Ga	98.8(1)
C2-N*	1.476(3)	C4-N-Ga	113.9(2)
C3*-Ga-C15	126.9(1)	C3-N-Ga	114.0(2)
C3*-Ga-C11	108.8(1)	N-C2-N*	106.7(3)
C15-Ga-C11	113.6(1)	N-C3-Ga*	108.7(2)

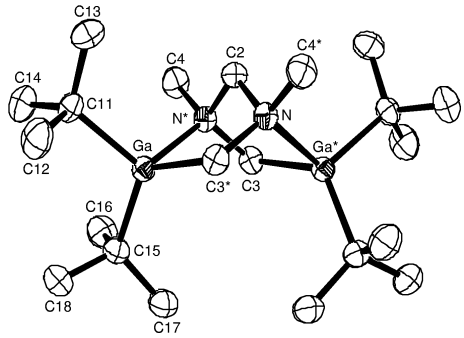


Fig. 1. Molecular structure of compound **1** (ORTEP drawing with 50% probability ellipsoids). Hydrogen atoms omitted for clarity. Symmetry transformation used to generate equivalent atoms: *y*, *x*, −*z*.

The methylene bridge between the two N atoms causes the Ga$_2$C$_2$N$_2$ six-membered ring to adopt the boat conformation typical for the norbornane skeleton with the two N atoms at the bow and stern positions. This leads to small endocyclic angles at the gallium atoms [82.8(1)°] which are slightly more compressed than those in the corresponding aluminum compound [^{t}Bu$_2$*Al*CH$_2$*N*(Me)]$_2$ CH$_2$ [84.1(1)°] [16] and its methyl analogue [Me$_2$Ga CH$_2$N(Me)]$_2$CH$_2$ [85.1(1)°] [15]. Due to the same reason, the angle at the methylene group in the six-membered ring [108.7(2) °] is much wider relative to the corresponding C–C–C angle in the C_{2v} symmetric hydrocarbon norbornane, 102.7° [18a] or 102.6(1)° [18b], but only slightly larger than the gallium-nitrogen heteronorbornane with methyl groups at gallium in [Me$_2$GaCH$_2$N(Me)]$_2$CH$_2$ [106.3(2)°] [15]. These small angles at the Ga atoms lead to a strongly distorted tetrahedral coordination geometry. This can also be seen from the C11-Ga-C15 angle enclosed by the two ^{t}butyl groups at 113.6(1)° and the extremely wide angle C3*-Ga-C15 at 126.9(1)° to the *endo*-^{t}butyl group whereas the angle

C3*-Ga-C11 to the *exo*-^{t}butyl group is comparatively small at 108.8(1)°. As it is expected due to the impacts of the sterically bulky ^{t}butyl groups, the angle to the *endo*-^{t}butyl group is nearly 5° larger than that in $[Me_2GaCH_2N(Me)]_2CH_2$ [122.0(2)°] [15] while the angle to the *endo*-^{t}butyl group is 4° smaller than the corresponding angle in $[Me_2GaCH_2N(Me)]_2CH_2$ [112.9(2)°] [15].

There is also a large difference in the C-N bond lengths. The endocyclic C1-N* bonds [1.510(3) Å] are much longer than the ones pointing to the exocyclic methyl carbon [C4-N 1.489(2) Å] or to the N,N-bridging methylene unit [C2-N 1.476(3) Å]. The former two are slightly longer than those in $[Me_2GaCH_2N(Me)]_2CH_2$ [1.503(4) and 1.475(4) Å, respectively] [15]. It should be noted that the geometries of NCN bridges do not change when the methyl groups on Ga are replaced by ^{t}butyl groups, all have the same N-C-N angles at 106.7° and N-C bond lengths at 1.476 Å.

The endocyclic bond Ga-N at 2.144(2) Å and Ga-C3 at 2.041(2) Å are only slightly longer than those in $[Me_2GaCH_2N(Me)]_2CH_2$ [Ga-N at 2.124(3) Å, Ga-C at 2.026(3) Å] [15], and much longer than the gas phase values of simple reference compounds as $Me_3Ga–NMe_3$ [Ga–N 2.09(3), Ga–C 1.992(6) Å] [19].

Experimental Section

General remarks

All reactions and manipulations were carried out under a dry nitrogen atmosphere with standard Schlenk and high vacuum techniques using double manifolds or in a glove box under argon. Solvents were purified and dried by standard methods immediately prior to use. NMR data were collected on a Bruker ARX300 (^{1}H 300.1 MHz, ^{13}C 75.5 MHz) in C_6D_6 as solvent dried over K/Na alloy. Chemical shifts are quoted relative to TMS. A Nonius Kappa-CCD X-ray diffractometer ($\lambda = 0.71073$ Å) was used to collect the reflections for single crystal structure determination. Bis(lithiomethyl-methylamino)methane [17] and $^tBu_2GaCl$ [20] were prepared by literature methods.

*Synthesis of $[^tBu_2GaCH_2N(Me)]_2CH_2$ (**1**)*

A solution of $^tBu_2GaCl$ (0.50 g, 2.28 mmol) in 20 ml hexane was added dropwise to a suspension of bis(lithiomethyl-methylamino)methane (0.13 g, 1.14 mmol) in hexane (40 ml) at −78 °C with vigorous stirring. The reaction mixture was stirred overnight at this temperature and then allowed to warm up to ambient temperature. The mixture was filtered through a sintered glass filter (porosity no. 4), and the resulting clear solution was concentrated under vacuum until it became slightly cloudy. Upon warming up to room temperature the solution became clear again. The vessel with this solution was immersed in a 1 l Dewar container filled with ethanol and allowed to cool slowly to −25 °C overnight. Colourless well formed crystals were obtained in this way. Yield: 0.29 g, 55.72%. M.p. 182 °C. ^{1}H NMR (C_6D_6): $\delta = 0.93/1.14$ (s, 36H, $GaCCH_3$), 2.24 (s, 6H, NCH_3), 2.74/2.78 (s, 4H, $GaCH_2N$), 2.89 (s, 2H, NCH_2N). – ^{13}C NMR (C_6D_6): $\delta = 22.7/24.1$ ($GaCCH_3$), 32.4/33.7 ($GaCCH_3$), 44.9 (NCH_3), 45.8/45.9 ($GaCH_2N$), 80.8 (NCH_2N). Analysis for $C_{21}H_{48}Ga_2N_2$ (468.07 g mol^{-1}): calcd. C 53.89, H 10.34, N 5.98; found C 52.81, H 10.18, N 5.88.

Table 2. Crystal and refinement data of **1**.

Cryst. system	trigonal	$2\theta_{max}$ [°]	55.76
Space group	$P3_121$	measd. refl.	12739
a [Å]	8.866(1)	unique refl.	1765
b [Å]	8.866(1)	observed refl	1673
c [Å]	27.475(1)	R_{int}	0.053
V [Å^3]	1870.4(3)	parameters	122
$\rho_{calcd.}$ [g cm^{-3}]	1.247	BASF[a]	0.54(2)
Z	3	$R[I > 2\delta(I)]/wR^2$	0.0251/0.0650
μ [mm^{-1}]	2.167	ρ_{fin} (min/max) [eÅ^3]	−0.266/0.881
temp. [K]	198(2)	CCDC-No.	252173
$T_{min/max}$	0.4104/0.8631		

[a] Contribution of the first twin component.

Crystal structure analysis

A single crystal of compound **1** was mounted under inert perfluoropolyether at the tip of a glass fibre and was cooled in the cryostream of the diffractometer. Structure solutions were carried out using direct methods and the refinements of the structure were undertaken with the program SHELXTL 6.10 [21]. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms isotropically with a riding model. Further details of data collections and refinements are listed in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication No. 252173. 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; email: deposit@ccdc.cam.ac.uk].

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