SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF CHIRAL DIMETHYLGALLIUM ALKOXIDES CONTAINING DIASTEREOISOMERICALLY PURE N,N-DIMETHYLAMINO ALCOHOLS

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Abstract

The reaction of trimethylgallium, GaMe₃, with optically active amino alcohols (-)-(1R,2S)-2-dimethylamino-1-phenylpropanol and (+)-(2S,3R)-4-dimethylamino-3-methyl-1,2-diphenyl-2-butanol provides the dimeric dimethylgallium alkoxide [(CH₃)₂GaOCH(C₆H₅)CH(CH₃)N(CH₃)₂]₂ (1) and the monomeric compound (CH₃)₂GaOCC₆H₅(CH₂C₆H₅)CH(CH₃)CH₂N(CH₃)₂ (2) via a methane elimination reaction. ¹H, ¹³C NMR, mass spectra as well as X-ray crystal structure analyses of these new compounds are reported and discussed. The X-ray crystal structures confirm that the absolute configurations of the asymmetric centers in the O,N-chelating bidental ligands are retained upon formation of the corresponding coordinatively saturated complexes. Differences concerning chemical shifts of the methyl groups bound to Ga observed in the ¹H NMR spectra are explained by dynamic dissociation processes of the Ga-N bond in the four- and five-coordinated gallium compounds.

Introduction

Organometallic compounds of group 13 have been found attractive reagents in a wide range of organic processes such as alkylation of aldehydes [1], saturated [2] and unsaturated ketones [3] and oxiranes [4]. Although dialkylaluminium compounds such as the alkoxides (CH₃)₂AlO(CH₂)₂N(CH₃)₂ and (CH₃)₂AlOCH₂C(CH₃)₂OCH₃ proved to be efficient alkylation reagents [5], the real potential of organometallic compounds in organic synthesis has not yet been exhausted. During the past several years, the application of organometallic complexes in regio- and stereospecific organic synthesis [6] has led to a great interest in preparation and characterization of these chiral metal reagents. As part of our interest in intramolecularly base-stabilized, nonracemic chiral organogallium compounds, two dialkylgallium complexes have been prepared by reaction of trimethylgallium with optically active amino alcohols in a 1:1 stoichiometry. In this paper we report on the synthesis, spectroscopic investigations and structural characterization of the new compounds.

Materials and Methods

General procedures:

All reactions were carried out in an atmosphere of dry, oxygen-free argon. CHN analyses were performed on a Perkin Elmer 240 C elemental analyzer. Mass spectra (electron impact ionization) were obtained on the instrument Varian MAT 311 A (70 eV). NMR spectra were recorded on the spectrometer Bruker ARX 200 (¹H NMR at 200 MHz in C₆D₆; ¹³C{¹H} NMR in C₆D₆); chemical shifts are referenced to (CH₃)₄Si with positive shifts referring to lower field.

Preparation of [(CH₃)₂GaOCH(C₆H₅)CH(CH₃)N(CH₃)₂]₂ (1):

3.03 g (26.4 mmol) of Ga(CH₃)₃ were dissolved in 30 ml of diethyl ether and an ethereal solution (80 ml) of 4.73 g (26.4 mmol) of (-)-(1R,2S)-2-dimethylamino-1-phenylpropanol was added dropwise with stirring. After further stirring for 12 h, the solvent was distilled off. The resulting residue was purified by fractionated crystallization from diethyl ether at room temperature. Colorless crystals were obtained. Yield: 5.9 g (80%). M.p. (sealed) 110°C. Anal. Found: C, 52.87; H, 8.04; N, 5.17. C₁₃H₂₂GaNO calcd: C, 56.16; H, 7.98; N, 5.04. ¹H NMR (δ, ppm): -0.12 (s, 6H, GaCH₃), 0.62 (d, ³J = 6.9 Hz, 3H, CH₃), 1.71 (s, 6H, NCH₃), 2.45 (m, 1H, NCH), 5.11 (d, ³J = 4.6 Hz, 1H, CHPh), 7.08 - 7.58 (m, 5H, aromatic H). ¹³C{¹H}NMR (δ, ppm): -5.68 (GaCH₃), 9.39 (CH₃), 43.46 (NCH₃), 67.67 (NCH), 75.18 (CHPh), 126.38, 126.74, 128.30, 144.66 (aromatic C). MS (EI, 120°C, 70 eV, m/z (%)): 262/264 (43.7) [M-CH₃]⁺, 99/101 (18.7) [Ga(CH₃)₂]⁺, 72 (100) [C₄H₁₀N]⁺.

Preparation of $(\text{CH}_3)_2\text{GaOCC}_6\text{H}_5(\text{CH}_2\text{C}_6\text{H}_5)\text{CH}(\text{CH}_3)\text{CH}_2\text{N}(\text{CH}_3)_2$ (**2**):

3.55 g (30.9 mmol) of $\text{Ga}(\text{CH}_3)_3$ were dissolved in 25 ml of pentane and a solution of 8.76 g (30.9 mmol) of (+)-(2S,3R)-4-dimethylamino-3-methyl-1,2-diphenyl-2-butanol in 65 ml of pentane was added dropwise with stirring. After the addition was complete (1.5 h), the resulting cloudy mixture was stirred for further 12 h. The solvent was distilled off to yield a residue, which was washed with pentane (3x) leaving behind a white solid. An ethereal solution of 3.0 g of the desired compound was cooled to -30°C , affording transparent crystals. Yield: 8.0 g (68%). M.p. (sealed) 150°C . Anal. Found: C, 65.42; H, 7.96; N, 4.37. $\text{C}_{21}\text{H}_{30}\text{GaNO}$ calcd: C, 66.00; H, 7.91; N, 3.66%. ^1H NMR (δ , ppm): -0.27 (s, 3H, GaCH_3), -0.11 (s, 3H, GaCH_3), 0.74 (d, $^3J = 7.4$ Hz, 3H, CH_3), 0.97 (m, 1H, CH), 1.45 (s, 3H, NCH_3), 1.56 (s, 3H, NCH_3), 1.94 (m, 1H, NCH_2), 2.48 (dd, $^2J = 12.8$ Hz, $^3J = 9.3$ Hz, 1H, NCH_2), 3.22 (d, $^2J = 13.4$ Hz, 1H, CH_2Ph), 3.42 (d, $^2J = 13.4$ Hz, 1H, CH_2Ph), 7.00 - 7.76 (m, 10H, aromatic H). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): -7.22 (GaCH_3), -4.71 (GaCH_3), 18.86 (CH_3), 40.43 (CH), 45.36 (NCH_3), 48.48 (CH_2N), 48.52 (NCH_3), 64.60 (CH_2Ph), 80.30 (C_q), 125.78, 126.09, 127.15, 127.63, 128.89, 131.62, 139.75, 146.88 (aromatic C). MS (EI, 120°C , 70 eV, m/z (%)): 366/368 (6.5) $[\text{M}-\text{CH}_3]^+$, 290/292 (34.6) $[\text{M}-\text{C}_7\text{H}_7]^+$, 99/101 (7.3) $[\text{Ga}(\text{CH}_3)_2]^+$, 91 (2.7) $[\text{C}_7\text{H}_7]^+$, 77 (2.0) $[\text{C}_6\text{H}_5]^+$, 58 (100) $[\text{C}_3\text{H}_8\text{N}]^+$.

Table I: Crystallographic data for **1** and **2**

compound	1	2
empirical formula	$[\text{C}_{13}\text{H}_{22}\text{GaNO}]_2$	$\text{C}_{21}\text{H}_{30}\text{GaNO}$
f_w , g/mol	556.08	382.18
cryst dim., mm	$0.24 \times 0.33 \times 0.39$	$0.18 \times 0.23 \times 0.27$
temperature, K	163(2)	187(2)
crystal system	tetragonal	orthorhombic
space group	$P 4_3 2_1 2$	$P 2_1 2_1 2_1$
a, Å	9.113(2)	13.360(3)
b, Å	9.113(2)	9.2343(13)
c, Å	34.409(9)	16.412(4)
V, Å ³	2857.3(11)	2024.7(7)
Z	4	4
ρ_{calc} , g cm ⁻³	1.293	1.254
μ , cm ⁻¹	1.908	1.395
F(000)	1168	808
radiation	Mo K α , $\lambda = 0.71069$	
2 θ range, deg	4 - 55	2 - 55
index ranges	$0 \leq h < 11, 0 \leq k < 11, 0 \leq l < 44$	$-17 \leq h < 17, 0 \leq k < 10, 0 \leq l < 21$
scan type	$\omega - 2\theta$	$\omega - 2\theta$
reflections collected	3681	4428
independent reflections	3251 [R(int) = 0.1163]	4101 [R(int) = 0.0366]
absorption correction	none	DIFABS [8] (min.: 0.877, max.: 1.144)
observed reflections	3245	4081
number of variables	150	217
GOF *	1.054	1.012
final R indices ** ($I > 2 \sigma(I)$)	$R_1 = 0.0421, R_w = 0.0805$	$R_1 = 0.0428, R_w = 0.0912$
absolute structure parameter	-0.03(2)	0.01(2)
largest diff. peak and hole, e/Å ³	0.322 and -0.347	0.303 and -0.404

* $\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$,
 ** R indices: $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$,
 $w = q / [(\sigma F_o)^2 + (\alpha P)^2 + bP + d + e \sin \theta]$.

X-ray Structure Analysis of 1 and 2:

The details of the crystal data with a summary of intensity data collection parameters and structural refinement for 1 and 2 are presented in table I. Atomic coordinates and equivalent isotropic displacement parameters for 1 and 2 are listed in table II. Data collection was carried out with an Enraf-Nonius CAD-4 automatic diffractometer, controlled by a PC and fitted with a low-temperature equipment. The cell parameters were obtained from a least squares treatment of the SET4 setting angles of 25 reflections in the range of $14.5^\circ < 2\theta < 24.3^\circ$ (1) and $16.7^\circ < 2\theta < 22.5^\circ$ (2). Both raw data sets were corrected for Lorentz and polarisation effects [7] and 1 for absorption effects [8]. The structures were solved with direct methods (SHELXS 86 [9]) and refined by full-matrix least squares using SHELXL 93 [10], which minimizes R_w (based on F^2). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in idealized positions (C-H 0.96 Å, $U_{iso} = 0.08$ Å²). Scattering factors were taken from the ref. [11-13]. All calculations were performed on a IBM Risk 6000 computer. The ORTEP [14] program was used to obtain the drawings. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository numbers CSD-404593 (1) and CSD-404594 (2), respectively.

Table II: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for 1 and 2 with estimated standard deviations.

Compound 1					Compound 2				
Atom	x/a	y/b	z/c	U_{eq}^*	Atom	x/a	y/b	z/c	U_{eq}^*
Ga	7914(1)	5483(1)	5065(1)	25(1)	Ga	1421(1)	1744(1)	1659(1)	25(1)
C(1)	7676(6)	3606(5)	5345(2)	43(1)	C(1)	226(3)	682(5)	2049(3)	42(1)
C(2)	9465(5)	6901(5)	5202(1)	36(1)	C(2)	2202(3)	2975(5)	2408(2)	38(1)
O	6602(3)	6129(3)	4667(1)	24(1)	O	1077(2)	2607(3)	684(2)	22(1)
C(3)	6735(4)	5786(4)	4276(1)	27(1)	C(3)	1703(2)	3004(4)	39(2)	20(1)
C(31)	5609(5)	4615(5)	4154(1)	29(1)	C(4)	1141(3)	2699(4)	-756(2)	21(1)
C(32)	4957(5)	3699(5)	4425(1)	34(1)	C(5)	1390(3)	3348(4)	-1505(2)	28(1)
C(33)	3920(5)	2657(6)	4312(2)	48(1)	C(6)	902(3)	2978(4)	-2211(2)	33(1)
C(34)	3499(5)	2567(6)	3930(2)	56(2)	C(7)	148(3)	1951(5)	-2200(2)	36(1)
C(35)	4103(6)	3476(6)	3660(2)	53(2)	C(8)	-127(3)	1324(4)	-1472(2)	32(1)
C(36)	5155(5)	4496(5)	3770(2)	42(1)	C(9)	366(3)	1700(4)	-757(2)	25(1)
C(4)	8361(4)	5456(5)	4188(1)	32(1)	C(10)	1985(3)	4634(4)	131(2)	26(1)
C(41)	8668(6)	4944(5)	3772(1)	46(1)	C(11)	1137(3)	5699(4)	85(2)	25(1)
N	9006(4)	4523(4)	4499(1)	30(1)	C(12)	1080(3)	6687(5)	-557(2)	36(1)
C(5)	8724(5)	2936(5)	4443(1)	41(1)	C(13)	327(4)	7720(5)	-579(3)	49(1)
C(6)	10608(5)	4728(6)	4519(2)	49(1)	C(14)	-370(4)	7801(5)	24(3)	49(1)
					C(15)	-342(3)	6816(5)	662(3)	45(1)
					C(16)	420(3)	5772(4)	688(3)	32(1)
					C(17)	2700(3)	2108(4)	72(2)	26(1)
					C(18)	3362(3)	2203(5)	-689(3)	39(1)
					C(19)	2503(3)	518(4)	268(2)	29(1)
					N	2407(2)	201(3)	1158(2)	27(1)
					C(20)	2010(3)	-1297(4)	1254(3)	40(1)
					C(21)	3414(3)	253(4)	1538(3)	37(1)

* U_{eq} is one third of the trace of the orthogonalized U tensor

X-ray structures:

The X-ray structure of **1** shows dimeric units with a twofold rotational symmetry and gallium in a penta-coordinate environment (Table III, Figure 1). This structure pattern is known from several related compounds [16] and therefore not surprising. The crystal structure of a closely similar compound ($[(\text{CH}_3)_2\text{Al}(\text{O}-(\text{R})-\text{CHC}_6\text{H}_5-(\text{S})-\text{CH}((\text{S})-\text{NHCH}_3)\text{CH}_3)]_2$) was published earlier [17]. A closer look at both structures reveals that they are nearly, but not exactly isotopic, since they differ in the number of atoms ($-\text{N}(\text{CH}_3)_2$ vs. $-\text{NHCH}_3$). Compound **1** crystallizes in the space group $\text{P}4_32_12$ (No.96), while Oliver and coworkers claim the enantiomorphous space group $\text{P}4_12_12$ (No.92) for the structure of the aluminium derivative. This is probably a mistake, since the atomic coordinates as well as the published drawing of the molecule show 1S,2R configuration for the ligand, while the text refers to the 1R,2S compound.

Figure 1: Molecular structure of **1**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% level.

Compound **2**, in contrast, is monomeric in the solid state (Table III, Figure 2). This is remarkable, since this means that there is another factor that prevents dimerization via formation of a four-membered Ga_2O_2 ring. In the crystal structures known so far, monomeric units usually result from one of the following effects: (i) the formation of intermolecular hydrogen bonds (ligands of $-\text{O}-\text{R}-\text{NH}_2$ type [18]), which saturate the primary donor atom (O) of the ligand, or (ii) mesomeric delocalization between the primary and secondary donor atoms [19], which reduces the negative charge of the primary donor atom and thus may decrease the tendency of dimerization. The only exception from this pattern, to our knowledge, is the aluminium analogue of **2**, published very recently [20]. The authors attribute the formation of a monomeric unit to the high stability of the six-membered chelate ring. Related dimeric structures with six-membered rings are known, however [16(k), 21]. We suspect that the presence of both a phenyl and a benzyl group in the direct neighborhood of the oxygen atom prevents the formation of dimers via this atom for steric reasons, rendering the metal atom in a tetra-coordinate environment.

Since a coordination number of four is the minimum required for a stable complex in this context, it is clear that the Ga-N coordinative bond is essential in **2**, while it is just an additional stabilizing factor in **1**. This can be verified by comparison of the bond lengths (2.11 vs. 2.36 Å, respectively), which shows that the corresponding bond in **1** is much weaker than in **2** and, furthermore, the weakest of the five bonds to Ga in the dimer. The consequences of this situation for the coordination behavior of the molecules in solution is

discussed in the NMR section below. The Ga-N bond distance observed for **2** is in the typical range of Ga-N dative bond lengths for tetrahedrally coordinate gallium [15(a), 18(a), 22].

Figure 2.: Molecular structure of **2**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% level.

^1H and ^{13}C NMR spectroscopy:

The ^1H and ^{13}C NMR spectra of the compounds are consistent with the reactions and structures described. The resonances at 3.47 ppm and 8.10 ppm for the OH protons of the corresponding ligands are missing in the spectra of the complexes formed, so there is no evidence of hydroxy protons of the starting amino alcohols. Only one diastereoisomer is detected for compound **1** and **2**, respectively, in the ^1H and ^{13}C NMR spectra, indicating diastereoisomerically pure complexes.

In the ^1H NMR spectrum of both, compound **1** as well as the corresponding ligand, the expected single set of resonances for all proton containing groups can be observed: The CH_3 -, NCH_2 - and CHPh -groups of the free ligand are detected as a doublet, a quartet and a doublet, respectively, and show the same coupling pattern at similar chemical shifts when complex **1** is formed. The NMe_2 -group at 1.71 ppm as well as the GaMe_2 -unit at -0.12 ppm are found as only one sharp signal, respectively. This seems to be somewhat surprising considering the different environments of the two methyl groups on both the gallium and nitrogen atom in the solid state structure. An explanation which is in line with the NMR data found, concerning the collapse of the methyl groups of both, the GaMe_2 - and NMe_2 - moiety, in solution, is the following: The weak Ga-N dative bond in **1** may undergo dissociation in solution, permitting transition from the five-coordinate to an intermediate four-coordinate gallium complex, which enables rapid rotation around the O-C bond without disruption of the Ga_2O_2 ring [16]. The rapid exchange between these possible conformations gives rise to a single magnetic environment on the NMR time scale. In contrast to **1**, in the similar dimeric Al compound $[(\text{CH}_3)_2\text{Al}(\text{O}(\text{R})\text{CHC}_6\text{H}_5-(\text{S})\text{-CH}((\text{S})\text{-NHCH}_3)\text{CH}_3)]_2$ [17] the methyl groups bound to aluminium were found to be nonequivalent at 22°C. As the temperature is increased coalescence of the AlMe_2 signals occurs. This indicates a lower energy of activation for the metal-nitrogen bond breaking in **1** and therefore a weaker M-N bonding at room temperature.

In comparison to 1, compound 2 reveals a totally different behavior in solution. In the ^1H NMR spectrum of compound 2, two sets of resonances are observed at room temperature for the NMe_2 -, NCH_2 - and CH_2Ph -moieties, respectively. In the free ligand only one signal for the NMe_2 -group, a multiplet for the NCH_2 -unit and a sharp signal for the CH_2Ph -moiety are detected. When complex 2 is formed, signal splitting and a change in the coupling pattern of each of these groups take place. Therefore the NMe_2 - group is observed as two signals, the NCH_2 -protons are detected as a part of an ABC pattern of the $-\text{CHCH}_2$ -unit linked to the amine, and the CH_2Ph -moiety as an AB pattern. The higher energy necessary for the dissociation of the Ga-N dative bond in the four-coordinate species 2 prevents break-up of the metal nitrogen bond, therefore fluxional behavior and free rotation around the Ga-O bond at room temperature becomes impossible. This provides a satisfactory explanation for the maintenance of the six-membered ring system in solution and the chemical shift nonequivalence of the NMe_2 - and NCH_2 -signals, respectively, observed in the ^1H and ^{13}C NMR spectra. The nonequivalence of the methylene protons of the CH_2Ph -group may be attributed to a hindered rotation of the benzyl group, caused by strong interaction with the GaMe_2 -unit. In the analogous aluminium complex [20] these protons collapse with equivalent chemical shifts, whereas when the bulkiness of the alkyl groups bound to the metal increases for example in the analogous AlEt_2 compound [20], diastereotopic behavior of the methylene protons can be observed. Therefore a more restricted rotation around the CH_2Ph bond and stronger interaction between the benzyl group and the GaMe_2 -unit compared to the AlMe_2 - group can be assumed.

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