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Synthesis and Crystal Structure of the Bis(cyclopentadienyl)gallium Ethoxide Dimer

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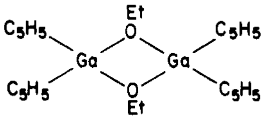
The reaction of C_5H_5Li with $GaCl_3$ in Et_2O at ambient temperature affords the ethoxy-bridged dimer $[(\eta^1\text{-}C_5H_5)_2GaOEt]_2$, 2. The structure of 2 has been determined by single-crystal X-ray diffraction. Compound 2 crystallizes in the monoclinic system $P2_1/n$ with a = 9.194 (5) Å, b = 9.778 (5) Å, c = 13.184 (7) Å, and β = 95.51 (4)°. The structure of 2 involves two ethoxy bridges and four terminal η^1-cyclopentadienyl groups. The Ga_2O_2 rhombus is planar.

Introduction

Cyclopentadienyl derivatives of the main-group elements are of interest because of the variety of bonding modes that have been observed.[1] In the preceding paper, Beachley et al.[2] described the preparation and structure of tris(cyclopentadienyl)gallium, 1. Independently we have prepared 1 using a virtually identical procedure, viz., the reaction of $GaCl_3$ with C_5H_5Li in Et_2O solution. Beachley et al. noted, and we concur, that careful temperature control is necessary to obtain 1 and that the desired reaction temperature is 0 °C. However, in some of our experiments we allowed the reaction to take place at ambient temperature. Under these conditions, the product is the novel ethoxy-bridged dimer, 2. In this paper we describe the synthesis and X-ray structure of 2. To the best of our knowledge, this represents the first structural information on a simple alkoxygallium compound. Moreover, the only cyclopentadienyl-substituted gallium compound investigated previously by X-ray crystallography is the dimethyl(μ-cyclopentadienyl)gallium polymer.[3]



2

Experimental Section

General Considerations. All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. All solvents were dried and freshly distilled immediately prior to use. Gallium trichloride was procured commercially and used as supplied, and C_5H_5Li was prepared by treatment of an Et_2O solution of C_5H_6 with an equimolar quantity of n-BuLi in n-hexane solution.

Medium-resolution mass spectra were measured on a Du Pont-Consolidated Model 21-491 instrument at an ionizing voltage of 70 eV.

Preparation of $[(\eta^1\text{-}C_5H_5)_2GaOEt]_2$, 2. A solution of $GaCl_3$ (5.0 g, 28.4 mmol) in 20 mL of Et_2O was added dropwise to a slurry of C_5H_5Li (85.2 mmol) in 200 mL of Et_2O/n-hexane at ambient temperature. Filtration of the reaction mixture and removal of the solvent and volatiles afforded 1.95 g of a yellow oil. Colorless single crystals of 2 (0.66 g, 1.35 mmol) suitable for X-ray diffraction study were grown from an Et_2O solution of the yellow oil held at −10 °C: yield of 2, 9.5%. The mass spectrum of 2 exhibited a weak parent peak at m/e 490. The base peak occurs at m/e 199 and is attributable to $[(C_5H_5)_2Ga]^+$. Other peaks of significance appear at m/e 331, 315, and 295.

Table I. Intensity Collection and Crystal Data for $[(\eta^1\text{-}C_5H_5)_2GaOEt]_2$, 2

formula	$C_{24}H_{30}Ga_2O_2$
mol wt	489.98
cryst class	monoclinic
space group	$P2_1/n$
a, Å	9.194 (4)
b, Å	9.778 (4)
c, Å	13.184 (6)
β, deg	95.51 (3)
U, Å^3	1179.8
Z	2 (dimers)
ρ(calcd), g cm^{-3}	1.38
cryst size, mm	0.60 × 0.40 × 0.25
μ(Mo Kα), cm^{-1}	24.25
radiatn	graphite-monochromated Mo radiation, λ = 0.71069 Å
reflctns measd	2095
reflctns obsd	1547
data omissn factor	$I > 3.0\sigma(I)$
2θ range, deg	$2.0 < 2\theta < 50.0$
no. of parameters varied	127
R^a	0.038
$R_w{}^a$	0.040

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega|F_o|^2]^{1/2}$.

X-ray Crystal Structure of $[(\eta^1\text{-}C_5H_5)_2GaOEt]_2$, 2. A single crystal of 2 was sealed under nitrogen in a Lindemann capillary prior to mounting on an Enraf-Nonius CAD-4 diffractometer. Lattice parameters were determined from a least-squares fit of the angular settings of 15 reflections, 10° < 2θ < 20° and subsequently refined by using accurately centered data with 2θ < 36°. The lattice parameters indicated a monoclinic cell, for which systematic absences uniquely determined the space group as $P2_1/n$. From a total of 2095 unique measured reflections, collected by using ω–2θ scans, 1567 were considered observed ($I > 3.0\sigma(I)$). After correction for Lorentz and polarization, but not for absorption, the structure was solved by direct methods (MULTAN)[4] which revealed the positions of the Ga atoms. The remaining non-hydrogen atoms were located from a subsequent difference-Fourier synthesis and refined by using anisotropic temperature factors. A subsequent difference-Fourier map revealed the positions of all hydrogen atoms which were positionally refined with a fixed isotropic temperature factor. A final least-squares refinement (full-matrix) converged smoothly to give final residuals R = 0.038 and R_ω = 0.040. No chemically significant peaks were

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(1) For a summary of structural information on group 3 cyclopentadienyl compounds, see: Baxter, S. G.; Cowley, A. H.; Lasch, J. G. *ACS Symp. Ser.* **1983**, *No. 232*, 111.

(2) Beachley, O. T., Jr.; Getman, T. E.; Kirss, R. U.; Hallock, R. B.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 751.

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Table II. Bond Lengths (Å) and Bond Angles (deg) for $[(\eta^1\text{-}C_5H_5)_2GaOEt]_2$, 2

Bond Lengths			
Ga(1)–O(1)	1.940 (3)	C(5)–C(1)	1.438 (9)
Ga(1)–O(1)′	1.906 (3)	C(6)–C(7)	1.466 (8)
Ga(1)–C(1)	2.016 (5)	C(7)–C(8)	1.322 (8)
Ga(1)–C(6)	2.016 (5)	C(8)–C(9)	1.41 (1)
C(1)–C(2)	1.457 (8)	C(9)–C(10)	1.335 (9)
C(2)–C(3)	1.322 (9)	C(10)–C(6)	1.457 (8)
C(3)–C(4)	1.38 (1)	O(1)–C(11)	1.386 (7)
C(4)–C(5)	1.368 (9)	C(11)–C(12)	1.31 (1)
Bond Angles			
O(1)–Ga(1)–C(1)	109.3 (2)	C(2)–C(3)–C(4)	110.6 (7)
O(1)–Ga(1)–C(6)	113.7 (2)	C(3)–C(4)–C(5)	109.6 (7)
O(1)–Ga(1)–O(1)′	79.5 (2)	C(1)–C(5)–C(4)	106.4 (7)
C(1)–Ga(1)–C(6)	122.2 (2)	C(7)–C(6)–C(10)	104.0 (5)
C(1)–Ga(1)–O(1)′	110.3 (3)	C(6)–C(7)–C(8)	108.9 (6)
C(6)–Ga(1)–O(1)′	113.8 (3)	C(7)–C(8)–C(9)	109.0 (7)
Ga(1)–O(1)–Ga(1)′	100.5 (2)	C(8)–C(9)–C(10)	110.1 (6)
C(2)–C(1)–C(5)	105.8 (6)	C(6)–C(10)–C(9)	107.8 (7)
C(1)–C(2)–C(3)	107.4(7)		

Angle between C(1)–C(6)–Ga(1) and Ga(1)–O(1)–O(1)′ Planes = 114.0 (5)

Table III. Fractional Coordinates for $[(\eta^1\text{-}C_5H_5)_2GaOEt]_2$, 2

atom	*x/a*	*y/b*	*z/c*
Ga(1)	−0.01777 (6)	0.03705 (6)	0.39079 (4)
C(1)	0.1463 (6)	−0.0183 (8)	0.3084 (4)
C(2)	0.0601 (6)	−0.0977 (8)	0.2308 (5)
C(3)	0.0362 (8)	−0.019 (1)	0.1492 (5)
C(4)	0.1054 (9)	0.106 (1)	0.1649 (6)
C(5)	0.1782 (7)	0.1089 (9)	0.2604 (6)
C(6)	−0.1941 (6)	0.1409 (6)	0.3294 (4)
C(7)	−0.2928 (6)	0.0398 (8)	0.2777 (4)
C(8)	−0.4068 (7)	0.0233 (9)	0.3304 (6)
C(9)	−0.3938 (7)	0.1136 (9)	0.4145 (6)
C(10)	−0.2720 (7)	0.1878 (7)	0.4141 (5)
O(1)	0.0636 (3)	0.1084 (4)	0.5214 (2)
C(11)	0.143 (1)	0.2265 (8)	0.5451 (6)
C(12)	0.129 (1)	0.3415 (9)	0.4947 (7)
H(1)	0.2101 (6)	-0.0705 (8)	0.3504 (4)
H(2)	0.0234 (6)	-0.1972 (8)	0.2379 (5)
H(3)	−0.0248 (8)	-0.047 (1)	0.0834 (5)
H(4)	0.0995 (9)	0.186 (1)	0.1129 (6)
H(5)	0.2426 (7)	0.1883 (9)	0.2922 (6)
H(6)	−0.1542 (6)	0.2321 (6)	0.2870 (4)
H(7)	−0.2738 (6)	−0.0125 (8)	0.2115 (4)
H(8)	−0.4922 (7)	−0.0457 (9)	0.3123 (6)
H(9)	−0.4680 (7)	0.1198 (9)	0.4676 (6)
H(10)	−0.2379 (7)	0.2642 (7)	0.4653 (5)
H(11)	0.227 (1)	0.2182 (8)	0.5027 (6)
H(12)	0.178 (1)	0.2239 (8)	0.6143 (6)
H(13)	0.042 (1)	0.3599 (9)	0.5328 (7)
H(14)	0.093 (1)	0.3409 (9)	0.4232 (7)
H(15)	0.203 (1)	0.4264 (9)	0.5117 (7)

present in the final difference map. All calculations were made by using the SHELX 76 system.[5] Pertinent crystallographic data are summarized in Table I, and compilations of atomic positional parameters and selections of bond lengths and bond angles appear in Tables II and III. Thermal parameters and tables of calculated structure factors are available as supplementary material.

Results and Discussion

The products of the reaction of C_5H_5Li with $GaCl_3$ depend on the reaction temperature. As pointed out by Beachley et al.,[2] at 0 °C the product is tris(cyclopentadienyl)gallium, 1. However, we have found that at ambient temperature the product is the ethoxy-bridged dimer $[(\eta^1\text{-}C_5H_5)_2GaOEt]_2$, 2. We presume that without external cooling the reaction temperature can increase to a point sufficient for the $GaCl_3$-promoted cleavage of Et_2O. However, we cannot exclude the possibility that EtO^- ions arose from adventitious ethoxide.

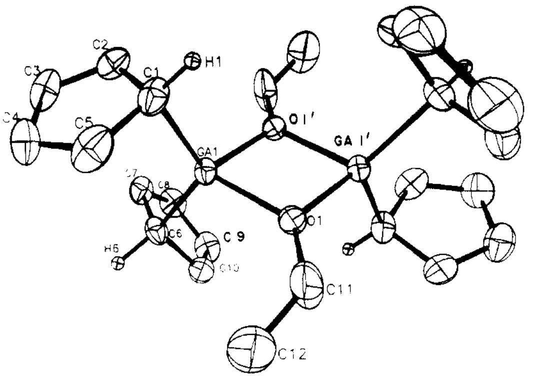

Figure 1. ORTEP diagram showing the non-hydrogen atoms of $[(\eta^1\text{-}C_5H_5)_2GaOEt]_2$, **2**.

The X-ray crystallographic study revealed the presence of ethoxy-bridged dimers in the solid state (Figure 1). The dimer has a center of symmetry imposed crystallographically, and there are no short intermolecular contacts between dimers. The cyclopentadienyl groups are bonded to gallium in the η^1 manner. This is clear from the patterns of C–C bond lengths within each cyclopentadienyl ring which resemble those, for example, for the terminal C_5H_5 groups of $(C_5H_5)_3In$.[6] Moreover, the Ga(1)–C(1) or Ga(1)–C(6) distances for 2 (2.016 (5) Å) are significantly shorter than, e.g., the Ga(1)–C(5) (2.701 (6) Å) or Ga(1)–C(10) (2.805 (6) Å) distances. Our Ga(1)–C(1) or Ga(1)–C(6) bond length is also shorter than that in the $(Me_2GaC_5H_5)_n$ polymer (average 2.264 (2))[3] but closer to the sum of single-bond covalent radii for Ga and C (1.97 Å).[7]

The Ga_2O_2 four-membered ring has been found to be a structural feature of the compounds $[R_2GaOCH_2CH_2NMe_2]_2$, R = H (**3**) and Me (**4**),[8] and $[Ga(OH)Cl(C_{14}H_{17}N_3)]_2Cl_2{\cdot}H_2O$ (**5**).[9] The average Ga–O bond length for **2** (1.923 (3) Å) is slightly shorter than those for **3** (1.982 (3) Å), **4** (1.995 (3) Å), and **5** (1.962 Å). Moreover, the bond angles at oxygen for **2** (100.5 (2)°) are smaller than for the pentacoordinate gallium derivatives **3** (105.3 (1)°) and **4** (105.4 (1)°).

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Supplementary Material Available: Listings of thermal parameters and observed structure factor amplitudes for **2** (11 pages). Ordering information is given on any current masthead page.

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