3074 *Organometallics* **1997,** *16,* 3074−3076

Synthesis and Characterization of $(MesGaO)_9$ (Mes = $Me_3C_6H_2$) and Crystal Structure of the First Galloxane Comparable to Catalytically Active Aluminum Compounds[†]

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Received February 5, 1997[⊗]

Summary: The thermolysis of $(Mes_2GaOH)_2 \cdot THF$ *in toluene or 1,4-dioxane at 100 °C resulted in the formation of* $(MesGaO)_9$ *(**1**). A byproduct of this reaction is* Mes_3Ga*. Compound **1** was characterized by electron impact mass spectroscopy and single-crystal X-ray structural analysis. The structure consists of two six-membered* $(MesGaO)_3$ *rings connected by three* μ_2*-(MesGaO) units.*

Controlled reactions of organoaluminum or -gallium compounds with water lead to the formation of alumoxanes or galloxanes with the general formulae $(RMO)_n$ or $(R_2MOMR_2)_n$ (M = Al, Ga).[1] The alkyl-substituted alumoxanes were studied in the 1960s as catalysts for polymerization reactions.[2−7] When Sinn and Kaminsky, in 1980, found methylalumoxane (MAO) to be a highly active cocatalyst for group 4 metallocenes (e.g., Cp_2ZrMe_2) in alkene polymerization,[8] considerable impetus was given to structural information on alumoxanes in order to elucidate their role in these systems. Therefore, manifold variations of organic substituents on aluminum have been introduced or the exchange of the metal by gallium has been made to determine the characteristics of metalloxanes.[1] On this basis, Barron et al. found that the hydrolysis of $^tBu_3Al$ leads to hydroxides, oxide hydroxides, or oxides.[9−12] In contrast, structural information concerning the analogous gallium compounds are limited to few hydroxides and oxide hydroxides.[11,13−17] Although Barron et al. have characterized the nonameric galloxane $(^tBuGaO)_9$, there has been no X-ray structural investigation on galloxanes.[18]

Recently, we have shown that controlled hydrolysis of Mes_3Ga in THF solution leads to the formation of $(Mes_2GaOH)_2 \cdot THF$.[19] We now report the synthesis and characterization of $(MesGaO)_9$ (**1**) formed by thermolysis of $(Mes_2GaOH)_2 \cdot THF$ (eq 1).

$$9(Mes_2GaOH)_2 \cdot THF \xrightarrow[\substack{-9THF \\ -18MesH}]{\Delta} 2(MesGaO)_9 \qquad (1)$$

Due to the high thermal stability of the hydroxide, no reaction was observed in refluxing THF. Therefore, we performed condensation reactions in toluene or 1,4-dioxane (as coordinating solvent) at 100 °C. In both solvents, the yield of the nonameric galloxane was about 60%. The main byproduct under these reaction conditions was trimesitylgallium. The ^1H NMR spectrum of **1** shows two sets of mesityl protons in the ratio of 2:1 (δ 6.64, 6.59 ppm for the ring protons, δ 2.57, 2.49 ppm for the *o*-CH_3 protons, and δ 2.07, 2.00 ppm for the *para*-CH_3 protons, respectively), indicating that the mesityl groups in **1** are magnetically nonequivalent. The electron impact (EI) mass spectrum shows the molecular ion (*m/z* 1844 **1**; *m/z* 1605, 100, **1** − Mes − MesH). Single crystals suitable for an X-ray structural determination were obtained from THF. The molecular structure of **1** is shown in Figure 1.

[†] Dedicated to Professor Roald Hoffmann on the occasion of his 60th birthday.

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

(1) Generally, alumoxanes and galloxanes are species containing an oxygen bridge connecting two metal atoms M−O−M (M = Al, Ga). Oligomeric aluminum or gallium alkoxides bridged by alkoxy groups M−O(R)−M and compounds containing no organic group are (by definition) not included in this classification. See: (a) Pasynkiewicz, S. *Polyhedron* **1990**, *9*, 429. (b) Atwood, J. L. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH Publishers, Inc.: New York, 1993; p 219.

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S0276-7333(97)00086-1 CCC: $14.00

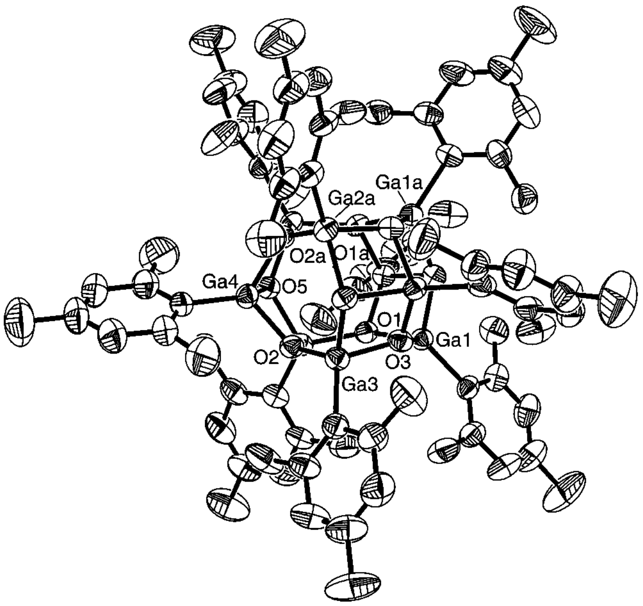

Figure 1. ORTEP plot of [$(MesGaO)_9$ + 10THF + $Me_3C_6H_3$] **1**. The mesitylene molecule and the nine noncoordinated THF molecules are omitted for clarity. Important average bond distances (Å): Ga−C 1.990 , Ga−O ($(MesGaO)_3$) 1.910 , Ga−O (μ_2-(MesGaO)) 1.967.

For reasons of clarity, lattice solvent molecules are omitted (nine noncoordinating THF molecules are located between the mesityl groups and one THF molecule is placed between four $(MesGaO)_9$ units in the layer). In addition, a single nonameric unit cocrystallizes with a single mesitylene (C_9H_{12}) molecule. To avoid a decay of the crystals due to loss of crystal solvent they were mounted on a glass fiber at −50 °C.[20] The nonameric mesitylgalloxane **1** crystallizes in the orthorhombic space group *Pccn*. The structure can be described having two six-membered $(MesGaO)_3$ rings connected by three μ_2-MesGaO units. A similiar structure was found for the analogous $(^tBuAlO)_9$, which is isostructural to $(NaO^tBu)_9$.[9] All gallium atoms of this cage are coordinated by three μ_3-oxygen atoms. The average gallium−carbon bond length (1.990 Å) is in the range of known mesityl-substituted gallium compounds.[19] The average Ga−O bond length of the two $(MesGaO)_3$ rings is 1.910 Å, whereas the three Ga−O bond distances in the μ_2-(MesGaO) units are remarkably longer (1.967 Å average). This bond lengthening is probably induced by the electrostatic competition of a fourth oxygen atom for each gallium atom in the bridging position between the six-membered rings (average Ga(4)···O(5′), Ga(5)···O(5), Ga(5′)···O(4) 3.524 Å). Furthermore, it seems noteworthy that the μ_2-(MesGaO) units between the rings are located closer to the bottom than to the top ring system shown in Figure 1 (Ga−O 1.871 versus 1.944 Å).

To obtain additional information on condensation reactions and the formation of Mes_3Ga, we performed solvent-free thermolysis of $(Mes_2GaOH)_2$·THF at atmospheric pressure and *in vacuo* (7.5×10^{-3} Torr) at various temperatures. According to eq 1, the elimination of mesitylene starts at the decomposition point of $(Mes_2GaOH)_2$·THF (172 °C, atmospheric pressure) whereas sublimation of Mes_3Ga can be observed *in vacuo* beginning at ca. 110 °C. Investigations of the volatiles collected in cooling traps (−196 °C) gave different ratios of mesitylene compared to THF at various temperatures (3:1 to 6:1). Moreover, the solid residue exhibits two characteristic OH vibrations in the IR spectra (3671 and 3645 cm^{-1}), clearly indicating hydroxide groups and remaining THF molecules. Therefore, we propose eq 2 as a competing reaction to eq 1.

$$n(\mathrm{Mes_2GaOH})_2\cdot\mathrm{THF} \xrightarrow{10^{-4}\ \mathrm{mbar},\ \Delta} n\underset{\mathbf{2}}{\mathrm{Mes_3Ga}} + \underset{\mathbf{3}}{[\mathrm{MesGa(OH)_2\cdot THF}]_n} \quad (2)$$

However, intermediates of composition such as $[Mes_2Ga(OH)\text{-}MesGa(OH)_2\cdot THF]_n$ (**4**) cannot be ruled out. At various reaction conditions (temperature and heating time), the yields of **1** (20−70%), **2** (15−30%), and the hydroxides (**3** or **4**, 15−50%) vary in the solid residue. The EI mass spectrum of the residue shows only the molecular ion of mesitylene (*m*/*z* 120). In the ^1H NMR spectrum, only the signals of **1**, **2**, and mesitylene can be detected. We assume decomposition of the intermediates **3** and **4**, respectively, in solution due to mesitylene and Mes_3Ga formation *in vacuo*. However, it has been impossible up to now to establish a precise condensation mechanism. The obvious temperature dependance of the condensation reaction can be deduced from the constant product distribution at a constant temperature and the variety of product yields at different temperatures (see above).

However, the experiments indicate that the equilibria postulated for the methylalumoxane system[1,21] are feasable for the related gallium systems as well. The existence of hydroxidic intermediates during condensation reactions has been established. Therefore, possible interactions between hydroxide groups and the catalytically active species in polymerization reactions of olefins with metallocenes should not be neglected.[22] This is indicated by the nonexistence of cocatalytic properties of **1** in the polymerization of ethylene with Cp_2ZrMe_2. Recently, Barron et al. introduced the idea of the "latent Lewis acidity" which might be responsible for the cocatalytic activity of $(^tBuAlO)_n$.[23] However, no crystallographic data are available for any nonameric metalloxane for comparing the structural parameters of **1** with those of the homologous aluminum compounds.

Experimental Section

General Considerations. All experiments were performed using standard Schlenk techniques under a dry nitrogen atmosphere due to the extreme sensitivity of the reactants and products toward air and moisture.[19] A Braun MB 150-GI glovebox was used to store the compounds and to prepare the samples for spectroscopic characterization. All solvents were dried over sodium/benzophenone, freshly distilled, and degassed prior to use. $(Mes_2GaOH)_2$·THF was prepared as previously reported.[19]

Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität

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Göttingen. NMR spectra were recorded on a Bruker AM 200 and were externally referenced to tetramethylsilane. FT-IR spectra were measured on a Bio-Rad FTS-7 as Nujol mulls between KBr plates in the range 4000−400 cm^{-1}. EI mass spectra were measured on a Finnigan MAT 8230 mass spectrometer.

Preparation of (MesGaO)$_9$ (1): Method a. A suspension of (Mes$_2$GaOH)$_2$·THF (2.0 g, 2.7 mmol) in toluene or 1,4-dioxane (30 mL) was heated to 100 °C for 6 h. After removing the volatiles under reduced pressure, the white solid was washed with *n*-hexane (15 mL), filtered, and dried *in vacuo*. Crystallization from THF gave **1** (0.7 g) in 61% yield. Mp > 350 °C. The filtrate contained 0.4 g of Mes$_3$Ga. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 6.64 (s, 12 H, Ar−H), 6.59 (s, 6 H, Ar−H), 2.57 (s, 36 H, 2,6-CH$_3$), 2.49 (s, 18 H, 2,6-CH$_3$), 2.07 (s, 18 H, 4-CH$_3$), 2.00 (s, 9 H, 4-CH$_3$) ppm. MS (70 eV): *m/e* 1844 ((MesGaO)$_9$, 10), 1724 ((MesGaO)$_9$ − MesH, 65), 1605 ((MesGaO)$_9$ − MesH − Mes, 100). IR (Nujol mull): 3015 (s), 1719 (m), 1601 (vs), 1558 (s), 1412 (s), 1293 (m), 1094 (vs), 1028 (vs), 947 (m), 848 (s), 737 (vs), 663 (vs), 589 (s), 572 (s), 551 (vs), 491 (m), 464 (s), 404 (vs). Anal. Calcd for C$_{81}$H$_{99}$Ga$_9$O$_9$ (1844.15): C, 52.76; H, 5.41. Found: C, 52.5; H, 5.6.

Preparation of (MesGaO)$_9$ (1): Method b. (Mes$_2$GaOH)$_2$·THF (0.8 g, 1.1 mmol) was heated at atmospheric pressure to 190 °C. At 172 °C, elimination of mesitylene and THF could be observed. The volatiles were collected in a cold trap and characterized by ^{1}H NMR. After removal of the volatiles at 90 °C under reduced pressure, the white solid was washed with *n*-hexane (15 mL), filtered, and dried *in vacuo.* Yield 0.3 g of **1** (71%). From the filtrate, 0.1 g of Mes$_3$Ga was obtained. Spectroscopic data and elemental analysis are consistent with those of method a.

Condensation of (Mes$_2$GaOH)$_2$·THF *in vacuo*. (Mes$_2$GaOH)$_2$·THF (0.8 g, 1.1 mmol) was heated *in vacuo* (7.5 × 10^{-3} Torr) to temperatures between 110 and 160 °C. Subliming Mes$_3$Ga was removed on a cold finger held at 30 °C. The volatiles (mesitylene and THF) were collected in a cold trap (−196 °C). The reaction time at each temperature was 8 h. At various temperatures, different amounts of Mes$_3$Ga, volatiles, and solid residue were obtained. The total assay of each reaction was correct. Spectroscopic data of the solid residue: ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 6.89−6.44 (m, Ar−H), 2.94−2.00 (m, 2,4,6-CH$_3$ ppm. MS (70 eV): *m/e* 120 (MesH, 100). IR (Nujol mull): 3671 (s, ν(OH)), 3645 (s, ν(OH)), 3509 (s, broad, ν(OH)), 3016 (s), 1756 (m), 1719 (m), 1601 (vs), 1556 (s), 1411 (s), 1292 (m), 1094 (vs), 1029 (vs), 947 (m), 846 (vs), 835 (m), 736 (vs), 708 (vs), 687 (s), 663 (vs), 588 (s), 571 (s), 543 (vs), 492 (m), 464 (s), 403 (vs).

X-ray Structure Determination of 1. The crystal of **1** was mounted in an oil drop on a glass fiber at low temperatures. Due to a phase transition of the crystals at −93 °C, data were collected at −80 °C[24] on a Stoe−Siemens−Huber diffractometer with monochromated Mo Kα radiation (λ = 0.710 73 Å) using a SMART-CCD area detector. The structure was solved by direct methods using SHELXS-90.[25] The structure was refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$.[26] The R values are defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically positioned and treated as riding. All five THF molecules present suffer from severe disorder. Similarity restraints were applied to geometrically equivalent bond lengths and angles of the lattice THF molecules. They were refined as puckered C$_5$H$_{10}$ five-membered rings because it was impossible to identify the oxygen atom. Two THF molecules in general positions were refined to three disordered positions with site occupation factors of 0.4/0.4/0.2 and 0.45/0.35/0.2, respectively, and two THF molecules in general positions were refined to two disordered positions with site occupation factors 0.6/0.4 and 0.65/0.35, respectively. The single THF molecule at the center of inversion was refined by suppressing the special position constraints.

Table 1. Crystallographic Data for 1

compd	**1**
empirical formula	C$_{126}$H$_{183}$Ga$_9$O$_{18}$
fw	2613.2
temp (K)	193(2)
cryst size (mm)	0.7 × 0.7 × 0.6
cryst syst	orthorhombic
space group	*Pccn*
a (Å)	18.78(3)
b (Å)	20.63(2)
c (Å)	33.65(3)
α (deg)	90
β (deg)	90
γ (deg)	90
cell volume, V (nm^3)	13.04(3)
Z	4
ρ_c (g·mm^{-3})	1.331
μ (mm^{-1})	1.888
F(000)	5448
2θ range (deg)	5−45
no. of data measd, unique	20 787, 11 026 (R$_{int}$ = 0.0373)
R,[a] wR2[b] ($I > 2\sigma I$)	0.0691, 0.1470
R, wR2 (all data)	0.0973, 0.1608
goodness of fit, S[c]	1.259
weight factors a, b[d]	0.029, 35.790
no. of refined parameters	1026
restraints	4045
largest diff peak, hole (e·nm^{-3})	462/−543

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]^{1/2}$. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma(n - p)]^{1/2}$. [d] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [F_o^2 + 2F_c^2]/3$.

Acknowledgment. This work has been financially supported by the BMBF, the Deutsche Forschungsgemeinschaft, and the Hoechst AG.

Supporting Information Available: Tables of crystal data, fractional coordinates, anisotropic displacement parameters, and bond lengths and angles and fully labeled figures showing 50% thermal ellipsoids and hydrogen atom coordinates of **1** (14 pages). Ordering information is given on any current masthead page.

OM970086D

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