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Structural Evidence of the Epoxide Oxygen Propensity to Double Coordination[†]

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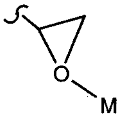
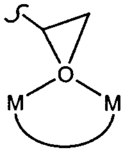
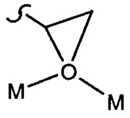
The availability and exceptional reactivity of epoxides cause these derivatives to constitute an important and much studied class of reagents in polymerization and synthetic chemistry and be of interest in both academic research and commercial development. Despite a pivotal role of Lewis acid−epoxide adducts in the ring-opening transformations, there is a relative obscurity of the structurally characterized metal epoxide complexes.[1] The transition states used for mechanistic considerations are usually comprised of the monodentate coordination mode of an epoxide to Lewis acid, **I**. The mechanisms involving the double coordination are very rare and usually concern the activation of epoxides with bidentate Lewis acids of a rigid structure with properly placed active centers, **II**.[2] It is interesting to note that for the first time, the possibility of double activation of epoxides by a diprotic molecule was proposed by Hine et al. in order to explain the unusual catalytic activity of 1,8-biphenylenediol, **IIa**, for the reaction of an epoxide with a nucleophile.[3] Only recently, Gabbai et al. reported the first structurally characterized complex consisting of the epoxide chelated by a bifunctional Lewis acid, 1,2-bis(chloromercurio)tetrafluorobenzene, **IIb**.[4] However, to our knowledge, there is a lack of structurally authenticated intermediates with the doubly coordinated epoxide by nonconstrained Lewis acid centers, **III**.



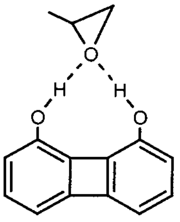
I



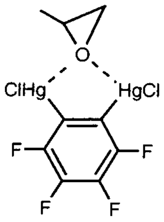
II



III



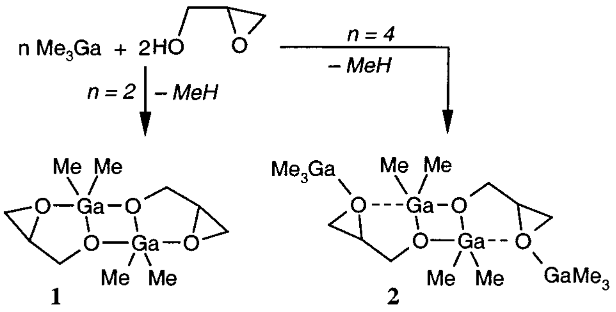
IIa



IIb

Herein, we report the synthesis and structural characterization of gallium−epoxide complexes derived from GaMe$_3$ and 2,3-epoxy-1-propanol, and for first time, we demonstrate that epoxides can be double activated by independent Lewis acid centers.

Scheme 1



The reaction of GaMe$_3$ with 1 equiv of *rac*-2,3-epoxy-1-propanol (CH$_2$Cl$_2$, −78 °C) allows for the isolation of complex **1** almost quantitatively (Scheme 1). Compound **1** is a viscous liquid at room temperature and was characterized by cryoscopic molecular weight determination and ^{1}H NMR spectroscopy.[5] The data indicate that the structure of **1** in solution is of the same morphology as the related dialkylgallium alkoxides derived from donor functionalized alcohols,[6] e.g., dimeric $[R_2Ga(\mu\text{-}O,O')]_2$ complexes. The relatively complex ^{1}H NMR spectrum probably results from the presence of *R,S* and *R*,R** diastereoisomers in the postreaction mixture and the nonrigid structure of **1** in solution.[7]

The 2,3-epoxy-1-propanol reacts with 2 equiv of GaMe$_3$ at −78 °C to yield the tetranuclear adduct **2** (Scheme 1). Compound **2** is stable as a solid under inert atmosphere; however, in solution it slowly decomposes at ambient temperature. The X-ray crystallographic analysis revealed an unprecedented structure of **2** in the solid state, which consists of the epoxide oxygen atoms double coordinated to different Lewis acid centers (Figure 1).[8]

The structure of **2** in the solid state may be viewed as the Lewis acid−base adduct of GaMe$_3$ with dimeric compound **1**, in which

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(5) Selected spectroscopic data for **1** and **2**. ^{1}H NMR (C$_6$D$_6$, 300 MHz); **1**, δ −0.01 (12H, s, Ga−CH$_3$), 2.05−2.45 (2H, m, br), 3.20−4.40 (8H, m, br); **2**, δ −0.15 (30H, s, br, Ga−CH$_3$), 2.10−2.60 (6H, m, br), 3.10−3.70 (4H, m, br).

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10.1021/ic015572e CCC: $20.00

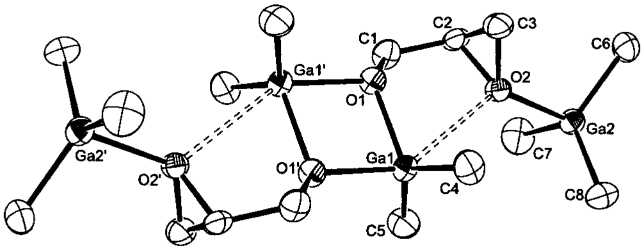
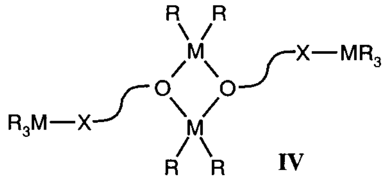


Figure 1. View of the molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Ga(1)−O(1) 1.951(3), Ga(1)−O(1′) 1.991(3), Ga(1)−O(2) 2.886(3), Ga(2)−O(2) 2.162(3), O(1)−C(1) 1.436(5), O(2)−C(2) 1.460(5), O(2)−C(3) 1.474(5), C(2)−C(3) 1.442(7), O(1′)-Ga(1)−O(2) 145.9(1), Ga(1)−O(2)−Ga(2) 127.8(1), O(1)−Ga(1)−C(4) 111.5(2), O(1)−Ga(1)−C(5) 111.3(2), O(1′)−Ga(1)−C(4) 105.4(2), O(1′)−Ga(1)−C(5) 106.5(2).

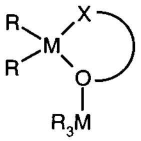
two $GaMe_3$ moieties are additionally coordinated to the epoxide oxygen of the chelating glycidolate anions. Several points are worth of noting regarding the structure and bonding in adduct **2**. The epoxide oxygen atoms O(2) and O(2′) fit well into the plane defined by the central Ga_2O_2 ring (rms deviation of the fitted atoms is equal to 0.010 Å) and interact with the gallium atoms, giving rise to five-coordinate metal centers. The Ga(1)O(1)C(1)C(2)O(2) ring is puckered, as demonstrated by the C(1) atom being 0.629(6) Å out of the O(1)Ga(1)O(2)C(2) plane, presumably in order to attain a proper position for the epoxide oxygen coordination to the metal center through an sp^3-like lone pair and to minimize ring strain. The coordination sphere of the central gallium atoms can be described as distorted trigonal bipyramidal, with the angle defined by the axial substituents of 145.9°(1). The Ga(1)−O(1), 1.951(3) Å, and Ga(1)−O(1′), 1.991(3) Å, bridge-bond distances differ in length, which is a typical feature of the dimeric five-coordinate group 13 organometallic alkoxides, $[R_2M(\mu\text{-}O,O')]_2$.[6,7] The observed nonequivalency of the Ga−O bridging distances in **2** is smaller than that in the related derivative of ethylene glycol monomethyl ether, $[Me_2Ga(\mu\text{-}OC_2H_4OCH_3)]_2$ (the corresponding Ga−O distances are 1.934(6) and 2.012(7) Å, and the Ga−O axial distance is 2.624(6) Å),[6b] which is consistent with the diversified trans influence of axial substituents,[9] i.e., the terminal axial bond in **2** is weaker than that in the α-hydroxy ether derivatives and the trans influence effects the intramolecular geometry less. The Ga(1)−O(2) bond distance of 2.886(3) Å is significantly shorter than the sum of the van der Waals radii of oxygen and gallium (3.39 Å),[10,11] however, it is noticeably longer than the corresponding bond distances in the dialkylgallium derivatives of α-hydroxy ethers.[6a,b] We also note that there is significant widening of O(1)−Ga(1)−C angles by 5−6° compared to O(1′)−Ga(1)−C angles. Thus, these observations strongly implicate the presence of a secondary stereoelectronic interaction between the epoxide oxygen and the gallium fifth coordination site in compound **2**.

The most striking feature of the molecular structure of **2** is the fact that the epoxide utilizes the oxygen lone electron pairs to bond the two metal centers. The fact that the epoxide oxygen in compound **2** binds two Lewis acid centers at once instate to form the open-shell structure with nonchelating glycidolate ligands and all four-coordinate metal centers indicates, in our opinion, the distinct propensity of an epoxide moiety to the double activation. It seems likely that the observed secondary interactions play an important role in the selective epoxide ring-opening transformations. For example, α-hydroxy epoxides are often used as model compounds for regio- and stereoselective transformations involving group 13 metal alkyls.[12,13]

Moreover, the solid-state structure of **2** is intriguing, as previous studies on the related reactions involving aluminum or gallium alkyls and various donor-functionalized alcohols have shown the formation of the open-shell dimeric four-coordinate complexes **IV** or monomeric adducts **V**.[14] Thus, it is reasonable to assume that the observed structure of **2** results from the propensity of the epoxide oxygen to double coordinate. It is also obvious that compound **2** exists in solution as an equilibrium between the close-shell five-coordinate and open-shell four-coordinate dimeric isomers, which is predominantly shifted to the latter form.



IV



V

In conclusion, the reported studies provide model complexes used to investigate mechanistic aspects of ring-opening transformations mediated by organometallic compounds. Additional studies are in progress to obtain further insight concerning the epoxide/Lewis acid complex formation and organometallic-mediated epoxide ring-opening reactions.

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Supporting Information Available: X-ray experimental details and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Crystal data for **2**: $C_{16}H_{40}Ga_4O_4$, triclinic, space group $P\bar{1}$, $Z = 1$, $a = 7.5689(2)$, $b = 7.8002(2)$, $c = 12.2351(5)$ Å, $\alpha = 84.952(1)$, $\beta = 79.449(1)$, $\gamma = 63.927(2)°$, $V = 637.84(4)$ Å^3, $T = 150$ K, $\mu = 4.19$ mm^{-1}, 4596 reflections collected, 2898 unique ($R_{int} = 0.068$). Several attempts to isolate suitable monocrystals always resulted in twinned crystals with twin index $i = 7$. Refined fractional contribution of the minor twin component was equal to 0.089(4). The structure was refined by full-matrix least-squares on F^2 including intensities of superimposed reflections of the twin. Final R indices (all data): $wR_2 = 0.1141$, $R_1 = 0.0534$.

(9) Recently, we demonstrated that the trans influence of axial substituents strongly effects the intramolecular geometry of the five-coordinate group 13 metal complexes: Lewiński, J.; Goś, P.; Kopeć, T.; Lipkowski, J.; Luboradzki, R. *Inorg. Chem. Commun.* **1999**, *2*, 374.

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(11) Based on a variable temperature X-ray analysis, we note that the Ga(1)−O(2) distance shows significant lengthening with the temperature increase (0.042 Å/100 K) when compared to all remaining bonds in compound **2**; this phenomenon will be discussed in detail elsewhere.

(12) For recent representative examples involving organoaluminum reagents promoted ring-opening reaction of 2,3-epoxy-1-ols see: Nicolaou, K. C.; Baran, F. S.; Jautelat, R.; He, Y.; Fong, K. C.; Choi, H. S.; Yoon, W. H.; Zhong, Y. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 549; Benedetti, F.; Berti, F.; Norbedo, S. *Tetrahedron Lett.* **1999**, *40*, 1041; Benedetti, F.; Berti, F.; Norbedo, S. *Tetrahedron Lett.* **1998**, *39*, 7971; Balasubramaniam, R. P.; Moss, D. K.; Wyatt, J. K.; Spence, J. D.; Nantz, M. H. *Tetrahedron* **1997**, *53*, 7429; Sasaki, M.; Matsumori, N.; Maruyama, T.; Nonomura, T.; Murata, M.; Tachibana, K.; Yasumoto, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1672.

(13) For example, the double activation of an epoxide moiety is probably involved in the enantioselective epoxide ring-opening reactions promoted by gallium heterobimetallic complexes (thought this has not been considered by the authors): Iida, T.; Yamamoto, N.; Matsunaga, S.; Woo, H.-G.; Shibasaki, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 2223; Iida, T.; Yamamoto, N.; Sasaki, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1997**, *119*, 4783.

(14) See for example: Atwood, D. A.; Gabbai, F. P.; Lu, J. L.; Remington, M. P.; Rutherford, D.; Sibi, M. P. *Organometallics* **1996**, *9*, 2308; McMahon, C. N.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1998**, 3301, and references therein.