

Supporting Information for

A Homogeneous Ga(III) Compound Selectively Catalyzes the Epoxidation of Alkenes

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Expanded Experimental Section

Materials

Unless stated otherwise, all chemicals were purchased from Sigma-Aldrich and used as received. Anhydrous ethanol and diethyl ether (ether) were bought from Pharmco-Aaper and Fisher Scientific, respectively. Deuterated acetonitrile (CD_3CN) was purchased from Cambridge Isotopes. $[\text{Ga}(\text{phen})_2\text{Cl}_2]\text{Cl}$ was prepared and characterized as previously described.¹⁻³ The Ga(III) complex crystallized upon adding ether to a saturated solution of the compound in acetonitrile (MeCN). The identity and purity of the Ga(III) catalyst were confirmed by nuclear magnetic resonance (NMR).

Preparation of Custom-Made Peracetic Acid (PAA_R)

The more basic grade of peracetic acid (PAA_R) was prepared through a slightly modified version of a reported procedure.⁴ 17 g of 50% H_2O_2 (0.25 mol) was slowly added to glacial acetic acid (150 g, 2.5 mol), which was stirred in a polyethylene bottle at room temperature. After 5 min, 5.0 g of Amberlite IR-120 was added. The resultant mixture was allowed to stir behind a blast shield for 24 h. After this duration, the solution was filtered, and the molar concentration of PAA was determined by its integrated ^{13}C NMR resonance relative to that of acetic acid. The solution was stored in a standard $-20\text{ }^\circ\text{C}$ freezer when not in use. The content of PAA was determined to be 7.1% (molar) by ^{13}C NMR analysis; this molar concentration was replicated in multiple batches.

CAUTION: Peracids and mixtures of peroxides and organic solvents are potentially explosive and should be handled with care. The dangers can be minimized by using minimal amounts of these materials, using proper protective equipment including blast shields, and working at lower temperatures.

Instrumentation

Proton and carbon-13 nuclear magnetic resonance (^1H NMR, ^{13}C NMR) spectra were acquired on a 400 MHz AV Bruker NMR spectrometer at 294 K. All resonances were referenced to internal standards. Gas chromatography (GC) was obtained on a ThermoScientific Trace GC Ultra spectrometer with a flame ionization detector (FID).

Mass spectrometry was performed on an Ultra Performance LC System (ACQUITY, Waters Corporation, Milford, MA) coupled to a quadrupole time-of-flight mass spectrometer (Q-

TOF Premier, Waters Corporation, Milford, MA) via direct probe analysis operated in the positive ion mode. All samples were run as MeCN solutions.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on a SPECTRO CIROS ICP-OES spectrometer in Auburn University's Department of Agronomy and Soils. All samples were prepared and run as solutions in 10% (by volume) aqueous HCl.

X-Ray Crystallography

The crystal was mounted in paratone oil on a glass fiber and aligned on a Bruker SMART APEX CCD X-ray diffractometer. Intensity measurements were performed using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a sealed tube and monocapillary collimator. SMART (v 5.624) was used to determine the preliminary cell constants and control the data acquisition. The intensities of reflections of a sphere were collected through the compilation of three sets of exposures (frames). Each set had a different ϕ angle for the crystal, with each exposure spanning 0.3° in ω . A total of 1800 frames were collected with exposure times of 40 s per frame. After the data were corrected for Lorentz and polarization effects, the structure was solved using direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at idealized positions $0.95 \text{ \AA}$ from their parent atoms prior to the final refinement. Further details regarding the data acquisition and analysis are included on Table S1.

Reactivity Studies

All reactions were run in acetonitrile (MeCN) at 0°C under N_2 . The reaction mixtures were stirred for 1 h, at which point excess ether was added to precipitate the gallium compounds. With all substrates, the quenched reaction mixtures were sequentially filtered through plugs of neutral alumina, basic alumina, and silica gel to remove the remaining PAA and metal salts. The workup did not remove organic starting materials or products from the reaction mixture, as assessed by analyzing control mixtures of alkenes and epoxides that were subjected to the same protocol. All products were identified by their GC retention times and NMR. The yields of the products were quantified relative to an internal standard of 1,2-dichlorobenzene, which was found to be unreactive under these conditions. All reactions were run at least four times to ensure reproducibility. The results were also found to be reproducible with different batches of both $[\text{Ga}(\text{phen})_2\text{Cl}_2]\text{Cl}$ and PAA_R .

Isolated Yields

Isolated yields were obtained for cyclohexene, cyclooctene, and 1-octene.

Cyclohexene oxide. [Ga(phen)₂Cl₂]Cl (0.054 g, 0.10 mmol) and cyclohexene (0.842 g, 10.0 mmol) were dissolved in 2 mL of MeCN. After the solution was put under N₂ and cooled to 0 °C, PAA_R (11.4 g, 20.0 mmol) was added dropwise. After 1 h, the reaction solution was filtered through plugs of silica gel and K₂CO₃. Cyclohexene oxide was isolated from the filtrate through distillation, yielding 0.38 g of product (39% vs. 46% GC yield).

Cyclooctene oxide. [Ga(phen)₂Cl₂]Cl (0.0540 g, 0.10 mmol) and cyclooctene (1.18 g, 10.0 mmol) were dissolved in 2 mL of MeCN. The solution was put under N₂ through nitrogen bubbling and cooled to 0 °C. Subsequently, PAA_R (11.4 g, 20.0 mmol) was added slowly. After 1 h, the reaction mixture was filtered through silica gel and K₂CO₃. Cyclooctene oxide was distilled from the filtrate (0.97 g, 77% vs. 87% GC yield).

1-Octene oxide. [Ga(phen)₂Cl₂]Cl (0.054 g, 0.10 mmol) and 1-octene (1.14 g, 10.0 mmol) were dissolved in 2 mL of MeCN. The reaction mixture was put under N₂ and cooled to 0 °C. Once the temperature equilibrated, 11.4 g of PAA_R (20.0 mmol) was added dropwise. 1 h after the addition was completed, the reaction mixture was filtered through plugs of silica gel and K₂CO₃. 1-Octene oxide was distilled from the filtrate (0.47 g, 37% vs. 41% GC yield).

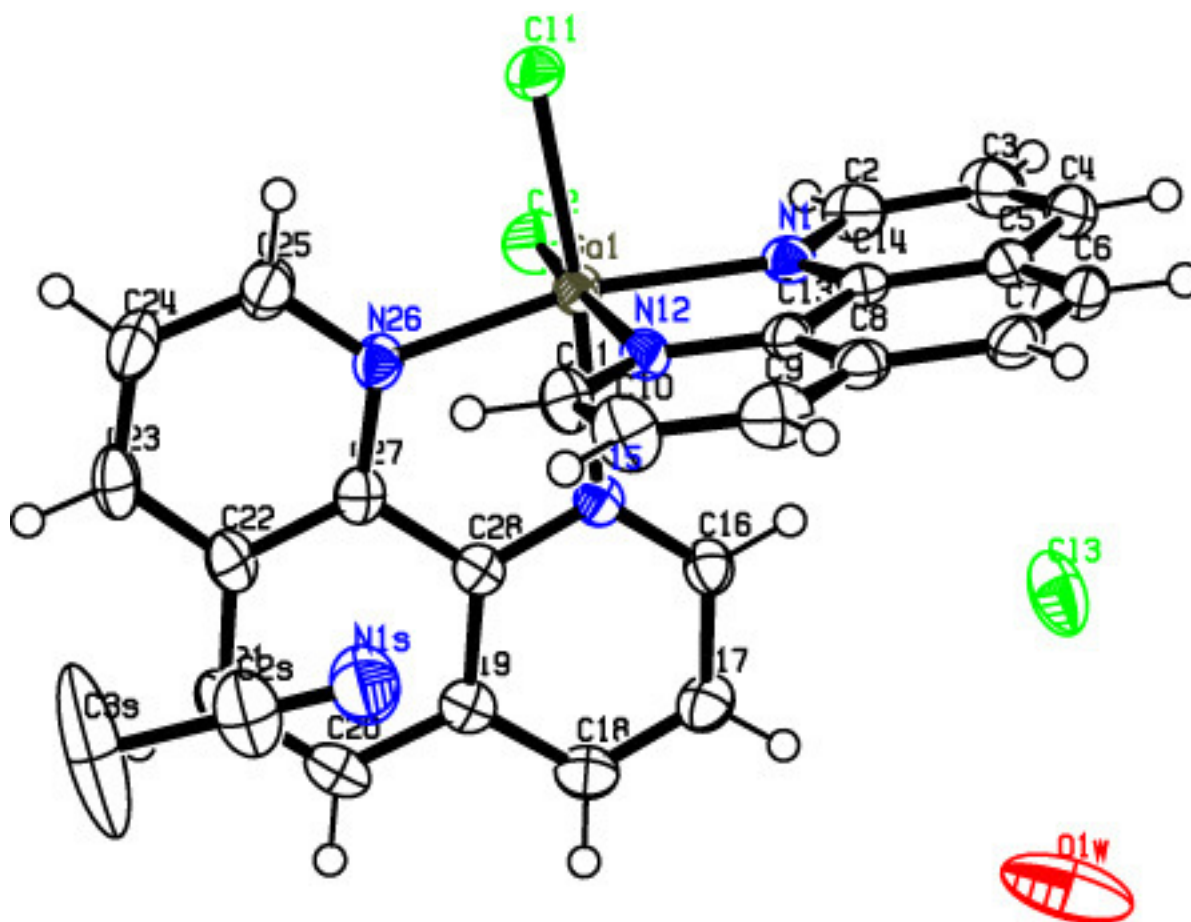


Figure S1. ORTEP representation of $[\text{Ga}(\text{phen})_2\text{Cl}_2]\text{Cl}\cdot 0.5\text{MeCN}\cdot \text{H}_2\text{O}$ showing all assigned atoms. All thermal ellipsoids are drawn at 50% probability. The outer-sphere MeCN molecule (defined by atoms C3s, C2s, and N1s) resides on a mirror plane, accounting for its half occupancy. The positions of the hydrogen atoms on the MeCN and the H_2O molecules could not be assigned with certainty.

Table S1. Selected crystallographic data for [Ga(phen)₂Cl₂]Cl.

Parameter	[Ga(phen) ₂ Cl ₂]Cl•0.5MeCN•H ₂ O
Formula	C ₅₀ H ₃₉ Cl ₆ Ga ₂ N ₉ O ₂
MW	1150.04
Crystal system	Orthorhombic
Space group	<i>P</i> _{bcn} (#60)
a (Å)	12.7377(11)
b (Å)	23.275(2)
c (Å)	16.5439(15)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å ³)	4904.8(8)
Z	4
Cryst color	Yellow
T (K)	183
Reflns collected	47811
Unique reflns	4661
R1 (F, I > 2σ(I))	0.0476
wR2 (F ² , all data)	0.121

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Table S2. Bond lengths (Å) and bond angles (°) for [Ga(phen)₂Cl₂]⁺.

Bond Length		Angle	
Ga-N(1)	2.085(2)	N(1)-Ga-Cl(1)	94.19(6)
Ga-N(12)	2.127(2)	N(1)-Ga-Cl(2)	95.09(7)
Ga-N(15)	2.134(2)	N(12)-Ga-Cl(1)	88.16(6)
Ga-N(26)	2.084(2)	N(12)-Ga-Cl(2)	171.58(6)
Ga-Cl(1)	2.2849(7)	N(15)-Ga-N(26)	78.57(9)
Ga-Cl(2)	2.2642(8)	N(15)-Ga-Cl(1)	169.26(6)
Angle		N(15)-Ga-Cl(2)	90.47(6)
N(1)-Ga-N(12)	78.73(8)	N(26)-Ga-Cl(1)	94.32(7)
N(1)-Ga-N(15)	91.51(8)	N(26)-Ga-Cl(2)	93.61(7)
N(1)-Ga-N(26)	166.86(9)	Cl(1)-Ga-Cl(2)	98.07(3)

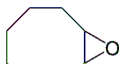
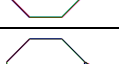
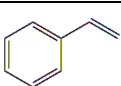
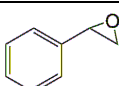
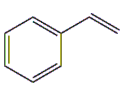
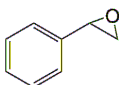
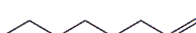
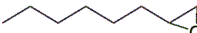
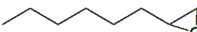
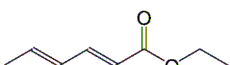
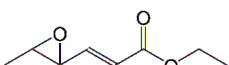
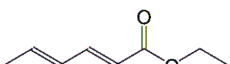
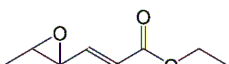
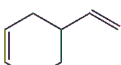
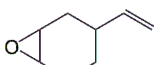
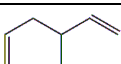
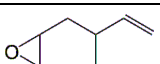
The Ga(III)-N bond distances and the L-Ga(III)-L bond angles are similar to those reported for [Ga(phen)₂Br₂]⁺.⁵ The major difference between the two structures is that the bonds between the Ga(III) and the nitrogen atoms on the 10-positions of the phenanthroline ligands are slightly longer in the chloride structure, averaging 2.13 Å as opposed to the 2.10 Å average for the bromide structure.

Table S3. Summary of ICP-OES Analysis.

Analyte	Blank Sample Conc. [ppm]	28 ppm [Ga(phen) ₂ Cl ₂]Cl [ppm]	122 ppm [Ga(phen) ₂ Cl ₂]Cl [ppm]
Ag	<0.002 ^a	<0.001	<0.001
Al	<0.019	<0.030	<0.040
As	<0.010	<0.003	<0.000
B	0.013	0.579	0.653
Ba	<0.001	<0.000	0.001
Ca	0.265	0.402	0.457
Cd	<0.000	<0.000	<0.000
Co	<0.000	<0.001	<0.002
Cr	<0.001	<0.002	<0.001
Cu	<0.000	<0.002	<0.000
Fe	0.041	0.033	0.034
K	4.658	2.697	1.640
Mg	0.143	0.175	0.182
Mn	<0.009	<0.008	0.014^b
Mo	0.029	0.014	<0.004
Na	3.382	3.844	3.613
Ni	<0.002	<0.012	<0.007
P	<0.037	<0.029	<0.027
Pb	<0.001	<0.001	<0.005
S	0.895	0.975	0.882
Se	0.067	0.069	0.061
Si	0.032	0.268	0.265
Ti	0.004	<0.002	<0.001
Zn	0.007	0.125	0.049
Zr	<0.015	<0.008	<0.003

^aThe “<” means the given value is below the limit of accurate detection for that analyte. ^bCorresponds to a 0.01% impurity in the 122 ppm sample.

Table S4. Yields of Epoxide Products (%) in Control Reactions.

Substrate	Product	Catalyst	2 PAA _C	2 PAA _R
		None	2	4
		5.0 mM GaCl ₃	3	4
		0.1 mM [Mn(phen) ₂ Cl ₂]	13 (±3)	14 (±2)
		None	12 (±3)	15 (±3)
		5.0 mM GaCl ₃	12 (±3)	16 (±3)
		0.1 mM [Mn(phen) ₂ Cl ₂]	22 (±3)	26 (±4)
		None	0	0
		5.0 mM GaCl ₃	0	0.3
		None	0	0
		5.0 mM GaCl ₃	1	2
		0.1 mM [Mn(phen) ₂ Cl ₂]	10 (±3)	13 (±4)
		None	0	0
		5.0 mM GaCl ₃	0	0
		None	3	7
		5.0 mM GaCl ₃	4	7

The conditions are identical to those described for the reactions in Table 1, with the exceptions of the identity and concentration of the catalyst. For the above reactions, the ratio of alkene/PAA was 1:2 when 2 equiv. of PAA were used and 1:1 when 1 equiv. of terminal oxidant was added, with the concentration of alkene set at 500 mM. All reactions were run in MeCN at 0 °C under N₂. The yields, defined here as the percentage of alkene converted to the epoxide, were measured at 1 h through a comparison of the GC integration of the epoxide peak to that of an internal standard, 1,2-dichlorobenzene. No other organic products were observed in the above reactions.

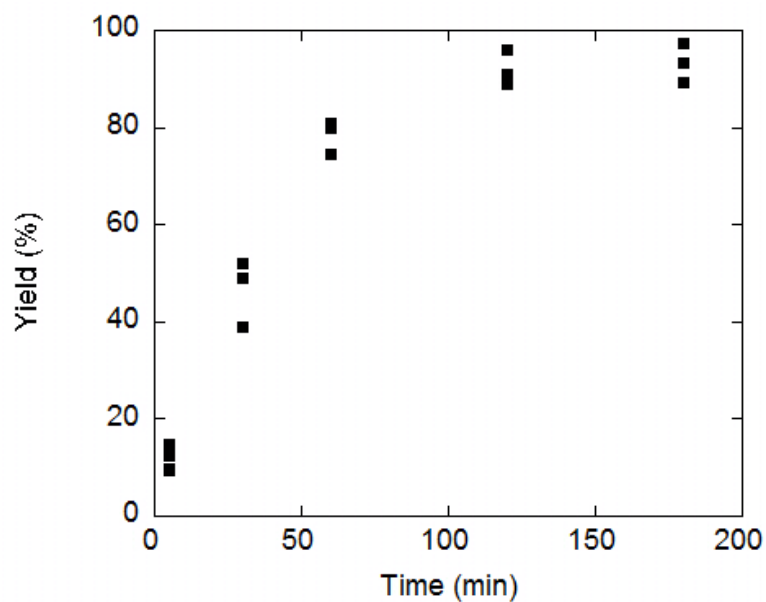


Figure S2. The yield of cyclooctene oxidation by PAA_R as a function of time. The reaction conditions are identical to those listed under Table 1 in the manuscript (0 °C, MeCN, 5.0 mM [Ga(phen)₂Cl₂]Cl, 500 mM cyclooctene, 1000 mM PAA_R). The plot shows the overlaid results from three independent reactions.

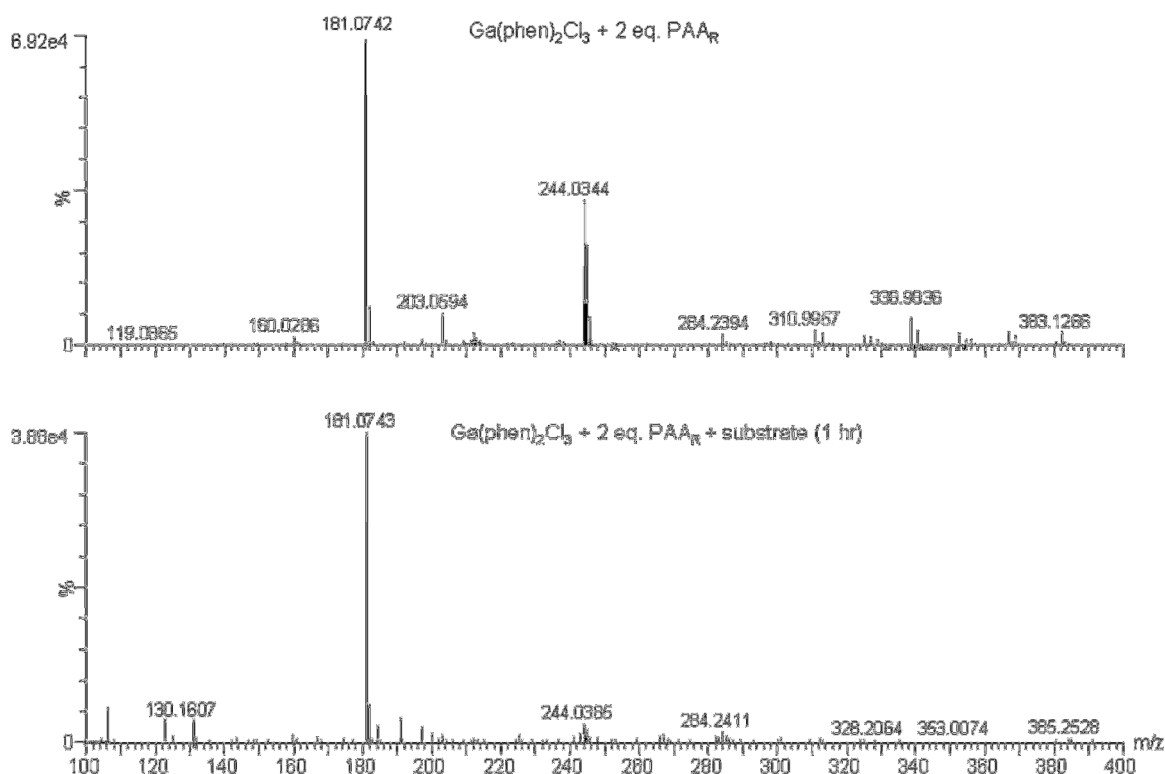


Figure S3. Mass spectrometric analysis of the reaction between cyclooctene and two equiv. of PAA_R at t = 5 s (top) and t = 60 min (bottom). The reaction conditions are identical to those listed under Table 1 in the manuscript (0 °C, MeCN, 5.0 mM [Ga(phen)₂Cl₂]Cl, 500 mM cyclooctene, 1000 mM PAA_R). The m/z feature at 244.0344 was assigned to [Ga(phen)₂(CH₃CO₂)²⁺], indicating that the chlorides are displaced almost instantaneously by the acetic acid in solution. At t = 60 min, this feature has almost completely disappeared; the major feature of this spectrum has m/z = 181.0743, which corresponds to protonated phen. Since the GaCl₃ salt by itself is unable to catalyze significant alkene epoxidation (Table S3), we propose that the increased solution acidity that results from the reduction of peracetic acid to acetic acid promotes the dissociation of the phen ligands from the Ga(III), halting the catalytic activity.

Summary of Alkene Epoxidation with a Lower Loading of [Ga(phen)₂Cl₂]Cl

The ability of PAA_R to oxidize cyclohexene was tested with a 0.1% loading of the [Ga(phen)₂Cl₂]Cl catalyst. The initial concentrations of the alkene, terminal oxidant, and Ga(III) were 500 mM, 1000 mM, and 0.50 mM respectively; the other reaction conditions were identical to those of the other reactions reported in this manuscript. 98% of the cyclohexene was oxidized at 1 h. The following products were identified: 3-cyclohexenol (39% individual yield), 1,2-cyclohexanediol (51% individual yield), cyclohexene oxide (8% individual yield).

The reaction between cyclohexene oxide and [Ga(phen)₂Cl₂]Cl did not yield any ring-opened products. The reaction between cyclohexene oxide and PAA_R did not result in any decomposition of the epoxide. These results suggest that a new Ga(III) oxidant is forming with the lower catalytic loading. We speculate that this new oxidant is responsible for the allylic oxidation and the dihydroxylation observed with the 0.1% loading.

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