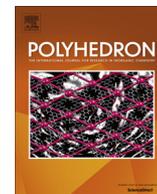




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## Expanding the scope of gallium-catalyzed olefin epoxidation

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## ABSTRACT

The broader use of Ga(III) complexes in the catalysis of olefin epoxidation was explored with a variety of studies. Two Ga(III) complexes with N-donor ligands were found to catalyze olefin epoxidation by peracetic acid in water. The stability of the catalyst more strongly influences the observed reactivity in water than in acetonitrile. Analysis of olefin epoxidation in buffered aqueous solutions indicates that either acidic or basic conditions are necessary for catalysis. The functional group tolerance was assessed using a variety of organic substrates. Alcohols, ketones, and alkylhalides survive the reaction conditions. Other common terminal oxidants were tested as possible replacements for peracetic acid but were not found to benefit from the presence of a Ga(III)-containing catalyst.

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## 1. Introduction

Much effort has been devoted to developing chemical processes capable of operating in water instead of an organic solvent [1,2]. The use of water as a solvent can potentially minimize the wastes generated by a reaction as well as its cost. Another key issue in reaction development is chemical selectivity. An ideal reaction will target a single type of chemical functionality on a substrate while leaving the remainder of the molecule unmodified. Improving the chemical selectivity also reduces waste by eliminating the need for additional steps to install and remove protecting groups and by minimizing the amounts of generated side-products.

Most reported homogeneous catalysts for olefin epoxidation are studied in organic solvents, such as acetonitrile (MeCN) [3]. The metal catalysts used in these studies generally are either unstable, insoluble, or otherwise non-functional in water [4,5]. Most reports of metal-catalyzed olefin epoxidation in solvent systems with high concentrations of water rely on simple salts [6,7]. In these systems, the structure of the catalytic species is ill-defined, with mixtures of oligonuclear complexes being implicated in some cases [6]. Furthermore, additives have been found to influence the reactivity strongly, possibly by significantly altering the composition of the catalyst [6,7]. A similar ambiguity with respect to the structure of the relevant catalyst was identified in a recent system that used a polyoxomolybdate “nanoball” to catalyze the epoxidation of olefins in water [8]. The regio- or stereoselective oxidation of alkenes is simply not feasible in water with these systems, given the possible agency of multiple oxidants and/or the lack of a ligand

capable of directing the catalyzed oxidation toward a specific product. Water-soluble iron complexes with porphyrin derivatives have been used to catalyze the asymmetric epoxidation of styrene derivatives in mixtures of water and methanol, but the activity is negligible in pure water [4]. A manganese-containing analog with the same porphyrin derivative has higher activity but produces epoxides with relatively low enantiomeric excesses [9]. The development of “green” olefin epoxidation reactions therefore remains a fertile area for exploration and improvement.

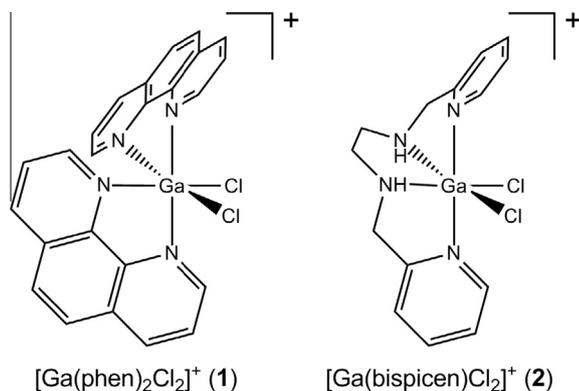
The functional group tolerance of olefin epoxidation can likewise be improved. Many first-row transition metal catalysts for olefin epoxidation are also capable of promoting allylic C–H activation and produce alcohols and ketones in addition to the target epoxides [9–13]. In rare circumstances, symmetric dihydroxylation is observed [14,15]. Other alkene epoxidation reactions can oxidize alcohols or amines in addition to C–C double bonds [16].

Recent work in our laboratory explored the use of gallium(III) complexes with  $N_4Cl_2$  inner-spheres as catalysts for olefin epoxidation in MeCN (Scheme 1) [17–20]. In this chemistry, the activity was correlated to the electronic character of the ligand, with the most electron-poor ligands providing the best short-term activity [18]. The more highly chelating ligands better stabilize the  $[GaN_4]^{3+}$  cores seemingly needed for catalysis. Although  $[Ga(phen)_2Cl_2]Cl$  (**1**) led to greater yields of cyclohexene oxide from cyclohexene than  $[Ga(bispiden)Cl_2]Cl$  (**2**) at 1 h, the two compounds have approximately equal activity when the oxidation reactions are allowed to proceed for 3 h [18]. At 1% mol loadings, both **1** and **2** are selective for the epoxide and do not promote C–H activation. At lower loadings, allylic C–H oxidation is observed for **1** but not **2**.

The Ga(III) complexes displayed excellent stability and solubility in water, with even the ethylenediamine complex  $[Ga(en)_2Cl_2]$

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Scheme 1.

Cl showing no sign of either ligand dissociation or speciation to  $[\text{Ga}(\text{en})_3]^{3+}$  and  $[\text{Ga}(\text{en})\text{Cl}_n]^{3-n}$  species in pure  $\text{D}_2\text{O}$  [18]. These properties encouraged us to assess the catalytic capabilities of **1** and **2** in aqueous solutions in the present work. We further investigated the functional group tolerance of **2**. Lastly, we performed a more systematic analysis of alternative terminal oxidants.

## 2. Materials and methods

### 2.1. Materials

Except where noted otherwise, chemicals were purchased from Sigma–Aldrich and used as received. Anhydrous acetonitrile (MeCN) was purchased from Acros Organics and stored in a glovebox free of moisture and oxygen. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 50% wt) was bought from Fisher. Iodosobenzene was purchased from TCI. Dry nitrogen ( $\text{N}_2$ ) and oxygen ( $\text{O}_2$ ) were purchased from Airgas. Chloroform-*d* ( $\text{CDCl}_3$ ) and acetonitrile-*d*3 ( $\text{CD}_3\text{CN}$ ) were bought from Cambridge Isotopes. *N,N'*-Bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen),  $[\text{Ga}(\text{phen})_2\text{Cl}_2]\text{Cl}$  (**1**), and  $[\text{Ga}(\text{bispicen})\text{Cl}_2]\text{Cl}$  (**2**) were prepared as previously described [17,18,21]. The purities of all materials were confirmed by  $^1\text{H}$  nuclear magnetic resonance (NMR).

### 2.2. Preparation of custom-made peracetic acid ( $\text{PA}_R$ )

A more basic grade of peracetic acid ( $\text{PA}_R$ ) that lacks the sulfuric acid impurity found in commercially available sources of PA was prepared through a modified version of a reported procedure [17,22]. At room temperature, 17 g of 50%  $\text{H}_2\text{O}_2$  (0.25 mol) was slowly added to glacial acetic acid (150 g, 2.5 mol). After 5 min, 5.0 g of Amberlite IR-120 was added to the mixture and stirred for 24 h. The solution was subsequently filtered to remove the resin. The formation of PA was determined by  $^{13}\text{C}$  NMR, and its concentration was determined by comparing the intensities of the PA and acetic acid resonance peaks. The solution was stored at  $-20^\circ\text{C}$  when not in use. The content of PA was determined to be 6.6% (molar) by  $^{13}\text{C}$  NMR analysis.

**Caution:** Peracids and mixtures of peroxides and organic solvents can potentially explode and should be handled with care. The dangers can be minimized by using small amounts of these materials, using proper protective equipment such as a blast shield, and working at lower temperatures.

### 2.3. Instrumentation

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on either a 400 MHz or a 250 MHz AV Bruker NMR spectrometer at 295 K. Fischer Scientific

AB15 and Thermo Scientific Orion 3 Star pH meters were used to prepare and calibrate the described buffered aqueous solutions. A Thermo Scientific Trace GC Ultra Gas Chromatograph and Thermo Scientific TR-1 and TG-WAXMS columns were used for gas chromatography (GC). High-resolution mass spectrometry (HR-MS) data were collected at the Mass Spectrometer Center at Auburn University on a Bruker microflex LT MALDI-TOF mass spectrometer via direct probe analysis operated in the positive ion mode.

### 2.4. Reactivity

For the reactions performed in unbuffered water, the initial concentrations of Ga(III) catalyst, alkene, and peracetic acid were 5.0 mM, 500 mM, and 500 mM, respectively. The reactions were stirred vigorously at 298 K for 60 min, at which point methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) was added to extract the organic products and remaining alkene starting material. The extracts were filtered through a plug of silica gel to remove the metal complex and most of the PA and then analyzed by GC. This work-up was found to have a negligible impact on the ratios of the organic products and remaining starting material [17]. All reported numbers are the averages of at least three independent reactions. All error values and bars represent one standard deviation.

### 2.5. Study of pH-dependence on olefin epoxidation

The concentrations of the buffer components in each solution used in the variable pH study were 0.5 M. Acetic acid was used to buffer the pH 4.0 and pH 5.0 solutions. Piperazine-*N,N'*-bis(2-ethanesulfonic acid) (PIPES) was used for solutions buffered to pH 6.0. 4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) was used to prepare the pH 7.0 and pH 8.0 solutions. Boric acid was used in the pH 9.0 and pH 10.0 solutions. For all reactions catalyzed by **1**, the initial concentrations of catalyst, cyclohexene, and PA were 0.75 mM, 75 mM, and 151 mM, respectively. Reactions catalyzed by **2** had initial catalyst, cyclohexene, and PA concentrations of 0.85 mM, 85 mM, and 169 mM respectively. The reactions were stirred vigorously at 298 K for 60 min, at which point the organic products were extracted using  $\text{CH}_2\text{Cl}_2$ . Extracts were filtered through a silica gel plug in order to remove residual Ga(III) catalyst and much of the PA. The samples were then immediately analyzed by GC; the immediate analysis was found to be critical for obtaining reproducible results.

## 3. Results and discussion

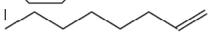
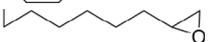
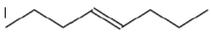
### 3.1. Catalysis of olefin epoxidation in water

Prior work from our laboratory found that Ga(III) complexes with  $\text{N}_4\text{Cl}_2$  coordination spheres catalyze the oxidation of alkenes to epoxides in MeCN [17–19]. The compounds  $[\text{Ga}(\text{phen})_2\text{Cl}_2]\text{Cl}$  (**1**) and  $[\text{Ga}(\text{bispicen})\text{Cl}_2]\text{Cl}$  (**2**) were selected as representative examples of Ga(III) complexes with bidentate and polydentate N-donor ligands. Each compound has been structurally characterized [17,18]. Complexes **1** and **2** were subsequently tested for their ability to accelerate the epoxidation of alkenes by peracetic acid (PA) in water. A less acidic grade of PA was used in order to facilitate comparison to previously studied alkene epoxidations in acetonitrile (MeCN) [17–19]. All reactions occurred under air at ambient temperature and pressure. Previous reactions in MeCN were run under either air or  $\text{N}_2$ , but the presence of  $\text{O}_2$  and atmospheric moisture did not impact the reactivity to a significant degree [19].

Complex **2** was found to be an effective catalyst for the epoxidation of electron-rich substrates by PA (Table 1), and the high selectivity for the epoxide product that was previously observed in

**Table 1**

Yields of aqueous alkene epoxidations catalyzed by  $[\text{Ga}(\text{phen})_2\text{Cl}_2]\text{Cl}$  (**1**) and  $[\text{Ga}(\text{bispicen})\text{Cl}_2]\text{Cl}$  (**2**).

Substrate	Product	Yield with <b>1</b> (%)	Yield with <b>2</b> (%)
		56 ( $\pm 5$ )	76 ( $\pm 5$ )
		1.5 ( $\pm 0.5$ )	3.1 ( $\pm 1.2$ )
			46 ( $\pm 3$ )
			40 ( $\pm 7$ )

Reaction conditions:  $\text{H}_2\text{O}$ , air, 298 K,  $[\text{Ga}(\text{III})]_0 = 5.0$  mM,  $[\text{alkene}]_0 = 500$  mM,  $[\text{PA}]_0 = 500$  mM. The yields were measured at 60 min by GC. All measurements are the averages of the yields of at least three separate experiments.

MeCN is maintained in  $\text{H}_2\text{O}$ . The four alkene substrates that were investigated were cleanly converted to epoxides; no other organic products were observed when the reactions were allowed to proceed for 1 h. The instability of PA in water would introduce errors into longer-term reactions [23], and we therefore elected not to study longer-term reactions. The uncatalyzed reaction proceeds in water but is slow without a catalyst. Without a Ga(III) complex present, the reaction between 170 mM PA and 85 mM cyclooctene yields a 54% yield of cyclooctene oxide at 24 h. As was observed in the MeCN chemistry, mixtures of **2** and PA do not efficiently oxidize terminal olefins, as evidenced by the poor yields of 1-octene oxide from 1-octene. More electron-rich alkenes, such as cyclooctene, are oxidized to greater extents. As has been observed in other systems, cyclooctene is more reactive than cyclohexene [5,8,10,17–19], likely due to its greater ring strain [24]. The substrate *trans*-4-octene can potentially be converted to a mixture of *cis*-4-octene oxide and *trans*-4-octene oxide if the oxygen atom is not transferred to the alkene in a concerted manner. That only the *trans*-4-octene oxide product is observed suggests that this does not occur and provides support for our previously calculated mechanism for Ga(III)-catalyzed olefin epoxidation [20].

The phen complex **1** was tested as a catalyst for the epoxidation of the most reactive substrate, cyclooctene, but the 56% yield of cyclooctene oxide is noticeably lower than the 76% yield measured for **2**. Even though **1** was considerably more effective than **2** at

catalyzing the conversion of 1-octene to 1-octene oxide in MeCN [17,18], the yield of epoxide from this substrate in  $\text{H}_2\text{O}$  was also lower for **1** than it is for **2**. Consequently, further substrates were not investigated for **1**.

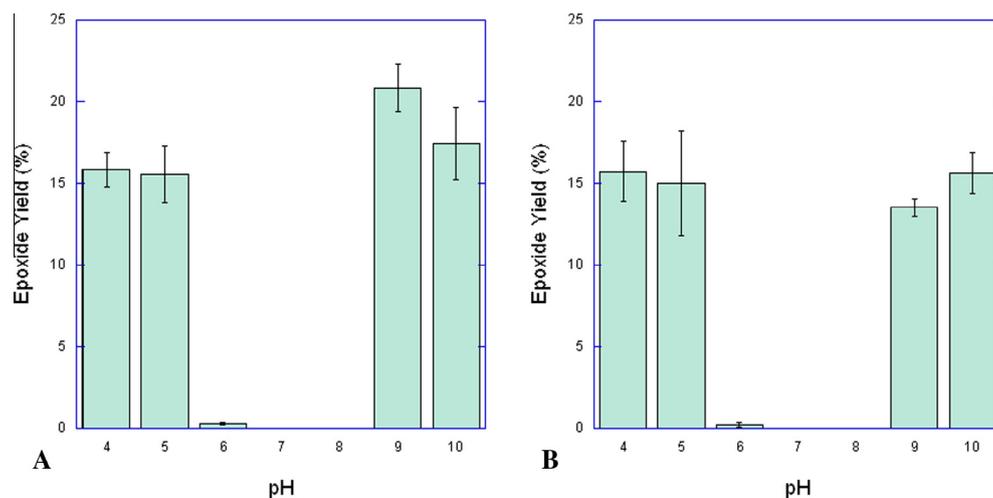
Complex **2** was previously documented to be less active than **1** over the course of 1 h when the alkene epoxidations were performed in MeCN [18]. Although the phen compound is initially more efficient at catalyzing these reactions, it loses its reactivity more quickly. When a more electron-rich substrate, such as cyclohexene, is oxidized, compound **2** becomes the superior catalyst when the reaction time is extended to 3 h. That compound **2** catalyzes the epoxidation of both cyclooctene and 1-octene more efficiently in  $\text{H}_2\text{O}$  over only 1 h suggests that the stability of the Ga(III) catalyst is a more important factor for olefin epoxidation in  $\text{H}_2\text{O}$  than it is in MeCN. The electronic character of the N-donor ligands, conversely, is seemingly less important in  $\text{H}_2\text{O}$  than it is in MeCN.

### 3.2. pH dependence

Previous reactivity studies with Ga(III)-containing catalysts have shown that the use of a less-acidic grade of PA gave improved epoxide yields relative to commercially available formulations containing residual sulfuric acid [17]. The effect of pH on the ability of **1** and **2** to catalyze the epoxidation of cyclohexene by PA was investigated using buffered solutions over the pH range 4–10 (Fig. 1). The reactions were performed with much lower concentrations of catalyst, alkene, and PA due to the need to maintain the desired pH. As a consequence, the yields of cyclohexene oxide are much lower than those of previous reactions in MeCN [17–19] and  $\text{H}_2\text{O}$  (Table 1). The yields of the control reactions are comparatively high but are noticeably lower than those for the Ga(III)-catalyzed reactions (12% at pH 4.0, 9% at pH 9.0 and 10.0).

Both **1** and **2** show negligible activity between pH 6.0 and pH 8.0 but function in both highly acidic and basic conditions (Fig. 1). As was seen with reactions in unbuffered water, no detectable organic side products were observed at any pH at 1 h. Unexpectedly, the reactivities are approximately the same for both acidic and basic solutions. Compound **2** may be slightly more active than **1** under basic conditions.

The greater catalysis at basic conditions may be attributed to the deprotonation of PA to peracetate; PA has a  $\text{pK}_a$  of 8.2. A prior computational analysis suggested that PA needs to coordinate to



**Fig. 1.** Yields of cyclohexene epoxidation reactions in aqueous solutions buffered to various pH values. (A) Reaction conditions:  $[\text{Ga}(\text{phen})_2\text{Cl}_2] = 0.75$  mM,  $[\text{alkene}]_0 = 75.0$  mM,  $[\text{PA}]_0 = 151$  mM. (B)  $[\text{Ga}(\text{bispicen})\text{Cl}_2]\text{Cl} = 0.85$  mM,  $[\text{alkene}]_0 = 85$  mM,  $[\text{PA}]_0 = 169$  mM. For both series of experiments, the reactions were performed under air at 298 K. The yields were measured by GC at 60 min. All measurements are the yields of at least three separate measurements.

the Ga(III) center in order to facilitate the oxygen atom transfer to the alkene [20]. Anionic ligands are generally more effective at competing for vacant coordination sites on cationic metal centers [25], and the deprotonation of PA to peracetate should facilitate the binding of the terminal oxidant to the Ga(III). The heightened activity at acidic pH values, conversely, may be a consequence of keeping the acetic acid ( $pK_a = 4.8$ ) administered with the PA in its protonated form, which would have a lesser affinity for Ga(III). Between pH 6 and pH 8, the acetic acid would be predominantly acetate, which would out-compete PA for the coordination sites on the Ga(III) center.

### 3.3. Functional group tolerance

Transition metal catalysts for olefin epoxidation often enable reactions with other functional groups. The functional group tolerance of reactions using the Ga(III)-containing catalysts had not yet been fully explored. Prior work suggested that the mixtures of Ga(III) complexes and PA are not capable of rapidly opening epoxides since the epoxides are the only observed organic products for the first 5 h [18].

Various derivatized cyclohexanes were tested as substrates in MeCN using **2** as the catalyst. The initial concentrations of **2**, PA<sub>R</sub>, and substrate were 5.0 mM, 500 mM and 500 mM, respectively. Cyclohexanol, cyclohexanone, and chlorocyclohexane each remain unchanged. When the reactions are provided the standard 60 min, no organic compounds aside from unreacted starting material are observed. 1,2-Diaminocyclohexane was also explored as a substrate, but we were unable to isolate it and its putative products cleanly from the reaction mixtures. Cyclohexanecarboxyaldehyde reacts with PA to yield a complex mixture of organic products; the addition of **2** does not noticeably alter this reactivity. From these studies, we can predict that alkene substrates with amine and/or aldehyde groups will not react cleanly with mixtures of PA and Ga(III) complexes.

### 3.4. Alternative terminal oxidants

Even if the  $[GaN_4]^{3+}$  cores of the catalysts were to be further stabilized, the instability of PA in H<sub>2</sub>O would still limit the reaction times to 1 h [23]. Finding an alternative terminal oxidant to PA is therefore essential for obtaining further advances in aqueous gallium-catalyzed olefin epoxidation. Heretofore, only O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and two grades of PA were tried as terminal oxidants for Ga(III)-catalyzed olefin epoxidation [17,18]. Other common oxygen transfer agents include iodosobenzene (PhIO), oxone, and *meta*-chloroperbenzoic acid (MCPBA). These terminal oxidants were tested in primarily organic solvents using complex **2** as the catalyst

**Table 2**  
Yields of cyclooctene and 1-octene epoxidation by other terminal oxidants with and without **2**.

Terminal oxidant	Cyclooctene (%)	1-Octene (%)
O <sub>2</sub>	0/0	0/0
H <sub>2</sub> O <sub>2</sub>	0/0 <sup>a</sup>	0/0
PhIO <sup>b</sup>	0/0	0/0
Oxone <sup>c</sup>	11/8	0/0
MCPBA	100/100	17/16

Reaction conditions: MeCN, air, 298 K,  $[Ga(III)]_0 = 1.0$  mM/  $0.0$  mM,  $[alkene]_0 = 100$  mM,  $[terminal\ oxidant]_0 = 200$  mM. The yields were measured at 30 min by GC. All measurements are the averages of the yields of at least three separate experiments. The yields of the Ga(III)-catalyzed reactions are listed first.

<sup>a</sup> Reaction also attempted in H<sub>2</sub>O, yielding identical results.

<sup>b</sup> Reactions with both alkenes occurred in MeOH.

<sup>c</sup> Reaction performed in 3:1 H<sub>2</sub>O/MeCN.  $[Ga(III)]_0 = 0.5$  mM,  $[alkene]_0 = 50$  mM,  $[oxone]_0 = 100$  mM.

(Table 2). PhIO and oxone were completely ineffective in pure MeCN due to their poor solubility. Switching to alternative solvent systems did not substantially improve the activity, and poor yields of epoxides are observed in both the presence and absence of **2**. The reaction between cyclooctene and MCPBA, conversely, proceeds quantitatively without a catalyst. The reaction between 1-octene and MCPBA only proceeds to ~15% without a catalyst, but the presence of **2** did not substantially improve this number. Since the addition of **2** failed to improve the reactivity in all cases, most of these terminal oxidants were not tried in reactions in H<sub>2</sub>O. H<sub>2</sub>O<sub>2</sub> was tested as a terminal oxidant for Ga(III)-catalyzed cyclooctene epoxidation in pH 4.0 H<sub>2</sub>O; as with the MeCN system, no epoxide was observed.

Previous attempts to analyze the mechanism of Ga(III)-catalyzed olefin epoxidation were largely limited to a computational study which predicted the agency of a Ga(III)-peracetate complex [20]. Although the Ga(III)-peracetate oxidant was calculated to be relatively stable, we were unable to observe this species experimentally. The large excesses of acetic acid present in all grades of PA would preclude the isolation of clean samples of peracetate intermediates. MCPBA is an attractive terminal oxidant for mechanistic studies since it is available in a form that is comparatively pure. The perbenzoic acid is the major component (~75%) in commercially available supplies of MCPBA, whereas PA is a minor component in both commercially available and custom-prepared solutions of this oxidant.

Regrettably, we were unable to observe a *meta*-chloroperbenzoate analog of the calculated Ga(III)-peracetate oxidant. Substrate-free reactions between MCPBA and **2** were monitored by <sup>1</sup>H NMR. The observed resonances correspond to the starting materials, and no evidence for a *meta*-chloroperbenzoate-Ga(III) adduct was observed. This result suggests that the failure of Ga(III) to improve the oxidation of 1-octene by MCPBA (Table 2) may be a consequence of the inability of this peracid to coordinate to the metal center. We speculate that MCPBA is too bulky to coordinate to the Ga(III)-bispicen complex. The noted inability of H<sub>2</sub>O<sub>2</sub> to coordinate to Ga(III) may partly explain why this molecule is also ineffective as a terminal oxidant [26].

## 4. Conclusions

Two previously discovered Ga(III) complexes with N-donor ligands were found to be capable catalysts for olefin epoxidation in water. The activity was better with the more highly chelating but more electron-rich bispicen ligand, suggesting that the stability of the catalyst is more important than its electronic character in aqueous olefin epoxidation. The activity is poor around neutral pH but improves substantially under both basic and acidic conditions. Although a number of functional groups survive the reaction conditions in MeCN, aldehydes react, and the stability of amines could not be readily assessed. Lastly, we did not locate a common terminal oxidant that could benefit from the presence of Ga(III) and substitute for PA. We hypothesize that these other terminal oxidants may be unable to coordinate to the Ga(III) center.

## Acknowledgement

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