Inorganic Chemistry

Article

pubs.acs.org/IC

Catalysis of Alkene Epoxidation by a Series of Gallium(III) Complexes with Neutral N-Donor Ligands

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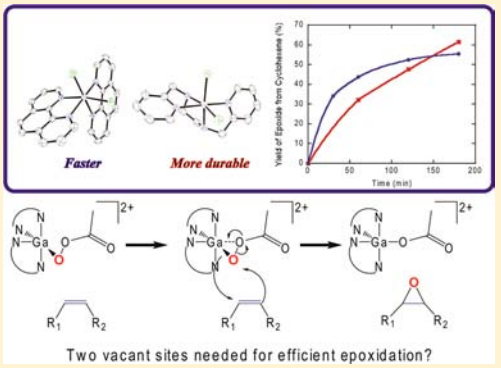
Supporting Information

ABSTRACT: Six gallium(III) complexes with N-donor ligands were synthesized to study the mechanism of Ga^{III}-catalyzed olefin epoxidation. These include 2:1 ligand/metal complexes with the bidentate ligands ethylenediamine, 5-nitro-1,10-phenanthroline, and 5-amino-1,10-phenanthroline, as well as 1:1 ligand/metal complexes with the tetradentate *N,N′*-bis(2-pyridylmethyl)-1,2-ethanediamine, the potentially pentadentate *N,N,N′*-tris(2-pyridylmethyl)-1,2-ethanediamine, and the potentially hexadentate *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine. In solution, each of the three pyridylamine ligands appears to coordinate to the Ga^{III} through four donor atoms. The six complexes were tested for their ability to catalyze the epoxidation of alkenes by peracetic acid. Although the complexes with relatively electron-poor phenanthroline derivatives display faster initial reactivity, the gallium(III) complexes with the polydentate pyridylamine ligands appear to be more robust, with less noticeable decreases in their catalytic activity over time. The more highly chelating trispicen and tpen are associated with markedly decreased activity.



INTRODUCTION

The coordination chemistry of gallium has been investigated to serve a number of applications, including the development of volatile precursors for gallium oxide, nitride, selenide, arsenide, and sulfide layers in chemical vapor deposition[1−7] as well as ^{68}Ga-containing radiopharmaceuticals suitable for positron emission tomography.[8−11] Gallium(III) compounds have also garnered attention for their ability to act as homogeneous Lewis acid catalysts.[7,12−16] One trend observed in the aforementioned catalysis is that cationic gallium(III) species tend to promote faster and more extensive reactivity.

Recently, our group reported that the previously known compound $[Ga(phen)_2Cl_2]Cl$ (phen = 1,10-phenanthroline)[17−19] could catalyze the epoxidation of alkenes by peracetic acid.[20] This is a rare example of gallium accelerating an oxidation−reduction reaction[21−24] and, to the best of our knowledge, represents the first instance of a homogeneous Ga^{III} catalyst for olefin epoxidation. The reactivity proceeded more quickly and at a lower temperature than analogous reactions catalyzed by aluminum(III) complexes.[25−27] We attributed the activity of $[Ga(phen)_2Cl_2]^+$ to the presence of the neutral and relatively electron-poor phen ligands,[28−30] which appear to remain bound to the Ga^{III} during the catalysis.[20] Without these ligands, oxidation does not proceed; $GaCl_3$ by itself is not a competent catalyst. Neutral N-donor ligands do not commonly coordinate to Al^{III}, which instead prefers to ligate harder bases. These ligands' affinities for Ga^{III}, however, are considerably higher.[31] Although complexation of Ga^{III} to polydentate neutral N-donor ligands could result in enhanced catalytic activity for group 13 metals, this chemistry has never been systematically studied.

Here, we report the syntheses and characterizations of six gallium(III) complexes with neutral N-donor ligands (Scheme 1). The ligands were selected to interrogate the influences of ligand denticity and electronics on the catalytic activity. One noted shortcoming with the $[Ga(phen)_2Cl_2]^+$ system is that its catalysis essentially ends after approximately 1 h.[20] Replacing the two bidentate phen ligands with a single more highly coordinating molecule extends the lifetime of the catalysis and increases the optimum yield of the epoxides, although the activity decreases if the ligand has the capacity to bind in a penta- or hexadentate fashion. The more electron-poor ligands promote more extensive alkene epoxidation, with the best activity being associated with 5-nitro-1,10-phenanthroline (NO_2-phen).

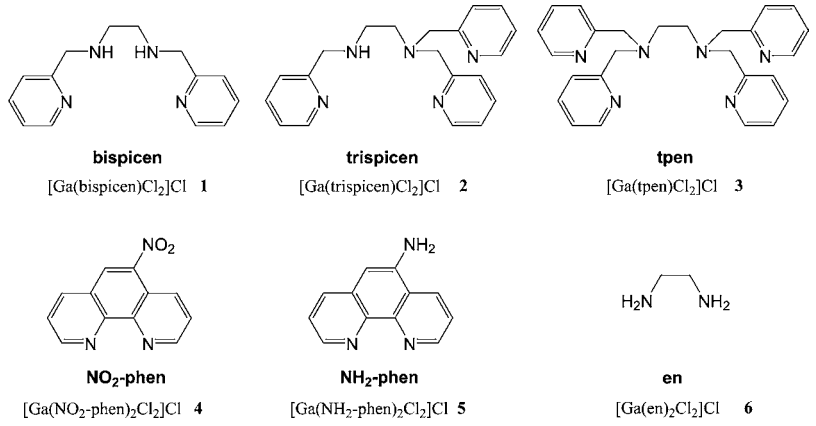
EXPERIMENTAL SECTION

Materials. Cyclooctene, cyclohexene, styrene, 1-octene, 4-vinylcyclohexene, 1,2-ethanediamine (en), 5-amino-1,10-phenanthroline (NH_2-phen), 5-nitro-1,10-phenanthroline (NO_2-phen), and gallium trichloride ($GaCl_3$) were purchased from Sigma-Aldrich and used as received. Methylene chloride (CH_2Cl_2) was bought from Macron Chemicals. Anhydrous acetonitrile (MeCN) and methanol (MeOH) were procured from Acros. Diethyl ether (ether) was obtained from J. T. Baker. Deuterated chloroform ($CDCl_3$), acetonitrile (CD_3CN), dimethyl sulfoxide (DMSO-d_6), water (D_2O), and methanol (CD_3OD) were purchased from Cambridge Isotopes.

Received: December 13, 2012
Published: April 26, 2013

   dx.doi.org/10.1021/ic400570h | *Inorg. Chem.* 2013, 52, 5814−5823

Scheme 1



Peracetic acid (PAA_R) was prepared through a previously described procedure that uses an acidic resin as the catalyst in place of the commercially used sulfuric acid.[32] 50% H_2O_2 (17 g, 0.25 mol) was slowly added to 150 g of glacial acetic acid (2.5 mol) in a room temperature (RT) polyethylene bottle. After the addition was complete, 5.0 g of Amberlite IR-120 was added, and the reaction mixture was stirred behind a blast shield for 24 h at RT. After that time, the solution was filtered to remove the resin and yield the 7.5 wt % PAA_R solution used for the reactivity experiments. The solution was stored in a freezer when not in use. The concentration of PAA_R was determined by comparing the intensities of the ^{13}C NMR resonances of CH_3CO_3H and CH_3CO_2H.

Caution! *Peracids and their mixtures with organic solvents are potentially explosive and should be handled judiciously. The potential hazards can be minimized by using minimal amounts of these materials at lower temperatures and by using proper protective equipment, such as blast shields.*

Instrumentation. All ^1H NMR spectra were acquired on either a 250, 400, or 600 MHz AV Bruker NMR spectrometer at 294 K. All resonances were referenced to internal standards. Atlantic Microlabs (Norcross, GA) performed all elemental analyses. A Shimadzu IR Prestige-21 FT-IR spectrophotometer was used for the described IR spectroscopy. Gas chromatography (GC) data were obtained using a ThermoScientific Trace GC Ultra spectrometer with a flame ionization detector. High-resolution mass spectrometry (HR-MS) data were collected at the Mass Spectrometer Center at Auburn University using a Bruker microflex LT MALDI-TOF mass spectrometer via direct probe analysis operated in the positive-ion mode.

X-ray Crystallography. X-ray diffraction data were acquired using a Bruker SMART APEX CCD X-ray diffractometer and Mo Kα radiation. Crystalline samples were mounted in Paratone-N oil on glass fibers. The program *SMART* (version 5.624) was used for the preliminary determination of cell constants and data collection control. Determination of the integrated intensities and global cell refinement was performed with the Bruker *SAINT* software package using a narrow-frame integration algorithm. The program suite *SHELXTL* (version 5.1) was used for space group determination, structure solution, and refinement.[33] Refinement was performed against F^2 by weighted full-matrix least squares, and empirical absorption corrections (*SADABS*) were applied.[34] H atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Crystallographic data are provided in both Table 1 and the Supporting Information.

Syntheses. The ligands *N,N′*-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen), *N,N,N′*-tris(2-pyridylmethyl)-1,2-ethanediamine (trispicen), and *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine (tpen) were prepared as described previously.[35−37] The identities and purities of these compounds were confirmed by NMR.

*cis-Dichloro[N,N′-bis(2-pyridylmethyl)-1,2-ethanediamine]-gallium(III) Chloride (**1**).* $GaCl_3$ (0.164 g, 0.931 mmol) and bispicen (0.227 g, 0.937 mmol) were dissolved in 10 mL of CH_2Cl_2 and stirred at RT under N_2. After 2 h, ether was added to the cloudy solution, precipitating 0.360 g of the product as a white powder (82%). Colorless crystals were grown from the slow diffusion of ether into a saturated solution of the complex in MeOH. ^1H NMR (CD_3OD, 400 MHz): δ 9.41 (2H, d, J = 5.2 Hz), 8.24 (2H, t, J = 7.6 Hz), 7.77 (2H, t, J = 6.4 Hz), 7.71 (2H, d, J = 7.6 Hz), 4.88 (2H, d, J = 17.2 Hz), 4.18 (2H, d, J = 17.2 Hz), 2.69 (2H, d, J = 9.2 Hz), 2.53 (2H, d, J = 9.2 Hz). ^{13}C NMR (CD_3OD, 150 MHz): δ 153.7, 147.0, 143.0, 125.8, 124.6, 51.5, 47.0. IR (KBr, cm^{-1}): 3416 (s), 3389 (s), 3100 (s), 3040 (s), 2991 (s), 2914 (s), 2850 (s), 2482 (w), 2395 (w), 2270 (w), 2166 (w), 1665 (w), 1612 (s), 1578 (m), 1481 (s), 1440 (s), 1363 (s), 1300 (s) 1262 (m), 1226 (s), 1160 (m), 1099 (s), 1048 (s), 1033 (s), 980 (m), 906 (w), 849 (m), 821 (w), 777 (s), 723 (m), 649 (m), 567 (m), 506 (m), 480 (m), 425 (m). Elem anal. Calcd for $C_{14}H_{18}N_4GaCl_3{\cdot}H_2O$: C, 38.53; H, 4.62; N, 12.84. Found: C, 38.32; H, 4.53; N, 12.51.

*Dichloro[N,N,N′-tris(2-pyridylmethyl)-1,2-ethanediamine]-gallium(III) Chloride (**2**).* $GaCl_3$ (0.189 g, 1.074 mmol) and trispicen (0.359 g, 1.079 mmol) were dissolved in 10 mL of CH_2Cl_2 (2 mL). The resultant solution was stirred for 2 h at RT under N_2. The addition of ether deposited the product as a pale-yellow powder (0.356 g, 65%). ^1H NMR (CD_3OD, 400 MHz): δ 9.40 (1H, d, J = 4.4 Hz),

Table 1. Select Crystallographic Data for [Ga(bispicen)Cl_2]Cl (1) and [Ga(trispicen)Cl](GaCl$_4$)(Cl) (7)

parameter	[Ga(bispicen)Cl_2]Cl·3H_2O	[Ga(trispicen)Cl](GaCl$_4$)(Cl)·MeCN
formula	$C_{14}H_{24}Cl_3GaN_4O_3$	$Ga_{22}H_{26}Cl_6Ga_2N_6$
MW	472.45	727.64
cryst syst	monoclinic	triclinic
space group	$P2_1/c$(No. 14)	$P\bar{1}$ (No. 2)
a (Å)	13.7249(5)	9.2381(7)
b (Å)	7.3885(3)	12.0453(9)
c (Å)	20.7913(8)	14.7889(11)
α (deg)	90	88.9220(10)
β (deg)	105.600(1)	79.7160(10)
γ (deg)	90	69.0670(10)
V (Å^3)	2030.70(14)	1510.5(2)
Z	4	2
cryst color	colorless	colorless
T (K)	296	296
reflns collected	63556	59468
unique reflns	4194	7113
R1(F) [$I > 2\sigma(I)$][a]	0.0301	0.0293
wR2(F^2) (all data)[a]	0.0828	0.0708

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

dx.doi.org/10.1021/ic400570h | *Inorg. Chem.* 2013, 52, 5814−5823

9.17 (1H, d, J = 4.4 Hz), 8.45 (1H, d, J = 5.2 Hz), 8.26 (2H, m), 7.96 (2H, m), 7.83 (2H, m), 7.61 (1H, d, J = 5.2 Hz), 7.55 (1H, t, J = 4.4 Hz), 7.16 (1H, d, J = 3.6 Hz), 4.56 (1H, d, J = 15.6 Hz), 4.49 (1H, d, J = 15.6 Hz), 4.08 (1H, d, J = 14.4 Hz), 3.58 (4H, m), 3.20 (1H, m), 2.93 (1H, m), 2.84 (1H, m). ^{13}C NMR (CD_3OD, 150 MHz): δ 148.5, 147.9, 147.5, 146.0, 144.7, 144.6, 143.5, 128.8, 128.1, 127.9, 127.1, 126.3, 126.2, 124.7, 61.2, 61.1, 56.8, 53.1, 47.5. IR (KBr, cm^{-1}): 3487 (s), 3387 (s), 3334 (s), 3115 (s), 2850 (s), 2657 (s), 2476 (m), 2392 (m), 2271 (m), 2157 (m), 2034 (w), 1936 (w), 1882 (w), 1815 (w), 1747 (w), 1611 (s), 1478 (s), 1438 (s), 1363 (s), 1298 (s), 1230 (s), 1159 (s), 1107 (s), 1040 (s), 1031 (s), 977 (s), 910 (w), 849 (m), 777 (s), 720 (m), 646 (m), 565 (m), 492 (m), 424 (m). Elem anal. Calcd for $C_{20}H_{23}N_5GaCl_3$: C, 47.15; H, 4.55; N, 13.75. Found: C, 47.44; H, 4.45; N, 13.36.

*Dichloro[N,N,N′,N′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine]gallium(III) Chloride (**3**).* $GaCl_3$ (0.134 g, 0.761 mmol) and tpen (0.324 g, 0.763 mmol) were dissolved in 10 mL of CH_2Cl_2 under N_2. The resultant solution was stirred for 2 h at RT, after which excess ether was added to precipitate 0.388 g of the product as a white powder (85%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 9.61 (2H, d, J = 5.4 Hz), 8.64 (2H, d, J = 4.8 Hz), 8.19 (2H, t, J = 8.2 Hz), 7.85 (2H, m), 7.74 (2H, t, J = 6.8 Hz), 7.60 (4H, m), 7.39 (2H, m), 5.09 (2H, d, J = 16.2 Hz), 4.65 (2H, d, J = 13.2 Hz), 4.20 (2H, d, J = 11.4 Hz), 3.60 (4H, m), 3.00 (2H, m). ^{1}H NMR (CD_3CN, 400 MHz): δ 9.52 (2H, d, J = 5.2 Hz), 8.63 (2H, d, J = 5.6 Hz), 8.21 (2H, t, J = 8.0 Hz), 7.83 (2H, t, J = 5.6 Hz), 7.75 (2H, t, J = 6.4 Hz), 7.62 (4H, d, J = 7.6 Hz), 7.41 (2H, m), 4.93 (2H, d, J = 16.0 Hz), 4.56 (2H, d, J = 13.6 Hz), 3.97 (2H, d, J = 16.4 Hz), 3.61 (2H, d, J = 13.6 Hz), 3.48 (2H, d, J = 5.2 Hz), 3.27 (2H, d, J = 5.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.9, 151.5, 149.9, 147.0, 142.8, 137.5, 127.5, 126.6, 125.6, 124.2, 56.6, 56.4, 46.3. IR (KBr, cm^{-1}): 3045 (m), 3008 (s), 2945 (s), 2907 (s), 2863 (s), 2815 (s), 2800 (s), 2764 (s), 2695 (m), 2550 (w), 2300 (w), 1905 (w), 1859 (w), 1796 (w), 1662 (w), 1588 (s), 1572 (s), 1472 (s), 1433 (s), 1364 (s), 1345 (s), 1298 (s), 1245 (s), 1209 (m), 1170 (s), 1126 (s), 1085 (m), 1045 (m), 1016 (w), 989 (s), 902 (m), 864 (m), 839 (m), 786 (s), 765 (s), 732 (m), 687 (w), 662 (w), 617 (m), 593 (w), 546 (w), 470 (w). MS (ESI). Calcd for $[Ga(tpen)Cl_2]^+$: m/z 563.1008. Found: m/z 563.0988. Elem anal. Calcd for $C_{26}H_{28}N_6GaCl_3$: C, 51.99; H, 4.70; N, 13.99. Found: C, 51.70; H, 4.65; N, 14.00.

*Dichlorobis[5-nitro(1,10-phenanthroline)]gallium(III) Chloride (**4**).* $GaCl_3$ (0.169 g, 0.959 mmol) and NO_2-phen (0.437 g, 1.94 mmol) were combined in 10 mL of CH_2Cl_2 under N_2. After the solution was stirred for 2 h at RT, ether was added, precipitating 0.332 g of the product as a pale-yellow powder (51%). ^{1}H NMR (CD_3OD, 600 MHz): δ 10.35 (2H, m), 9.82 (1H, d, J = 12.0 Hz), 9.50 (1H, d, J = 8.4 Hz), 9.44 (1H, s), 9.33 (2H, m), 9.03 (1H, d, J = 8.4 Hz), 8.67 (2H, m), 8.06 (1H, d, J = 3.6 Hz), 8.02 (1H, d, J = 3.6 Hz), 7.86 (2H, m). ^{13}C NMR (CD_3OD, 150 MHz): δ 155.9, 153.4, 151.8, 149.6, 148.0, 147.2, 146.6, 146.3, 146.0, 144.6, 141.4, 140.0, 139.5, 139.0, 133.2, 131.1, 129.6, 129.3, 129.0, 128.4, 128.1, 127.1, 126.8, 124.9, 124.5. IR (KBr, cm^{-1}): 3422 (m), 3113 (w), 3071 (m), 3004 (w), 2970 (w), 2934 (w), 2871 (w), 2337 (w), 1970 (w), 1946 (w), 1841 (w), 1627 (m), 1586 (m), 1540 (s), 1522 (s), 1507 (s), 1490 (m), 1453 (m), 1421 (s), 1388 (m), 1349 (s), 1335 (s), 1261 (w), 1207 (m), 1181 (m), 1153 (m), 1117 (m), 1104 (m), 1038 (w), 992 (w), 974 (w), 920 (m), 838 (s), 823 (s), 810 (m), 751 (m), 734 (s), 721 (s), 652 (m), 619 (w), 541 (w), 507 (w), 429 (w). Elem anal. Calcd for $C_{24}H_{14}N_6GaCl_3{\cdot}3H_2O$: C, 42.34; H, 2.96; N, 12.35. Found: C, 42.56; H, 2.73; N, 12.11.

*Dichlorobis[5-amino(1,10-phenanthroline)]gallium(III) Chloride (**5**).* $GaCl_3$ (0.104 g, 0.589 mmol) and NH_2-phen (0.228 g, 1.18 mmol) were dissolved in 10 mL of MeCN under N_2. The solution was allowed to stir for 2 h at RT. After that time, excess ether was added to precipitate 0.287 g of the product as a yellow powder (87%). ^{1}H NMR (DMSO-d_6, 250 MHz): δ 10.00 (1H, t, J = 5.2 Hz), 9.54 (2H, m), 9.06 (1H, d, J = 8.0 Hz), 8.88 (1H, d, J = 8.5 Hz), 8.55 (1H, m), 8.40 (1H, d, J = 8.2 Hz), 8.28 (1H, m), 7.71 (2H, m), 7.45 (1H, m), 7.25 (2H, m), 7.10 (1H, s). ^{1}H NMR (CD_3OD, 600 MHz): δ 10.18 (1H, d, J = 16.5 Hz), 9.74 (1H, d, J = 16.2 Hz), 9.39 (1H, t, J = 6.9 Hz), 8.91 (1H, d, J = 7.8 Hz), 8.75 (1H, m), 8.46 (1H, m), 8.27 (1H, d, J = 7.8 Hz), 8.21 (1H, m), 7.66 (2H, m), 7.40 (1H, m), 7.25 (2H, m), 7.14 (1H, s). ^{13}C NMR (DMSO-d_6, 62.5 MHz): δ 148.2, 145.1, 144.9, 144.7, 144.5, 142.6, 138.9, 138.3, 137.2, 136.9, 136.4, 136.0, 132.4, 132.0, 129.6, 128.8, 126.6, 126.3, 125.5, 125.2, 122.8, 122.3, 101.0, 100.8. IR (KBr, cm^{-1}): 3399 (s), 3339 (s), 3208 (s), 3080 (m), 1640 (s), 1620 (s), 1604 (s), 1586 (m), 1522 (w), 1494 (s), 1465 (m), 1435 (s), 1350 (w), 1323 (w), 1287 (w), 1226 (w), 1164 (w), 1146 (w), 1122 (w), 1087 (w), 913 (w), 851 (w), 826 (w), 802 (w), 725 (s), 665 (w), 653 (w), 427 (w). Elem anal. Calcd for $C_{24}H_{18}N_6GaCl_3{\cdot}H_2O$: C, 49.31; H, 3.45; N, 14.38. Found: C, 49.56; H, 3.43; N, 14.51.

*Dichlorobis(1,2-ethanediamine)gallium(III) Chloride (**6**).* $GaCl_3$ (0.214 g, 1.22 mmol) and ethylenediamine (165 μL, 2.46 mmol) were dissolved in 10 mL of MeCN under N_2. As the reaction was stirred for 2 h, a white precipitate began to form. The addition of ether deposited more solid. A total of 0.320 g of the product was isolated as a white powder (79%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 3.07 (8H, s). ^{1}H NMR (D_2O, 600 MHz): δ 3.14 (8H, s). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 36.57. ^{13}C NMR (D_2O, 150 MHz): δ 39.31. IR (KBr, cm^{-1}): 3420 (s), 3225 (s), 2978 (s), 2912 (s), 2804 (s), 2747 (s), 2711 (s), 2677 (s), 2634 (s), 2575 (m), 2521 (m), 2420 (m), 2280 (w), 2055 (m), 1624 (m), 1602 (m), 1504 (s), 1342 (w), 1182 (w), 1085 (m), 1034 (s), 1008 (w), 973 (w), 917 (w), 786 (w), 568 (m), 467 (m), 445 (w), 431 (w). Elem anal. Calcd for $C_8H_{16}N_4GaCl_3{\cdot}2H_2O$: C, 14.46; H, 6.07; N, 16.86. Found: C, 14.61; H, 6.03; N, 16.71.

Reactivity Studies. All reactions were run in MeCN at 273 K under N_2, with the initial concentrations of the catalyst, alkene, and PAA_R being 5.0 mM, 500 mM, and 1.0 M, respectively. Most reactions were allowed to proceed for 1 h. At the end of each reaction, excess ether was added to precipitate the gallium(III) compound, effectively quenching catalysis. For the studies focusing on the catalytic activity as a function of time, aliquots were taken at the indicated time points. Each portion was quenched with excess ether and filtered through a plug of silica gel to remove the remaining PAA_R and gallium(III) salts. Control studies confirmed that this workup removed neither the olefin starting material nor the epoxide product from the solution. The remaining alkene and epoxide products were quantified relative to an internal standard of 1,2-dichlorobenzene, which is inert under the reaction conditions. All reactions were run at least three times to ensure reproducibility. All reported values are the averages of the results from these reactions. The errors represent 1 standard deviation.

RESULTS

Synthesis and Characterization. Syntheses of the gallium(III) complexes (Scheme 1) proceed in a straightforward manner, and simple mixing of the $GaCl_3$ salt and ligand in RT CH_2Cl_2 or MeCN is sufficient to ensure complexation. The compounds with the polydentate pyridylamine ligands (bispicen, trispicen, and tpen) can be isolated in high purities and yields (77−85%) through precipitation from CH_2Cl_2/ether mixtures. Compounds **1**−**3** tend to be hygroscopic and noticeably moistened upon prolonged exposure to air. The compounds with the bidentate ligands (NO_2-phen, NH_2-phen, and en) are prepared in moderate-to-high yields (51−87%) through precipitation. The en complex **6** is the least soluble of the six gallium(III) compounds in organic solvents. Complexes **4**−**6** appear to be more hygroscopic than compounds **1**−**3**, and we were unable to exclude water from the elemental analyses of the former. When syntheses of **1**−**6** were run under air instead of N_2, much lower yields of the desired products were obtained.

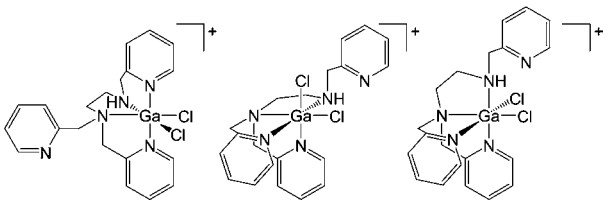
The gallium(III) complexes are diamagnetic and nearly colorless, as anticipated. The 294 K ^{1}H NMR spectrum of the bispicen complex **1** has four resonances in the aromatic region, indicating that its two pyridine rings are equivalent at this temperature. The doublet at 9.41 ppm is assigned to the protons on the 6-positions of the pyridine rings. These

dx.doi.org/10.1021/ic400570h | Inorg. Chem. 2013, 52, 5814−5823

resonances tend to be exquisitely sensitive to metal-ion coordination, and their chemical shifts can be used to assess whether the affiliated pyridine rings bind to Ga^{III}.[38] The resonances at 4.88 and 4.18 ppm indicate that the picolylic methylene protons are diastereotopic. The splitting pattern is inconsistent with a trans ligand conformation, which has a sufficiently high symmetry to render all of the picolylic protons equivalent. The splitting pattern is more consistent with a C_2 symmetry for the gallium(III) complex in solution. The ^{13}C NMR spectrum features only seven resonances, providing further evidence that the halves of the bispicen ligand are equivalent in solution. The NMR data suggest that **1** retains the cis-α ligand conformation observed in its crystal structure (vida infra) in solution.

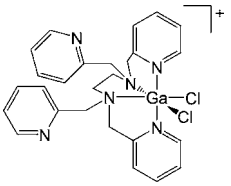
The ^1H NMR spectrum of the trispicen complex **2** has two doublets at 9.40 and 9.17 ppm, which are comparable in energy to the 9.41 ppm resonance observed for **1**. We have therefore assigned these as corresponding to the protons on the 6-positions of Ga^{III}-bound pyridine rings. The integrated intensity of each of these doublets corresponds to one proton, suggesting that the two associated pyridine rings are inequivalent at 294 K. The resonance for the third pyridine ring's 6-position proton appears at a significantly lower chemical shift (8.45 ppm), suggesting that it does not coordinate to Ga^{III}. The inequivalence of the two coordinated pyridine rings is supported by the acquired ^{13}C NMR spectrum. If the pyridine rings were equivalent, we would observe 14 ^{13}C resonances at most; instead, 19 resonances can be unambiguously identified. The conformation of the four coordinated N donors cannot be assigned with certainty; Scheme 2 shows three possible solution structures in which the two chlorides are coordinated cis to each other.

Scheme 2. Possible Solution Structures of 2



The tpen complex **3** likewise appears to have the pyridylamine ligand coordinated to the metal in a hypodentate fashion. The ^1H NMR spectra in CD_3CN and $CDCl_3$ strongly resemble each other, suggesting that MeCN does not displace the chlorides to an observable degree. The NMR spectra are consistent with a structure with two pendant pyridine rings. This is again most apparent from consideration of the protons on the 6-positions of the pyridine moieties, which are evenly split between doublet resonances at ~9.6 (bound) and ~8.6 (unbound) ppm. There are four doublets that can be reasonably assigned to methylene protons; as with **1**, this pattern is consistent with a C_2 symmetry and a cis-α conformation of the N donors. The number of resonances in the ^{13}C NMR data suggests that the halves of the tpen ligand are equivalent in solution, supporting the assignment of a C_2-symmetric species. HR-MS analysis of **3** detects a $[Ga(tpen)Cl_2]^+$ cation; consequently, we believe that the Ga^{III} center in **3**, like those in **1** and **2**, is primarily coordinated by a N_4Cl_2 set of donor atoms in solution. The mode of tpen coordination that is most consistent with the data is depicted in Scheme 3. The

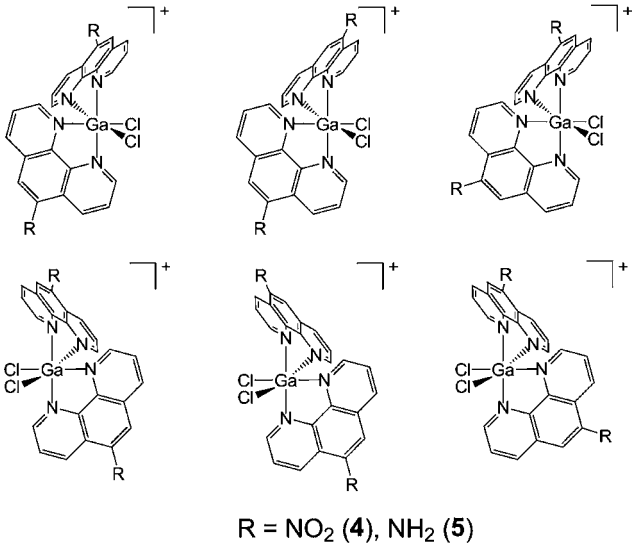
Scheme 3. Proposed Solution Structure of 3



exchange between the pendant and bound pyridine rings appears to be slow; we observe neither broadening nor coalescing of the ^1H NMR signals as samples of **3** in CD_3CN are heated from 294 to 324 K.

The solution structures of the two gallium(III) complexes with the phen derivatives are more difficult to interpret. Potentially, two 5-derivatized phen ligands could coordinate to the metal ion to form six isomers of *cis*-$[Ga(R\text{-phen})_2Cl_2]^+$; these six are comprised of three pairs of enantiomers (Scheme 4). Given that the cis conformation is present in the structures

Scheme 4. Possible Conformations of the phen Ligands in Complexes 4 and 5



of both $[Ga(phen)_2Cl_2]^+$ and $[Ga(phen)_2Br_2]^+$,[20,39] we suspect that additional trans isomers are not present in significant quantities, although the data certainly cannot preclude such a possibility. The ^1H and ^{13}C NMR spectra of the two gallium(III) complexes with NO_2-phen and NH_2-phen, **4** and **5**, display more resonance features than would be anticipated from the uncoordinated ligands. This demonstrates that the isomers of the gallium(III) complexes, like complex **3**, have limited fluxionality at RT. Rapid isomerization of **4** and **5** would result in 7 and 8 observable ^1H NMR resonances, respectively; instead, we observe 10 and 12 features. As with **3**, we do not observe any ^1H NMR resonances broadening or shifting as samples of **4** are heated to 324 K. Given the number of multiplets observed in the ^1H NMR spectra, we currently believe that **4** and **5** each exist as a mixture of multiple cis isomers in solution.

The ^1H and ^{13}C NMR spectra of the en complex **6** each contain a single resonance, consistent with the presence of a single compound with two chemically equivalent en ligands. These NMR spectra are distinct from those of free en in both DMSO-d_6 and D_2O, indicating that the ligand is indeed

dx.doi.org/10.1021/ic400570h | Inorg. Chem. 2013, 52, 5814−5823

chelating the metal ion. The data in D_2O suggest that the Ga^{III}–N bonds remain intact in solvents that can potentially ligate the Ga^{III} center.

IR Spectroscopy. IR measurements provide support for the modes of coordination suggested by the NMR data. The IR spectrum of noncoordinated pyridine features a C–N stretch at 1578 cm^{-1}; coordination to a metal ion typically shifts this frequency to the 1590–1615 cm^{-1} range.[40] All three complexes have intense bands where the C–N stretches of coordinated pyridine rings are expected (1612, 1611, and 1588 cm^{-1} for **1**–**3**, respectively). The IR spectra of complexes **1**–**3** display stronger absorbances in the 1560–1580 cm^{-1} region as the number of pyridine rings increases, with complexes **1** and **3** having weak and strong bands at 1578 and 1572 cm^{-1}, respectively. The presence of this peak for **1** is unexpected and may result from either another vibrational mode or the partial dissociation of the ligand during the preparation of the KBr pellet. Complex **2** lacks a distinct band in the 1560–1580 cm^{-1} range, but its 1611 cm^{-1} feature has a prominent shoulder that extends into this region.

X-ray Crystallography. Crystals of **1** were grown from the slow diffusion of ether into saturated MeOH solutions (Table 1). The X-ray diffraction data confirm that the composition of **1** is $[Ga(bispicen)Cl_2]Cl$ (Figure 1). The outer-sphere chloride is

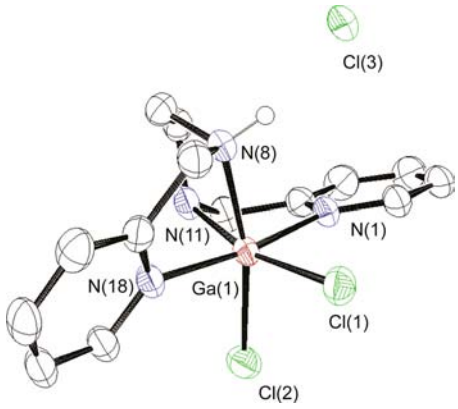


Figure 1. ORTEP representation of the complex $[Ga(bispicen)Cl_2]Cl$. All H atoms, except for the one located on N(8), and three noncoordinated water molecules have been removed for clarity. All thermal ellipsoids are drawn at 50% probability.

3.19 Å from one of the amine N atoms, N(8); this may be consistent with a N–H···Cl hydrogen bond.[41] In the cation, the bispicen ligand is bound to Ga^{III} in a cis-α conformation, which is commonly seen in the ligand's complexes with transition-metal ions,[42–46] and contributes to an overall distorted octahedral coordination geometry around the metal center. In gallium chemistry, the cis-α conformation of four N donors has also been observed in complexes with N_4O_2 coordination spheres.[11,31] The Ga–N and Ga–Cl bond lengths observed for **1** are typical for a hexacoordinate gallium(III) complex with a N_4Cl_2 donor atom set.[20,47,48] The Ga–N bond lengths differ only slightly, and the symmetry of the cation is approximately C_2.

A small number of crystals were also grown from saturated solutions of **2** in mixtures of MeOH and MeCN (Table 1). The structural data, however, correspond to the formula $[Ga(trispicen)Cl](GaCl_4)(Cl)$ (**7**; Figure 2), as opposed to $[Ga(trispicen)Cl_2]Cl$. Given that only the latter composition is consistent with the NMR, IR, and elemental analysis data for

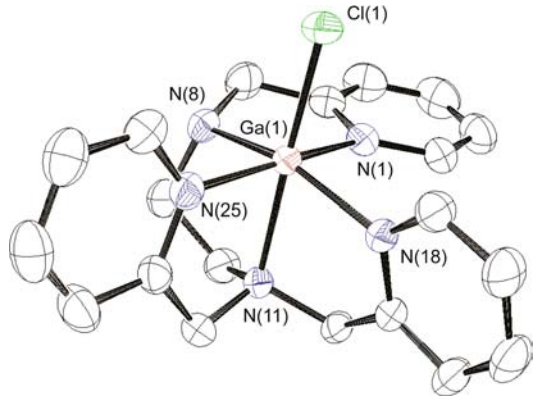


Figure 2. ORTEP representation of the dication $[Ga(trispicen)Cl]^{2+}$. All H atoms, the Cl^- and $[GaCl_4]^-$ counteranions, and a noncoordinated MeCN molecule have been removed for clarity. All thermal ellipsoids are drawn at 50% probability.

freshly isolated solid samples of **2**, we believe that **2** at least partially converts to **7** over the prolonged period of time required for crystal growth. Only small yields of **7** were obtained, limiting our ability to characterize the compound and its reactivity. The IR spectrum of **7** is distinct from that of **2** and notably lacks a feature between 1560 and 1580 cm^{-1} that can be readily assigned to an uncoordinated pyridine ring. In the structure of **7**, the bound trispicen is κ-5 rather than κ-4. Two different counteranions are in the outer sphere: $[GaCl_4]^-$ and Cl^-. The presence of the tetrachlorogallate(III) anion indicates that some of the Ga^{III} in the sample had dissociated from the trispicen ligand over the time required for crystallization.

The crystals that grew from saturated solutions of **3** were likewise consistent with decomposition products rather than the formula anticipated from the NMR and elemental analysis of the freshly precipitated product. In some cases, the Ga^{III} centers in the crystals were coordinated by bispicen, with unit cell parameters that were identical to those of the aforementioned crystals of **1**. In other cases, gallium(III) complexes with trispicen were isolated from the solutions. Both degradation products contain ligands that are missing picolyl arms. Water molecules are present in these crystal structures, which may suggest that these portions are being lost through hydrolytic processes. Attempts to grow the crystals in the strict absence of air and moisture were unsuccessful.

Short-Term Reactivity. The six gallium(III) compounds were tested for their ability to catalyze the epoxidation of alkenes by PAA_R (Table 2). A 1% loading of catalyst and 2 equiv of PAA_R per 1 equiv of substrate were used, primarily to facilitate comparison to our previous results with $[Ga(phen)_2Cl_2]Cl$.[20] For each catalyzed oxidation reaction, the epoxide is the sole organic product observed at 1 h; no allylic oxidation or dihydroxylation is observed with 1% mole catalytic loading. In all cases, the percentage of the alkene substrate that has been consumed is equal within error to the yield of the epoxide product, suggesting that the GC analysis has accounted for all organic products. As anticipated, the more electron-deficient terminal alkenes react less readily, as evidenced by the lower yields of epoxides.

Three trends can be observed in the epoxidation activities. First, the gallium(III) complexes with phen derivatives promote alkene epoxidation to much greater extents. In particular, compounds **4** and **5** promote the oxidation of 1-octene to 1-octene oxide to much higher degrees than any of the other four

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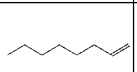
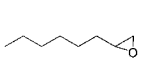
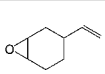
Table 2. Alkene Conversions/Yields of Epoxides (%) of Reactions Catalyzed by 1−6[a]

Substrate	Product	$[Ga(phen)_2Cl_2]Cl$[b]	**1**	**2**	**3**	**4**	**5**	**6**
		*46 (±5)* 46 (±8)	*31 (±4)* 32 (±4)	*27 (±2)* 25 (±2)	*14 (±1)* 15 (±1)	*56 (±4)* 56 (±7)	*43 (±2)* 40 (±3)	*41 (±2)* 40 (±3)
		*90 (±3)* 87 (±4)	*80 (±3)* 82 (±2)	*66 (±4)* 68 (±5)	*32 (±2)* 31 (±3)	*93 (±3)* 94 (±2)	*87 (±3)* 84 (±2)	*85 (±5)* 83 (±5)
		*10 (±1)* 11 (±2)	*7 (±0.4)* 7 (±0.6)	*3 (±0.2)* 3 (±0.2)	*0* 0	*13 (±1)* 13 (±1)	*10 (±1)* 9 (±1)	*10 (±1)* 9 (±1)
		*38 (±4)* 41 (±3)	*2 (±0.2)* 2 (±0.3)	*2 (±0.2)* 2 (±0.2)	*0* 0	*51 (±3)* 47 (±3)	*34 (±3)* 35 (±3)	*2 (±0.2)* 2 (±0.2)
		*59 (±8)* 61 (±6)	*40 (±4)* 37 (±3)	*26 (±4)* 28 (±4)	*17 (±2)* 17 (±2)	*70 (±6)* 72 (±4)	*52 (±5)* 50 (±5)	*38 (±2)* 39 (±3)

[a]Standard reaction conditions: MeCN, 273 K, N_2, $[Ga^{III}]$ = 5.0 mM, $[alkene]_0$ = 500 mM, and $[PAA_R]_0$ = 1.0 M. The alkene conversion, defined as the percentage of alkene that has been consumed by the reaction, was measured at 1 h via GC. The alkene conversions are italicized in the above table. The yield of epoxide, defined as the percentage of alkene converted to the epoxide, was measured at 1 h via GC. Because the substrate is in a 100-fold excess relative to the catalyst, the above yields of epoxides also serve as turnover numbers. [b]From ref 20.

newly reported gallium(III) complexes. The increases in the yields of the other epoxide products are much less pronounced. Second, the use of more electron-deficient ligands tends to result in more epoxidation. Comparison of the activities of $[Ga(phen)_2Cl_2]Cl$, **4**, and **5** reveals that the installation of a more electron-withdrawing NO_2 group on the 5-positions of the phen ligands increases the turnover rate, whereas the addition of an electron-donating NH_2 group reduces the yield of the epoxide at 1 h. Third, as the maximum denticity of the ligand increases past κ-4, the gallium(III) complexes become less able to quickly catalyze olefin epoxidation. Within the series of complexes with pyridylamine ligands, the catalytic activity associated with the tetradentate ligand bispicen is fastest; conversely, the complex with the potentially hexadentate tpen, **3**, is the worst catalyst.

In the previously studied alkene oxidation catalyzed by $[Ga(phen)_2Cl_2]Cl$, the selectivity for the epoxide product is lost upon switching to a lower catalyst loading. With a 0.1% catalyst loading of the phen complex, the most heavily represented products result from allylic C−H oxidation and bishydroxylation.[20] A loss of selectivity for the epoxide is also observed for the oxidation of cyclohexene catalyzed by **1** but with a substantially different product distribution. With a 0.1% loading of **1**, 3.0 M cyclohexene is oxidized by 6.0 M PAA_R to predominantly *trans*-1,2-cyclohexanediol (49%), with cyclohexene oxide as a minor product (6%) and the remainder of the substrate failing to react (45%). Unexpectedly, 2-cyclohexenol is not observed. Another potential product of allylic C−H oxidation, 2-cyclohexenone, is not formed in the olefin oxidations catalyzed by low concentrations of either **1** or $[Ga(phen)_2Cl_2]Cl$.[20]

Time Scale of Reactivity. The ability of the gallium(III) complexes to catalyze the epoxidation of olefins by PAA_R was monitored beyond 1 h in order to assess whether a more highly chelating ligand could extend the lifetime of the reactivity. Figure 3 shows the yields as a function of time for the epoxidations of five olefins catalyzed by the bispicen complex **1**. There is no noticeable initiation period, although this may occur on a much shorter time scale. The data show that the catalytic activity of **1** is maintained past 1 h; the observed increases in the yields beyond this time point are too large to be attributed to the uncatalyzed reactions between the olefins and terminal oxidant.[20] The most reactive substrate, cyclooctene, is fully converted to cyclooctene oxide by 2 h. Beyond 5 h, diol products consistent with the subsequent opening of the epoxide are observed. With cyclohexene as the substrate, cyclohexene oxide is the sole organic product until 5 h, forming in 75% yield from the alkene. By 6 h, noticeable amounts of *trans*-1,2-cyclohexanediol are observed in addition to the epoxide.

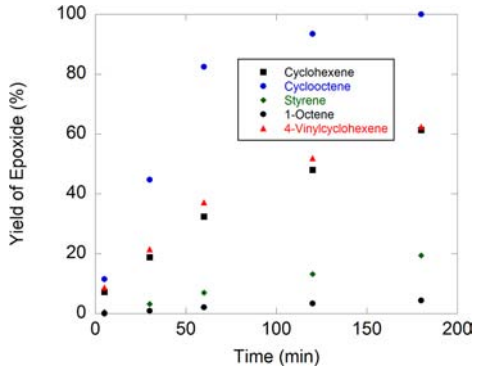


Figure 3. Yields of alkene epoxidations by PAA_R catalyzed by the bispicen complex **1** as a function of time. The reaction conditions are identical with those listed for Table 2.

MS of the cyclohexene epoxidation at 3 h reveals that the Ga^{III}-bispicen adduct is still intact. At both 5 min and 3 h, the most intense feature has *m*/*z* 369.0817, consistent with $[Ga(bispicen\text{-}H)(CH_3CO_2)]^+$ (predicted *m*/*z* 369.0842). This suggests that the two chloride ions in **1** are displaced by acetate shortly after the beginning of the reaction. Under ionization conditions, one of the amine protons is likely lost, explaining both the reduced mass and the 1+ charge of the observed ion.

The trispicen and tpen complexes **2** and **3** likewise appear to retain their catalytic activity for longer periods of time than

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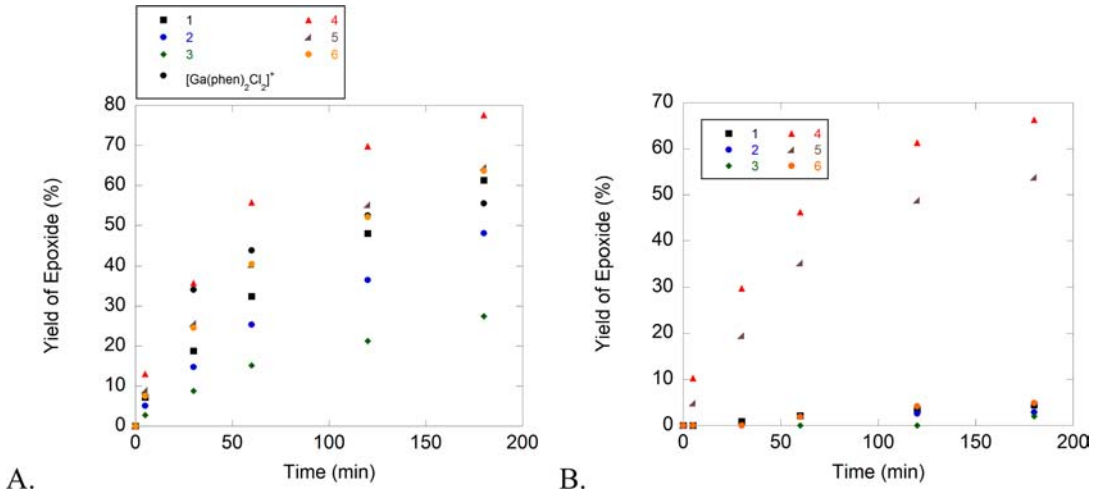


Figure 4. Yields of alkene epoxidation by PAA_R catalyzed by **1**−**6** and $[Ga(phen)_2Cl_2]Cl$ as a function of time. Panel A shows the oxidation of cyclohexene, whereas B shows the oxidation of 1-octene. The reaction conditions are identical with those listed for Table 2. The data for $[Ga(phen)_2Cl_2]Cl$ are from ref 20.

$[Ga(phen)_2Cl_2]Cl$, as assessed by their abilities to catalyze the oxidation of cyclohexene by PAA_R. Figure 4A compares the longer term reactivities of compounds **1**−**6** and $[Ga(phen)_2Cl_2]Cl$, using the oxidation of cyclohexene to cyclohexene oxide as a standard.[20] The plot shows that the activities of the complexes with the bidentate ligands have decreased substantially by 3 h. Catalysts **1**−**3**, although slower, appear to retain more of their activity, with the overall catalytic activity of **1** becoming approximately equivalent to those of **5** and $[Ga(phen)_2Cl_2]Cl$ by 3 h. As anticipated, compounds **2** and **3** are much less active than **1** throughout the 3 h. MS analyses of **2** and **3** at 3 h do not reveal any peaks consistent with the ligand hydrolysis observed in the crystals grown from solutions of **3**. Although **3**, for instance, eventually decomposes to **1** and **2** (Figure 2), we did not observe m/z features for either of these compounds in the 3 h data for reactions using **3** as a catalyst. As with **1**, the peaks observed at 3 h are consistent with acetate adducts.

The plots of the cyclohexene oxide yields versus time for catalysts **4**−**6** are more curved than those observed for compounds **1**−**3**, suggesting that the former set is less durable under the reaction conditions. The slowing of these three reactions cannot be attributed to depletion of the substrate, which only becomes noticeable as the reaction yield exceeds ∼80% (cyclooctene reaction in Figure 3). Despite this loss of activity, catalyst **4** remains the best catalyst of the six at the 3 h time point. Losses of activity for **4** and **5** are also observed over time when 1-octene is used as the standard (Figure 4B), but with this particular substrate, the durabilities of **1**−**3** do not come close to compensating for their slower activity.

DISCUSSION

The syntheses of the gallium(III) complexes are generally straightforward in that no special measures are necessary to form adducts between the N-donor ligands and the metal ion and that pure products can be isolated without chromatography. The obtained yields range from moderate (51%) to high (85%). One complication with the syntheses is that the compounds are hygroscopic, and prolonged exposure to moisture appears to degrade the pyridylamine ligands, as evidenced by the crystallized decomposition products of **3**. The complexes with the phen derivatives are likely isolated as mixtures of cis isomers (Scheme 4).

Three pyridylamine ligands were investigated: bispicen, trispicen, and tpen (Scheme 1). The bispicen molecule is a well-established tetradentate ligand.[35,49−51] The tpen ligand typically coordinates metal ions in a hexadentate fashion, although tetra- and pentadentate modes of coordination have been observed.[52−56] With respect to previously reported group 13 chemistry, there exists a heptacoordinate complex of tpen with In^{III}, with the tpen itself providing six of the donor atoms in the inner sphere.[57] The coordination chemistry of trispicen is much less established, but a singly methylated derivative, *N*′-methyl-*N*,*N*,*N*′-tris(2-pyridylmethyl)-1,2-ethanediamine, is pentadentate in its structurally characterized complexes with Mn^{II} and Fe^{II}.[37,58] NMR analysis of **1**−**3** suggests that all three ligands predominantly coordinate Ga^{III} through four N donors, with one and two pyridine rings failing to ligate the metal in **2** and **3**, respectively. This is supported by IR analysis of freshly precipitated powder samples of these compounds.

Although the crystal structure of **1** (Figure 1) is consistent with its NMR spectra and elemental analysis, crystals grown from solutions of **2** are not consistent with the initially obtained $[Ga(trispicen)Cl_2]Cl$. The crystal structure of the isolated **7** (Figure 2) demonstrates that the coordination of trispicen to Ga^{III} is not strictly limited to the hypodentate mode supported by the NMR data. In one of the complex ions within the asymmetric unit, $[Ga(trispicen)Cl]^{2+}$, the ligand is pentacoordinate, whereas in the other complex ion, $[GaCl_4]^-$, the trispicen ligand is entirely absent from the Ga atom. The $[Ga(trispicen)Cl]^{2+}$ dication represents only the second example of a structurally characterized Ga^{III} ion with a N_5X coordination sphere (X = F, Cl, Br, I).[59] This coordination sphere may initially be surprising because the Ga atom does not obey the octet rule, having five clear Ga−N bonds. The Ga atom does not strictly obey the octet rule, however, and there exist an abundance of hexacoordinate gallium(III) species, including several examples with $[GaN_6]^{3+}$ coordination spheres that would seem to deviate even further into hypervalence.[60−62]

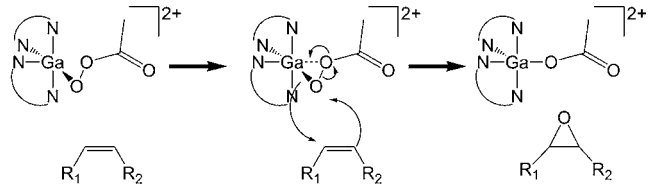
The capability of the trispicen and tpen ligands to more fully coordinate the Ga^{III} ion may explain the decreased epoxidation activities exhibited by **2** and **3** (Table 2 and Figure 4). Focusing analysis on the complexes with the three pyridylamine ligands,

dx.doi.org/10.1021/ic400570h | *Inorg. Chem.* 2013, 52, 5814−5823

the bispicen complex **1** promotes the most extensive epoxidation of all substrates except 1-octene, which essentially does not react with either **1**, **2**, or **3** present as the catalyst. The tpen-containing **3** is the worst catalyst of the three compounds, with 1 h yields that are less than half of those measured for **1**. On the basis of the results, we speculate that the pendant pyridine rings in **2** and **3** may compete with the terminal oxidant for the coordination sites vacated by the initially bound chloride anions. Previous work suggests that the affinities of pyridine rings to Ga^{III} are comparable to those of carboxylate ligands.[31] Reducing the number of pendant pyridine donors would alleviate the competition between intramolecular and intermolecular binding and facilitate the coordination of PAA to the Ga^{III} center necessary for catalysis. Alternatively, the steric bulk provided by the additional binding arms in **2** and **3** may hinder coordination of the terminal oxidant and/or limit the accessibility of the alkene substrate to the reactive portion of the active oxidant.

The results may suggest that two available coordination sites are needed to activate PAA most efficiently, which is reminiscent of the Sharpless-type mechanism proposed for the epoxidation of alkenes by mixtures of $[Al(H_2O)_6]^{3+}$ and H_2O_2.[27,63] In the mechanistic scheme proposed by Shul'pin et al. for this Al^{III} catalysis, coordination of both O atoms of H_2O_2 to the metal center precedes a concerted O-atom transfer from the bound oxidant to an uncoordinated alkene.[27] If two coordination sites are likewise needed for the activation of PAA by the Ga^{III} centers of the current catalysts, **2** would be anticipated to be an inferior catalyst to **1**, in accordance with our results (Table 2). Scheme 5 illustrates a possible

Scheme 5



mechanism for the epoxidation reactions that highlights the potential benefit of a second coordination site for PAA. The illustrated mechanism assumes that the N-donor ligands remain fully bound during the reaction; this assumption has not been experimentally confirmed. We are currently assessing the feasibility of various mechanistic pathways through computational analysis and experiments involving gallium(III) complexes with sterically encumbered bispicen derivatives.

The higher catalytic activities of the complexes with the phen derivatives suggest that the Ga^{III} centers enable catalysis through their abilities to act as Lewis acids. That more electron-rich alkenes tend to react more readily would suggest an electrophilic oxidant, which would be stabilized and rendered less active by more electron-rich ligands. The electrophilicity of the oxidant in the Ga^{III} catalysis is also consistent with the inability of H_2O_2 and *t*-BuOOH to serve as terminal oxidants for the epoxidation reactions. Carbonyl groups are widely considered to be electron-withdrawing functional groups. When PAA is used as the terminal oxidant, its carbonyl group may reduce the electron density on the transferred O atom sufficiently to allow O-atom transfer to the alkene substrate. The acetate produced upon O-atom transfer would also be a better leaving group than the hydroxide or *tert*-butyloxide resulting from H_2O_2 or *t*-BuOOH.

1,10-Phenanthroline is widely viewed as being electron-poor relative to amine N-donor ligands[28−30] and should render chelated metal ions more electron-deficient. Complexes **4** and **5** are notable for their ability to catalyze the oxidation of 1-octene; the other four gallium(III) compounds reported in this manuscript, conversely, cannot promote this reaction to a significant degree. The addition of electron-withdrawing nitro groups onto the phen ligands improves the yields of the epoxidation reactions; conversely, the installation of electron-donating amino groups decreases the yields (Table 1).

Although the complexes with the phen ligands are more active over shorter durations, the compounds with the pyridylamine ligands can potentially achieve superior turnover numbers over longer periods of time because of the greater stability provided by chelate effects. One noted shortcoming with the $[Ga(phen)_2Cl_2]Cl$ catalyst is that it decomposed to unreactive gallium(III) salts and free phen within approximately the first hour of the epoxidation reactions.[20] The phen appears to slowly dissociate from the Ga^{III} center under acidic conditions. The stability of the Ga^{III} catalyst can be increased by using a single tetradentate ligand in place of two bidentate ligands. The ability of bispicen, trispicen, and tpen to sustain the catalysis over longer periods of time confirms that this is a viable strategy for Ga^{III}-catalyzed olefin epoxidations (Figures 3 and 4). Compound **1** is catalytically equivalent to $[Ga(phen)_2Cl_2]Cl$ when the yields of cyclohexene epoxidation are measured at 3 h (Figure 4). Unlike the phen compound, the Ga^{III}-bispicen adduct remains intact at 3 h. The observed decomposition of **2** and **3** (Figures 2 and S1 in the SI) suggests that the pyridylamine-containing complexes do have finite catalytic lifetimes. Compounds **1**−**3** appear to retain their intact polydentate ligands through the 3 h necessary for the alkene epoxidation, however, suggesting that the ligand degradation is slow relative to the alkene epoxidation.

The reactivity with the 1% catalyst loading is selective for the epoxide product for short durations, with the epoxide accounting for the entirety of the observed organic product. The reactions using **1** as the catalyst do start to produce *trans*-1,2-cyclohexanediol from cyclohexene between 5 and 6 h after the start of the reaction. As with the olefin oxidation catalyzed by $[Ga(phen)_2Cl_2]Cl$,[20] the selectivity for the epoxide product is lost when the catalyst loading of **1** is reduced to 0.1%. Oddly, the chemistry associated with **1** differs from that promoted by the phen compound in that the lower concentration of **1** does not promote allylic C−H activation. Instead, bishydroxylation is overwhelmingly favored under such circumstances. When cyclohexene oxide is used as a substrate with the standard reaction conditions and a 1% mole loading of gallium (3.0 mM **1**, 6.0 M PAA_R, 0 °C, 7 h), no diol is observed, suggesting that cyclohexene may be converted directly to *trans*-1,2-cyclohexanediol as opposed to a two-step reaction involving epoxidation followed by ring opening. We speculate that another Ga^{III}-based oxidant is responsible and are continuing to investigate this side reactivity through experimental and computational methods. The mechanism displayed in Scheme 5 certainly does not explain all of the observed oxidative activity of the gallium(III) complexes.

dx.doi.org/10.1021/ic400570h | *Inorg. Chem.* 2013, 52, 5814−5823

CONCLUSIONS

Six new gallium(III) complexes with N-donor ligands have been prepared and tested as catalysts for the epoxidation of alkenes by PAA_R. A comparison of the compounds' activities provides three major insights into Ga^{III}-catalyzed alkene epoxidation. First, more electron-deficient ligands are found to support more rapid catalytic turnover, with phen derivatives leading to superior initial activity over ligands with amine and pyridine chelating groups. The gallium(III) complexes with phen derivatives are markedly better at activating the electron-deficient substrate 1-octene, and $[Ga(NO_2\text{-phen})_2Cl_2]Cl$ is the best catalyst of the six under all characterized reaction conditions. Second, more highly coordinating ligands, such as the tetradentate bispicen, can prolong the catalytic activity by stabilizing the ligand−metal adduct. Third, it is found that the more highly chelating N-donor ligands, trispicen and tpen, decrease the catalytic activity. The additional binding arms may compete with terminal oxidant for the coordination sites, or they may impede the reactivity through steric effects.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data for $[Ga(trispicen)Cl]Cl_2$, which forms upon decomposition of **3**, mass spectrometry of **3**, ^1H and ^{13}C NMR spectra for **1**−**6**; IR spectra for **1**−**7**, figure showing 1,2-cyclohexanediol production over 7 h, mass spectrometry of the gallium adducts in **1**−**3**-catalyzed epoxidations of cyclohexene at 3 h, and CIF file of CCDC reference numbers 913806−913808. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for funding provided by Auburn University and a Doctoral New Investigator grant from the Petroleum Research Fund, sponsored by American Chemical Society (Grant #49532-DNI3).

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