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Synthesis and Characterization of α-Diimine Complexes of Group 13 Metals and Their Catalytic Activity toward the Epoxidation of Alkenes

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Ⓢ *Supporting Information*

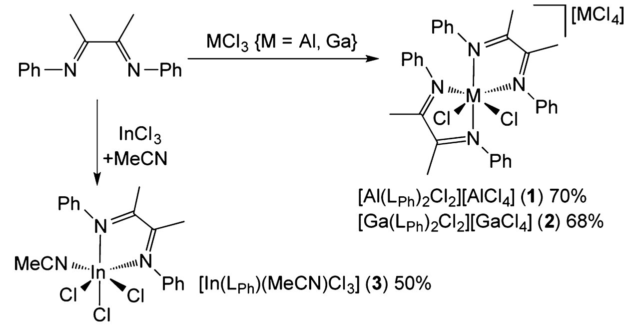
ABSTRACT: Complexes of group 13 metal (Al, Ga, In) ions with neutral α-diimine ligands have been prepared and characterized. The Al^{III} and Ga^{III} $[M(\alpha\text{-diimine})_2Cl_2][MCl_4]$ complexes catalyze the epoxidation of alkenes by peracetic acid under ambient conditions. The two complexes display nearly identical reactivity, demonstrating that inexpensive and highly abundant aluminum is a viable catalytic metal for these reactions.

The discovery of catalysts that do not rely on precious metals is essential for the development of more sustainable industrial processes. Aluminum is among the most abundant elements in the earth's crust, making it an inexpensive and attractive choice for catalyst development. However, because of its relative lack of redox activity, it has rarely been used to catalyze the oxidation of organic molecules.[1−5]

α-Diimines comprise a class of easily prepared and highly modifiable ligands. The N−C−C−N backbone can be derivatized with a wide array of substituents to tune the steric and electronic properties of metal complexes. Although complexes of these ligands with aluminum and the other group 13 elements gallium and indium are well represented in the literature,[6] to the best of our knowledge, none have been used as catalysts. Not coincidentally, most group 13 coordination complexes with α-diimines contain reduced and anionic forms of the parent ligand. Neutral ligands have been found to be essential for the catalytic activities of group 13 metal complexes for a variety of reactions.[7] We have been investigating the coordination chemistry of *N*-aryl-substituted α-diimine ligands $[ArN{=}C(CH_3)C(CH_3){=}NAr]$ and previously reported the synthesis of aluminum(III) complexes with singly and doubly reduced forms of the ligands.[8] Herein, we report the synthesis and characterization of a trio of group 13 metal complexes with *N*,*N*′-bisphenyl-2,3-dimethyl-1,4-diazabutadiene (L_{Ph}). We also show that both the aluminum(III) and gallium(III) complexes catalyze the selective epoxidation of alkenes by peracetic acid (PA).

Reaction of equimolar amounts of L_{Ph} and MCl_3 in 1,2-dimethoxyethane (DME) affords $[M(L_{Ph})_2Cl_2][MCl_4]$ in 70% (**1**; M = Al) or 68% (**2**; M = Ga) yield (Scheme 1). Both **1** and **2** precipitate from solution during the course of the reactions as yellow powders that are sufficiently pure for catalysis. Both compounds are indefinitely stable in the solid state when stored under an N_2 environment at −25 °C and are stable under air for several hours. In acetonitrile (MeCN), **2** does decompose within ~4 h to an unidentified species, as observed by UV−vis spectroscopy. Conversely, **1** is much more stable in MeCN, showing no discoloration over 24 h (see the Supporting Information, SI). Reaction of L_{Ph} with $InCl_3$ in DME results in a metal complex with only one α-diimine ligand, $[In(L_{Ph})Cl_3]$,[9] which can be crystallized from MeCN/diethyl ether at −25 °C to provide $[In(L_{Ph})(MeCN)Cl_3]$ (**3**) in 50% yield (Scheme 1).

Scheme 1. Syntheses of Complexes 1−3



The formulations of **1**−**3** were corroborated by X-ray crystallography. Single crystals of all three compounds were grown from the slow diffusion of diethyl ether into concentrated MeCN solutions at −25 °C. **1** and **2** crystallize as cation−anion pairs, with the anion being a MCl_4^- tetrahedron and the cation being $[M(L_{Ph})_2Cl_2]^+$, with the metal ions coordinated in slightly distorted octahedral geometries (Figure 1 and the SI). The chloride ligands in both cations of **1** and **2** are in a *cis* arrangement, giving the ions near C_2 symmetry. The general structural motif is similar to that observed for the $[M(bipy)_2Cl_2]^+$ cations (bipy = 2,2′-bipyridine).[10] Complex **3** crystallizes with an octahedral indium(III) ion, with the three chloride ligands coordinated in a *fac* conformation (see the SI). The average C−C and C−N bond distances in the α-diimine ligands in **1**−**3** are 1.506 and 1.282 Å, respectively, supporting neutral ligands.[11]

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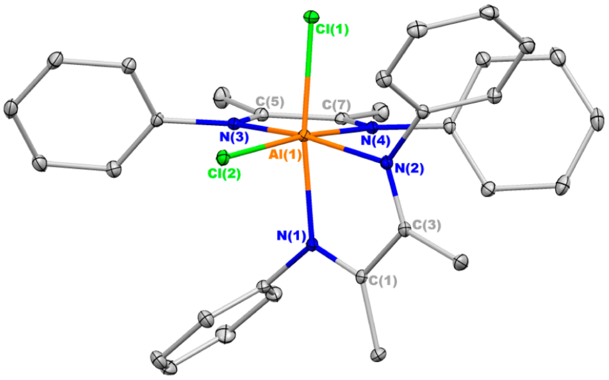
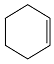
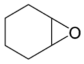
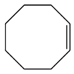
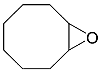
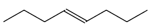
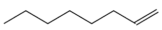
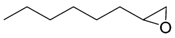
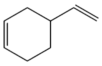
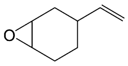


Figure 1. Solid-state structure of one of the $[Al(L_{Ph})_2Cl_2]^+$ cations of **1**. Ellipsoids are projected at 30% probability, and hydrogen atoms are omitted for clarity.

Table 1. Alkene Conversions/Yields of Epoxides for Reactions Catalyzed by 1 and 2 after 1 h[a]

Substrate	Product		Conversion (%)	Yield (%)
		**1**	71 (±4)	68 (±4)
		2	69 (±6)	66 (±6)
		**1**	88 (±3)	83 (±3)
		2	90 (±3)	86 (±3)
		**1**	56 (±1)	56 (±1)
		2	58 (±1)	58 (±1)
		**1**	5.1 (±1.0)	5.1 (±1.0)
		2	4.6 (±0.4)	4.6 (±0.4)
		**1**	57 (±5)	54 (±4)
		2	40 (±2)	37 (±2)

[a] Standard reaction conditions: MeCN, 295 K, air, [M^{III}] = 2.3 mM, $[alkene]_0$ = 230 mM, $[PA]_0$ = 230 mM. The conversion and yield were determined by GC.

Compounds **1** and **2** were readily characterized by ^{1}H and ^{13}C NMR spectroscopies, with the spectra indicating that the compounds are diamagnetic. For both complexes, the crude reaction products and crystallized samples have identical ^{1}H NMR spectra, suggesting that the solid-state structures are reflective of bulk materials. The spectra are consistent with the pseudo-C_2 symmetries observed in the crystal structures, with both compounds having two signals attributable to the $CH_3C{=}N$ protons along with multiple aromatic environments, all of which are multiplets or unresolved broad signals. We attribute the broad aromatic signals to hindered rotation about the $N-C_{Ph}$ bonds. The rotation slows enough at lower temperature (5 °C for **1** and −10 °C for **2**) to allow the resolution of all signals as more defined multiplets (see the SI). At higher temperatures, rotation becomes more rapid, causing several signals to coalesce. The $CH_3C{=}N$ signals do not change as the sample is heated from 5 to 75 °C, suggesting that the ligands remain firmly bound to the metal ion across this temperature range in MeCN. The ^{27}Al NMR spectrum of **1** has two unique signals, a sharp signal at 103.7 ppm ($\Delta\nu_{1/2}$ = 5 Hz, $AlCl_4^-$) and a broader, less intense signal at 29.9 ppm ($\Delta\nu_{1/2}$ = 119 Hz, $[Al(L_{Ph})_2Cl_2]^+$), supporting two independent aluminum ions in solution.

The aluminum and gallium cations of **1** and **2** share a N_4Cl_2 coordination sphere with the $[Ga(phen)_2Cl_2]Cl$ complex (phen = 1,10-phenanthroline), which was structurally characterized by the Goldsmith group.[12a] Given that this complex was catalytically active for alkene epoxidation, we decided to screen our complexes for similar reactivity. Gratifyingly, both **1** and **2** proved to be competent catalysts for the epoxidation of electron-rich alkenes by PA at ambient temperature and pressure using only a 1.0 mol % catalyst loading (Table 1). Compared to $[Ga(phen)_2Cl_2]Cl$, both **1** and **2** are more efficient at oxidizing electron-rich substrates but much poorer at catalyzing the epoxidation of electron-deficient alkenes.[12a] Although the reactivities are excellent for a main-group catalyst, certain transition-metal complexes display superior activity under similar conditions.[13] Cyclooctene is the most reactive substrate and is oxidized to a near-quantitative yield. More electron-deficient alkenes, such as 1-octene, are much less reactive, with yields of about 5%. In substrates with multiple oxidizable C═C bonds, the more highly substituted one is oxidized preferentially. The ring C═C bond of 4-vinylcyclohexene is oxidized almost exclusively. Ethyl sorbate is oxidized in <2% yield with **2**, but what little oxidation that does occur is localized on the C═C bond that is farther from the electron-withdrawing ester group. The substrate *trans*-4-octene is oxidized to a single epoxide product, suggesting that the oxygen atom is added to both carbon atoms in the alkene in a concerted manner. This suggests a mechanism similar to that proposed for the $[Ga(phen)_2Cl_2]Cl$ system,[12c] indicating that catalysis likely proceeds through a 1:1 M^{III}/peracetate complex from which the oxygen atom transfers to both carbon atoms in the alkene C═C bond simultaneously (see the SI). In general, the reactions appear to be slightly less selective for the epoxide than previously studied reactions with gallium(III) catalysts.[12] Side products are observed for the oxidation of cyclohexene, 4-vinylcyclohexene, and cyclooctene and account for approximately 2−5% of the oxidized organic products. Regrettably, we were unable to identify these trace compounds. In the case of cyclohexene, the gas chromatography (GC) retention time of the side product was inconsistent with those of 2-cyclohexenol, 2-cyclohexenone, or *trans*-1,2-cyclohexanediol. This suggests that neither allylic oxidation nor epoxide ring opening occurs to a detectable degree during the 1 h reaction.

Even with these trace side products, the epoxidation of olefins by **1** is unusually clean and represents unprecedented catalytic activity for an aluminum(III) complex. The $[Al(H_2O)_6]^{3+}$ ion has been shown to catalyze the epoxidation of *α*,*β*-unsaturated ketones with H_2O_2.[4] However, elevated temperatures and long reaction times (24 h) were required for reasonable conversions (21−88%). Further, the selectivity for the epoxide over other oxidation products is poor (3−56%). Aluminum oxide has also been shown to be catalytically active for the epoxidation of cyclooctene with H_2O_2.[1] Although selectivities for this system range from fair to good (55−95% for epoxide), the conversions are low (<40%), even at high temperatures (80 °C). In our control experiments, we found that $Al(OTf)_3$ catalyzes alkene oxidation, although a 10-fold higher loading of $Al(OTf)_3$ is needed to obtain a conversion similar to that for **1**. Furthermore, the reactivity is not selective for any product. When cyclohexene is the substrate, most of the organic products cannot be readily identified, and cyclohexene oxide represents only 10% of the converted olefin.

Compounds **1** and **2** differ only in the metal ion, allowing for a direct comparison of the catalytic competencies of aluminum and gallium. Remarkably similar reactivities were observed for both complexes across most substrates, with the only reactions that differ substantially being those of 4-vinylcyclohexene, which is oxidized more extensively by **1**. The catalysis cannot be attributed to the ligand; control reactions with 6.4 mM L_{Ph} did not increase the yield of cyclohexene epoxidation beyond that of the uncatalyzed reaction. The epoxidation of cyclohexene was monitored over 2 h (see the SI). Both **1** and **2** behave similarly, and at every time point, the yields of cyclohexene oxide are within experimental error of each other. Compounds **1** and **2** remain catalytically active for a longer period of time relative to the $[Ga(phen)_2Cl_2]Cl$ complex,[12] as evidenced by epoxide yields that plateau later and at higher values. Despite their greater apparent stability relative to the phen complex, the reactivities of both **1** and **2** do decrease over time, and the increases in the yields of epoxide from 90 to 120 min are in the range of that of the uncatalyzed reaction between cyclohexene and PA. Visual observation of the reactions suggests that the $Al^{III}L_{Ph}$ and $Ga^{III}L_{Ph}$ adducts decompose over time. The reaction between metal-free L_{Ph} and PA immediately yields a dark-red species. Solutions of **1** and **2**, conversely, are initially yellow but gradually become pink over the course of their reactions with PA.

In conclusion, we have prepared group 13 complexes with neutral α-diimine ligands. The aluminum(III) and gallium(III) complexes have been shown to be catalytically active for the epoxidation of alkenes. This work represents the first instances in which main-group complexes with α-diimine ligands served as catalysts. The reactivity and selectivity of **1** as a catalyst for olefin epoxidation are unprecedented for aluminum(III). The results show that, at parity of ligand, aluminum is as catalytically effective as gallium for olefin epoxidation. Even though the activity of **1** pales in comparison to those of the most successful manganese-containing catalysts, the high abundance and low cost of aluminum relative to gallium and non-iron transition metals make it an economically attractive lead for future research.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental details, ^1H and ^{13}C NMR spectra of **1** and **2**, ^1H NMR spectrum of **3**, ^{27}Al NMR spectrum of **1**, VT-NMR spectra of **1** and **2**, crystal structures of **2** and **3**, plots of the yield of cyclohexene oxide versus time for **1** and **2**, tables of control reactions, and a suggested mechanism. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01136.

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Notes

The authors declare no competing financial interest.

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