

Synthesis and characterization of manganese(III) and high-valent manganese-oxo complexes and their roles in conversion of alkenes to cyclic carbonates



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ABSTRACT

A novel manganese(III) complex (**2**) of an amido-amine ligand (**1**) was successfully synthesized and characterized using various analytical techniques such as ¹H NMR and single-crystal X-ray diffraction. X-ray crystallography data of **2** has demonstrated that the complex is a six-coordinated species. Electrospray ionization mass spectrometry (ESI-MS) also showed the characteristic peak (*m/z* 401.6, negative ion mode) of **2** indicating the formation of the complex. **2** was successfully employed to convert a variety of olefins to cyclic carbonate in the presence of carbon dioxide (CO₂), an oxidant (e.g. *tert*-butylhydroperoxide, TBHP) and a co-catalyst (tetrabutylammonium bromide, TBAB) in a single-pot under mild reaction conditions. Upon reaction with an oxidant, **2** generated a non-heme high-valent manganese-oxo species (**3**), which was responsible for conversion of alkene to epoxide, and further cycloaddition of CO₂ occurs in the presence of **2** and TBAB. The effect of reaction conditions (temperature and pressure), oxidants, and alkenes were systematically investigated for cyclic carbonate synthesis. High turnover numbers (50–240) and yield were obtained when various alkenes were employed. Additionally, **3** was characterized using various spectroscopic and mass spectrometry techniques. Fourier transform infrared spectrum (FT-IR) of **3** indicated a peak at 839 cm⁻¹ corresponding to manganese-oxo stretching. Isotope labeling studies of the oxo group of **3** revealed a peak shift to 804 cm⁻¹ upon exchange of the ¹⁶O with ¹⁸O. **3** was also characterized by ESI-MS. ¹⁸O isotope studies were performed to understand the role of **3** in the catalytic cycle and to further establish the mechanism of the reaction.

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1. Introduction

Carbon dioxide (CO₂) is an environmentally benign, renewable resource that can be utilized in chemical reactions for sustainable development [1]. One such example is the synthesis of cyclic carbonates using CO₂ and epoxide as reagents, which is a 100% atom economic reaction and incorporates other “green” principles [2]. Cyclic carbonates are important organic compounds useful in the production of chemicals and polymers, used as aprotic polar solvents and in lithium ion batteries [3]. Industrially, cyclic carbonates are produced by the cycloaddition of CO₂ to epoxides in

the presence of phosphonium or quaternary ammonium salts as catalysts [4]. Over the years numerous homogenous and heterogeneous active catalytic systems have been developed and successfully employed in this reaction [5] and efforts are currently underway to develop catalysts, which can be employed in mild temperature and pressure conditions [6].

Synthesis of cyclic carbonates from olefins via in situ formation of epoxides, however, provides a safe, economic, and energy efficient pathway by reducing the need of synthesizing toxic epoxides externally [7]. Though introduced in 1962 [8], only a few reports are available about the carboxylation of olefins towards cyclic carbonate synthesis. In 1986, Aresta et al. reported the first homogeneous rhodium(I) complex catalyzed one-pot synthesis of styrene carbonate from styrene, CO₂ and, oxygen (O₂) at 40 °C [9]. Almost two decades later, researchers began using different

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catalytic systems based on ionic liquid and tetrabutylammonium bromide (TBAB) employed in a multi-step carbonate formation, which significantly improved the product yields [10]. Sun et al. synthesized a heterogeneous catalyst consisting of Au/SiO₂ and zinc bromide that effectively produced cyclic styrene carbonate from styrene [11]. A metal free catalytic system containing *N*-bromosuccinamide (NBS) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and hydrogen peroxide (H₂O₂) in water was also employed for conversion of alkene to cyclic carbonate [12]. He et al. reported a one-component production of cyclic carbonate from olefin using sodium phosphotungstate/TBAB and a base. Quantitative amount of the corresponding benzoate derivative was observed, along with the product [13]. Additionally, recent reports of using highly active quaternary metal-based salts have also been reported [14]. Under the guidance of these reports, the field of alkene to cyclic carbonate synthesis is gaining greater attention in research.

However, low selectivity towards the carbonates, formation of side products, and longer reaction times are a few of the challenges that propelled the development of an alternate active catalytic system. Additionally, stability of the catalysts under an oxidizing environment and high temperature and pressure conditions are important factors when choosing a catalyst. Metal complexes of first row transition elements, such as manganese and iron being less toxic [15] and biologically abundant [16], are ideal when developing “green” catalysts. Therefore, due to these characteristics and variable redox chemistry, novel manganese-based complexes may provide a solution to the previous challenges of alkene to cyclic carbonate conversion via in situ epoxide formation.

The manganese-oxo species, which are produced in many biological systems, participate in various important biochemical processes [17]. High valent manganese-oxo species are believed to play role in the oxidation of water to oxygen in membrane bound protein (Photosystem II) in photosynthesis [18]. Manganese-oxo species [18d], particularly manganese(V)-oxo complexes, involving various ligands of corroles [19], porphyrins [20], corrolazines [21] and non-heme amide-based ligands [22] have been implicated in different reactions such as water oxidations and purification, C–H bond activation, and oxo transfer reactions. Oxo transfer reactions, predominantly epoxidation reactions, using manganese-based complexes have been well established in the literature over the past few decades [23] and such complexes are suitable for conversion of alkene to cyclic carbonate oxidatively. Previously, we have used amido-macrocylic ligand-based metal complexes for the catalytic conversion of CO₂ and epoxides to industrially important cyclic carbonate [24]. Other researchers have also incorporated acyclic tetradentate ligands that possess a similar diamido skeleton. Complexes of manganese, iron, nickel, chromium, cobalt, ruthenium etc. have been synthesized and utilized in reactions for nitrosyl transfer, alkene oxidation, and alkene epoxidation [25]. Additionally, we have synthesized a cobalt(III)-complex of an acyclic amido-amine ligand [26], which was found

to effectively produce cyclic carbonate from epoxide and CO₂. Using the similar ligand (1), we report synthesis and characterization of novel manganese(III)-complex (2) that was employed for alkene to cyclic carbonate synthesis oxidatively in a single pot. 2 was chosen such that an alkene can be easily converted to an epoxide via formation of a non-heme high-valent manganese-oxo intermediate (3) (Fig. 1) upon reaction with an oxidizing agent, for example TBHP. When pressurized with CO₂, 2 has enough Lewis acidity for catalytic cycloaddition of CO₂ to epoxide, in the presence of a co-catalyst, producing a cyclic carbonate in a single pot (Scheme 1).

The catalytic system showed excellent activity with various substrates at turnover numbers (TONs) as high as 240. To the best of our knowledge no reports are available involving manganese complexes for the single-pot conversion of alkene to cyclic carbonates via in situ formation of epoxide. Various oxidants and substrates were used for the cyclic carbonate formation. Reaction conditions such as temperature and pressure were also verified in order to obtain optimum reaction conditions. 3 was isolated and characterized using various spectroscopic techniques and isotope labeling studies, which enabled us to establish the mechanistic pathway of the reaction.

2. Experimental

2.1. General

All chemicals used in this study were purchased from Sigma-Aldrich, USA and Acros organics, USA and were used as received unless otherwise noted. Tetrahydrofuran (THF) was dried using sodium and benzophenone [27]. CO₂ (99.9%) was obtained from Airgas. H₂¹⁸O (95% ¹⁸O-enriched) was purchased from Cambridge Isotope Laboratories, Andover, MA, USA. Syntheses of cyclic carbonates were performed in a 50 mL Parr reactor autoclave connected with a 4840 controller. ¹H and ¹³C NMR spectra were obtained using a 600 MHz Bruker or a JEOL ECS 400 MHz instrument equipped with a 5 mm triple resonance inverse probe. The spectra were collected at 25 °C, and chemical shifts were reported in ppm relative to TMS as external standard. Infrared spectra were obtained using a Thermo Scientific Nicolet 6700 FT-IR spectrometer. Electrospray ionization mass spectra (ESI-MS) were obtained using an Agilent 1000 series MSD VL spectrometer. Product analysis for the conversion of alkene to cyclic carbonate was performed using an Agilent technologies 6890N network Gas Chromatography (GC) system and equipped with Agilent technologies 5975 inert XL mass selective detector. Ultraviolet–visible spectra (UV–vis) were recorded using a Varian Cary 5000 UV–vis–NIR spectrophotometer. Cyclic voltammetry was conducted using Pine Bipotentiostat and following a conventional three electrode method. An Ag/AgCl reference electrode was used for the measurement. Elemental analysis was performed at the Midwest Microlab LLC, Indianapolis, USA.

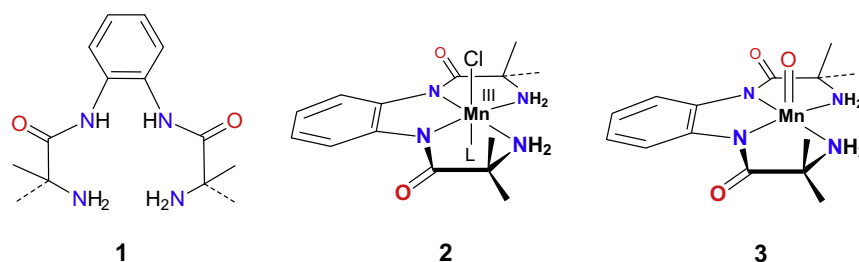


Fig. 1. Structure of the amido-amine ligand (1), manganese(III) (2) (L = Cl, 2a; L = methanol, 2b) and manganese(V)-oxo (3) complexes used in this study. Note: For simplicity charges and counter ions are omitted for 2 and 3; when L = solvent (methanol), 2 is neutral.

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