



Original article

Appended corrole manganese complexes: Catalysis and axial-ligand effect



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ABSTRACT

A series of *N*-base appended corroles and their manganese complexes were synthesized and their binding constants with three different nitrogenous ligands, triethylamine, *N*-methylimidazole and pyridine, were evaluated by spectroscopy. Kinetic studies indicated that the presence of appended *N*-donor ligands may cause a significant enhancement of the rate of oxygen atom transfers (OAT) from (oxo)manganese(V) corrole to alkene, and the stronger axial ligand binding has impact on the rate of the oxidation reaction. Turnover frequency (TOF) for the catalytic oxidation of alkenes by appended manganese corroles varies with the following ligand order: acetamido < pyridyl < imidazolyl. The influence of the external axial ligands on the catalytic epoxidation was investigated by using appended acetamido manganese corrole as catalyst, with the results revealing that *N*-methylimidazole gave the best enhancement on the yields of total oxidation products among the investigated nitrogenous ligands.

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1. Introduction

Corrole is a ring-contracted porphyrin analog having one direct pyrrole–pyrrole link [1]. It represents a distinctive family of macrocyclic compounds with unique structural, chemical, and photophysical properties [2–5]. Unlike porphyrin [6], corrole contains three protons in the inner core of the ring which renders it a tri-anionic ligand capable of stabilizing metals in high oxidation states [7]. This feature is mainly responsible for metallocorroles acting as potent catalysts in a variety of chemical reactions, such as epoxidation, cyclopropanation, asymmetric sulfoxidation, aziridination, and oxygen atom transfer reactions [8].

Manganese complexes of corroles and related macrocycles are typically employed in various oxygenation reactions to get insights into the reaction mechanism owing to their efficiency and specificity [8–12]. Manganese corroles are found to be effective catalysts for selective epoxidation of olefins at less-substituted double bond [13], as well as selective oxidation of unactivated C–H bonds in alkanes

[14]. It has recently been reported that mild and room temperature oxidation of electron rich alcohols to carbonyl compounds may be achieved through manganese corroles bearing electronegative substituents [15]. Significantly less attention, however, has been paid to the catalytic effects of axial ligation in metallomacrocycles. The catalytic activity and selectivity of metalloporphyrins and related transition metal complexes in biomimetic oxidation of cytochrome P-450 is substantially affected by the fifth coordination [16]. The *N*-donor axial ligands are the most common ones used in the metalloporphyrin catalyzed oxidation systems. Importantly, the rate of oxidation reactions catalyzed by metalloporphyrins could be strongly enhanced by the addition of an axial ligand, such as pyridine or imidazole bases [17,18]. For asymmetric epoxidation, addition of axial ligands to catalytic reaction systems is a convenient and efficient way to enhance enantioselectivity [19,20]. Metalloporphyrins with covalently linked axial ligand “tails” are often used in the biomimetic modeling [21]. The use of a covalently linked axial ligand may avoid the problem of exogenous ligand oxidation competing with the substrate oxidation. Despite the significant effect of axial ligation in metalloporphyrin catalyzed systems, similar investigations on metallocorroles are scarce, and to the best of our knowledge, only one such report is found in the literature [22] and, in addition, no report exists for the catalysis by ligand-appended metallocorroles. Herein, we wish to report the synthesis of

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manganese corroles with covalently attached nitrogenous ligands and their catalytic activities. The catalytic epoxidation of alkenes revealed that the presence of appended *N*-donor ligands will significantly enhance the rate of OAT from (oxo)manganese(V) corroles to alkenes.

2. Experimental

The appended corroles were prepared as shown in Scheme 1 starting from 5-(pentafluorophenyl)-dipyrromethane **1** [23]. The *trans*-*A*₂*B* corroles **2** and **3** were prepared by our previously reported procedure [24]. The synthetic detail, including synthesis, characterization and catalysis data, are given in Supporting information.

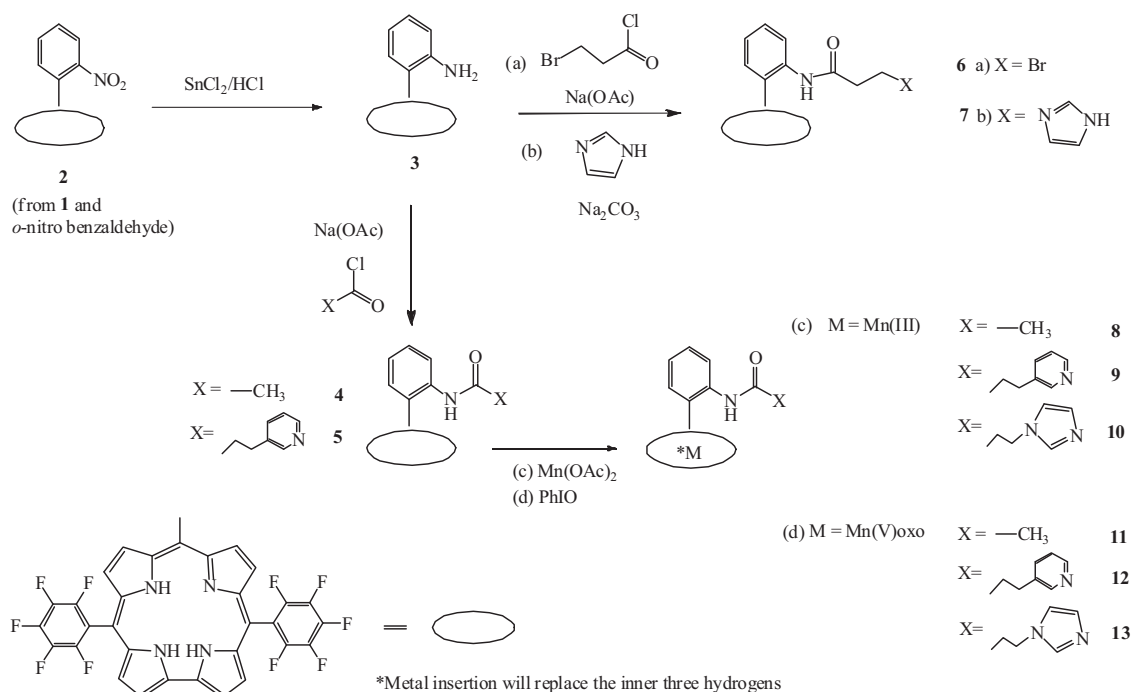
3. Results and discussion

All synthesized appended corroles and their manganese complexes were characterized by spectroscopic methods. The Soret-band of appended manganese corroles **8**, **9** and **10** appeared at about 400 nm and 420 nm (Fig. S1 in Supporting information), while the Q-band of **9**, **10** exhibited a significant red shift due to the coordination between the tailed, appended ligand and the manganese. The most definitive difference upon appended ligand coordination is the dramatic increase in the absorbance at about 490 nm.

Axial ligation exerts a profound effect on the physicochemical properties of metalloporphyrins similar to metalloporphyrins [19,20]. The spectral changes in manganese(III) corrole **8** on addition of *N*-methylimidazole is shown in Fig. S2 in Supporting information. Excellent isosbestic points were observed, indicating a clean transformation of **8** to its axial coordinated product. Quantitative analysis of the spectroscopic titration data revealed that **8** formed a 1:1 complex with *N*-methylimidazole, and the binding constant was found to be 1.87×10^4 L/mol. The complexes **9** and **10** also formed a 1:1 complex with *N*-methylimidazole, but their binding constants were two orders of magnitude less than that of **8**. This is due to the coordination between the appended nitrogenous ligand and the core metal in **9** and **10**. The binding constants between Mn(III) corrole and *N*-methylimidazole follows the order

$K_b\mathbf{8} > K_b\mathbf{9} > K_b\mathbf{10}$ (Table S1 in Supporting information). The binding constant for pyridine and **8** is 19.4 L/mol, which is comparable to the binding between pyridine and corrole (OMC)Mn [25] (where OMC = octamethylcorrole). The binding between pyridine and **9**, **10** was too weak to be measured reliably. The binding constant for triethylamine and **8**, **9** was determined to be 1.08×10^2 L/mol and 2.20 L/mol, respectively, and the binding between triethylamine and **10** was too weak to be measured. It is obvious that these appended manganese(III) corroles exhibit good binding tendency with *N*-methylimidazole among the examined *N*-donor ligands, and the binding ability of triethylamine is stronger than pyridine. Manganese(III) corroles are generally four-coordinated, as in the case of the complex **8**, where the coordination of acetamido-ligand is not possible with the manganese center. However, complex **8** will turn to five-coordinated state in the presence of the external axial ligand. The presence of the appended ligand in complexes **9** and **10** will increase the coordination number from four to five, and only one nitrogenous ligand can coordinate with Mn(III) to form a maximum of five-coordinated complex.

High valent (oxo)manganese(V) corroles are the active oxidants in the catalytic cycle of manganese corroles-catalyzed oxidation reactions of alkenes [13,26] and sulfides [27]. In order to investigate the effects of a tailed axial ligand on the reactivity of the (oxo)manganese(V) corroles, we prepared (oxo)manganese(V) corroles **11**, **12** and **13** by using PhIO as oxidant [26] and performed kinetic studies on their reactions with styrenes. The UV–vis spectra of these (oxo)manganese(V) corroles resemble those found in literatures [8,27]. At room temperature, these metal-oxo species decompose gradually and eventually return to the corresponding manganese(III) corroles as indicated by UV–vis data. Addition of styrene can significantly speed up the reduction of these (oxo)manganese corroles. The UV–vis changes of **11** upon mixing with styrene in CH₂Cl₂ is shown in Fig. S3 in Supporting information. With excess styrene, the reactions followed *pseudo*-first order kinetics. The rate constants (k_{obs}) and the *pseudo*-first order reaction activation energy (E_A) of the OAT can be derived according to the rate law and Arrhenius equation. The rate



Scheme 1. Synthesis of appended free base corroles and their manganese complexes.

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