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Recent developments and perspectives in the ruthenium-catalyzed olefin epoxidation

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1. Introduction

Olefin epoxidation constitute one of the key transformations in synthetic organic chemistry. Extreme reactivity makes these highly strained cyclic ethers important intermediates in carbon–carbon as well as carbon-hetero atom bond-forming reactions in pharmaceutical,[1] agrochemical and perfume industry[2] as well as in natural product synthesis.[3] Nucleophilic opening of epoxide provides an easy pathway for nucleophile addition across a double bond. Many naturally occurring epoxides exhibit important biological properties.[4] Transition metal catalyzed epoxidation received considerable interest since epoxidation using common oxidants like peroxy acids, organic peroxides, iodoso reagents, amine oxides, periodates etc. are found to be more selective and productive in the presence of these catalytic systems. Sharpless asymmetric epoxidation using titanium tartrate complexes forms the best known example.[5] Ruthenium complexes constituted a major area of epoxidation catalysts which showed remarkable developments in the last few decades.[6] The developments in the field of homogeneous ruthenium-catalyzed epoxidations have been well reviewed up to 2009.[7] Heterogeneous ruthenium-catalyzed epoxidation is also an inevitable area which also witnessed significant achievements in which catalyst developments involved skillful derivatization, immobilization etc. of the already reported homogeneous catalysts. This review combines developments in both homogeneous (from 2009 to 2015) and heterogeneous (from 1998 to 2015) ruthenium-catalyzed epoxidations.

2. Ruthenium complexes as epoxidation catalysts

Like all other transition metals, ruthenium also possesses easily interchangeable multiple number of oxidation states. This property makes the metal capable of facile ligand exchange or substitution in the complexed state providing easy accessibility for metal-oxo species, the key intermediate in olefin epoxidation which plays the role of oxygen donor to alkenes making valuable catalysts. Homogeneous ruthenium complexes with ligands such as porphyrin,[8] polypyridyl,[9] Schiff base,[10] oxazoline,[11] pyrazolyl[12] etc. formed a vast range of ruthenium-catalyzed epoxidation catalysts. Heterogeneous catalysis which is a more economical mode also made valuable contributions. Heterogenization of ruthenium complexes was always found to be challenging since strategies were needed which maintain the properties of ligands such as lability, enantiopurity or even relative orientation which have significant effect on reactivity, enantioselectivity, regioselectivity or chemoselectivity of the epoxidations. Anchoring of the catalyst on to a polymer was one of the strategies available which only required either of the ligands to contain a reactive functional group or a polymerizable moiety. Immobilization of catalysts in channels of highly porous materials like zeolites or molecular sieves was another efficient method in which characteristic pore sizes provided shape selectivity also.

2.1. Ligand-based ruthenium(II)-catalyzed epoxidations

2.1.1. Ruthenium complexes with N_4-coordination environment

2.1.1.1. Ruthenium porphyrin complexes.

a) Encapsulated or supported ruthenium porphyrin complexes

The developments in porphyrin based metal catalysts were mainly inspired by a wide variety of metalloporphyrins found in nature which catalyze highly selective biological transformations. These reactions make use of multiple numbers of redox reactions happening at the metal centre which are stabilized and maintained by the porphyrin ligand. One of the earliest reports available on the ruthenium-porphyrin catalyzed epoxidation of alkenes was by Quinn et al. in 1985 where a dioxo(tetramesity1porphyrinato) ruthenium(VI) complex, [Ru(TMP)(O)$_2$] was found to catalyze the epoxidation of alkenes using oxygen as the oxidant.[13] In 1998, Liu et al. introduced a new heterogeneous epoxidation catalyst Ru/M-41(m) **1** by immobilizing ruthenium *meso*-tetrakis (2,6-dichlorophenyl)porphyrin complex, (Ru^{II}(TDCPP)(CO)(EtOH)) **3** in (3-aminopropyl)triethoxysilane modified MCM-41 molecular sieves (APTES-MCM-41m) **2** (Fig. 1) which are found to catalyze epoxidations stereospecifically in good yields.[14]

Encapsulation was performed by stirring **2** with **3** for one hour in dichloromethane (DCM). The catalytic activity of the complex was explored for a few alkenes using 2,6-dichloropyridine-*N*-oxide(Cl_2pyNO),**4** as the oxidant (Scheme 1).

Excellent to moderate yields were observed in epoxidation of a variety of alkenes. The catalyst has provided complete stereospecific transformation in the case of *cis*-alkenes whereas found to be inactive towards *trans*-alkenes. Epoxidation of (+)-limonene furnished about 61% of 8,9-epoxide along with *cis*- and *trans*-1,2-epoxides in yields of 27% and 10%, respectively. While 3,4,6-tri-*O*-

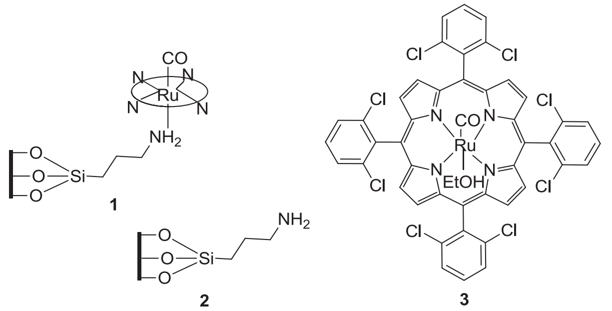

Fig. 1. Ruthenium-porphyrin complex **1** obtained by ligand substitution in **3** with **2**. Reproduced with permission from *J. Org. Chem.* **1998**, *63*, 7364–7369.