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Bioinspired Mn-aminopyridine catalyzed epoxidations of olefins with various oxidants: Enantioselectivity and mechanism

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ABSTRACT

This mini-review summarizes the progress in the asymmetric epoxidation of olefins in the presence of manganese aminopyridine complexes, achieved in the last decade. The major breakthroughs in catalyst design, that eventually led to the emergence of highly enantioselective (> 99% *ee*) and efficient (> 1000 TON) catalysts, are discussed. The mechanistic studies carried out in recent years are given particular attention.

1. Introduction

The asymmetric epoxidation of olefins is one of most important oxidative transformations in organic chemistry since the resulting scalemic epoxides are considered as useful building blocks and intermediates for the fine chemical and pharmaceutical industries [1,2]. Catalyst systems based on transition metal complexes have been hitherto regarded as the most prominent catalysts, capable to carry out this challenging reaction with high efficiency and enantioselectivity transformation [2–6]. Since the milestone discoveries of Katsuki [7], and of Jacobsen [8], manganese-salen complexes have attracted great attention as asymmetric epoxidation catalysts [9]. A new era of Mn-catalyzed epoxidations commenced in 2003, when Stack and co-workers discovered Mn-bpmen (**1a**) and Mn-bpmcn (**2a**) complexes containing tetradentate C_2-symmetrical aminopyridine ligands (Fig. 1) to efficiently catalyze epoxidation of terminal alkenes with peracetic acid [10]. Subsequently, this area expanded greatly; various modifications of the Stack's ligand system were reported, most of them were successfully applied to enantioselective olefin epoxidations with environmentally benign and atom-economic oxidant – hydrogen peroxide. Besides H_2O_2, other oxidants, such as peracids, alkyl hydroperoxides and iodosylarenes, were tested and showed noticeable promise in asymmetric epoxidations. Mn aminopyridine complexes captured significant attention and was periodically reviewed in recent years [3–14].

In spite of extensive catalytic studies, the mechanisms of epoxidations on Mn aminopyridine complexes are insufficiently explored, apparently due to the broad variety of available oxidation states for manganese (II–VII), high reactivity of the catalytically active sites and hence their low steady-state concentration, entailing difficulties in their direct spectroscopic observation. The present account demonstrates the achievements of manganese aminopyridine complexes as catalysts for asymmetric epoxidations, with particular focus on the recent advances in the mechanistic investigations of those catalyst systems.

2. Asymmetric epoxidations of olefins catalyzed by Mn aminopyridine complexes

While in the earliest communication only two catalytically active Mn aminopyridine complexes were presented [10], in subsequent contribution Stack and co-workers screened nineteen Mn(II) complexes as catalysts in the epoxidation of 1-octene with peracetic acid [15]. As compared to the known salen [8], Me_4cyclam [16], tpa [17], terpyridine and bipyridine ligands, originally designed Mn-bpmcn (**2a**) demonstrated the highest

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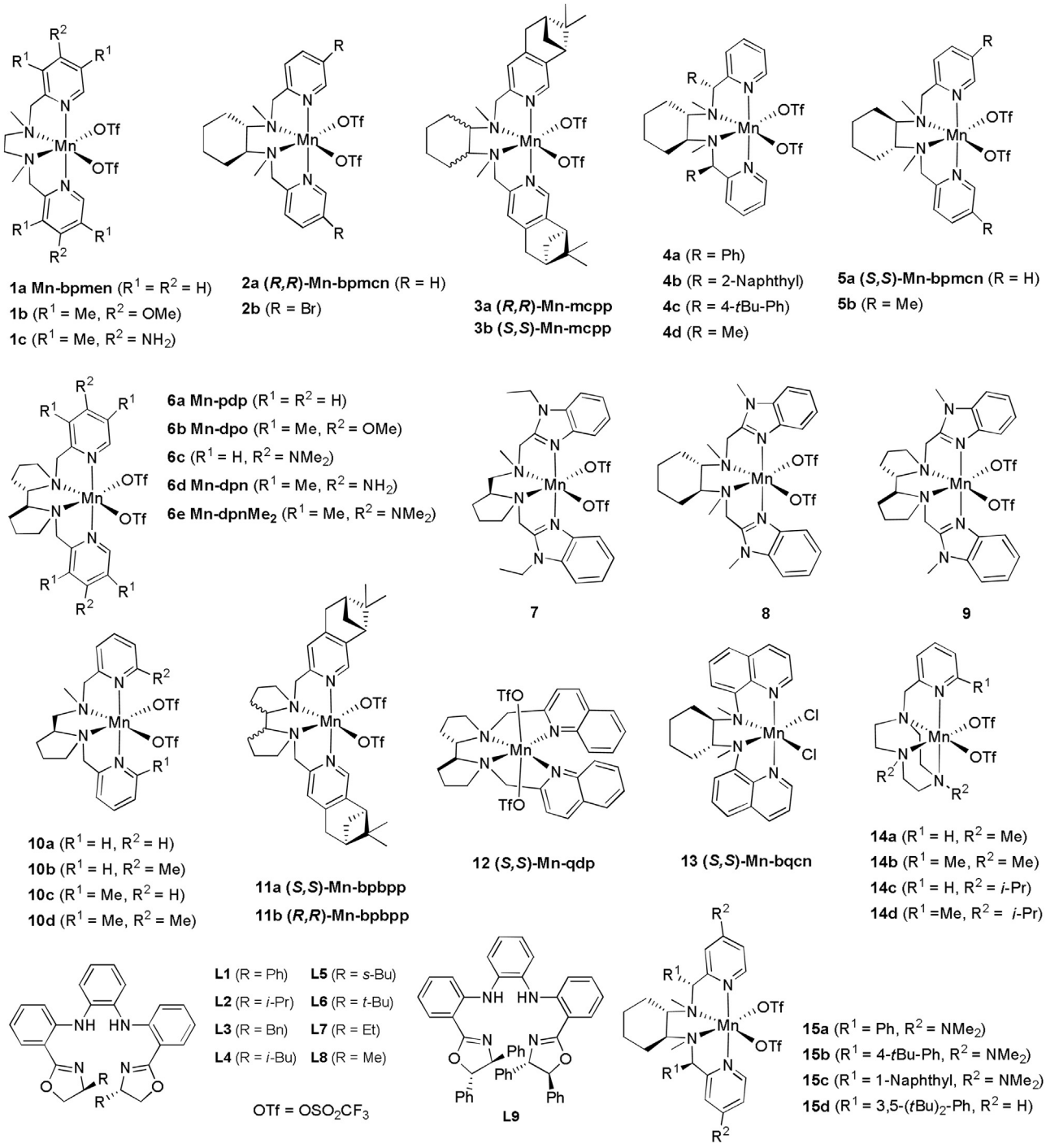

Fig. 1. Structures of aminopyridine and related manganese(II) complexes [10,18–23,25–30,33,34,55,57] and ligands [31,32].

efficiency, achieving over 900 TON over 5 min and giving 1-octene oxide in 92% yield [15]. The first example of asymmetric epoxidations on these Mn aminopyridine catalysts (with peracetic acid as terminal oxidant) came from Costas and co-workers, who synthesized (*R*,*R*)-Mn-mcpp (**3a**) and (*S*,*S*)-Mn-mcpp (**3b**) complexes containing pinene rings fused to the 4 and 5 positions of the two pyridine moieties of the parent mcp ligand (Fig. 1) [18]. Several olefins were tested as substrates, and the highest asymmetric induction was documented in styrene epoxidation (46% *ee* at 0 °C, TON = 200, Table 1, entry 2) on catalyst **3b**.

In 2009 Sun and co-workers contributed a novel family of manganese(II) complexes **4a–4c** (Fig. 1), with tetradentate *N*-donor ligands featuring with 1,2-diamino-cyclohexane backbone with two additional centers of chirality [19]. Catalysts **4a–4c** efficiently epoxidized (1 mol% catalyst loading, TON up to 100) various unfunctionalized olefins (with up to 46% *ee*, see Table 1, entry 5) and substituted chalcones (with up to 89% *ee*) with hydrogen peroxide (6 equiv.) in the presence of 5 equiv. of additive – acetic acid. More recently, Abdi with co-workers contributed a Mn-bpmcn (**2a**) related complex **4d** (Fig. 1) which the authors tested in epoxidations of various olefins with hydrogen peroxide in the presence of acetic acid [20]. The catalyst exhibited rather high efficiencies (TON = 800–1000) and moderate to good enantioselectivities (43–88% *ee*).