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Review

Tris(pyrazol-1-yl)methane metal complexes for catalytic mild oxidative functionalizations of alkanes, alkenes and ketones

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ABSTRACT

This work concerns recent advances (since 2005) in the oxidative functionalization of alkanes, alkenes and ketones, under mild conditions, catalyzed by homoscorpionate tris(pyrazol-1-yl)methane metal complexes. The main types of such homogeneous or supported catalysts are classified, and the critical analysis of the most efficient catalytic systems in the different reactions is presented. These reactions include the mild oxidation of alkanes (typically cyclohexane as a model substrate) with hydrogen peroxide (into alkyl hydroperoxides, alcohols, and ketones), the hydrocarboxylation of gaseous alkanes (with carbon monoxide and potassium peroxodisulfate) into the corresponding C_{n+1} carboxylic acids, as well as the epoxidation of alkenes and the Baeyer–Villiger oxidation of linear and cyclic ketones with hydrogen peroxide into the corresponding esters and lactones. Effects of various reaction parameters are highlighted and the preferable requirements for a prospective homogeneous or supported C-scorpionate-M-based catalyst in oxidative transformations of those substrates are identified.

Abbreviations: AC, activated carbon; acac, acetylacetonate; aq., aqueous; BPO, benzoyl peroxide; bpy, bipyridine; bqdi, *o*-benzoquinonediimine; BV, Baeyer–Villiger; CNT, carbon nanotubes; CX, carbon xerogel; CyH, cycloalkane or cyclohexane; DCE, 1,2-dichloroethane; dmgly, *N*,*N*-dimethylglycinate; dmpa, *N*,*N*-dimethylpicolylamine; GC, gas chromatography; H_2(gma), glyoxal-bis(2-mercaptoanil); HIDA, *N*-hydroxyiminodiacetic acid; HIDPA, *N*-hydroxyimino-2,2-dipropionic acid; HMT, hexamethylenetetramine; Hpca, pyrazinecarboxylic acid; ILs, ionic liquids; mCPBA, *m*-chloroperoxybenzoic acid; MOR, mordenite; PDMS, polydimethylsiloxane membrane; PTA, 1,3,5-triaza-7-phosphaadamantane; pz, pyrazolyl; r.t., room temperature; TBHP, *tert*-butylhydroperoxide; tea, triethanolamine; TFA, trifluoroacetic acid; TOF, turnover frequency; TON, turnover number; UHP, urea-hydrogen peroxide adduct.

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1. Introduction

Metal complex-catalyzed oxidation reactions are quantitatively the most important homogeneously catalyzed reactions in chemical industry [1–4]. In recent years, much work has been dedicated to the search for efficient, selective, environmentally benign and economic catalytic oxidation processes [5–7] toward a sustainable development of chemical processes.

The use of metallic complexes with C-scorpionate poly(pyrazol-1-yl)methane ligands as catalysts is experiencing significant development [8–13] and was included in a few reviews appearing up to 2005 [10–12]. A more recent article [13] is dedicated to metal complexes with heteroscorpionate ligands based on the bis(pyrazol-1-yl)methane moiety and their catalytic applications, mainly polymerization reactions. In a complementary way, the current review focuses on *tris*- rather than on *bis*-(pyrazol-1-yl)methane complexes and on different types of catalysis.

It is believed that the interchange between bidentate and tridentate coordination modes of poly(pyrazol-1-yl)methane ligands (on the basis of the meaning of the usual *scorpionate* designation, Fig. 1 for tris(pyrazol-1-yl)methanes), is at the core of the structural and chemical versatility of many metal complexes of this kind and is essential for their catalytic applications.

The present review mainly concerns the significant advances in the last years on the use in oxidation catalysis of transition metal complexes containing homoscorpionate tris(pyrazol-1-yl)methane ligands RC(R′pz)$_3$ (pz = pyrazolyl; R = H or substituent at the methine carbon; R′ = H or substituent at the pz ring), as well as the pyrazole (Hpz) derivatives formed by reaction of such C-scorpionates. Partial oxidation of light saturated hydrocarbons is a field which remains underexplored due to their considerable inertness, in spite of constituting huge potential carbon stocks on earth [14–25]. Their conversion into added value functionalized products, under mild conditions and using environmentally benign oxidants, is still a serious challenge. Tris(pyrazol-1-yl)methane complexes have already been successfully applied as catalyst or catalyst precursors for relevant alkane oxidation reactions, namely peroxidative oxygenations, *i.e.*, with peroxides (usually hydrogen peroxide) to give alcohols and ketones, and carboxylations to produce carboxylic acids. The latter are not typical oxidation reactions since they also involve C—C bond formation, but they are also mentioned on account of their synthetic interest. All these types of alkane reaction are promising toward the eventual exploration of alkanes as unconventional starting materials for synthesis.

The epoxidation of alkenes catalyzed by tris(pyrazol-1-yl)methane complexes, an important synthetic reaction for both commodity and fine chemicals [1–7], is also discussed, as well as the application of this class of metal complexes as catalysts (or catalysts precursors) for the Baeyer–Villiger (BV) oxidations, *viz.*, the transformation of cyclic and acyclic ketones into lactones and esters, respectively, which has also become an important research topic in the last years due to the wide applications of the products [26–29].

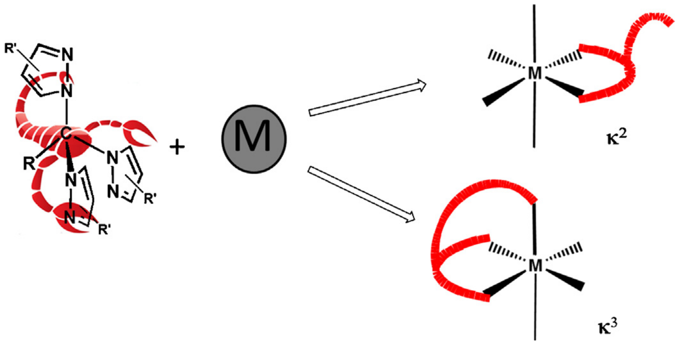
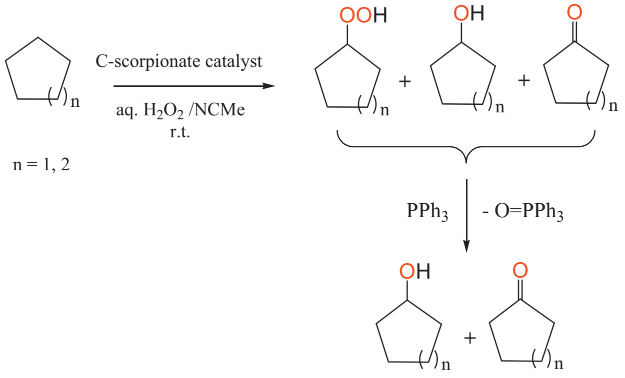


Fig. 1. Schematic structure of tris(pyrazol-1-yl)methanes and their coordination modes and comparison with a scorpion and its attack on a prey.



Scheme 1. Oxidation of cycloalkanes to cycloalkanols and cycloalkanones catalyzed by tris(pyrazol-1-yl)methane metal complexes.

The review mainly deals with homogeneous catalytic systems, but supported catalysts are also included. The immobilization of a metal scorpionate catalyst (or catalyst precursor) on an inert support (*e.g.*, zeolite, silica or carbon material) is a suitable procedure to combine the advantages of homogeneous and heterogeneous catalysis.

The scorpionate catalysts or catalyst precursors and the reactions they catalyze, as well as the substrates and products, are summarized in Table 1, and the molecular structures of such complexes are shown in Fig. 2.

2. Homogeneous oxidations of alkanes

Strategies for efficient and highly selective single-pot oxidative functionalization of alkanes (typically the cyclic ones) to the corresponding alkanols and alkanones have been reported by using catalytic systems based on transition metal complexes with tris(pyrazol-1-yl)methane-type scorpionates, as discussed below for the types of oxidants applied.

2.1. With hydrogen peroxide

The C-scorpionate ligands, bearing three pyrazolyl moieties, easily change their denticity during the reaction since they can undergo partial decoordination upon protonation in the commonly used acidic medium (with generation of unsaturated metal centers). They (*via* their N and/or O atoms) can also assist proton-transfer steps that are believed (see below the mechanistic discussion) to be involved in key processes (such as the metal-promoted generation of the hydroxyl radical from H_2O_2) thus promoting the observed catalytic behavior of their complexes in water/NCMe medium. These may also be the reasons why the catalytic activities of the tris(pyrazol-1-yl)methane complexes are rather higher [30–36] than those exhibited by the corresponding metal salts. Moreover, in some cases, they form water soluble complexes, favoring the use of an aqueous reaction medium.

Tris(pyrazol-1-yl)methane complexes of V(III, IV or V), Fe(II), Cu(II), Re(III or VII) and Au(III) (Fig. 2) exhibit catalytic ability for the peroxidative oxidation of cyclohexane (and cyclopentane in the cases tested) to give, in a single-pot, the corresponding alcohols and ketones (final products) *via* formation of the cycloalkyl hydroperoxide (primary product) according to Schemes 1 and 2 (see below, at the end of this section, mechanistic considerations). The organohydroperoxide (ROOH) is often present in the final reaction solution, mixed with the alcohol and the ketone. The formation