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Title: Stereospecific sp<sup>3</sup> C–H Oxidation with *m*-CPBA: a Co<sup>III</sup> Schiff Base Complex as Pre-catalyst vs. its Co<sup>III</sup>Cd<sup>II</sup> Heterometallic Derivative

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Stereospecific sp<sup>3</sup> C–H Oxidation with *m*-CPBA: a Co<sup>III</sup> Schiff Base Complex as Pre-catalyst vs. its Co<sup>III</sup>Cd<sup>II</sup> Heterometallic Derivative

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Graphical Abstract



#### Highlights

- Co<sup>III</sup> and Co<sup>III</sup>/Cd<sup>II</sup> Schiff base complexes catalyse stereospecific hydroxylation of *cis*-1,2-dimethylcyclohexane with *m*-CPBA in the presence of an acidic promoter.
- The heterometallic Co<sup>III</sup>/Cd<sup>II</sup> complex is considerably more active than the homometallic Co<sup>III</sup> one exhibiting higher yields of products and excellent stereospecificity.
- The acidity of the promoter is crucial for achievement of high catalytic activity.
- Catalytic systems have been studied by isotopic labelling, kinetic isotope effects and radical trap experiments.

#### Abstract

The mono- and binuclear Schiff base complexes [CoL<sub>3</sub>]·DMF (1) and [CoCdL<sub>3</sub>Cl<sub>2</sub>]·0.5H<sub>2</sub>O (2) were facilely synthesized using zerovalent cobalt and cadmium chloride (for 2) as starting materials and the pre-formed pro-ligand HL (2-methoxy-6-[(methylimino)methyl]phenol, the product of condensation of *o*-vanillin and methylamine) in air. The compounds were characterized by single crystal X-ray diffraction analysis and spectroscopic methods in solution and in the solid state. Both complexes demonstrate a profound catalytic activity in the stereoselective oxidation of cis-1,2dimethylcyclohexane (model substrate) with *m*-CPBA (*m*-chloroperbenzoic acid) under mild conditions in the presence of promoters of various acidity (HNO<sub>3</sub>, TFA and HOAc). The heterometallic binuclear Co<sup>III</sup>Cd<sup>II</sup> pre-catalyst (2) was more active than the mononuclear Co<sup>III</sup> one (1), exhibiting higher products yields up to 51% and excellent stereospecificity (up to 99.2%) retention of stereoconfiguration). This result could be associated with a synergistic effect of two different metals in **2**. Based on the large obtained kinetic isotope effect and H<sub>2</sub><sup>18</sup>O labelling studies. the overall reaction mechanism was proposed to proceed without the participation of free alkyl radicals. The acidity of the promoter was shown to influence catalytic parameters for both 1 and 2 so that the better parameters are achieved with the acid possessing lower  $pK_a$  values (a stronger acid). The comparison of the catalytic behaviours of 1 and 2 is discussed in detail considering relevant examples from the literature.

**Keywords:** homogeneous catalysis, stereoselective C-H oxidation, *m*-chloroperbenzoic acid, metal complex catalysis, <sup>18</sup>O isotopic labelling

#### 1. Introduction

Oxidation of inactivated sp<sup>3</sup> C–H bonds that is routinely carried out in biology remains a formidable challenge in chemistry [1, 2]. In spite of impressive efficiency of natural enzymes such as cytochrome P450 [3, 4] Rieske dioxygenase [5] or methane monooxygenase (MMO) [6], which have ability to insert oxygen into C–H bonds with exciting selectivity under ambient conditions [5, 7], examples of man-made sp<sup>3</sup> C–H oxidation catalytic systems with selectivities comparable to those of the natural systems are limited [8-10]. The explanation is that strong activators (e.g. oxidizing agents) and specific conditions are needed to overcome the inert character of very strong, nonpolar bonds. The application of such methods often requires laborious isolation procedures with subsequent purification of desired isomers and shows low regio-, stereo- and/or chemoselectivities. Therefore, catalysts, which are able to perform selective functionalization of alkanes C–H bonds under mild reaction conditions, are highly desired.

Complexes of transition metals proved to be efficient catalysts for a broad range of organic reactions, including direct C–H functionalization [11, 12]. Further, the use of catalysts comprising dissimilar metal ions (heterometallic complexes) may offer advantages over the homometallic catalytic systems [13, 14]. Metals of different kinds may participate in the same catalytic cycle, thus enhancing the catalytic activity (*synergistic effect*) [13, 14]. The second metal can also play an indirect role by influencing the redox potential of the main catalytic centre or changing its coordination preferences, as it happens, for instance, in the Ca/Mn active centre of the photosystem II and its models [15, 16].

While considerable efforts have been made towards alkane oxidation using homometallic complexes as catalysts, the catalytic properties of heterometallic compounds in these reactions received significantly less attention. Ligands having N,O-donor sites, such as aminoalcohols, are attractive for the construction of polynuclear heterometallic compounds [12, 17] and, among them, Schiff bases occupy special place due to their rich structural diversity [18]. It has been shown that Schiff base complexes serve as efficient catalysts in a wide range of reactions [12, 18, 19]. Earlier we reported a pronounced catalytic activity of monometallic Schiff base complexes of copper, manganese and iron in the mild alkanes C–H bonds oxidation [20-22]. The catalytic activity of heterometallic Cu/Fe and Co/Fe Schiff base complexes in the same reaction was found to be considerably higher [23, 24] and, moreover, in the latter case the activity was associated to heterometallic species  $[Co_2Fe(Sae)_4]^+$  (H<sub>2</sub>Sae = salicylidene-2-ethanolamine), illustrating a synergistic effect of two different metals [24].

Recently, we reported the catalytic activity of an isoindole-based Co complex in the mild oxidation of alkanes that proceeds with pronounced stereoselectivity when m-chloroperbenzoic acid (m-CPBA) is used as an oxidant [25]. In the search for understanding of the origin of stereoselectivity of the C-H bonds oxidation governed by the catalytically active metal complex, we have now explored the catalytic behaviour of two related  $Co^{III}$  complexes,  $[CoL_3] \cdot DMF$  (1) and (2)  $[CoCdL_3Cl_2] \cdot 0.5H_2O$ with Schiff (HL a base ligand \_ 2-methoxy-6-[(methylimino)methyl]phenol, Scheme 1; DMF - N,N-dimethylformamide) in alkanes oxidation reactions. It should be noted that heterometallic systems for alkane oxidation with m-CPBA are virtually unknown and the effects of acidic or basic promoters on the catalytic performance have not been studied yet.

The title compounds 1 and 2 have been synthesized as part of our ongoing research on transition metal complexes of Schiff base ligands aimed at preparing compounds of various nuclearity and structures with diverse potential applications. In these studies, we successfully apply *direct synthesis* of coordination compounds based on a spontaneous self-assembly, in which one of the metals is introduced as a powder (zerovalent state) and oxidized by aerial dioxygen during the synthesis [23, 26-30]. In continuing our research line, herein we report the synthesis and catalytic activity of mononuclear complex 1 and binuclear heterometallic compound 2, in the stereoselective hydroxylation of *cis*-1,2-dimethylcyclohexane (*cis*-1,2-DMCH) with *m*-CPBA as oxidant using different acidic promoting agents under mild conditions.

#### 2. Experimental

2-Hydroxy-3-methoxy-benzaldehyde (*o*-Vanillin) was purchased from Aldrich and used as received. All other chemicals were purchased from local suppliers and used without additional treatment. All synthetic experiments were carried out in air. Elemental analyses for CHN were provided by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm<sup>-1</sup>) were recorded using a BX-FT IR Perkin Elmer instrument in KBr pellets. The <sup>1</sup>H NMR spectra of **1**, **2** and HL in DMSO-*d*<sub>6</sub> were measured at room temperature using a Mercury 400 Varian spectrometer at 400 MHz. The chemical shift ( $\delta$ ) values in ppm are referenced to internal Me<sub>4</sub>S; the coupling constants (*J*) are given in Hz. ESI–MS(±) spectra were run on a LCQ Fleet mass spectrometer equipped with an electrospray (ESI) ion source (Thermo Scientifc), using ca. 10<sup>-5</sup> M solutions of **1** and **2** in acetonitrile. The pro-ligand HL was synthesized according to a slightly modified reported procedure [31]. In the syntheses, the condensation reaction between *o*-vanillin and CH<sub>3</sub>NH<sub>2</sub>·HCl was utilized without isolation of the resulting Schiff base.

#### 2.1. Synthesis of CoL<sub>3</sub>·DMF (1)

*o*-Vanillin (0.3 g, 2.0 mmol) in methanol (10 mL) was stirred with CH<sub>3</sub>NH<sub>2</sub>·HCl (0.14 g, 2.0 mmol) and dimethylaminoethanol (0.1 mL) in a 50 mL conical flask at 333 K for 30 min. SnCl<sub>2</sub>·2H<sub>2</sub>O (0.23 g, 1.0 mmol) dissolved in 10 mL DMF and Co powder (0.06 g, 1.0 mmol) were added to the resulting yellow solution of the Schiff base, and the mixture gradually turned green-brown as it was stirred magnetically at 333 K until dissolution of the cobalt powder was observed (1.5 h). (Total dissolution of the metal powder was not achieved due to adhesion of a small fraction of the metal particles to the stirring bar.) The resultant brown solution was filtered and left to stand at room temperature. Dark brown needles of **1** were formed by the following day. They were filtered off, washed with methanol and dried in air. Yield (based on Co): 74%. Anal. Calcd for C<sub>30</sub>H<sub>37</sub>CoN<sub>4</sub>O<sub>7</sub> (624.56): C 57.69, H 5.97, N 8.97%. Found: C 57.45, H 5.72, N 8.93%.

#### 2.2. Synthesis of $CoCdL_3Cl_2 \cdot 0.5H_2O(2)$

*o*-Vanillin (0.23 g, 1.5 mmol) in 10 mL ethanol was stirred with CH<sub>3</sub>NH<sub>2</sub>·HCl (0.10 g, 1.5 mmol) and dimethylaminoethanol (0.1 mL) in a 50 mL conical flask at 333 K for 30 min. CdCl<sub>2</sub>·2.5H<sub>2</sub>O (0.11 g, 0.5 mmol) dissolved in 5 mL ethanol was added to the resulting yellow solution of the Schiff base, and the solution was stirred magnetically at 333 K for 30 min. After that, Co powder (0.03 g, 0.5 mmol) was added to the flask and the mixture that gradually turned brown was stirred until dissolution of the cobalt powder was observed (1.3 h). (Total dissolution of the metal powder was not achieved due to adhesion of a small fraction of the metal particles to the stirring bar.) The resultant brown solution was filtered and left to stand at room temperature. Dark brown-green prisms of **2** were formed by the following day. They were filtered off, washed with ethanol and dried in air. More product was obtained from the mother liquor upon slow evaporation in air for several days. Yield: 63%. Anal. Calcd for C<sub>27</sub>H<sub>31</sub>CdCl<sub>2</sub>CoN<sub>3</sub>O<sub>6.50</sub> (743.78): C 43.60, H 4.20, N 5.65%. Found: C 43.31, H 4.26, N 5.34%.

#### 2.3. Single-crystal X-ray diffraction

Crystallographic data for **1** and **2** were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer fitted with Cu K $\alpha$  radiation. Following analytical absorption corrections and solution by direct methods, the structures were refined against  $F^2$  with full-matrix least-squares using the program SHELXL-2014 [32]. The non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms in both structures were introduced at calculated positions and refined using of a riding model with isotropic displacement parameters based on those of the parent atom. The site occupancy of the solvent water molecule in **2** was constrained to 0.5 after trial

refinement. CCDC 1566104 (1) and 1566105 (2) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Crystal data for 1: C<sub>30</sub>H<sub>37</sub>CoN<sub>4</sub>O<sub>7</sub>, M = 624.56, orthorhombic, *Pna*2<sub>1</sub>, *a* = 13.5398(7) Å, *b* = 10.8076(6) Å, *c* = 20.0218(11) Å, *V* = 2929.8(3) Å<sup>3</sup>, T = 100(2) K, *Z* = 4, 26041 reflections measured, 4304 independent reflections ( $R_{int} = 0.1116$ ),  $R_1 = 0.0500$ ,  $wR_2 = 0.1130$  [ $I > 2\sigma(I$ ]], GoF = 1.029, absolute structure parameter -0.038(5).

Crystal data for **2**: C<sub>27</sub>H<sub>31</sub>CdCl<sub>2</sub>CoN<sub>3</sub>O<sub>6.50</sub>, M = 743.78, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 14.090(2) Å, *b* = 16.887(2) Å, *c* = 13.179(2) Å,  $\beta$  = 110.804(2)°, *V* = 2931.3(7) Å<sup>3</sup>, T = 100(2) K, *Z* = 4, 14806 reflections measured, 5209 independent reflections (*R*<sub>int</sub> = 0.0793), *R*<sub>1</sub> = 0.0654, *wR*<sub>2</sub> = 0.1529 [*I* > 2 $\sigma$ (*I*)], GoF = 1.060.

#### 2.4. Alkanes catalytic oxidation

Typically, the reactions were carried out in thermostated cylindrical vials under vigorous stirring in open air. At first, 0.9–2.1 mg of solid pre-catalyst **1** or **2** was weighed into the reaction flask, then 3.4 or 3.5 mL of CH<sub>3</sub>CN, 0.5 mL of CH<sub>3</sub>NO<sub>2</sub> stock solution (internal standard; 1 mL of CH<sub>3</sub>NO<sub>2</sub> mixed with 9 mL of CH<sub>3</sub>CN), 2.1–50  $\mu$ L of promoting agent (HNO<sub>3</sub>, HOAc and TFA were used as aqueous solutions or used in a form of stock solutions in acetonitrile) and 70  $\mu$ L of *cis*-1,2-dimethylcyclohexane (*cis*-1,2-DMCH) were added. When solid adamantane (68 mg) was used as substrate, it was added into the vial before the addition of CH<sub>3</sub>CN. Then, the solution of *m*-chloroperbenzoic acid (*m*-CPBA) in CH<sub>3</sub>CN (30 mg in 1 mL of acetonitrile) was prepared and it was dropwise added to a warm (40 °C) solution of organic compounds with *m*-chloroperbenzoic acid at elevated temperatures may be explosive!). The total volume of the reaction solution was 5 mL. According to developed methods [33], obtained samples were quenched at r. t. with excess of solid PPh<sub>3</sub> and directly analyzed by GC and GC-MS. The index of the retention of stereoconfiguration (RC) was calculated considering that the commercial substrate, *cis*-1,2-dimethylcyclohexane, contained 0.86% of *trans*-isomer.

#### 2.5. Gas Chromatography

A Perkin-Elmer Clarus 600 gas chromatograph equipped with two non-polar capillary columns (SGE BPX5; 30 m × 0.32 mm × 25  $\mu$ m), one having an EI-MS (electron impact) detector and the other one with a FID detector, was used for analyses of the reaction mixtures. The following GC sequence has been used: 50 °C (3 min), 50–120 °C (8 degrees per minute), 120–300 °C (35 degrees

per minute), 300 °C (3.11 min), 20 min total run time; 200 °C injector temperature. For analysis of oxidation products of highly-boiling compounds, such as adamantane, different conditioning was employed: 50 °C (3 min), 50–150 °C (30 degrees per minute), 150–300 °C (14 degrees per minute), 300 °C (2.95 min), 20 min total run time; 200 °C injector temperature. Helium was used as the carrier gas with a constant 1 mL per minute flow. All EI–MS spectra were recorded with 70 eV energy.

#### 2.6. GC–MS

The identification of peaks at chromatograms was made by comparison of respective EI massspectra with those from the NIST v.2.2 database. The mass-spectra patterns of some products (tertiary *cis*- and *trans*-1,2-dimethylcyclohexanoles) were not found in the NIST database, and identification of these products was made by comparing with the reported previously mass-spectra [34].

#### 3. Results and discussion

#### 3.1. Synthesis and IR spectra

The reaction of *o*-vanillin and CH<sub>3</sub>NH<sub>2</sub>·HCl in ethanol in the presence of dimethylaminoethanol produces a yellow coloured solution of the Schiff base HL. The heterometallic complex **2** was readily prepared by interaction of cobalt powder, cadmium chloride and ethanol solution of the preformed HL in the  $Co^0$  : CdCl<sub>2</sub> : HL = 1 : 1 : 3 mole ratio. The dissolution of the metal powder is easily achieved under moderate heading and stirring of the reaction mixture in open air. Earlier, we have shown that oxidation of zerovalent metal in ligand solution and formation of its coordination compound are stipulated by the presence of a proton-donating species and O<sub>2</sub> from the air, which is reduced to give H<sub>2</sub>O [35]. This approach of using zerovalent metal as an initial reagent was further developed into a synthetic scheme to prepare heterometallic compounds [26]. However, in the attempt to obtain a Co/Sn heterometallic complex, the pure Co(III) compound **1** was isolated instead.

The infrared spectra of **1** and **2** are very informative and show similar patterns (Figure S1). The presence of adsorbed or lattice water molecules can be detected by the intense broad bands centred at about 3440 cm<sup>-1</sup> in both spectra. Several bands observed above and below 3000 cm<sup>-1</sup> are assigned to aromatic =C-H and alkyl -C-H stretching, respectively. The characteristic v(C=N) absorption of the Schiff base which appears at 1634 cm<sup>-1</sup> as a strong intense band in the IR spectrum of HL (Figure S1), is detected at 1632 (**1**) and 1628 (**2**) cm<sup>-1</sup>. A number of sharp and intense peaks are found in the aromatic ring stretching (1600–1400 cm<sup>-1</sup>) and C-H out-of-plane

bending regions (800–700 cm<sup>-1</sup>) of both complexes. A sharp intense band at 1664 cm<sup>-1</sup> in the IR spectrum of **1** corresponds to the C=O stretching frequency of DMF.

#### 3.2. Structural Description

The cobalt(III) complex **1** is built of discrete CoL<sub>3</sub> molecules and DMF molecules of crystallization. The molecule of **1** is chiral and has no crystallographically imposed symmetry (Figure 1). There are two pairs of enantiomers in every crystal cell. The ligand moieties are deprotonated at the phenol O atom and octahedrally coordinate the Co(III) atom through the three azomethine N and three phenolate O atoms in a *mer* configuration. As can be seen in Figure 1 viewed along the pseudo-3-fold axis, two of the ligands are pointed 'up' and one 'down'. Three crystallographically non-equivalent salicylaldimine ligands have Co–O and Co–N bond lengths in the ranges 1.881(4)–1.913(4) and 1.932(5)–1.936(5), respectively, with average Co–O and Co–N bond lengths being of 1.893 and 1.934 Å, respectively (Table S1). The *trans* angles at the metal atom vary from 172.0(2) to 176.7(2), the *cis* angles are equal to 84.9(2)–94.1(2)° (Table S1). The geometrical parameters of **1** are similar to those of isomorphous CoL<sub>3</sub>. THF (CSD refcode WEQTES) with the same ligand [36]. In the solid state, CoL<sub>3</sub> molecules form layers in the *ab* plane divided by the DMF molecules (Figure S2). Interactions between complex molecules are weak, the closest Co…Co intermolecular separation exceeds 7.08 Å. No  $\pi$ – $\pi$  stacking is observed.

In the heterometallic molecule of **2**, the Co atom retains its octahedral coordination by three deprotonated Schiff base ligands with almost the same geometric parameters: Co–O and Co–N bond lengths are in the ranges 1.876(6)-1.921(6) and 1.938(7)-1.948(7) Å, respectively; the *trans* angles at the metal atom vary from 172.0(2) to 176.7(2), the *cis* angles are equal to  $84.9(2)-94.1(2)^{\circ}$  (Figure 2, Table S2). The cadmium atom has two quite short bonds with the phenolato oxygen atoms, O(11) and O(31) [2.291(6), 2.218(6) Å], of the two deprotonated Schiff bases and two longer bonding distances to the chlorine atoms [Cl1: 2.417(2), Cl2: 2.391(2) Å] in a distorted tetrahedral geometry. The angles at the metal atom vary from 66.4(2) to 130.29(16) (Table S2). In addition, Cd(1) is weakly bonded to the oxygen atom O(12) at 2.724(7) Å, which implies that the Cd(1) coordination sphere approximates an irregular square pyramid with Cl(1) atom in the apex. The  $\mu$ -phenolato-bridges between metal centers result in the cobalt-cadmium separation of 3.315(2) Å.

The dinuclear units show no significant intermolecular interactions in the solid state. Numerous C– $H\cdots$ Cl contacts in the crystal lattice of **2** with the H $\cdots$ Cl distances of above 2.68 Å should arise

from van der Waals close packing. Oxygen atom of the water solvent molecule, O1, appears to act as a donor to Cl2 atom as evidenced by the O···Cl distance of about 3.20(1) Å.

#### 3.3. Characterization of 1 and 2 in solution by NMR and ESI Mass Spectrometry

The diamagnetic nature of Co(III) complexes is helpful in their characterization by NMR spectroscopy. The data on the room temperature <sup>1</sup>H NMR spectra of 1, 2 and HL in DMSO- $d_6$ (Figure S3) are summarized in Table 1 with proton labels as shown in Scheme 1. Assignments of the signals in the spectra of 1 and 2 were made by comparison with the respective signals in the spectrum of the pro-ligand interpreted before [31]. The mer arrangement of the three deprotonated bidentate Schiff bases around the cobalt(III) centre in 1 causes asymmetry of all three ligands. The <sup>1</sup>H NMR spectrum of complex **1** shows the presence of three different ligand environments, thus confirming retention of the mer-octahedral geometry of Co(III) in DMSO solution. The -CH=Nprotons of the deprotonated Schiff base ligands appear as three singlets in a 1:1:1 ratio at  $\delta$  7.94, 7.79 and 7.46 ppm in its spectrum. Nine CH<sub>3</sub>O and nine CH<sub>3</sub> protons are seen at two different positions each at  $\delta$  3.62, 3.54 and 3.21, 3.19 ppm, respectively, in a 1 : 2 ratio. Nine protons of the rings are observed as four doublets, a triplet and a multiplet in the range 6.91–6.24 ppm due to three chemically different aromatic rings. The spectrum of 2 is very similar to that of 1 and contains the same set of signals in the 8 to 2.5 ppm region. A definite conclusion on possible dissociation of the heterometallic molecule in DMSO cannot be made due to the fact that cadmium coordination to phenolato O atoms has a negligible effect on the remaining protons of the aromatic rings while the metal contact to the methoxo oxygen atom O12 is too long.

Electrospray ionization mass spectrometry (ESI-MS) was used as a powerful tool for speciation analysis of **1** and **2** in solution. The investigation of diluted (ca.  $1 \times 10^{-5}$  M) solutions of the complexes in acetonitrile showed that the behaviours of the mono- (**1**) and binuclear (**2**) compounds clearly differ. The most intense peak in the spectra of both compounds was recognized as  $[(Co^{III}L_3)_2Na]^+$  at m/z = 1125. Two other intense peaks in the spectrum of **2** correspond to  $[Co^{III}L_2]^+$ and  $[Co^{III}L_3]^+$  species at m/z = 387 and 556, respectively. The same species are found in the spectrum of **1**, however, with considerably lower intensities.  $[Co^{III}L_3Na]^+$  is present in both spectra at 383 m/z. A transformation process for **1** proceeds further revealing decomposition of the initial Schiff base ligand and possible reduction of  $Co^{III}$  ions:  $[Co^{III}(o-Van-H)_3Co^{II}(o-Van-H)(o-Van)]^+$  at m/z = 934 and  $[Co^{II}(o-Van-H)_2Na]^+$  at 383 m/z (o-Van is o-vanillin; o-Van-H is deprotonated ovanillin) show 30 and 20% peak intensities, respectively. Three species at m/z = 700, 1308 and 1434 in the spectrum of **2** were assigned to heterometallic particles  $[Co^{III}L_3CdCl]^+$ ,  $[(Co^{III}L_3)_2CdCl_2Na]^+$ 

and  $[(Co^{III}L_3)_2Cd_2Cl_3]^+$ , respectively. Not seen for **1**, the species at 166 and 937 *m/z* in the spectrum of **2** were identified as the free ligand,  $[(HL)H]^+$ , and  $[Co^{III}_2L_5]^+$ , respectively. Both spectra also show numerous peaks within a 100–160 *m/z* range with low intensities. The data obtained support existence of the mono- and binuclear cores of **1** and **2** in CH<sub>3</sub>CN solution and also reveal the presence of remarkable aggregation processes. Formation of larger particles is particularly evident in the case of heterometallic **2**.

It should be stressed, however, that metal ions and metal complexes might undergo gas-phase ligand replacement and intramolecular charge transfer reactions under the ESI-MS conditions. Therefore, the structure may be altered during the ESI process and the original species information is lost [37, 38].

#### 3.4. Alkanes catalytic oxidation with m-chloroperbenzoic acid

#### 3.4.1. General observations.

Oxidation of *cis*-1,2-dimethylcyclohexane (*cis*-1,2-DMCH) is a catalytic process which can be successfully used as a model reaction to study the bond and stereoselectivities of the catalytic C–H activation systems [12, 39-41]. Compounds **1** and **2** were investigated as pre-catalysts for the stereospecific oxidation of *cis*-1,2-dimethylcyclohexane with *m*-chloroperbenzoic acid using different acids as promoting agents (Scheme 2). To reduce the overoxidation effects we used a 3.7 excess of alkane substrate relative to the oxidant in all the tests. No alkane oxidation products (or only traces) were obtained in the absence of the pre-catalysts. The main observed reaction product of the studied reaction was the tertiary 3° *cis*-alcohol (tertiary alcohol having the methyl groups in *cis* position to each other). The by-products, tertiary 3° *trans*-alcohol and ketones that appeared from the activation of 2° C–H bonds of *cis*-1,2-DMCH, were also detected. As known in similar situations [25, 42], ketones usually result from overoxidation of secondary alcohols. Hence, it is assumed that in the present case the formation of the ketones occurs *via* the subsequent oxidation of alcohols and not by direct C–H bonds oxidation of the alkane (this assumption is in agreement with cyclohexane oxidation curves, see below).

Promoting agents can have a strong influence on the oxidation process [12]. The role of a strong protic acid, such as nitric acid, can be associated to the stabilization of transition states of metal catalysts or to the creation of an unsaturated coordination environment around the metal. Nitric and trifluoroacetic (TFA) acids are recognized promoters for efficient oxidations of alkanes with  $H_2O_2$  [12]. A weaker carboxylic acid, such as acetic acid (HOAc), can serve as a co-catalyst in the same type of reactions which can proceed with high stereoselectivity. In these cases, HOAc facilitates the

HVMO (high-valent metal-oxo) species formation under the carboxylic-acid-assisted mechanism [5, 43]. Therefore, in this study the influence of three typical acid promoters of various acidities, namely nitric, acetic and trifluoroacetic acids, was investigated.

The accumulations of the tertiary *cis*-alcohols with time upon *cis*-1,2-DMCH oxidation with *m*-chloroperbenzoic acid in the presence of pre-catalysts **1** and **2** and acidic promoters, are shown in Figures S4–S6. For nitric acid, two concentrations of the pre-catalysts have been tested. For **1**, the maximum observed initial reaction rates  $W_0$  are almost equal in both studied concentrations of **1**, being of  $8.7 \times 10^{-5}$  and  $8.9 \times 10^{-5}$  M s<sup>-1</sup> for [**1**]<sub>0</sub> of  $2.9 \times 10^{-4}$  and  $5.4 \times 10^{-4}$  M, respectively, providing the TOF (turnover frequency) values of 1080 and 593 h<sup>-1</sup>. For **2**, the following parameters have been obtained:  $W_0 = 3.8 \times 10^{-5}$  M s<sup>-1</sup> (TOF = 507 h<sup>-1</sup>) for [**2**]<sub>0</sub> =  $2.7 \times 10^{-4}$  M and  $W_0 = 1.5 \times 10^{-4}$  M s<sup>-1</sup> (TOF = 964 h<sup>-1</sup>) for [**2**]<sub>0</sub> =  $5.6 \times 10^{-4}$  M. Considering the observed yields and stereoselectivities (see the Supporting Info), the lower concentrations of the pre-catalysts showed better performance and were used through all the following tests.

Nitric acid is the most efficient promoter (Figure 3), affording the *cis/trans* ratios of 59 and 78 for **1** and **2**, respectively (after 1 h). Notably, the latter corresponds to 99.2% retention of stereoconfiguration (RC index, see the Experimental part for details), accounting for an almost absolute stereospecificity of the  $2/HNO_3$  heterometallic catalytic system. The products yields are also higher when the pre-catalyst **2** is used (36 and 51% for **1** and **2**, respectively). In both systems with **1** and **2** the yields of chlorobenzene by-product do not exceed 0.6% (Figure 3).

The catalytic systems containing TFA and HOAc promoters appear to be much less efficient (Figures 3, S7 and S8), showing the highest yield up to 26% (2/HOAc system) with the maximum *cis/trans* ratio of 9 (1/TFA system). Moreover, these systems yield elevated amounts of chlorobenzene by-product up to 14% for 2/HOAc (compare with 0.4 and 0.6% for 1/HNO<sub>3</sub> and 2/HNO<sub>3</sub> systems, respectively).

The highest normalized bond selectivity  $3^\circ$ :  $2^\circ$  of 40 was observed for the 2/HNO<sub>3</sub> system (Table 2). When using TFA and HOAc, the bond selectivity becomes lower with the lowest value of 25 for 1/HOAc catalytic system.

The catalytic systems containing TFA and HOAc promoters appear to be much less efficient (Figures 3, S7 and S8), showing the highest yield up to 26% (2/HOAc system) with the highest *cis/trans* ratio of 9 (1/TFA system). At the same time, these systems yield elevated amounts of chlorobenzene by-product up to 14% for 2/HOAc (compare with 0.4 and 0.6% for 1/HNO<sub>3</sub> and 2/HNO<sub>3</sub> systems, respectively).

The highest normalized bond selectivity  $3^\circ$ :  $2^\circ$  of 40 was observed for the 2/HNO<sub>3</sub> system (Table 2). When using TFA and HOAc, the bond selectivity becomes lower with the lowest value of 25 for 1/HOAc catalytic system.

#### 3.4.2. Chlorobenzene formation kinetics during cis-1,2-DMCH oxidation.

Chlorobenzene is a side product of oxidations with *m*-CPBA that results from the decarboxylation of the *m*-chlorobenzoate radical, a typical intermediate [44, 45]. The rate of this decarboxylation is known to be high (*ca.*  $10^6 \text{ s}^{-1}$ ) and comparable to those for H atom abstraction processes [44, 46]. The *m*-chlorobenzoate radical is formed through homolytic *m*-CPBA O–O bond splitting and is related to a free radical process, which is less selective than metal-mediated ones [8]. Chlorobenzene was considered an indicator for a contribution of low-selective reaction mechanisms when using *m*-CPBA [25, 47-49]. Similar oxidants, such as peroxyphenylacetic acid produce toluene instead of chlorobenzene in the same radical decarboxylation [50, 51]. Hence, we were interested in finding possible correlations between accumulation of chlorobenzene and overall selectivity of the catalytic system.

In the reactions of oxidation of cycloalkanes with *m*-chloroperbenzoic acid catalysed by compounds of cobalt [52], nickel [48, 49, 53] and ruthenium [54] with pyridylalkylamine ligands, the high amounts of formed chlorobenzene (over 40% based on the oxidant) suggested significant involvement of the homolytic O–O splitting pathway in the respective oxidation processes, what is reflected by a low ratio of tertiary : secondary bond selectivity of 5 : 1 (for methylcyclohexane) [48]. Much lower amounts of chlorobenzene (up to 3.3%) were observed when using cobalt isoindole complex as a catalyst, in the absence of any promoter [25]. In the latter case, pronounced stereo- and bond selectivities were observed.

The accumulations of chlorobenzene (Figures 3, S10 and S11) for the case of HNO<sub>3</sub> promoter show similar amounts of chlorobenzene (up to 0.6%) for both **1** and **2**, with the respective reaction rates  $W_0$  PhCl of  $4.3 \times 10^{-7}$  and  $6.0 \times 10^{-7}$  M s<sup>-1</sup>, respectively. Considering the yield of tertiary *cis*-alcohols of up to 51% and assuming that the principal pathway of the reaction occurs through the heterolysis of the *m*-CPBA O–O bond, one can estimate the ratio between heterolysis and homolysis processes as *ca*. 85 : 1. For TFA and HOAc promoters, much higher concentrations of chlorobenzene were observed (Figure 3). The initial reaction rates  $W_0$  PhCl corresponding to the systems **1**/TFA, **1**/HOAc, **2**/TFA and **2**/HOAc, *i.e.*  $3.2 \times 10^{-6}$ ,  $9.5 \times 10^{-6}$ ,  $3.7 \times 10^{-6}$  and  $5.7 \times 10^{-6}$  M s<sup>-1</sup>, respectively, are higher than those for **1**/HNO<sub>3</sub> and **2**/HNO<sub>3</sub>.

The plot of the *cis/trans* ratio *vs.* yield of chlorobenzene in *cis*-1,2-DMCH oxidation, observed after 90 min, is depicted in Figure 4, top. For each pre-catalyst, the higher chlorobenzene amounts correspond to lower stereoselectivity. In general, although pre-catalyst **2** produces larger amounts of chlorobenzene with TFA and HOAc promoters with the same *cis/trans* ratio as **1**, the nitric acid promoter is more efficient with the heterometallic complex **2**. The  $W_0$  PhCl values built as a function of the acidity parameter  $pK_a$  (Figure 4, bottom; 8.80, 12.65 and 23.51  $pK_a$  values [55] were used for HNO<sub>3</sub>, TFA and HOAc, respectively) show a linear dependence for complex **1** and a non-linear for **2**. The nearly equal initial formation rates  $W_0$  PhCl for **1** and **2** when using HNO<sub>3</sub> or TFA promoters suggest that the chlorobenzene formation kinetics depends more on the acidity of the pre-catalyst affords a higher reaction rate of chlorobenzene formation (Figure S12). The latter observation points out that chlorobenzene forms through metal-catalysed processes, rather than in the metal-free transformation of *m*-CPBA.

#### 3.4.3. Adamantane oxidation.

Both  $1/\text{HNO}_3$  and  $2/\text{HNO}_3$  systems afford higher yields of products in the adamantane oxidation with *m*-chloroperbenzoic acid than those for *cis*-1,2-DMCH, namely 68 ( $W_0 = 7.9 \times 10^{-5} \text{ M s}^{-1}$ ) and 65% ( $4.2 \times 10^{-5} \text{ M s}^{-1}$ ) for **1** and **2**, respectively (after 1 h) (Figure S9). 1-Adamantanol is the main product, as illustrated by the 3° : 2° bond normalized selectivities of 22 : 1 (**1**) and 23 : 1 (**2**). These values are close to those obtained for *cis*-1,2-dimethylcyclohexane oxidation (Table 2). Chlorobenzene amounts are *ca*. twice lower than those found in systems with *cis*-1,2-DMCH, showing 0.3% yields for both **1** and **2**. For secondary products, low alcohol/ketone (A/K) ratios varying from 0.5 to 1.6 are observed for both pre-catalysts.

Formation of *N*-(1-adamantyl)acetamide by-product was revealed in adamantane oxidation (Scheme 3). The amounts of this by-product are comparable to those of adamantane-1,3-diol (Figure S15). Earlier, the formation of low quantities of *N*-(1-adamantyl)acetamide was detected in the adamantane oxidation catalysed by the isoindole cobalt complex and using *m*-CPBA as an oxidant in the absence of promoting agent [25]. *N*-(1-adamantyl)acetamide can be prepared through the interaction of hydroxylated or halogenated adamantane with acetonitrile in the presence of acids, nitrosium salts and some other reagents [56]. Direct formation of *N*-(1-adamantyl)acetamide from alkane (adamantane) is known, but typically requires harsh conditions [56] and/or expensive reagents [57, 58]. We presume that in our case the formation of *N*-(1-adamantyl)acetamide proceeds *via* the Ritter type reaction and may involve 1-adamantanel as an intermediate. The absence of

amidated products in the adamantane oxidation with  $H_2O_2$  under similar conditions (a copper complex as catalyst, HNO<sub>3</sub> promoter, acetonitrile solvent) [21] suggests that the nature of the catalyst and the application of *m*-CPBA as oxidizing agent are essential.

#### 3.4.4. Kinetic isotope effect and <sup>18</sup>O labelling tests.

To gain a greater insight into the performance of  $1/\text{HNO}_3$  and  $2/\text{HNO}_3$  catalytic systems, the competitive oxidation reactions with equimolar mixtures of deuterated and normal cyclohexanes (0.05 M each) in the presence of <sup>18</sup>O labelled water (1 M) was performed. The accumulations of all four products (normal and deuterated cyclohexanols and cyclohexanones) are depicted in Figure 5. An overall shape of the accumulation curves is typical for the consecutive reactions  $C_6H_{12} \rightarrow C_6H_{11}OH \rightarrow C_6H_{10}=O$  (A $\rightarrow$ B $\rightarrow$ C type). The initial periods of kinetic curves, where total accumulations ( $C_6H_{11}OH + C_6H_{10}=O$ ) obey a linear law, were fitted to equations [59]

$$B(t) = \frac{A_0 k_1 \left( e^{-k_1 t} - e^{-k_2 t} \right)}{k_2 - k_1} \quad C(t) = A_0 \left( 1 - \frac{k_2 e^{-k_1 t}}{k_2 - k_1} - \frac{k_1 e^{-k_2 t}}{k_1 - k_2} \right)$$

where B(t) and C(t) are concentrations of cyclohexanol and cyclohexanone after reaction time t, and  $A_0$  is the initial concentration of cyclohexane (constants  $k_1$  and  $k_2$  correspond to  $A \rightarrow B$  and  $B \rightarrow C$  reactions, respectively). It was found, that in all cases alcohols are oxidized much faster than initial alkanes, as evidenced by  $k_2/k_1$  ratios varying from 34 to 145. This explains low alcohol/ketone (A/K) ratios between 0.27 and 1.44, observed at 90 min time. Thus, a correct value of KIE (kinetic isotope effect) should be determined from the ratio of  $k_{1H}/k_{1D}$  constants, but not from simple measuring of  $C_6H_{11}OH$  and  $C_6D_{11}OH$  concentrations at some point. Using the  $k_{1H}/k_{1D}$  method, the KIE values were found to be 5.7(3) and 6.2(2) for 1 and 2, respectively. Considering the estimated standard deviations, one may assume that the KIE values for both complexes are equal. Such high values of KIE are comparable to those observed for the systems operating *via* iron and ruthenium high-valent metal-oxo (HVMO) C–H attacking species [60], and suggest that the H atom abstraction could be among the rate determining steps [61].

The mean incorporations of oxygen from  $H_2^{18}O$  in the normal and deuterated cyclohexanols are 2.0(1) and 2.9(1.4)% for **1** and 3.5(2) and 2.9(3)% for **2** for C<sub>6</sub>H<sub>11</sub>OH and C<sub>6</sub>D<sub>11</sub>OH, respectively. The main difference between the pre-catalysts lies in the <sup>18</sup>O incorporation into normal alcohol, which is almost twice higher for **2**, giving larger amounts of <sup>18</sup>O-labelled normal alcohol (Figure 6).

As the reaction samples were quenched with Ph<sub>3</sub>P, which readily reacts with ROOH peroxides [33] and HVMO species [62] to form Ph<sub>3</sub>P=O in the following ways:

 $ROOH + Ph_3P \rightarrow ROH + Ph_3P=O$  $M^n=O + Ph_3P \rightarrow M^{n-2} + Ph_3P=O$ 

it was interesting to see whether <sup>18</sup>O oxygen appears in Ph<sub>3</sub>P=O. The phosphine oxide contained up to 53 and 42% of <sup>18</sup>O for **1** and **2**, respectively (at 90 min), showing gradual accumulations of <sup>18</sup>O with time (Figure S13). A blank test revealed that Ph<sub>3</sub>P=O does not exchange oxygen with H<sub>2</sub><sup>18</sup>O in acetonitrile when HNO<sub>3</sub> promoter was used. Formation of large portions of Ph<sub>3</sub>P=<sup>18</sup>O is expected for catalytic systems that function *via* a free radicals pathway, when Ph<sub>3</sub>P reduces labelled hydroperoxide, such as cyclohexyl hydroperoxide C<sub>6</sub>H<sub>11</sub><sup>18</sup>O<sup>18</sup>OH [63-67]. However, the free radical systems are not expected to transfer <sup>18</sup>O from H<sub>2</sub><sup>18</sup>O to alkyl hydroperoxides and, moreover, no traces of C<sub>6</sub>H<sub>11</sub>OOH were detected in the GCMS chromatograms in the present case [68].

A gradual accumulation of  $Ph_3P=^{18}O$  over time (Figure S13) accounts for the existing of some <sup>18</sup>Ocontaining species, which concentration increases with time. This can be due to formation of catalytic <sup>18</sup>O-labelled intermediates as well as a non-catalytic oxygen exchange. Considering the growth of <sup>18</sup>O incorporation into  $Ph_3P=O$  during the time period up to 90 min, while the oxidation reaction stops after 20 mins, the version of a non-catalytic oxygen exchange looks more reasonable. However, the nature of this exchange and the species responsible for  $Ph_3P=O$  labelling were not identified. No <sup>18</sup>O-labelled *m*-chlorobenzoic acid was detected, while peracids are known [69] not to exchange oxygen with water (a blank test confirmed the absence of such an oxygen exchange). Finally, a different character of the <sup>18</sup>O accumulations into the alcohols (low level, nearly constant) and  $Ph_3P=O$  (high level, continuous growth) implies different pathways of <sup>18</sup>O appearance in the respective products.

Formation of the chlorocyclohexane by-product was observed for both  $1/\text{HNO}_3$  and  $2/\text{HNO}_3$  catalytic systems, both for deuterated and normal cyclohexane substrates (Figure 7). The amount of chlorinated normal cyclohexane ( $C_6H_{11}$ Cl) is sufficient for its detection as a regular peak in the chromatogram, while that of  $C_6D_{11}$ Cl is considerably lower and can be detected only by a targeted search for its mass-spectrum (Figures 7, S16). From the fact that both deuterated and normal chlorination by-products were detected, one may rule out the reduction of chlorobenzene as a source of chlorocyclohexane. Further, as chlorocyclohexane was detected for complex 1, which does not contain chloride anions in its structure, *m*-CPBA (or its derivatives, *m*-chlorobenzoic acid and chlorobenzene) is the single origin of chlorine in the chlorocyclohexanes. Similar observations were made earlier [25]. A possible explanation could be that the C–Cl bond splits at the stage of

chlorobenzene radical formation (see below; Scheme 4) releasing the chlorine radical Cl• which further attacks cyclohexane or its short-lived alkyl radical to give chlorocyclohexane.

The KIE values found for **1** and **2** lie in the range observed for other catalysts in reactions of alkanes oxidation with *m*-CPBA (Table 3), being close to porphyrin complexes of iron (**4b**; at low temperature), and porphyrin (**5**) and isoindole (**3**) complexes of cobalt. Cobalt perchlorate **8** also exhibits a rather high KIE of 8 (Table 3), although with low yields of products (ca. 1%) based on the substrates [42]. Compounds of iron are proposed mostly to oxidize alkanes through high-valent metal-oxo (HVMO) intermediates of Fe(IV) or Fe(V), showing the KIE with values around 3.5 (Table 3). Complexes of ruthenium **9** and **10**, for which participation of Ru(IV)=O intermediates is proposed, also show KIE of the same magnitude. There are, however, exceptions such as the Fe(IV) complex **22**, which exhibits KIE of 25 during the stoichiometric oxidation (Table 3). Remarkably, the incorporations of oxygen from H<sub>2</sub><sup>18</sup>O into the hydroxylation products span over a wider range.

#### 3.4.5. Radical trap experiments.

To establish the involvement of the alkyl radicals into *cis*-1,2-DMCH oxidation, we used a radical trap, CBrCl<sub>3</sub>, to see how it influences the catalytic activity. The catalytic system 2/HNO<sub>3</sub> that showed the highest stereoselectivity among the systems tested (cis/trans = 87 at 90 min, Figure S5), was chosen for this test. When the reaction was initiated with addition of 0.1 M of CBrCl<sub>3</sub> (1 equiv. relative to substrate), the *cis/trans* ratio dropped to 24 (after 90 min) and the yield of tertiary alcohols decreased to 10% based on the cis-1,2-DMCH (compare to 53% of 3° alcohols in the system without addition of CBrCl<sub>3</sub>). Several by-products were observed, some of them presumably being chlorinated and brominated cis-1,2-DMCH according to their mass-spectra. The peaks I and II (Figure 8) can be tentatively assigned to Cl and ClBr derivatives of the alkane substrate based on the characteristic peaks near 146 and 111 m/z in the respective EI mass spectra (Figures S17 and S18). The strong peaks III–V with similar mass spectra (Figures S19–S21) were identified as brominated derivatives of *cis*-1,2-dimethylcyclohexane [25]. Peak VI also looks like a Cl-derivative (see a typical pattern at 145 m/z, Figure S22). Peak VII is recognized as 8-hydroxy-octanone, and although the reference spectrum reveals differences from that of VII (Figure S23), one could assign this peak to a halogen-free product. Detection of 1-bromo-3-chlorobenzene is in agreement with the presence of *m*-chlorobenzyl radicals, formed through the decarboxylation of *m*-chlorobenzoate ones [44]. However, the CBrCl<sub>3</sub> trap was found to react with PPh<sub>3</sub> to form CHCl<sub>3</sub> and CHBrCl<sub>2</sub> (Figure 8, inset), where hydrogen probably comes from the alkane. Both CHCl<sub>3</sub> and CHBrCl<sub>2</sub> were found only at trace levels when the samples were injected before PPh<sub>3</sub> addition. The possibility of spontaneous reaction between PPh<sub>3</sub> and CBrCl<sub>3</sub> while passing through a hot (200 °C) GC injector is

ruled out because CBrCl<sub>3</sub> reacts with PPh<sub>3</sub> rather slowly requiring at least 20 min of treatment at room temperature for complete disappearance of the CBrCl<sub>3</sub> peak (Figure S25).

The observation that CBrCl<sub>3</sub> is able to induce a metal-free oxidation and halogenation of *cis*-1,2-DMCH (in open air) was unexpected. The test performed in the absence of **2** and *m*-CPBA revealed notable amounts of tertiary alcohols and Br-derivatives at the beginning of the reaction, then leading to Cl- and Br-derivatives as the main products (Figure 8). If the cyclohexane substrate was used, no alkane functionalization products were detected. It is well known that the energy of C–Br bond in CBrCl<sub>3</sub> is rather low (55.3 kcal mol<sup>-1</sup>) [85] and the bond undergoes homolysis under sunlight or heating to form highly reactive Br• and Cl<sub>3</sub>C• radicals [85]. The latter easily react with alkyl radicals and alkanes themselves. We assume that these processes take place in the metal-free *cis*-1,2-DMCH/HNO<sub>3</sub>/CBrCl<sub>3</sub>/O<sub>2</sub> system. Considering the great similarity between the patterns of halogenated products **I–VI** in the cases of metal/oxidant-free and **2**/*m*-CPBA systems (Figure 8), we believe that in the latter case the halogenated products are formed through a metal-free pathway, while the tertiary *cis*-alcohol and 1-bromo-3-chlorobenzene come from the metal-catalysed route. Hence, the radical trap (CBrCl<sub>3</sub>) competes with the main pathway of the reaction in the **2**/HNO<sub>3</sub>/*m*-CPBA system rather than interferes with it. Nevertheless, it can be suggested that the alkyl and *m*-chlorobenzyl radicals are present in the catalytic mixtures.

#### 3.4.6. Discussion.

Coordination of *m*-CPBA or peroxyphenylacetic acid (PPAA) to a coordination compound is generally described as a process which may lead to a) oxygenation without elimination of HVMO species, b) homolytic or c) heterolytic splitting of the O–O bond (Scheme 4) [8]. The two latter pathways afford HVMO species or respective M–O• radicals. The mechanism of this type was studied for complexes of manganese [51], iron [72, 76], cobalt [25, 50, 86], nickel [48, 49, 53, 87-91], and ruthenium [92], and is in accordance with DFT, catalytic and spectroscopic data. We accepted this general pathway as a basis and attempted to recognize the dominant route for the systems with pre-catalysts 1 and 2. As the starting cobalt oxidation state in 1 and 2 is 3+, the heterolysis pathway should lead to Co(V) species. The existence of such intermediates, while possible, is rather doubtful considering the very high activity even of Co(IV) compounds (see below). The mechanisms of similar cobalt-catalysed oxidations with *m*-CPBA are presumed to involve HVMO cobalt intermediates (for instance, **3** and **5** in Table 3) [25, 50, 71, 93, 94], particularly as a source of stereoselectivity. However, in contrast to numerous Fe(IV)=O and Fe(V)=O HVMO complexes, which possess rich chemistry and sufficient stability to make their

isolation and study possible [95, 96], the respective compounds of Co(IV) and Co(V) remain elusive. The high reactivity of HVMO cobalt species causes their very short lifetimes and, therefore, difficulties in reliable characterization. There are reports by Nam and co-workers that Co(IV)=O species can be stabilized within heterobimetallic Co/M assemblies, where M is a redoxinactive metal such as Sc(III), Ce(III), Y(III) or Zn(II) [97, 98]. For example, the existence of a Co(IV)=O-Sc(III) core was proposed (one may see that such a core resembles the Co/Cd core in **2**) [97, 98]. Later, however, some of these data were re-investigated and the possibility of their interpretation as Co(III) species was suggested [99]. Recently a Co(IV) complex was trapped by spectroscopic methods, where it was obtained by photo- or chemical oxidation of a Co(II) complex with 1,4,7,10- tetramethyl-1,4,7,10-tetraazacyclotridecane ligand [100]. Although this HVMO cobalt compound was not isolated (it decayed within 4 min), it was shown to possess strong oxidative properties, particularly in the C–H bonds oxidation [100].

Based on the above discussions, we presume that the main oxidation pathway in 1/promoter/*m*-CPBA and 2/promoter/*m*-CPBA systems likely involves Co(II) and/or Co(III) species and the "concerted" route (Scheme 4), although participation of Co(IV) ones cannot be excluded. The expected short lifetime of Co(IV) intermediates suggests that their potential oxygen exchange with  $H_2^{18}O$  (expected for HVMO compounds) cannot be a sufficient explanation of <sup>18</sup>O incorporation into a hydroxylated product. Hence, as *m*-CPBA did not reveal notable <sup>18</sup>O enrichment when treated with  $H_2^{18}O$ , one may suggest that water is able to exchange its oxygen with one of the Co/*m*-CPBA intermediates.

The main pathway of the reaction of *m*-CPBA with the cobalt centre is believed not to lead to the elimination of free aroyloxyl ArC(O)O• or aroylperoxyl ArC(O)O0• radicals (homolytic *m*-CPBA splitting, Scheme 4). Elimination of the ArC(O)O• radical from the cobalt-based intermediate (Scheme 5) should be considered as a minor process, strongly influenced by the acidity of the promoter. Such a scheme explains a pronounced dependence of chlorobenzene formation both on the pre-catalyst concentration and  $pK_a$  of the acid promoter. The free aroyloxyl radical initiates a series of metal-free reactions between radical species, *m*-CPBA and alkane (Scheme 5) [44, 45]. The aroylperoxyl ArC(O)OO• radical, known to result from the reaction of aroyloxyl radical with *m*-chloroperbenzoic acid, was stated to hydroxylate alkanes *via* a concerted mechanism with retention of initial stereoconfiguration of the alkane substrate [44]. The aryl radical, formed through the decarboxylation of the aroyloxyl radical, abstracts H atom from the tertiary bond of alkane, producing chlorobenzene as well as a free alkyl radical [8]. The latter affords a mixture of *cis*- and

*trans*-isomers [33, 41] before reacting with  $O_2$  [33], finally yielding both stereoisomers of tertiary alcohols (Scheme 5).

Although the details of this mechanism are to be established, the analysis of the combined catalytic parameters (yields and stereoselectivities, Tables 2 and 4) clearly shows advantages of the Co/Cd heterometallic system (2) over the Co mononuclear pre-catalyst (1). Moreover, the <sup>18</sup>O incorporation parameters in cyclohexane oxidation were also found to be different for pre-catalysts 1 and 2. These observations can be understood in terms of the *synergistic catalytic effect of different metals*, already recognized for various combinations of metals in diverse catalytic processes, including alkane oxidation [12, 13]. It is known that redox-inactive metals, such as cadmium, can catalyse peroxidative oxidation where the catalytic effect occurs via interaction of two peroxide molecules coordinated to the same metal centre [101-104]. Further, the properties (and, therefore, catalytic activity) of a redox-active metal centre can be influenced by another redox-inactive one, located at close proximity [15, 16, 105]. When each kind of metal participates specifically on the overall reaction mechanism, a cooperative effect of the two metals (often without an obvious understanding) can occur [13]. In the Scheme 5, we propose that the most probable role of the cadmium centre in the pre-catalyst **2** is in influencing the coordination geometry and redox properties of the cobalt atom, facilitating, e.g., its interaction with *m*-CPBA.

There are some catalytic systems capable of oxidizing *cis*-1,2-dimethylcyclohexane with *m*-CPBA under conditions relevant to the present study (Table 4). The *cis/trans* ratio shown by the 2/HNO<sub>3</sub> system is among the highest ones, also disclosing one of the highest  $3^{\circ}$  :  $2^{\circ}$  selectivities. The heterometallic Co/Fe complex with Schiff base ligand **3** exhibits the *cis/trans* ratio of 17. Good products yields are also provided by a series of organometallic complexes of cobalt [67]. Complex **4** from the series that bears tetramethylcyclobutadiene ligand is given in Table 4 as a representative example. Complexes **5** and **6** with silsesquioxane ligands show moderate stereoselectivity in **6**/HNO<sub>3</sub> system only, while in the absence of the nitric acid promoter both complexes act as nonselective catalysts. The isoindole cobalt complex **7** is reported to catalyse stereoselective reactions in the absence of any promoter (Table 3) with yields based on the substrate up to 15% [25]. A number of complexes with porphyrin ligands and various transition metals were tested towards stereoselective oxidation under promoter-free conditions (**8–13**) and showed pronounced *cis/trans* ratios and yields based on the oxidant (Table 4). Perchlorate salts of the same metals (**14–16**) were also shown to catalyse the stereoselective reaction. Although significant yields based on the oxidant were achieved in the catalytic systems **8–16**, the obtained products yields based on *cis*-1,2-DMCH

did not exceed 1%. In contrast, the catalytic systems  $1/\text{HNO}_3/m$ -CPBA and  $2/\text{HNO}_3/m$ -CPBA are able to reach 15% yield based on the substrate. The negligible stereoselectivity of iron(III) chloride (17) can be slightly improved using an 8-fold excess of the polydentate amine ligand L<sup>6</sup> relative to the iron salt (18).

#### 4. Conclusions

We have explored the catalytic properties of the mononuclear Co (1) and heterometallic binuclear  $Co^{III}Cd^{II}$  (2) Schiff base complexes in the stereoselective reaction of *cis*-1,2-dimethylcyclohexane oxidation with *m*-CPBA oxidant and promoters of different acidity (HNO<sub>3</sub>, TFA and HOAc) under mild conditions. Both complexes reveal a notable activity, with yields of the products up to 15% and 51% based on 1,2-DMCH and *m*-CPBA, respectively, and retention of stereoconfiguration of alkane substrate up to 99.2%. The heterometallic  $Co^{III}Cd^{II}$  complex (2) is more active than the mononuclear  $Co^{III}$  complex (1), exhibiting higher products yields and a higher stereoselectivity. This finding can be understood in terms of the *synergistic catalytic effect of different metals*, so that the cadmium atom in the pre-catalyst 2 may play a role in suppressing the minor non-selective radical mechanism or in stabilizing stereoselective intermediates.

We have investigated the influence of the nature of an acidic promoter and found that the best catalytic parameters can be achieved with the acid possessing the lowest  $pK_a$  value (strongest acid). The chlorobenzene side product formation, associated with a non-selective radical mechanism, depends on the  $pK_a$  of the promoter. From the pronounced stereo- and bond selectivities, high kinetic isotope effects in the cyclohexane oxidation (5.7 and 6.2 for **1** and **2**, respectively) and incorporation of oxygen from H<sub>2</sub><sup>18</sup>O into the cyclohexanel, we presume that the mechanism of

studied reaction proceeds *via* a non-free-radical pathway, with possibility of involvement of Co(IV) high-valent metal-oxo species.

The present work provides novel insights into the *m*-CPBA chemistry, as well as into the C–H catalytic oxidation using this oxidant. The use of heterometallic pre-catalyst 2 is shown to have advantages over the mononuclear 1 and other known homometallic catalysts in terms of yields, bond- and stereoselectivity.

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**Figure 1**. Molecular structure of complex **1**, showing the principal atom numbering scheme. Non-H atoms are shown with 50% probability displacement ellipsoids.



**Figure 2**. Molecular structure of complex **2**, showing the principal atom numbering scheme. Non-H atoms are shown with 50% probability displacement ellipsoids.



**Figure 3**. The activities of the catalytic systems comprising the substrate, cis-1,2-DMCH (0.1 M), oxidant, *m*-CPBA (0.027 M), pre-catalyst ( $[1]_0 = 2.9 \times 10^{-4}$  M;  $[2]_0 = 2.7 \times 10^{-4}$  M) and acidic promoter ( $5.5 \times 10^{-3}$  M), in acetonitrile at 40 °C. Data are shown for the probe taken 1 h after the reaction start. The *cis/trans* ratio is the ratio of *cis*- to *trans*-tertiary alcohol products. The yield of oxygenates refers to the sum of all tertiary and secondary alcohols and ketones. Both oxygenates and chlorobenzene yields are based on the oxidant.



**Figure 4.** Top: the tertiary alcohols *cis/trans* ratio vs. the chlorobenzene yield after 90 min of the reaction time (the conditions are as those of Figure 3 caption). Bottom: dependences of the initial rate of chlorobenzene formation on the  $pK_a$  values [55] of the respective acids in acetonitrile.



**Figure 5**. Alcohols and ketones accumulations (open and solid symbols, respectively) over the reaction time during the oxidation of the equimolar mixture of  $C_6H_{12}$  (0.05 M, circles) and  $C_6D_{12}$  (0.05 M, squares) with *m*-chloroperbenzoic acid (0.027 M) using HNO<sub>3</sub> promoter (5.5 × 10<sup>-3</sup> M) and  $H_2^{18}O$  (1 M) and catalysed by **1** (top;  $[\mathbf{1}]_0 = 2.9 \times 10^{-4}$  M ) and **2** (bottom;  $[\mathbf{2}]_0 = 2.7 \times 10^{-4}$  M) in acetonitrile at 40 °C. Insets show the respective accumulations of sums of alcohol and ketone of normal (red triangles) and deuterated (blue squares) cyclohexane. The respective fits are shown as solid lines (see text).



**Figure 6**. Accumulations of <sup>18</sup>O-labelled alcohols over the reaction time in the oxidation of equimolar mixtures of  $C_6H_{12}$  and  $C_6D_{12}$  (0.05 M each) with *m*-CPBA (0.027 M), in the presence of

 $H_2{}^{18}O$  (1 M) and HNO<sub>3</sub> (5.5  $\times$  10<sup>-3</sup> M) catalysed by 1 (2.9  $\times$  10<sup>-4</sup> M) or 2 (2.7  $\times$  10<sup>-4</sup> M) in acetonitrile at 40 °C.



**Figure 7**. Fragment of the chromatogram (90 min), showing alcohols and ketones (main reaction products) as well as chlorobenzene and chlorocyclohexanes (by-products) during the oxidation of the equimolar mixture of deuterated and normal cyclohexane (conditions are as those stated in Figure 6 caption). The EI mass-spectrum of the  $C_6D_{11}Cl$  (see Figure S16 for its reference spectrum) is observed in the background of the spectrum of  $C_6H_{11}OH$ .



**Figure 8**. The fragments of the chromatograms exhibiting the main reaction products of *cis*-1,2-DMCH (0.1 M) oxidation in the presence of CBrCl<sub>3</sub> (0.1 M) and HNO<sub>3</sub> ( $5.5 \times 10^{-3}$  M), in the presence or absence of **2** ( $2.7 \times 10^{-4}$  M) and *m*-CPBA (0.027 M), in acetonitrile at 40 °C. The inset shows the initial periods of the chromatograms recorded for **2**/HNO<sub>3</sub>/*m*-CPBA system, before and after addition of PPh<sub>3</sub>.



Scheme 1. 2-Methoxy-6-[(methylimino)methyl]phenol, HL.



**Scheme 2**. The *cis*-1,2-DMCH oxidation affords the formation of  $3^{\circ}$  *cis*- (retention) and *trans*-(inversion) alcohols (main reaction products) and the products of oxidation of secondary C–H bonds as well as the ring cleavage by-product 2,7-octanedione. Typical products originated from *m*-CPBA are *m*-chlorobenzoic acid, chlorobenzene and carbon dioxide.



**Scheme 3**. The oxidation of adamantane leads mainly to tertiary alcohol formation, but also the products of secondary C–H bonds oxidation are formed. The tertiary alcohol can be overoxidized to produce diol or amidated to give *N*-(1-adamantyl)acetamide.



Scheme 4. Generally accepted plausible routes of interaction of *m*-CPBA and related peracids with metal compounds (n is the oxidation state of M and m is the charge of the  $M^n$  species). For *m*-chloroperbenzoic acid Ar is the *m*-chlorobenzyl fragment.



**Scheme 5**. Proposed general reaction mechanism that includes three main parts depending on the expected stereoselectivity of the process. RH and ROH are alkane substrate and alcohol product, respectively.

Assign.	1		2		HL		
H1	_		_		13.39 s	Н	
Н5	7.94; 7.79; 7.46 s	3Н	7.92; 7.79; 7.45 s	3Н	8.44 s	Н	
H2 H4	( 01 ( 042 ···	6H	6.96.6.24	6H	6.92 (8.0) d	2H	
H3	0.91–0.243 m	3H	0.80–0.24 m	3Н	6.74 (7.8) t	Н	
H6	3.62; 3.54 s	9H	3.61; 3.53 s	9H	3.78 s	3Н	
H7	3.21; 3.19 s	9H	3.21; 3.1 s	9H	3.47 s	3Н	

**Table 1**. <sup>1</sup>H NMR spectral data ( $\delta$ , ppm; *J*, Hz) for [CoL<sub>3</sub>]·DMF (**1**), [CoCdL<sub>3</sub>Cl<sub>2</sub>]·0.5H<sub>2</sub>O (**2**) and HL at room temperature.

**Table 2**. The  $3^\circ$  :  $2^\circ$  bond normalized selectivities (shown as a single number of excess of  $3^\circ$ ) during *cis*-1,2-dimethylcyclohexane oxidation.<sup>a</sup>

	Pre-catalyst			
Promoter	1	2		
HNO <sub>3</sub>	32 / 32 <sup>b</sup>	40 / 36 <sup>c</sup>		
TFA	26	32		
HOAc	25	36		

<sup>a</sup> general conditions:  $[1]_0 = 2.9 \times 10^{-4}$  or  $[2]_0 = 2.7 \times 10^{-4}$  M,  $[cis-1,2-dimethylcyclohexane]_0 = 0.1$  M, [m-chloroperbenzoic acid]\_0 = 0.027 M, [acid promoter]\_0 =  $5.5 \times 10^{-3}$  M, acetonitrile, 40 °C; <sup>b</sup>  $[1]_0 = 5.4 \times 10^{-4}$  M; <sup>c</sup>  $[2]_0 = 5.6 \times 10^{-4}$  M.

	Catalyst	KIE <sup>a</sup>	<sup>18</sup> O	from	Temp. <sup>c</sup>	Oxidant	ref.
			$H_2{}^{18}\mathrm{O}{}^{\mathrm{b}}$				
1	[Co <sup>III</sup> L <sub>3</sub> ]·DMF	5.7(3)	2.0(1)		40	<i>m</i> -CPBA	this work
2	$[Co^{III}Cd^{II}L_3Cl_2]\cdot 0.5H_2O$	6.2(2)	3.5(2)		40	<i>m</i> -CPBA	this work
3	$[Co^{II}(L^1)_2](NO_3)_2$	7.2(2)	3.5 <sup>d</sup>		40	<i>m</i> -CPBA	[25]
<b>4</b> a	$[Fe^{III}(L^2)](CF_3SO_3)_5$	3.9	34(3) / 4	7(4) <sup>e</sup>	25	<i>m</i> -CPBA	[70]
<b>4</b> b	$[Fe^{III}(L^2)](CF_3SO_3)_5$	6.4	62(6) / 7	8(6) <sup>e</sup>	-40	<i>m</i> -CPBA	[70]
5	$[Co^{III}(L^3)](CF_3SO_3)$	8(1)	10(1)		r.t. <sup>f</sup>	т-СРВА	[71]
6	$[Fe^{III}(L^3)](CF_3SO_3)$	n.r. <sup>g</sup>	18(2)		r.t.	т-СРВА	[71]
7	[Fe <sup>III</sup> (L <sup>4</sup> )Cl]	n.r.	4(1)		r.t.	m-CPBA	[72]
8	Co <sup>II</sup> (ClO <sub>4</sub> ) <sub>2</sub>	8(1)	11		r.t.	m-CPBA	[42]
9	$[Ru^{III}(L^5)Cl_2](ClO_4)$	4.3	9		r.t.	m-CPBA	[54]
10	$[Ru^{III}(L^6)Cl_2](ClO_4)$	3.1	100		r.t.	m-CPBA	[54]
11	$[Ni^{II}(L^6)(OAc)(H_2O)](BPh_4)$	2.8 <sup>h</sup>	n.r.		r.t.	m-CPBA	[73]
12	$[Fe^{III}_2O(L^7)(OAc)_2](ClO_4)_2$	3.2	n.r.		25	<i>m</i> -CPBA	[74]
13	$[Fe^{III}_2(L^8)(O)(OBz)]ClO_4$	3.0 <sup>h</sup>	n.r.		r.t.	m-CPBA	[75]
14a	$[Fe^{II}(L^9)(CH_3CN)](ClO_4)_2$	4.2	n.r.		r.t.	m-CPBA	[76]
14b	$[Fe^{II}(L^9)(CH_3CN)](ClO_4)_2$	1.5	n.r.		r.t.	$H_2O_2$	[76]
15	Fe <sup>III</sup> (ClO <sub>4</sub> ) <sub>3</sub>	1.5	n.r.		r.t.	$H_2O_2$	[60]
16	$[(n-C_4H_9)_4N]_4[\gamma-$	3.2	n.r.		60	$H_2O_2$	[77]
	$HPV_2W_{10}O_{40}]$						
17	$[Fe^{II}(CF_3SO_3)_2(L^{10})]$	4.3 <sup>i</sup>	45		25	$H_2O_2$	[78]
18	$[Fe^{III}(L^{11})](ClO_4)_2$	6.5(5)	n.r.		25	$H_2O_2$	[79]
19	$[Fe^{III}(L^{12})(H_2O)](ClO_4)_2 \cdot H_2O$	3.9(1)	n.r.		r.t.	$H_2O_2$	[80]
20	$Mn^{II}(L^{13})(CF_3SO_3)_2$	2.5	0		25	CH <sub>3</sub> CO <sub>3</sub> H	[81]
21	-	5	_		80	$[Co^{III}(L^{14})(OOtBu)]$	[82]
22	-	25	-		-40	$[Fe^{IV}(O)(L^{15})(CH_3CN)]^{2+}$	[83]
23	-	3.6(4)	-		-60	$[(L^{16})Fe^{IV}(\mu -$	[84]
						N)Fe <sup>IV</sup> (O)( $L^{16++}$ )]	

**Table 3**. Selected catalytic systems for *cis*-1,2-dimethylcyclohexane oxidation showing KIE and  $^{18}$ O-labelling data.

<sup>a</sup> KIE (kinetic isotope effect) obtained in the oxidation of the C<sub>6</sub>H<sub>12</sub>/C<sub>6</sub>D<sub>12</sub> equimolar mixture, unless stated otherwise. <sup>b</sup> Incorporation of <sup>18</sup>O (in %) into the normal cyclohexanol during of  $C_6H_{12}$  oxidation in the presence of  $H_2^{18}O$ , unless stated otherwise. <sup>c</sup> Reaction temperature. <sup>d</sup> incorporation of <sup>18</sup>O (in %) into the 3° cis-alcohol during the oxidation of cis-1,2-DMCH. <sup>e</sup> Incorporations of <sup>18</sup>O (in %) into C<sub>6</sub>H<sub>11</sub>OH and C<sub>6</sub>D<sub>11</sub>OH, observed in the courses of the respective oxidation reactions. <sup>f</sup> room temperature. <sup>g</sup> not reported. <sup>h</sup> KIE obtained from the oxidations of C<sub>6</sub>D<sub>12</sub> and C<sub>6</sub>H<sub>12</sub> conducted separately. <sup>i</sup> Oxidation of 1 : 3 mixture of C<sub>6</sub>H<sub>12</sub>/C<sub>6</sub>D<sub>12</sub>. L<sup>1</sup> = O,O'-(3-amino-1*H*-isoindole-1,1-diyl)bis(propan-2-one oxime).  $L^2$ = *meso*-tetrakis(2,3,5,6-tetrafluoro-4trimethylammonio)porphyrin.  $L^3 = meso$ -tetrakis(2,6-difluorophenyl)porphinato dianion.  $L^4 =$  $L^5$ *meso*-tetrakis(2,6-difluorophenyl)porphinato dianion. bis(4-ethoxycarbonyl-2-= pyridylmethyl)(2-pyridylmethyl)amine.  $L^6 = tris(2-pyridylmethyl)amine. L^7 = 1,2-bis[2-di(2-pyridylmethyl)amine)$ 

pyridyl)-methyl-6-pyridyl]ethane.  $L^8 = 3,3$ '-Bis[N,N-bis(2-pyridylmethyl)aminomethyl]-1,1'-bi-2naphthol. HObz = benzoic acid.  $L^9 = [N-(1-methyl-2-benzimidazolyl)methyl-N-(2-pyridyl)methyl-N-(bis-2-pyridylmethyl)amine]. <math>L^{10} = 1-(2-pyridylmethyl)-4,7$ -dimethyl-1,4,7-triazacyclononane. H $L^{11}$  = polydentate N-donor ligand. H $L^{12} = 2$ -[bis(pyridin-2-ylmethyl)]amino-N-quinolin-8-yl-acetamide.  $L^{13} = N,N'$ -dimethyl-N,N'-bis(8-quinolyl)-ethane-1,2-diamine. H $_2L^{14} = N,N$ -bis[2-(2-pyridyl)ethyl]-pyridine-2,6-dicarboxamide).  $L^{15} = tris(2-quinolyl)methyl)amine. L^{16} = meso-tetraphenylporphyrin.$ 

	Catalyst	promoter	Yield, <sup>a</sup> %	$\mathrm{TON}^b$	<i>cis/trans</i> ratio <sup>c</sup>	$3^\circ$ : $2^\circ$ ratio	Solvent	Ref.
1	[CoL <sub>3</sub> ]·DMF	HNO <sub>3</sub>	36	36	59	32:1	CH <sub>3</sub> CN	this work
2	$[CoCdL_3Cl_2] \cdot 0.5H_2O$	HNO <sub>3</sub>	51	59	78	40:1	CH <sub>3</sub> CN	this work
3	$[Co_4Fe_2O(L^1)_8]\cdot 4DMF\cdot H_2O$	HNO <sub>3</sub>	n.r.	n.r.	17	n.r.	CH <sub>3</sub> CN	[24]
<b>4</b> a	$[(C_4Me_4)Co(C_6H_6)]PF_6$	HNO <sub>3</sub>	21	109	22	n.r. <sup>d</sup>	CH <sub>3</sub> CN	[106]
<b>4</b> b	$[(C_4Me_4)Co(C_6H_6)]PF_6$	_	13	66	7	n.r.	CH <sub>3</sub> CN	[106]
5	[(PhSiO <sub>1.5</sub> ) <sub>12</sub> (NiO) <sub>6</sub> (NaCl)]	_	42	34	1	n.r.	CH <sub>3</sub> CN	[107]
6a	[(PhSiO <sub>1.5</sub> ) <sub>10</sub> (CoO) <sub>5</sub> (NaOH)]	HNO <sub>3</sub>	30	158	25	n.r.	CH <sub>3</sub> CN	[108]
6b	[(PhSiO <sub>1.5</sub> ) <sub>10</sub> (CoO) <sub>5</sub> (NaOH)]	_	30	156	1	n.r.	CH <sub>3</sub> CN	[108]
7	$[Co(L^2)_2](NO_3)_2$	_	57	46	56	35:1	CH <sub>3</sub> CN	[25]
8	[Fe(L <sup>3</sup> )](CF <sub>3</sub> SO <sub>3</sub> ) <sub>5</sub>		83	21	>300	16:1	$\begin{array}{l} CH_{3}CN \ / \\ CH_{2}Cl_{2} \end{array}$	[70]
9	[Mn(L <sup>4</sup> )](ClO <sub>4</sub> )	_	56	11	>40	10 : 1	CH <sub>3</sub> CN / CH <sub>2</sub> Cl <sub>2</sub>	[42]
10	$[Fe(L^4)](ClO_4)$	_	75	15	>55	11:1	CH <sub>3</sub> CN / CH <sub>2</sub> Cl <sub>2</sub>	[42]
11	[Co(L <sup>4</sup> )](ClO <sub>4</sub> )	_	67	13	>60	34:1	CH <sub>3</sub> CN / CH <sub>2</sub> Cl <sub>2</sub>	[42]
12	[Co(L <sup>5</sup> )](CF <sub>3</sub> SO <sub>3</sub> )	-	70	4	>65	53 : 1	CH <sub>3</sub> CN / CH <sub>2</sub> Cl <sub>2</sub>	[71]
13	[Fe(L <sup>5</sup> )Cl]		77	1	>72	58 : 1	$\begin{array}{l} CH_{3}CN \ / \\ CH_{2}Cl_{2} \end{array}$	[72]
14	Mn(ClO <sub>4</sub> ) <sub>2</sub>	-	37	7	>25	8:1	CH <sub>3</sub> CN / CH <sub>2</sub> Cl <sub>2</sub>	[42]
15	Fe(ClO <sub>4</sub> ) <sub>2</sub>	_	14	3	>10	10:1	CH <sub>3</sub> CN / CH <sub>2</sub> Cl <sub>2</sub>	[42]
16	Co(ClO <sub>4</sub> ) <sub>2</sub>	_	89	18	>81	41:1	CH <sub>3</sub> CN / CH <sub>2</sub> Cl <sub>2</sub>	[42]
17	FeCl <sub>3</sub>	_	n.r.	n.r.	1.4	n.r.	CH <sub>3</sub> CN	[109]
18	FeCl <sub>3</sub> / L <sup>6</sup>	_	n.r.	n.r.	4	n.r	CH <sub>3</sub> CN	[109]

#### Table 4. Selected systems for catalytic oxidation of *cis*-1,2-dimethylcyclohexane with *m*-CPBA.

<sup>a</sup> Overall yields based on the oxidant. <sup>b</sup> TONs (turnover numbers), mols of products (sum of tertiary and secondary products) per mol of catalyst. <sup>c</sup> Mols of 3<sup>°</sup> *cis*-alcohol per mol of *trans*-alcohol. <sup>d</sup> Not O,O'-(3-amino-1H-isoindole-1,1reported.  $H_2L^1$ = salicylidene-2-ethanolamine.  $L^2 =$ divl)bis(propan-2-one oxime).  $L^3$ = meso-tetrakis(2,3,5,6-tetrafluoro-4trimethylammonio)porphyrin.  $L^4 = meso$ -tetrakis(pentafluorophenyl)porphinato dianion.  $L^5 = meso$ -N,N'-bis(2-pyridylmethylene)-1,4tetrakis(2,6-difluorophenyl)porphinato dianion.  $L^6$ = diaminodiphenyl ether.