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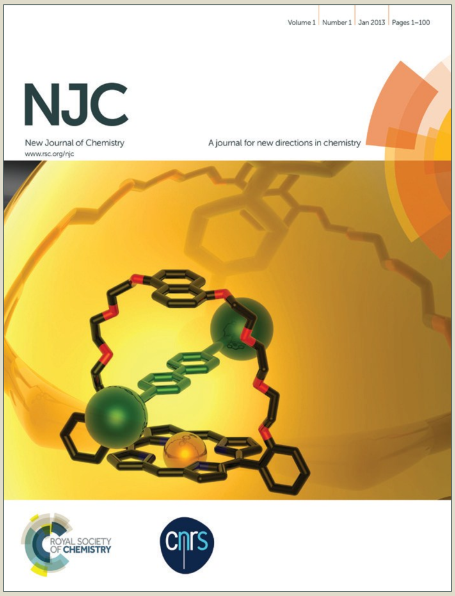

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Copper(II) and iron(III) complexes with arylhydrazone of ethyl 2-cyanoacetate or formazan ligands: *E/Z* isomerization assisted by cooperative coordination and ionic interaction, catalysts for oxidation of alcohols

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Abstract

The aquasoluble [Cu(1κ*N*,O^2:2κ*O*-HL^1)(S)]$_2$ [S = CH_3OH (**1**), $(CH_3)_2NCHO$ (**2**)] and [Cu(κ*N*-HL^1)(en)$_2$]·CH_3OH·H_2O (**3**) Cu^{II} complexes were prepared by reaction of Cu^{II} nitrate hydrate with the new (*E/Z*)-4-(2-(1-cyano-2-ethoxy-2-oxoethylidene)hydrazinyl)-3-hydroxybenzoic acid ($\mathbf{H_3L^1}$), in the presence (for **3**) or absence (for **1** and **2**) of ethylenediamine (en), while the Fe^{III} complex [Fe(κN^3-HL^2)$_2$] (**4**) was isolated by treatment of iron(III) chloride hexahydrate with the new (1*E*,1*E*)-N',2-di(1*H*-1,2,4-triazol-3-yl)diazenecarbohydrazonoyl cyanide ($\mathbf{H_3L^2}$), and characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction. Cooperative *E,Z* → *E* isomerization of $\mathbf{H_3L^1}$, induced by coordination and ionic interactions, occurs upon interaction with Cu^{II} in the presence of en. Complexes **1**−**4** are catalyst precursors for the solvent-free microwave (MW) assisted selective oxidation of primary or secondary alcohols and diols to the corresponding aldehydes, ketones and diketones, respectively, with yields in the 5−99 % range (TONs up to 4.96×10^2) after 60 min of MW irradiation at 120 °C. Temperature, time and organic radical influence were studied and also the regioselectivity oxidation of the catalytic systems involving the primary and secondary alcohols.

Keywords: Arylhydrazone of ethyl 2-cyanoacetate; Formazan; Cu^{2+} or Fe^{3+} complexes; *E/Z* isomerization; Oxidation of alcohols.

Introduction

Arylhydrazones of active methylene compounds (AHAMCs, Scheme 1) are versatile ligands in the synthesis and design of coordination compounds.[1] The preparative procedures for these complexes are usually rather straightforward giving high yields of the final products. AHAMC complexes have been applied as *i)* catalysts for the oxidation of alkanes[2] and alcohols[2,3] and C−C bond formations (e.g., Henry reaction),[4] *ii)* as biological active compounds *in vitro* antifungal[5a] and antiproliferative[5b] tests, *iii)* materials for optical recording media[6a] and spin-coating films,[6b] and *iv*) molecular switches in response to changes in pH[7] and auxiliary ligands.[3]

A particular property of AHAMCs is their ability to undergo reversible *E/Z* isomerism (Scheme 1) with the isomers often being isolable species with good solid-state stability, what makes them good candidates for the construction of molecular electronics, switches, rotors and similar nanomachines.[8] Thus, *E/Z* isomerization of AHAMCs can be important for their physical and pharmacological properties, as well as in their reactions and catalysis. The reported *E/Z* isomerizations in hydrazones are regulated by pH,[7] resonance-assisted hydrogen bonding [X···H−Y ↔ Y···H−X (X, Y = N, O, S, etc.), RAHB],[4] coordination-coupled proton transfer,[9a] UV light,[9b,c]

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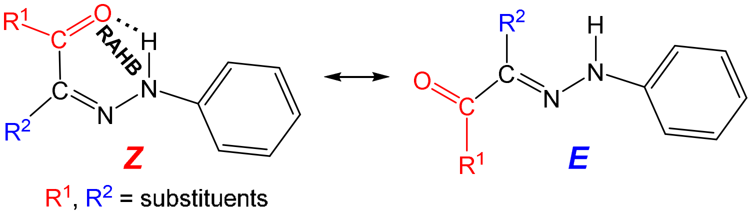
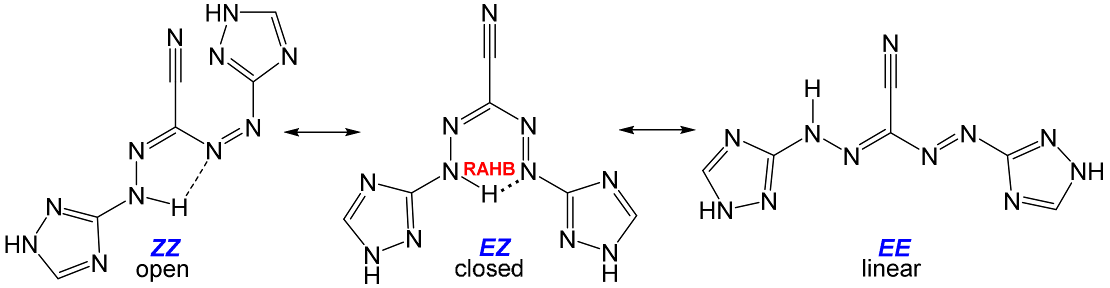
cooperative RAHB and ionic interaction,[4c] auxiliary ligands[3] or solvation,[2] but no cooperative coordination and ionic interaction assisted control of this process has been reported, and this possibility is explored in this work.



Scheme 1. *E/Z* isomerization of AHAMCs.

Formazans, which contain the azo-hydrazone bond system (Scheme 2), are colored compounds due to their *E/Z* isomerization (Scheme 2) as well as π–π* electronic transitions and form a distinct class of organic dyes with certain properties.[10] They exhibit a number of biological properties, such as antiviral,[11a,b] antimicrobial,[11c,d] anti-inflammatory, analgesic,[11e] antifungal,[11f] anticancer and anti-HIV[11g] ones. The wide variability of substituents in formazan molecules and relative ease of their synthesis make it possible to study the influence of the ligand fine structure on the design of metal complexes. In contrast to the well-studied coordination chemistry of close analogues of β-diketiminates, the number of publications devoted to structurally characterized formazan complexes is very limited. [10,12] Thus, in order to promote the versatility of coordination chemistry of formazan ligands, we decided to focus on a functionalized form, in particular its 1,2,4-triazole (heterocycle) substituted derivative (Scheme 2), in view of the promising coordination feature of this compound towards iron(III).



Scheme 2. A new heterocyclic formazan and its *E/Z* isomerization.

On the other hand, transition metal complexes catalyzed oxidation of alcohols play an important role in catalysis and since carbonyl compounds are widely used in organic synthesis, the development of new oxidative protocols continues to receive attention in spite of the availability of several methods to achieve such objectives.[13] Recently, several copper(II) complexes of AHAMCs are successfully applied in the oxidation of alcohols to corresponding carbonyl compounds.[2,3] However, complexes of formazan ligands have not yet been reported for such a purpose. Hence, one relevant objective of the current work was the design of a formazan compound that could act as a

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multidentate *N*-donor ligand for a metal center that would behave as a catalyst for the oxidation of structurally different alcohols.

Taking the above considerations, herein we report: *i*) the syntheses of new Cu^{II} complexes from (*E/Z*)-4-(2-(1-cyano-2-ethoxy-2-oxoethylidene)hydrazinyl)-3-hydroxybenzoic acid (**H_3L^1**); *ii)* the synthesis of a new Fe^{III} complex from (1*E*,1*Z*)-N',2-di(1*H*-1,2,4-triazol-3-yl)diazenecarbohydrazonoyl cyanide (**H_3L^2**); *iii*) the cooperation of ionic interactions and coordination for regulating the of *E*/*Z* isomerization in AHAMC ligand upon its treatment with Cu^{II}; *iv*) the evaluation of the catalytic activity of the prepared new Cu^{II} and Fe^{III} complexes in the model MW-assisted and TEMPO-mediated solvent-free oxidation by peroxide of structurally different alcohols to the corresponding carbonyl compounds.

Results and Discussion

Synthesis and characterization of $H_3L^{1,2}$, Cu^{II} and Fe^{III} complexes

(*E/Z*)-4-(2-(1-cyano-2-ethoxy-2-oxoethylidene)hydrazinyl)-3-hydroxybenzoic acid (**H_3L^1**) was synthesized via the Japp-Klingemann reaction[14] between the 4-carboxy-2-hydroxybenzenediazonium chloride and ethyl 2-cyanoacetate in water-ethanol (5/25, *v/v*) containing sodium hydroxide and sodium acetate, and characterized by ESI-MS, IR and NMR spectroscopies and elemental analysis. The ^1H NMR spectrum of H_3L^1 in DMSO-d_6 at room temperature consists of two sets of signals at 12.79 and 13.16 ppm indicating the existence of a mixture of the two isomeric *E*- and *Z*-hydrazone forms (Scheme 3), respectively. The mole ratio of the isomeric forms has been determined by the relative integration of the $NN\underline{H}$ signal of each isomer (Figure S1 in Supplementary Information), showing 65 % for the *Z*-hydrazone and 35 % for the *E*-isomer. Possibly due to RAHB between carbonyl group and hydrogen of hydrazone moiety compared to the cyano group (Scheme 3), the *Z*-hydrazone form dominates. These two isomeric forms were also confirmed by ^{13}C NMR spectra of H_3L^1 in DMSO-d_6, which also consists of two sets of signals, (Figure S2 in Supplementary Information). The IR spectrum of H_3L^1 reveals ν(OH) at 3409 and 3088 cm^{-1}, ν(NH) at 2780 and 2462 cm^{-1}, ν(C=O) at 1693 and 1610 cm^{-1}, and ν(C=N) at 1512 cm^{-1}. Elemental analysis and ESI-MS in methanol (peak at *m/z* 278.2 $[Mr+H]^+$) support the proposed formulation.

The reaction of the *E/Z*-isomeric mixture of H_3L^1 with copper(II) nitrate hydrate in methanol and methanol-dimethylformamide mixture (20/1, v/v) lead to the dinuclear *Z*-hydrazone complexes $[Cu(1\kappa N,O^2:2\kappa O\text{-}HL^1)(CH_3OH)]_2$ (**1**) and $[Cu(1\kappa N,O^2:2\kappa O\text{-}HL^1)\{(CH_3)_2NCHO\}]_2$ (**2**), respectively. The mononuclear complex $[Cu(\kappa N\text{-}HL^1)(en)_2]\cdot CH_3OH\cdot H_2O$ (**3**) was obtained upon *E/Z*→*E* conversion by reaction of the *E/Z*-isomeric mixture of H_3L^1 with the copper salt, in methanol, in the presence of ethylenediamine (en) (Scheme 3, Figure 1). Compounds **1**−**3** have been isolated as air-stable crystalline solids and were characterized by IR spectroscopy, ESI-MS and

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elemental analysis. In the IR spectra of **1**, **2** and **3**, the *v*(C=O) and *v*(C=N) signals appear at 1671 and 1577, 1643 and 1567, 1652 and 1584 cm^{-1}, respectively, values that are significantly shifted relative to the corresponding signals of H_3L^1 (see above). The ESI mass spectra of **1**, **2** and **3** dissolved in CH_3OH, show parent peaks at m/z = 678.52 $[Mr{-}2CH_3OH{+}H]^+$, 678.62 $[Mr{-}2(CH_3)_2NCHO{+}H]^+$ and 460.02 $[Mr{-}CH_3OH{-}H_2O{+}H]^+$ (Figures S3-S5 in Supplementary Information). Elemental analyses are consistent with the proposed formulations, which are also supported by single crystal X-ray diffraction (see below).

The cooperation of coordination and ionic interactions provides an unprecedented strategy towards an easy [(*E,Z*) → *E* or *Z*] isomeric resolution of H_3L^1 to give the copper(II) complexes $[Cu(1\kappa N,O^2{:}2\kappa O\text{-}HL^1)(CH_3OH)]_2$ (**1**) and $[Cu(1\kappa N,O^2{:}2\kappa O\text{-}HL^1)\{(CH_3)_2NCHO\}]_2$ (**2**) (*Z* form) and $[Cu(\kappa N\text{-}HL^1)(en)_2]{\cdot}CH_3OH{\cdot}H_2O$ (**3**) (*E* form). Usually, copper(II) can directly coordinate the AHAMC ligands, destroying the RAHB system and entering the chelating pocket,[1] as obtained in the cases of **1** and **2**. But, to achieve the coordination of those ligands to other transition metal ions, deprotonating agents have to be used for the weakening/destroying RAHB system, in most of the cases.[1]

Ethylenediamine (en) has been used as auxiliary ligand,[1] deprotonating agent,[1,2] nucleophile,[2,4b] etc., in the synthesis and design of coordination compounds of AHMAC ligands. It was expected that the reaction of Cu^{II} with H_3L^1, in the presence of en, would give a copper(II) complex with the hydrazone ligand in the *Z*-form, as this is isolated in basic medium in many cases.[1a] However, a different result was obtained (Scheme 3). The isolation of the *E*-form in complex **3** in basic medium can be explained on the basis of the higher coordination ability of en to copper leading to the initial formation of $[Cu(en)_2]^{2+}$, preventing the expected N,N,O-chelation of H_3L^1 which thus coordinates in the monodentate fashion via the cyano group. The coordination of this group promotes deprotonation of the ligand, the positive charges of Cu^{2+} ion in **3** being neutralized by the negative charges of the deprotonated nitrogen and oxygen atoms of the hydrazone and carboxylate groups (Scheme 3). The intramolecular distance in **3** between Cu^{2+} and N^- is 5.120 Å (Scheme 3), whereas the intermolecular distance between Cu^{2+} and O^- of the carboxylate group of a neighbouring molecule is 4.170 Å (see below for X-ray analysis). Both distances fall in the recognized range of ionic interaction distances.[15] Moreover, deprotonation of hydrazone moiety gives an intramolecular hydrogen bonding system, which may additionally support the *E*-form (Scheme 3). Thus, cooperation of coordination and ionic interaction in the reaction of Cu^{II} with H_3L^1 in the presence of en leads to (*E,Z*) → *E* isomeric resolution. Isolated isomers is of particular significance for material[7a] and synthetic chemistries.[7b] Thus, we found that cooperative coordination and ionic interaction assisted *E/Z*-isomerization and can be used to control physical or chemical properties of AHAMC ligands and their complexes.

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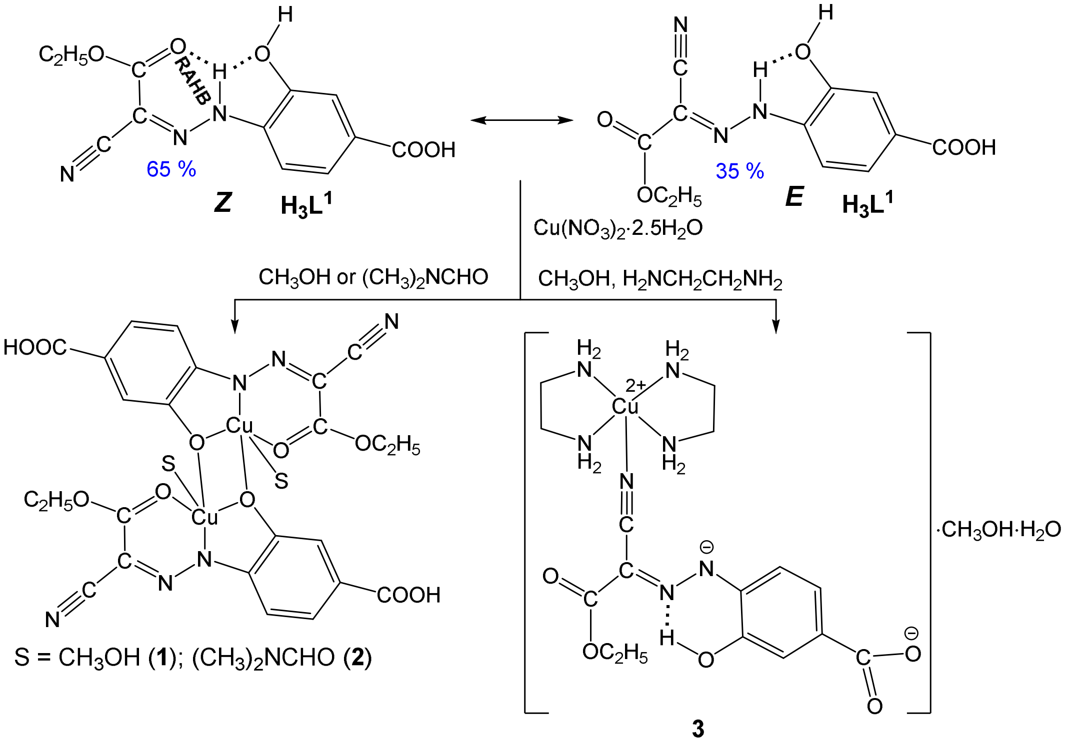

Scheme 3. *E/Z* isomerization of H_3L^1 in the synthesis of **1**−**3**.

It is known that active methylene compounds can be deprotonated and allowed to react with two equivalents of diazonium salts in aqueous solution to give formazan ligands.[12a] Using this strategy, we also prepared the new formazan (*1Z,1E*)-*N*',2-di(1*H*-1,2,4-triazol-3-yl)diazene-carbohydrazonoyl cyanide (H_3L^2), from reaction of 1*H*-1,2,4-triazole-3-diazonium chloride with methyl 2-cyanoacetate in basic medium (Scheme 4). The molar ratios of formazan isomers, tautomers and conformers are dependent on the character and position of the substituents and on the aggregate state.[12] The inclusion of a triazole moiety can provide additional isomers and tautomeric forms due to rotation around the C=N and N=N double bonds or proton migration to the heteroatom of this substituent, respectively. In fact, according to the ^1H NMR spectrum of H_3L^2, it has a linear *EE*-configuration (Scheme 2) at pH ~ 7.5, with the NH group proton not involved in hydrogen bonding appearing at 8.15 ppm (Figure S6 in Supplementary Information). In agreement, the ^{13}C-NMR spectrum of H_3L^2 shows only one signal that supports the linear *EE*-configuration (Figure S7 in Supplementary Information). The IR spectrum of H_3L^2 shows the *v*(C≡N) vibration at 2215 cm^{-1}, while *v*(NH) and *v*(C=N) are observed at 3125 and 2907, and 1695, 1611 and 1539, correspondingly.

Slow evaporation of a methanol-water (4/1, v/v) solution at pH 2 (HCl) of H_3L^2 and Fe^{III} chloride hydrate furnishes dark red crystals of the monomeric complex $[Fe(\kappa N^3\text{-}HL^2)_2]$ (**4**) (Scheme 4). Elemental analyses and ESI-MS (peak at 518.2 $[Mr+H]^+$) support the formulation (Figure S8 in Supplementary Information), while IR spectrum reveals absorption bands at 3360 and 2923 *v*(N−H), 2223 *v*(C≡N), 1647, 1636 and 1545 *v*(C=N). No signal was observed in the ^1H or ^{13}C

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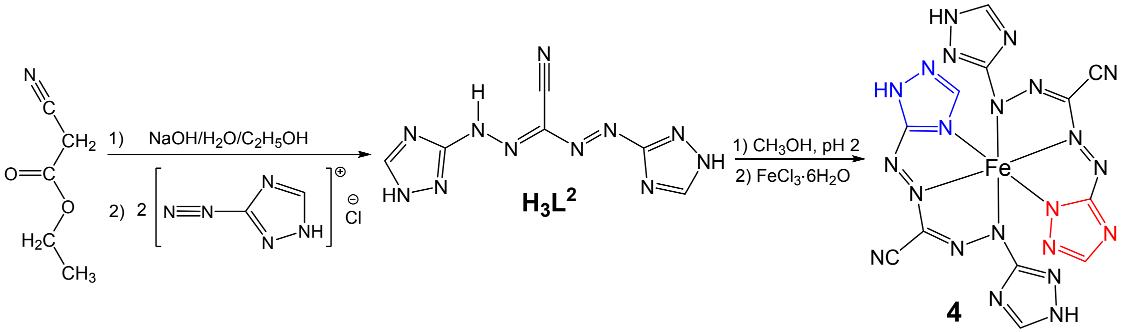
NMR spectra of **4**, according to the paramagnetic character of the trivalent metal ion (Fe^{3+}). Magnetic susceptibility measurements of **4** via the Evans method at pD of 4 (see Supplementary Information, Table S1)[16] revealed a susceptibility, μ_{eff} (μ_β), of 5.1 corresponding to a spin of 5/2. Moreover, **4** was characterized by cyclic voltammetry at a platinum electrode at 25 °C in a 0.2 M [^{n}Bu$_4$N][BF$_4$]/NCMe solution. It exhibits a single-electron (as measured by controlled potential electrolysis) irreversible reduction wave at 0.03 V *vs*. SCE (Figure S9) assigned to the $Fe^{III} \rightarrow Fe^{II}$ transition. This potential value is very similar to those reported for mononuclear Fe^{III} complexes with ligands derived from 3-amino-2-pyrazinecarboxylic acid.[17]



Scheme 4. Synthesis of $\mathbf{H_3L^2}$ and **4**.

To determine the dissociation constants of $H_3L^{1,2}$ and the stability constants of their complexes (**1**−**4**), pH-metric titrations in aqueous media were performed. The obtained values were $pK_1 = 4.30 \pm 0.04$, $pK_2 = 6.77 \pm 0.01$, $pK_3 = 10.51 \pm 0.03$ (for H_3L^1), $pK_1 = 7.75 \pm 0.02$, $pK_2 = 9.70 \pm 0.05$, $pK_3 = 11.13 \pm 0.03$ (for H_3L^2), $\lg\beta = 13.73 \pm 0.04$ (for **1**), $\lg\beta = 13.82 \pm 0.06$ (for **2**), $\lg\beta = 13.15 \pm 0.09$ (for **3**) and $\lg\beta = 17.85 \pm 0.05$ (for **4**). The details of the performed calculations can be followed in the Electronic Supplementary Information (Tables S2−S7). According to previous performed quantum-chemical calculations in the Hückel approximation,[1c,14a] we conclude that pK_1, pK_2 and pK_3 concern the deprotonation of –COOH, −OH and =N–NH– groups of H_3L^1, respectively (Scheme 3). In the case of H_3L^2, pK_1 concerns the proton abstraction from the hydrazone group (=N–NH–), while pK_2 and pK_3 refer to the stepwise deprotonation of the –NH– moiety in the triazol ring of the molecule (Scheme 4). The results of pH-metric titration show that the complexes are very stable and their stability follows the order: **4** > **2** > **1** > **3**. On account of the stronger coordination ability of dimethylformamide in comparison to methanol, complex **2** is more stable than **1**. The comparison of stability constants of the complexes with their pH-metric titration curves (Figure S10) reveals that the more H^+ ions are released during complex formation, the more stable is the obtained complex.

X-ray diffraction analysis

Crystals of **1**−**4** suitable for X-ray diffraction analysis were obtained upon crystallization from methanol (for **1** and **3**), methanol-dimethylformamide (20/1, v/v) (for **2**) or methanol-water mixtures

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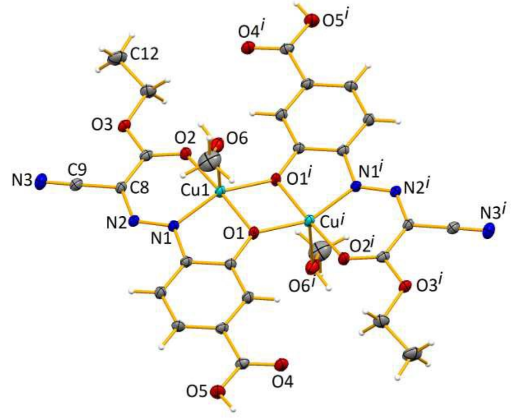
(4:1, v/v) (for **4**) (Schemes 3 and 4). Representative plots are depicted in Figure 1. Crystallographic data and refinement parameters are given in Table S8 (Supplementary Information), selected bond distances and angles in Table S9.

In **1** and **2** (Figure 1) the copper atoms are bridged by the phenolate oxygen atoms of the chelating $(HL^1)^{2-}$ ligands thus giving rise to Cu_2O_2 cores with Cu···Cu separations of 2.9830(3) (**1**) and 2.96669(8) (**2**) Å; inversion centres lie in the middle of these cores. The geometry around the copper atoms are that of basal edge-sharing distorted square pyramids (τ_5 = 0.32 and 0.28, for **1** and **2**, respectively),[18a] the copper atoms being shifted 0.184 (**1**) and 0.055 (**2**) Å above the least-square basal planes towards the apical position occupied by the coordinated methanol or dimethylformamide molecules. Compound **2** can also be considered as a 1D polymeric species by way of longer range interactions between each metal cation and the O-carbonyl atoms of vicinal molecules [Cu···O, 2.871(4) Å], the copper cations thus presenting octahedral N_1O_5 coordination environments (Figure S11). Such a polymeric chain is stabilized by H-bond contact involving the hydroxyl moiety of the carboxylic groups and the oxygen atoms of the coordinated dimethylformamides [O4–H4O–O6: $d_{D\cdots A}$ = 2.668(4) Å, $\angle_{D-H\cdots A}$ = 161(6)º].

Contrasting with the aforementioned cases, in **3** (Figure 1) the hydrazone ligand $(HL^2)^{2-}$ binds the $\{Cu(en)_2\}^{2+}$ complex cation through the cyanide N-atom, the metal thus presenting an *all*-N square-pyramidal (τ_5 = 0.10)[18a] coordination geometry. Despite the different coordination modes, the hydrazone ligands in **1**−**3** are nearly planar but with the least-square plane of the carboxylic (or carboxylate) groups twisted, by 3.50, 20.31 or 10.77º, in this order, relatively to the plane defined by the $O_{hydroxyl}NO_{ketone}$ atoms (the chelating atoms in **1** and **2**). The $CuN_{hydrazone}$ bond distances assume values of 1.920(2) (**1**), 1.908(3) (**2**) and 2.329(2) Å (**3**), the latter clearly evidencing its axial position in the coordination sphere of the metal. The equatorial CuN_{en} lengths in **3** ranges from 2.005(2) to 2.015(2) Å.



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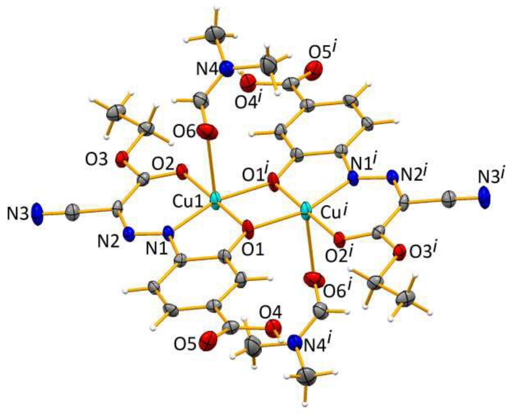

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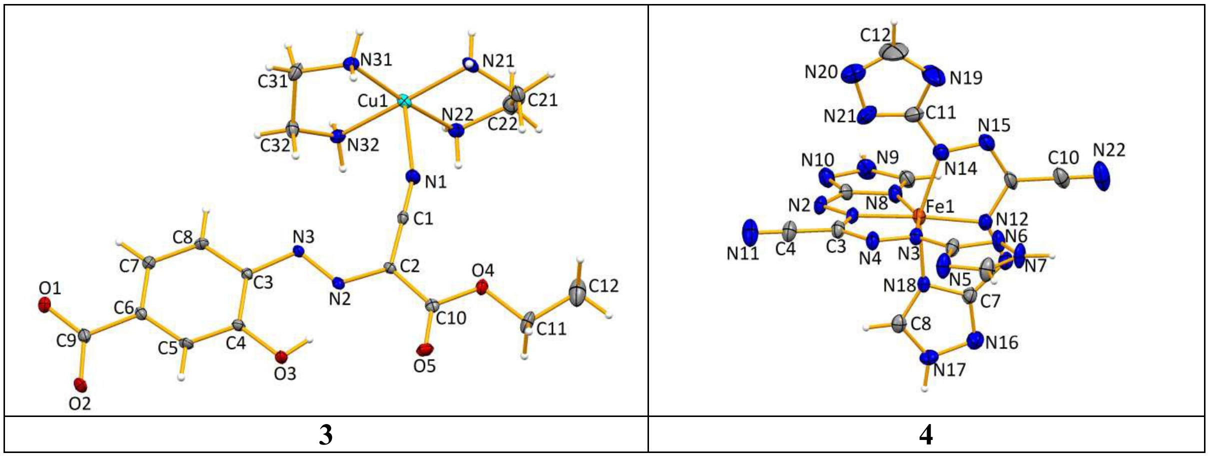

3 **4**

Figure 1. X-ray molecular structures of complexes **1**−**4** with partial atom numbering schemes. Ellipsoids are drawn at 30% probability level. Solvent molecules in **3** are omitted for clarity. Symmetry operation to generate equivalent atoms: *i*) 2-x,-y,1-z (**1**), -x,-y,1-z (**2**).

The molecules of **1** are involved in hydrogen bond interactions, the most relevant ones concerning the mutual interaction of carboxylic acid groups of vicinal molecules giving rise to 8-membered R_2^2 rings, and the contacts between the hydroxyl group of coordinated methanol which act as donor to the cyanide N-atom of a neighbouring molecule by means of 16-membered R_2^2 rings. These two types of interactions extend the structure of **1** to the second dimension (Figure S11). Also the molecules of **2** are involved in H-bond interactions, with relevance for the 12-membered R_4^4 ring connecting the copper and the crystallization water molecules. The methanol molecules, in turn, act as acceptors from amine groups and as donors to carboxylate moieties.

Each deprotonated formazan ligand in **4** chelates the iron cation through two N-hydrazone and one N-triazole atoms, as it is usual in iron complexes with these species,[10d] affording a distorted 6-coordinated environment around the metal (octahedral quadratic elongation, OQE, of 1.027; octahedral angle elongation, OAE, of 93.84),[18b] and giving rise to four fused CN_3Fe five-membered metallacycles. The crystal structure of **4** is stabilized by hydrogen bonding interactions between the triazole hydrogens and the nitrogens of formazan and other triazole moieties in adjacent units (Figure S11, Supplementary Information).

Catalytic Activity of 1−4 in Microwave-assisted Oxidation of Alcohols to Carbonyl Compounds

Complexes **1**−**4** were tested as catalyst precursors for the solvent-free microwave (MW) assisted oxidation of primary or secondary benzyl alcohols (benzyl alcohol, cinnamyl alcohol, 1-phenylethanol or benzhydrol), secondary aliphatic alcohols (cyclooctanol, cyclohexanol, isoborneol or fenchyl alcohol) and secondary aliphatic dialcohols (1,2-cyclohexanediol or 1,4-cyclohexanediol) to the corresponding aldehydes, ketones or diketones using aqueous *tert*-butyl hydroperoxide (Bu^tOOH) as oxidizing agent, under low power (20 W) MW irradiation (Scheme 5). Typical homogenous reaction conditions were performed (unless stated otherwise) using 2.5 mmol

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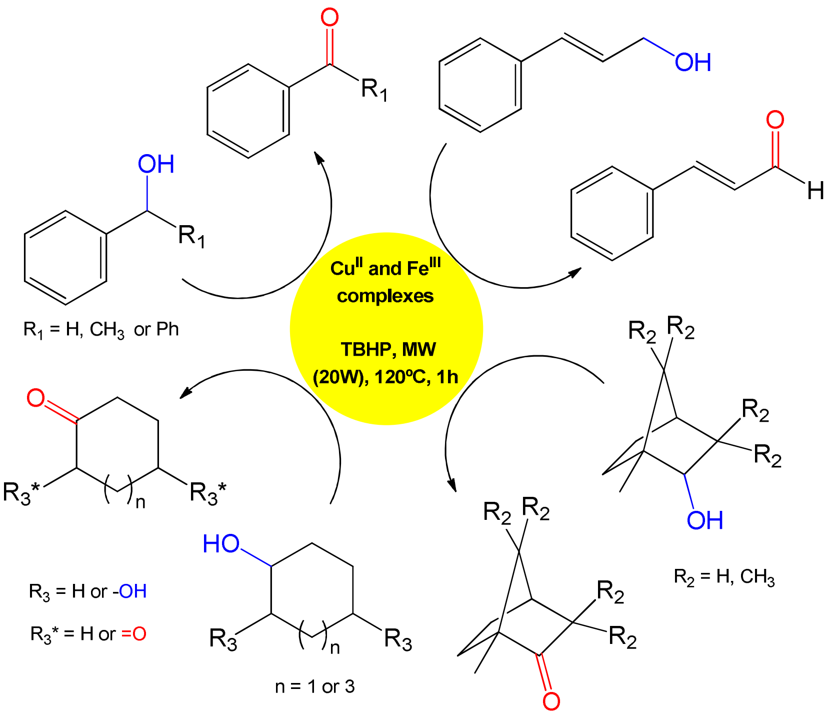
of alcohol substrate, 5 µmol (0.2 mol % *vs*. substrate) of **1**−**4**, 5 mmol of Bu^tOOH (2 equiv, 70 % in H_2O), 0.5−2 h reaction time in a solvent-free medium.



Scheme 5. MW-assisted oxidation of alcohol substrates to the corresponding aldehydes or ketones.

Influence of two important reaction parameters such as the time and temperature[3,19] were investigated using 1-phenylethanol as model substrate (Tables S10 and S11).

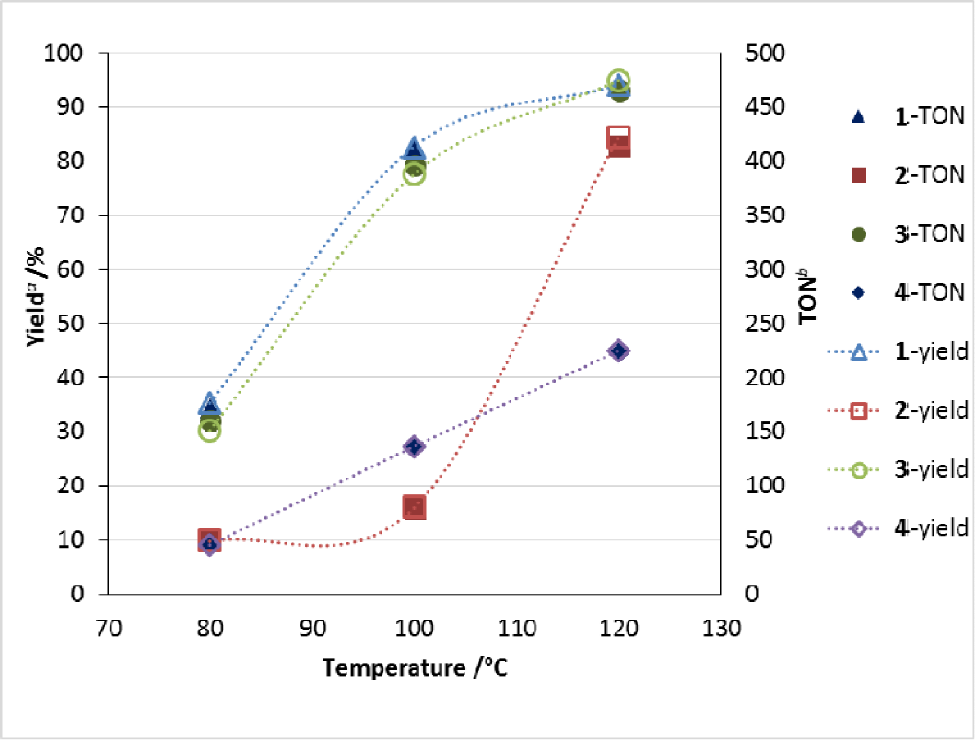


Figure 2. Dependence on the temperature for MW-assisted solvent-free oxidation of 1-phenylethanol using **1**−**4** as catalyst precursors. Reaction conditions: 2.5 mmol of 1-phenylethanol,

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5 µmol (0.2 mol % *vs*. substrate) of **1**–**4**, 5 mmol of Bu^{t}OOH (2 equiv., 70% in H_2O), 0.5 h reaction time, 80, 100 and 120 °C reaction temperature, MW irradiation (up to 20 W power). ^{a}Moles of acetophenone per 100 mol of alcohol substrate (GC yield), >99% selectivity. ^{b}Turnover number = moles of product/mol of catalyst precursor.

The catalytic performance of **1**–**4** to produce acetophenone is enhanced increasing temperature. **1** and **3** exhibited the highest activities at 120 ºC, reaching 94.0 and 95.0% yield, respectively, with corresponding TON (moles of product per mol of catalyst precursor) values of 4.71×10^2 and 4.66×10^2, respectively, after 0.5 h of MW irradiation. High selectivity towards the formation of acetophenone was found (> 99%), and no traces of by-products were detected by GC analyses of the final reaction mixtures (only unreacted alcohol, apart from the ketone product).

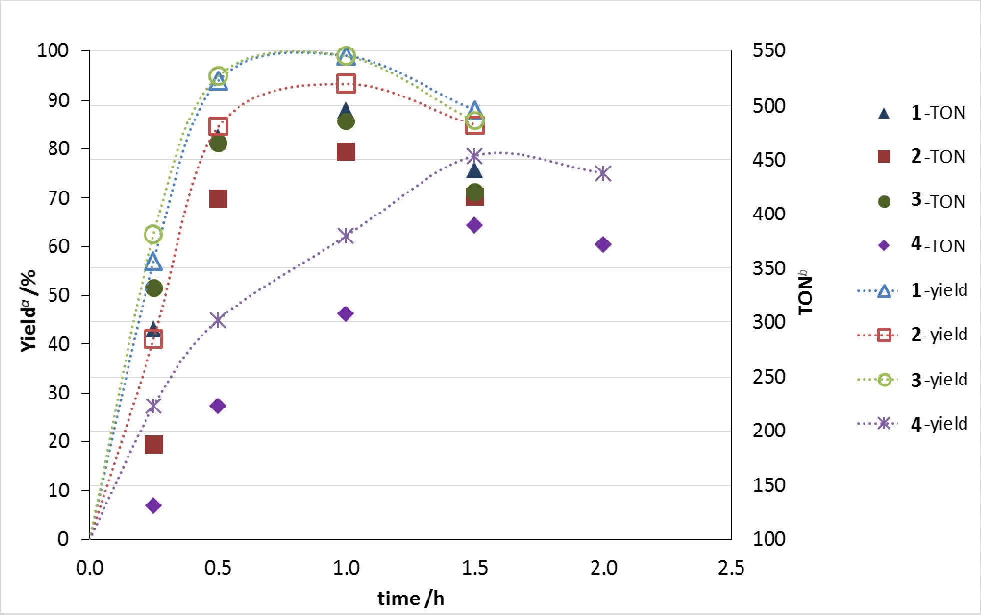

Figure 3. Time reaction studies in MW-assisted solvent-free oxidation of 1-phenylethanol using **1**–**4** as catalyst precursors. Reaction conditions: 2.5 mmol of 1-phenylethanol, 5 µmol (0.2 mol % *vs*. substrate) of **1**–**4**, 5 mmol of Bu^{t}OOH (2 equiv., 70% in H_2O), 0.25, 0.5, 1.0, 1.5 and 2.0 h reaction time, 120 °C reaction temperature, MW irradiation (up to 20 W power). ^{a}Moles of acetophenone per 100 mol of alcohol substrate (GC yield), >99% selectivity. ^{b}Turnover number = moles of product/mol of catalyst precursor.

It was found that 1h of MW irradiation is the best compromise since yields reach a maximum and then slightly decrease conceivably due to overoxidation (Figure 3). **1** and **3** exhibit the maximum yields (99.9 %) and highest TON values (4.96×10^2 and 4.85×10^2, respectively).

The molecular structures of **1** and **2** are very similar, only differing in one site of each Cu coordination sphere, where it can be found the solvent species, methanol or dimethylformamide (DMF) in **1** and **2**, respectively (see Scheme 3). The higher labiality of methanol relative to DMF, can afford more availability for the metal centre and thus account for the higher acetophenone yield obtained in the presence of **1**.

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Iron(III) in some reports is known to be better than Cu(II) towards alcohol oxidation,[13f,g] but in our work **4** exhibited the lowest catalytic performance. Coordination sphere of **4** is saturated by N donor atoms of the formazan ligands (see Scheme 4), constituting a more stable structure and then increasing the inertness of this pre-catalyst.

The Cu(II) complex bearing one arylhydrazone of ethyl 2-cyanoacetate ligand, coordinated via metal-cyano group (structure **3**, Scheme 3), evidenced the higher catalytic activity. This fact is based on the ability of the coordinated species to leave the metallic centre and dispose free coordination sites, turning it in a more convenient compound to react with the alcohol substrates and oxidant. It should be noted that besides **1** and **3** reached similar yield values for production of acetophenone, structure **1** bears two metal species and **3** just one. Then, if we take into account the activity per metal centre **3** is the most effective pre-catalyst towards oxidation of 1-phenylethanol.

The catalytic performance of **1−4** in the homogeneous oxidation using Bu^{t}OOH of 1-phenylethanol was studied in the presence of the 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) radical. The results are presented in Figure 4. TEMPO additive provided a slightly decrease in TON values for all catalytic systems under similar reaction conditions.

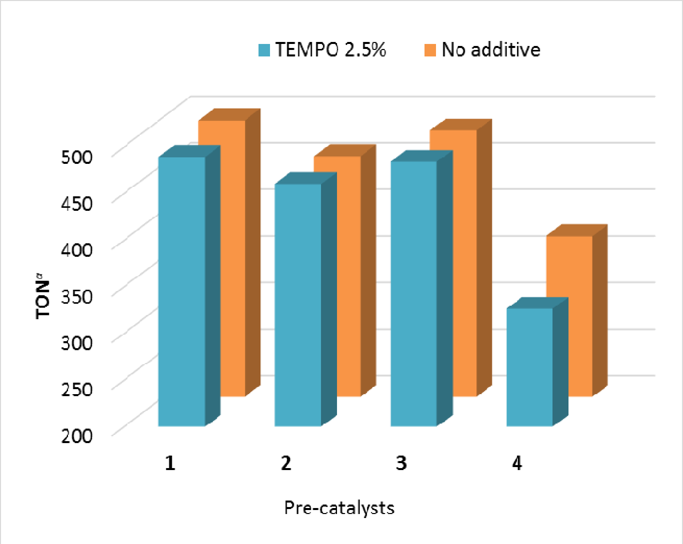

Figure 4. MW-assisted solvent-free oxidation of 1-phenylethanol using **1−4** as catalyst precursors in absence and presence of TEMPO (2.5 mol % vs. substrate). Reaction conditions: 2.5 mmol of 1-phenylethanol, 5 µmol (0.2 mol % *vs*. substrate) of **1−4**, 5 mmol of Bu^{t}OOH (2 equiv., 70% in H_2O), 62.5 µmol of TEMPO (2.5 mol % vs. substrate), 1.0 h reaction time, 120 °C reaction temperature, MW irradiation (up to 20 W power). ^{a}Turnover number = moles of product/mol of catalyst precursor.

1-Phenylethanol blank tests (in the absence of a pre-catalyst) and trials using **$H_3L^{1,2}$** (with no coordinated metal) were performed under the same optimized reaction conditions and no significant acetophenone production was observed (Table S10, entries 31-33).

In order to get insights regarding the mechanism of alcohol oxidation with TBHP, known C and O-radical traps ($CBrCl_3$ and Ph_2NH) were introduced to the catalytic system.[20] This led to a significant decrease of the catalytic activity in the presence of **1−4** (Table S10, entries 34-41). This

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fact suggests that C· and O· radicals (H-atom abstractor of the alcohol function group) where trapped by the introduced radical scavengers, interrupting the probably metal-mediated Bu^{t}OO· and Bu^{t}O· formation.[21] The proposed mechanism is resumed by equations (1-6) where M is the catalyst metal centre.[22] It should be noted that for the Fe(III) catalyst equations (1) and (2) are in reverse order. This mechanism was proposed for different transition metals (*e.g.*, M = V, Mn, Fe, Co or Cu)[19] where the ability to undergo a unit change of the metal oxidation state ($M^{n+}/M^{(n+1)+}$) appears to be particularly favorable. Such a type of radical mechanism has also been reported for copper-catalyzed peroxidative oxidation of other substrates, such as aromatic aldehydes[22e] and amines.[22f]

$$M^{n+} + {}^tBuOOH \rightarrow M^{(n+1)+}{-}OH + {}^tBuO^{\cdot} \qquad (1)$$

$$M^{(n+1)+} + {}^tBuOOH \rightarrow M^{n+} + {}^tBuOO^{\cdot} + H^+ \qquad (2)$$

$$M^{(n+1)+}{-}OH + {}^tBuOOH \rightarrow M^{(n+1)+}{-}OO{-}{}^tBu + H_2O \qquad (3)$$

$${}^tBuO^{\cdot} + R_2CHOH \rightarrow {}^tBuOH + R_2C^{\cdot}{-}OH \qquad (4)$$

$${}^tBuOO^{\cdot} + R_2CHOH \rightarrow {}^tBuOOH + R_2C^{\cdot}{-}OH \qquad (5)$$

$$M^{(n+1)+}{-}OO{-}{}^tBu + R_2C^{\cdot}{-}OH \rightarrow R_2C{=}O + {}^tBuOOH + M^{n+} \qquad (6)$$

For comparison of MW irradiation *vs.* conventional heating mode (silicone bath), same optimized reaction parameters were applied on **1** and **3** catalytic systems for the oxidation our selected alcohol substrate model, 1-phenylethanol (Figure 5). MW irradiation affords an enhanced acetophenone yield with both precatalysts, since 94.0 % (**1**) and 95.0 % (**3**) yield is reach just after 30 min and full conversion within 1 h of reaction in contrast with conventional heat at 30 min (52.5 and 53.3 % for **1** and **3**, respectively) and 1 h (97.6 and 94.4 % for **1** and **3**, respectively). It is necessary to carry out the reaction to 3 h to obtain full conversion with the conventional heat mode. It is worthwhile to notice the low MW irradiation power (less than 20 W) also turn this synthetic protocol more desirable than the conventional heat one, which requires about 1500-2000 W to achieve a 120 °C reaction temperature.

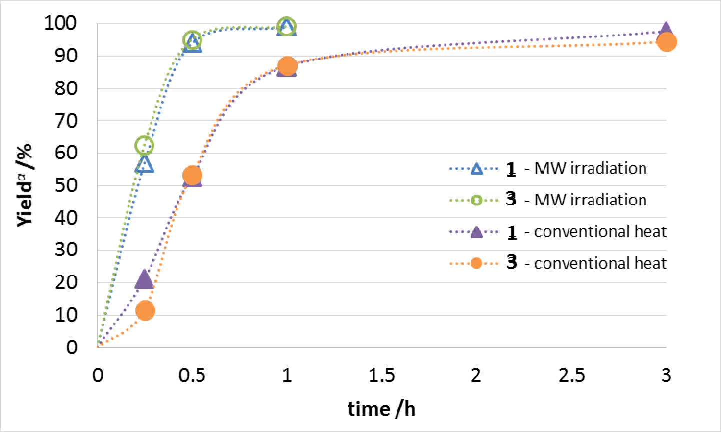

Figure 5. Solvent-free oxidation of 1-phenylethanol using **1** or **3** as catalyst precursors using conventional heat or MW irradiation. Reaction conditions: 2.5 mmol of 1-phenylethanol, 5 μmol

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(0.2 mol % *vs*. substrate) of **1** or **3**, 5 mmol of $\mathrm{Bu^{t}OOH}$ (2 equiv., 70% in H_2O), 0.25, 0.5, 1.0 and 3.0 h reaction time, 120 °C reaction temperature, conventional heat (silicone bath) or MW irradiation (up to 20 W power). ^{a}Moles of aldehyde or ketone per 100 mol of alcohol substrate (GC yield), >99% selectivity.

Since the best catalytic performances were obtained in presence of **1** or **3** at 120 ºC and 1 h MW irradiation in absence of TEMPO, the oxidation of other alcohol substrates was tested under the same optimized reaction parameters (Figure 6, Table S11).

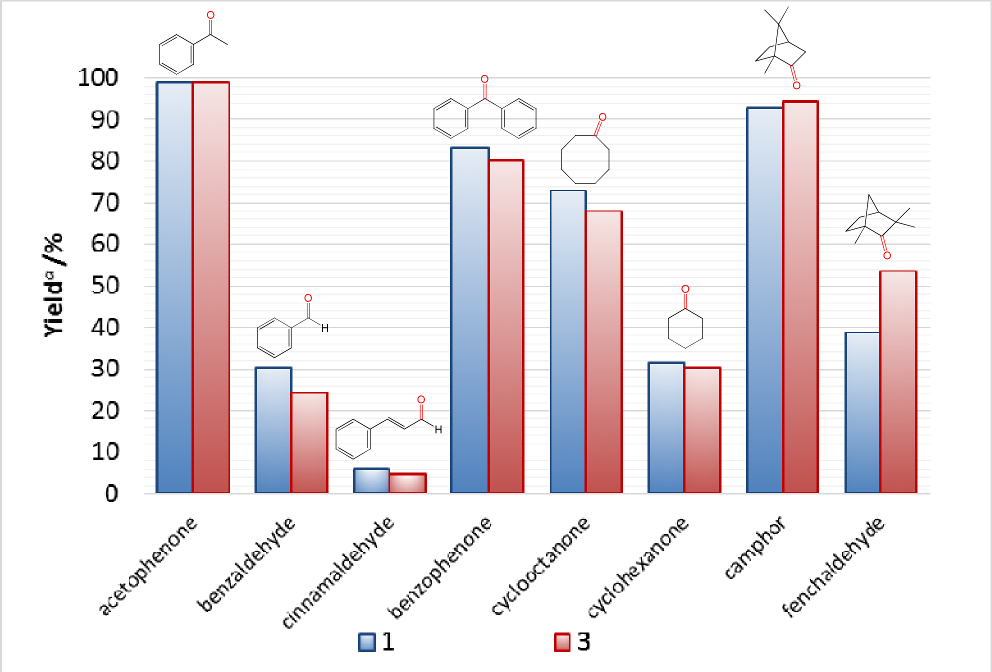

Figure 6. MW-assisted solvent-free oxidation of 1-phenylethanol, benzyl alcohol, cinnamyl alcohol, bezhydrol, cyclooctanol, cyclohexanol, isoborneol and fenchyl alcohol using **1** or **3** as catalyst precursors. Reaction conditions: 2.5 mmol of alcohol substrate, 5 µmol (0.2 mol % *vs*. substrate) of **1** or **3**, 5 mmol of $\mathrm{Bu^{t}OOH}$ (2 equiv., 70% in H_2O), 1.0 h reaction time, 120 °C reaction temperature, MW irradiation (up to 20 W power). ^{a}Moles of aldehyde or ketone per 100 mol of alcohol substrate (GC yield), >99% selectivity.

Oxidation, with peroxide, of primary aromatic alcohols (benzyl alcohol and cinnamyl alcohol) end up to be much less profitable than secondary ones (1-phenylethanol and benzhydrol). Despite the less steric hindrance of primary alcohols that should turn the substrate more suitable to react, lower conversions were obtained, maybe due the higher stability of the radical intermediate formed from secondary alcohols ($R_2C^{\cdot}$–OH> $RHC^{\cdot}$–OH) upon the H abstraction illustrated in equations 4 and 5.

For the tested ring membered aliphatic secondary alcohols (Table S11), cyclooctanone was obtained in higher yields than cyclohexanone, in accord with the greater instability/reactivity of the 8-carbon member ring in comparison with the 6 one. Moreover, camphor is produced in higher yield from isoborneol than fenchaldehyde from fenchyl alcohol. A possible justification relies on the difference of the steric hindrance of -OH group in the alcohol substrate.

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It was also studied the regioselective oxidation of 1,2- and 1,4-cyclohexanediol by **1** and **3** under the optimized reaction conditions (Figure 7). The corresponding diketones were obtained, and again similar activities were observed for both catalyst precursors. Vicinal diketones (51.5 and 56.0% for **1** and **3**, respectively) were formed in higher yields than 1,4-diketones (18.1 and 23.4% for **1** and **3**, respectively). This tendency was expected in *vic*-diols since after one H· abstraction, the remaining H of the other –OH functional group has increased acidity (higher pK_a) and then became more easy to be captured by radicals from the peroxide.

High selectivity for diketones were achieved. This suggests the presence of only traces of by products, such as hydroxyl ketones, or even hydroxyoxepanones (Baeyer-Villiger mechanism type) has reported in other works.[23]

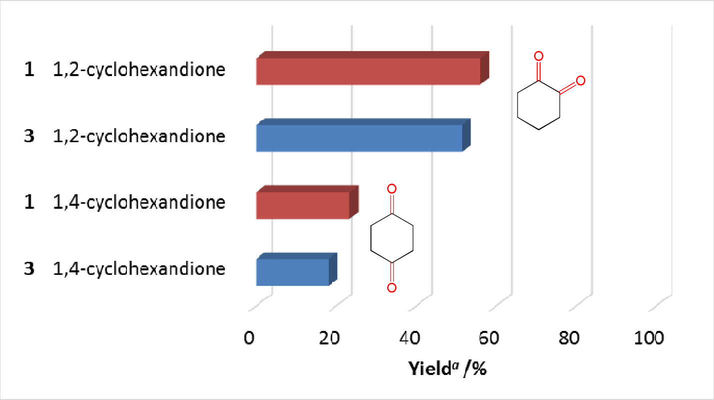

Figure 7. MW-assisted solvent-free oxidation of 1,2-cyclohexanediol and 1,4-cyclohexanediol catalysed by **1** or **3**. Reaction conditions: 2.5 mmol of alcohol substrate, 5 μmol (0.2 mol % *vs.* substrate) of **1** or **3**, 5 mmol of Bu^{t}OOH (2 equiv., 70% in H_2O), 1.0 h reaction time, 120 °C reaction temperature, MW irradiation (up to 20 W power). ^{a}Moles of aldehyde or ketone per 100 mol of alcohol substrate (GC yield), *ca* 94 % selectivity.

Conclusions

Three copper(II) complexes bearing arylhydrazone ligands and an iron(III) compound with formazan groups were synthesized and fully characterized. A new type of *E*/*Z* → *E* isomerization assisted by unprecedented cooperation of coordination and ionic interaction was found in the formation of a copper(II) complex in the presence of ethylenediamine. Although the free heterocyclic formazan compound occurred in the *EE*-configuration, its iron(III) complex showed that moiety with the *EZ*-configuration.

The obtained complexes act as effective catalyst precursors, highlighting binuclear Cu-complexes, for the mild and selective homogeneous oxidation, by peroxide, of benzyl and aliphatic primary and secondary alcohols and cyclic 1,2- and 1,4-diols to corresponding aldehydes, ketones and diketones in a solvent-free MW-assisted process. Efforts to increase the catalytic activities using TEMPO were unsuccessful, which end up to reveal an opposite desired effect. Curiously the oxidation products from more substituted alcohols (secondary) achieved higher yields and TONs in comparison with the less substituted ones (primary). The regioselective applicability, minute scale

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reaction, use of low power MW irradiation and solvent-free system are significant factors converging towards green standards and energy saving catalytic systems aiming more sustainable scalable chemical processes.

Experimental Section

Materials and instrumentation

All the synthetic work was performed in air and at room temperature. All the chemicals were obtained from commercial sources (Aldrich) and used as received. Infrared spectra (4000–400 cm^{-1}) were recorded on a Vertex 70 (Bruker) instrument in KBr pellets. 1D (^{1}H, ^{13}C{^{1}H}) NMR spectra were recorded on Bruker Advance II 300.13 (75.468 carbon-13) and 400.13 (100.61 carbon-13) MHz (UltraShield^{TM} Magnet) spectrometers at ambient temperature. Magnetic measurements of complex **4** in solution was performed at room temperature (r.t.) by ^{1}H NMR using the Evans' method[18] on a Bruker Avance 300 spectrometer operating at 300.13 MHz at a constant temperature of 298.15 K. The measurement for **4** was performed in standard 5 mm NMR tube containing the paramagnetic sample dissolved in D_2O with an inert reference of *tert*-butyl alcohol, against a reference insert tube filled with the same solvent (*tert*-butyl alcohol in D_2O) and their shift measured in Hz. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from *m/z* 100 to 1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80–105 V). The acidity of the solutions was measured using a CG825 pH-meter with an ESL-43-07 glass electrode adjusted by standard buffer solutions and an EVL-1M3.1 silver-silver chloride reference electrode. The ionic strength was maintained constant (0.1 M) by adding a calculated amount of KCl. The absorbance of the solutions was measured on a Lambda 40 spectrophotometer (Perkin Elmer) in 1 cm quartz cells. The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface. Cyclic voltammograms (CV) were obtained in a 0.2 M [^{n}Bu$_4$N][BF$_4$]/NCMe solution, at a platinum disc working electrode (d = 0.5 mm). Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the above mentioned composition, in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. For both CV and CPE experiments, a Luggin capillary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential. The CPE experiments were monitored regularly by cyclic voltammetry, thus assuring that no significant potential drift occurred during the electrolyses. Ferrocene was used as an internal standard for the

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measurement of the oxidation potentials of the complexes; the redox potential values are quoted relative to the SCE by using as internal reference the ferrocene/ferricinium couple ([Fe(η^5-C_5H_5)$_2$]$^{0/+}$; *E* = 0.42 V *vs.* SCE in NCMe).[24]

Synthesis of (*E/Z*)-4-(2-(1-cyano-2-ethoxy-2-oxoethylidene)hydrazinyl)-3-hydroxybenzoic acid (H_3L^1)

The arylhydrazone H_3L^1 was synthesized via the Japp-Klingemann reaction[14] between the aromatic diazonium salt of 4-amino-3-hydroxybenzoic acid and ethyl 2-cyanoacetate in water solution containing sodium acetate.

For the synthesis of H_3L^1, 4-amino-3-hydroxybenzoic acid (1.53 g, 10.00 mmol) was dissolved in 50 mL water, and 0.40 g (10.00 mmol) of NaOH was added. The solution was cooled in an ice bath to 273 K and 0.69 g (10.00 mmol) of $NaNO_2$ was added; 2.00 mL HCl was then added in 0.5 mL portions for 1 h. The temperature of the mixture should not exceed 278 K. Ethyl 2-cyanoacetate (1.13 mL, 10.00 mmol) was added to 30 mL water-ethanol (5/25, *v/v*) solution of sodium hydroxide (0.2 g, 10.0 mmol) and sodium acetate (0.82 g, 10.00 mmol). The resulting solution was stirred and cooled to *ca.* 273 K, and a suspension of diazonium salt (see above) was added in three portions under vigorous stirring for 1 h. A yellow precipitate of the title compound was formed in *ca.* 1 h, filtered off, dried in air and recrystallized from methanol.

H_3L^1. Yield: 870 mg (based on ethyl 2-cyanoacetate), yellow powder soluble in water, methanol, ethanol, acetone and insoluble in chloroform. Anal. Calcd for $C_{12}H_{11}N_3O_5$ (*Mr* = 277.07): C, 51.99; H, 4.00; N, 15.16; found: C, 51.81; H, 3.94; N, 15.22 %. ESI-MS: *m/z*: 278.2 [*Mr*+H]$^+$. IR (KBr): 3409 and 3088 *ν*(OH), 2780 and 2462 *ν*(NH), 2180 *ν*(C≡N), 1693 *ν*(COOH), 1610 *ν*(C=O) and 1512 *ν*(C=N) cm^{-1}. ^{1}H NMR of a mixture of isomeric *E*- and *Z*-hydrazone forms (300.130 MHz) in DMSO-d_6, internal TMS, δ (ppm): *E*-Hydrazone, 1.27−1.33 (s, 3H, CH_3), 3.83 (s, 1H, COOH), 4.29−4.35 (2H, CH_2), 7.48−7.54 (3H, Ar−H), 11.02 (s, 1H, O−H) 12.79 (s, 1H, N−H). *Z*-Hydrazone, 1.27−1.33 (s, 3H, CH_3), 3.86 (s, 1H, COOH), 4.29−4.35 (2H, CH_2), 7.48−7.54 (3H, Ar−H), 11.03 (s, 1H, O−H) 13.16 (s, 1H, N−H). ^{13}C{^{1}H} NMR (75.468 MHz, DMSO-d_6). *E*-Hydrazone, δ: 13.87 (CH_3), 52.93 (CH_2), 106.27 (Ar−H), 113.90 (C=N), 115.60 (C≡N), 127.66 (2Ar−H), 132.30 (Ar−COOH), 132.33 (Ar−NHN=), 145.31 (Ar−OH), 161.69 (C=O), 166.73 (COOH). *Z*-Hydrazone, δ: 13.87 (CH_3), 62.25 (CH_2), 106.45 (Ar−H), 121.79 (C=N), 116.35 (C≡N), 127.70 (2Ar−H), 132.30 (Ar−COOH), 132.33 (Ar−NHN=), 145.33 (Ar−OH), 161.26 (C=O), 166.73 (COOH).

Synthesis of (1*E*,1*Z*)-N',2-di(1*H*-1,2,4-triazol-3-yl)diazenecarbohydrazonoyl cyanide (H_3L^2)

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Synthesis of $\mathbf{H_3L^2}$ was performed according to a known procedure;[12a] reaction of methyl 2-cyanoacetate with two equivalent of 1*H*-1,2,4-triazole-3-diazonium chloride lead to formazan ligand.

Two equivalent of 1*H*-1,2,4-triazol-3-amine (1.68 g, 20.00 mmol) were dissolved in 70 mL water. The solution was cooled in an ice bath to 273 K and 4.00 mL of HCl was added; 1.38 g (20.00 mmol) of $NaNO_2$ in 5 mL water was then added in 0.5 mL portions for 1 h. 10 mL water solution of NaOH (1.20 g, 30.00 mmol) were added to a mixture of 10.00 mmol (0.99 mL) of methyl 2-cyanoacetate with 20 mL of ethanol. The solution was cooled in an ice bath to *ca*. 273 K, and 1*H*-1,2,4-triazole-3-diazonium chloride (see above) was added in three portions under vigorous stirring for 1 h. The reaction mixture was then transferred to a beaker and acidified by HCl (33 % w/w) to pH ~7.5. The orange product $\mathbf{H_3L^2}$ precipitated, whereupon it was filtered off, dried in air and recrystallized from methanol.

$\mathbf{H_3L^2}$. Yield: 680 mg (based on methyl 2-cyanoacetic acid), yellow powder soluble in water, methanol, ethanol and insoluble in chloroform. Anal. Calcd for $C_6H_5N_{11}$ (*Mr* = 231.18): C, 31.17; H, 2.18; N, 66.65; found: C, 31.04; H, 2.09; N, 66.34 %. ESI-MS: *m/z*: 232.2 $[Mr\text{+H}]^+$. IR (KBr): 3125 and 2907 *ν*(NH), 2215 *ν*(C≡N), 1695, 1611 and 1539 *ν*(C=N) cm^{-1}. ^1H NMR (300.130 MHz) in DMSO-d_6, internal TMS, δ (ppm): *EE linear isomer*, 8.15 (s, 1H, NH hydrazone), 8.34 and 8.52 (2H, 2CH of triazole moieties), 8.82 and 8.86 (2H, 2NH of triazole moieties). $^{13}C\{^1H\}$ NMR (75.468 MHz, DMSO-d_6). *EE linear isomer*, δ: 110.09 (C≡N), 143.79 (C−NH of triazole moiety), 145.36 (C−NH of triazole moiety), 145.84 (C−N=N), 157.06 (C−NH), 163.54 (N=$\underline{C}$−C≡N).

Syntheses of complexes

Syntheses of 1 and 2. 27.7 mg (0.1 mmol) of H_3L^1 was dissolved in 5 mL methanol (or methanol-dimethylformamide mixture (20/1, v/v) in the case of **2**), then 23.3 mg (0.1 mmol) of $Cu(NO_3)_2\cdot 2.5H_2O$ were added. The mixture was stirred and heated to 80 °C for 5 min, then left for slow evaporation at room temperature. Dark blue crystals of the product started to form after *ca*. 3 d at room temperature; they were then filtered off and dried in air.

1: Yield, 4.0 mg, 62 % (based on Cu). Dark blue crystalline compound soluble in ethanol, methanol, acetonitrile, DMSO and water. Anal. Calcd for $C_{26}H_{26}Cu_2N_6O_{12}$ (*Mr* = 741.61): C, 42.11; H, 3.53; N, 11.33. Found: C, 42.14; H, 3.39; N, 11.27. ESI-MS: *m/z*: 678.52 $[Mr{-}2CH_3OH\text{+H}]^+$. IR (KBr, selected bands, cm^{-1}): 3400 and 2982 *ν*(O−H), 2224 *ν*(C≡N), 1671 *ν*(C=O) and 1577 *ν*(C=N).

2: Yield, 3.3 mg, 51 % (based on Cu). Dark brown crystalline compound soluble in ethanol, methanol, acetonitrile, DMSO and water. Anal. Calcd for $C_{30}H_{32}Cu_2N_8O_{12}$ (*Mr* = 823.71): C, 43.74; H, 3.92; N, 13.60. Found: C, 43.24; H, 3.61; N, 13.40. ESI-MS: *m/z*: 678.62

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[*Mr*−2(CH$_3$)$_2$NCHO+H]$^+$. IR (KBr, selected bands, cm^{-1}): 3497 *ν*(O−H), 2218 *ν*(C≡N), 1697 and 1643 *ν*(C=O) and 1567 *ν*(C=N).

Synthesis of 3. 27.7 mg (1.0 mmol) of H$_3$L^1 were dissolved in 5 mL methanol, then 23.3 mg (0.1 mmol) of Cu(NO$_3$)$_2$·2.5H$_2$O and 12 μL (0.2 mmol) ethylenediamine were added. The mixture was stirred for 30 min at 80 °C and left for slow evaporation; the dark brown crystals of the product started to form after *ca*. 3 d at room temperature; they were then filtered off and dried in air.

3: Yield, 3.0 mg, 47 % (based on Cu). Dark brown crystalline compound soluble in ethanol, methanol, acetonitrile, DMSO and water. Anal. Calcd for C$_{17}$H$_{31}$CuN$_7$O$_7$ (*Mr* = 509.02): C, 40.11; H, 6.14; N, 19.26. Found: C, 39.94; H, 5.97; N, 19.45. ESI-MS: *m/z*: 460.02 [*Mr*−CH$_3$OH−H$_2$O+H]$^+$. IR (KBr, selected bands, cm^{-1}): 3611, 3298, 3223 and 3144 *ν*(O−H), 2969, 2934, 2908 and 2884 *ν*(N−H), 2363 *ν*(C≡N), 1652 and 1624 *ν*(C=O) and 1584 *ν*(C=N).

Synthesis of 4. 23.1 mg (0.1 mmol) of H$_3$L^2 were dissolved in 5 mL methanol-water mixture (4/1, v/v), then 1 mL 0.01 M HCl (pH 2) and 23.2 mg (0.1 mmol) of FeCl$_3$·6H$_2$O were added. The mixture was stirred for 5 min, then left for slow evaporation at room temperature, dark red crystals of **4** suitable for X-rays started to form after *ca*. 3 d.

4: Yield, 2.4 mg, 43 % (based on Fe). Dark red crystals soluble in ethanol, acetonitrile, DMSO, DMF and water. Anal. Calcd for C$_{12}$H$_9$FeN$_{22}$ (*Mr* = 517.19): C, 27.87; H, 1.75; N, 59.58. Found: C, 27.71 H, <2.00; N, 59.09. ESI-MS: *m/z*: 518.2 [*Mr*+H]$^+$. IR (KBr, selected bands, cm^{-1}): 3360 and 2923 *ν*(N−H), 2223 *ν*(C≡N), 1647, 1636 and 1545 *ν*(C=N).

X-ray structure determinations

X-ray quality crystals of **1** - **4** were immersed in cryo-oil, mounted in a Nylon loop and measured at 296 K. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-Kα (λ 0.71073Å) radiation. Data were collected using omega scans of 0.5º per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT[25a] on all the observed reflections. Data were corrected for absorption effects using the multi-scan method (SADABS).[25a] Structures were solved by direct methods by using SIR-97 package[25b] and refined with SHELXL-2014.[25c] Calculations were performed using the WinGX System-v2014.1.[25d] The hydrogen atoms attached to carbon atoms were inserted at geometrically calculated positions and included in the refinement using the riding-model approximation, while those attached to nitrogen atoms were located in the difference Fourier synthesis but were included in the final refinement at positions calculated from the geometry of the molecules using the riding model, with isotropic vibration parameters. Uiso(H) were defined as 1.5Ueq of the parent nitrogen atoms and of the parent carbon atoms for the methyl groups, or 1.2Ueq of the carbon atoms for phenyl and methylene residues. The hydrogen atoms of the water and methanol molecules (in **3**) have been located from the final Fourier difference map,

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and the isotropic thermal parameter were set at 1.5 times the average thermal parameter of the belonging oxygen atom. Some DFIX and DANG restrains were applied for the NH groups and/or the water molecule. PLATON/SQUEEZE[25e] was used to treat disordered molecules in the asymmetric unit of **3**. These were removed from the model and not included in the empirical formula.

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General procedure for the oxidation of alcohols with TBHP

In a typical experiment, the alcohol substrate, 1-phenylethanol, benzylic alcohol, cinnamyl alcohol, benzhydrol, cyclooctanol, cyclohexanol, isoborneol, fenchyl alcohol, 1,2-cyclohexanediol or 1,4-cyclohexanediol (2.5 mmol), Bu^tOOH (70 % aqueous solution, 5.0 mmol) and catalyst precursor **1−4** (10 μmol, 0.2 mol% *vs.* substrate) were introduced to a cylindrical Pyrex tube, which was then placed in the focused microwave reactor. In the simultaneous oxidation of benzylic alcohol and 1-phenylethanol experiment an equimolar amount was used (1.25+1.25 mmol). In the TEMPO-mediated experiments, TEMPO (62.5 μmol, 2.5 mol% *vs.* substrate) was added to the reaction mixture. The system was stirred and irradiated (up to 20 W) for 15, 30, 60, 90 or 120 min at 80, 100 or 120 ºC. After the reaction, the mixture was allowed to cool down to room temperature. 150 μL of benzaldehyde (internal standard) and 2.5 mL of MeCN (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred during 10 min and then a sample (0.5 μL) was taken from the organic phase and analysed by GC using the internal standard method. Blank tests indicate no traces of acetophenone are generated in a pre-catalyst-free system. For the conventional heating method, experiments were carried out in 5 mL round-bottomed flasks eqquiped with a reflux condenser under silicone heating bath. Reaction parameters were applied as mentioned above.

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Supporting Information Available: $^1H/^{13}C$ NMR spectrum of $H_2L^{1,2}$. Crystal data, experimental parameters and selected details of the refinement calculations, tables listing bond distances and angles and hydrogen bond geometry. This material is available free of charge via the Internet or from the authors. CCDC 1412834−1412837 contain the supplementary crystallographic data for complexes **1−4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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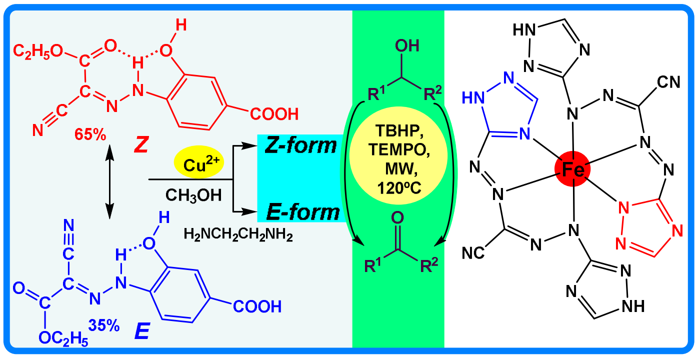
TOC graphic and synopsis

Cooperative coordination and ionic interactions assisted *E/Z* isomerization in arylhydrazone ligand lead to a variety of Cu^{II} complexes, which effectively catalyse the homogeneous oxidation of alcohols to carbonyl compounds (see scheme). A new Fe^{III} complex with heterocyclic formazan ligand is also catalytic active in alcohols oxidation.



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