

DOI:10.1002/ejic.201500440



Trinuclear Cu^{II} Structural Isomers: Coordination, Magnetism, Electrochemistry and Catalytic Activity towards the Oxidation of Alkanes

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Keywords: N,O ligands / Copper / Magnetic properties / Electrochemistry / Oxidation

The reaction of the Schiff base (3,5-di-tert-butyl-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (H_3L) with copper(II) nitrate, acetate or metaborate has led to the isomeric complexes $[Cu_3(L)_2(MeOH)_4]$ (1), $[Cu_3(L)_2(MeOH)_2]$ -2MeOH (2) and $[Cu_3(L)_2(MeOH)_4]$ (3), respectively, in which the ligand L exhibits dianionic $(HL^{2-}, \text{ in 1})$ or trianionic $(L^{3-}, \text{ in 2 and 3})$ pentadentate $1\kappa O, O', N: 2\kappa N', O''$ chelation modes. Complexes 1–3 were characterized by elemental analysis, IR spectroscopy, single-crystal X-ray crystallography, electrochemical methods and variable-temperature magnetic susceptibility measurements, which indicated that the intra-trimer antiferromagnetic coupling is strong in the three com-

Introduction

The chemistry of trinuclear copper(II) complexes has been intensively studied owing to their potential biological activities, for example, laccase,^[1] methane monooxygenase,^[2] ascorbate oxidase,^[3] as well as for their active role as model systems to gain an understanding of the magnetic interactions and magneto-structural correlations in molecular systems.^[4] In general, trinuclear Cu^{II} complexes can be classified into three types: 1) open triangular, 2) closed triangular and 3) linear, depending upon the arrangement of the metal centres.^[5] Open triangle trinuclear Cu^{II} complexes plexes and that there exists very weak ferromagnetic intermolecular interactions in 1 but weak antiferromagnetic intermolecular interactions in both 2 and 3. Electrochemical experiments showed that in complexes 1–3 the Cu^{II} ions can be reduced, in distinct steps, to Cu^I and Cu⁰. All the complexes act as efficient catalyst precursors under mild conditions for the peroxidative oxidation of cyclohexane to cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone, leading to overall yields (based on the alkane) of up to 31% (TON = 1.55×10^3) after 6 h in the presence of pyrazinecarboxylic acid.

have important structural and magnetic properties in relation to their role in the active site of multi-copper oxidases,^[6] whereas closed and linear triangle Cu^{II} ions have been predominantly studied in order to investigate magnetic interactions.^[7] Although the magnetic interactions of Cu^{II} complexes have been well explored, only a few Schiff-base complexes containing the diazene bridge with a trinuclear array of copper centres have been reported.^[7c,7d,8]

The main aim of this work was thus to prepare other types of trinuclear Cu^{II} complexes with a diazene bridge and to examine the effect of different copper salts in reactions with Schiff bases, which are known to stabilize metal complexes in various oxidation states and nuclearities^[9] and, in particular, can play an important role in the synthesis of multinuclear copper complexes.^[8,10] Another aim was to explore their possible catalytic applications in the field of alkane functionalization (see below).^[11–14]

In addition to the biological and magnetic importance of multinuclear copper complexes, their catalytic applications have also been established.^[10a,11g-1] In particular, the search for mild, efficient and direct routes for the oxidative functionalization of inert alkanes (relatively cheap and abundant materials) to more valuable organic products is of high industrial significance.^[12] An example^[11d-11i,12c-12f,12h-12j,13] is the catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone, which are important reagents for the

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201500440.



production of adipic acid and caprolactam used for the manufacture of Nylon-6,6, for which the need for alternatives to the current industrial route, using more active and selective catalytic systems under milder reaction conditions, has been recognized.^[11a,11d,12c,14]

A promising approach consists of the design and development of new bio-inspired catalysts.^[2b,11e-11i,12h-12k,13h] Among various metals with a recognized biological function, copper is cheap and widespread in nature, being present in the active sites of many oxidation enzymes often as di-, tri- or polynuclear Cu centres,^[15] such as particulate methane monooxygenase (pMMO), a multi-copper enzyme that catalyses the hydroxylation of alkanes.^[16] Recently, several multi-copper(II) complexes have been found to exhibit a high catalytic activity in the oxidation of cycloalkanes by hydrogen peroxide to the corresponding alkyl hydroperoxides, alcohols and ketones under mild conditions.^[11e-11i,17]

Herein we report the synthesis of three structural isomers of new trinuclear Cu^{II} complexes with a Schiff base containing a diazene bridge by using three different copper salts and explore their magnetic and electrochemical properties as well as their catalytic activity towards the oxidation of alkanes.

copper(II) structural isomers, depending on the metal salt used (Scheme 1). The reaction of H_3L in methanol at room temperature with $Cu(NO_3)_2 \cdot 2.5H_2O$ in the presence of triethylamine, $Cu(OOCCH_3)_2 \cdot H_2O$ or CuB_2O_4 (copper metaborate) resulted in the formation of the green trinuclear copper(II) complexes $[Cu_3(L)_2(MeOH)_4]$ (1), $[Cu_3(L)_2-$ (MeOH)_2]·2MeOH (2) or $[Cu_3(L)_2(MeOH)_4]$ (3), respectively. It is well known^[18] that hydrazone-based ligands exhibit keto-enol tautomerism in solution (Scheme 1) and complex formation takes place by deprotonation of the enol form. The trianionic (L^{3-}) form of the ligand has two coordination pockets, one bidentate and one tridentate, and binds simultaneously to two metal ions, similarly to what has been found for *N*-substituted salicylhydrazide complexes^[19] (Scheme 1).

In all the complexes, it is the trianionic form (L^{3-}) of the ligand that coordinates to the Cu^{II} centres. In the linear trinuclear complex 1, the copper cations exhibit square-pyramid and square planar geometries, in 2, the terminal and central Cu^{II} ions present square-planar and distorted tetrahedral geometries, respectively, and in 3, the ligands stabilize a linear trinuclear copper(II) complex in which the metal ions are in square-planar and octahedral environments.

Results and Discussion

The Schiff base (3,5-di-tert-butyl-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (H₃L) was obtained by the condensation reaction of 3,5-di-tert-butyl-2-hydroxybenzalde-hyde with salicylhydrazide and was used to synthesize three

Crystal Structures

Overall Features

Crystals of compounds 1–3 suitable for X-ray diffraction were obtained upon slow evaporation of their methanolic



Scheme 1. Synthesis of complexes 1-3.



	1	2	3
Empirical formula	C48H66Cu3N4O10	$C_{48}H_{74}Cu_3N_4O_{14}$	C ₄₈ H ₆₆ Cu ₃ N ₄ O ₁₀
M _r	1049.66	1121.73	1049.66
Crystal system	triclinic	monoclinic	monoclinic
Temperature [K]	150(2)	296(2)	150(2)
Space group	$P\overline{1}$	C2/c	$P2_1/c$
a [Å]	6.6851(9)	26.7119(10)	19.7555(12)
b [Å]	10.2750(11)	14.8620(5)	11.3640(6)
c [Å]	18.641(2)	13.9824(4)	11.1664(8)
a [°]	83.106(7)	90	90
β ^[°]	82.419(7)	98.562(2)	100.038(2)
γ [°]	79.292(9)	90	90
$V[Å^3]$	1241.1(3)	5489.0(3)	6991.5(7)
Z	1	4	2
$D_{\text{calcd.}} [\text{g cm}^{-3}]$	1.404	1.357	1.412
μ (Mo- K_a) [mm ⁻¹]	1.332	1.215	1.340
Reflections collected/unique/observed	7153/4131/2252	19578/5261/3877	20434/5186/3799
R _{int}	0.0873	0.0653	0.0633
Final $R1^{[a]}$, $wR2^{[b]}$ with $I \ge 2\sigma(I)$	0.1017, 0.2674	0.0533, 0.1374	0.0424, 0.0945
Goodness-of-fit on F^2	1.103	1.027	0.944

Table 1. Crystal data and structure refinement details for complexes 1-3.

[a] $R = \Sigma ||F_{o}| - |F_{c}|| \Sigma ||F_{o}|$. [b] $wR(F^{2}) = [\Sigma w(|F_{o}|^{2} - |F_{c}|^{2})^{2} / \Sigma w ||F_{o}|^{4}]^{\frac{1}{2}}$.

solutions at room temperature. The crystallographic data and processing parameters are summarized in Table 1, and selected dimensions and hydrogen-bonding geometries are presented in Tables S1 and S2 in the Supporting Information. Representative crystal structures are displayed in Figures 1–3 and packing diagrams in Figures 4–6.





Figure 1. Structural representation of 1 with partial atomic labelling scheme. Hydrogen atoms have been omitted except for those involved in hydrogen-bonding interactions (dashed lines). Symmetry codes to generate equivalent atoms: i) 2 - x, 2 - y, 1 - z; ii) 1 - x, 1 - y, 1 - z; iii) 1 - x, 2 - y, 1 - z; iv) 1 + x, y, z; v) 1 + x, 1 + y, z.

Complexes 1–3 are trinuclear with H_3L coordinating to the metal cations in the trianionic (L^{3-}) form by means of both phenolate O atoms, the enolate O atom and both the N atoms in a $1\kappa O, O', N: 2\kappa N', O''$ -bridging chelate fashion. In 1 and 3, the central metal cations are located at inversion centres and in 2 it lies on a two-fold axis. The asymmetric units of the compounds contain half of the molecules, namely one and a half copper cations, one L^{3-} ligand and Figure 2. Structural representation of **2** with partial atomic labelling scheme. Hydrogen atoms have been omitted except for those involved in hydrogen-bonding interactions (shown as dashed lines). Symmetry codes to generate equivalent atoms: *i*) 1 - x, *y*, 1/2 - z; *ii*) *x*, *y*, 1/2 + z; *iii*) 1 - x, -y, 1 - z; *iv*) *x*, -y, -1/2 + z.

one (in 2) or two (in 1 and 3) methanol molecules. One noncoordinated methanol molecule could also be found in the asymmetric unit of 2.

In compounds **1** and **2**, the central metal cations are in N_2O_2 environments, assuming perfect square-planar and distorted tetrahedral geometries, respectively ($\tau_4 = 0.00$ and 0.83,^[20a] respectively), whereas in **3**, the central metal cation is in the middle of an almost perfect N_2O_4 octahedron





Figure 3. Structural representation of **3** with partial atomic labelling scheme. Hydrogen atoms have been omitted except for those involved in hydrogen-bonding interactions (shown as dashed lines). Symmetry codes to generate equivalent atoms: *i*) 2 - x, -y, 1 - z; *ii*) x, 0.5 - y, 0.5 + z; *iii*) x, 0.5 - y, -0.5 + z; *iv*) x, -0.5 - y, 0.5 + z; *v*) 2 - x, 0.5 + y, 0.5 - z; *vi*) 2 - x, -0.5 + y, 0.5 - z; *vi*) 2 - x, -0.5 + y, 1.5 - z.

(quadratic elongation of 1.043 and angle variance of 19.04°²).^[20b] The terminal metals are in N₁O₄ distorted square-pyramidal (in 1, $\tau_5 = 0.31$)^[20c] or slightly distorted N₁O₃ square-planar environments (in 2 and 3, $\tau_4 = 0.10$).

The central copper cations are incorporated into two sixmembered CuOCCCN rings, whereas the terminal copper cations feature in one five-membered CuOCNN ring and one six-membered CuOCCCN ring. The minimum intramolecular Cu···Cu distance decreases in the order 4.662(1) > 4.651(2) > 4.643 Å (3), whereas the shortest intermolecular distance between the metals decreases as 5.332(1) > 5.210(3) > 5.153 Å (2).

Each Schiff-base ligand is almost planar, the leastsquares planes of the aromatic rings making angles of 7.35 (1), 5.51 (2) and 7.50° (3), and the CNNC torsion angles being 169.41 (1), 172.71 (2) and -168.16° (3). In compounds 1 and 3, the terminal metal cations are almost in the same plane as the ligands, but the central copper atoms are totally out of plane, as indicated by the CCOCu and CCNCu torsion angles of the six-membered metallacycles, which range from 31.87 to 33.67°. In 2, however, these angles are -17.81 and 11.13°, respectively, and, indeed, both metal cations lie in the plane of the Schiff-base ligand. These variations in the coordination parameters of the metals also affect other structural factors, as expressed by the Cu- $O_{\text{phenolate}}$ bond lengths (Table 1), which range from 1.878(8) to 1.907(8) Å, the differences between these distances in each compound being 0.034 (1), 0.012 (2) and 0.049 Å (3). The Cu-O_{enolate} bond lengths average 1.938(4) Å and the Cu-N lengths vary between 1.902(3) and 2.014(3) Å, the values in each compound diverging by 0.094 (1), 0.031 (2) and 0.116 Å (3).

Extensive hydrogen-bonding interactions were found in all the structures (for compounds 2 and 3, see Table S2 in the Supporting Information). In compound 1, a 2D network results from contacts involving the methanol ligands; they act as donors to a methanol ligand and a phenolate moiety of a vicinal molecule, and as acceptors from a methanol ligand of nearby molecules (Figures 1 and 4). The 1D chain in 2 (Figure 5) results from non-coordinated methanol molecules, which simultaneously act as donor to a phenolate group of an adjacent trimer and as acceptor from a coordinated methanol ligand of another close molecule. Compound 3 also features a 2D network constructed from the interaction of each trimer with neighbouring analogues with each methanol ligand donating to phenolate groups (Figure 6).



Figure 4. Fragment of the 2D network in compound 1, viewed along the crystallographic a axis.



Figure 5. Fragment of the 1D chain in compound 2, viewed along the crystallographic *a* axis. The non-coordinated methanol molecules are drawn by the space-filled model.



Figure 6. Fragment of the 2D network in compound 3, viewed along the crystallographic a axis.



Magnetism

Variable-temperature magnetic susceptibility determinations were carried out on powdered samples of the three complexes in a field of 1000 Oe in the temperature range 2-300 K. As shown in Figure S1 in the Supporting Information, the $\chi_{\rm M}T$ value of 0.93 cm³ K mol⁻¹ for 1 at 300 K is lower than the spin-only value expected for three isolated copper(II) ions $(1.125 \text{ cm}^3 \text{ K mol}^{-1}, \text{ assuming } g = 2.0).$ Upon cooling, the $\chi_{\rm M}T$ value clearly decreases from room temperature down to about 100 K, which indicates strong antiferromagnetic intramolecular interactions. Between 100 and 10 K, the $\chi_{\rm M}T$ product plateaus at 0.53 cm³ K mol⁻¹ and then increases below 6 K, reaching a value of 0.63 cm³ K mol⁻¹ at 2 K. The magnetic data was analysed by using a symmetric linear S = 1/2 trimer model. Equation (1) is derived from the Hamiltonian $\hat{H} = -2J(\hat{S}_1\hat{S}_2 +$ $\hat{S}_2\hat{S}_3$ – $2J'\hat{S}_1\hat{S}_3$ [J' is assumed to be zero due to the large distance between the external copper(II) ions].^[8c] In Equation (1), N, k and β represent the usual constants. However, this model could not reproduce the increase in $\chi_{\rm M}T$ observed below 6 K, so we included intermolecular interactions (zj') modelled with the molecular field approximation, see Equation (2). With this improvement, the magnetic properties could be well fitted over the whole temperature range, with g = 2.01, $J = -108.7 \text{ cm}^{-1}$, $zj' = 0.42 \text{ cm}^{-1}$ and $R = 3.34 \times 10^{-5}$. The results indicate that the intratrimer antiferromagnetic coupling is strong and that a very weak ferromagnetic intermolecular interaction exists.

$$\chi = \frac{Ng^2\beta^2}{3kT} \times \frac{10e^{-J/kT} + e^{-2J/kT} + 1}{2e^{-J/kT} + e^{-2J/kT} + 1}$$
(1)

$$\chi_{M} = \frac{\chi}{1 - (2zj^{*}/Ng^{2}\beta^{2})\chi}$$
(2)

Similarly to 1, the room-temperature $\chi_{\rm M}T$ values for 2 (0.87 cm³ K mol⁻¹) and 3 (0.96 cm³ K mol⁻¹) are also smaller than those expected for three non-interacting copper(II) ions (see Figure S2 in the Supporting Information). However, unlike 1, the decrease in the $\chi_{\rm M}T$ product continues to 2 K, reaching 0.43 and 0.44 cm³ K mol⁻¹ for 2 and 3, respectively. These results suggest intramolecular antiferromagnetic exchange and an odd number of spins in the ground state.^[8c] The same Hamiltonian for 1 was used to describe this symmetric linear S = 1/2 trimer magnetic coupling model, however, it is necessary to consider the mole fraction of the paramagnetic impurity (ρ), the Weiss-like temperature correction (θ) and temperature-independent paramagnetism (*Na*) for a better fitting, see Equation (3).^[8c]

$$\chi_{M} = \frac{Ng^{2}\beta^{2}}{3k(T-\theta)} \times \frac{10e^{-J/kT} + e^{-2J/kT} + 1}{2e^{-J/kT} + e^{-2J/kT} + 1}(1-\rho) + \frac{3Ng^{2}\beta^{2}}{4k(T-\theta)}\rho + N\alpha$$
(3)

Analysis of the exchange by using Equation (3) gave g = 1.97, $J = -126.4 \text{ cm}^{-1}$, $\theta = -0.21 \text{ K}$, $\rho = 0.013$, $Na = 0.00016 \text{ cm}^3 \text{mol}^{-1}$ and $R = 6.99 \times 10^{-6}$ for **2**, and g = 2.02,

 $J = -130.8 \text{ cm}^{-1}$, $\theta = -0.37 \text{ K}$, $\rho = 0.031$, $N_a = 0.0044 \text{ cm}^3 \text{mol}^{-1}$ and $R = 4.21 \times 10^{-6}$ for 3. Because the coordination geometries of copper in the three complexes are not always the same, it is hard to analyse the magneto-structural correlations in detail. Nevertheless, the absolute value of *J* increases in the order 1 < 2 < 3, ascribing approximately to the order of decreasing Cu1…Cu2 distance: 1 (4.662 Å) > 2 (4.651 Å) > 3 (4.643 Å). The results confirm that the shorter the Cu1…Cu2 distance, the stronger the antiferromagnetic exchange.

Electrochemical Behaviour of 1-3

The redox properties of 1-3 were investigated by cyclic voltammetry (CV) at a Pt disc electrode in a 0.2 M [nBu₄N][BF₄]/MeCN solution at room temperature. All compounds exhibit similar voltammograms: two singleelectron (per Cu ion, as measured by controlled potential electrolysis) irreversible reduction waves (see Figure S3 in the Supporting Information for complex 1), assigned to the $Cu^{II} \rightarrow Cu^{I}$ (wave I) and $Cu^{I} \rightarrow Cu^{0}$ (wave II) reductions, at the reduction peak potentials given in Table 2 (${}^{I}E_{p}$ red ranges from -0.37 to -0.61 V vs. SCE, and ${}^{II}E_{p}{}^{red}$ between -1.21and -1.69 V vs. SCE). A new irreversible anodic wave (wave III, ${}^{I}E_{p}^{ox}$ in the range -0.27 to -0.22 V vs. SCE) is also observed upon scan reversal after the second cathodic process (see Figure S4 for complex 2), which corresponds to the oxidation of the cathodically generated Cu⁰ species. No anodic waves were detected for any of the complexes in a first anodic sweep without a previous reduction scan, which indicates that neither a metal- nor a ligand-centred oxidation is observed.

Table 2. Cyclic voltammetric data^[a] for complexes 1-3.

	$E_{\rm p}$ [V] (I ^{red})	$E_{\rm p}$ [V] (II ^{red})	$E_{\rm p} [{\rm V}] ({\rm I}^{\rm ox})^{[{\rm b}]}$
1	-0.56	-1.53	-0.26
2	-0.37	-1.21	-0.27
3	-0.61	-1.69	-0.22

[a] Potential values in volts (± 0.02 V) vs. SCE in a 0.2 M [*n*Bu₄N][BF₄]/MeCN solution at a Pt disc (d = 0.5 mm) working electrode and determined by using the [Fe(κ^5 -C₅H₅)₂]^{0/+} redox couple ($E_{1/2}^{\text{ox}} = 0.42$ V vs. SCE)^[21] as internal standard at a scan rate of 200 mV s⁻¹. [b] Anodic wave generated upon scan reversal following the second reduction wave (II^{red}).

Similar behaviour has previously been reported^[22] for trinuclear triangular copper(II) compounds containing the $[Cu_3(\mu^3-OH)(\mu-pz)_3]^{2+}$ (pz = pyrazolate) core stabilized by different carboxylate ligands and additional solvent or Hpz moieties.

The occurrence of a single-electron reduction per Cu^{II} (or Cu^I) atom was confirmed by exhaustive controlled potential electrolysis (CPE) at a potential slightly cathodic relative to that of the peak potential of wave I (or II), which corresponds to a charge consumption of 3 Fmol^{-1} . The CPE performed for the second reduction wave led to the deposition of metallic copper, which is clearly observed by its sharp oxidation (with desorption) wave at E_{p}^{ox} in the



range of -0.27 to -0.22 V versus SCE, as shown in Figure S4 in the Supporting Information for compound **2**.

Because each of the cathodic waves involves the reduction of three metal ions, without differentiation of distinct waves at different potentials, no metal-metal electronic communication has been detected. Nevertheless, the occurrence of such an interaction, to a limited extent, cannot be ruled out in view of the considerable broadness of the reduction waves, which may result from the overlap of other waves at similar, but distinct, reduction potentials corresponding to sequential metal reductions, that is, $Cu^{II}Cu^{II}Cu^{II} \rightarrow Cu^{I}Cu^{II}Cu^{II} \rightarrow Cu^{I}Cu^{I}Cu^{II} \rightarrow Cu^{I}Cu^{I}Cu^{I}$ for wave I, and similarly for further reductions to Cu^{0} at wave II.^[22] Moreover, cathodically induced Cu–ligand bond cleavage can also occur.^[23]

Catalytic Activity

Complexes 1–3 exhibit good catalytic activity in the oxidation of cyclohexane (CyH) with aqueous hydrogen peroxide (Table 3) under mild conditions to yield a mixture of cyclohexyl hydroperoxide (CyOOH, main primary product), cyclohexanol and cyclohexanone (Scheme 2, a). The alcohol and ketone are the final products after autodecomposition, the metal-assisted decomposition of the hydroperoxide or, alternatively, following Shul'pin's method,^[13a–13d,13g] upon reduction with PPh₃ (Scheme 2, b).



Scheme 2. Oxidation of cyclohexane to cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone with H_2O_2 catalysed by the Cu complexes (a), and reduction of cyclohexyl hydroperoxide to cyclohexanol in the presence of PPh₃ (b).

The catalytic systems were based on the Cu^{II} complexes 1-3 with hydrogen peroxide (30% aqueous solution) as the oxidizing agent in acetonitrile in the presence of an acid cocatalyst [nitric, trifluoroacetic, or pyrazinecarboxylic (Hpca)] under atmospheric pressure at room temperature.

Complex **2** provided the best activity, achieving overall yields, in the presence of pyrazinecarboxylic acid (Hpca), of

up to 31% (relative to the alkane, Table 3, entry 3) after 6 h reaction time and overall turnover numbers (TON) of up to 1.8×10^3 (6×10^2 per Cu atom, Table 3, entry 4). The accelerating effect of pyrazinecarboxylic acid in metal-catalysed oxidation reactions has been observed previous-ly.^[14f-14j] Complex **2** is also the easiest one to be reduced (Table 2), as shown by cyclic voltammetry (see above), which conceivably facilitates the Cu^{II}-catalysed oxidations of H₂O₂ and CyOOH (see the mechanistic considerations below).

Table 3. Peroxidative oxidation of cyclohexane^[a] with H_2O_2 (selected data) catalysed by 1–3.

Entry	Additive	Total yield [%] ^[b] (Total TON ^[c])			
	(amount [mol-%] vs. substrate)	1	2	3	
1	_	2.5 (26)	5.0 (50)	2.2 (22)	
2	HNO ₃ (2.5)	19 (190)	23 (230)	13 (130)	
3	Hpca (2.5)	27 (270)	31 (310)	17 (170)	
4 ^[d]	Hpca (2.5)	$12(1.2\times10^3)$	$18 (1.8 \times 10^3)$	$10 (1.0 \times 10^3)$	
5	TFA (2.5)	21 (210)	25 (250)	12 (120)	
6	Ph ₂ NH (100)	0.6 (6)	0.3 (3)	0.5 (5)	
7	CBrCl ₃ (100)	0.7 (7)	1.6 (16)	0.3 (3)	

[a] Reaction conditions (unless stated otherwise): cyclohexane (5.0 mmol), 1–3 (5 μ mol, 0.1 mol-% vs. substrate), H₂O₂ (10.0 mmol), room temp. [b] Molar yield (%) based on substrate, that is, moles of cyclohexanol + cyclohexanone per 100 mole of cyclohexane, determined by GC analysis (upon treatment with PPh₃). [c] Turnover number (moles of products per mole of catalyst precursor). [d] 1–3: 0.01 mol-% vs. cyclohexane.

Yields of up to 31% in the oxidation of an inert alkane are considered high and are also much higher than that of the industrial process (4% to reach a good selectivity, at ca. 150 °C)^[11a,11d] in spite of the mild conditions of our system (ambient temperature, atmospheric pressure, with an aqueous green oxidant and very low loads of catalyst). Similar yields (28%) have been obtained with the trinuclear Cu^{II} compound [Cu₃(μ ³-OH)(μ -pz)₃(EtCOO)₂(H₂O)]^[17c] or the mono-copper(II) complex [Cu(H₂tea)(N₃)] (H₂tea = triethanolamine).^[17f]

Moreover, a high selectivity towards the formation of cyclohexanol and cyclohexanone is exhibited by our systems, because no traces of byproducts were detected by GC–MS analysis of the final mixtures obtained under the optimized conditions. These features are important for the establishment of a greener catalytic process for cyclohexane oxidation.

The copper salts used for the synthesis of 1–3, Cu- $(NO_3)_2$, Cu $(OAc)_2$ or CuB₂O₄, exhibited poor activity (maximum total yields of 4, 3 and 4%, respectively) under the cyclohexane oxidation conditions of Table 3, which points to the relevance of the polydentate N,O ligands, conceivably associated with their involvement in the proton-transfer steps.^[17,25d–25f]

The previously recognized promoting effect of an acid^[13e,13f,17,22,24] on the peroxidative oxidation of alkanes catalysed by homogeneous or supported^[24g–24j] metallic species is also observed in these systems (Table 3). In fact, the presence of an acid co-catalyst (either organic or min-



eral) has a strong promoting effect of the catalytic activity (Table 3, entries 2–5) of **1–3**. The role of the acid may be associated with,^[17] for example, the promotion of coordinative unsaturation upon ligand protonation, its involvement in proton-transfer steps, the acceleration of the oxidation reaction, the facilitation of the formation of peroxo complexes or the prevention of the decomposition of H₂O₂ to water and oxygen (i.e., suppressing eventual catalase activity in the acidic medium).

As observed for other copper and metal catalytic systems,^[13e-13h,17,22,23] the introduction of a carbon or oxygen radical trap (e.g., CBrCl₃ or Ph₂NH) into the reaction mixture resulted in a marked decrease in the product yield. This behaviour, along with the formation of cyclohexyl hydroperoxide (typical intermediate product in radical-type reactions), supports a free-radical mechanism^[25,26] for the oxidation of cyclohexane in this study.

Conclusions

The different structural environments of the copper(II) centres present in the starting materials for the synthesis of the trinuclear complexes 1–3 result in different structural isomers with distinct metal coordination environments. Variable-temperature magnetic susceptibility measurements showed that complexes 1–3 exhibit a strong antiferromagnetic exchange interaction between the Cu^{II} ions. The order of observed antiferromagnetic exchange interactions (*J* values) increases with decreasing distance between the copper ions. The complexes exhibit irreversible Cu^{II} \rightarrow Cu^I and Cu^I \rightarrow Cu⁰ reduction waves in cyclic voltammetry measurements, and therefore there is no evidence of any electronic communication between the metals.

All of the complexes 1–3 behaved as catalyst precursors for the efficient peroxidative oxidation of cyclohexane by aqueous hydrogen peroxide in acetonitrile in the presence of an acid co-catalyst at room temperature. The products of the oxidation, cyclohexanol and cyclohexanone, were obtained in good yields (overall yield of 31% for 2, maximum TON 1.8×10^3) via the formation of the corresponding cycloalkyl hydroperoxide intermediate (CyOOH) following a radical mechanism, as substantiated by radical-trap experiments. Moreover, the use of an aqueous medium at room temperature and of an environmentally friendly catalyst is a significant step forward in the development of green catalytic systems for cyclohexane oxidation.

Experimental Section

General Materials and Procedures: All the synthetic work was performed in air. The reagents and solvents were obtained from commercial sources and used as received, that is, without further purification or drying. Three different metal sources, namely Cu- $(NO_3)_2 \cdot 2.5H_2O$, Cu(COOCH₃)₂·H₂O and CuB₂O₄, were used for the synthesis of complexes 1–3. CuB₂O₄ was prepared according to a literature method.^[27] CHN elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined with a Leica Gallen III instrument. IR spectra (4000–400 cm⁻¹) were recorded with a Bruker Vertex 70 spectrometer in KBr pellets. ¹H NMR spectra were recorded at room temperature with a Bruker Avance II + 400.13 MHz (Ultra-ShieldTM Magnet) spectrometer. The chemical shifts are reported in ppm using tetramethylsilane as internal reference.

The magnetic susceptibility measurements were carried out on polycrystalline samples with a Quantum Design MPMS-XL5 SQUID magnetometer in the temperature range of 2-300 K and at an applied field of 2000 Oe. Diamagnetic corrections for all constituent atoms were estimated from Pascal's constants.^[28] GC measurements were carried out by using a FISONS Instruments GC 8000 series gas chromatograph with an FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm) and the Jasco-Borwin v.1.50 software. The temperature of injection was 240 °C. The initial temperature was maintained at 100 °C for 1 min, then raised at a rate of 10 °C/min to 180 °C and held at this temperature for 1 min. Helium was used as the carrier gas. GC-MS analyses were performed by using a Perkin-Elmer Clarus 600 C instrument (He as the carrier gas) equipped with a $30 \text{ m} \times 0.22 \text{ mm} \times 25 \text{ }\mu\text{m}$ BPX5 (SGE) capillary column. The electrochemical experiments were performed with an EG&G PAR 273A potentiostat/galvanostat connected to a computer through a GPIB interface. Cyclic voltammograms (CV) were obtained in 0.2 м solutions of [nBu₄N][BF₄] in MeCN at a platinum disc working electrode (d = 0.5 mm) at room temperature. Silver and platinum wires were employed as pseudo-reference electrode and counter-electrode, respectively. 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 the 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 CV, thus assuring no significant potential drift occurred along the electrolyses. The electrochemical experiments were performed under N₂ at room temperature. The potentials of the complexes were measured by CV in the presence of ferrocene as the internal standard, and the redox potentials are normally quoted relative to the SCE by using the $[Fe(\kappa^5-C_6H_5)_2]^{0/+}$ redox couple $(E_{1/2}^{ox} = 0.42 \text{ V})$ vs. SCE)^[21] in a 0.2 M [nBu₄N][BF₄]/MeCN solution. Mass spectra were recorded with a Varian 500-MS LC Ion Trap Mass Spectrometer equipped with an electrospray (ESI) ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with a nebulizer pressure of 35 psi. Scanning was performed from m/z = 100-1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80 - 105 V).

Typical Procedures for the Catalytic Oxidation of Cyclohexane and Product Analysis: The peroxidative oxidation reactions were carried out as follows: the catalyst precursor $(0.5-10 \mu mol)$ and acid (HNO₃, Hpca or TFA; 125 µmol) were dissolved in MeCN (3.00 mL) with vigorous stirring. Cyclohexane (0.54 mL, 5.00 mmol) and 30% H₂O₂ (1.02 mL, 10.00 mmol) were then added and the reaction solution was stirred for 6 h at room temperature and normal pressure. In the experiments with radical traps, CBrCl₃ (5.00 mmol) or NHPh₂ (5.00 mmol) was added to the reaction mixture. The product analysis was carried out as follows: cycloheptanone (internal standard, 90 µL), diethyl ether (to extract the substrate and the organic products from the reaction mixture, 10.00 mL) and an excess of triphenylphosphine (to reduce the cyclohexyl hydroperoxide formed to the corresponding alcohol and hydrogen peroxide to water, following a method developed by

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Shul'pin)^[13a-13d,13g] were added. The mixture obtained was stirred for 10 min and then a sample (1 μ L) was taken from the organic phase and analysed by GC using the internal standard method. Blank tests indicated that no oxidation took place in the absence of the Cu complex or the oxidant.

Synthesis of the Pro-ligand H₃L: The Schiff base pro-ligand (3,5-di-*tert*-butyl-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (H₃L) (Scheme 1) was prepared by condensation of the corresponding salicylhydrazide with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde according to a previously reported procedure.^[29] Yield 86%. IR (KBr): $\tilde{v} = 3328 [v(OH)]$, 2957 [v(NH)], 1658 [v(C=O)], 1590 [v(C=N)] cm⁻¹. ¹H NMR ([D₆]DMSO): $\delta = 12.20$ (s, 1 H, OH), 12.08 (s, 1 H, OH), 11.65 (s, 1 H, NH), 8.62 (s, 1 H, -CH=N), 7.89–6.98 (m, 6 H, C₆H₄), 1.41 (s, 9 H, CH₃), 1.28 (s, 9 H, CH₃) ppm. C₂₂H₂₈N₂O₃ (368.47): calcd. C 71.71, H 7.66, N 7.60; found C 71.67, H 7.62, N 7.57.

Synthesis of the Trinuclear Cu^{II} Complexes

[Cu₃(L)₂(MeOH)₄] (1): An excess of Cu(NO₃)₂·2.5H₂O (0.93 g, 4.00 mmol) was added to a methanolic solution (30 mL) of H₃L (0.368 g, 1.00 mmol) and the reaction mixture was stirred for 15 min at 50 °C. Triethylamine (0.202 g, 2 mmol) was then added to the reaction mixture and stirring was continued for a further 10 min. The resultant dark-green solution was filtered and the filtrate was left to stand in air. After 2 d, green single crystals suitable for X-ray diffraction analysis were isolated, washed three times with cold methanol and dried in open air, yield 0.264 g (72%, with respect to H₃L). IR (KBr): $\tilde{v} = 3441$ [v(OH)], 1609 [v(C=N)], 1251 [v(C–O) enolic], 1167 [v(N–N)] cm⁻¹. MS (ESI, +): *mlz* (%) = 470 (100) [NaCu(L)(H₂O)]⁺. C₄₈H₆₆Cu₃N₄O₁₀ (1): C 54.92, H 6.34, N 5.34; found C 54.87, H 6.30, N 5.31.

[Cu₃(L)₂(MeOH)₂]·2MeOH (2): An excess of Cu(OOCCH₃)₂·H₂O (0.80 g, 4.00 mmol) was added to a methanolic solution (30 mL) of H₃L (0.368 g, 1.00 mmol) and the reaction mixture was stirred for 30 min at 50 °C. The resultant dark-green solution was filtered and the filtrate was left to stand in air. After 3 d, green single crystals suitable for X-ray diffraction analysis were isolated, washed three times with cold methanol and dried in open air, yield 0.28 g (76%, with respect to H₃L). IR (KBr): $\tilde{v} = 3436$ [v(OH)]. 1609 [v(C=N)], 1252 [v(C–O) enolic], 1170 [v(N–N)] cm⁻¹. MS (ESI, +): *m/z* (%) = 461 (100) [Cu(L)(MeOH)]⁺. C₄₈H₆₆Cu₃N₄O₁₀ (2): C 54.92, H 6.34, N 5.34; found C 54.84, H 6.28, N 5.29.

[Cu₃(L)₂(MeOH)₄] (3): An excess of CuB₂O₄ (0.6 g, 4.00 mmol) was added to a methanolic solution (30 mL) of H₃L (0.368 g, 1.00 mmol) and the reaction mixture was heated at reflux for 1 h. The resultant dark-green solution was filtered and the filtrate was left to stand in air. After 2 d, green single crystals suitable for X-ray diffraction analysis were isolated, washed three times with cold methanol and dried in open air, yield 0.192 g (52%, with respect to H₃L). IR (KBr): $\tilde{v} = 3424$ [v(OH)], 1610 [v(C=N)], 1254 [v(C–O) enolic], 1171 [v(N–N)] cm⁻¹. MS (ESI, +): *mlz* (%) = 470 (100) [NaCu(L)(H₂O)]⁺. C₄₈H₆₆Cu₃N₄O₁₀ (3): C 54.92, H 6.34, N 5.34; found C 54.86, H 6.28, N 5.27.

X-ray Measurements: Single crystals of complexes 1–3 suitable for X-ray diffraction were immersed in cryo-oil, mounted in Nylon loops and analysed at 150 (1 and 3) or 296 K (2). Intensity data were collected with a Bruker AXS-KAPPA APEX II diffractometer with graphite-monochromated Mo- K_a ($\lambda = 0.71073$ Å) radiation. Data were collected by using omega scans of 0.5° per frame and a

full sphere of data was obtained. Cell parameters were obtained by using the SMART^[30a] software and refined by using the SAINT^[30b] software on all the observed reflections. Absorption corrections were applied by using SADABS.^[30a] Structures were solved by direct methods by using SHELXS-97^[30c] and refined with SHELXL-97.^[30c] Calculations were performed by using WinGX (Version 1.80.03).^[30d] The hydrogen atoms attached to carbon atoms were inserted at geometrically calculated positions and included in the refinement by using the riding-model approximation; $U_{iso}(H)$ was defined as $1.2U_{eq}$ of the parent carbon atoms for phenyl residues and $1.5U_{eq}$ of the parent carbon atoms for the methyl groups. The hydroxy H-atoms of methanol molecules were located from the final difference Fourier map, and the isotropic thermal parameters were set at 1.5 times the average thermal parameters of the Oatoms. Disordered molecules are present in the structure of 2. Because no obvious major site occupations were found for those molecules, it was not possible to model them. PLATON/ SQUEEZE^[30e] was used to correct the data and a potential volume of 788.5 Å³ was found with 131 electrons per unit cell worth of scattering. These were removed from the model and included in the empirical formula as one water molecule per asymmetric unit. Least-squares refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic parameters for the remaining atoms were employed. The crystallographic data are summarized in Table 1 and selected bond lengths and angles are presented in Table S1 in the Supporting Information.

CCDC-1042432 (for 1), -1042433 (for 2), and -1042434 (for 3) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Acknowledgments

The authors are grateful to the Fundação para a Ciência e a Tecnologia, Portugal (FCT) (project number PEst-OE/QUI/UI0100/ 2013) for financial support. M. S. acknowledges FCT for a postdoctoral fellowship (grant number SFRH/BPD/86067/2012). The authors are also thankful to the Portuguese NMR Network (IST-UL Centre) for access to the NMR facility.

- a) H. Claus, *Microelectron. J.* 2004, *35*, 93–96; b) E. C. M. Tse,
 D. Schilter, D. L. Gray, T. B. Rauchfuss, A. A. Gewirth, *Inorg. Chem.* 2014, *53*, 8505–8516; c) K. Piontek, M. Antorini, T. Choinowski, *J. Biol. Chem.* 2002, *277*, 37663–37669.
- [2] a) S. I. Chan, V. C.-C. Wang, J. C.-H. Lai, S. S.-F. Yu, P. P.-Y. Chen, K. H.-C. Chen, C.-L. Chen, M. K. Chan, Angew. Chem. Int. Ed. 2007, 46, 1992–1994; Angew. Chem. 2007, 119, 2038;
 b) A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, M. Haukka, M. F. C. Guedes da Silva, A. J. L. Pombeiro, Angew. Chem. 2005, 117, 4419–4423; c) R. L. Lieberman, A. C. Rosenzweig, Dalton Trans. 2005, 3390–3396; d) C. Di Nicola, Y. Y. Karabach, A. M. Kirillov, M. Monari, L. Pandolfo, C. Pettinari, A. J. L. Pombeiro, Inorg. Chem. 2007, 46, 221– 230.
- [3] a) E. I. Solomon, J. W. Ginsbach, D. E. Heppner, M. T. Kieber-Emmons, C. H. Kjaergaard, P. J. Smeets, L. Tian, J. S. Woertink, *J. Chem. Soc. Faraday Trans.* 2011, 148, 11–39; b) A. Di Venere, E. Nicolai, N. Rosato, A. Rossi, A. Finazzi Agrò, G. Mei, *FEBS J.* 2011, 278, 1585–1593; c) E. I. Solomon, A. J. Augustine, J. Yoon, *Dalton Trans.* 2008, 3921–3932; d) A. Mes-

serschmidt, H. Leucke, R. Huber, J. Mol. Biol. 1993, 230, 997-1014.

- [4] a) B. Le Guennic, S. Petit, G. Chastanet, G. Pilet, D. Luneau, N. Ben Amor, V. Robert, *Inorg. Chem.* 2008, 47, 572–577; b) I. Gautier-Luneau, D. Phanon, C. Duboc, D. Luneau, J.-L. Pierre, *Dalton Trans.* 2005, 3795–3799; c) L. Rigamonti, A. Cinti, A. Forni, A. Passini, O. Piovesana, *Eur. J. Inorg. Chem.* 2008, 3633–3647; d) M. U. Anwar, L. K. Thompson, L. N. Dawe, *Dalton Trans.* 2011, 40, 1437–1440; e) R. D. Köhn, L. T. Laudo, Z. Pan, F. Speiser, G. Kociok-Köhn, *Dalton Trans.* 2009, 4556–4568.
- [5] a) L. Gutierrez, G. Alzuet, J. A. Real, J. Cano, J. Borras, A. Castiñeiras, *Inorg. Chem.* 2006, 45, 3608–3614; b) Q. Wang, X. Wu, W. Zhang, T. Sheng, P. Lin, J. Li, *Inorg. Chem.* 1999, 38, 2223–2226; c) M. González-Álvarez, G. Alzuet, J. Borrás, B. Macías, A. Castiñeiras, *Inorg. Chem.* 2003, 42, 2992–2998; d) S. Thakurta, J. Chakraborty, G. Rosair, J. Tercero, M. S. Fallah, E. Garribba, S. Mitra, *Inorg. Chem.* 2008, 47, 6227–6235.
- [6] a) R. Costa, A. Garcia, R. Sanchez, J. Ribas, X. Solans, V. Rodriguez, *Polyhedron* **1993**, *12*, 2697–2704; b) J. Liu, Y. Song, Z. Yu, J. Zhuang, X. Huang, X. You, *Polyhedron* **1999**, *18*, 1491–1494.
- [7] a) P. J. van Koningsbruggen, J. G. Haasnoot, W. Vreugdenhil, J. Reedijk, O. Kahn, *Inorg. Chim. Acta* 1995, 239, 5–12; b) C. B. Ma, W. G. Wang, X. F. Zhang, C. N. Chen, Q. T. Liu, H. P. Zhu, D. Z. Liao, L. C. Li, *Eur. J. Inorg. Chem.* 2004, 3522–3532; c) W.-S. Wu, W.-D. Cheng, D.-S. Wu, H. Zhang, Y.-J. Gong, Y. Lu, *Inorg. Chem. Commun.* 2006, 9, 559–562; d) V. A. Milway, L. Zhao, T. S. M. Abedin, L. K. Thompson, Z. Xu, *Polyhedron* 2003, 22, 1271–1279.
- [8] a) S. Mukhopadhyay, D. Mandal, P. B. Chatterjee, C. Desplanches, J. P. Sutter, R. J. Butcher, M. Chaudhury, *Inorg. Chem.* 2004, 43, 8501–8509; b) L. Gutierrez, G. Alzuet, J. A. Real, J. Cano, J. Borrás, A. Castiñeiras, *Inorg. Chem.* 2000, 39, 3608–3614; c) L. Zhao, L. K. Thompson, Z. Xu, D. O. Miller, D. R. Stirling, *J. Chem. Soc., Dalton Trans.* 2001, 1706–1710; d) S. S. Tandon, L. N. Dawe, V. A. Milway, J. L. Collins, L. K. Thompson, *Dalton Trans.* 2007, 1948–1953.
- [9] a) M. Sutradhar, L. M. Carrella, E. Rentschler, *Eur. J. Inorg. Chem.* 2012, 4273–4278; b) M. Sutradhar, T. R. Barman, E. Rentschler, *Inorg. Chem. Commun.* 2014, 39, 140–143; c) M. Sutradhar, T. R. Barman, S. Ghosh, M. G. B. Drew, *J. Mol. Struct.* 2013, 1037, 276–282; d) M. Sutradhar, T. R. Barman, G. Mukherjee, M. G. B. Drew, S. Ghosh, *Polyhedron* 2012, 34, 92–101; e) M. Sutradhar, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, E. C. B. A. Alegria, C.-M. Liu, A. J. L. Pombeiro, *Dalton Trans.* 2014, 43, 3966–3977; f) M. Sutradhar, T. R. Barman, S. Ghosh, M. G. B. Drew, *J. Mol. Struct.* 2012, 1020, 148–152; g) T. R. Barman, M. Sutradhar, M. G. B. Drew, E. Rentschler, *Polyhedron* 2013, 51, 192–200.
- [10] a) M. Sutradhar, M. V. Kirillova, M. F. C. Guedes da Silva, C.-M. Liu, A. J. L. Pombeiro, *Dalton Trans.* 2013, 42, 16578–16587; b) M. Sutradhar, T. R. Barman, J. Klanke, M. G. B. Drew, E. Rentschler, *Polyhedron* 2013, 53, 48–55; c) K. T. Mahmudov, M. Haukka, M. Sutradhar, A. Mizar, M. N. Kopylovich, A. J. L. Pombeiro, *J. Mol. Struct.* 2013, 1033, 127–130; d) K. T. Mahmudov, M. F. C. Guedes da Silva, M. Glucini, M. Renzi, K. C. P. Gabriel, M. N. Kopylovich, M. Sutradhar, F. Marchetti, C. Pettinari, S. Zamponi, A. J. L. Pombeiro, *Inorg. Chem. Commun.* 2012, 22, 187–189.
- [11] a) Ullmann's Encyclopedia of Industrial Chemistry, 6th ed., Wiley-VCH, Weinheim, Germany, 2002; b) R. Whyman, Applied Organometallic Chemistry and Catalysis, Oxford University Press, Oxford, UK, 2001; c) R. A. Smiley, H. L. Jackson, Chemistry and the Chemical Industry, CRC Press, Boca Raton, FL, 2002; d) K. Weissermel, H. J. Arpe, Industrial Organic Chemistry, 2nd ed., VCH Verlagsgesellschaft, Weinheim, Germany 1993; e) J.-E. Bäckvall, Modern Oxidation Methods, Wiley-VCH, Weinheim, Germany, 2004; f) G. P. Chiusoli, P. M. Maitlis (Eds.), Metal-catalysis in Industrial Organic Processes,

Royal Society of Chemistry, Cambridge, UK, 2006, chapter 2; g) K. R. Gruenwald, A. M. Kirillov, M. Haukka, J. Sanchiz, A. J. L. Pombeiro, *Dalton Trans.* 2009, 2109–2120; h) M. V. Kirillova, A. M. Kirillov, A. N. C. Martins, C. Graiff, A. Tiripicchio, A. J. L. Pombeiro, *Inorg. Chem.* 2012, *51*, 5224–5234; i) U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R. S. da Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinacé, E. L. Pires, *Appl. Catal. A* 2001, *211*, 1–17; j) R. A. Sheldon, I. Arends, U. Hanefeld, *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, Germany, 2007.

- [12] a) E. G. Derouane, J. Haber, F. Lemos, F. R. Ribeiro, M. Guisnet, Catalytic Activation and Functionalization of Light Alkanes, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1998, vol. 44; b) R. H. Crabtree, J. Chem. Soc., Dalton Trans. 2001, 2437-2450; c) J. Clark, D. Macquarrie, Handbook of Green Chemistry and Technology, Backwell, Oxford, 2002; d) R. H. Crabtree, J. Organomet. Chem. 2004, 689, 4083-4091; e) A. E. Shilov, G. B. Shul'pin, Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2000; f) G. B. Shul'pin, in: Transition Metals for Organic Synthesis (Eds.: M. Beller, C. Bolm), 2nd ed., Wiley-VCH, New York, 2004, vol. 2, chapter 2, p. 215–242; g) E. G. Derouane, V. Parmon, F. Lemos, F. R. Ribeiro, Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges, and Opportunities, Springer, Dordrecht, The Netherlands, 2005, vol. 191; h) A. E. Shilov, G. B. Shul'pin, Chem. Rev. 1997, 97, 2879-2932; i) G. B. Shul'pin, Mini-Rev. Org. Chem. 2009, 6, 95-104; j) M. M. Díaz-Requejo, P. J. Pérez, Chem. Rev. 2008, 108, 3379-3394; k) A. A. Fokin, P. R. Schreiner, Chem. Rev. 2002, 102, 1551-1594; 1) A. J. L. Pombeiro, in: Advances in Organometallic Chemistry and Catalysis, (Ed.: A. J. L. Pombeiro, Wiley, Hoboken, NJ, 2013, chapter 2, p. 15-25; m) M. Sutradhar, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, A. J. L. Pombeiro, Coord. Chem. Rev. 2015, DOI: 10.1016/ j.ccr.2015.01.020.
- [13] a) G. B. Shul'pin, C. R. Chim. 2003, 6, 163–178; b) G. B. Shul'pin, Y. N. Kozlov, L. S. Shul'pina, A. R. Kudinov, D. Mandelli, Inorg. Chem. 2009, 48, 10480-10482; c) G. B. Shul'pin, Y. N. Kozlov, L. S. Shul'pina, P. V. Petrovskiy, Appl. Organomet. Chem. 2010, 24, 464–472; d) G. B. Shul'pin, J. Mol. Catal. A 2002, 189, 39-66; e) L. M. D. R. S. Martins, A. J. L. Pombeiro, in: Advances in Organometallic Chemistry and Catalysis (Ed.: A. J. L. Pombeiro), Wiley-VCH, Weinheim, Germany, 2013, ch. 22, p. 285-294; f) L. M. D. R. S. Martins, A. J. L. Pombeiro, Coord. Chem. Rev. 2014, 265, 74-88; g) G. B. Shul'pin, Dalton Trans. 2013, 42, 12794-12818; h) J. A. L. da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, Coord. Chem. Rev. 2011, 255, 2232-2248; i) M. Sutradhar, N. V. Shvydkiy, M. F. C. Guedes da Silva, M. V. Kirillova, Y. N. Kozlov, A. J. L. Pombeiro, G. B. Shul'pin, Dalton Trans. 2013, 42, 11791–11803; j) M. Sutradhar, M. V. Kirillova, M. F. C. Guedes da Silva, L. M. D. R. S. Martins, A. J. L. Pombeiro, Inorg. Chem. 2012, 51, 11229-11231.
- [14] a) G. B. Shul'pin, G. V. Nizova, *React. Kinet. Catal. Lett.* 1992, 48, 333–338; b) G. B. Shul'pin, D. Attanasio, L. Suber, J. Catal. 1993, 142, 147–152; c) U. Schuchardt, D. Mandelli, G. B. Shul'pin, *Tetrahedron Lett.* 1996, 37, 6487–6490; d) G. B. Shul'pin, G. V. Nizova, Y. N. Kozlov, L. G. Cuervo, G. Süss-Fink, Adv. Synth. Catal. 2004, 346, 317–332; e) K. S. Anisia, A. Kumar, Appl. Catal. A 2004, 273, 193–200; f) G. B. Shul'pin, M. C. Guerreiro, U. Schuchardt, *Tetrahedron* 1996, 52, 13051–13062; g) G. V. Nizova, G. B. Shul'pin, *Tetrahedron* 2007, 63, 7997–8001; h) U. Schuchardt, D. Mandelli, G. B. Shul'pin, D. Attanasio, L. Suber, Russ. Chem. Bull. 1993, 42, 55–59; j) A. M. Kirrillov, G. B. Shul'pin, *Coord. Chem. Rev.* 2013, 257, 732–754.
- [15] a) R. S. Brissos, S. Garcia, A. Presa, P. Gamez, *Comments Inorg. Chem.* 2011, *32*, 219–245; b) P. Gamez, P. G. Aubel, W. L. Driessen, J. Reedijk, *Chem. Soc. Rev.* 2001, *30*, 376–385; c)

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L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Chem. Rev.* **2004**, *104*, 1013–1046; d) E. A. Lewis, W. B. Tolman, *Chem. Rev.* **2004**, *104*, 1047–1076; e) S. Itoh, in: *Comprehensive Coordination Chemistry* (Eds.: J. A. McCleverty, T. J. Meyer, L. Que, W. B. Tolman), 2nd ed., Elsevier, Dordrecht, The Netherlands, **2003**, vol. 8, ch. 8.15; f) D. H. Lee, in: *Comprehensive Coordination Chemistry* (Eds.: J. A. McCleverty, T. J. Meyer, L. Que, W. B. Tolman), 2nd ed., Elsevier, Dordrecht, The Netherlands, **2003**, vol. 8, chapter 8.17; g) J. J. R. Fraústo da Silva, R. J. P. Williams, *The Biological Chemistry of the Elements*, Oxford University Press, Oxford, UK, **2001**.

- [16] a) R. A. Himes, K. D. Karlin, *Curr. Opin. Chem. Biol.* 2009, 13, 119–131; b) R. L. Lieberman, A. C. Rosenzweig, *Nature* 2005, 434, 177–182; c) S. J. Elliot, M. Zhu, L. Tso, H.-H. T. Nguyen, J. H.-K. Yip, S. I. Chan, *J. Am. Chem. Soc.* 1997, 119, 9949–9955; d) H. H. Nguyen, A. K. Shiemke, S. J. Jacobs, B. J. Hales, M. E. Linstrom, S. I. Chan, *J. Biol. Chem.* 1994, 269, 14995–15005.
- [17] a) A. M. Kirillov, M. V. Kirillova, A. J. L. Pombeiro, Coord. Chem. Rev. 2012, 256, 2741-2759; b) K. T. Mahmudov, M. N. Kopylovich, M. F. C. Guedes da Silva, P. J. Figiel, Y. Y. Karabach, A. J. L. Pombeiro, J. Mol. Catal. A 2010, 318, 44-50; c) S. Contaldi, C. Di Nicola, F. Garau, Y.Y. Karabach, L. M. D. R. S. Martins, M. Monari, L. Pandolfo, C. Pettinari, A. J. L. Pombeiro, Dalton Trans. 2009, 4928-4941; d) C. Di Nicola, F. Garau, Y. Y. Karabach, L. M. D. R. S. Martins, M. Monari, L. Pandolfo, C. Pettinari, A. J. L. Pombeiro, Eur. J. Inorg. Chem. 2009, 666-676; e) A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, M. Haukka, M. F. C. Guedes da Silva, A. J. L. Pombeiro, Angew. Chem. Int. Ed. 2005, 44, 4345-4349; Angew. Chem. 2005, 117, 4419; f) A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, Y. Y. Karabach, M. Haukka, M. F. C. Guedes da Silva, A. J. L. Pombeiro, Adv. Synth. Catal. 2006, 348, 159–174; g) Y. Y. Karabach, A. M. Kirillov, M. F. C. Guedes da Silva, M. N. Kopylovich, A. J. L. Pombeiro, Cryst. Growth Des. 2006, 6, 2200-2203; h) Y. Y. Karabach, A. M. Kirillov, M. Haukka, M. N. Kopylovich, A. J. L. Pombeiro, J. Inorg. Biochem. 2008, 102, 1190-1194; i) T. C. O. MacLeod, M. N. Kopylovich, M. F. C. Guedes da Silva, K. T. Mahmudov, A. J. L. Pombeiro, Appl. Catal. A 2012, 439-440, 15-23; j) M. V. Kirillova, Y. N. Kozlov, L. S. Shul'pina, O. Y. Lyakin, A. M. Kirillov, E. P. Talsi, A. J. L. Pombeiro, G. B. Shul'pin, J. Catal. 2009, 268, 26-38; k) M. V. Kirillova, A. M. Kirillov, D. Mandelli, W. A. Carvalho, A. J. L. Pombeiro, G. B. Shul'pin, J. Catal. 2010, 272, 9-17; l) M. N. Kopylovich, M. J. Gajewska, K. T. Mahmudov, M. F. C. Guedes da Silva, M. V. Kirillova, P. J. Figiel, J. Sanchiz, A. J. L. Pombeiro, New J. Chem. 2012, 36, 1646-1654.
- [18] a) M. Sutradhar, A. J. L. Pombeiro, *Coord. Chem. Rev.* 2014, 265, 89–124; b) M. Sutradhar, T. R. Barman, G. Mukherjee, M. G. B. Drew, S. Ghosh, *Inorg. Chim. Acta* 2010, 363, 3376–3383; c) T. Ghosh, B. Mondal, T. Ghosh, M. Sutradhar, G. Mukherjee, M. G. B. Drew, *Inorg. Chim. Acta* 2007, 360, 1753–1761.
- [19] a) S.-X. Liu, S. Lin, B.-Z. Lin, C.-C. Lin, J.-Q. Huang, Angew. Chem. 2001, 40, 1084–1087; b) S. Lin, S.-X. Liu, Z. Chen, B.-Z. Lin, S. Gao, Inorg. Chem. 2004, 43, 2222–2224; c) P. J. Rohith, K. Lee, M. S. Lah, Chem. Commun. 2004, 2660–2661; d) M. Sutradhar, M. F. C. Guedes da Silva, D. S. Nesterov, J. Jezierska, A. J. L. Pombeiro, Inorg. Chem. Commun. 2013, 29, 82–84; e) M. Sutradhar, M. F. C. Guedes da Silva, A. J. L. Pombeiro, Inorg. Chem. Commun. 2013, 29, 82–84; e) M. Sutradhar, M. F. C. Guedes da Silva, A. J. L. Pombeiro, Inorg. Chem. Commun. 2013, 30, 42–45; f) M. Sutradhar, A. J. L. Pombeiro, in: Ligands: Synthesis, Characterization and Role in Biotechnology (Eds.: P. Gawryszewska, P. Smoleński), Nova Publishers, New York, 2014, p. 275–288.
- [20] a) L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* 2007, 955–964; b) K. Robinson, G. V. Gibbs, P. H. Ribbe, *Science* 1971, *172*, 567–570; c) A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* 1984, 1349–1356.

- [21] a) A. J. L. Pombeiro, M. F. C. Guedes da Silva, M. A. N. D. A. Lemos, *Coord. Chem. Rev.* 2001, 219, 53–80; b)
 M. E. N. P. R. A. Silva, A. J. L. Pombeiro, J. J. R. Fraústo da Silva, R. Herrmann, N. Deus, T. J. Castilho, M. F. C. Guedes da Silva, *J. Organomet. Chem.* 1991, 421, 75–90; c)
 M. E. N. P. R. A. Silva, A. J. L. Pombeiro, J. J. R. Fraústo da Silva, R. Herrmann, N. Deus, R. E. Bozak, *J. Organomet. Chem.* 1994, 480, 81–90.
- [22] a) S. Contaldi, C. Di Nicola, F. Garau, Y. Y. Karabach, L. M. D. R. S. Martins, M. Monari, L. Pandolfo, C. Pettinari, A. J. L. Pombeiro, *Dalton Trans.* 2009, 4928–4941; b) C. Di Nicola, F. Garau, Y. Y. Karabach, L. M. D. R. S. Martins, M. Monari, L. Pandolfo, C. Pettinari, A. J. L. Pombeiro, *Eur. J. Inorg. Chem.* 2009, 666–676.
- [23] a) E. Reisner, V. B. Arion, M. F. C. Guedes da Silva, R. Lichtenecker, A. Eichinger, B. K. Keppler, V. Y. Kukushkin, A. J. L. Pombeiro, *Inorg. Chem.* 2004, 43, 7083–7093; b) E. Reisner, V. B. Arion, B. K. Keppler, A. J. L. Pombeiro, *Inorg. Chim. Acta* 2008, 361, 1569–1583; c) A. J. L. Pombeiro, C. Amatore, *Trends in Molecular Electrochemistry*, Marcel Dekker/ FontisMedia, New York, 2004; d) P. Zanello, *Inorganic Electrochemistry*, Royal Society of Chemistry, Cambridge, UK, 2003.
- [24] a) M. N. Kopylovich, A. C. C. Nunes, K. T. Mahmudov, M. Haukka, T. C. O. MacLeod, L. M. D. R. S. Martins, M. L. Kuznetsov, A. J. L. Pombeiro, Dalton Trans. 2011, 40, 2822-2836; b) D. S. Nesterov, E. N. Chygorin, V. N. Kokozay, V. V. Bon, R. Boča, Y. N. Kozlov, L. S. Shul'pina, J. Jezierska, A. Ozarowski, A. J. L. Pombeiro, G. B. Shul'pin, Inorg. Chem. 2012, 51, 9110-9122; c) D. S. Nesterov, V. N. Kokozay, V. V. Dyakonenko, O. V. Shishkin, J. Jezierska, A. Ozarowski, A. M. Kirillov, M. N. Kopylovich, A. J. L. Pombeiro, Chem. Commun. 2006, 4605-4607; d) G. S. Mishra, T. F. S. Silva, L. M. D. R. S. Martins, A. J. L. Pombeiro, Pure Appl. Chem. 2009, 81, 1217-1227; e) R. R. Fernandes, J. Lasri, A. M. Kirillov, M. F. C. Guedes da Silva, J. A. L. Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, Eur. J. Inorg. Chem. 2011, 3781-3790; f) M. N. M. Milunovic, L. M. D. R. S. Martins, E. C. B. A. Alegria, A. J. L. Pombeiro, R. Krachler, G. Trettenhahn, C. Turta, S. Shova, V. B. Arion, Dalton Trans. 2013, 42, 14388-14401; g) G. S. Mishra, E. C. B. Alegria, L. M. D. R. S. Martins, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, J. Mol. Catal. A 2008, 285, 92-100; h) L. M. D. R. S. Martins, M. Peixoto de Almeida, S. A. C. Carabineiro, J. L. Figueiredo, A. J. L. Pombeiro, ChemCatChem 2013, 5, 3847-3856; i) L. M. D. R. S. Martins, A. Martins, E. C. B. A. Alegria, A. P. Carvalho, A. J. L. Pombeiro, Appl. Catal. A 2013, 464-465, 43-50; j) M. Peixoto de Almeida, L. M. D. R. S. Martins, S. A. C. Carabineiro, T. Lauterbach, F. Rominger, A. S. K. Hashmi, A. J. L. Pombeiro, J. L. Figueiredo, Catal. Sci. Technol. 2013, 3, 3056-3069
- [25] a) M. V. Kirillova, Y. N. Kozlov, L. S. Shul'pina, O. Y. Lyakin, A. M. Kirillov, E. P. Talsi, A. J. L. Pombeiro, G. B. Shul'pin, J. Catal. 2009, 268, 26–38; b) M. V. Kirillova, A. M. Kirillov, M. F. C. Guedes da Silva, A. J. L. Pombeiro, Eur. J. Inorg. Chem. 2008, 3423–3427; c) M. V. Kirillova, A. M. Kirillov, P. M. Reis, J. A. L. Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, J. Catal. 2007, 248, 130–136; d) M. L. Kuznetsov, A. J. L. Pombeiro, Inorg. Chem. 2009, 48, 307–318; e) M. V. Kirillova, M. L. Kuznetsov, V. B. Romakh, L. S. Shul'pina, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, G. B. Shul'pin, J. Catal. 2009, 267, 140–157; f) M. V. Kirillova, M. L. Kuznetsov, Y. N. Kozlov, L. S. Shul'pina, A. Kitaygorodskiy, A. J. L. Pombeiro, G. B. Shul'pin, ACS Catal. 2011, 1, 1511–1520.
- [26] G. B. Shul'pin, G. Süss-Fink, J. Chem. Soc. Perkin Trans. 2 1995, 2, 1459–1463.
- [27] J. Liu, S. Wen, X. Zou, F. Zuo, G. J. O. Beran, P. Feng, J. Mater. Chem. A 2013, 1, 1553–1556.
- [28] O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993.

- [29] a) R. Dinda, P. Sengupta, M. Sutradhar, T. C. W. Mak, S. Ghosh, *Inorg. Chem.* 2008, 47, 5634–5640; b) M. Sutradhar, G. Mukherjee, M. G. B. Drew, S. Ghosh, *Inorg. Chem.* 2007, 46, 5069–5075; c) M. Sutradhar, G. Mukherjee, M. G. B. Drew, S. Ghosh, *Inorg. Chem.* 2006, 45, 5150–5161.
- [30] a) APEX2, Bruker AXS Inc., Madison, WI, 2004; b) SAINT, Bruker AXS Inc., Madison, WI, 2004; c) G. M. Sheldrick, Acta

Crystallogr., Sect. A **2008**, *64*, 112–122; d) L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–837; e) A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

Received: April 22, 2015 Published Online: July 17, 2015