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Half-Sandwich Scorpionate Vanadium, Iron and Copper Complexes: Synthesis and Application in the Catalytic Peroxidative Oxidation of Cyclohexane under Mild Conditions

Telma F. S. Silva,[a,c] Elisabete C. B. A. Alegria,[a,b] Luísa M. D. R. S. Martins,[a,b] and Armando J. L. Pombeiro[a,]*

[a] Centro de Química Estrutural, Complexo I, Instituto Superior Técnico,TU Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal
Fax: (+351)-21-846-4455; e-mail: pombeiro@ist.utl.pt
[b] Departamento de Engenharia Química, ISEL, R. Conselheiro Emídio Navarro, 1950-062 Lisbon, Portugal
[c] Área Científica de Física, ISEL, R. Conselheiro Emídio Navarro, 1950-062 Lisbon, Portugal

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Abstract: The new half-sandwich scorpionate complexes [hydridotris(1-pyrazolyl)methane]vanadium trichloride, ([$VCl_3\{HC(pz)_3\}$] **1** (pz = pyrazolyl), [tris(1-pyrazolyl)methanesulfonate]vanadium trichloride, [$VCl_3\{SO_3C(pz)_3\}$] **2**, [hydrido(1-pyrazolyl)-methane]iron dichloride, [$FeCl_2\{HC(pz)_3\}$] **3**, lithium [tris(1-pyrazolyl)methanesulfonate]dichloroferrate, Li[$FeCl_2\{SO_3C(pz)_3\}$] **4**, and [tris(1-pyrazolyl)methanesulfonate]copper chloride, [$CuCl\{SO_3C(pz)_3\}$] **5** were synthesized, characterized and shown to act, as well as the related (tripyrazolylmethane)copper dichloride, [$CuCl_2\{HC(pz)_3\}$] **6**, as selective catalysts (or catalyst precursors) for the peroxidative oxidation (with hydrogen peroxide) of cyclohexane to cyclohexanol and cyclohexanone, under mild conditions (at room temperature and using an aqueous solution of H_2O_2). The iron complexes are the most active ones (reaching TON values up to *ca.* 690), the effects of a variety of factors are reported and the reaction is shown to proceed *via* both C- and O-centred radical mechanisms, conceivably involving a metal-based oxidant.

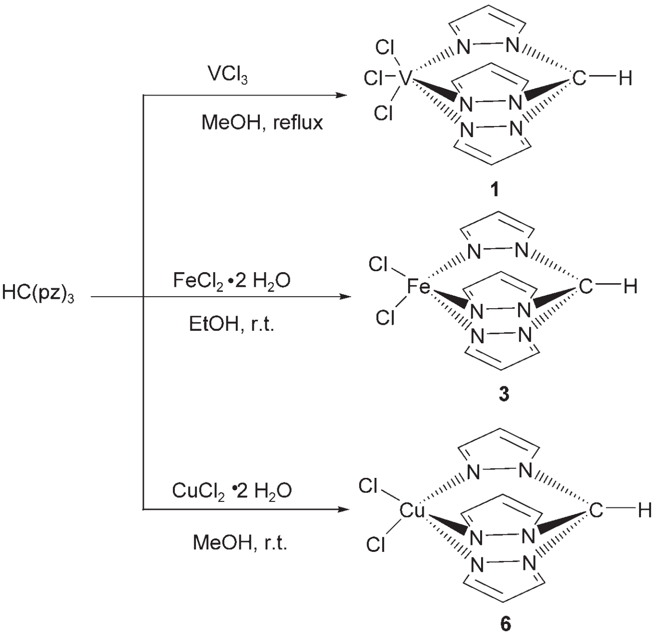
Keywords: copper; cyclohexane; iron; oxidation; scorpionates; vanadium

Introduction

Transition metal complexes stabilized by tripodal capping ligands, which also contain labile monodentate ligands, are potentially useful in catalytic processes with biological or industrial significance.[1] We have been interested in the coordination chemistry of the "scorpionate" nitrogen donor ligands, in particular the N_3-tripodal neutral hydrotris(1-pyrazolyl)methane [$HC(pz)_3$, Tpm], its derivatives with substituted pyrazolyl groups [for example, $HC(3,5\text{-}Me_2pz)_3$, Tpm^{Me}] and the C-substituted sulfonate derivative tris(pyrazolyl)methanesulfonate [$SO_3C(pz)_3^-$, Tpms] with the ability to promote the solubility of its complexes in polar solvents and also with the advantage of being more resistant to hydrolysis.[1c,2] Hence, we have recently reported[3] the synthesis and properties of several Re complexes with the above ligands.

Nevertheless, the coordination chemistry of tris(1-pyrazolyl)methanes has so far been reported only sparsely.[1,4] The lack or rarity of half-sandwich Tpm or Tpms complexes with vanadium, iron or copper, as well as the knowledge of the important role played by these metals in catalytic organic chemistry[5] and in biology[6] encouraged us to attempt the preparation of complexes with such metals and ligands. We now report the results of these studies which led to the preparation of the half-sandwich complexes [$VCl_3\{HC(pz)_3\}$] **1**, [$VCl_3\{SO_3C(pz)_3\}$] **2**, [$FeCl_2\{HC(pz)_3\}$] **3**, Li[$FeCl_2\{SO_3C(pz)_3\}$] **4** and [$CuCl\{SO_3C(pz)_3\}$] **5**. To our knowledge, complexes **1** and **2** constitute the first examples of half-sandwich Tpm and Tpms complexes of vanadium.

Functionalization reactions of saturated hydrocarbons, in particular oxidations, provide rather promising methods towards the use of such unreactive compounds as raw materials for organic syntheses.[5,7] An example with industrial significance concerns the oxidation products of cyclohexane, i.e., cyclohexanol and cyclohexanone, that are important raw materials for the production of adipic acid and caprolactam used for the manufacture of nylon.[8] The industrial process uses homogeneous cobalt species as catalysts and dioxygen as oxidant, at a considerably high temperature (150 °C), forming, e.g., cyclohexanone in a low yield (*ca.* 4%) to achieve a good selectivity[8], and the need to search for more active systems under milder conditions has been recognized[9–12]. Besides O_2, hydrogen peroxide is the preferred oxidant since it simply produces water as sub-product, but the conversions and turnovers of the cyclohexane oxidation are still commonly low.[11] In pursuit of our interest[12] on the peroxidative oxidations of alkanes, and encouraged by the successfully application of scorpionate Re complexes as catalysts in the peroxidative oxidation of ethane (to acetaldehyde) and cyclohexane.[13] we have explored, in the current study, the catalytic activity, for such a type of reaction, of the above hydrotris(1-pyrazolyl)methane and tris(1-pyrazolyl)methanesulfonate V, Fe and Cu complexes **1–5**, as well as the known[14] related $[CuCl_2\{HC(pz)_3\}]$ **6**. We now report the unprecedented use of scorpionate complexes as catalysts of these metals for cyclohexane oxidation, under mild conditions, to cyclohexanol and cyclohexanone, thus also widening our studies on alkane functionalization catalyzed by bioinspired complexes.[12] The activity of the full-sandwich compound $[Cu\{HC(pz)_3\}_2]Cl_2$ **7** was also investigated for comparison.



Scheme 1.

Results and Discussion

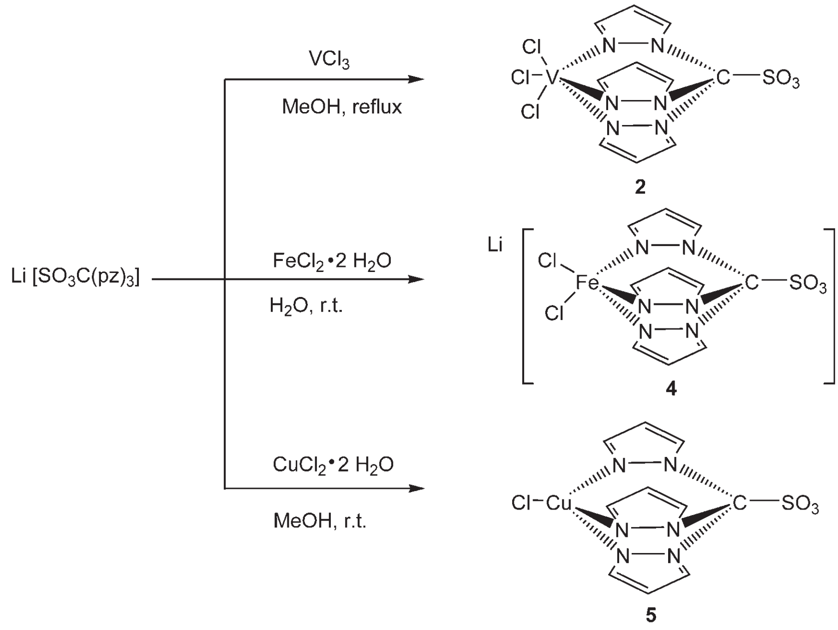
Synthesis and Spectroscopic Characterization

Complexes $[VCl_3\{HC(pz)_3\}]$ **1** (pz = pyrazolyl), $[VCl_3\{SO_3C(pz)_3\}]$ **2**, $[FeCl_2\{HC(pz)_3\}]$ **3**, $Li[FeCl_2\{SO_3C(pz)_3\}]$ **4**, $[CuCl\{SO_3C(pz)_3\}]$ **5** and $[CuCl_2\{HC(pz)_3\}]$ **6** were synthesized directly from the corresponding metal chlorides, VCl_3 (**1**, **2**), $FeCl_2{\cdot}2H_2O$ (**3**, **4**) or $CuCl_2{\cdot}2H_2O$ (**5**, **6**[14]) in an alkanol solvent or water (**4**), in the presence of the appropriate scorpionate, hydrotris(1-pyrazolyl)methane, $HC(pz)_3$ (**1**, **3**, **6**), or lithium tris(1-pyrazolyl)methanesulfonate, $Li[SO_3C(pz)_3]$ (**2**, **4**, **5**) (Scheme 1 and Scheme 2). All the complexes are new with the exception of **6**.[14]

In all of them the scorpionate ligand is η^3 coordinated by N atoms of the pyrazolyl rings. The vanadium(III and IV) complexes **1** and **2** are hexacoordinate, whereas the Fe(II) compounds **3** and **4** are pentacoordinate. Penta- and tetracoordination are displayed by Cu(II) complexes **6** and **5**, respectively. Complexes **1** and **2** appear to provide, to the best of our knowledge, the first examples of half-sandwich, hydrotris(1-pyrazolyl)methane and tris(1-pyrazolyl)methanesulfonate complexes of V. Moreover, complexes **2** and **3** display a high solubility in water [in spite of the water insolubility of the uncoordinated hydrotris(1-pyrazolyl)methane], an important feature towards their application as catalysts or catalyst precursors in aqueous media, under mild conditions, and which may also be of particular significance for further biological activity tests.

All the complexes have been characterized by elemental analysis, IR, NMR or EPR spectroscopies and FAB-mass spectrometry.

The IR spectra of the hydrotris(1-pyrazolyl)methane complexes (**1**, **3** and **6**) exhibit a medium band at 3123–3150 cm^{-1} assigned to the ν(CH) stretching mode of the methine proton of the ligated $HC(pz)_3$, which appears at values comparable to those of the uncomplexed ligand and of $[Fe\{HC(pz)_3\}(NCS)_2]$, the other known[15] five-coordinate Fe(II) compound with this ligand. Moreover, those complexes display ν(C=C) and ν(C=N) bands of their pyrazolyl groups at the normal[3,15] range of *ca.* 1635–1520 cm^{-1}. For the tris(1-pyrazolyl)methanesulfonate complexes **2**, **4** and **5**, ν(S=O) and ν(S−C) of the methanesulfonate group, as well as ν(C=C) and ν(C=N) of the pyrazolyl rings are observed at the usual ranges[2b,16,17] of 1105–1038, 636–623 and 1635–1512 cm^{-1}, respectively, being comparable to those quoted, e.g., for the Fe(II) or Cu(I) complexes $[Fe\{SO_3C(pz)_3\}_2]$, $[Ph_4P]_2[Fe(CN)_3\{SO_3C(pz)_3\}]$,[16] $[Cu\{SO_3C(pz)_3\}(PPh_3)]$[18] and $[Cu\{SO_3C(pz)_3\}(CO)]$.[2a] In all the complexes, the presence of the chloro ligands is confirmed by the corresponding IR ν(M−Cl) bands in the 383–321 cm^{-1} range.



Scheme 2.

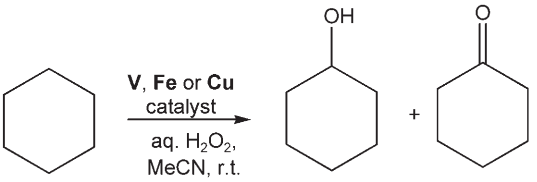
In **3** and **4**, the equivalence of the pyrazolyl groups is indicated by both ^{1}H and ^{13}C{^{1}H} NMR spectra which display a single resonance for each type of protons or of carbons, i.e., for the 3, 4 or 5 position in the ring. Moreover, in the ^{1}H NMR spectrum of **3**, the methane proton appears at $\delta = 9.05$ (in D_2O), a value similar to that exhibited, e.g., by [Fe{HC(pz)$_3$}(NCS)$_2$] (8.90 ppm[15]).

The EPR spectrum of **2** shows the expected 8-line pattern of a paramagnetic V(IV) monomeric species (^{51}V, I = 7/2) with typical values[19a,b] of the *g* and *a* parameters. The EPR spectra of powders of the Cu(II) complexes **5** and **6** also exhibit the usual pattern (^{63}Cu, I = 3/2), similar that of [Cu{HC(pz)$_3$}$_2$][NO$_3$]$_2$.[19c]

The FAB$^+$-MS of **1**, **3**, **5** and **6** exhibit the molecular ion [M]$^+$ and the fragmentation pathways occur by cleavage of the metal-ligand bonds and rupture of bonds within the HC(pz)$_3$ (**1**, **3**, **6**) or SO$_3$C(pz)$_3^-$ (**4**, **5**) ligands. Hence, fragments such as [M−Cl]$^+$, [M−Cl−pz]$^+$ and those derived upon further loss of pyrazolyl and chlorines are detected. Coupling of pyrazolyl with metal fragments has also been observed, e.g., [M+pz]$^+$ and [M−Cl+pz]$^+$.

Oxidation of Cyclohexane to Cyclohexanol and Cyclohexanone

Complexes **1–6** act as catalysts or catalyst precursors for the oxidation of cyclohexane, in acetonitrile, to a cyclohexanol and cyclohexanone mixture, by aqueous hydrogen peroxide (30% aqueous solution), usually in acidic medium, at room temperature, according to the overall reaction of Eq. (1). No cyclohexane oxidation by hydrogen peroxide takes place in the absence of the metal complex or the oxidant. A high selectivity towards the formation of those products is exhibited by these systems since no traces of by-products were detected by GC analysis of the final reaction mixtures. The reactions were typically performed under dinitrogen.



(1)

The iron(II) complexes (**3** and **4**) display the highest catalytic activities, with a maximum overall turnover number (TON, moles products/mol catalyst) of 522 or 600 (Table 1) upon 6 h reaction time, in acidic medium. A higher TON (686) can be achieved upon 1 h reaction in the presence of 3-chloroperoxobenzoic acid as a radical initiator (see below). The yields can reach values up to *ca.* 13% for **3** and *ca.* 25% for **4**, based on the alkane, although under different conditions from those that lead to the highest TONs. Since an excess of H_2O_2 is used, the yields relative to this oxidant are lower, not exceeding *ca.* 6% or 8% (for **3** or **4**, respectively). The iron catalysts are followed by the V ones (**1** and **2**), with overall TONs of 167 and 121, respectively, while the Cu(II) complexes (**5** and **6**) are less active (TONs of 43 and 32).

Table 1. Peroxidative oxidation of cyclohexane to cyclohexanol and cyclohexanone catalysed by the scorpionate complexes [$VCl_3\{HC(pz)_3\}$] 1, [$VCl_3\{SO_3C(pz)_3$] 2, [$FeCl_2\{HC(pz)_3\}$] 3, Li[$FeCl_2\{SO_3C(pz)_3\}$] 4, [$CuCl\{SO_3C(pz)_3\}$] 5, [$CuCl_2\{HC(pz)_3\}$] 6 and [$Cu\{HC(pz)_3\}_2$]Cl_2 7 (selected data).[a]

Entry[b]	Catalyst	$\frac{n(H_2O_2)}{n(\text{catalyst})}\times 10^{-3}$	$\frac{n(\text{catalyst})}{n(C_6H_{12})}\times 10^{5}$	TON[c]			
				Cyclohexanol (A)	Cyclohexanone (K)	Total[d]	A/K[e]
1 (1)	**1**	1	200	48.3	15.4	63.7	3.1
2 (4)	**1**	40	5	73.9	93	167	0.79
3 (5)	**2**	1	200	12.3	37.3	49.6	0.33
4 (8)	**2**	40	5	35.4	85.6	121	0.41
5 (9)	**3**	1	200	21.5	43.6	65.1	0.49
6 (12)	**3**	40	5	174	348	522	0.50
7 (14)[f]	**3**	40	5	254	432	686	0.59
8 (13)	**4**	1	200	41.2	81.1	122	0.51
9 (16)	**4**	40	5	223	377	600	0.59
10 (20)	**5**	40	5	25.4	17.5	42.9	1.5
11 (24)	**6**	40	5	18.3	13.4	31.7	1.4

[a] For more examples, see Supporting Information Tables S1-Table S5; *reaction conditions (unless stated otherwise):* $n(H_2O_2)/n(C_6H_{12})=2$; $n(HNO_3)/n(\text{catalyst})=10$ (**1**, **2**, **5** and **6**), 1000 (**3**, **4**); C_6H_{12} (5 mmol); NCMe (3.0 mL); 6 h reaction time; 20 °C.

[b] Numbers in brackets correspond to those of entries in the Supporitng Information, Table S1, unless started otherwise.

[c] Turnover number (moles of product per mol of catalyst); yields (%) can be estimed as TON × [$n(\text{catalyst})/n(C_6H_{12})$] × 100, e.g., 12.7, 9.9, 13.0 and 24.5% for entries 1, 3, 5 and 8, respectively.

[d] Cyclohexanol + cyclohexanone.

[e] Alcohol (cyclohexanol)/ketone (cyclohexanone) molar ratio.

[f] Number in brackets corresponds to entry number in Supporting Information, Table S5; in the presence of 3-$ClC_6H_4C(=O)OOH$; TON values quoted after 1 h reaction time.

For comparative purposes, the full sandwich Cu(II) compound [$Cu\{HC(pz)_3\}_2$]Cl_2 **7** was also tested and shown to display a lower activity (TON of 18) than the related Cu(II) half-sandwich complexes (**5** and **6**) under the same experimental conditions, which points to the relevance of labile monodentate ligands for the catalytic processes. Accordingly, the higher activity of the iron complexes relative to the vanadium ones, with the same types of ligands, conceivably can be associated, in part, to the coordinative unsaturation of the pentacoordinate iron centres, with a vacant coordination position.

The starting iron(II) and vanadium(III and IV) complexes, on reaction with H_2O_2, should be oxidized to higher oxidation states conceivably with formation of new peroxo-complexes which may be the active species in the system. In some cases, a colour change of the reaction solution was observed upon addition of the peroxide, but we failed to fully characterize the metal products. In particular, upon reaction of complex **2** and H_2O_2 in acetonitrile, a V(V) oxoperoxo-complex appeared to be present in the isolated solid mixture, as shown by ^{51}V NMR ($\delta=-528.2$ rel. to $VOCl_3$, a value comparable to those reported[20a] for oxoperoxovanadate complexes) and IR (988 and 785 cm^{-1}, assigned to $\nu(V{=}O)$ and $\nu(OO)$,[20b] respectively). However, these isolated species are almost inactive (overall TON *ca.* 0.9) and conceivably are formed upon decomposition, during the work-up, of the active and unstable peroxo-compounds generated *in situ*.

The iron scorpionate complexes **3** and **4** of this study are much more active (on the basis of TON values) in the peroxidative oxidation of cyclohexane than the iron, iron-chromium hydroxides and hydroxo-complexes (maximum TON of *ca.* 30 in the presence of acid) we have investigated earlier[12f] and non-heme iron(II) complexes containing polydentate nitrogen ligands.[10,11]

The obtained TONs in this work for the vanadium complexes **1** and **2** are also higher than those observed[12g] when using other V catalysts with N,O ligands, such as Amavadin, i.e., Ca[$V(HIDPA)_2$] [$HIDPA^{3-}$ = basic form of 2,2′-(hydroxyimino)dipropionic acid] and the related Ca[$V(HIDA)_2$] [$HIDA^{3-}$ = basic form of 2,2′-(hydroxyimino)diacetic acid] or [$VO\{N(CH_2CH_2O)_3\}$] complexes, which have been shown[12g,21] to be particularly active for oxidative functionalization reactions of alkanes. The activities of the half-sandwich copper compounds **5** and **6** are comparable to those observed for some polynuclear copper(II) triethanolamine complexes,[12c] although being somehow hampered by their low solubility in the reaction medium.

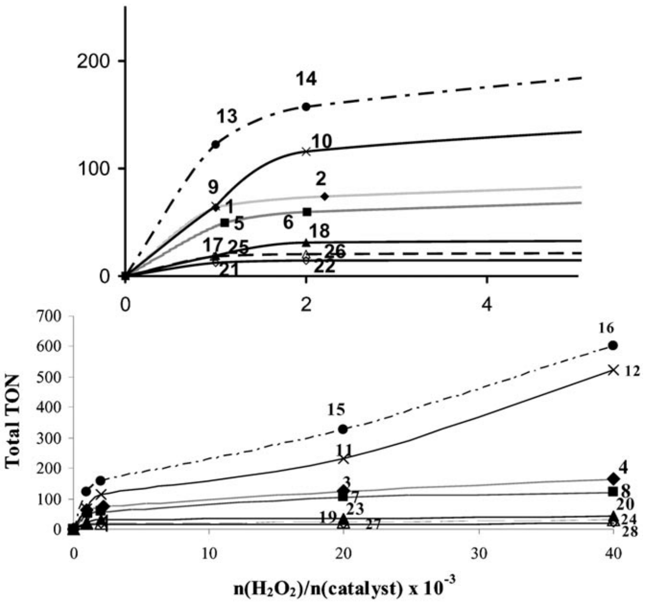


Figure 1. Effect of H_2O_2 amount (H_2O_2/catalyst molar ratio) on the overall TON, using, as catalyst precursor, [VCl_3{HC(pz)$_3$}] 1 (◆), [VCl_3{SO_3C(pz)$_3$}] 2 (■), [$FeCl_2${HC(pz)$_3$}] 3 (×), Li[$FeCl_2${SO_3C(pz)$_3$}] 4 (●), [CuCl{SO_3C(pz)$_3$}] 5 (△), [$CuCl_2${HC(pz)$_3$}] 6 (▲) or [Cu{HC(pz)$_3$}$_2$]Cl_2 7 (◇). Reaction conditions and point numbers are those of the Table S1 entries.

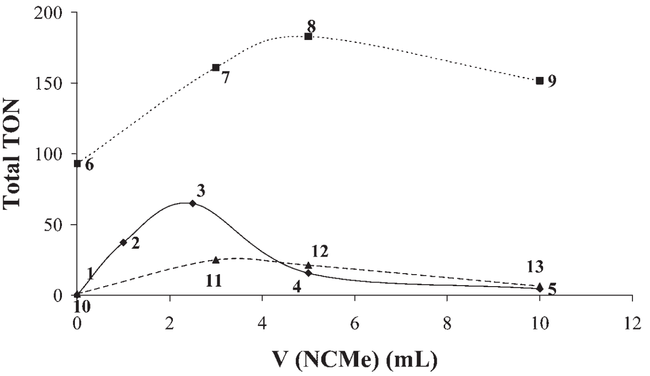


Figure 2. Effect of the amount of the NCMe solvent on the overall TON, using [VCl_3{HC(pz)$_3$}] **1** (◆), [$FeCl_2${HC(pz)$_3$}] **3** (■) or [$CuCl_2${HC(pz)$_3$}] **6** (▲) as catalyst precursors. Reaction conditions and point numbers are those of the Table S3 entries.

The effects of a variety of factors such as the relative amounts of H_2O_2, HNO_3, catalyst and solvent, reaction time and radical traps, on the activity of catalysts were studied towards the optimization of the processes, the results being shown in the Supporting Information, Table S1 to Table S5 as well as in Figure 1, Figure 2, Figure 3, Figure 4 and Figure 5, and discussed below.

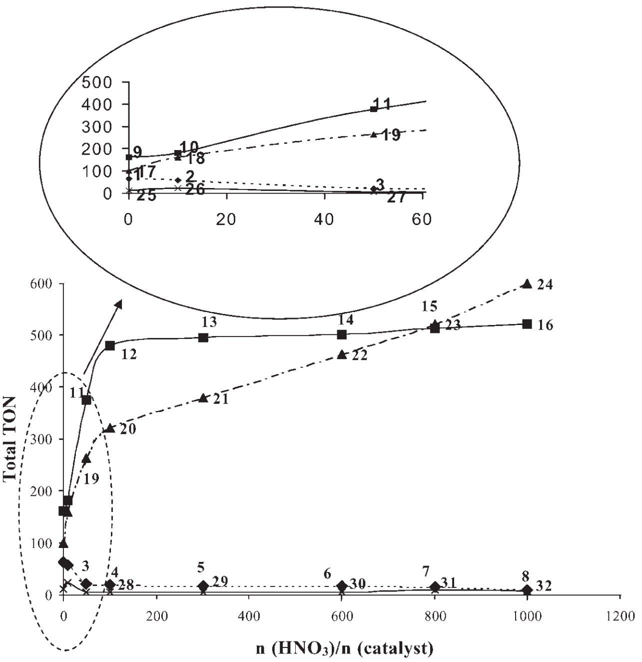


Figure 3. Effect of acid amount (HNO_3/catalyst molar ratio) on the overall TON using, as catalyst precursor, [VCl_3{HC(pz)$_3$}] **1** (◆), [$FeCl_2${HC(pz)$_3$}] **3** (■), Li[$FeCl_2${SO_3C(pz)$_3$}] **4** (▲) and [$CuCl_2${HC(pz)$_3$}] **6** (×). Reaction conditions and point numbers are those of the Table S4 entries.

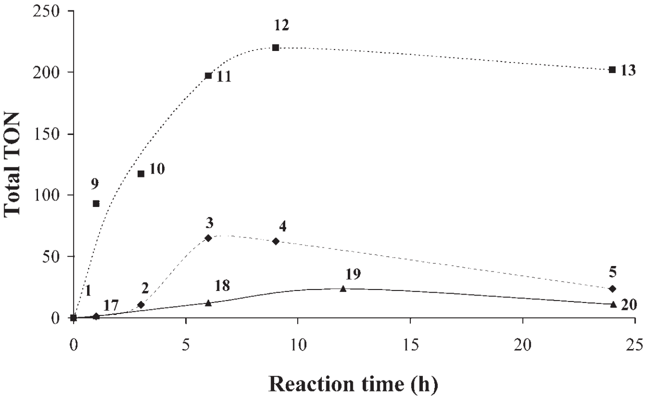


Figure 4. Effect of the reaction time on the overall TON using, as catalyst precursor, [VCl_3{HC(pz)$_3$}] **1** (◆), [$FeCl_2${HC(pz)$_3$}] **3** (■) or [$CuCl_2${HC(pz)$_3$}] **6** (▲). Reaction conditions and point numbers are those of the Table S5 entries.

Effect of the H_2O_2-to-Catalyst Molar Ratio and Type of Oxidant

The amount of hydrogen peroxide has a relevant effect. For all the complexes, the increase of the H_2O_2/catalyst molar ratio, by reducing the amount of catalyst used, results in an increase of the TON (Supporting Information, Table S1, Table S2, and

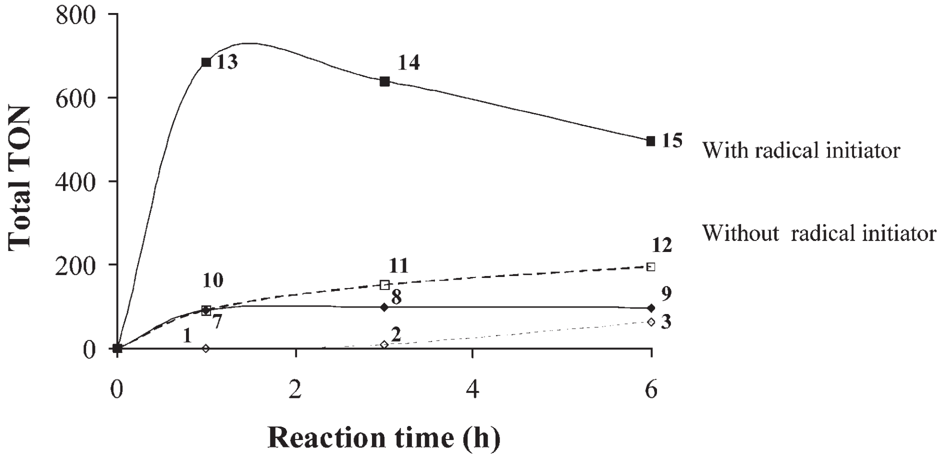


Figure 5. Effect of the presence of the radical initiator 3-chloroperoxybenzoic acid [$3\text{-}ClC_6H_4(C{=}O)OOH$], along the time, on the overall TON using [$VCl_3\{HC(pz)_3\}$] **1** as the catalyst precursor, without radical initiator (◇), with radical initiator (◆); and [$FeCl_2\{HC(pz)_3\}$] **3** as the catalyst precursor, without radical initiator (□), with radical initiator (■).

Figure 1). Hence, e.g., the overall TON for **4** or **3** increases from 122 or 65 to 600 or 522, respectively, upon changing that ratio from 1,000 to 40,000 (entries 13 or 9 and 16 or 12, Supporting Information, Table S1).

We have also tested, for the most active catalysts **3** and **4**, the effects of different oxidants. Although benzoyl peroxide $(PhCOO)_2$ can also act as an oxidant, in the presence of any of these complexes, producing basically only cyclohexanone, the TONs are much lower than those obtained under the same reaction conditions but by using hydrogen peroxide. The replacement of H_2O_2 by $K_2S_2O_8$, $(NH_4)_2S_2O_8$ or *t*-BuOOH results in suppression of the catalytic activity. Moreover, performing the oxidation reaction in air or in an atmosphere of O_2 results in a marked lowering of activity for all catalysts (e.g., a TON drop of *ca.* 50–75% for the Fe catalysts **3** and **4**, and an even more pronounced one to the other metal catalysts). This shows that O_2 does not play a dominant oxidizing role. In fact, in our systems, hydrogen peroxide behaves as the most effective oxidizing agent among those tested, which is particularly significant since it is a "green" oxidant whose by-products are just water and dioxygen.

Effect of the Amount and Type of Solvent

Acetonitrile is the typical solvent used in this type of reactions due to its high resistance to oxidizing agents and also in view of the solubility of the alkane and organic products therein. Moreover, it has been reported[22] that acetonitrile, upon reaction with H_2O_2, forms the peroxycarboximidic acid $MeC(=NH)OOH$ that is a good oxygen transfer agent.

The amount of acetonitrile in the reaction mixture has a significant effect on the TONs of products (Supporting Information, Table S3 and Figure 2). In the absence of acetonitrile, the formation of the products is usually not observed (however, see below). The increase of the volume of this solvent promotes the activity (consistent with a higher amount of the alkane in the liquid phase) which, however, reaches a maximum TON, e.g., for *ca.* 5 mL of acetonitrile for catalysts **3** and **6** (Supporting Information, entries 8 and 12, Table S3). Beyond this volume, the TON decreases, conceivably corresponding to a dilution effect of reagents and/or intermediates.

Nevertheless, interestingly, the most active iron catalyst **3** still exhibits quite a notorious activity in the absence of MeCN (Figure 2). This behaviour is favoured by the good solubility of that catalyst in water, and in the aqueous H_2O_2 medium used the catalytic system operates without the need to add any organic solvent.

Effect of the Amount of Nitric Acid

It is known that the peroxidative oxidation of cyclohexane catalysed, e.g., by some iron-chromium hydroxides and hydroxo complexes,[12f] vanadium[12g,23] and copper[12d] complexes with N,O ligands proceeds more efficiently in acidic medium.

In the current study, the cyclohexane oxidation in the presence of catalysts **1**–**6** proceeds even in the absence of acid (Supporting Information, Table S2), as reported for other V[12g,23], Fe[12f] and Cu[12c] systems. However, distinct behaviours in the presence of HNO_3 are observed (Supporting Information, Table S4, Figure 3). For the more active iron complexes $[FeCl_2\{HC(pz)_3\}]$ **3** and $Li[FeCl_2\{SO_3C(pz)_3\}]$ **4**, the addition of HNO_3 results in an enhancement of activity, e.g., for **4** the overall TON increases from 100 to 600 on changing the acid-to-catalyst molar ratio from 0 to 1,000 (Figure 3). For **3**, a pronounced increase of TON with the amount of acid is observed up to $n(HNO_3)/n(catalyst)=1{,}000$ beyond which no considerable effect has been detected (Figure 3). In the cases of the V and Cu catalysts $[VCl_3\{HC(pz)_3\}]$ **1** and $[CuCl_2\{HC(pz)_3\}]$ **6**, respectively, with lower activities, the acid has not a substantial effect (Figure 3).

The favourable effect of acid for the most active Fe catalysts presumably can be associated with (i) the activation of the metal centre by further unsaturation upon protonation of the scorpionate ligand (decrease of its hapticity), (ii) the enhancement of oxidative properties of metal complexes, (iii) the stabilization of H_2O_2 towards decomposition to water and oxygen, and promotion of peroxo (or hydroperoxo)-complexes formation.

Effect of Reaction Time, Radical Initiator and Radical Traps

The effect of the reaction time was studied for complexes **1, 3** and **6** (Supporting Information, Table S5, Figure 4). The overall TON usually increases during the first 6–8 h whereafter only a small drop is observed, conceivably due to overoxidation. The highest initial rate is exhibited by the most active complex (iron catalyst **3**).

The peroxidative oxidation of cyclohexane appears to proceed mainly by mechanisms that involve both carbon- and oxygen-centred radicals since the formation of cyclohexanol and cyclohexanone products is suppressed when the reactions that correspond to the highest TONs for complexes **2**, **3**, **4** or **5** are carried out in the presence of a radical trap[24] for carbon (such as trichlorobromomethane, $CBrCl_3$), in a stoichiometric amount relative to substrate, or a radical trap for oxygen (such as diphenylamine, Ph_2NH), in a stoichiometric amount relative to H_2O_2.

The effect of 3-chloroperoxybenzoic acid, $3\text{-}ClC_6H_4C(=O)OOH$, in a stoichiometric amount relative to the substrate, acting as a possible radical initiator,[25] was studied for the systems catalyzed by complexes **1** and **3** in the presence of H_2O_2. That peroxy acid greatly accelerates the reaction (Figure 5) leading, after 1 h, to the highest TON and TOF values (686 and 686 h, respectively, for complex **3**) achieved in this study. However, the TON drops beyond this time suggesting that a radical trap effect of that peroxy acid predominates after the initial accelerating radical initiator effect. Moreover, if $3\text{-}ClC_6H_4C(=O)OOH$ is tested as the oxidant, instead of H_2O_2, no catalytic activity (or only a very low one) is detected.

Mechanistic Considerations

The peroxidative oxidation (by H_2O_2) reaction is believed to proceed *via* a radical mechanism involving both O- and C-centred radicals (see the above-mentioned effect of radicals traps) and possibly a metal-based oxidant (such as $M{-}OOH$ or $M{=}O$, see below) as supported by the high catalytic activity (TON values can approach 700) in the absence of air, which has not yet been accounted for by a Fenton-type chemistry typically operating under air *via* free radical chain auto-oxidation. The limited product selectivity (the alcohol/ketone ratio A/K is within the 0.3–3.5 range, Table 1 and Supporting Information, Table S1), which eventually would corroborate the unselective radical chain auto-oxidation mechanism (expected A/K of *ca.* 1),[10c] is not conclusive. In addition, the presence of some amount of ROOH at the end of the reaction (catalysts **2** and **5**, see below) affects the A/K ratio which thus reflects the total amounts of alcohol and ketone, formed during the reaction and upon decomposition, in the chromatograph, of the remaining RCOOH (to give additional similar molar amounts of A and K).[9d] Therefore, the obtained A/K ratio expresses a lower selectivity than that in fact achieved along the reaction. Moreover, we are using an excess of H_2O_2, what is favourable to further oxidation of the alcohol to the ketone (accordingly, for the most active systems, the cyclohexanone yield is roughly double of that of cyclohexanol, i.e., an A/K of *ca.* 0.5).

Metal-peroxo intermediates can be entailed in pathways that account for the formation of the products without requiring the involvement of molecular oxygen, in agreement with the catalytic activity of our systems in the absence of air and the lowering of that activity by the presence of O_2. In fact, $M^n{-}OOH$ species, which have also been invoked in some peroxidative alkane oxidations systems, can undergo, in principle, any of the following further reactions:[10,26] (i) attack at the alkane (RH), thus acting as a metal-based oxidant, to yield $M^n{-}OH+ROH$ or $M^{n+1}+R(-H){=}O+H_2O$; (ii) homolytic O−O bond cleavage to give $M^{n+1}{=}O$ and the hydroxyl radical $HO^\bullet$, both of them able to react with the alkane (yielding $R^\bullet+M^n{-}OH$ or H_2O, respectively); (iii) O−O bond heterolysis to form a high valent $M^{n+2}{=}O$ species (and hydroxide HO^-) which could attack the alkane; (iv) $M{-}O$ bond homolysis to yield $HOO^\bullet$ which could disproportionate[26c] to H_2O_2 and O_2. The radical $R^\bullet$ formed in (ii) or (iii) could react with the metal peroxide $M^n{-}OOH$ to yield $M^{n-1}+ROOH$ (cyclohexyl hydroperoxide) or $M^{n+1}=O+ROH$.[26d]

The promoting effect of 3-chloroperoxybenzoic acid, $3\text{-}ClC_6H_4C(=O)OOH$, can be associated to the metal-assisted formation of the reactive hydroxyl radical (upon homolytic scission of the O−O bond),[27,28]of an oxo-metal (*M*=O) active species (by heterolytic O−O bond cleavage)[27,29] or of the reactive acylperoxy radical 3-$ClC_6H_4C(=O)OO^{\bullet}$[29,30] (which can oxygenate the alkane RH to give the alcohol ROH and the corresponding acyloxy radical 3-$ClC_6H_4COO^{\bullet}$).

Decomposition of ROOH to give the alcohol and the ketone has been often proposed[5,9d,21c,31–34] *via* metal-assisted formation of the alkyloxy $RO^{\bullet}$ and alkylperoxy $ROO^{\bullet}$ radicals (the former yielding ROH upon H-abstraction from the alkane, and the latter decomposing to $ROH + R(-H)=O + O_2$ or to $RO^{\bullet}$).

Nevertheless, we cannot rule out the participation, to some extent, of a Fenton-type chemistry for example, as a source of the hydroxyl radical (an active oxidant, able to generate the cyclohexyl radical by H-abstraction from alkane). Dominant Fenton-type chemistry has been reported[11] for the oxidation of cyclohexane (used in a large excess) by H_2O_2, under air and in the presence of various non-heme iron complexes with polydentate N ligands, although the possibility of operating a metal-based oxidation mechanism has also been suggested[11d] for the more active and selective systems.

Most of the metal-assisted reactions suggested above involve a change in the metal oxidation state of one unit and hence are particularly favourable for complexes in which the metal can exhibit the corresponding available oxidation states of comparable stability, as expected for V(IV/V), Fe(II/III) or Cu(I/II). However, the mechanism (iii) involves a metal oxidation of two units and thus is not expected for the Cu(II) systems and cannot occur with V(IV). Nevertheless, it would be possible for V(III) and, although less probable, for Fe(II) systems. Thus, different metals can follow distinct mechanisms. This is also suggested by the detection of ROOH in some of our systems but not in others. In fact, the involvement of ROOH is corroborated for complexes of V and Cu (**2** and **5**, respectively) by the pronounced increase (of *ca.* 75% or 45%, respectively, for the conditions of entries 4 and 10, Table 1) in the amount of alcohol with a concomitant decrease in the amount of ketone when the final reaction solution, before GC analysis, is treated with an excess of PPh_3, according to a method reported by Shul'pin et al.[9d,31]. However, in the case of the Fe catalysts **3** and **4**, no appreciable change in the amounts of products was observed upon addition of PPh_3, suggesting that either ROOH had already decomposed (further reacted) in the presence of these catalysts or the reaction does not proceed *via* that hydroperoxide.

Conclusions

We have found a simple and convenient route for the formation of half-sandwich scorpionate vanadium, iron or copper complexes directly from the commercially available metallic salts, that has allowed the synthesis of the first hydrotris(1-pyrazolyl)methane and tris(1-pyrazolyl)methanesulfonate V complexes of this type, thus contributing towards the still little explored coordination chemistry of such types of scorpionate ligands.

We have also opened up the possibility of applying such a type of complexes as catalyst precursors for the single-pot cyclohexane oxidation to cyclohexanol and cyclohexanone under mild conditions, at room temperature and with an environmentally friendly oxidant (H_2O_2). The iron complexes $Li[FeCl_2\{SO_3C(pz)_3\}]$ **4** and $[FeCl_2\{HC(pz)_3\}]$ **3** provide the best catalysts and their activity is promoted by acid reaching remarkable TON values up to *ca.* 690 or yields (based on the alkane) up to *ca.* 25%. The use of H_2O_2 as oxidant and of acetonitrile-water as the solvent medium leads to the highest catalytic activity, but the hydrosoluble Fe complex **3** can operate effectively in water without requiring the presence of any organic solvent. This feature that allows the uncommon use of water as the only solvent is particularly significant in terms of developing a "green" catalytic system and deserves to be further explored by preparing and testing other hydro-soluble scorpionate complexes.

The reactions proceed *via* radical mechanisms with possible involvement of both C-centred and O-centred radicals, and of a metal-based oxidant.

Experimental Section

General Materials and Procedures

Vanadium trichloride (Acros), copper(II) chloride (Merck), cyclohexane (Merck), acetonitrile (Riedel-de-Haën), hydrogen peroxide (30%) (Fluka), nitric acid (65%) (Riedel-de-Haën), cyclopentanone, cycloheptanone (Riedel-de-Haën), 3-chloroperoxybenzoic acid (Aldrich) and triphenylphosphine (Merck) were used as received from the supplier. Anhydrous iron(II) chloride, $FeCl_2{\cdot}2\,H_2O$[35], hydrotris(pyrazolyl)methane, $HC(pz)_3$[36], lithium tris(l-pyrazolyl)methanesu1fonate, $Li[SO_3C(pz)_3]$[2a], complexes **6**[14] and **7**[37] were obtained according to published methods. All manipulations and reactions were performed under an atmosphere of dinitrogen using standard vacuum and inert-gas flow techniques. Solvents were purified by standard procedures and freshly distilled immediately prior to use.

$\{^1H\}$-NMR and ^{13}C NMR spectra were recorded at 22 °C on a Varian Unity 300 spectrometer, δ values are in ppm relative to $SiMe_4$. Coupling constants are in Hz; abbreviations: s = singlet, d = doublet. EPR spectra were recorded on a Bruker ESP 300E X-band spectrophotometer equipped with an ER 4111 VT variable-temperature unit. Infrared spectra (4000–400 cm^{-1}) were recorded on a Nicolet Impact 400D, a Perkin–Elmer 1330 or a Jasco FT/IR-430 spectrophotometer, in KBr pellets; wavenumbers are in cm^{-1}; abbreviations: vs, very strong; s, strong; m, medium; w, weak. Far infrared spectra (400–200 cm^{-1}) were recorded on a Vertex 70 spectrophotometer, in polyethylene pellets. FAB mass spectra were obtained on a Trio 2000 spectrometer by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (*ca.* 1.28×10^{15}J) Xe atoms. Nominal molecular masses were calculated using the most abundant isotopes, i.e., ^{51}V (100%), ^{56}Fe (63%), ^{63}Cu (69%) and ^{35}Cl (76%), and the expected natural abundance isotope cluster patterns were observed for the various ion clusters. Mass calibration for data system acquisition was achieved using CsI. The C, H, N, S elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Gas chromatographic (GC) measurements were carried out using a Fisons Instruments GC 8000 series gas chromatograph with a FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm). The temperature of injection was 240 °C. The initial temperature was maintained at 100 °C for 1 min, then raised 10 °C min^{-1} to 180 °C and held at this temperature for 1 min. Helium was used as the carrier gas.

Synthesis and Characterization of the Complexes

$[VCl_3\{HC(pz)_3\}]$ (1): To a solution of vanadium trichloride (0.10 g, 0.64 mmol) in methanol (10 mL) was added, with constant stirring, an equimolar amount of $HC(pz)_3$ (0.13 g, 0.64 mmol) in methanol (10 mL). The resulting green solution was stirred overnight under reflux. The precipitate formed was filtered off, washed with Et_2O and dried under vacuum; yield: 0.11 g (46%). IR (KBr pellet): ν = 3122 [s, ν(C−H)], 1629 and 1513 [s, ν(C=C), ν(N=C), $C(pz)_3$], 383, 359 and 321 cm^{-1} [ν(V−Cl)]; ^{1}H NMR (DMSO-d_6): δ = 8.95 [s, br, 1H, $HC(pz)_3$], 7.89 [s, br, 3H, H(3) or H(5), $HC(pz)_3$], 7.67 [s, br, 3H, H(4), $HC(pz)_3$], 6.41 [s, br, 3H, H(5) or H(3), $HC(pz)_3$]; FAB$^+$-MS: m/z = 372 ([M]$^+$), 337 ([M]$^+$−Cl), 302 ([M−2 Cl]$^+$), 235 ([M−2 Cl−pz]$^+$); anal. calcd. for $VCl_3C_{10}H_{10}N_6$: C 32.6, H 2.7, N 22.6; found: C 32.7, H, 3.1, N 21.3%.

$[VCl_3\{SO_3C(pz)_3\}]$ (2): To a solution of vanadium trichloride (0.20 g, 1.27 mmol) in methanol (10 mL) was added, with constant stirring, an equimolar quantity of $Li[SO_3C(pz)_3]$ (0.38 g, 1.27 mmol) in methanol (10 mL). The resulting deep purple solution was stirred overnight under reflux. The final blue solution was concentrated and upon addition of Et_2O a blue solid precipitated. The solid was collected by filtration, washed with Et_2O and dried under vacuum: yield: 0.29 g (51%). This complex is soluble in water. IR (KBr pellet): ν = 3170, 3148 [s, ν(C−H), $^-SO_3C(pz)_3$], 1528 and 1440 [s, ν(C=C) and ν(N=C), $^-SO_3C(pz)_3$], 1105, 1075 and 1057 [s, ν(S=O), $^-SO_3C(pz)_3$], 635 [m, ν(S−C), $^-SO_3C(pz)_3$], 355, 347 and 320 cm^{-1} [ν(V−Cl)]; EPR (CH_2Cl_2, r.t.): a = 98.2 G, g = 1.9981; FAB$^+$-MS: m/z = 384 ([M−pz]$^+$), 312 ([M−pz−2 Cl]$^+$), 282 ([M−2 pz−Cl]$^+$); anal. calcd. for $VCl_3C_{10}H_9N_6SO_3$: C 26.6, H 2.0, N 18.6, S 7.1; found: C 26.3, H 2.5, N 18.1, S 7.3%.

$[FeCl_2\{HC(pz)_3\}]$ (3): To an ethanol (10 mL) solution of $FeCl_2\cdot 2H_2O$ (281 mg, 1.73 mmol) was added slowly an equimolar amount of $HC(pz)_3$ (331 mg, 1.73 mmol) in ethanol (12 mL). A pink solid precipitated and the solution became almost colourless. The solid was filtered off, washed several times with methanol and dried under vacuum; yield: 0.38 g (64%). This complex is soluble in water. IR (KBr pellet): ν = 3150 [s, ν(C−H)], 1634 and 1515 [s, ν(C=C), ν(N=C), $HC(pz)_3$], 363 and 327 cm^{-1} ν(Fe−Cl); ^{1}H NMR (D_2O): δ = 9.05 [s, 1H, *H*$C(pz)_3$], 8.42 [s, br, 3H, H(3) or H(5), $HC(pz)_3$], 7.63 [s, br, 3H, H(4), $HC(pz)_3$], 6.86 [s, br, 3H, H(5) or H(3), $HC(pz)_3$]; ^{13}C{^{1}H} NMR: δ = 157.68 [s, C(3), $HC(pz)_3$], 112.09 [s, C(5), $HC(pz)_3$], 140.67 [s, C(4), $HC(pz)_3$], 71.10 [s, $HC(pz)_3$]; ^{13}C NMR: δ = 157.68 [d, J_{CH} = 197.3, C(3), $HC(pz)_3$], 140.67 [d, J_{CH} = 195.3, C(5), $HC(pz)_3$], and 112.09 [d, J_{CH} = 184.2, C(4), $HC(pz)_3$]; FAB$^+$-MS: *m/z* = 338 ([M]$^+$), 269 ([M−2 Cl]$^+$), 237 ([M−Cl−pz]$^+$); anal. calcd. for $FeCl_2C_{10}H_{10}N_6$: C 35.5, H 3.5, N 24; found: C 35.3, H 3.6, N 24.1%.

$Li[FeCl_2\{SO_3C(pz)_3\}]$ (4): Reaction of $FeCl_2\cdot 2H_2O$ (250 mg, 1.53 mmol) in water (8 mL) with an equimolar amount of $Li[SO_3C(pz)_3]$ (459 mg, 1.53 mmol) in aqueous solution (5 mL) immediately led to the precipitation of a pink solid which was filtered off, washed with methanol and dried under vacuum; yield: 0.44 g (67%); IR (KBr pellet): ν = 3177, 3128 and 3054 [m, ν(C−H), $^-SO_3C(pz)_3$], 1635 and 1512 [s, ν(C=C) and ν(N=C), $^-SO_3C(pz)_3$], 1098, 1090 and 1056 [vs, ν(S=O, $^-SO_3C(pz)_3$], 623 [s, ν(S−C), $^-SO_3C(pz)_3$], 381 and 370 cm^{-1} ν(Fe−Cl); ^{1}H NMR (DMSO-d_6): δ = 8.08 [s, br, H(5), $^-SO_3C(pz)_3$], 6.28 [s, br, H(3), $^-SO_3C(pz)_3$], 7.35 [s, br, H(4), $^-SO_3C(pz)_3$]; FAB$^+$- MS: *m/z* = 423 ([M+pz−2 Cl]$^+$), 256 ([M−Cl+2 pz]$^+$); anal. calcd. for $LiFeCl_2C_{10}H_9N_6SO_3$: C 31.0, H 2.9, N 21.0; found: C 30.5, H 2.9, N 19.7%.

$[CuCl\{SO_3C(pz)_3\}]$ (5): To a solution of $CuCl_2\cdot 2H_2O$ (0.15 g, 0.87 mmol) in methanol (15 mL) was added, with constant stirring, an equimolar amount of $Li[SO_3C(pz)_3]$ (0.26 g, 0.87 mmol) in methanol (10 mL). The blue solution was stirred overnight at room temperature. The formed precipitate was collected by filtration, washed with Et_2O and dried under vacuum; yield: 0.25 g (61%). IR (KBr pellet): ν = 3167.3, 3139.1 and 3109.5 [m, ν(C−H), $^-SO_3C(pz)_3$], 1531.9 and 1519.5 [s, ν(C=C) and ν(N=C), $^-SO_3C(pz)_3$], 1077.1, 1054.4 and 1037.6 [vs, ν(S=O), $^-SO_3C(pz)_3$], 632.6 cm^{-1} [s, ν(S−C), $^-SO_3C(pz)_3$]; Far IR (polyethylene pellet): ν = 278.4 [s, ν(Cu−Cl)]; EPR (solid, 90 K): a = 174.0 G, g = 2.0784; FAB$^+$-MS: *m/z* = 392 ([M]$^+$), 312 ([M−SO$_3$]$^+$), 178 ([M−SO$_3$−2 pz]$^+$), 491 ([M+pz]$^+$), 558 ([M+2 pz]$^+$); anal. calcd. for $CuClC_{10}H_9N_6SO_3\cdot Et_2O$: C 36.1, H 3.6, N, 18.1, S 6.9%; found: C 36.0, H 3.3, N 17.8, S 7.2%.

$[CuCl_2\{HC(pz)_3\}]$ (6): A reported[14] procedure was followed although with a considerable reduction of the reaction time (from 12[14] to 2 h) which resulted in an improved yield (65% compared to 43%[14]). EPR (solid, 90 K): a = 75.7 G, g = 2.1278; FAB$^+$-MS: *m/z* = 349 ([M]$^+$), 314 ([M−Cl]$^+$), 279 ([M−2 Cl]$^+$), 209 ([M−2 Cl−pz]$^+$).

Catalytic Activity Studies

The oxidation reactions were carried out in Schlenk tubes and under dinitrogen. In typical conditions the reaction mixtures were prepared as follows: 0.010 mmol of the catalyst (complexes **1–7**) were dissolved in 2.50 mL of MeCN. The required amount of this solution for the desired oxidant/catalyst molar ratio was transferred to a second flask, whereafter MeCN was added until a total solution volume of 3.00 mL. Then 5.00 mmol of H_2O_2 in a 30% H_2O solution (0.50 mL) and 5.00 mmol of cyclohexane (0.54 mL) were added (in this order) and the reaction solution was stirred for 6 h at the desired temperature (commonly room temperature) and normal pressure. In the experiments with HNO_3, this acid was added immediately before the addition of the substrate.

For the products analysis, 90 μL of cyclopentanone (internal standard) and 6.5 mL of diethyl ether (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 (1 μL) was taken from the organic phase and analyzed by GC by the internal standard method. The amount of alkyl hydroperoxide (if formed) was estimated from the variations in the alcohol and ketone yields, determined by GC analyses, on addition of PPh_3 to the final reaction, according to a method reported by Shul'pin et al.[9d,31] Blank experiments confirm that no cyclohexanol or cyclohexanone are formed without the metal catalyst. Moreover, only traces of these products are detected by GC analysis immediately performed after addition of 3-choroperoxybenzoic acid to an acetonitrile solution of cyclohexane and metal catalyst **1**, thus showing that the peroxo acid does not oxidize the alkane in the GC injector.

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