

Review

C-Homoscorpionate Oxidation Catalysts—Electrochemical and Catalytic Activity

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Academic Editor: Georgiy B. Shul'pin

Received: 18 November 2016; Accepted: 23 December 2016; Published: 1 January 2017

Abstract: A survey of the electrochemical properties of homoscorpionate tris(pyrazol-1-yl)methane complexes is presented. The relationship between structural features and catalytic efficiency toward the oxidative functionalization of inexpensive and abundant raw-materials to added-value products is also addressed.

Keywords: C-scorpionate; cyclic voltammetry; redox potential; catalyst; oxidation; electrochemical parameter; alkane; alkene; alcohol; ketone

1. Introduction

Scorpionate compounds (Figure 1), in particular, poly(pyrazol-1-yl)borates, $R^1BX_n(R^2pz)_{3-n}$ (pz = pyrazol-1-yl, $n = 0$ or 1), and poly(pyrazol-1-yl)methanes, $R^1CX_n(R^2pz)_{3-n}$ ($n = 0$ or 1), are undoubtedly among the most important N -donor ligands in coordination chemistry [1–8]. The latter are considerably less well studied than the analogous borate species [3]. However, in the last two decades, mainly driven by improved syntheses [9,10], coordination behavior and physicochemical properties of poly(pyrazol-1-yl)methanes have attracted considerable interest [5–8] in order to perform the precise tuning of target scorpionates towards a desired function [3,6,7]. Applications of this highly versatile class of metal compounds range from organic synthesis, analytical, bio-inorganic or catalytic chemistry to material sciences [3,6–8,11–18].

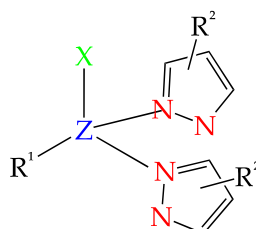


Figure 1. General scorpionate structure: poly(pyrazol-1-yl)borates for $Z = B$; poly(pyrazol-1-yl)methanes for $Z = C$.

The development of sustainable efficient catalytic processes for the activation of abundant and inexpensive raw-materials into high-added-value products remains a great challenge for both academic and industrial purposes. In this respect, the use of metal complexes bearing C-scorpionate poly(pyrazol-1-yl)methane ligands as catalysts is currently experiencing significant development [6–8,16]. Transition metals are important in this topic participating e.g., in redox

processes, which can be applied in specific steps. The electronic interaction between transition metals and scorpionate ligands can play a key role in improving the redox process, and the type of scorpionate ligand can be determinant in achieving the desired properties in such complexes. Thus, one advantage of this catalytic system (over e.g., the metallocene based one) is the ease of modifying the scorpionate ligand to change the steric and electronic properties of the metal complex and therefore, its catalytic performance.

Industrially important reactions catalyzed by C-scorpionate complexes include [6–8,17–22] (i) mild partial oxidation of alkanes to alkyl hydroperoxides, alcohols and ketones; (ii) epoxidation of alkenes; (iii) oxidation of primary or secondary alcohols to aldehydes or ketones, respectively; (iv) the Baeyer-Villiger oxidation of linear or cyclic ketones to the corresponding esters and lactones, respectively; (v) the single pot carboxylation of gaseous alkanes into the corresponding C_{n+1} carboxylic acids; (vi) the stereo-selective nitroaldol Henry C–C coupling reaction; and (vii) olefin polymerization.

Whereas the main catalytic applications of metal complexes with tris(pyrazol-1-yl)borates or heteroscorpionate ligands based on the bis(pyrazol-1-yl)methane moiety are found in olefin polymerization reactions [1,6], tris(pyrazol-1-yl)methane-type complexes of several transition metals are mainly used as catalysts or catalyst precursors for alkane, alkene, alcohol, and ketone oxidation reactions directed toward single-pot organic synthesis [7]. Their use as catalysts for the C–C coupling Henry reaction (a non-redox process) [8] has also proved to be a very promising strategy, in particular for those metals (e.g., Zn) that exhibit no redox flexibility but can behave as Lewis acid catalysts.

Moreover, tris(pyrazol-1-yl)methane metal complexes can exhibit remarkable versatile catalytic activity for oxidation reactions [16]. It is believed that the interchange between bidentate and tridentate coordination modes of the C-scorpionate ligands is at the core of the structural and chemical versatility of many metal complexes of this kind and is essential for their catalytic applications.

Electron transfer plays a fundamental role in governing the pathway of most of the above chemical reactions. In fact, the activity of metal-based catalysts depends largely on their ligand environment and coordination geometry, which also rule their oxidation/reduction properties, with the redox potential as a determining parameter. Thus, quantification of the net electron donation of the ligands to a metal center would allow predicting metal-centered redox potentials, and vice-versa, providing a powerful tool for the design of metal-based catalysts within a desired redox window.

Determination of redox potentials can be conveniently done by e.g., the easy and fast cyclic voltammetry technique, provided the redox signals lie within the available solvent/electrolyte potential window and the species have a sufficient lifetime for signal detection. However, to date, the useful information associated to the redox potential of a metal complex has not yet found a common application as a characterization or identification tool [23]. Moreover, a survey of the redox properties of known C-homoscorpionate metal complexes is missing.

Systematic approaches to establish redox potential/structure relationships, following the recognition of full additive ligand (L) effects on that potential have been proposed [24–28]. For example, Lever's parametrization approach (Equation (1)) [27,28] allows for the prediction of an $M^{n+1/n}$ redox potential (E) of a six-coordinate metal complex in V vs. SHE (standard hydrogen electrode), where E_L is an additive ligand parameter obtained by a statistical analysis on the known redox potentials of a high number of $M^{n+1/n}$ complexes [27,28]. The slope, S_M , and intercept, I_M , are dependent upon the metal and redox couple, the polygon of the complex, the spin state, and the stereochemistry [23].

$$E = S_M (\Sigma E_L) + I_M / \text{V vs. SHE} \quad (1)$$

On the other hand, Equation (1) can be applied to estimate the E_L value of a ligand (L) provided one knows the redox potential of a complex with that ligand L bound to a $M^{n+1/n}$ metal redox couple with known I_M and S_M parameters, and the E_L values of the co-ligands.

Herein, the electrochemical properties of homoscorpionate tris(pyrazol-1-yl)methane metal complexes that act as catalysts for the above industrial oxidation reactions are presented.

Moreover, the E_L ligand parameter, a measure of the electron donor character of ligand L (the lower its value, the stronger that character), is used to establish redox/structure as well as redox/catalytic activity relationships, a very important tool for the design of improved catalysts to address some of the problems presented by current large-scale industrial partial oxidation processes.

2. C-Homoscorpionates and Their Metal Catalysts

Firstly reported by Trofimenko (1966) [29,30] as “a new and fertile field of remarkable scope”, B-scorpionate tris(pyrazol-1-yl)borates (Tp, Figure 2a) indeed were revealed to be a class of compounds that became a precious ligand system in modern coordination chemistry [1,2].

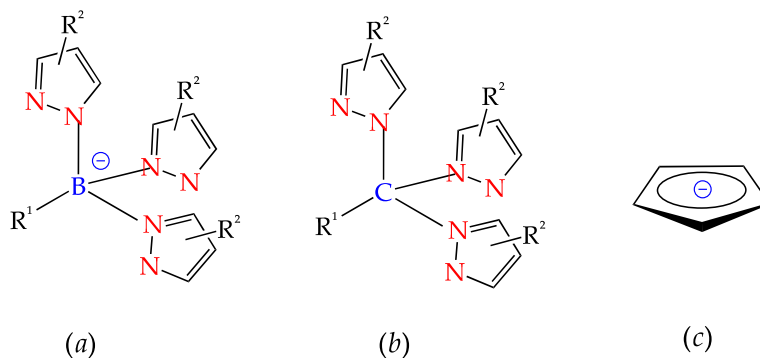


Figure 2. Structural general representation of tris(pyrazol-1-yl)borate (a); tris(pyrazol-1-yl)methane (b); and cyclopentadienyl (c) ligands.

Although discovered earlier by Hückel et al. (1937) [31], the analogous C-scorpionate tris(pyrazol-1-yl)methanes (Tpm, Figure 2b) remained dormant with respect to coordination chemistry until 1966 [32], mainly due to synthetic difficulties and usually very low yields associated with the preparation of functionalized tris(pyrazol-1-yl)methanes where substituents on the pyrazolyl rings are larger than methyl. In fact, until Elguero’s report (1984) of an improved synthetic strategy [33] and its subsequent application in the formation of functionalized derivatives bearing bulky substituents [34,35], only few (less than 20) reports appeared pertaining to first-row transition metal complexes of tris(pyrazol-1-yl)methanes, mostly homoleptic ones.

It is commonly agreed to compare [2,3,30,36–38] the main characteristics of tris(pyrazol-1-yl) type scorpionate ligands with other face-capping ligands. In particular, the parallel between Tp and cyclopentadienyl (Cp, Figure 2c) ligands is established in that both are mononegative, six-electron (ionic model) or five-electron donor (covalent model) ligands. They are also formally isolobal [2,3]. The former are weak-field hard σ -N donors which tend to behave as fac-capping chelating ligands (i.e., occupy three coordination positions), while Cp are typically 5-fold π -donors and tend to form tetrahedral complexes [3,38].

Importantly, it has been shown that there is no systematic trend in comparative electron donor ability of Tp relative to Cp [39]. Their electron-donating abilities are dependent upon the identity and oxidation state of the metal center as well as the properties of the other ligands in the complex [40]. Tris(pyrazol-1-yl)borates are also bulkier than the formally analogous Cp and, in six-coordinate environments, enforce nearly octahedral coordination to the metal with N-M-N bite angles close to the ideal value (90°). This has been suggested to be the primary source of the different reactivity between comparable Tp and Cp complexes [40,41]. For example, the greater steric profile of Tp ligands has permitted the isolation of molecular species whose pentamethylcyclopentadienyl congeners proved too reactive [42]. In addition, Tp is coordinatively flexible, presenting κ^2 - or κ^3 -coordination modes (i.e., the scorpionate feature). The carbon analogues to Tp, tris(pyrazol-1-yl)methanes, maintain the tripodal face capping aspect and the same electro-donor ability, but differ from Tp and Cp in the charge they hold (Figure 2).

Since 2005 a considerable interest in the development of a fast and efficient synthetic route for hydrotris(pyrazol-1-yl)methane, $\text{HC}(\text{pz})_3$ (pz = pyrazol-1-yl), Tpm [10], as well as on the design and synthesis of brand new poly-functionalized C-homoscorpionates, $\text{R}^1\text{C}(\text{R}^2\text{pz})_3$, overcoming the lack in the chemistry of such species (Figure 3), has been found [43–45]. For example, new tris(pyrazol-1-yl)methanes functionalized at the methine carbon atom (in order to vary the coordination behavior and physicochemical properties) were successfully prepared: $\text{CH}_3\text{SO}_3\text{CH}_2\text{C}(\text{pz})_3$ [43] or $\text{PyCH}_2\text{OCH}_2\text{C}(\text{pz})_3$ (Py = pyridine) [44]. The functionalization of pyrazol-1-yl rings (to modulate the coordination properties) was also achieved, as well as those derivatives that combine the two types of functionalization: e.g., $\text{SO}_3\text{C}(3\text{-Phpz})_3^-$ [45], $\text{HOCH}_2\text{C}(3\text{-Phpz})_3$ [44], or $\text{PyCH}_2\text{OCH}_2\text{C}(3\text{-Phpz})_3$ [44].

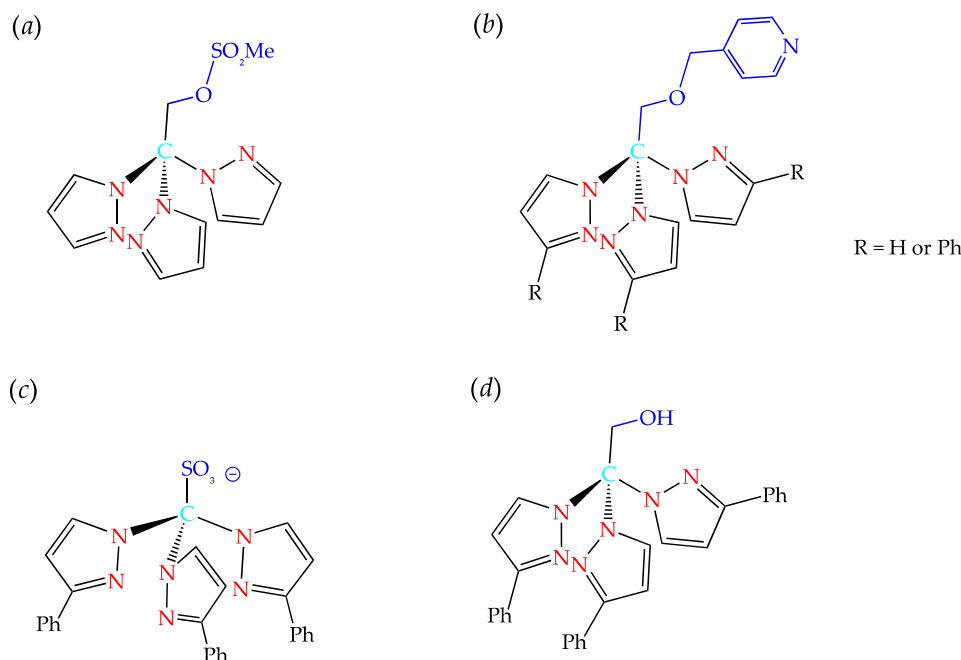


Figure 3. Structures of functionalized tris(pyrazol-1-yl)methanes: (a) $\text{CH}_3\text{SO}_3\text{CH}_2\text{C}(\text{pz})_3$; (b) $\text{PyCH}_2\text{OCH}_2\text{C}(\text{pz})_3$ (Py = pyridine) or $\text{PyCH}_2\text{OCH}_2\text{C}(3\text{-Phpz})_3$; (c) $\text{SO}_3\text{C}(3\text{-Phpz})_3^-$ and (d) $\text{HOCH}_2\text{C}(3\text{-Phpz})_3$.

A systematic investigation of the coordination behavior of new C-scorpionates, as well as some of the known ones, toward a variety of transition metals (e.g., V [44,46–49], Mo [17,19,50], Re [51,52], Fe [44,46,49,53], Ru [54], Co [12,13], Ni [44,49,55], Pd [44], Cu [43,45,46,56,57], Ag [14], Au [58] or Zn [44,56]) followed, leading to new classes of complexes exhibiting different types of coordination modes (Figures 4 and 5). Like the pincer of a scorpion, these versatile tripodal ligands bind metal centers with nitrogen atoms from two pyrazolyl rings attached to the central carbon atom; the third pyrazolyl attached to carbon rotates forward like a scorpion's tail to “sting” the metal; hence the name of “scorpionates” (Figure 4).

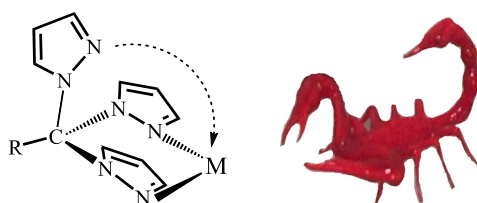


Figure 4. κ^2 – κ^3 interchange coordination modes of a tris(pyrazol-1-yl)methane scorpionate ligand and comparison with a scorpion.

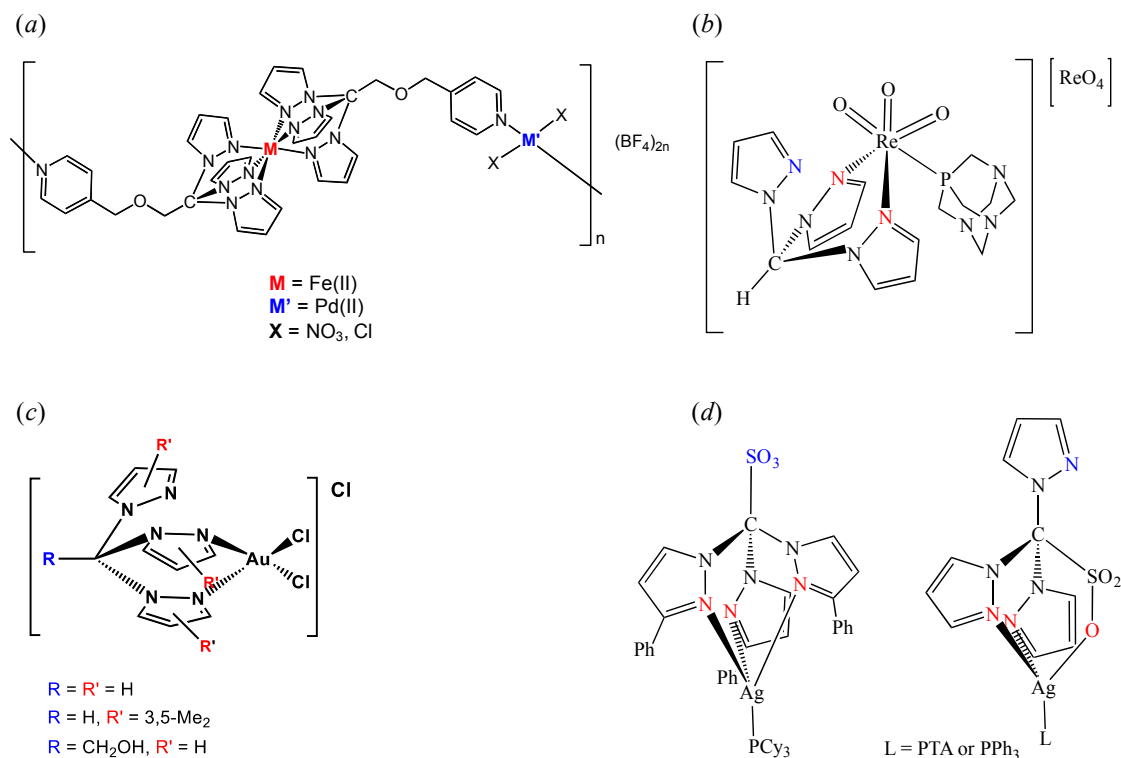


Figure 5. Selected C-homoscorpionate complexes exhibiting: (a) tetradentate coordination ability of the scorpionate ligand; (b) κ^2 -coordination of the scorpionate ligand at an octahedral geometry; (c) κ^2 -coordination of the scorpionate ligand at a square planar geometry (d) N_3 - or N_2O -coordination of the scorpionate ligand.

Some of the above new C-homoscorpionates (with three identical pyrazol-1-yl rings), such as e.g., $\text{PyCH}_2\text{OCH}_2\text{C}(\text{pz})_3$ (Figure 5a) exhibit extended coordination ability, including tetradentate characteristics [44], where the extra coordination moiety has different affinity towards metal centers. Therefore, it leads to a sort of metal-supported scorpionate ligand that forms easily heterobimetallic species, opening to a large variety of applications (such as catalysis or supramolecular chemistry).

On the other hand, tris(pyrazol-1-yl)methane derivatives bearing bulky substituents at the pyrazol-1-yl rings (especially at the 3-position), when ligating a metal center, such a bulky species provides a steric control on the other coordination position(s) of the complex, selecting the suitable ligands on the opposite side, namely preventing the formation of full-sandwich complexes (with two such scorpionate ligands) [45]. Moreover, they also offer the opportunity to tailor the coordination behavior toward different metal centers. This important feature is directly correlated to further research in catalytic synthetic chemistry.

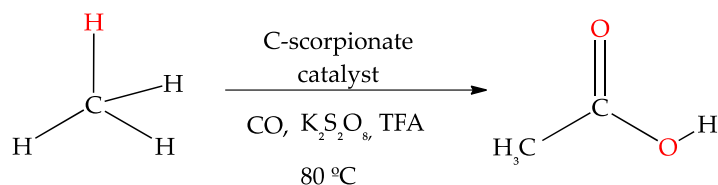
It was also found, from electrochemical experiments [57,59], that changes on the functionalized methine group of tris(pyrazol-1-yl)scorpionates have a much smaller influence on the ligand properties than when performed at the pyrazol-1-yl rings (see below).

The coordination versatility of tris(pyrazol-1-yl)methanes, namely the interchange between bidentate and tridentate coordination modes (Figure 5b,c for κ^2 -coordination) was found to be tuned by metal center as well as by the electronic properties of the co-ligands present at the coordination sphere. In addition, the tripodal functionalized coordination flexibility (e.g., N_3 - or N_2O -coordination modes for sulfonated derivatives, Figure 5d) involving the functionalized methine carbon [7,8,14,45,49,50] is also tailored by such co-ligands, an important pre-requisite for their catalytic activity.

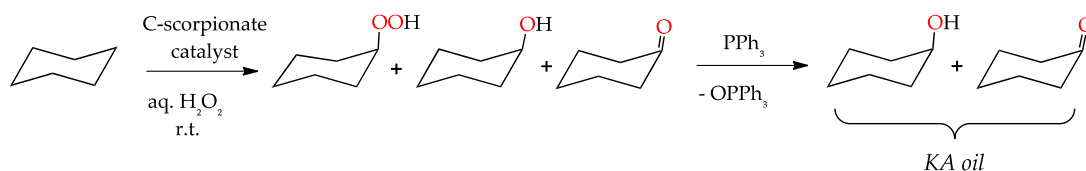
One might consider that the coordination behavior of the tris(pyrazol-1-yl)methane complexes would mirror that exhibited by the corresponding tris(pyrazol-1-yl)borate compounds, the major difference being in the charge between the methane and the borate counterpart. However, large

differences appear in some cases [60]: for example, the $\text{RC}(\text{pz})_3$ ligands react with Group 6 metal hexacarbonyls to afford insoluble and non-volatile species, whereas $[\text{M}(\text{RB}(\text{pz})_3)(\text{CO})_3]$ are very soluble and sublime easily. The tripodal ligand $\text{HC}(\text{pz})_3$ produces a relatively strong ligand field, consistent with the rather short metal–nitrogen bond lengths in the complexes. The pyrazol-1-yl group acts as moderately strong σ donor and a weak out-of-plane π donor, with the π interaction in the plane of the amine ligand probably being close to zero [61].

The main applications of C-homoscorpionate complexes as catalysts for oxidative reactions, where the involvement of metal redox processes is crucial for the catalytic activity, are the important and challenging single-pot oxidation of gaseous (e.g., direct oxidation of methane to carboxylic acids, Scheme 1) [47,62] and liquid (e.g., cyclohexane to the correspondent alcohol-ketone mixture, Scheme 2) alkanes [7,8,13,43,46–49,53,57,58,63–68]. Indeed, oxidation of alkanes has been the object of considerable research [69–78], but still constitutes a serious challenge to modern chemistry, owing to the high inertness of these substrates. Currently, alkanes are mainly applied as fuels but it would be desirable to direct their application to the synthesis of organic products of a high added value. The feasibility of this approach is supported by the industrial application of cyclohexane in the production of cyclohexanone and cyclohexanol (KA oil, Scheme 2), with dioxygen as oxidizing agent and catalysts based on cobalt [79]. However, this industrial process has a very low yield to ensure an acceptable selectivity. Another case is the industrial production of acetic acid, a known commodity of large-scale demand. Currently mainly obtained by the improved Cativa™ methanol carbonylation process [69,71,80], it nevertheless requires three steps from natural gas and considerably harsh, pollutant rich and costly conditions. The above examples explain the interest in finding more efficient processes and in understanding the involved mechanisms [81–83].



Scheme 1. One-pot carboxylation of methane to acetic acid catalyzed by C-scorpionate complexes [7,8,47,62].



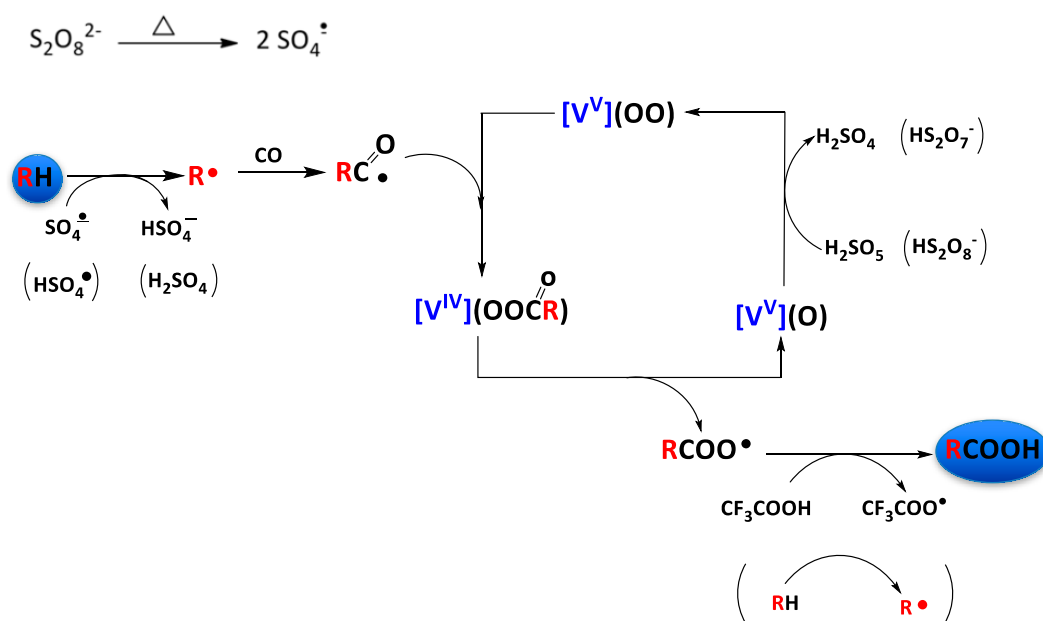
Scheme 2. Peroxidative oxidation of cyclohexane to cyclohexanone and cyclohexanol (KA oil) in aqueous medium, catalyzed by C-scorpionate catalysts [7,8,13,43,46–49,57–68].

Among the new catalysts recently found for the above reactions are C-homoscorpionate metal complexes which have been successfully applied either as catalysts for oxygenations, with H_2O_2 , to produce the respective alcohols and ketones or, with $\text{K}_2\text{S}_2\text{O}_8$, to directly yield carboxylic acids [7,8].

The reactions leading to the above oxygenated species are believed to proceed mainly via both carbon- and oxygen-centered radicals. Interestingly, although occurring via the formation of reactive radicals, such reactions are rather selective [7,8,16]. The C-scorpionate catalyst initially activates not the alkane but reacts with another reactant, usually the oxidant (e.g., hydrogen-peroxide) [7,8]. The formed reactive species (e.g., hydroxyl radical) attacks the alkane molecule without any participation in the latter process of the metal complex. Thus, the metal catalyst does not take part in the direct “activation” of the carbon-hydrogen bond by the radical.

A possible mechanism [69,70] for the generation of carboxylic acids is represented in Scheme 3 for an oxo-V complex: a potassium peroxodisulfate salt ($\text{K}_2\text{S}_2\text{O}_8$) is essential for the formation of alkyl

radicals whereas the scorpionate catalyst is not needed for this purpose. Nevertheless, no carboxylic acid is detected in the absence of the catalyst. Under the experimental conditions, peroxodisulfate undergoes thermolysis into sulfate (or its protonated form $\text{HSO}_4^\bullet$ if in acidic medium) radicals which are known alkane hydrogen abstractors, leading to $\text{R}^\bullet$. Further conversion of alkyl radical to carboxylic acid includes carbonylation of the former by CO to form the acyl radical $\text{RCO}^\bullet$. The latter may then be converted, in the presence of the metal catalyst, by its oxygenation to give $\text{RCOO}^\bullet$, involving a peroxo metal species (Scheme 3) derived from the reaction of catalyst with HS_2O_8^- or with H_2SO_5 (peroxomonosulfuric acid) formed upon reaction of HS_2O_8^- with TFA or hydrolysis by traces of water. Then $\text{RCOO}^\bullet$ abstracts a hydrogen atom from, for example, excess TFA or alkane to afford the desired carboxylic acid.

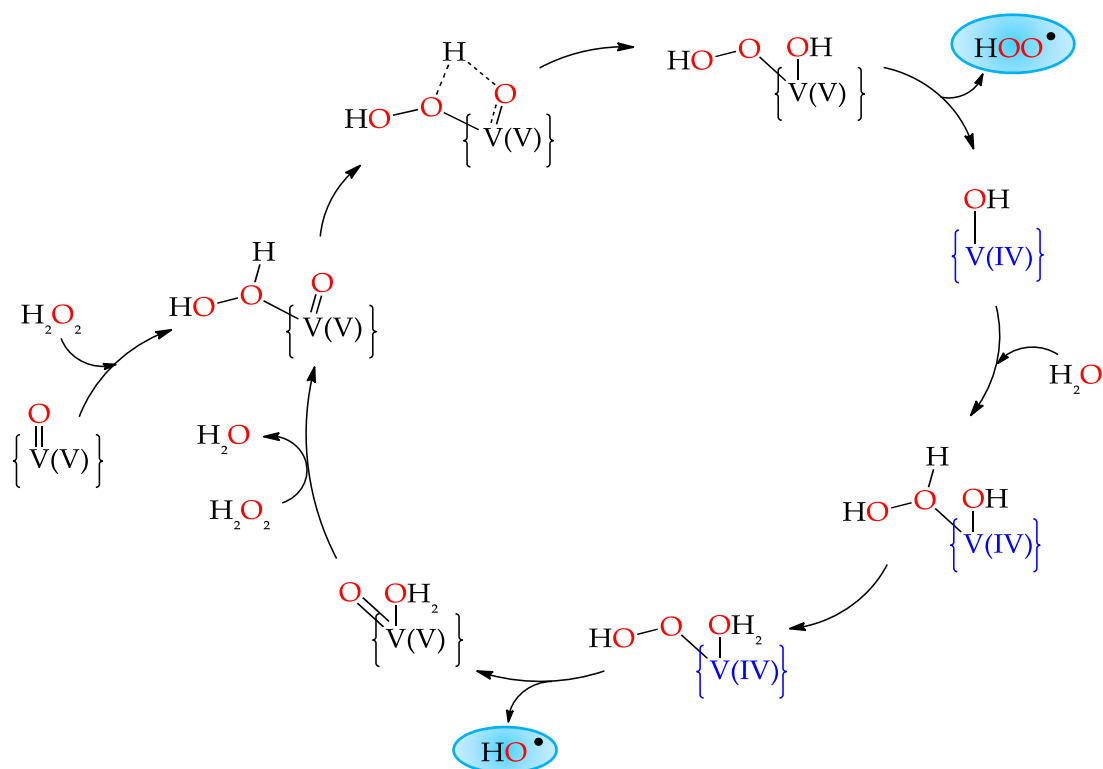


Scheme 3. Proposed mechanism for the carboxylation of an alkane to the corresponding carboxylic acid catalyzed by a C-homoscorpionate oxo-V complex.

In the case of the oxidation of alkanes with hydrogen peroxide, detailed investigation of the effects of various experimental parameters in this reaction, the use of radical traps, kinetic and selectivity studies complemented with theoretical calculations [73,84–86] indicated the interest of using controlled amounts of water and acid, and assured the involvement of hydroxyl ($\text{OH}^\bullet$) and alkyl ($\text{R}^\bullet$) radicals in a radical type mechanism (see Equations (2)–(10) and Scheme 4 for a more detailed formation of hydroxyl and hydroperoxyl radicals).

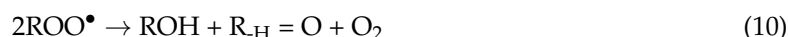
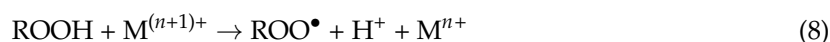
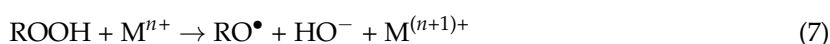
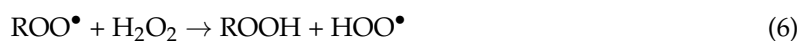
The proposed route for the metal-catalyzed decomposition of hydrogen peroxide (Haber–Weiss mechanism) [70,87] includes the following two key stages (Equations (2) and (3)) of formation of the oxygen-centered radicals $\text{HOO}^\bullet$ and $\text{HO}^\bullet$:





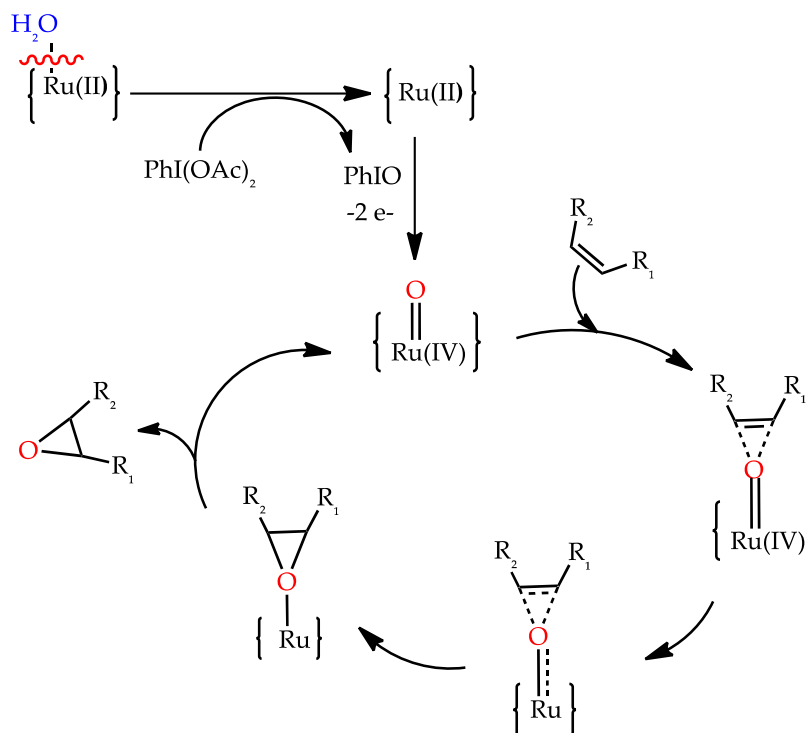
Scheme 4. Proposed mechanism for the formation of $\text{OH}^\bullet$ and $\text{HOO}^\bullet$ radicals in the oxidation of an alkane with hydrogen peroxide, catalyzed by a C-homoscorpionate oxo-V complex.

It is the hydroxyl radical (derived from the reduction of H_2O_2 by the reduced form of the metal catalyst, Equation (2) and Scheme 4 for a C-homoscorpionate oxo-V complex) that reacts with the alkane generating the alkyl radical $\text{R}^\bullet$ (Equation (4)) which, in turn, reacts with dioxygen (Equation (5)) to form the alkylperoxyl radical $\text{ROO}^\bullet$. The latter gives rise to the alkyl-hydroperoxide (ROOH) (Equation (6)) which, in the presence of both the reduced and oxidized forms of the metal catalyst, decomposes (Equations (7)–(10)) to the ketone and/or the alcohol.



The use of C-homoscorpionate complexes to catalyze epoxidation of alkenes, a very useful synthetic transformation to produce fine chemicals [79,80], is also significant. Selective catalytic epoxidation of *cis*-cyclooctene to 1,2-epoxy-cyclooctane was achieved in the presence of tris(pyrazol-1-yl)methane Mo(VI) complexes [19,20,88], in particular if water is rigorously excluded from the reaction mixture. Other alkene substrates such as *R*-(+)-limonene, 1-octene, *trans*-2-octene, cyclododecene, 3-carene, and 4-vinyl-1-cyclohexene are also selectively converted into the corresponding epoxides.

In the presence of the sacrificial oxidant $\text{PhI}(\text{OAc})_2$, aqua $\text{Ru}(\text{II})$ tris(pyrazol-1-yl)methane compounds catalyze the aerobic epoxidation of a wide variety of alkenes [89]. The mechanistic pathway for the epoxidation (Scheme 5) proceeds via the formation of an active metal–oxo intermediate through the mediation of iodobenzene diacetate. The active catalytic species is a formally $\text{Ru}(\text{IV})=\text{O}$ one, resulting from the oxidation of the aqua $\text{Ru}(\text{II})$ complex by $\text{PhI}(\text{OAc})_2$. The electrophilic metal bound oxo group subsequently interacts with the incoming olefinic double bond with transfer of the oxo group. The involvement of a concerted transition state for the transfer of the oxygen atom from the metal-oxido complex to the olefinic double bond is suggested [89,90].



Scheme 5. Proposed mechanism for the epoxidation of alkenes catalyzed by a C-homoscorpionate aqua-Ru complex.

From the above, it turns out that an effective catalyst for the above oxidation reactions requires the ability to undergo reversible redox processes involving electron transfer at accessible potentials. This redox potential—oxidative catalytic activity relationship will be addressed in detail in the following section.

3. Electrochemical Properties of C-Scorpionate Metal Complexes

The electrochemical approach is a very powerful tool for fundamental chemical characterization of species that can be oxidized or reduced. By continuously changing the working potential, its cycling or keeping constant, enables not only the determination of the respective oxidation or reduction potentials but also revelation of the reversibility of the redox processes, the nature, kinetics and equilibrium constants of the follow-up reactions, the stability and structure of intermediates, the type and yield of products, etc. In fact, an electron transfer in a coordination compound can induce very diverse chemical reactivity, ultimately with catalytic significance.

Some C-homoscorpionate complexes underwent systematic electrochemical investigation usually by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) techniques, at platinum working electrodes (disk or gauze, respectively). Glassy carbon working electrodes for CV were also used [89]. Experiments were performed in a three-electrode system whose potential was

controlled vs. a Luggin capillary connected to a silver wire pseudo-reference electrode and a Pt auxiliary electrode. The complexes were added to a 0.1–0.2 M [$^n\text{Bu}_4\text{N}$][X] (X = BF_4 , PF_6 or ClO_4) or $[\text{Et}_4\text{N}][\text{ClO}_4]$ /aprotic non-aqueous medium (e.g., CH_2Cl_2 , NCMe, DMF or DMSO), at room temperature, under dinitrogen [46,49–54,89,91–93].

Their measured redox potentials in volts vs. saturated calomel electrode (V vs. SCE) and the eventual reversibility of the redox process, are indicated in Table 1.

Table 1. Cyclic voltammetric data ^a for metal C-homoscorpionate complexes.

C-Scorpionate Compound	Redox Potential/V vs. SCE			Ref.
	$I_{E_p}^{ox}$ ($I_{E_{1/2}}^{ox}$)	$I_{E_p}^{red}$ ($I_{E_{1/2}}^{red}$)	$II_{E_p}^{red}$ ($II_{E_{1/2}}^{red}$)	
$[\text{VCl}_3\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]$	(1.14)	-	-	[91]
$[\text{VO}_2\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]^b$	-	−0.46	−1.82	[47]
$[\text{VOCl}_2\{\kappa^3\text{-CH}_3\text{SO}_2\text{OCH}_2\text{C}(\text{pz})_3\}]^c$	(1.35)	−0.78	-	[49]
$[\text{VO}_2\{\kappa^3\text{-HC}(\text{pz})_3\}][\text{BF}_4]^b$	-	−0.28	−1.70	[47]
$[\text{VO}_2\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}][\text{BF}_4]$	-	−0.37	−1.75	[47]
$\text{Li}[\text{Mo}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}(\text{CO})_3]$	(0.18)	-	-	[50]
$[\text{Mo}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}\text{I}(\text{CO})_3]$	0.44	-	-	[50]
$[\text{Mo}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}\text{H}(\text{CO})_3]$	0.09	-	-	[50]
$[\text{ReCl}_2\{\kappa^3\text{-HC}(\text{pz})_3\}(\text{PPh}_3)][\text{BF}_4]^d$	(0.54)	(−0.74)	-	[51]
$[\text{ReCl}_3\{\kappa^3\text{-HC}(\text{pz})_3\}]$	1.14	−0.62	−1.70	[52]
$[\text{ReCl}_3\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}]$	(1.25)	(−0.13)	(−0.72)	[52]
$[\text{ReCl}_4\{\kappa^2\text{-HC}(\text{pz})_3\}]$	1.79	(−0.06)	−1.50	[52]
$[\text{ReO}_3\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]$	-	−0.83	-	[52]
$[\text{ReO}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}(\text{HMT})]^b$	(0.86)	−0.83	-	[21]
$[\text{ReOCl}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}(\text{PPh}_3)]\text{Cl}$	1.45	(−0.94)	(−1.41)	[52]
$[\text{ReO}_3\{\kappa^2\text{-HC}(\text{pz})_3\}(\text{PTA})][\text{ReO}_4]^b$	-	(−0.62)	-	[21]
$[\text{ReO}_3(\text{Hprz})(\text{HMT})][\text{ReO}_4]^b$	-	(−0.33)	-	[21]
$[\text{FeCl}_2\{\kappa^3\text{-CH}_3\text{SO}_2\text{OCH}_2\text{C}(\text{pz})_3\}]^c$	(1.06)	−0.38	-	[49]
$[\text{FeCl}_3\{\kappa^3\text{-HC}(\text{pz})_3\}]^d$	(−0.11)	-	-	[92]
$[\text{FeCl}_3\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}]^d$	(−0.20)	-	-	[92]
$[\text{FeCl}_3\{\kappa^3\text{-HC}(3\text{-iPrpz})_3\}]^d$	(−0.04)	-	-	[92]
$[\text{Ru}(p\text{-cymene})\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]\text{Cl}$	(0.95)	(−0.97)	-	[54]
$[\text{Ru}(p\text{-cymene})\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}][\text{BF}_4]$	(0.96)	(−0.97)	-	[54]
$[\text{Ru}(p\text{-cymene})\{\kappa^3\text{-SO}_3\text{C}(3\text{-Phpz})_3\}]\text{Cl}$	1.02	(−1.00)	-	[54]
$[\text{Ru}(\text{benzene})\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]\text{Cl}$	(1.07)	(−0.87)	-	[54]
$[\text{Ru}(\text{benzene})\{\kappa^3\text{-SO}_3\text{C}(3\text{-Phpz})_3\}]\text{Cl}$	(1.37)	(−0.92)	-	[54]
$[\text{Ru}(\text{HMB})\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]\text{Cl}$	0.95	(−1.11)	-	[54]
$[\text{Ru}(\text{cod})\text{Cl}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]$	(0.96)	(−1.10)	-	[54]
$[\text{Ru}(\text{cod})\text{Cl}\{\kappa^3\text{-SO}_3\text{C}(3\text{-Phpz})_3\}]$	(0.99)	(−1.27)	-	[54]
$[\text{RuCl}\{\kappa^3\text{-HC}(\text{pz})_3\}(\text{bqdi})][\text{ClO}_4]^c$	(0.82)	(−0.79)	−1.39	[89]
$[\text{Ru}(\text{H}_2\text{O})\{\kappa^3\text{-HC}(\text{pz})_3\}(\text{bqdi})][\text{ClO}_4]_2^c$	(0.44)	-	-	[89]
$[\text{Ru}\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}(\text{NCCH}_3)_3][\text{BF}_4]_2^c$	(0.42)	-	-	[93]
$[\text{Ru}\{\kappa^3\text{-HC}(3,5\text{-Ph}_2\text{pz})_3\}(\text{NCCH}_3)_3][\text{BF}_4]_2^c$	(0.71)	-	-	[93]
$[\text{Co}(\text{OSO}_3\text{H})(\text{OCH}_3)(\text{HOCH}_3)\{\kappa^3\text{-HC}(\text{pz})_3\}]^b$	1.03	−0.40	-	[12]
$[\text{Co}\{\kappa^3\text{-HOCH}_2\text{C}(\text{pz})_3\}_2](\text{NO}_3)_2$	(0.58)	−0.68	-	[12]
$[\text{Co}\{\kappa^3\text{-HOCH}_2\text{C}(\text{pz})_3\}_2][\text{Co}\{\kappa^3\text{-HOCH}_2\text{C}(\text{pz})_3\}(\text{H}_2\text{O})_3]_2(\text{Cl})_6 \cdot 6\text{H}_2\text{O}$	(0.60)	−0.67	−1.21	[12]
$[\text{CoCl}_2(\text{H}_2\text{O})\{\kappa^3\text{-PyCH}_2\text{OCH}_2\text{C}(\text{pz})_3\}]$	1.28	−0.60	-	[12]
$[\text{CoCl}_2(\text{H}_2\text{O})\{\kappa^3\text{-CH}_3\text{SO}_2\text{OCH}_2\text{C}(\text{pz})_3\}]^c$	1.10	−0.64	-	[12]
$[\text{CuCl}_2\{\kappa^3\text{-CH}_3\text{SO}_2\text{OCH}_2\text{C}(\text{pz})_3\}]^c$	-	−0.70	-	[49]
$[\text{AuCl}_2\{\kappa^2\text{-HC}(\text{pz})_3\}]\text{Cl}^c$	-	−0.02	−0.60	[57]
$[\text{AuCl}_2\{\kappa^2\text{-HOCH}_2\text{C}(\text{pz})_3\}]\text{Cl}^c$	-	−0.01	−0.58	[57]
$[\text{AuCl}_2\{\kappa^2\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}]\text{Cl}^c$	-	−0.11	−0.69	[57]

^a Values in V $\pm$ 0.02 relative to SCE; in CH_2Cl_2 ; scan rate of 200 mV·s^{−1}. Values for reversible waves are given in brackets. bqdi = *o*-benzoquinonediimine; 3-*i*Pr = *iso*-propyl group; ^b In dimethyl sulfoxide (DMSO);

^c In acetonitrile (NCMe); ^d In dimethylformamide (DMF). SCE = saturated calomel electrode.

All authors found that C-homoscorpionate ligands are electrochemically inert in the potential range of -2.0 V to 2.0 V vs. SCE, at the used experimental conditions [46,49–54,89,91–93], thus no ligand centered oxidation or reduction has been reported to date.

Most of the metallic compounds bearing tris(pyrazol-1-yl)methane ligands exhibit at least a single-electron (determined by exhaustive CPE) oxidation wave, assigned to the $d^n \rightarrow d^{n-1}$ metal oxidation. Exceptions are, as expected, V(V), Re(VII), Ni(II), Cu(II), Au(III), and Zn(II) complexes. The said oxidation waves can meet the reversibility criteria [94] or be irreversible due to chemical reactions that follow the electron-transfer process (Table 1). Most of the C-homoscorpionate complexes also exhibit (Table 1) a reduction wave which usually is followed, at a lower potential, by a second one. These waves often (e.g., for V, Re, Fe, Ru or Co complexes) correspond to single-electron processes, being assigned to the $d^n \rightarrow d^{n+1}$ and $d^{n+1} \rightarrow d^{n+2}$ metal reductions.

The highest known first oxidation potential of all C-scorpionate metal complexes is shown by the 15-electron Re(IV) complex $[\text{ReCl}_4\{\kappa^2\text{-HC}(\text{pz})_3\}]$ ($^1E_p^{\text{ox}} = 1.79$ V vs. SCE, Table 1) per its electron deficiency. Such oxidation potential value is even higher than the one of the oxo-Re(V) 16-electron complex $[\text{ReOCl}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}(\text{PPh}_3)]\text{Cl}$ ($^1E_p^{\text{ox}} = 1.45$ vs. SCE, Table 1) in spite of the higher metal oxidation state of the latter. The presence of the strong electron-donor oxo-ligand provides another reason for the lower oxidation potentials of this oxo-complex. $[\text{ReCl}_4\{\kappa^2\text{-HC}(\text{pz})_3\}]$ is also the one that exhibits the most favorable (highest) reduction potential ($^1E_{1/2}^{\text{ox}} = -0.06$ V vs. SCE, Table 1) in accord with its low electron-count. Harder to reduce are the oxo-Re species $[\text{ReO}_3\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]$ and $[\text{ReOCl}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}(\text{PPh}_3)]\text{Cl}$, in agreement with the presence of the strong electron-donor oxide ligand and with their higher electron count. Among the rhenium complexes, Re(III) 16-electron complexes $[\text{ReCl}_3\{\kappa^3\text{-HC}(\text{pz})_3\}]$ and $[\text{ReCl}_3\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}]$ are those that present the lowest oxidation potential ($^1E_p^{\text{ox}} = 1.14$ and $^1E_{1/2}^{\text{ox}} = 1.25$ V vs. SCE, Table 1), consistent with the lower metal oxidation state. In contrast with the measured values, complex $[\text{ReCl}_3\{\kappa^3\text{-HC}(\text{pz})_3\}]$ would be expected to have a higher oxidation potential than the analogous $[\text{ReCl}_3\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}]$, on account of the weaker electron-donor character of $\text{HC}(\text{pz})_3$ in the former in comparison with $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ in the latter. However, the irreversible character of the oxidation wave of the former (indicative of a chemical reaction following the electron-transfer step, with a resulting shift of the oxidation potential) preclude a reliable comparison between the measured potentials for these complexes.

In the case of Mo(0 or II) complexes a second single-electron oxidation process is detected (not shown in Table 1) in the potential range of 0.18 to 0.6 V vs. SCE. In $\text{Li}[\text{Mo}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}(\text{CO})_3]$ yields the 16-electron Mo(II) complex $[\text{Mo}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}(\text{CO})_3]^+$, its irreversibility being associated to fast coordination of a solvent molecule, leading to an electronically saturated product.

The irreversibility of the first oxidation wave of compounds $[\text{MoI}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}(\text{CO})_3]$ and $[\text{MoH}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}(\text{CO})_3]$ signals the instability of the resulting cationic Mo(III) complexes, which then rapidly decompose with probable CO loss [95] and, for the hydride compound, by deprotonation [96–98]. The first oxidation potentials of all these tricarbonyl complexes are much lower than that of the parent hexacarbonyl compound, on account of the replacement of three carbonyls in the latter by the more electron-donating C-scorpionate ligands [24,27,28]. Moreover, the first oxidation potential of $[\text{MoH}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}(\text{CO})_3]$ in comparison with $[\text{MoI}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}(\text{CO})_3]$ reflects the stronger electron-donor character of the hydride relatively to the iodide ligand [28].

These Mo (0 or II) compounds have not yet been used for catalytic oxidation reactions. Nevertheless, their low oxidation potentials (first oxidation wave in the range 0.09 – 0.44 V vs. SCE, Table 1) and the detected easy coordination/decoordination of substrates are promising features for a possible good oxidative catalytic performance.

The interest in electron transfer induced reactivity of C-scorpionate metal compounds is demonstrated in the following catalytic systems where such complexes provide unprecedented examples.

3.1. Oxidation of Alkanes to Alcohols and Ketones

In the case of the oxidation of alkanes with peroxides, the availability of reducible metal species, easily detectable by electrochemical experiments, was found very important for the catalytic performance of C-homoscorpionate complexes.

As previously mentioned, the formation of RO• and ROO• radicals (Equations (2) and (3), and Scheme 4) involves the reaction of both reduced and oxidized forms of the metal catalyst and is a key step for the occurrence of the C–H abstraction from the alkane. Therefore, C-homoscorpionate complexes that undergo redox processes at accessible potential values are expected to display better oxidative catalytic performance than those harder to oxidize or reduce.

In fact, V(V) complexes $[\text{VO}_2\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]$ and $[\text{VO}_2\{\kappa^3\text{-HC}(\text{pz})_3\}][\text{BF}_4]$, whose accessible potential values for the first single-electron [V(V) to V(IV)] reduction process are -0.46 and -0.48 V vs. SCE, lead to quite similar (19% and 18.6%, respectively [47]) KA oil yields (among the highest values obtained for this class of catalysts) by catalytic oxidation of cyclohexane. The turnover number (TON, moles of product per mole of catalyst) values also follow the trend: 117 and 112, respectively, for $[\text{VO}_2\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]$ and $[\text{VO}_2\{\kappa^3\text{-HC}(\text{pz})_3\}][\text{BF}_4]$.

A further example comes from V(III or IV) complexes. $[\text{VCl}_3\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]$ is easier to oxidize than $[\text{VOCl}_2\{\kappa^3\text{-CH}_3\text{SO}_2\text{OCH}_2\text{C}(\text{pz})_3\}]$ (1.14 vs. 1.35 V, Table 1) and thus yields higher KA oil amounts (13% (TON = 121) [46] vs. 7% (TON = 89) in the presence of $[\text{VOCl}_2\{\kappa^3\text{-CH}_3\text{SO}_2\text{OCH}_2\text{C}(\text{pz})_3\}]$ [49]). Moreover, trichlorovanadium(III) $[\text{VCl}_3\{\kappa^3\text{-HC}(\text{pz})_3\}]$ leads to higher yield (18%) and TON (167) values [47] than the related $[\text{VCl}_3\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]$ (13% yield and a TON of 121, [46,47]), in accordance with its lower oxidation state and the neutral scorpionate ligand in $[\text{VCl}_3\{\kappa^3\text{-HC}(\text{pz})_3\}]$.

Likewise, for the Co(II) complexes $[\text{CoCl}_2(\text{H}_2\text{O})\{\kappa^3\text{-PyCH}_2\text{OCH}_2\text{C}(\text{pz})_3\}]$ and $[\text{CoCl}_2(\text{H}_2\text{O})\{\kappa^3\text{-CH}_3\text{SO}_2\text{OCH}_2\text{C}(\text{pz})_3\}]$; the latter presents lower oxidation potential (1.10 V vs. SCE, Table 1) and thus exhibits better catalytic performance: 10.5% vs. 3.2% yield of KA oil in the presence of $[\text{CoCl}_2(\text{H}_2\text{O})\{\kappa^3\text{-PyCH}_2\text{OCH}_2\text{C}(\text{pz})_3\}]$ [12] which is oxidized at 1.28 V vs. SCE (Table 1).

A similar behavior is found for the chloro-Au(III) complexes: $[\text{AuCl}_2\{\kappa^2\text{-HC}(\text{pz})_3\}]\text{Cl}$ and $[\text{AuCl}_2\{\kappa^2\text{-HOCH}_2\text{C}(\text{pz})_3\}]\text{Cl}$ which present very close reduction potentials for the first irreversible two electrons $\text{Au(III)} \rightarrow \text{Au(I)}$ reduction process (Table 1) and are the most active, leading to 8.1% and 10.3%, respectively, of KA oil [57]. The hardest to reduce (-0.11 V vs. SCE, Table 1) yields only 7.5% of the oxygenated mixture under the same conditions [64]. The lower reduction potential of $[\text{AuCl}_2\{\kappa^2\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}]\text{Cl}$ in comparison with the one of $[\text{AuCl}_2\{\kappa^2\text{-HC}(\text{pz})_3\}]\text{Cl}$ is consistent with the stronger electron-donor ability of the methyl-substituted $\kappa^2\text{-HC}(3,5\text{-Me}_2\text{pz})_3$ ligand than that of $\kappa^2\text{-HC}(\text{pz})_3$ [24]. However, an accurate comparison cannot be established due to the irreversibility of the reduction waves (the reduction potential is not the thermodynamic one). Moreover, whereas the CH_2OH substituent at the apical methine carbon appears to have limited influence on the redox potential of the gold complexes (Table 1), the replacement of hydrogens by an electron donor group (Me) at the pyrazolyl rings of the C-scorpionate leads to an electronically richer Au(III) center, resulting in a measurable (ca. 0.1 V) cathodic shift of the potential. A second irreversible reduction (Table 1) assigned to the $\text{Au(I)} \rightarrow \text{Au(0)}$ reduction leads to the appearance of gold metal at the platinum electrodes surface after exhaustive controlled potential electrolysis and an irreversible anodic wave (in the range 0.44–0.50 V vs. SCE) observed upon scan reversal after the second reduction wave, corresponding to the oxidation of the Au(0) species formed in the second reduction process.

3.2. Oxidation of Alkanes to Carboxylic Acids

The catalytic activity of the only to date tested [51] Re(III) complexes, $[\text{ReCl}_3\{\kappa^3\text{-HC}(\text{pz})_3\}]$ and $[\text{ReCl}_2\{\kappa^3\text{-HC}(\text{pz})_3\}(\text{PPh}_3)][\text{BF}_4]$, for the direct oxidation of ethane to acetic acid follows their oxidation behavior (Table 1 and Figure 6): $[\text{ReCl}_2\{\kappa^3\text{-HC}(\text{pz})_3\}(\text{PPh}_3)][\text{BF}_4]$ presents considerably lower oxidation potential ($E_{1/2}^{\text{ox}} = 0.54$ V vs. SCE) and leads to higher acetic acid yield (16%) and TON (8) values than $[\text{ReCl}_3\{\kappa^3\text{-HC}(\text{pz})_3\}]$ ($E_{1/2}^{\text{ox}} = 1.14$ V vs. SCE; 5% acetic acid yield and TON = 2) [51,52].

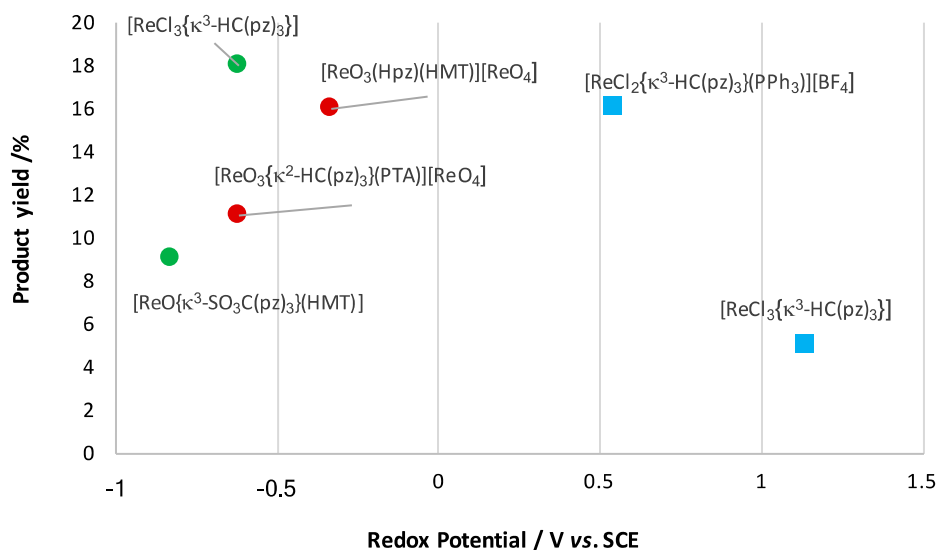


Figure 6. Yields of: (■) acetic acid produced from the one-pot oxidation of ethane catalyzed by the Re(III) complexes vs. their Re(III) oxidation potentials; (●) 6-methylhexanolide obtained from Baeyer-Villiger (BV) oxidation of 2-methylcyclohexanone, vs. their Re(VII) oxidation potentials; and (●) 6-methylhexanolide from BV oxidation of 2-methylcyclohexanone, vs. their Re(III) oxidation potentials.

3.3. Baeyer-Villiger Oxidation of Ketones

The regioselective Baeyer-Villiger (BV) oxidation of 2-methylhexanone to 6-methylhexanolide (as a result of the formal insertion of the oxygen atom between the carbonyl and the more substituted C_α atom) was found [21] to be favored by strong Lewis acid Re catalysts (Table 1 and Figure 6). The non-radical mechanism of BV ketone oxidation proceeds via the activation of the ketone, upon coordination to the metal catalyst, to nucleophilic attack of the peroxide oxidant, followed by heterolytic peroxo-bond cleavage and carbanion migration. In fact, for the same Re oxidation state (III (●) or VII (●)), Figure 6 higher lactone yields are obtained when the catalyst presents a higher (more positive) reduction potential. The electron deficiency of the catalyst (stronger Lewis acid character) activates to a greater extent the carbonyl group of the ketone for the nucleophilic attack by hydrogen peroxide.

3.4. Oxidation of 1,2-Diols

The Fe(III)/Fe(II) redox potentials of the chloro-iron(III) complexes follow the trend $[\text{FeCl}_3\{\kappa^3\text{-HC}(3\text{-iPrpz})_3\}]$ (3-*iPr* = *iso*-propyl group on the 3-position of pyrazole rings) > $[\text{FeCl}_3\{\kappa^3\text{-HC}(\text{pz})_3\}]$ > $[\text{FeCl}_3\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}]$ (Table 1), which represents a decrease in Lewis acidity of the iron(III) center along this series. In $[\text{FeCl}_3\{\kappa^3\text{-HC}(3\text{-iPrpz})_3\}]$, the sterically hindering *iso*-propyl group weakens the coordination of nitrogen of pyrazol-1-yl ring conferring an enhanced Lewis acidity of the iron(III) center. The electron-releasing methyl groups on the pyrazol-1-yl ring in $[\text{FeCl}_3\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}]$ increase the electron density on pyrazol-1-yl nitrogen and hence decreases the Lewis acidity of the iron(III) center [92].

The catechol dioxygenase activity of the above iron(III) complexes was tested and the electrochemical properties of the catecholate adducts of the complexes reveal that a systematic variation in the ligand donor atom type significantly influences the Lewis acidity of the iron(III) center and hence the interaction of the complexes with simple and substituted catechols.

The rate of oxygenation increases upon increasing the Lewis acidity of the iron(III) center by modifying the ligand substituents. One of the pyrazolyl arms in the catecholate adducts is sterically constrained by the 6,6'-chelate ring system and appears to dissociate from the coordination sphere upon binding to the catecholate substrate, which is followed by dioxygen attack at the equatorial plane leading to the formation of benzoquinone [92].

3.5. Carboxylation of Alkanes

The catalytic activity of C-homoscorpionate V(V) complexes for the one-pot carboxylation of methane to acetic acid (Scheme 1) was found [47] to be in accordance with the order of their V(V) $\rightarrow$ V(IV) reduction potentials, which follows the electron-donor characters of the scorpionate ligands and the charge of the complex (see Table 1 and Figure 7). The stronger vanadium(V) Lewis acid (the easiest to reduce) favors the carboxylation mechanism represented in Scheme 3 and allows the highest product yield (under the same experimental conditions of the other two V(V) complexes) to be achieved. Moreover, turnover number values follow the yields trend [47].

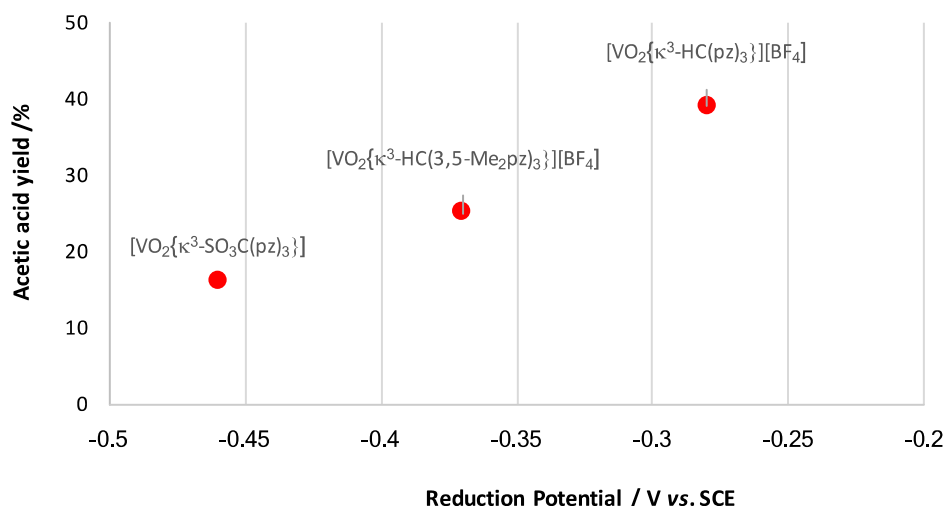


Figure 7. Yields of acetic acid produced from the one-pot carboxylation of methane catalyzed by the V(V) complexes $[\text{VO}_2\{\kappa^3\text{-HC}(\text{pz})_3\}][\text{BF}_4]$, $[\text{VO}_2\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}][\text{BF}_4]$ and $[\text{VO}_2\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}][\text{BF}_4]$ vs. their V(V) to V(IV) reduction potentials.

3.6. Epoxidation of Alkenes

For the *o*-benzoquinonediimine (bqdi) Ru(II) complexes $[\text{RuCl}\{\kappa^3\text{-HC}(\text{pz})_3\}(\text{bqdi})][\text{ClO}_4]$ and $[\text{Ru}(\text{H}_2\text{O})\{\kappa^3\text{-HC}(\text{pz})_3\}(\text{bqdi})][\text{ClO}_4]_2$, electrochemical and DFT calculations established [89] that the redox non-innocent bqdi was stabilized in its fully oxidized quinone state in both the chloro complex ($[\text{Ru}\{\kappa^3\text{-HC}(\text{pz})_3\}(\text{bqdi})(\text{Cl})]^+$) and the aqua ($[\text{Ru}\{\kappa^3\text{-HC}(\text{pz})_3\}(\text{bqdi})(\text{H}_2\text{O})]^{2+}$) derivative. The chloro complex exhibits metal based Ru(II)/(III) oxidation and bqdi centered reduction.

The aqua complex $[\text{Ru}(\text{H}_2\text{O})\{\kappa^3\text{-HC}(\text{pz})_3\}(\text{bqdi})][\text{ClO}_4]_2$ exhibits two one electron oxidations at pH 7, suggesting the formation of a $\{\text{Ru}(\text{IV})=\text{O}\}$ species, the supposed active species of the alkene epoxidation catalytic cycle (see Scheme 5). Thus, $[\text{Ru}(\text{H}_2\text{O})\{\kappa^3\text{-HC}(\text{pz})_3\}(\text{bqdi})]^{2+}$ functions as an efficient pre-catalyst for the selective epoxidation of a wide variety of alkenes in the presence of iodobenzene diacetate as the sacrificial oxidant.

3.7. Redox Potential Parametrization

The values of the Ru(II/III) oxidation potential (in the range of 0.95–1.37 V vs. SCE, Table 1) of $[\text{Ru}(\text{L})(\text{L}')]\text{X}$ complexes [L = *p*-cymene, benzene, hexamethylbenzene (HMB), or cyclooctadiene (cod), L' = tris(pyrazol-1-yl)methanesulfonate or the 3-phenylpyrazolyl-substituted derivative, X = Cl or BF_4] reflect [54] the electron-donor characters of their ligands: for the cationic complexes, with the common $[\text{Ru}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]^+$ center, the order of the oxidation potentials follows that (in the opposite direction) of the electron-releasing character of the corresponding variable ligand (cymene > benzene) as measured by the electrochemical Lever E_L ligand parameter (+1.48 and +1.59 V vs. NHE for cymene and benzene, respectively) [54].

As mentioned in the introduction, E_L is a measure of the electron-donor character of the ligand, the stronger this character, the lower is E_L . Moreover, the experimental oxidation potentials are in accordance with those predicted from the knowledge of E_L values for cymene [54], benzene [54] and $\kappa^3\text{-SO}_3\text{C}(\text{pz})_3$ (Table 2) [52] by applying the Lever method. Accordingly, the higher oxidation potentials of $[\text{Ru}\{\kappa^3\text{-SO}_3\text{C}(3\text{-Phpz})_3\}(\text{benzene})]\text{Cl}$ or $[\text{RuCl}\{\kappa^3\text{-SO}_3\text{C}(3\text{-Phpz})_3\}(\text{cod})]$, bearing the 3-phenyl substituted tris(pyrazol-1-yl)methanesulfonate ligand, than those of the analogous $[\text{Ru}(\text{benzene})\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]\text{Cl}$ or $[\text{RuCl}(\text{cod})\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]$ reflect the expected weaker electron-donor character of $\{\kappa^3\text{-SO}_3\text{C}(3\text{-Phpz})_3\}^-$ ligand in comparison with that of $\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}^-$. Hence, the former ligand should present a higher E_L value than the latter [52] (Table 2).

Table 2. Electrochemical E_L Lever ligand parameter for C-homoscorpionate ligands.

Tris(pyrazol-1-yl)methane	$E_L/\text{V vs. SHE}^a$
$\text{HC}(\text{pz})_3$	0.14
$\{\text{SO}_3\text{C}(\text{pz})_3\}^-$	−0.09
$\{\text{SO}_3\text{C}(3\text{-Phpz})_3\}^-$	−0.05

^a for each coordinated pyrazol-1-yl group.

The electrochemical E_L Lever parameters for tris(pyrazol-1-yl)methane ligands [23,51,52,54] to date, found possible to estimate from the oxidation potential values of C-homoscorpionate complexes, by applying the linear (valid for octahedral complexes) relationship (1) and considering its extension to square-planar coordination and to full- and half-sandwich complexes [28,99–103], are presented in Table 2. These values correspond to partial E_L parameters assigned to each metal ligated arm (2-electron-donor) of the scorpionate ligand. Thus, the overall E_L value of a scorpionate ligand will depend on its coordination mode to the metal center in a complex.

Since the E_L parameter is a measure of the electron donor character of a ligand (the lower the parameter value, the stronger is that character), each ligated pyrazol-1-yl arm in $\{\text{SO}_3\text{C}(\text{pz})_3\}^-$ ($E_L = -0.09$ V vs. SHE, Table 2) is clearly a stronger electron donor than in $\text{HC}(\text{pz})_3$ ($E_L = 0.14$ V vs. SHE), indicating a much stronger electron-releasing ability of the anionic CSO_3^- group at $\{\text{SO}_3\text{C}(\text{pz})_3\}^-$ than the methine HC group in the neutral $\text{HC}(\text{pz})_3$. That is consistent with the above reported electrochemical behavior for V, Re, and Au complexes. Moreover, the value of -0.05 V vs. SHE (for each coordinating pyrazolyl arm) agrees with the expected slightly weaker electron-donor character of $\text{SO}_3\text{C}(3\text{-Phpz})_3^-$ relative to $\text{SO}_3\text{C}(\text{pz})_3^-$ due to the phenyl substituent at the pyrazol-1-yl rings in the former ligand.

The above two series Ru(II) complexes, bearing the tris(pyrazol-1-yl)methanesulfonate ligand and its 3-phenyl substituted derivative, have not yet been tested as catalysts for partial oxidation reactions. Nevertheless, based on the reported electrochemical studies [54] we would expect a better oxidative catalytic performance for the tris(pyrazol-1-yl)methanesulfonate complexes $[\text{Ru}(p\text{-cymene})\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]\text{Cl}$ and $[\text{Ru}(\text{cod})\text{Cl}\{\kappa^3\text{-SO}_3\text{C}(\text{pz})_3\}]$.

A comparison of the effect of $\text{HC}(\text{pz})_3$ or $\text{HB}(\text{pz})_3$ ligands on the redox potential of a metal complex was reported for acetonitrile-Ru(II) complexes [93]. $[\text{Ru}\{\kappa^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}(\text{NCCH}_3)_3][\text{OTf}]$ exhibits a higher Ru(III)/(II) potential than its carbon analogue $[\text{Ru}\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}(\text{NCCH}_3)_3][\text{BF}_4]_2$ (0.59 and 0.42 V vs. SCE, respectively), indicating that the charged $\{\kappa^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}^-$ ligand stabilizes Ru(III) relative to Ru(II) compared to the neutral $\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}$. In contrast, the Ru(III)/(II) reduction potential observed for the $[\text{Ru}\{\kappa^3\text{-HB}(3,5\text{-Ph}_2\text{pz})_3\}(\text{NCCH}_3)_3][\text{BF}_4]$ complex (0.57 V vs. SCE) is lower than the same potential for the $[\text{Ru}\{\kappa^3\text{-HC}(3,5\text{-Ph}_2\text{pz})_3\}(\text{NCCH}_3)_3][\text{BF}_4]_2$ complex (0.71 V vs. SCE, Table 1), indicating that ligand charge is not as significant a factor as steric in determining the stability of ruthenium oxidation states for complexes with these bulky ligands. Since the redox potential of $[\text{Ru}\{\kappa^3\text{-HB}(3,5\text{-Ph}_2\text{pz})_3\}(\text{NCCH}_3)_3][\text{BF}_4]$ complex is smaller than that of the $[\text{Ru}\{\kappa^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}(\text{NCCH}_3)_3][\text{OTf}]$ complex, but the reverse is true for the $[\text{Ru}\{\kappa^3\text{-HC}(3,5\text{-Ph}_2\text{pz})_3\}(\text{NCCH}_3)_3][\text{BF}_4]_2$ and $[\text{Ru}\{\kappa^3\text{-HC}(3,5\text{-Me}_2\text{pz})_3\}(\text{NCCH}_3)_3][\text{BF}_4]_2$ complexes,

both electronic and steric factors of these ligands affect the redox potentials of their Ru(II) complexes. Overall, Ru(II) coordination by negatively charged $\{\kappa^3\text{-HB(3,5-R}_2\text{pz)}_3\}^-$ (R = Me or Ph) or neutral $\{\kappa^3\text{-HC(3,5-R}_2\text{pz)}_3\}$ ligands with varying steric bulk alters the Ru(III)/(II) potential by over 400 mV. The ability to alter the stability of ruthenium +2 or +3 oxidation states may be used to tune catalytic reactions.

The electronic and structural properties of scorpionate ligands, such as poly(pyrazol-1-yl)methane ligands, play an important role in the ability of several transition metal complexes to mediate C–H activation and functionalization as well as other partial oxidations. Thus, the knowledge of the redox behavior of a certain C-homoscorpionate catalyst, as well as its relationship with the structure of the catalyst, may allow tailoring of its structural design to present a favorable value of potential to enhance its catalytic performance. Moreover, tris(pyrazol-1-yl)methane ligands may act as more than simple spectators during chemical reactions experienced by their metal complexes, and have an important influence on their reactivity by means of temporary changes of denticity.

Of course, other factors are involved in the catalytic activity exhibited by the metal complex. Importantly, the tripodal C-scorpionate ligand, bearing three pyrazol-1-yl moieties (via their N atoms) is found to assist proton-transfer steps (see Scheme 4) that are involved in key catalytic oxidation processes. Such factors should additionally be considered in the design of a catalyst with expected improved activity for the above oxidation reactions.

Acknowledgments: The author gratefully acknowledges all the co-authors cited in the joint publications. The work in this area has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal, and its projects PTDC/QEQ-ERQ/1648/2014 and UID/QUI/00100/2013.

Conflicts of Interest: The author declares no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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