

## Scorpionate Complexes as Catalysts for Alkane Functionalization

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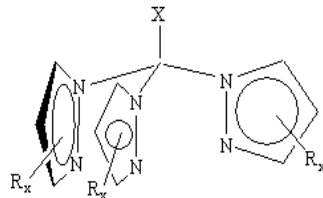
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### Abstract

A survey of the scorpionate tris(pyrazolyl)methane complexes synthesized by our group is presented, as well as their structural features and catalytic applications toward the functionalization of linear and cyclic light alkanes. This work has been initiated within the IPL research project n<sup>o</sup> 41.

### Introduction

Hydrotris(pyrazolyl)borate ligands are undoubtedly among the most important face-capping, six-electron N-donor ligands in coordination chemistry [1,2]. Compared to these anionic species, the isoelectronic, neutral analogues, hydrotris(pyrazolyl)methanes,  $\text{HC}(\text{R}_x\text{pz})_3$  (pz = pyrazolyl, Figure 1), formally derived by replacing the bridging  $(\text{BH})^-$  moiety with the CH group, are considerably less well developed [3-5].



**Figure 1** - Schematic structure of hydrotris(pyrazolyl)methanes (X = H).

The underdevelopment of this chemistry results from the relatively small number of such ligands currently available, the difficulties associated with their synthesis and the usually low yields. Recent breakthroughs in the synthesis of ring-substituted tris(pyrazolyl)methanes [6] offer the opportunity for the development of this useful and promising class of ligands which has been summarised in two review articles [4,5]. Some tris(pyrazolyl)methane complexes show interesting physicochemical properties with significance in fields spanning from catalysis to magnetic materials [4], constituting an emerging field of research.

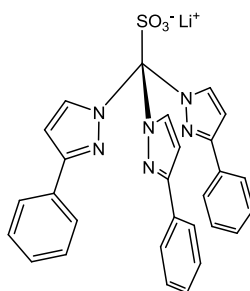
On the other hand, there is a growing interest to develop the multiple coordination modes of  $\text{HC}(\text{pz})_3$ . In fact, it is believed that further synthetic development toward the functionalization of the central methyne carbon atom would be greatly advantageous, as such changes to the backbone can dramatically influence the properties of the complexes, extend the coordination properties of the ligand and opening to a large variety of applications. One of enormous significance is performed by complexes soluble and stable under physiological conditions and

several examples of the use of poly(pyrazolyl)borate complexes to mimic enzymatic systems as well as biomedical applications as metallodrugs (in view of their anti-tumor properties or antibacterial activity) have been reported [1].

We have addressed the above aspects by synthesizing new functionalized species and by studying the coordination behaviour of the scorpionate tris(pyrazolyl)methane compounds at different transition metal centres. Moreover, we have further investigated the ability of the new prepared complexes to catalyse oxidation reactions of linear and cyclic light alkanes.

### Synthesis of functionalized tris(pyrazolyl)methane compounds

We aimed at the synthesis and investigation of the coordination behaviour of a new scorpionate compound that could combine the flexibility and water solubility of the sulfonato-functionalized class with the sterically demanding features of the 3-substituted tris(pyrazolyl) ligands [3]. For these purposes, we designed [7] a new tris(pyrazolyl)methanesulfonate derivative bearing a phenyl ring at the 3-position of pyrazolyl rings, the tris(3-phenylpyrazolyl)methanesulfonate ( $\text{Tpms}^{\text{Ph}}$ )<sup>-</sup> species (Figure 2).



**Figure 2** - Schematic structure of tris(3-phenylpyrazolyl)methane,  $\text{Li}(\text{Tpms}^{\text{Ph}})$  [7].

When ligating a metal center, such a bulky species would be expected to provide 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 “sandwich” complexes (with two of such scorpionate ligands) [8].

Starting from  $\text{Tpm}^{\text{Ph}}$  we were able to prepare the tris(3-phenylpyrazolyl)methanesulfonate species as the lithium salt,  $\text{Li}(\text{Tpms}^{\text{Ph}})$  in good yield, by deprotonation of the methyne carbon by BuLi, at low temperature, followed by sulfonation with the  $\text{SO}_3\text{NMe}_3$  adduct (Scheme 1).

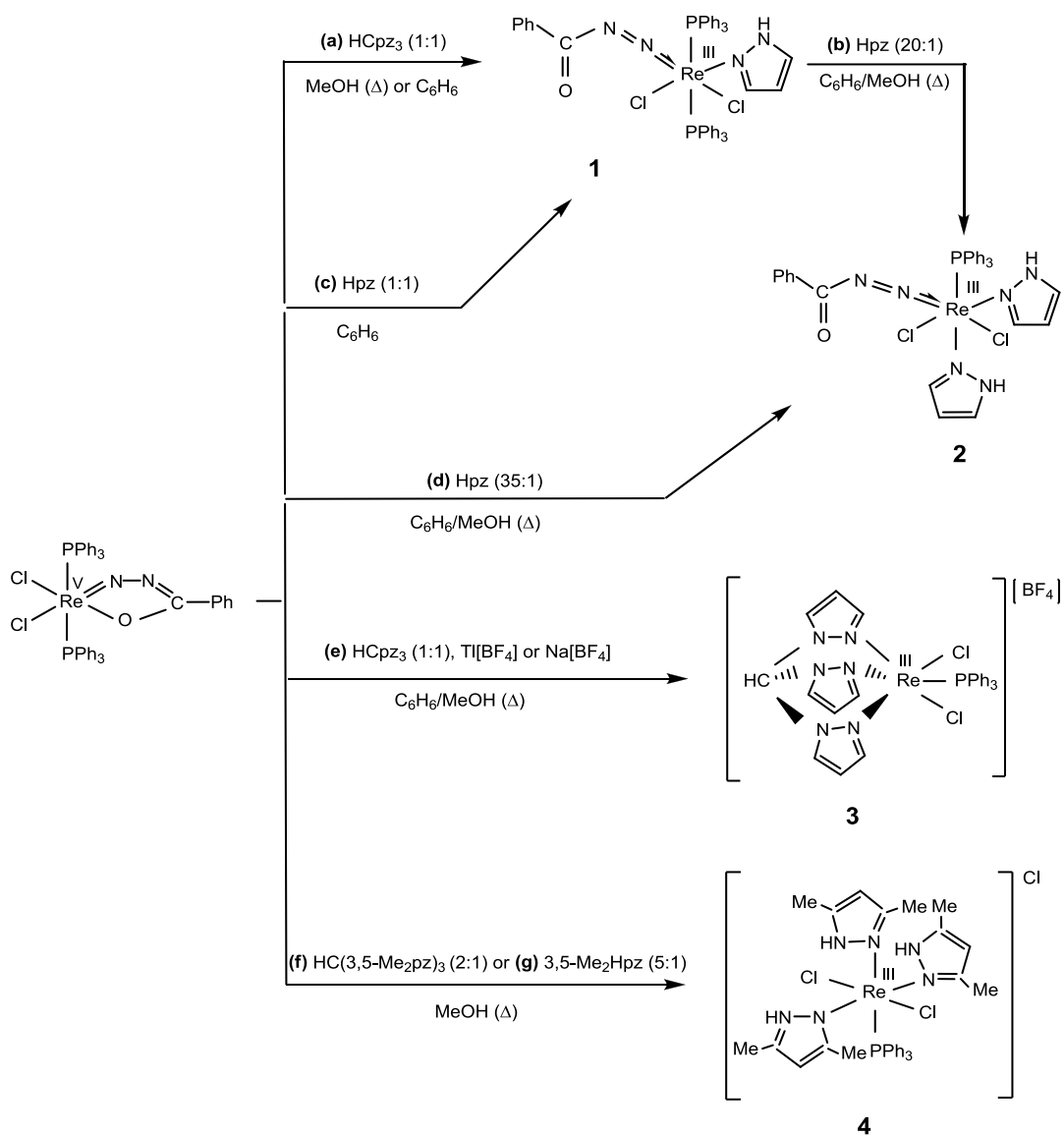


**Scheme 1** – Synthesis of tris(3-phenylpyrazolyl)methanesulfonate species as the lithium salt,  $\text{Li}(\text{Tpms}^{\text{Ph}})$  [7].

## Complexes bearing tris(pyrazolyl)methanes or derivatives

We have been interested on the coordination chemistry of  $\text{HC}(\text{pz})_3$  (Tpm) and the functionalized  $\text{HC}(\text{Me}_2\text{pz})_3$  ( $\text{Tpm}^{\text{Me}_2}$ ),  $\text{SO}_3\text{C}(\text{pz})_3^-$  ( $\text{Tpms}^-$ ) or  $\text{SO}_3\text{C}(3\text{-Phpz})_3^-$  ( $\text{Tpms}^{\text{Ph}-}$ ) [7] at Re, V, Fe or Cu centres [7, 9-11].

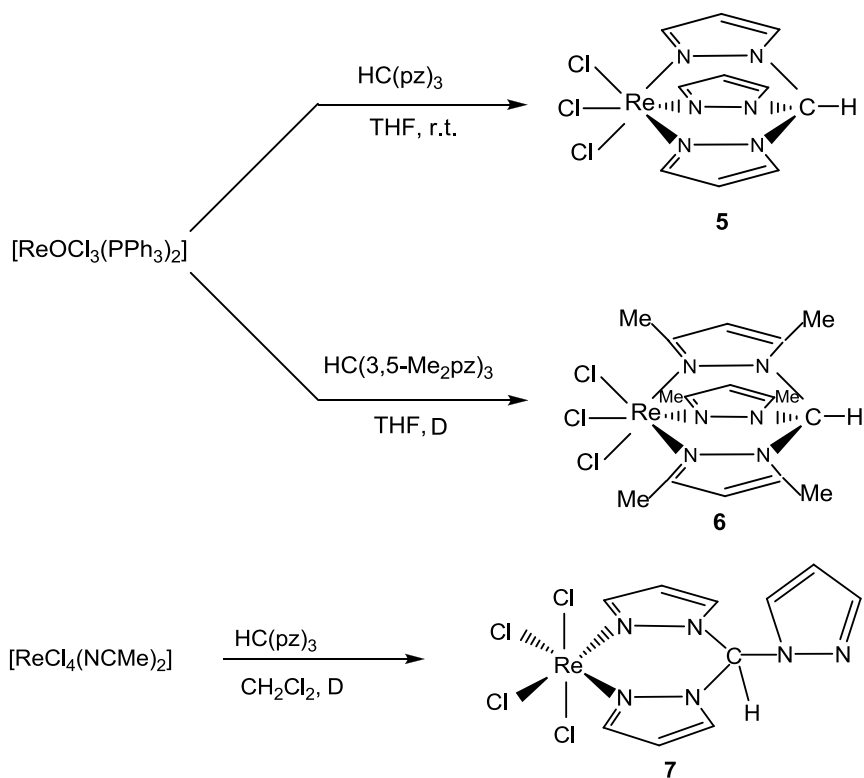
For instance, we were able to prepare [11] novel types of Re complexes with hydrotris(1-pyrazolyl)methanes or derived ones such as  $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})(\text{PPh}_3)_2]$  **1** (Hpz = pyrazole),  $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$  **2**,  $[\text{ReCl}_2(\text{HCpz}_3)(\text{PPh}_3)][\text{BF}_4]$  **3** and  $[\text{ReCl}_2(3,5\text{-Me}_2\text{Hpz})_3(\text{PPh}_3)]\text{Cl}$  **4** which were obtained by treatment of the chelate  $[\text{ReCl}_2\{\eta^2\text{-N,O-N}_2\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$  with hydrotris(1-pyrazolyl)methane  $\text{HCpz}_3$  (**1,3**), pyrazole Hpz (**1,2**), hydrotris(3,5-dimethyl-1-pyrazolyl)methane  $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ , (**4**) or dimethylpyrazole 3,5- $\text{Me}_2\text{Hpz}$  (**4**) (Scheme 2).



**Scheme 2** – Synthesis of Re(III) complexes derived from hydrotris(1-pyrazolyl)methanes [11].

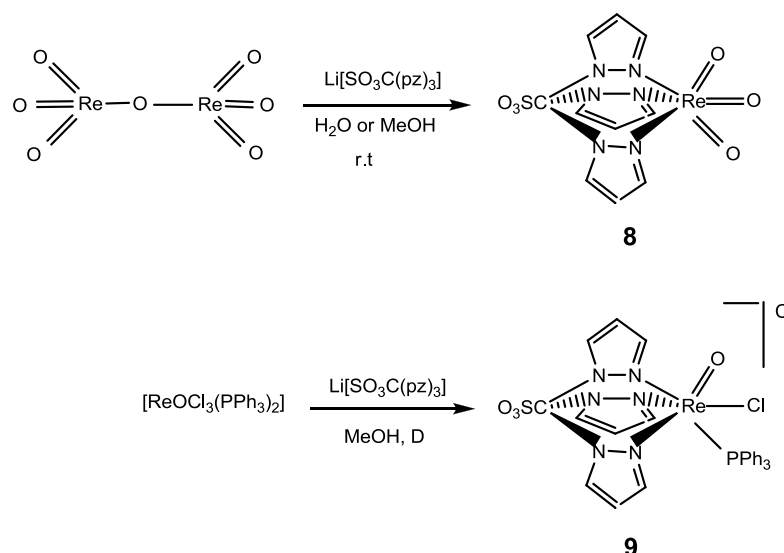
Rupture of a C(sp<sup>3</sup>)-N bond in HC(pz)<sub>3</sub> or HC(3,5-Me<sub>2</sub>pz)<sub>3</sub>, promoted by the Re centre, has occurred in the formation of **1** or **4**, respectively. All the reactions involved a formal two-electron reduction of Re(V) to Re(III).

Additionally, [ReCl<sub>3</sub>{HC(pz)<sub>3</sub>}] **5**, [ReCl<sub>3</sub>{HC(3,5-Me<sub>2</sub>pz)<sub>3</sub>}] **6** and [ReCl<sub>4</sub>{η<sup>2</sup>-HC(pz)<sub>3</sub>}] **7** were prepared by reaction of [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] or [ReCl<sub>4</sub>(NCMe)<sub>2</sub>] with hydrotris(pyrazolyl)methane (**5,7**) or hydrotris(3,5-dimethyl-1-pyrazolyl)methane (**6**), Scheme 3. Different coordination modes have been observed: while **5** and **6** present Tpm η<sup>3</sup>-coordinated, in **7** the Tpm acts as a bidentate ligand.



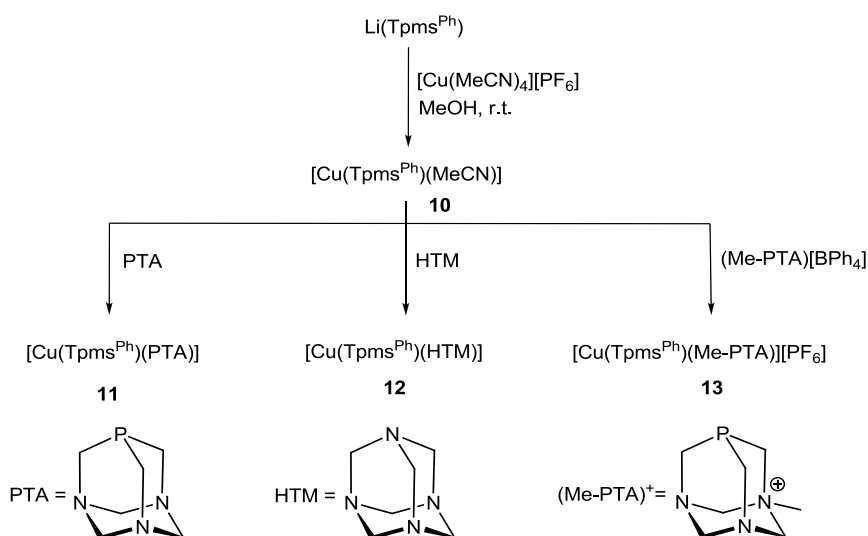
**Scheme 3** – Chloro-Re(III or IV) complexes bearing the hydrotris(pyrazolyl)methane ligand [10].

The use of water as an unconventional solvent in organometallic chemistry and catalysis, with relevant advantages over the common organic solvents, namely towards the development of "green" systems, has also been an object of our interest. Hence, we have been preparing hydro-soluble coordination compounds with water-soluble tris(pyrazolyl)methane scorpionates [7,9,10,12,13] with various metals, and studying their properties and chemical reactivity. The trioxo [ReO<sub>3</sub>{SO<sub>3</sub>C(pz)<sub>3</sub>}] **8** and oxo [ReOCl{SO<sub>3</sub>C(pz)<sub>3</sub>}(PPh<sub>3</sub>)Cl] **9** compounds were the first tris(pyrazolyl)methanesulfonate complexes of rhenium to be reported [10,13]. They were obtained by treatment of Re<sub>2</sub>O<sub>7</sub> or [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>], respectively, with Li[SO<sub>3</sub>C(pz)<sub>3</sub>] the C-substituted sulfonate derivative of HC(pz)<sub>3</sub>, which, like the hydrotris(1-pyrazolyl)borate, can behave as monoanionic polydentate N-donor ligand but with the ability to promote the solubility of its complexes in polar solvents and also with the advantage of being more resistant to hydrolysis.



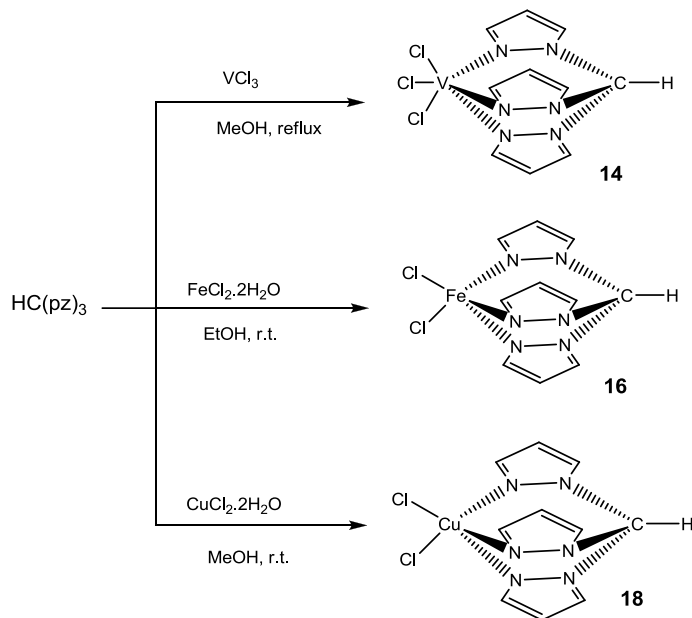
**Scheme 4** – Synthesis of the first tris(1-pyrazolyl)methanesulfonate Re complexes [10].

Moreover, the coordination behaviour toward a Cu(I) center of the new sterically hindered scorpionate tris(3-phenylpyrazolyl)methanesulfonate ( $\text{Tpms}^{\text{Ph}}$ ), in the presence of 1,3,5-triaza-7-phosphaadamantane (PTA), *N*-methyl-1,3,5-triaza-7-phosphaadamantane tetraphenylborate ((Me-PTA)[BPh<sub>4</sub>]) or hexamethylenetetramine (HMT) has been studied [7]. The reaction between  $\text{Li}(\text{Tpms}^{\text{Ph}})$  and  $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$  yields  $[\text{Cu}(\text{Tpms}^{\text{Ph}})(\text{MeCN})]$  **10** which, upon further acetonitrile displacement on reaction with PTA, HMT or (Me-PTA)[BPh<sub>4</sub>], gives the corresponding complexes  $[\text{Cu}(\text{Tpms}^{\text{Ph}})(\text{PTA})]$  **11**,  $[\text{Cu}(\text{Tpms}^{\text{Ph}})(\text{HMT})]$  **12** and  $[\text{Cu}(\text{Tpms}^{\text{Ph}})(\text{Me-PTA})][\text{PF}_6]$  **13** (Scheme 5). In the complexes **11** and **13**, which bear a phosphine ligand (*i.e.* PTA and Me-PTA, respectively), the new scorpionate ligand shows the typical N,N,N-coordination mode, whereas in **10** and **12**, bearing a N-donor ligand (*i.e.* MeCN and HMT, respectively), it binds the metal via the N,N,O chelating mode, involving the sulfonate moiety.

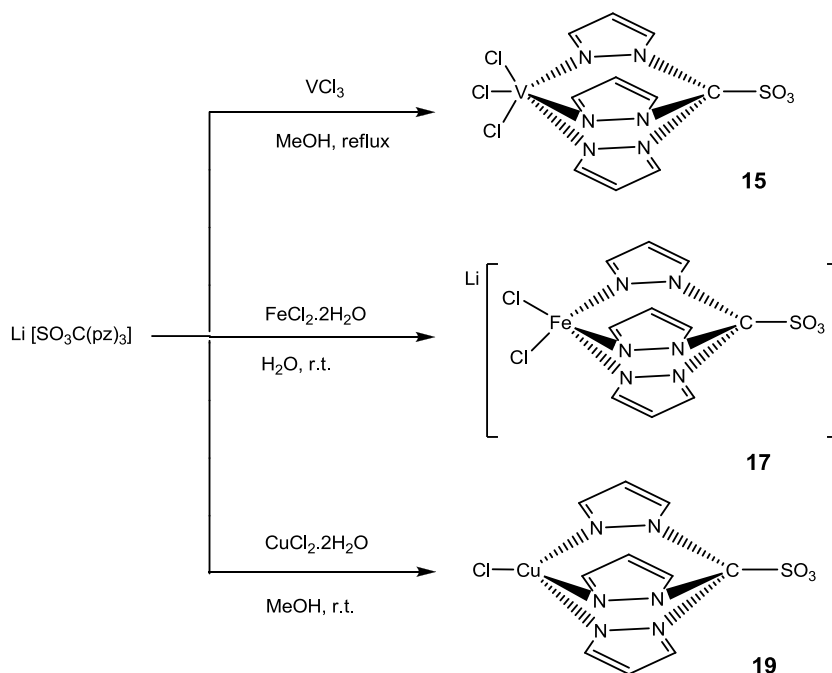


**Scheme 5** – Synthesis of the Cu(I) complexes bearing the new  $\text{Tpms}^{\text{Ph}}$  ligand [7].

We have also prepared [11] the first examples of half-sandwich scorpionate Tpm and TpmS complexes of vanadium  $[\text{VCl}_3\{\text{HC}(\text{pz})_3\}]$  **14** and  $[\text{VCl}_3\{\text{SO}_3\text{C}(\text{pz})_3\}]$  **15**, and expanded the coordination chemistry of both scorpionates toward iron and copper centres by synthesizing the complexes  $[\text{FeCl}_2\{\text{HC}(\text{pz})_3\}]$  **16**,  $\text{Li}[\text{FeCl}_2\{\text{SO}_3\text{C}(\text{pz})_3\}]$  **17** and  $[\text{CuCl}\{\text{SO}_3\text{C}(\text{pz})_3\}]$  **19** (Schemes 6 and 7).



**Scheme 6** - Synthesis of hydrotris(1-pyrazolyl)methane V(III), Fe(II) and Cu(II) complexes [11].



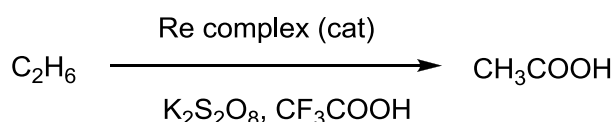
**Scheme 7** - Synthesis of tris(1-pyrazolyl)methanesulfonate V(IV), Fe(II) and Cu(II) complexes [11].

In all of them the scorpionate ligand is  $\eta^3$ -coordinated by N atoms of the pyrazolyl rings. Complexes **15** and **16** 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 ambient friendly conditions, and which may also be of particular significance for further biological activity tests.

### Catalytic applications of scorpionate tris(pyrazolyl)methane complexes

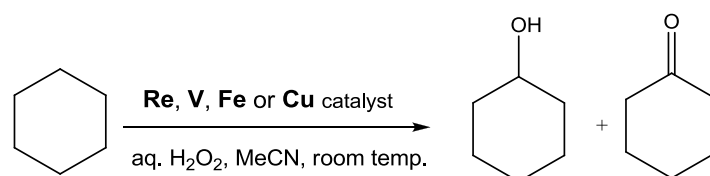
We have been interested in the application of the above scorpionate complexes as catalysts for some oxidation reactions of light alkanes such as ethane or cyclohexane [9,12-15]. We found [13,14] that the new pyrazole complexes [ReCl<sub>2</sub>{N<sub>2</sub>C(O)Ph}(Hpz)(PPh<sub>3</sub>)<sub>2</sub>] **2**, [ReCl<sub>2</sub>{N<sub>2</sub>C(O)Ph}(Hpz)<sub>2</sub>(PPh<sub>3</sub>)] **3** and [ReClF{N<sub>2</sub>C(O)Ph}(Hpz)<sub>2</sub>(PPh<sub>3</sub>)] **4**, and the tris(pyrazolyl)methane compounds [ReCl<sub>2</sub>(HCpz<sub>3</sub>)(PPh<sub>3</sub>)] [BF<sub>4</sub>] **5**, [ReCl<sub>3</sub>{HC(pz)<sub>3</sub>}] **7**, [ReOCl<sub>2</sub>{SO<sub>3</sub>C(pz)<sub>3</sub>}(PPh<sub>3</sub>)] **8** and [ReO<sub>3</sub>{SO<sub>3</sub>C(pz)<sub>3</sub>}] **9**, act as selective catalysts (or catalyst precursors), in a single-pot process, for the oxidation of ethane, in the presence of potassium peroxodisulfate K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, in trifluoroacetic acid (TFA), to give acetic acid (Scheme 8), in a remarkable yield (up to ca. 40 %) and under mild conditions (in some cases carboxylation can also occur to give propionic acid, but in a much lower yield).



**Scheme 8** – Oxidation of ethane to acetic acid catalysed by scorpionate Re complexes [14].

The formation of propionic acid is, however, promoted by using CO gas which in addition hampers the production of acetic acid, thus the selectivity being controlled by adjusting the pressure of this gas. Nevertheless, the CO pressure should always be kept below a maximum value beyond which an inhibiting effect occurs also for the formation of propionic acid. The ethane pressure is also an important factor and the highest product yields are observed for the 3-5 atm range. K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and TFA are the best oxidant and solvent, respectively, their replacement by related oxidants, e.g. (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, H<sub>2</sub>O<sub>2</sub> or *t*-BuOOH, or solvents resulting usually in much less effective systems. The fluoro-dipyrazole complex [ReClF{N<sub>2</sub>C(O)Ph}(Hpz)<sub>2</sub>(PPh<sub>3</sub>)] **4** provides the best catalyst for the oxidation of ethane to acetic acid. The presence of the fluoride ligand in **4** is particularly favourable since the analogous dichloro-complex [ReCl<sub>2</sub>{N<sub>2</sub>C(O)Ph}(Hpz)<sub>2</sub>(PPh<sub>3</sub>)] **3** exhibits ca. half of the activity.

The catalytic peroxidative oxidation of cyclohexane to cyclohexanone and cyclohexanol is also achieved by using most of the above catalyst precursors, under mild conditions (at room temperature and with an aqueous solution of H<sub>2</sub>O<sub>2</sub>, Scheme 9). Complex [ReClF{N<sub>2</sub>C(O)Ph}(Hpz)<sub>2</sub>(PPh<sub>3</sub>)] **4** provides the best catalyst for the oxidation in the absence of acid, while the tris(pyrazolyl)methanesulfonate compound [ReO<sub>3</sub>{SO<sub>3</sub>C(pz)<sub>3</sub>}] **9** becomes more active for the cyclohexane oxidation if performed in the presence of acid.

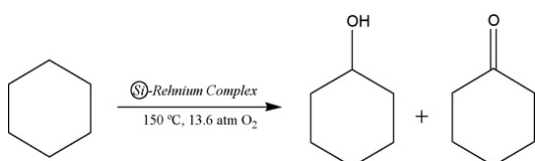


**Scheme 9** – Oxidation of cyclohexane to cyclohexanol and cyclohexanone catalysed by scorpionate Re, V, Fe or Cu complexes [9,13,14].

Further, the new scorpionate complexes  $[\text{VCl}_3\{\text{HC}(\text{pz})_3\}]$  **14**,  $[\text{VCl}_3\{\text{SO}_3\text{C}(\text{pz})_3\}]$  **15**,  $[\text{FeCl}_2\{\text{HC}(\text{pz})_3\}]$  **16**,  $\text{Li}[\text{FeCl}_2\{\text{SO}_3\text{C}(\text{pz})_3\}]$  **17** and  $[\text{CuCl}\{\text{SO}_3\text{C}(\text{pz})_3\}]$  **19** also shown to act, as well as the related  $[\text{CuCl}_2\{\text{HC}(\text{pz})_3\}]$  **18** [15], as selective catalysts (or catalyst precursors) for the peroxidative oxidation of cyclohexane to cyclohexanol and cyclohexanone, under the mentioned mild conditions [9]. The iron complexes are the most active ones (reaching TON values up to ca. 690). In addition, we have found that the hydro-soluble Fe complex **16** acts as a catalyst for the oxidative functionalization of cyclohexane in water as the sole solvent (without needing the presence of any organic solvent) what is of significance towards the establishment of an effective "green" process.

In all cases, the processes are shown to proceed via both C-centered and O-centered radical mechanisms, conceivably involving a metal-based oxidant.

On the other hand, aiming the development of rhenium heterogeneous catalytic systems (with the normal advantages over the homogenous ones *e.g.* in terms of easy catalyst separation and recovery) that could operate with the ideal "green" oxidant, *i.e.* dioxygen, for oxidative functionalization reactions of alkanes, we have immobilized our rhenium complexes on 3-aminopropyl functionalized silica gel support [16]. The pyrazole complexes  $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})(\text{PPh}_3)_2]$  **2**,  $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$  **3** and  $[\text{ReClF}\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$  **4**, catalyze the cyclohexane oxidation with dioxygen, to cyclohexanol and cyclohexanone (the main product), in the absence of solvent and additives and under relatively mild conditions (Scheme 10).



**Scheme 10** – Oxidation of cyclohexane to cyclohexanol and cyclohexanone catalysed by supported scorpionate Re complexes [16].

Complex **4** provides the best activity (ca. 16 % overall conversion towards the ketone and alcohol, at the  $\text{O}_2$  pressure of 19 atm, at 150 °C, 8 h reaction time). The reaction is further promoted by pyrazinecarboxylic acid. TGA analysis shows that the supported complexes are stable up to ca. 200 °C. The use of radical traps supports the involvement of a free-radical



mechanism via carbon- and oxygen-centred radicals. Complex **4** also catalyses the oxidation of other cycloalkanes to the corresponding cycloalkanols and cycloalkanones.

Further developments are currently being performed towards the optimization of the scorpionate tris(pyrazolyl)methane catalysts and the catalytic oxidation processes, in view of their industrial significance.

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*Partial Oxidation, under Mild Conditions, of Ethane to Acetic and Acetaldehyde and of Cyclohexane to Cyclohexanol and Cyclohexanone*, PT 103735 (priority date: 2007/05/11; award date: 2008/03/31).

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