Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Ni^{II}, Cu^{II} and Zn^{II} Complexes with a Sterically Hindered Scorpionate Ligand ($Tpms^{Ph}$) and Catalytic Application in the Diasteroselective Nitroaldol (Henry) Reaction

Bruno G.M. Rocha,[a] Tatiana C.O. Mac Leod,[a] M. Fátima C. Guedes da Silva,[a] Konstantin V. Luzyanin,[a] Luísa M.D.R.S. Martins,[a,b*] Armando J.L. Pombeiro[a*]*

[a] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049–001 Lisboa, Portugal. E-mail: fatima.guedes@tecnico.ulisboa.pt, pombeiro@tecnico.ulisboa.pt

[b] Chemical Engineering Department, ISEL, R. Conselheiro Emídio Navarro, 1959-007 Lisboa, Portugal. E-mail: lmartins@deq.isel.ipl.pt

Abstract

The Ni^{II} and Zn^{II} complexes $[MCl(Tpms^{Ph})]$ ($Tpms^{Ph} = SO_3C(pz^{Ph})_3$, pz = pyrazolyl; M = Ni **2** or Zn **3**) and the Cu^{II} complex $[CuCl(Tpms^{Ph})(H_2O)]$ (**4**) have been prepared by treatment of the lithium salt of the sterically demanding and coordination flexible tris(3-phenyl-1-pyrazolyl)methanesulfonate $(Tpms^{Ph})^-$ (**1**) with the respective metal chlorides. The $(Tpms^{Ph})^-$ ligand shows the N_3 or N_2O coordination modes in **2** and **3** or in **4**, respectively. Upon reaction of **2** and **3** with $Ag(CF_3SO_3)$ in acetonitrile the complexes $[M(Tpms^{Ph})(MeCN)](CF_3SO_3)$ (M = Ni **5** or Zn **6**, respectively) were formed. The compounds were obtained in good yields and characterized by analytic and spectral (IR, ^1H and $^{13}C\{^1H\}$ NMR, ESI-MS) data, density

functional theory (DFT) methods and {for **4** and [^{n}Bu$_4$N](Tpms^{Ph}) (**7**), the latter obtained upon Li^+ replacement by [^{n}Bu$_4$N]$^+$ in Li(Tpms^{Ph})} by single crystal X-ray diffraction analysis.

The Zn^{II} and Cu^{II} complexes (**3** and **4**, respectively) act as efficient catalyst precursors for the diastereoselective nitroaldol reaction of benzaldehydes and nitroethane to the corresponding β-nitroalkanols (up to 99% yield, at room temperature) with diastereoselectivity towards the formation of the *anti* isomer, whereas the Ni^{II} complex **2** only shows a modest catalytic activity.

Introduction

Originally introduced by Trofimenko in 1967,[1] the tris(pyrazol-1-yl)borate (Tp) ligands and their metal complexes became one of the most widely studied class of compounds in inorganic, organometallic and bioinorganic chemistries.[2-4] We have been interested in the study of the coordination chemistry of their carbon analogues, the tris(pyrazol-1-yl)methanes (Tpm),[5-21] as well as in the synthesis of new Tpm derivatives (Figure 1).[9, 17]

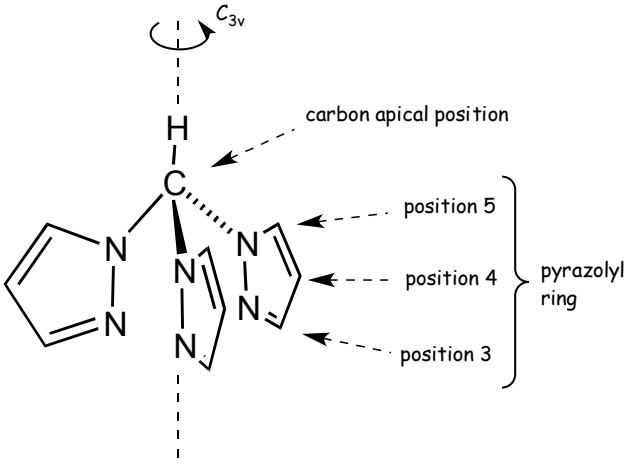


Figure 1. Functionalization points of hydrotris(pyrazol-1-yl)methane, Tpm.

Pyrazolyl rings containing bulky substituents at the 3-position can tune the coordination behaviour towards different metal centres, avoiding the formation of full-sandwich complexes, with favourable generation of one face-capped complexes. It is also expected that these 3-substituents have an effect on the electronic properties and its corresponding donor ability towards the binding metal site. Moreover, the possibility to functionalise the central methine carbon, by replacement of the acidic proton by other groups *e.g.*, leading to sulfonate derivatives of the type $^{-}SO_3C(pz^R)_3$ ($Tpms^R$),[3, 22-26] can confer a high stability and hydrosolubility to the corresponding metal complexes, an advantage in various fields of catalysis or enzyme modelling where physiological conditions are preferred. This ionic C-functionalized tris(pyrazolyl)methane derivative and related ones exhibit a relevant coordination versatility, acting as either tripodal or bipodal ligands (*i.e.*, with N_3, N_2O, N_2 or NO coordination modes)[17, 23-26] with the possibility of involving the sulfonate moiety in coordination (Figure 2 for R = Ph). Thus, these scorpionate ligands which could combine the flexibility and water solubility of the sulfonato-functionalized class with the sterically demanding features of the 3-substituted tris(pyrazolyl) ligands are worth for exploring the behaviour of the resulting complexes towards further reactivity.

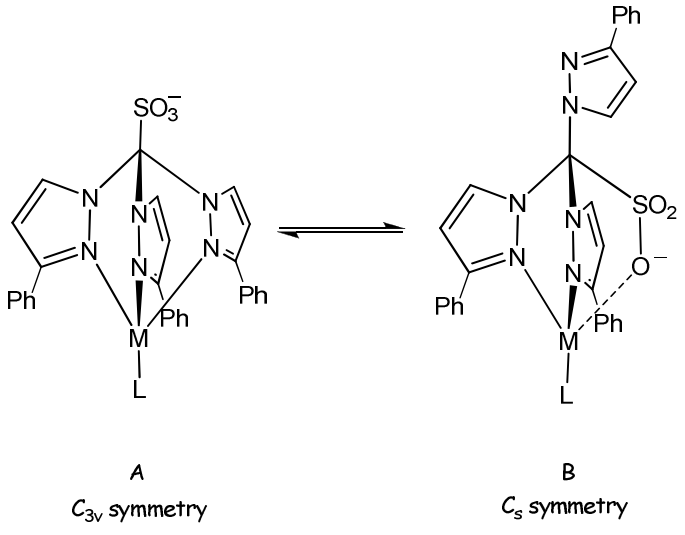
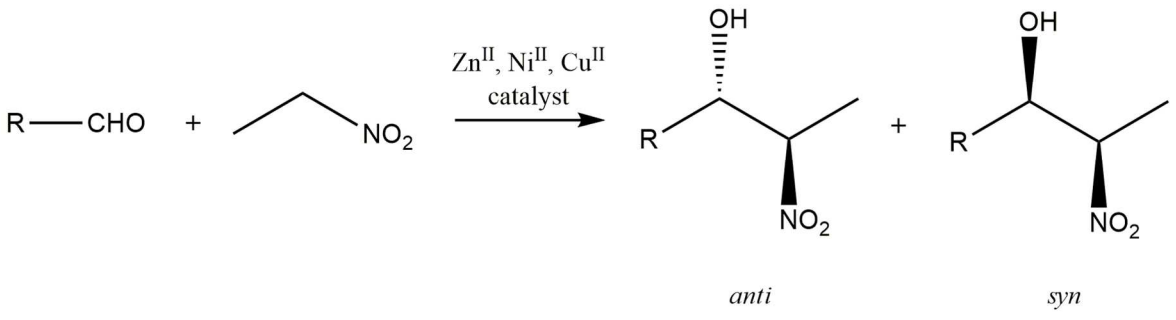


Figure 2. Schematic examples of N_3 and N_2O coordination modes for $Tpms^{Ph}$.

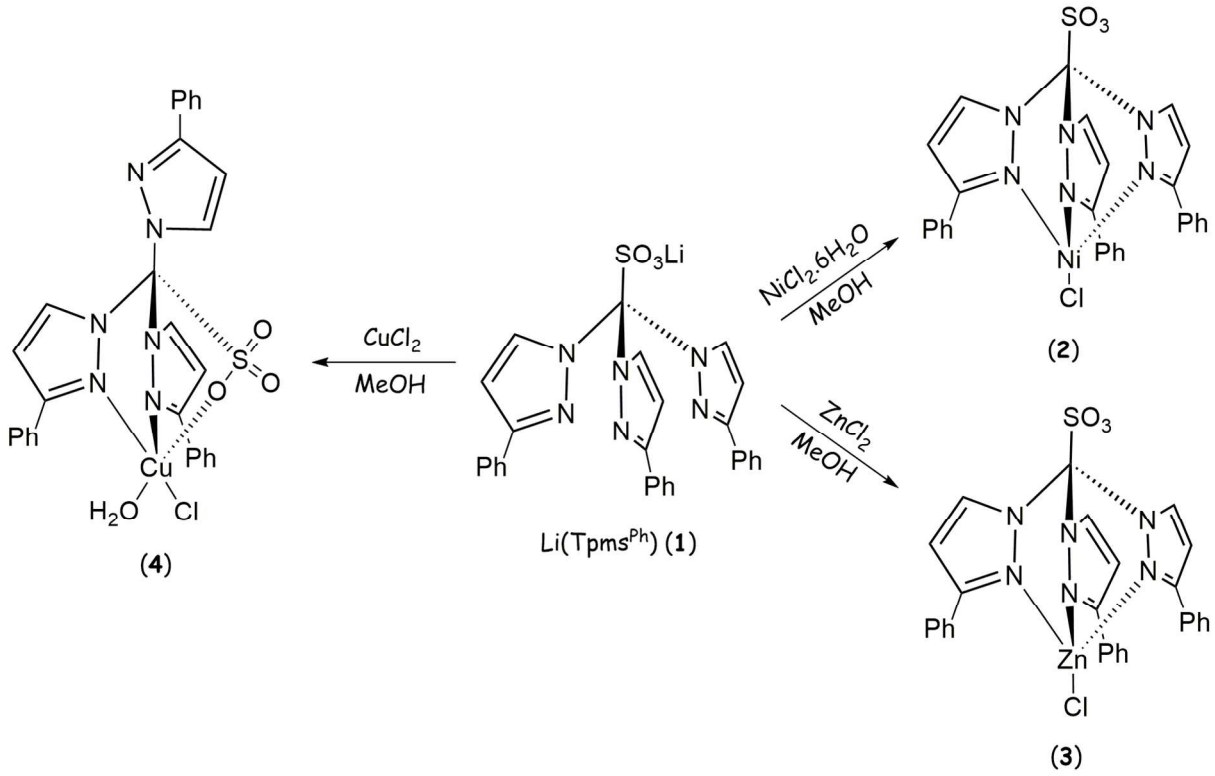
In addition, several applications of C-scorpionate complexes have been reported in catalysis,[27] namely in polymerization and oxidation reactions,[5, 6, 8, 10, 12, 14, 16, 28-35] and in this work we aimed to extend and explore the catalytic properties of the new complexes for the diastereoselective nitroaldol (Henry) reaction (Scheme 1) which is based on C-C coupling of an aldehyde with a nitroalkane to give β-nitroalkanols (*anti* and *syn*). This reaction is one of the most important carbon-carbon bond formation reactions to generate such species, which are common building blocks present in biologically active natural products and pharmaceuticals.[36-38] Due to the practical importance of this reaction, much attention has been paid to its diastereoselectivity, but the stereochemical control of the two newly generated carbon centres remains a difficult task to achieve. A stereoselective synthesis of either the *anti* or *syn* isomer would be desirable and efforts have been focused on the development of catalytic diastereo- or enantio-selective processes.[39] In particular, it is known that some Zn^{II} [40-42] and Cu^{II} [43, 44] complexes, with *N*,*O* or *O*,*O* ligands catalyse the Nitroaldol reaction, but the diastereoselectivity, which is usually limited, mainly for the *anti* isomer, has been less studied.



Scheme 1. Formation of β-nitroalkanols in the Henry reaction.

Results and discussion

Complexes [NiCl(Tpms^{Ph})] (**2**), [ZnCl(Tpms^{Ph})] (**3**) or [CuCl(Tpms^{Ph})(H_2O)] (**4**) were obtained, in good yields (Scheme 2), from reactions of Li(Tpms^{Ph}) (**1**) with $NiCl_2.6H_2O$ (**2**), $ZnCl_2$ (**3**) or $CuCl_2$ (**4**), respectively, in methanol, under air, at room temperature.



Scheme 2. Syntheses of complexes **2**-**4**.

Attempted reactions with the neutral tris(3-phenylpyrazol-1-yl)methane (Tpm^{Ph}) instead of the sulfonate derivative Tpms^{Ph}, under the same previous conditions, did not proceed showing the important role of the sulfonate moiety, not only in terms of solubility, but also in the reactivity of this type of ligand towards a metal centre.

The chloro ligand at **2**-**4** was detected by far IR at typical[25] M-Cl stretching frequencies in the 233 – 378 cm^{-1} range.

The binding mode of $Tpms^{Ph}$ in the synthetized complexes **2**-**4** was determined in both solid and liquid state on the basis of IR data[26], ^1H NMR spectroscopy (for **2** and **3**) and X-ray diffraction analysis (for **4**). The ^1H NMR spectra of solutions of **2** and **3** (in methanol-d_4), in the temperature range from 25 ^oC to -60 ^oC and -75 ^oC, respectively, show the expected resonances for the 4-H and 5-H protons of the three equivalent pyrazolyl rings, where only one unique set of signals was observed and no significant changes were detected with the temperature variation, revealing the N_3 type coordination mode of **1** in both compounds. This was corroborated by both solid and liquid state IR data where the ν_{SO} frequencies for complexes **2** and **3** are similar to that of the typical band of the uncoordinated sulfonate group[26] (ν_{SO} 1046 cm^{-1}), suggesting that $Tpms^{Ph}$ is coordinated to the nickel or zinc in the N_3 coordination mode, in both solid state and solution. In the case of **4**, the N_2O coordination mode of the scorpionate is suggested also by both solid and liquid state IR[26] and confirmed by X-ray diffraction analysis (Figure 5).

Moreover, DFT calculations of geometry optimization and vibrational frequencies undertaken for **1** (Supplementary Figures S1 and S2) and for the N_3 and N_2O coordination modes of $Tpms^{Ph}$ in complexes **2**-**4** (Table S1, Figures S3-S5, S7-S9 and S11-S13), without modelling the solvent effects, corroborate the above results. In fact, comparisons of the theoretical IR spectra for both coordination modes of $Tpms^{Ph}$ with the experimental ones, in particular in terms of intensity and form of the ν_{SO} bands (Figures S5, S9 or S13 *vs*. S6, S19 or S14, respectively),[26] support the N_3 coordination in **2** and **3**, and the N_2O coordination in **4**. For $Li(Tpms^{Ph})$ (**1**) the theoretical (Figure S2) and experimental[17] IR spectra are also similar.

For **2** and **3** the energy difference between the two optimized structures for the N_3 and N_2O $Tpms^{Ph}$ coordinations (Figures S3, S4; Table S1, entries 1-3, for **2**; Figures S7, S8; Table S1, entries 4-6, for **3**) suggests a greater stability for the former coordination mode. Moreover, the diamagnetic nature of the d^8 Ni^{II} complex **2** is accounted for by the distortion of the tetrahedral geometry (Figure S3) that is not observed in the case of the optimized geometry of the d^{10} Zn^{II} complex **3** (Figure S7). Other examples of diamagnetic tetrahedral-type Ni^{II} complexes are known.[45] For the Cu^{II} compound **4**, no significant energy difference between the N_3 and N_2O coordination modes is observed (Figures S11 and S12; Table S1, entries 7-9) with the applied basis set.

It is known in the chemistry of Tpm and Tp (trispyrazolyl borates) ligands that even a small difference in the electronic and/or steric properties of the substituents can influence markedly the binding properties.[17,21] In our case, the introduction of the phenyl substituent (electron-withdrawing group) in position 3 of the pyrazol ring results in different properties of the complexes when compared to Klaui's compounds $[NiX(Tpms^{tBu})]$ (X = Cl, Br)[24] with the ^{t}Bu group (electron-donor substituent with a greater steric hindrance) in the same position. In particular, in the later case, the Ni^{II} complexes, in contrast to ours, have a quite different colour (red) and are paramagnetic, but, similarly to our complexes, only the N_3 binding mode was observed.[24] Nevertheless, for the related $Tpms^{tBu}$-Zn^{II} and -Cu^{I} complexes, both N_3 and N_2 O coordination modes are present in solution.[24]

The acetonitrile compounds $[M(Tpms^{Ph})(MeCN)](CF_3SO_3)$ (M = Ni **5** or Zn **6**) were prepared upon replacement of the chloro ligand in **2** and **3**, respectively, by reaction with $Ag(CF_3SO_3)$ in acetonitrile, under an atmosphere of dinitrogen, at room temperature. The ^{1}H NMR spectra of **5** and **6** in methanol-d_4 show expected small shifts from the ^{1}H NMR spectra of the starting

complexes **2** and **3**, since the ligand exchange should not have a marked influence on the $(Tpms^{Ph})^-$ signals.

Description of X-ray structures

In complex $[CuCl(Tpms^{Ph})(H_2O)]$ (**4**), the anionic $Tpms^{Ph}$ group acts as a tridentate ligand with the *N,N,O* coordination mode to the Cu ion through the two pyrazolyl nitrogens N11 and N31 and the oxygen O1 of the sulfonate moiety (Figure 3); a chloride and a water molecule complete the coordination sphere around the metal which features an almost regular square pyramid ($\tau5$ = 0.05).[46] The $Cu\text{-}O_{sulfonate}$ distance in **4** [2.267(4) Å] is shorter than in the mononuclear Cu^I compounds $[Cu(Tpms^{Ph})(L)]$ [L = NCMe, hexamethylenetetramine or CNCy; 2.326(2), 2.412(2) or 2.377(2) Å, respectively][15,17], consistent with the higher oxidation state of copper. However, that distance is also shorter than that found in the trinuclear complex $[(\mu\text{-}Cu)\{Cu(\mu\text{-}OH)_2(Tpms^{Ph})\}_2]$ [2.361(4) Å],[15] what is symptomatic of constrictions around the metal imposed by the bridging ligands in this type of compounds. The average mean and the largest deviations from planarity of the pyrazolyl rings [0.010(6) and 0.022(4) Å, respectively] are greater than those found in **7** (see below); the non-coordinated phenyl pyrazolyl moiety is the one with larger planarity. The bite angles between the planes of the pyrazol rings relative to the attached phenyl rings assume values of 46.97, 38.77 and 10.50 º. These distortions are responses not only to the pyrazolyl binding but also to packing constrains (see Figure S15).

The copper atom is slightly away from the planes with Cu1–N11–N12–C1 and Cu1–N31–N32–C1 torsion angles of 4.02 and −16.35 º, respectively. The same conclusion can be drawn from the planes with Cu1–N11–N12–C12 and Cu1–N31–N32–C32 torsion angles of

−162.17 and 163.46, in this order, were the metal cation stands only 0.09 Å away from both planes.

The asymmetric unit of [^{n}Bu$_4$N](Tpms^{Ph}) (**7**) (Figure 4), obtained by reaction of Li(Tpms^{Ph}) with [^{n}Bu$_4$N]Br in CH_2Cl_2, consists of one anionic tris(3-phenylpyrazolyl)methanesulfonate group and one *n*-butyl ammonium cation. The crystal lattice is stabilized by non-classical hydrogen bonding interactions involving the oxygen atoms of the sulfonate moiety which act as acceptors not only from two vicinal cations [$d_{H\cdots A}$ (Å), ∠ DHA (º): C41–H41A···O12 2.57, 120; C61–H61A···O11 2.52, 119; C72–H72A···O12 2.48, 156], but also from a symmetry generated anion [$d_{H\cdots A}$ (Å), ∠ DHA (º): C32–H32···O13 2.42, 163]. The pyrazolyl rings remain nearly planar, with an average mean deviation from the plane of 0.005(2) Å and the largest deviation of 0.010(1) Å. An interesting feature in the structure of **7** refers to the bite angles between the planes of the pyrazolyl rings relative to the attached phenyl rings; they assume values of 26.18, 21.66 and 8.65 º and are considerably smaller than those found in complex **4** (see above).

Table 1 Crystallographic data of [CuCl(Tpms^{Ph})(H_2O)] (**4**) and [^{n}Bu$_4$N](Tpms^{Ph}) (**7**)

	(**4**)	(**7**)
Empirical formula	$C_{28}H_{23}ClCuN_6O_4S$	$C_{44}H_{57}N_7O_3S$
Formula weight	638.57	764.03
Crystal system	Monoclinic	Triclinic
Space Group	*P* 2_1/c	*P* $\bar{1}$
a (Å)	16.8172(11)	12.1291(3)
b (Å)	10.6453(6)	12.8720(3)
c (Å)	22.5966(14)	14.2573(4)
α	90.00	88.2280(10)
β	119.202(3)	85.036(2)
γ	90.00	70.4200(10)
V (Å^3)	3531.2(4)	2089.35(9)
Z	4	2

ρ_{calc} (g cm^{-3})	1.201	1.214
μ(Mo Kα) (mm^{-1})	0.790	0.125
F (000)	1308	820
Refl.Collected / unique	25402 / 6442	30978 / 7483
R_{int}	0.1248	0.0355
R1[a] ($I \geq 2\sigma$)	0.0677	0.0402
wR2[b] ($I \geq 2\sigma$)	0.1638	0.0961
GOF	0.883	1.025

[a] R$1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] wR2 = $[\sum[w(Fo^2 - Fc^2)2]/\sum[w(Fo^2)^2]]^{1/2}$.

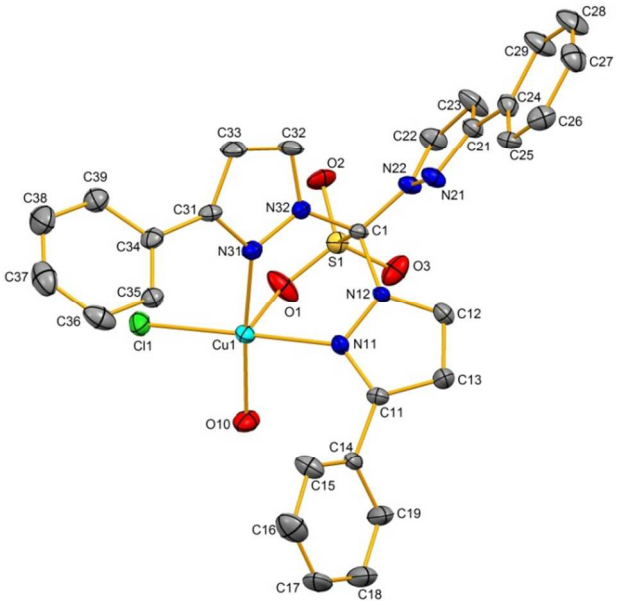


Figure 3. Molecular structure of [CuCl(Tpms^{Ph})(H_2O)] (**4**) with atomic numbering scheme. Ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cl1–Cu1 2.2262(16), O10–Cu1 1.966(4), O1–Cu1 2.267(4), N11–Cu1 2.036(4), N31–Cu1 1.986(4), N11–N12 1.368(5), N21–N22 1.380(6), N31–N32 1.357(6); O10–Cu1–N11 90.06(19), N31–Cu1–N11 84.55(18), O10–Cu1–Cl1 90.68(15), N31–Cu1–Cl1 94.62(14), O10–Cu1–O1 91.91(18), N31–Cu1–O1 89.21(16), N11–Cu1–O1 86.10(17), Cl1–Cu1–O1 97.20(13).

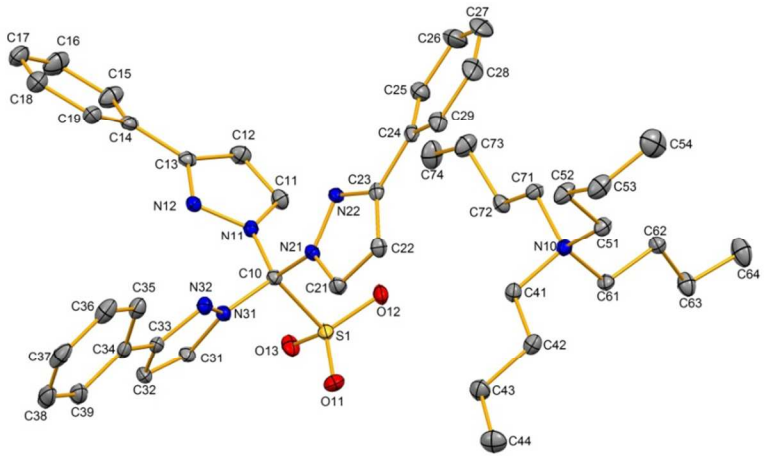


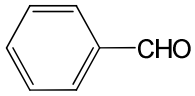
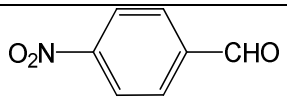
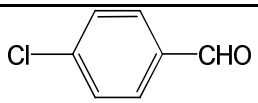
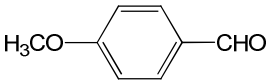
Figure 4. Molecular structure of [^{n}Bu$_4$N](Tpms^{Ph}) (**7**) with atomic numbering scheme. Ellipsoids are drawn at 30% probability and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: N11–N12 1.3637(18), N21–N22 1.3553(18), N31–N32 1.3592(18), C10–S1 1.8947(16).

Catalytic activity of complexes 2-4 in the Henry reaction

The catalytic activity of the scorpionate complexes **2**- **4** has been tested for the nitroaldol reaction. As a model system, we have chosen the reaction of benzaldehyde with nitroethane (Scheme 1) in methanol, since in our recent work[10, 47] it was found to be the best solvent for this reaction. The products of the Henry reaction are the mixture of the corresponding β-nitroalkanol diastereoisomers (*anti* and *syn* forms), according to ^{1}H NMR analysis (see experimental part). Comparison of the catalytic activity of **2**–**4** in the model system revealed that the nickel complex **2** is less active than the other two complexes tested (Table 2, entries 1-3). The Zn^{II} and Cu^{II} complexes, **3** and **4**, respectively, exhibit a good catalytic activity, with overall yields up to 99% even at room temperature, with an appreciable diastereoselectivity, that is unusual for this type of reaction. The yields of the model system using catalysts **3** and **4** are comparable but, in terms of selectivity, the Zn^{II} complex **3** acts as the best one showing predominance of the *anti* isomer (*anti*/*syn* molar ratios up to *ca*. 2.3) (Table 2, entries 2 and 3).

No significant nitroaldol reaction between benzaldehyde and nitroethane was observed in the absence of the metal complex, even in the presence of zinc chloride or zinc nitrate (Table 2, entries 4-6).

Table 2 Catalytic activity of [NiCl(Tpms^{Ph})] (**2**), [ZnCl(Tpms^{Ph})] (**3**) and [CuCl(Tpms^{Ph})(H_2O)] (**4**) in the Henry reaction.[a]

Entry	Catalyst	Substrate	Yield (%)[b]	Selectivity *anti*:*syn*[b]
1	**2**		31.5	52:48
2	**3**		**97.8**	**70:30**
3	**4**		**98.5**	57:43
4	-		0	-
5	$ZnCl_2$		0	-
6	$Zn(NO_3)_2$		0	-
7	**3**		**90.3**	56:44
8	**4**		**93.4**	51:49
9	**3**		83.9	74:26
10	**4**		**92.5**	51:49
11	**3**		12.6	**79:21**
12	**4**		32.7	68:32

[a] Reaction conditions: 5 μmol of catalyst precursor, methanol (2 mL), nitroethane (4 mmol) and aldehyde (1 mmol), under air, at room temperature. [b] Determined by ^{1}H NMR analysis (see Experimental part).

The reactions of various para-substituted aromatic aldehydes with nitroethane were also studied in the presence of catalysts **3** and **4**, and shown to provide the respective β-nitroalkanols with yields ranging up to 90% in the case of complex **3** and up to 93% for complex **4**. The maximum *anti:syn* selectivity obtained was *ca.* 4:1 (Table 2, entry 11). In this type of reaction it is expected[47] that the nature of substrates can greatly influence the yields and selectivity. Thus, benzaldehydes bearing the electron-withdrawing *para*-nitro or -chloro substituent (Table 2, entries 7-10) exhibit a higher reactivity compared to that of the benzaldehyde having the

electron-donor methoxy in the same position (Table 2, entries 11-14). This may relate with the increased electrophilicity of the aldehyde substrate with the former substituents. However, all the substituted benzaldehydes lead to lower product yields than the unsubstituted one, what can reflect steric effects.

In accord with our previous studies[10] and others,[47] the metal catalyst is expected to act as a Lewis acid centre, activating both the nitroethane (increasing its acidity) and aldehyde (increasing its electrophilic character). The scorpionate ligand can behave as a Brønsted base, promoting the deprotonation of the acidic nitroethane with the formation of a reactive nitronate species which, via a nucleophilic intramolecular attack to the aldehyde, forms a C–C bond resulting in the formation of the β-nitroalkanol.[48, 49]

In comparison with other reported metal catalysts[50-54] for the Henry reaction, complexes **3** and **4** are among the best ones in terms of activity combined with diastereoselectivity. The stereochemical control of the two newly generated carbon centres remains a challenge, in particular due to the epimerization of the nitro-substituent on the carbon chain.[55, 56] Although some expensive and enantio-differentiating catalysts can considerably overcome this difficulty,[49, 53] our catalysts are environmentally friendly, easier to prepare and/or cheaper than others, *e.g.* based on metals such as Rh,[50] La,[53, 54] Nd[53, 54] or using an ionic liquid.[51] Nevertheless, a higher selectivity has been reported[54] for a less accessible and more complex (also more expensive) Nd-Na heterobimetallic catalytic system.

Conclusions

This work contributed to the development of the C-scorpionate coordination chemistry by synthesising new late transition metal (Ni, Cu or Zn) complexes with the sterically hindered and water soluble tris(3-phenylpyrazol-1-yl)methanesulfonate ($Tpms^{Ph}$) ligand.

NMR and IR spectroscopies, ESI-MS and X-ray studies demonstrated that the use of this sterically hindered ligand favours the synthesis of half-sandwich complexes preferably to the full sandwich ones. Moreover, they also have shown the different coordination modes of the $Tpms^{Ph}$ ligand: it coordinates in a N_2O mode, involving the sulfonate moiety, to the copper(II) centre, but in a N_3 mode to the zinc(II) or nickel(II) centres.

Our results also show that the Zn^{II} and Cu^{II} complexes, **3** and **4** respectively, are effective catalyst precursors for the diastereoselective nitroaldol reaction, leading to β-nitroalkanols in high yield (up to 99%), with predominance of the *anti* diastereoisomer. The combination of Cu^{II} or Zn^{II} with the $Tpms^{Ph}$ ligand provides a Lewis acid metal centre (capable to promote the nitroethane deprotonation and the electrophilicity of benzaldehyde) and a Brönsted base (able to assist the proton loss from nitroethane) that seems to be particularly favourable for that reaction.

Computational studies of the geometry optimization and frequency calculations of the species with the different types of ligand coordination modes are in accord with their structural characterization.

Hence, this work provides a combination of complementary synthetic, structural and catalytic studies towards a better knowledge of the promising, but yet underdeveloped, chemistry of tris(pyrazol-1-yl)methanesulfonate complexes and their application in the nitroaldol (Henry) reaction.

Experimental Section

General Materials and Experimental Procedures: The complexation reactions were carried out in air and the ligand exchange reactions were carried out under dinitrogen, using standard Schlenk techniques. All solvents were dried, degassed and distilled prior to use. All the reagents were purchased from Aldrich and used without further purification. C, H, N and S analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets and in chloroform. Far infrared spectra (400-200 cm^{-1}) were recorded on a Vertex 70 spectrophotometer in cesium iodide pellets. Vibrational frequencies are expressed in cm^{-1}; abbreviations: s, m and w: strong, medium and weak, respectively. 1D (^{1}H, $^{13}C\{^{1}H\}$) and 2D (^{13}C-HSQC, $^{1}H,^{13}C$-APT) NMR experiments were performed on Bruker 300 and 400 UltraShield^{TM} spectrometers. ^{1}H and ^{13}C chemical shifts δ are expressed in ppm relative to $Si(Me)_4$. Coupling constants are in Hz; abbreviations: s, singlet; d, doublet; m, complex multiplet; vt, virtual triplet; br, broad. ESI^{+} mass spectra were obtained on a VARIAN 500-MS LC ion trap mass spectrometer (solvent: methanol; flow: 20 μL/min; needle spray voltage: ± 5 kV, capillarity voltage: ± 100 V; nebulizer gas (N_2): 35 psi; drying gas (N_2): 10 psi; drying gas temperature: 350 ºC). For the ESI-MS spectra description, M denotes the complex part of the compound.

X-ray structure determinations. X-ray quality single crystals of compounds **4** and **7** were immersed in cryo-oil, mounted in a Nylon loop and measured at a temperature of 150 (**7**) or 296 (**4**) K (Table 1). Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-Kα (λ 0.71073) radiation. Data were collected

using omega scans of 0.5º per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT[57] on all the observed reflections. Absorption corrections were applied using SADABS.[58] Structures were solved by direct methods by using the SHELXS–97[30] package and refined with SHELXL–97.[59] Calculations were performed using the WinGX System–Version 1.80.03.96.[60] Coordinates of hydrogen atoms bonded to carbon atoms were calculated following the stereochemical rules with C-H distances of 0.93 A for phenyl, 0.97 A for methylene and 0.96 A for methyl groups. The hydrogen atoms were included in the refinement using the riding-model approximation. Uiso(H) were defined as 1.2Ueq of the parent carbon atoms for phenyl and methylene residues and 1.5Ueq of the parent carbon atoms for the methyl groups. Hydrogen atoms attached to the coordinated water molecule were located in a difference Fourier synthesis but were included in the final refinement at positions calculated from the geometry of the molecule using the riding model, with Uiso(H) defined as 1.5Ueq of the parent oxygen atom. There were disordered molecules in the structure of **4**. Since no obvious major site occupations were found for those molecules, it was not possible to model them. PLATON/SQUEEZE [61] was used to correct the data and a potential volume 1002 $Å^3$ were found with 333 electrons per unit cell worth of scattering. These were removed from the model and not included in the empirical formula. CCDC 988720 (for **7**) and 988721 for (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details: All calculations were performed using the Gaussian 03 software package.[62] Geometry optimizations were performed using the B3LYP[63] hybrid functional and the

standard 6-31G(d,p)[64-68] and 3-21G[69-73] basis set, without symmetry constraints. Frequency calculations were performed to confirm the nature of the stationary points.

Synthesis of Li(Tpms^{Ph}) (1) and [^{n}Bu$_4$N](Tpms^{Ph}) (7). The lithium salt of (Tpms^{Ph})$^-$ was synthesized following the method reported by some of us[17] and characterised by the above methods. X-ray quality single crystals of [^{n}Bu$_4$N](Tpms^{Ph}) (**7**) were grown by slow diffusion of dry diethyl ether in a concentrated solution of **1** with [^{n}Bu$_4$N]Br in dichloromethane, under dinitrogen atmosphere.

Synthesis of [NiCl(Tpms^{Ph})] (2). To a methanolic solution (1.5 mL) of $NiCl_2.6H_2O$ (27 mg, 0.11 mmol) a solution of **1** (66 mg, 0.12 mmol, 1 equiv) in 1.5 mL of methanol was added dropwise and the mixture was stirred at room temperature for 18 h. The solvent was then evaporated under vacuum and the residue washed with $CHCl_3$. The precipitate was separated by filtration and the filtrate was evaporated under vacuum to give a pale green solid of **2** (49 mg, 66 % yield). **2** is soluble in $CHCl_3$ and acetone, slightly soluble in H_2O ($S_{25°C} \approx 1$ mg.mL^{-1}), MeOH, EtOH and CH_2Cl_2, but insoluble in Et_2O. It is stable in air when dried. $C_{28}H_{21}N_6SO_3NiCl$: (615.72) Calcd. C 54.62; H 3.44; N 13.65; S 5.21; found: C 54.35; H 3.51; N 13.49; S 5.15. ESI$^+$-MS *m/z*: 596 [Ni(Tpms^{Ph}) + OH]$^+$, 611 [Ni(Tpms^{Ph}) + CH_3OH]$^+$. IR (KBr and $CHCl_3$, selected bands, cm^{-1}): 1534 (m, ν(C=N)), 1502 (m), 1457 (s), 1354 (m), 1230 (s br), 1079 (s), 1046 (s, ν(S-O)), 900 (m), 862 (s), 754 (s), 695 (s), 640 (s, ν (C-S)) cm^{-1}. Far-IR (CsI pellet, cm^{-1}): 233 [m, ν(Ni–Cl)])]. ^{1}H NMR (methanol-d_4, δ): 8.16 (d, 3H, 5-H (pz)), 7.78 (d, 6H, *o*-H (Ph)), 7.34-7.25 (m, 9H, *m*-H and *p*-H (Ph)), 6.83 (d, 3H, 4-H (pz). ^{13}C{^{1}H} NMR (acetone-d_6,

δ): 151.2 (s, 3-C (pz)), 132.9 (s, 5-C (pz)), 131.2 (s, pz-C (Ph)), 129.5 (s, *p*-C (Ph)), 128.8 (s, *m*-C (Ph)), 127.3 (s, *o*-C (Ph)), 104.9 (s, 4-C (pz)), 102.2 (s, CSO_3).

Synthesis of [ZnCl(Tpms^{Ph})] (3). To a methanolic solution (1.5 mL) of $ZnCl_2$ (16 mg, 0.11 mmol) a solution (1.5 mL) of **1** (66 mg, 0.12 mmol, 1 equiv.) in methanol was added dropwise. The reaction mixture was stirred at room temperature for 18 h leading to a white suspension. The solvent was removed under vacuum, the solid residue was washed (extracted) with $CHCl_3$ and the obtained colourless solution was separated upon centrifugation. The solution was concentrated under vacuum giving rise to a white precipitate of (**3**) (51 mg, 68 % yield). **3** is soluble in H_2O ($S_{25°C} \approx 2$ mg.mL^{-1}), $CHCl_3$, MeOH, EtOH and acetone, slightly soluble in CH_2Cl_2 and MeCN, insoluble in Et_2O and toluene. **3**, $C_{28}H_{21}N_6SO_3ZnCl$: (622.41) Calcd. C 54.03; H 3.40; N 13.50; S 5.15; found: C 54.15; H 3.47; N 13.46; S 5.17. ESI$^+$-MS *m/z*: 602 [Zn(Tpms^{Ph}) + OH]$^+$, 617 [Zn(Tpms^{Ph}) + CH_3OH]$^+$. IR (KBr and $CHCl_3$, selected bands, cm^{-1}): 3152 (s), 3060 (m br), 1535 (m, ν(C=N)), 1501 (m), 1456 (s), 1396 (m), 1355 (m), 1269 (s br), 1046 (s) (s, ν(S-O)), 976 (m), 862 (s), 756 (s), 695 (s), 640 (s, ν (C-S)) cm^{-1}. Far IR (CsI pellet, cm^{-1}): 378 [m, ν(Zn–Cl)])]. ^{1}H NMR (methanol-d_4, *δ*): 8.09 (d, 3H, 5-H (pz)), 7.79 (d, 6H, *o*-H (Ph)), 7.35-7.26 (m, 9H, *m*-H and *p*-H (Ph)), 6.84 (d, 3H, 4-H (pz)). ^{13}C{^{1}H} NMR (acetone-d_6, *δ*): 153.4 (s, 3-C (pz)), 135.4 (s, 5-C (pz)), 134.1 (s, pz-C (Ph)), 129.2 (s, *p*-C (Ph)), 129.6 (s, *m*-C (Ph)), 126.9 (s, *o*-C (Ph)), 105.1 (s, 4-C (pz)), 101.5 (s, CSO_3).

Synthesis of [CuCl(Tpms^{Ph})(H_2O)] (4). To a methanolic solution (1.5 mL) of $CuCl_2$ (13 mg, 0.093 mmol) a solution (1.5 mL) of **1** (50 mg, 0.093 mmol, 1 equiv) in the same solvent was added. The resulting green solution was stirred in air at room temperature overnight. The solvent

was removed under vacuum and the crude residue was poured in THF and the solution filtered. The solution was then evaporated affording a light green powder of **4** (65 mg, 93 %). **4** is green, sparingly soluble in H_2O ($S_{25°C} \approx 1$ mg.mL^{-1}), soluble in THF, MeOH and EtOH, slightly soluble in $CHCl_3$, CH_2Cl_2 and MeCN, and insoluble in Et_2O and toluene. **4**, $C_{28}H_{23}N_6O_4SCuCl$: (638.57) Calcd. C 52.66; N 13.16; H 3.63; S 5.02; found: C 52.95; N 13.11; H 3.74; S 5.05. IR (KBr and $CHCl_3$, selected bands, cm^{-1}): 3464 (m, ν(O–H)), 3061, 2959, 2854 (m br), 1629 (m, δ(O–H)), 1535 (m, ν(C=N)), 1501 (m), 1456 (s), 1396 (m), 1356 (m), 1284 (s), 1229 (s), 1079 (s), 1046 (s, ν(S-O)), 900 (m), 862 (s), 756 (s), 695 (s), 639 (s, ν(C-S)), 540 (w) cm^{-1}. Far-IR (CsI pellet, cm^{-1}): 280 [m, ν(Cu–Cl)])]. ESI$^+$-MS *m/z*: 504 [{Cu(Tpms^{Ph}) – (SO_3)}]$^+$, 441 [{Tpms^{Ph} – SO_3}+ H]$^+$, 297 [Tpms^{Ph} – SO_3 – pz]$^+$, 145 [{Tpms^{Ph} – SO_3 – 2(pz)} + 2H]$^+$. X-ray quality single crystals were grown by slow diffusion, in air, of toluene in a concentrated solution of the titled compound in THF.

Synthesis of [Ni(Tpms^{Ph})(MeCN)](CF_3SO_3) (5). To a solution of **2** (50 mg, 0.08 mmol) in acetonitrile (3 mL), Ag(CF_3SO_3) (21 mg, 0.08 mmol, 1 equiv.) was added at room temperature, under a dinitrogen atmosphere and the mixture was stirred for 3 h, resulting in a light yellow suspension. Upon centrifugation and decantation, a white precipitate of AgCl and a yellow solution were separated out. The solution was evaporated to leave a white off solid of [Ni(Tpms^{Ph})(MeCN)](CF_3SO_3) (**5**) in quantitative yield. $C_{31}H_{24}N_7S_2O_6F_3Ni$: (770.39) Calcd. C 48.33; H 3.14; N 12.73; S 8.32; found: C 48.40; H 3.14; N 12.76; S 8.30. ESI$^+$-MS *m/z*: 620 [Ni(Tpms^{Ph})(MeCN)]$^+$, 611 [Ni(Tpms^{Ph}) + CH_3OH]$^+$. IR (KBr, selected bands, cm^{-1}): 2253 (m, ν(C≡N)), 1534 (m, ν(C=N)), 1502 (m), 1457 (s), 1354 (m), 1230 (s br), 1079 (s), 1046 (s, ν(S-O)), 900 (m), 862 (s), 754 (s), 695 (s), 640 (s, ν(C-S)) cm^{-1}. ^{1}H NMR (methanol-d_4, δ): 8.15 (d,

3H, 5-H (pz)), 7.78 (d, 6H, *o*-H (Ph)), 7.54-7.25 (m, 9H, *m*-H and *p*-H (Ph)), 6.83 (d, 3H, 4-H (pz), 2.07 (s, 3H, H_3CCN). $^{13}C\{^1H\}$ NMR (acetone-d_6, δ): 151.2 (s, 3-C (pz)), 132.9 (s, 5-C (pz)), 131.2 (s, pz-C (Ph)), 129.5 (s, *p*-C (Ph)), 128.8 (s, *m*-C (Ph)), 127.3 (s, *o*-C (Ph)), 115.3 (s, $H_3C\mathit{C}N$) 104.9 (s, 4-C (pz)), 102.2 (s, CSO_3), 12.03 (s, $H_3\mathit{C}CN$).

Synthesis of [Zn(Tpms^{Ph})(MeCN)](CF$_3$SO$_3$) (6). To a solution of **3** (50 mg, 0.08 mmol) in acetonitrile (3 mL), Ag(CF_3SO_3) (21 mg, 0.08 mmol, 1 equiv.) was added at room temperature, under a dinitrogen atmosphere and the mixture was stirred for 3 h resulting in a white suspension. Upon centrifugation and decantation, the white precipitate of AgCl was separated from the solution. The latter was evaporated to leave a white off solid of [Zn(Tpms^{Ph})(MeCN)](CF_3SO_3) (**6**) in quantitative yield. $C_{31}H_{24}N_7S_2O_6F_3Zn$: (777.08) Calcd. C 47.92; H 3.11; N 12.62; S 8.25; found: C 47.86; H 3.12; N 12.64; S 8.28. ESI$^+$-MS *m/z*: 626 [Zn(Tpms^{Ph})(MeCN)]$^+$. IR (KBr, selected bands, cm^{-1}): 3150 (s), 2252 (m, ν(C≡N)), 1533 (m, ν(C=N)), 1500 (m), 1455 (s), 1395 (m), 1355 (m), 1268 (s br), 1045 (s, ν(S-O)), 976 (m), 862 (s), 756 (s), 694 (s), 640 (s, ν(C-S)) cm^{-1}. ^{1}H NMR (methanol-d_4, δ): 8.08 (d, 3H, 5-H (pz)), 7.78 (d, 6H, *o*-H (Ph)), 7.36-7.26 (m, 9H, *m*-H and *p*-H (Ph)), 6.86 (d, 3H, 4-H (pz)), 2.01 (s, 3H, H_3CCN). $^{13}C\{^1H\}$ NMR (acetone-d_6, δ): 151.7 (s, 3-C (pz)), 134.2 (s, 5-C (pz)), 132.5 (s, pz-C (Ph)), 128.9 (s, *p*-C (Ph)), 127.6 (s, *m*-C (Ph)), 126.8 (s, *o*-C (Ph)), 115.8 (s, $H_3C\mathit{C}N$), 105.1 (s, 4-C (pz)), 101.4 (s, CSO_3), 12.01 (s, $H_3\mathit{C}CN$).

General procedure for the catalytic Nitroaldol (Henry) reaction studies. Specific conditions are provided in Table 2. The selected catalyst precursor **2** – **4** (5.0 μmol) was placed, under air, in a 5 mL vial. Methanol (2 mL), nitroethane (286 μL, 4 mmol) and the selected aldehyde (1

mmol) were added to the vial in that order. The reaction mixture was stirred during 24 h (see Table 2 for details) at room temperature and air atmospheric pressure. The reaction mixture was evaporated to dryness under a stream of dinitrogen, and the residue was dissolved in deuterated DMSO and analysed by ^{1}H NMR spectroscopy. The yield of β-nitroalkanol product (relatively to the aldehyde) was established using 1,2-dimethoxyethane as internal standard, taking into consideration the relative amounts of these compounds, as given by ^{1}H NMR spectra and previously reported.[74] The ratio between the *anti* and *syn* isomers was also determined by ^{1}H NMR spectroscopy. Control experiments were performed under the same reaction conditions but in the presence of $ZnCl_2$ or $Zn(NO_3)_2$ instead of any complex catalyst. The performed blank experiments confirmed that no products of nitroaldol reaction were obtained unless the catalyst was added.

Acknowledgments

This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal, and its PPCDT program (FEDER funded) through the research projects PTDC/QUI-QUI/102150/2008, PTDC/QUI-QUI/109846/2009, PTDC/EQU/EQU-122025-2010, PTDC/QUI-QUI/119561/2010 and Pest-OE/QUI/UI0100/2013. BR is grateful to the Group V of Centro de Química Estrutural and the FCT, for the fellowships BL/CQE-2012-026, BL/CQE-2013-010 and the PhD fellowship of CATSUS PhD program (SFRH/BD/52370/2013) respectively, while KVL to both the FCT and the Instituto Superior Técnico (IST) for the research contract (Ciência 2008 Initiative). Authors also thank the Portuguese NMR Network (IST-UTL NMR Centre) and National MS Network (IST Node) for providing access to the NMR and ESI-MS facilities, correspondingly.

1. Trofimenko S., *J. Am. Chem. Soc.*, 1967, **89**, 3170.
2. A. Looney, R. Han, K. Mcneill, G. Parkin, *J. Am. Chem. Soc.*, 1993, **115**, 4690.
3. S. Trofimenko, in *Scorpionates, The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press: London, 1999.
4. C. Pettinari, in *Scorpionates II: Chelating Borate Ligands*, Imperial College Press, World Scientific Pub, 2008.
5. G. S. Mishra, T. F. S. Silva, L. M. D. R. S. Martins, A. J. L. Pombeiro, *Pure Appl. Chem.*, 2009, **81**, 1217.
6. T. F. S. Silva, G. S. Mishra, M. F. C. Guedes da Silva, R. Wanke, L. M. D. R. S. Martins, A. J. L. Pombeiro, *Dalton Trans.*, 2009, **42**, 9207.
7. C. Dinoi, M. F. C. Guedes da Silva, E. Alegria, P. Smolenski, L. M. D. R. S. Martins, R. Poli, A. J. L. Pombeiro, *Eur. J. Inorg. Chem.*, 2010, **16**, 2415.
8. T. F. S. Silva, K. V. Luzyanin, M. V. Kirillova, M. F. C. Guedes da Silva, L. M. D. R. S. Martins, A. J. L. Pombeiro, *Adv. Synth. Catal.*, 2010, **352**, 171.
9. R. Wanke, M. F. C. Guedes da Silva, S. Lancianesi, T. F. S. Silva, L. M. D. R. S. Martins, C. Pettinari, A. J. L. Pombeiro, *Inorg. Chem.*, 2010, **49**, 7941.
10. C. Pettinari, F. Marchetti, A. Cerquetella, R. Pettinari, M. Monari, T. C. O. Mac Leod, L. M. D. R. S. Martins, A. J. L. Pombeiro, *Organometallics*, 2011, **30**, 1616.
11. C. Pettinari, F. Marchetti, G. Lupidi, L. Quassinti, M. Bramucci, D. Petrelli, L. A. Vitali, M. F. C. Guedes da Silva, L. M. D. R. S. Martins, P. Smolenski, A. J. L. Pombeiro, *Inorg. Chem.*, 2011, **50**, 11173.
12. T. F. S. Silva, M. F. G. da Silva, G. S. Mishra, L. M. D. R. S. Martins, A. J. L. Pombeiro, *J. Organomet. Chem.*, 2011, **696**, 1310.
13. T. F. S. Silva, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, A. R. Fernandes, A. Silva, P. M. Borralho, S. Santos, C. M. P. Rodrigues, A. J. L. Pombeiro, *Dalton Trans.*, 2012, **41**, 12888.
14. T. F. S. Silva, T. C. O. Mac Leod, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, M. A. Schiavon, A. J. L. Pombeiro, *J. Mol. Cat. A: Chem.*, 2013, **367**, 52.
15. B. G. M. Rocha, R. Wanke, M. F. C. Guedes da Silva, K. V. Luzyanin, L. M. D. R. S. Martins, P. Smolenski, A. J. L. Pombeiro, *J. Organomet. Chem.*, 2012, **714**, 47.
16. M. Peixoto de Almeida, L. M. D. R. S. Martins, S. A. C. Carabineiro, T. Lauterbach, F. Rominger, A. S. K. Hashmi, A. J. L. Pombeiro, J. L. Figueiredo, *Catal. Sci. Technol.*, 2013, **3**, 3056.
17. R. Wanke, P. Smolenski, M. F. C. Guedes da Silva, L. M. D. R. S. Martins, A. J. L. Pombeiro, *Inorg. Chem.*, 2008, **47**, 10158.
18. F. Marchetti, C. Pettinari, R. Pettinari, A. Cerquetella, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, T. F. S. Silva, A. J. L. Pombeiro, *Organomet.*, 2011, **30**, 6180.
19. E. C. B. Alegria, L. M. D. R. S. Martins, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *J. Organomet. Chem.*, 2005, **690**, 1947.
20. E. C. B. Alegria, L. M. D. R. S. Martins, M. Haukka, A. J. L. Pombeiro, *Dalton Trans.*, 2006, 4954.
21. C. Pettinari, R. Pettinari, *Coord. Chem. Rev.*, 2005, **249**, 525.
22. W. Klaui, M. Berghahn, G. Rheinwald, H. R. Lang, *Angew. Chem.-Int. Ed.*, 2000, **39**, 2464.
23. W. Klaui, D. Schramm, W. Peters, G. Rheinwald, H. Lang, *Eur. J. Inorg. Chem.*, 2001, **6**, 1415.

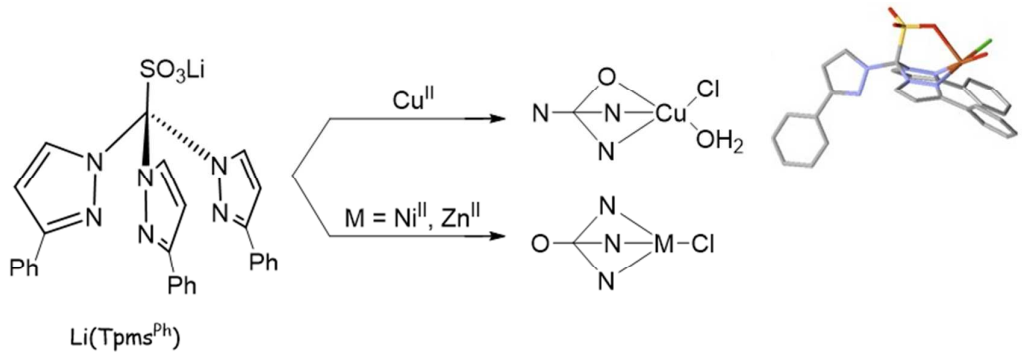
24. W. Klaui, M. Berghahn, W. Frank, G. J. Reiss, T. Schonherr, G. Rheinwald, H. Lang, *Eur. J. Inorg. Chem.*, 2003, **11**, 2059.
25. E. T. Papish, M. T. Taylor, F. E. Jernigan, M. J. Rodig, R. R. Shawhan, G. P. A. Yap, F. A. Jove, *Inorg. Chem.*, 2006, **45**, 2242.
26. T. B. Chenskaya, M. Berghahn, P. C. Kunz, W. Frank, W. Klaui, *J. Mol. Struct.*, 2007, **829**, 135.
27. L. M. D. R. S. Martins, A. J. L. Pombeiro, *Coord. Chem. Rev.*, 2014, **265**, 74.
28. E. C. B. Alegria, M. V. Kirillova, L. M. D. R. S. Martins, A. J. L. Pombeiro, *Appl. Catal. A Gen.*, 2007, **317**, 43.
29. A. Otero, J. Fernandez-Baeza, A. Lara-Sanchez, L. F. Sanchez-Barba, *Coord. Chem. Rev.*, 2013, **257**, 1806.
30. G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Determination.* In University of Göttingen; Göttingen, Germany, 1997 edn.
31. G. S. Mishra, E. C. B. Alegria, L. M. D. R. S. Martins, J. J. R. Frausto da Silva, A. J. L. Pombeiro, *J. Mol. Catal. A Chem.*, 2008, **285**, 92.
32. E. C. B. A. Alegria, L. M. D. R. S. Martins, M. V. Kirillova, A. J. L. Pombeiro, *Appl. Catal. A Gen.*, 2012, **443**, 27.
33. L. M. D. R. S. Martins, E. C. B. A. Alegria, P. Smolenski, M. L. Kuznetsov, A. J. L. Pombeiro, *Inorg. Chem.*, 2013, **52**, 4534.
34. L. M. D. R. S. Martins, A. Martins, E. C. B. A. Alegria, A. P. Carvalho, A. J. L. Pombeiro, *Appl. Catal. A Gen.*, 2013, **464**, 43.
35. L. M. D. R. S. Martins, M. Peixoto de Almeida, S. A. C. Carabineiro, J. L. Figueiredo, A. J. L. Pombeiro, *ChemCatChem*, 2013, **5**, 3847.
36. T. Suami, K. Tadano, A. Suga, Y. Ueno, *J. Carboh. Chem.*, 1984, **3**, 429.
37. T. M. Williams, H. S. Mosher, *Tetrahedron Lett.*, 1985, **26,** 6269.
38. V. J. Bulbule, V. H. Deshpande, S. Velu, A. Sudalai, S. Sivasankar, V. T. Sathe, *Tetrahedron*, 1999, **55**, 9325.
39. M. Shibasaki, M. Kanai, S. Matsunaga, N. Kumagai, in *Bifunctional Molecular Catalysis*, eds. T. Ikariya and M. Shibasaki, 2011, vol. 37, pp. 1-30.
40. B. M. Trost,V. S. C. Yeh, *Angew. Chem. Int. Ed.*, 2002, **41**, 861.
41. B. M. Trost, V. S. C. Yeh, H. Ito, N. Bremeyer, *Org. Lett.*, 2002, **4**, 2621.
42. C. Palomo, M. Oiarbide, A. Laso, *Angew. Chem. Int. Ed.* 2005, **44**, 3881.
43. D. A. Evans, D. Seidel, M. Rueping, H. W. Lam, J. T. Shaw, C. W. Downey, *J. Am. Chem. Soc.*, 2003, **125,** 12692.
44. M. D. Jones, C. J. Cooper, M. F. Mahon, P. R. Raithby, D. Apperley, J. Wolowska, D. Collison, *J. Mol. Catal. A Chem.*, 2010, **325**, 8.
45. S. Blanchard, F. Neese, E. Bothe, E. Bill, T. Weyhermuller and K. Wieghardt, *Inorg. Chem.*, 2005, **44**, 3636.
46. A. W. Addison, T. N. Rao, J. Reedijk, J. Vanrijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.*, 1984, **7**, 1349.
47. M. N. Kopylovich, T. C. O. Mac Leod, K. T. Mahmudov, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Dalton Trans.*, 2011, **40**, 5352.
48. J. Boruwa, N. Gogoi, P. P. Saikia, N. C. Barua, *Tetrahedron-Asym.*, 2006, **17**, 3315.
49. N. Qi, R.-Z. Liao, J.-G. Yu, R.-Z. Liu, *J. Comput. Chem.*, 2010, **31**, 1376.
50. S. Kiyooka, T. Tsutsui, H. Maeda, Y. Kaneko, K. Isobe, *Tetrahedron Lett.*, 1995, **36**, 6531.

51. T. Jiang, H. X. Gao, B. X. Han, G. Y. Zhao, Y. H. Chang, W. Z. Wu, L. Gao, G. Y. Yang, *Tetrahedron Lett.*, 2004, **45**, 2699.
52. A. Bulut, A. Aslan, O. Dogan, *J. Org. Chem.*, 2008, **73**, 7373.
53. S. Handa, K. Nagawa, Y. Sohtome, S. Matsunaga, M. Shibasaki, *Angew. Chem. Int. Ed.*, 2008, **47**, 3230.
54. T. Nitabaru, N. Kumagai, M. Shibasaki, *Tetrahedron Let.t*, 2008, **49**, 272.
55. D. Seebach, A. K. Beck, T. Mukhopadhyay, E. Thomas, *Helv. Chim. Acta*, 1982, **65**, 1101.
56. C. Palomo, M. Oiarbide, A. Mielgo, *Angew. Chem. Int. Ed.*, 2004, **43**, 5442.
57. P. Harding, D. J. Harding, S. Saithong, C. Pakawatchai, S. Youngme, *Acta Crystallogr. E*, 2006, **62**, M1616.
58. G. M. Sheldrick, *v 2.10. In Bruker AXS, Inc.*, 2003, Madison, Wisconsin, USA.
59. G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement.* In University of Göttingen: Göttingen, Germany, 1997 edn.
60. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 1.
61. A. L. Spek, *Acta Cryst. Sec. C*, 1990, **46**, C34.
62. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. V. Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision C.02, Gaussian Inc., Wallingford CT, 2004.
63. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
64. Ditchfie.R, W. J. Hehre, J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.
65. W. J. Hehre, R. Ditchfie J. A. Pople, *J. Chem. Phys.*, 972, **56**, 2257.
66. Harihara. Pc, J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
67. Harihara.Pc , J. A. Pople, *Mol. Phys.*, 1974, **27**, 209.
68. M. S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163.
69. J. S. Binkley, J. A. Pople, W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.
70. M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, W. J. Hehre, *J. Am. Chem. Soc.*, 1982, **104**, 2797.
71. W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. Defrees, J. A. Pople, J. S. Binkley, *J. Am. Chem. Soc.*, 1982, **104**, 5039.
72. K. D. Dobbs, W. J. Hehre, *J. Comput. Chem.*, 1986, **7**, 359.
73. K. D. Dobbs, W. J. Hehre, *J. Comput. Chem.*, 1987, **8**, 880.
74. A. Cwik, A. Fuchs, Z. Hell, J. M. Clacens, *Tetrahedron*, 2005, **61**, 4015.

Graphical Abstract

Ni^{II}, Cu^{II} and Zn^{II} Complexes with a Sterically Hindered Scorpionate Ligand ($Tpms^{Ph}$) and Catalytic Application in the Diasteroselective Nitroaldol (Henry) Reaction

Bruno G.M. Rocha,[a] Tatiana C.O. Mac Leod,[a] M. Fátima C. Guedes da Silva,[a] Konstantin V. Luzyanin,[a] Luísa M.D.R.S. Martins,[a,b] Armando J.L. Pombeiro[a*]*



The bulky scorpionate $(Tpms^{Ph})^-$ adapts its coordination mode to the electronic and steric preferences of the Ni^{II}, Cu^{II} or Zn^{II} centre forming complexes which catalyse (Cu^{II} and Zn^{II}) the nitroaldol reaction.