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Hydrosoluble Complexes Bearing Tris(pyrazolyl)methane Sulfonate Ligand: Synthesis, Characterization and Catalytic Activity for Henry Reaction

Abdallah G. Mahmoud, Luísa M. D. R. S. Martins *, M. Fátima C. Guedes da Silva * and Armando J. L. Pombeiro

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa Av. Rovisco Pais, 1049-001 Lisboa, Portugal

* Correspondence: luisammartins@tecnico.ulisboa.pt (L.M.D.R.S.M.); fatima.guedes@tecnico.ulisboa.pt (M.F.C.G.d.S.); Tel.: +351-218-419-389 (L.M.D.R.S.M.); +351-218-419-207 (M.F.C.G.d.S.)

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Abstract: The catalytic activity of the water-soluble scorpionate coordination compounds [Cu(κ-*NN*′*O*-Tpms)$_2$] (**1**), [Mn(Tpms)$_2$] (**2**) and Li[FeCl$_2$(κ-*NN*′*N*″-Tpms)] (**3**) [Tpms = tris(pyrazolyl)-methane sulfonate, $O_3SC(pz)_3{}^-$], were studied towards the (Henry) reaction between benzaldehyde and nitromethane or nitroethane in aqueous medium to afford, respectively, 2-nitro-1-phenylethanol or 2-nitro-1-phenylpropanol, the latter in the *syn* and the *anti* diastereoisomeric forms. Complex **1** exhibited the highest activity under the optimum experimental conditions and was used to broaden the scope of the reaction to include several aromatic aldehydes achieving yields up to 94%.

Keywords: C-scorpionate; Henry reaction; aqueous medium; catalysis

1. Introduction

Scorpionate is a term coined by Trofimenko [1] to describe a special class of poly(pyrazolyl) compounds, which are derived from two or more N-deprotonated pyrazole rings bound to a main group atom (e.g., boron, carbon, aluminium, indium, gallium, silicon, and germanium) through one of the ring nitrogens [1–6]. Tris(pyrazolyl)methanes (Tpm, Figure 1) were reported for the first time in 1937 [7]. However, up to mid-90s, their properties and coordination chemistry remained unexplored due to the difficulties of their preparation in good yields, until Reger has reviewed some effective synthetic protocols to prepare Tpm compounds in high yields [8–10].

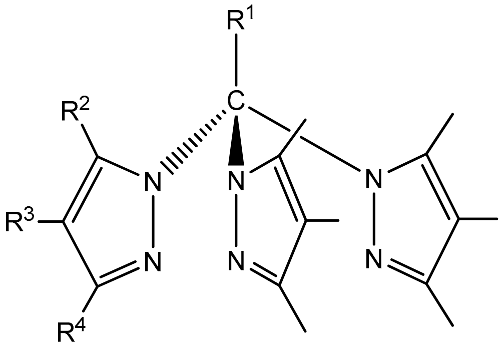
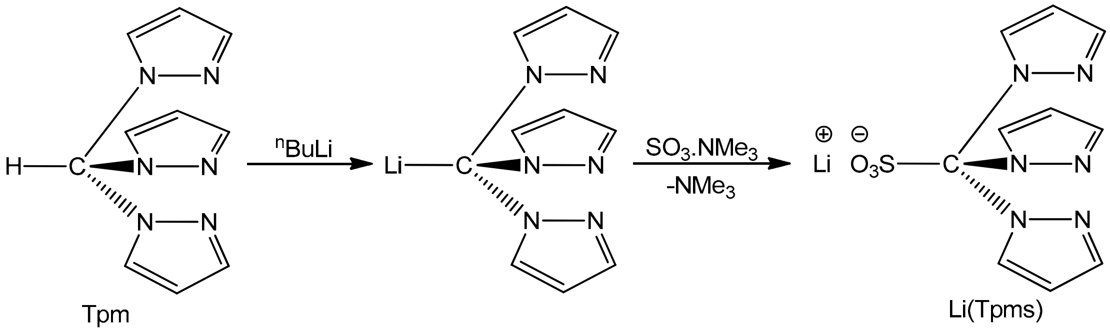


Figure 1. A schematic representation of tris(pyrazolyl)methane compounds.

Significant developments have been made in the application of C-scorpionate Tpm based complexes as catalysts due to their chelating versatility resulting from, e.g., a change between the bidentate and tridentate binding modes [2,11–14]. They have been reported as catalyst precursors for oxidation [12,13,15–18], hydroformylation [19], hydrogenation [20,21], alkane hydroxylation [22], benzene carbonylation [23], olefin polymerization [24–26], nitrene transfer reactions [27], nitroaldol condensation [11,28], azide-alkyne cycloaddition [29], and Heck C–C coupling [30,31].

Tpm based compounds are highly soluble and stable in all common organic solvents but not in water. In the beginning of this century, Kläui et al. [32] obtained a novel class of water soluble scorpionates by addition of sulfurtrioxide–trimethylamine complex to lithiated $HC(pz)_3$ to produce the anionic hydrosoluble tris(pyrazolyl)methane sulfonate (Tpms) (Scheme 1).



Scheme 1. Synthesis of tris(pyrazolyl)methane sulfonate.

The hydrophilic nature of Tpms and its complexes makes them potentially useful in the area of enzyme modelling and catalysis, where systems that operate in aqueous solution are actively sought after due to the inherently potential sustainable processes [11]. Although the coordination properties of Tpms have been well studied towards diverse metal centers, the use of Tpms-containing hydrosoluble complexes in aqueous medium catalysis is limited to scarce examples, in particular for oxidation [16,33–35], hydroformylation [19], and hydrogenation [20] reactions. The catalytic activity of Tpms-metal complexes for nitroaldol (Henry) reaction has not yet been investigated.

Nitroaldol condensation [36] is carried out by coupling a nitroalkane with an aldehyde or ketone to produce the corresponding β-nitro alcohol. This reaction has found various applications [37–39], the produced β-nitro alcohols can be converted into other valuable intermediates, including α-nitro ketones by oxidation [40], β-amino alcohols by reduction [41], or nitroalkenes by dehydration [42].

Activation of the carbonyl group using Lewis acidic metal compounds for catalytic Henry reaction is an approach that has been intensively studied and performed with (i) a well-defined complex [28,43–53], (ii) an in situ generated complex by addition of a metal salt and a ligand [54–59], or (iii) a metal organic framework (MOF) [60–62]. In some instances a base is used to facilitate the deprotonation of the nitroalkane [56,63,64].

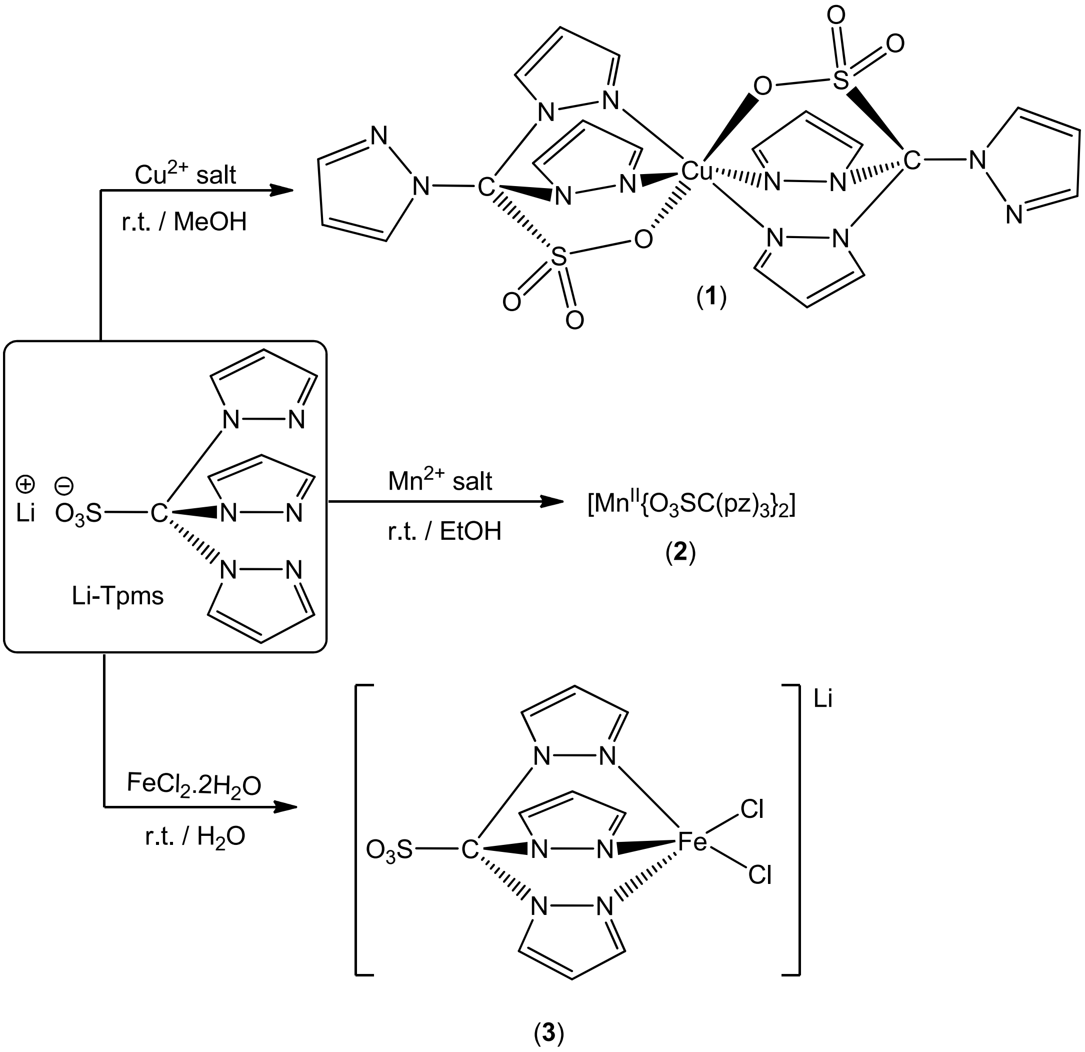
On the basis of the above considerations, herein we report the catalytic performance of well-defined hydrosoluble Cu(II), Mn(II), and Fe(II) complexes **1–3** bearing a Tpms ligand for Henry reaction in a homogeneous aqueous medium, for which a high Lewis acid character of the catalyst should constitute a favorable feature.

2. Results and Discussion

2.1. Synthesis and Characterization of Complexes

Reacting Cu(II), Mn(II) salts (e.g., chlorides, nitrates, or acetates) or iron(II) chloride with Li(Tpms), under air and at room temperature, lead to the formation of complexes $[Cu(\kappa\text{-}NN'O\text{-Tpms})_2]$ (**1**), $[Mn(Tpms)_2]$ (**2**), and $Li[FeCl_2(\kappa\text{-}NN'N''\text{-Tpms})]$ (**3**), respectively (Scheme 2). Compound **2** is new, whereas reports on **1** [65] and **3** [33] have been found. A different experimental procedure for obtaining

1 has been followed which led to the authentication of its structure by single crystal X-ray diffraction. A novel structure for Li(Tpms) was also obtained and is described in the Supplementary Material file.



Scheme 2. Synthesis of compounds **1**–**3**.

Complexes **1**–**3** are stable in air both in the solid state and in solution. While **2** and **3** show a good solubility in water, DMSO and MeCN, **1** can be dissolved only in hot water after stirring for several hours, or upon addition of few drops of 0.1 M NH_4OH to raise the pH to 9. The formulations of **1**–**3** were confirmed by spectroscopic and analytical data (see experimental section). As expected, compounds **1** and **2** are paramagnetic.

The IR spectra of the compounds exhibit a set of bands with diverse intensities typical of the Tpms ligand [66], in particular the ν(C=C) and ν(C=N) vibrations of the pyrazolyl groups in the range of *ca.* 1651–1506 cm^{-1}, in addition to the ν(S=O) in the range of 1064–1036 cm^{-1}.

ESI-MS spectra for the complexes were obtained in water solutions. In the negative mode a common peak corresponding to $[O_3SC(pz)_3]^-$ is revealed and represents the base peak; in the positive mode the spectra of the complexes do not show the $[M]^+$ molecular ion peak, but a set of other peaks assigned to the compounds fragmentations.

2.2. Description of the X-ray Crystal Structure

The molecular structure of **1** was established by single crystal X-ray diffraction (SCXRD) analysis. The crystals were obtained as described in the experimental section. Selected crystallographic data and structure refinement details are provided in Table S1. Selected bond distances and angles are listed in Table S2.

Complex **1** crystallized in the orthorhombic space group *Pbca*, its asymmetric unit comprising the copper metal cation and one Tpms unit (Figure 2). The metal presents a slightly distorted N_4O_2 octahedral geometry, with the ligands exhibiting κ-*NN′O* coordination modes. The N-donor atoms occupy the equatorial positions with Cu–N bond distances of 1.9829(16) and 1.9898(16) Å, and the O-atoms stand on the axial positions rendering Cu–O lengths of 2.3480(16) Å. The former values are shorter than those found in the Cu(I) complex [Cu(PPh$_3$)(κ-*NN′O*-Tpms)] [2.003(3) and 2.032(2) Å] [65], on account of the metal lower oxidation state in the latter. However, it is also lower than those found in the copper(II) complex with 2,2,2-tris(pyrazol-1-yl)ethyl methanesulfonate ligands, working as *NNN*-chelators [1.999(3)–2.347(3) Å] [67]. Although the long Cu–O dimension in **1** can be due to Jahn-Teller distortion [68–70], it is similar to that found in the Cu(I) complex [65]. The coordinated pyrazolyl rings and sulfonate group restrict the intra-ligand N–Cu–N and N–Cu–O angles to the range 83.32(7)°–86.28(7)°, it is therefore shorter than the expected 90°.

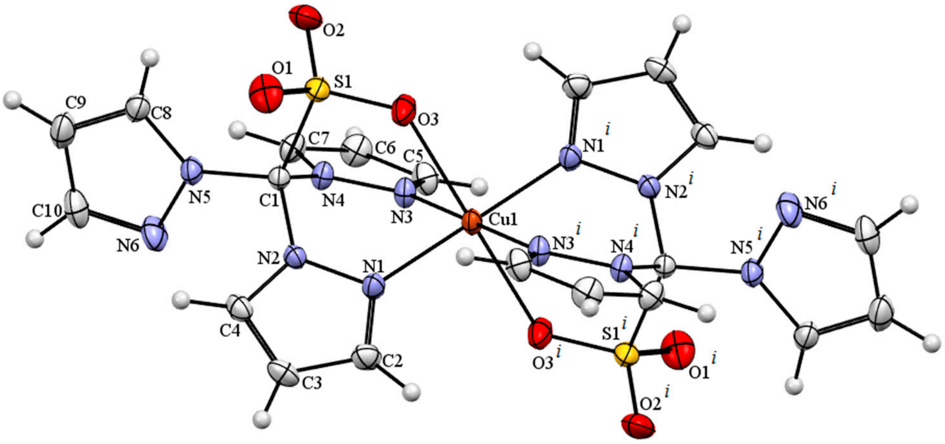
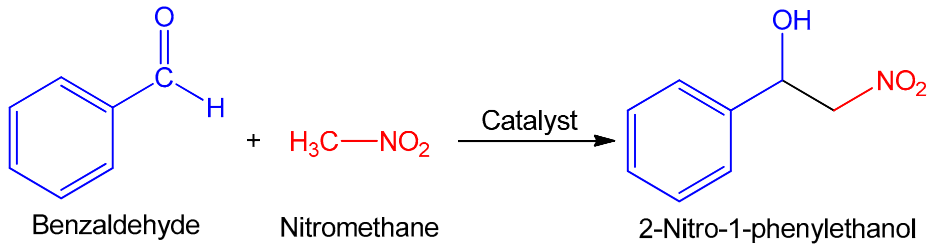


Figure 2. ORTEP diagram of **1** with displacement ellipsoids shown at 40% probability level and partial atom labelling scheme. Symmetry operation (*i*) to generate the equivalent atoms: -x,-y,1-z.

2.3. Catalytic Activity

Compounds **1–3** were tested, under atmospheric mild homogeneous reaction conditions, as catalysts for nitroaldol coupling of nitromethane with benzaldehyde in water to afford 2-nitro-1-phenylethanol. Using as a model the reaction of benzaldehyde with nitromethane (see Table 1), using 5 mol% of catalyst in water as sole solvent for 24 h and at 75 °C, the Cu(II) complex **1** exhibited the highest catalytic activity for the Henry reaction (Table 1, entries 1–3). Therefore, it was employed for further exploration of several reaction variables in order to find the optimum conditions to afford the highest yield of the product.

Table 1. Henry reaction of nitromethane with benzaldehyde catalyzed by **1–3** [a].



Entry	Catalyst	Cat. load [b] (mol%)	Time (h)	Temp. (°C)	Solvent	Yield [c] (%)	TON [d]
1	**1**	5	24	75	water	56	11
2	**2**	5	24	75	water	27	5
3	**3**	5	24	75	water	41	8
4	**1**	5	6	75	water	27	5
5	**1**	5	8	75	water	33	7
6	**1**	5	12	75	water	40	8
7	**1**	5	36	75	water	68	14
8	**1**	5	48	75	water	77	15
9	**1**	5	72	75	water	76	15
10	**1**	5	24	60	MeOH	61	12
11	**1**	5	24	60	EtOH	23	5
12	**1**	5	24	60	MeCN	7	1
13	**1**	5	24	60	CH_2Cl_2	<5	-
14	**1**	5	24	60	toluene	<5	-
15	**1**	5	24	60	water	49	10
16	**1**	5	24	60	water + MeOH	59	12
17	**1**	5	24	60	water + EtOH	47	9
18	**1**	5	24	60	water + MeCN	36	7
19	**1**	5	24	60	water + CH_2Cl_2	28	6
20	**1**	5	24	60	water + toluene	31	6
21	**1**	5	48	23	water/MeOH	51	10
22	**1**	5	48	60	water/MeOH	78	16
23	**1**	5	48	100	water/MeOH	89	18
24	**1**	0.5	48	60	water/MeOH	14	28
25	**1**	1	48	60	water/MeOH	39	39
26	**1**	3	48	60	water/MeOH	51	17
27 [e]	**1**	5	12	23	water	>99	20
28	$CuSO_4.5H_2O$	5	24	75	water	12	2
29	$Cu(OAc)_2.H_2O$	5	24	75	water	38	8
30	$CuCl_2.2H_2O$	5	24	75	water	18	4
31	$Cu(NO_3)_2.2.5H_2O$	5	24	75	water	26	5
32	**1**	5	24	60	solvent free	-	-
33	-	-	24	60	water/MeOH	-	-
34	$(C_2H_5)_3N$	5	12	23	water	41	8

[a] Reaction conditions: benzaldehyde (0.5 mmol, 1 equiv.), nitromethane (2.5 mmol, 5 equiv.), 2 mL of solvent, with 1:1 ratio in case of mixtures. [b] Calculated based on benzaldehyde. [c] Determined by ^1H NMR analysis of the products in crude form (see Figure S3). [d] Moles of 2-nitro-1-phenylethanol per mol of catalyst. [e] In the presence of 5 mol% triethylamine.

The reaction progression with time has been monitored in water using 5 mol% of the catalyst, at 75 °C (Table 1, entries 1 and 4–9). 2-Nitro-1-phenylethanol yield raised gradually with time up to 77% upon 48 h, and a further extension of the reaction time did not lead to a significant change.

Performing the reaction in different solvents (Table 1, entries 10–20, and Figure 3) revealed the following points: using solely a protic solvent (e.g., water, methanol, or ethanol) led to higher 2-nitro-1-phenylethanol yields than the use of other organic solvents for the same period of time (Table 1, entries 10–15); MeOH gave the highest yield of 61%. Generally, by using a 1:1 combination of water and organic co-solvent (Table 1, entries 16–20) better yields were obtained. A 1:1 mixture of water and MeOH gave a yield (59%) very close to that obtained using MeOH alone (Table 1, entries 10 and 16). Finally, the use of a 1:1 immiscible mixture of CH_2Cl_2 or toluene with water in a bi-phasic catalytic system gave lower product yields (28% and 31%, respectively) when compared to other miscible aqueous combinations (Table 1, compare entries 16–20).

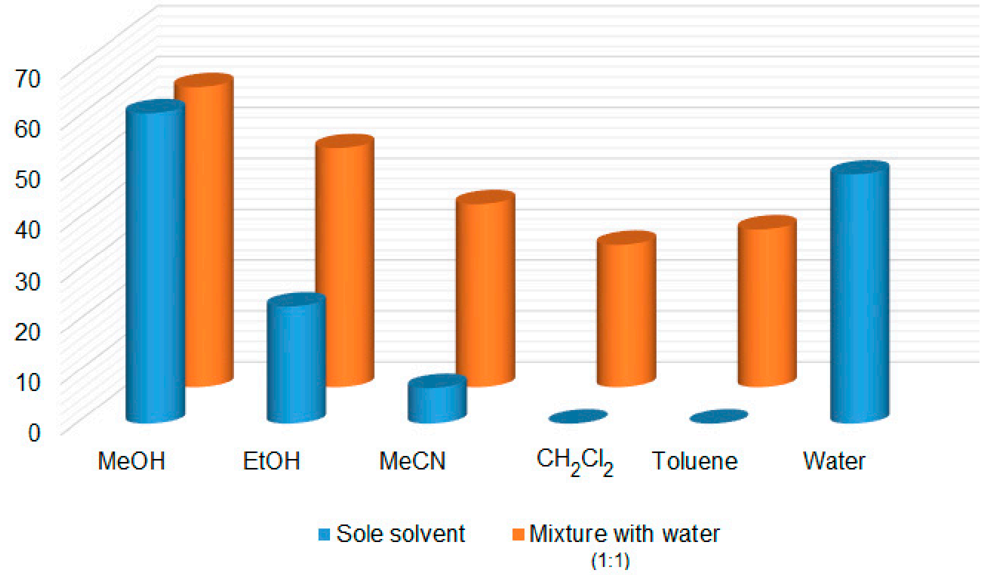


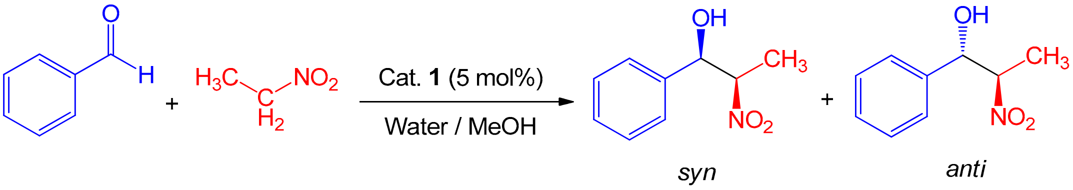
Figure 3. Effect of the solvent type on the reaction yield, using sole solvents (blue, in the front) and aqueous 1:1 combination (Orange, in the back).

It was observed that in a mixture of water and MeOH, the rise in temperature up to 100 °C led to an increase in the reaction yield to 89% after 48 h (Table 1, entries 21–23). Also, increasing the catalyst loading from 0.5 mol% to 5 mol% raised the reaction yield from 14% to 78% (Table 1, entries 22 and 24–26).

In the presence of an additional catalytic amount of a base (i.e., 5 mol% of catalyst **1** and a similar amount of triethylamine), the conversion was quantitative after only 12 h in water, at room temperature (Table 1, entry 27). With Cu(II) salts as catalysts, only 12 to 38% conversions were achieved after 24 h at 75 °C (Table 1, entries 28–31). The reaction does not show any progression under solvent-free conditions or in the absence of the catalytic metal species (Table 1, entries 32 and 33). With triethylamine and in the absence of catalyst **1**, a conversion of 41% was obtained after 12 h at room temperature (Table 1, entry 34).

By replacing nitromethane in the model reaction with nitroethane, the β-nitro alcohol is produced in the diastereoisomeric *syn* and the *anti* forms of 2-nitro-1-phenylpropanol (Table 2). In a water/MeOH (1:1) mixture, using 5 mol% of catalyst **1** at 100 °C a yield of 85% (maximum) was reached in 48 h exhibiting superior selectivity for the *syn* isomer (Table 2, entries 1–4). The presence of 5 mol% of triethylamine improved the reaction performance in terms of yield (97%) at ambient temperature and in a shorter time and but with a significant decrease in selectivity (Table 2, entry 5).

Table 2. Selected data for the Henry coupling of benzaldehyde with nitroethane catalyzed by complex **1** [a].



Entry	Time (h)	Temp. (°C)	Total yield [b] (%)	Selectivity [c] (*syn*:*anti*)	TON [d]
1	6	100	29	77:23	5.8
2	12	100	47	74:26	9.4
3	24	100	61	73:27	12.2
4	48	100	85	75:25	17.4
5 [e]	24	23	96	51:49	19.2

[a] Reaction conditions: benzaldehyde (0.5 mmol, 1 equiv.), nitroethane (2.5 mmol, 5 equiv.), 5 mol% of catalyst **1**, 2 mL of water/MeOH (1:1). [b] Calculated based on benzaldehyde. [c] Determined by ^1H NMR analysis of the products in crude form (see Figure S4). [d] Moles of 2-nitro-1-phenylpropanol per mol of catalyst. [e] In the presence of triethylamine (5 mol%).

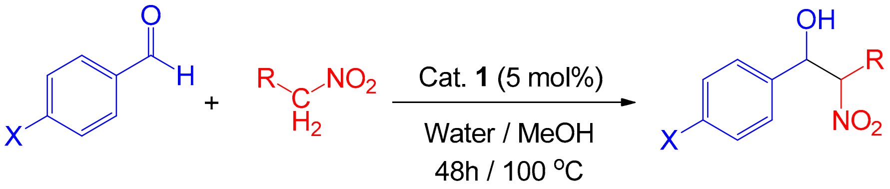
In accordance with previous studies, [71–74] the mechanism of the reaction involves metal assisted (upon coordination) deprotonation of nitroalkane to produce the nitronate species, and activation of the aldehyde for its electrophilic attack to the nitronate. Therefore, the Cu(II) complex **1** acts efficiently as a Lewis acid for the aforementioned activation process and, furthermore, the Tpms ligand can behave as a base to enhance the nitroalkane deprotonation.

Based on the study of several variables, it was found that the best reaction conditions to obtain the highest possible yield of β-nitro alcohols using catalyst **1** (5 mol%) is by heating the reaction mixture at 100 °C for 48 h in a mixture of water and MeOH.

The scope of the catalytic reaction was broadened to include different *para*-substituted aromatic aldehydes (Table 3) under the aforementioned optimum conditions.

Using either nitromethane or nitroethane, the reaction proceeded smoothly to afford the corresponding β-nitro alcohols with yields up to 94%, exhibiting higher selectivity towards the *syn* isomer if nitroethane was employed. The results show that the aromatic aldehydes with electron-donating substituents (OCH_3 or CH_3, Table 3, entries 1–4) exhibit a lower reactivity than those bearing electron-withdrawing groups (NO_2, Br or Cl, Table 3, entries 7–12) due to the higher electrophilicity of the aldehyde in the latter case. In comparison to the scarce examples found in the literature for the catalytic nitroaldol reaction in water, using catalysts based on different metals (Table S3), the conversions obtained in this work are comparable, or better in some cases, taking into consideration the indicated reaction conditions such as temperature, amount of catalyst, and reaction time [43,44,60–62,75–80].

Table 3. Selected data for the Henry coupling of nitroalkanes with various aldehydes catalyzed by complex **1** [a].



Entry	X	R	Yield [b] (%)	Selectivity [b] (*syn*:*anti*)	TON [c]
1	MeO	H	53	-	11
2		Me	47	68:32	9
3	Me	H	81	-	16
4		Me	74	72:28	15
5	H	H	89	-	18
6		Me	85	74:26	17
7	NO_2	H	94	-	19
8		Me	88	73:27	18
9	Br	H	91	-	18
10		Me	86	70:30	17
11	Cl	H	89	-	18
12		Me	86	71:29	17

[a] Reactions conditions (unless stated otherwise): 100 °C, 48 h in air, aldehyde (0.5 mmol), nitroalkane (2.5 mmol), 5 mol% of **1**, 2 mL of water and MeOH (1:1). [b] Determined by ^{1}H NMR analysis of crude products. [c] Moles of β-nitro alcohol per mol of catalyst.

3. Materials and Methods

3.1. General Procedures and Instrumentation

All synthetic procedures were performed in air. Reagents and solvents were obtained from commercial sources and used without further purification. Li(Tpms) [32] and complex **3** [33] were synthesized using the reported procedures.

C, H, N and S elemental analyses were carried out by the Microanalytical services of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were obtained in a Cary 630 FTIR spectrometer (Agilent, Santa Clara, CA, USA); wavenumbers are in cm^{-1}; abbreviations: s, strong; m, medium; w, weak. Electrospray mass spectra were obtained with a Varian 500 MS LC Ion Trap Mass Spectrometer equipped with an electrospray (ESI) ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. The compounds were observed in the negative and positive modes (capillary voltage = 80–105 V). ^{1}H spectra were obtained using Bruker Advance III 300 or 400 MHz UltraShield Magnet spectrometer (Bruker, Billerica, MA, USA), at ambient temperature.

3.2. Synthesis of Complexes

3.2.1. Synthesis of [Cu(Tpms)$_2$] (**1**)

To a MeOH solution (10 mL) of $Cu(NO_3)_2.2.5H_2O$ (38 mg, 0.165 mmol), Li(Tpms) (100 mg, 0.33 mmol) was added at room temperature to produce a blue-sky precipitate immediately. The solution was stirred for an additional 3 h. The blue-sky crystalline precipitate was filtered off, washed with MeOH, and dried under vacuum.

X-ray quality crystals of **1** were obtained after dissolving the compound (25 mg) in an acetonitrile: 0.1 M NH_4OH aqueous solution (10:1.5 mL) following slow evaporation in air. Compound **1** was also obtained when using different starting Cu^{2+} metal salts (e.g., acetate or chloride) or different stoichiometric ratios of the reagents.

Yield = 71%, based on copper (76 mg). Elemental analysis calcd (%) for $C_{20}H_{18}CuN_{12}O_6S_2$ (650.11 g/mol): C 36.95, H 2.79, N 25.85, S 9.86; found: C 37.24, H 2.83, N 25.72, S 9.89. FTIR (KBr pellet), ν (cm^{-1}): 3167 w [ν(C−H)]; 1635 m, 1506 w [ν(C=C) and ν(C=N)]; 1095 m, 1076 m, 1053 m, 1036 m [ν(S=O)]; 650 s [ν(S−C]; 479 m [ν(Cu−N]. ESI-MS$^{-/+}$ in H_2O (*m*/*z* assignment, % intensity): 293 ($[O_3SC(pz)_3]^-$, 100); 356 ($[Cu\{O_3SC(pz)_3\}]^+$, 100).

3.2.2. Synthesis of [Mn(Tpms)$_2$] (**2**)

To a solution of $Mn(NO_3)_2{\cdot}4H_2O$ (42 mg, 0.165 mmol) in EtOH (5 mL) was added, with constant stirring, Li(Tpms) (100 mg, 0.33 mmol) in EtOH (10 mL). A white precipitate was immediately observed, and the solution was stirred for 3 hours at room temperature. The solid was isolated by filtration, washed with cold EtOH, and dried under vacuum.

Yield = 68%, based on manganese (72 mg). Elemental analysis calcd (%) for $C_{20}H_{18}MnN_{12}O_6S_2.2H_2O$ (677.53 g/mol): C 35.45, H 3.27, N 24.81, S 9.77; found: C 35.83, H 2.98, N 24.33, S 10.19. FTIR (KBr pellet), ν (cm^{-1}): 3167 m [ν(C−H)]; 1636 m, 1532 w[ν(C=C) and ν(C=N)]; 1101 m, 1065 m, 1051 m, 1036 s [ν(S=O)]; 657 m, 639 s [ν(S−C)]; 446 m [ν(Mn−N]. ESI-MS$^{-/+}$ in H_2O (*m*/*z* assignment, % intensity): 293 ($[O_3SC(pz)_3]^-$, 100); 348 ($[Mn\{O_3SC(pz)_3\}]^+$, 100).

3.3. *General Procedure for β-Nitro Alcohols Synthesis*

In a typical experiment, a mixture of the nitroalkane (1.5 mmol), the catalyst (0.025 mmol) and 2 mL of solvent, was prepared with constant stirring for 15 minutes. Then, the aldehyde (0.5 mmol) was added. The solution stirred in atmospheric conditions and for the time intervals indicated in Tables 1–3. After the desired reaction time, 3 mL water were added to the solution and extracted with diethyl ether (3 × 10 mL). The combined extracts were dried over Na_2SO_4 (anhydrous), and the mixture filtered off. The diethyl ether was removed using vacuum, and the organic residue was analyzed by ^1H NMR spectroscopy, in $CDCl_3$, to calculate the yield of β-nitro alcohol as no other products were detected.

Using ^1H NMR spectroscopy to calculate the β-nitro alcohol yields constitutes an efficient way, as proved in several reports [45,63,75,80–83]. The ratio between the *anti* and *syn* diastereoisomers of 1-phenyl-2-nitropropanol, formed by the nitroaldol coupling using nitroethane, was also determined by ^1H NMR spectroscopy. Indeed, the vicinal coupling constants values between the α-O–C–*H* and the α-N–C–*H* protons identify the isomers (*anti*-isomer: J = 7–9 Hz; *syn*-isomer J = 3.2–4 Hz) [84,85].

3.4. *X-ray Structure Determination of Compounds*

An X-ray quality crystal of **1** and of Li(Tpms) were immersed in cryo-oil, mounted in a Nylon loop and measured at ambient temperature. Intensity data were collected in a Bruker AXS-KAPPA APEX II PHOTON 100 diffractometer (Bruker, Billerica, MA, USA) with graphite monochromated Mo-Kα (0.71069 Å) radiation. Data were collected using omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART [86] software and refined using Bruker SAINT [86] on all the observed reflections. SADABS program was used for applying absorption corrections [87]. The structure was solved by direct methods using SIR97 package [88] and refined with SHELXL-2014/7 [89]. The WinGX System-Version 2014.1 was used for the calculations [90]. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic ones for the remaining atoms were employed.

CCDC 1936856 (**1**) and 1936857 [Li(Tpms)] contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4. Conclusions

The tris(pyrazolyl)-methane sulfonate compounds [Cu(κ-*NN′O*-Tpms)$_2$] (**1**), [Mn(Tpms)$_2$] (**2**) and Li[FeCl$_2$(κ-*NN′N″*-Tpms)] (**3**) were the first Tpms complexes to be investigated as catalysts towards the nitroaldol (Henry) reaction between benzaldehyde and nitromethane to afford the corresponding 2-nitro-1-phenylethanol. Complex **1** was the most active (89% yield) under the following optimum reaction conditions: 5 mol% of catalyst, 1:1 water:MeOH solvent mixture, 100 °C, and for 48 h. Reacting benzaldehyde with nitroethane in the presence of **1**, and under the given experimental conditions, produced 2-nitro-1-phenylpropanol in the *syn* and the *anti* diastereoisomeric forms, with a total yield of 85% and a higher selectivity towards the former. The scope of the reaction was broadened to include several aromatic aldehydes, which were reacted with any of the nitroalkanes. Higher yields (up to 94%) were obtained with aldehydes possessing electron-withdrawing groups.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/7/611/s1: Figure S1: ORTEP diagram of Li(Tpms) with displacement ellipsoids drawn at 40% probability level and partial atom labelling scheme, Figure S2: Structural fragment representing the two chains of the 1D polymer of Li(Tpms), Figure S3: ^{1}H NMR spectrum (CDCl$_3$; 400 MHz) of crude product from nitroaldol condensation of benzaldehyde with nitromethane using 5 mol% of catalyst **1** (Table 1, entry 23), Figure S4: ^{1}H NMR spectrum (CDCl$_3$; 400 MHz) of crude product from nitroaldol condensation of benzaldehyde with nitroethane using 5 mol% of catalyst 1 (Table 2, entry 2), Table S1: Crystallographic data and structure refinement details for Li(Tpms) and 1, Table S2: Selected bond distances (Å) and angles (°) for Li(Tpms) and **1**, Table S3: Comparison of various catalytic systems for Henry reaction of benzaldehyde with nitroethane in aqueous medium.

Author Contributions: L.M.D.R.S.M. and A.G.M. conceived and designed the experiments; M.F.C.G.d.S. performed, solved and discussed the single-crystal X-ray diffraction data; A.G.M., M.F.C.G.d.S., L.M.D.R.S.M. and A.J.L.P. discussed the whole data and wrote the paper. All authors read and approved the manuscript.

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