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A pyridyl-triazole ligand for ruthenium and iridium catalyzed C=C and C=O hydrogenations in water/organic solvent biphasic systems

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ABSTRACT

The water soluble pyridyl-triazole ligand sodium 2-(1-((pyridin-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl) ethyl sulfate (Na**1**) has been successfully employed in combination with ruthenium and iridium for catalytic hydrogenation of C=C and C=O double bonds in water/toluene biphasic systems. Reaction of the ligand with $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ affords the new water soluble complex $[RuCl(\eta^6\text{-}p\text{-cymene})(\mathbf{1})]$ (**2**) which has been found to be catalytically active in the water/organic solvent biphasic hydrogenation using styrene and 2-cyclohexen-1-one as model substrates. Very conveniently, the iridium based catalytic system is prepared by simply stirring in water $[Ir(\eta^4\text{-COD})Cl]_2$ with Na**1** (Ir:Na**1** molar ratio = 1:4), the resulting solution is catalytically active and appears more efficient than **2**. With both the Ru- and Ir-based systems the catalytically active aqueous phases can be used at least three times without loss of activity.

1. Introduction

Homogeneous catalysts generally provide very good activities and selectivities, but their application in industrial processes is hampered by their difficult separation from the reaction products. Furthermore, recovery of homogeneous catalysts appears very often a challenging and expensive task. For all these reasons, the development of water soluble catalysts, whose separation from reagents and products could allow a prompt recycle of the catalytically active species, is highly desirable [1–5]. This provides an inexpensive answer to the challenge of preserving resources, making the process more environmentally friendly.

Nowadays water-soluble catalysts are increasingly employed either in water or in water/organic solvent biphasic mixtures.

The most commonly employed catalysts in water/organic phase biphasic systems are metal complexes modified with water soluble phosphines, such as TPPTS (triphenylphosphine-3,3′,3″-trisulfonic acid trisodium salt) which, for instance, is employed in the renowned OXEA (former Ruhrchemie/Rhône-Poulenc) hydroformylation process [4–8].

In the last years new species bearing different hydrophilic groups such as —COOH, $-NR_3^+$, —OH, etc. [1–4] and also natural compounds, such as aminoacids, peptides, proteins and sugars have been used as ligands in combination with transition metal species in order to obtain catalysts active in water [9–18].

For some time now, our research group has been involved in the synthesis of triazolyl ligands taking advantage of the copper-catalyzed azide-alkyne [3+2] cyclization (Scheme 1) [19–22]. Employing this efficient strategy we have synthesized a small library of N—N or N—S ligands which were successfully employed in palladium catalyzed Suzuki–Miyaura reactions [23,24]. As a part of this ongoing research we have recently reported the synthesis of the water soluble ligand Na**1** (Scheme 1) [25], which was successfully employed in aqueous phase palladium catalyzed S–M coupling reactions.

In the present work, we wish to report that Na**1** can be successfully employed as the ligand in combination with ruthenium and iridium to catalyze carbon–carbon and carbon–oxygen double bond hydrogenation in biphasic water/organic solvent mixtures.

2. Experimental

2.1. Materials and instrumentation

All reactions were carried out under inert atmosphere (argon) using standard Schlenk techniques. Commercial solvents (Sigma–Aldrich) were purified as described in the literature [26]. Sodium 2-(1-((pyridin-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl)

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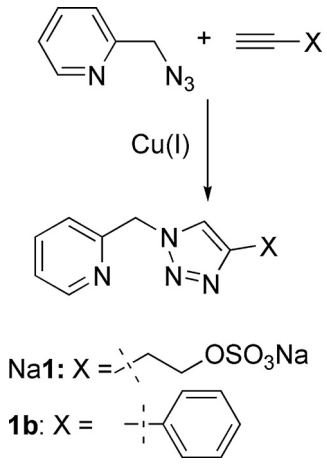

Scheme 1. General synthetic scheme for bidentate pyridyl-triazolyl ligands.

ethyl sulfate (Na**1**) was prepared as described in the literature [25]. $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ [27] and $[Ir(\eta^4\text{-COD})Cl]_2$ [28] were prepared according to literature methods. $[Ir(\eta^4\text{-COD})Cl]_2$ is also commercially available (Alfa Aesar).

^1H and ^{13}C NMR spectra were recorded in deuterated solvents (Sigma–Aldrich) on a Bruker Avance 300 spectrometer operating at 300.1 and 75.5 MHz, respectively; the chemical shift values are reported in δ units with reference to the residual solvent signal. The proton assignments were performed by standard chemical shift correlations as well as by ^1H 2D COSY experiments. The ^{13}C chemical shift values were assigned through DEPT-135 and 2D-heteronuclear correlation experiments (HMQC and HMBC).

ESI-MS analyses were performed using a Finnigan LCQ-Duo ion-trap instrument, operating in positive ion mode (sheath gas N_2, source voltage 4.0 kV, capillary voltage 21 V, capillary temperature 200 °C). Sample solutions were prepared by dissolving the Ru complex (1 mg) in methanol (1 mL) and then further diluting with methanol (1:30). Sample solutions were introduced into the ESI source by a syringe pump at 8 μL/min flow rate. All mass spectra were recorded on freshly prepared solutions. The ESI-MS data, reported below, have been confirmed by MS/MS experiments and isotope pattern analysis.

The solutions resulting from the catalytic experiments were analyzed by GLC on a 6850 Agilent Technologies gas-chromatograph employing HP-1 capillary column (30 m × 0.32 mm × 0.25 μm) or HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). GC–MS spectra were recorded on a HP 5890 series II gas-chromatograph interfaced to a HP 5971 quadrupole mass detector employing a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm). The reaction products were identified by comparison with commercial samples (Sigma–Aldrich). ICP-MS analyses were performed by using an Agilent 7500a-Series instrument.

2.2. Ruthenium catalyst synthesis **2**

In a 50 mL two-neck round-bottomed flask a mixture of sodium 2-(1-((pyridin-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl)ethyl sulfate (Na**1**) (118 mg, 0.39 mmol) and $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (118 mg, 0.20 mmol) was stirred in methanol (20 mL) at room temperature for 3 days under nitrogen. Then the mixture was filtered and taken to dryness in vacuo. The resulting yellow-orange solid was extracted with boiling ethanol and filtered; on standing overnight, orange microcrystals (155 mg, 72% yield) precipitate, mp 234 °C (dec). ^1H NMR (300 MHz, CD_3OD, 298 K) δ 9.11 (d, 1H, J = 5.8, H-1), 8.33 (s, 1H, H-7), 8.06 (td, 1H, J = 7.7 and 1.3 Hz, H-3), 7.77 (d, 1H, J = 7.2 Hz, H-4), 7.59 (m, 1H, J = 5.8 Hz, H-2), 6.10 (d, 1H, J = 15.8 Hz, H-6_A), 6.08 (d, 1H, J = 6.1 Hz, *p*-cym), 5.97 (d, 1H, J = 6.1 Hz, *p*-cym), 5.87 (d, 1H, J = 6.1 Hz, *p*-cym), 5.81 (d, 1H, J = 6.1 Hz, *p*-cym), 5.62 (d, 1H, J = 15.8 Hz, H-6_B), 4.28 (m, 2H, H-10), 3.11 (m, 2H, H-9), 2.92 (spt, 1H, J = 6.9 Hz, ArC<u>H</u>), 2.01 (s, 3H, ArC<u>H</u>$_3$), 1.31 (d, 6H, J = 6.9 Hz, CHC<u>H</u>$_3$). ^{13}C NMR (75.5 MHz, CD_3OD, 298 K) δ 159.5 (C-1), 154.7 (C-5), 149.7 (C-7), 141.8 (C-3), 130.1 (C-4), 127.4 (C-8 or C-2), 127.3 (C-8 or C-2), 107.9 (*p*-cym), 102.6 (*p*-cym), 89.0 (*p*-cym), 86.3 (*p*-cym), 85.6 (*p*-cym), 84.9 (*p*-cym), 67.1 (C-10), 55.4 (C-6), 32.2 (*p*-cym<u>C</u>H), 27.2 (C-9), 22.6 (CH<u>C</u>H$_3$), 22.3 (CH<u>C</u>H$_3$), 18.3 (*p*-cym<u>C</u>H$_3$). IR (KBr pellet) ν_{max}: 3591, 3461, 3127, 3073, 3022, 2947, 1603, 1468, 1431, 1254, 1218, 1005, 896, 773, 742, 581 cm^{-1}. Anal. Calc. for $C_{20}H_{25}ClN_4O_4RuS$ (554.0): C, 43.36; H, 4.55; N 10.11; Cl 6.40%. Found: C, 43.12; H, 4.54, N 9.88; Cl 6.15%.

2.3. Complex **2** aquation

5.5 mg (0.01 mmol) of complex **2** were dissolved in 1.0 mL of D_2O. The following is the description of the ^1H NMR spectrum registered immediately after dissolution. ^1H NMR of complex **2** (300 MHz, D_2O, 298 K) δ 9.03 (d, 1H, J = 5.8, H-1), 8.33 (s, 1H, H-7), 8.08 (td, 1H, J = 7.8 and 1.3 Hz, H-3), 7.78 (d, 1H, J = 7.2 Hz, H-4), 7.59 (m, 1H, J = 5.8 Hz, H-2), 6.08–6.00 (m, 3H, H-6_A and 2 H of *p*-cym), 5.90 (d, 1H, J = 6.1 Hz, *p*-cym), 5.88 (d, 1H, J = 6.1 Hz, *p*-cym), 5.62 (d, 1H, J = 15.8 Hz, H-6_B), 4.31 (m, 2H, H-10), 3.17 (m, 2H, H-9), 2.81 (spt, 1H, J = 6.9 Hz, ArC<u>H</u>), 2.07 (s, 3H, ArC<u>H</u>$_3$), 1.24 (d, 3H, J = 6.9 Hz, CHC<u>H</u>$_3$), 1.21 (d, 3H, J = 6.9 Hz, CHC<u>H</u>$_3$). On standing the signals relevant to complex **3** develop. The equilibrium is reached after 24 h. The ^1H NMR spectrum displays along with the above reported signals relevant to complex **2**, new signals attributed to the aquo species **3**, according to integration the **2**:**3** molar ratio is 0.45:0.55, respectively. ^1H NMR of complex **2** (300 MHz, D_2O, 298 K) δ 8.99 (d, 1H, J = 5.8, H-1), 8.37 (s, 1H, H-7), 8.15 (td, 1H, J = 7.8 and 1.3 Hz, H-3), 7.84 (d, 1H, J = 7.2 Hz, H-4), 7.72 (m, 1H, J = 5.8 Hz, H-2), 6.16–5.86 (overlapping multiplets attributed to 6_A and *p*-cym of **2** and **3**), 5.63 (d, 1H, J = 15.8 Hz, H-6_B), 4.31 (m, 2H, H-10), 3.17 (m, 2H, H-9), 2.81 (spt, 1H, J = 6.9 Hz, ArC<u>H</u>), 2.11 (s, 3H, ArC<u>H</u>$_3$), 1.25–1.19 (overlapping multiplets attributed to CHC<u>H</u>$_3$ of **2** and **3**).

2.4. Hydrogenation experiments with catalyst **2**

As an example the experimental details relevant to Entry 3 in Table 1 are reported. In a Schlenk tube, a toluene solution of styrene (374 mg, 3.6 mmol in 2.0 mL) was added to an aqueous solution of **2** (4.0 mg, 0.0072 mmol in 2.0 mL of water) under nitrogen atmosphere. The Schlenk tube was then transferred into a 150 mL stainless steel autoclave under nitrogen. The reactor was pressurized at p(H_2) = 4.0 MPa and then heated at 80 °C under magnetic stirring. After 6 h the autoclave was cooled to room temperature and the residual gas vented off.

The organic phase was carefully separated, dried on Na_2SO_4 and, after the addition of 0.5 mmol of mesitylene (as the internal GC

Table 1
Biphasic hydrogenation of styrene in the presence of the ruthenium catalyst **2**.[a]

Entry	p(H_2) (MPa)	t (h)	%Conv.[b] (TOF[c])		
			1st Run	2nd Run	3rd Run
1	4.0	1	25 (125)	64 (320)	60 (300)
2	4.0	3	62 (103)	96 (160)	99 (165)
3	4.0	6	100 (83)	100 (83)	100 (83)
4	3.0	6	98 (81)	99 (82)	99 (82)
5	2.0	6	78 (65)	92 (77)	88 (73)

[a] Reaction conditions: [RuCl(η⁶-*p*-cymene)(**1**)] = 4.0 mg (0.0072 mmol), styrene = 374 mg (3.59 mmol), T = 80 °C, H_2O = 2.0 mL, toluene = 2.0 mL, substrate:Ru (molar ratio) = 500:1.
[b] By GLC.
[c] Mol of hydrogenated product/mol of catalyst per hour.