



Copper(II) arylhydrazone complexes as catalysts for C–H activation in the Henry reaction in water



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ABSTRACT

Three new water-soluble copper(II) complexes $[\text{Cu}(\text{HL})(\text{H}_2\text{O})\{(\text{CH}_3)_2\text{NCHO}\}]$ (**1**), $[\text{Cu}(\text{H}_2\text{L})_2(\text{im})_4]\cdot\text{CH}_3\text{OH}$ (**2**) and $[\text{Cu}(\text{HL})(\text{CH}_3\text{OH})_2(\mu_2\text{-py})]$ (**3**) were synthesized from copper(II) nitrate and sodium (*Z*)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazinyl)benzene-sulfonate (NaH_2L), in the absence (for **1**) and presence of imidazole (*im*) (for **2**) or pyrazine (*py*) (for **3**), and fully characterized. The complexes **1–3** have been tested as stereoselective C–H activating catalysts for the model nitroaldol (Henry) condensation of nitroethane with various aldehydes in water. **1** was the most active catalyst affording 64–87% yields with *syn/anti* diastereoselectivities up to 77:23.

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1. Introduction

The C–H activation of alkanes in water with Pt complexes (the so-called Shilov reaction) remains a conceptual breakthrough which demonstrates the possibility to transform essentially inert and hydrophobic substrates into their water-soluble oxidation products of a much higher added value and reactivity [1]. In spite of the initial expectations, elaboration of new effective catalysts for such transformations is still far from perfection, and many efforts continue to be poured into the field [2]. One of the approaches is related to the preparation of suitable metal-organic catalytic species, which, on one hand, can provide (stereo)specific interaction with a hydrophobic substrate and a catalytic centre (e.g. a transition metal ion), while, on the other hand, facilitate interac-

tion with reaction media, where water is the preferable case due to a number of reasons [1c,3].

Arylhydrazones of active methylene compounds (AHAMC) modified with $-\text{SO}_3\text{H}$ and/or $-\text{COOH}$ substituents can be used as ligands for a number of copper(II) catalyzed C–H functionalizations in water [4]. Imidazole (*im*) and pyrazine (*py*) are also known to play an important role in the design of many C–H activating homogeneous catalysts, regulating their solubility, buffer capacity, stability and eventually the overall activity [4b,5]. Hence, the preparation of new heteroligand water-soluble copper homogeneous catalysts with the abovementioned ligands is of interest for the area of C–H (stereo)specific functionalization in aqueous media. The well studied and widely applied Henry coupling can be used as a model reaction to test the activity and stereoselectivity of the catalysts towards aliphatic nitroalkanes.

The Henry (nitroaldol) reaction concerns the interaction between the carbonyl carbon atom of an aldehyde and the α -carbon atom of an aliphatic nitro compound to give a new C–C bond. Using this simple transformation, one can construct a variety

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of biologically active polyfunctionalized compounds with several stereogenic centres from relatively cheap and available starting materials [6]. This reaction can be catalyzed by a base, transition *d* [7–11] or *f* [12] metal complexes as well as some organocatalysts [13]. Amongst these protocols, Cu-catalyzed Henry couplings have recently received much attention [7], but most of them are performed in harmful organic solvents. In order to avoid the organic solvents, one can prepare water-soluble copper complexes, e.g. by suitable functionalization of ligands, and study their catalytic performance towards the Henry reaction in water medium.

Thus, in this work we combine the abovementioned approaches towards the following aims: (i) to synthesize a new water-soluble AHAMC ligand bearing a $-\text{SO}_3\text{H}$ group, namely (*Z*)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazinyl)benzenesulfonate (NaH_2L); (ii) to prepare new aquasoluble Cu^{II} -AHAMC complexes, bearing imidazole and pyrazine ligands; (iii) to test the obtained complexes as catalysts or catalyst precursors for the Henry reaction in water medium, as well as in other solvents or under solvent-free conditions, for comparative purposes.

2. Experimental

2.1. Materials and instrumentation

All the chemicals were obtained from commercial sources (Aldrich) and used as received. The infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were done using a "2400 CHN Elemental Analyzer" by Perkin Elmer. The ^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance II + 300 (UltraShield™ Magnet) spectrometer operating at 300.130 and 75.468 MHz for proton and carbon-13, respectively. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference. Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument

(Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray 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. Scanning was performed from m/z 0–1200 in methanol solution. The compounds were observed in the negative or positive mode (capillary voltage = 80–105 V).

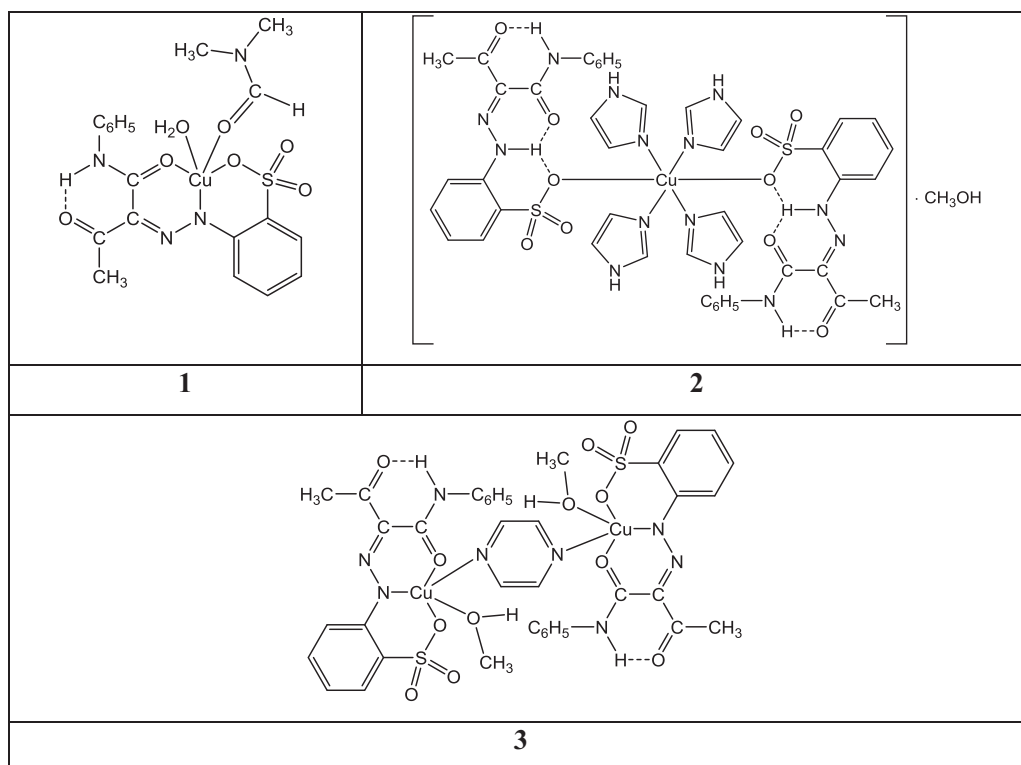
2.2. Synthesis of NaH_2L

NaH_2L was synthesized similarly to a well-established procedure [4], by azocoupling of 2-sulfo benzenediazonium chloride with acetoacetanilide in the presence of sodium hydroxide.

Diazotization: A 10 mmol (1.73 g) portion of 2-aminobenzenesulfonic acid was dissolved in 50 mL of water upon addition of 0.6 g of solid NaOH. The solution was cooled in an ice bath to 0°C and 10 mmol (0.69 g) of NaNO_2 were added with subsequent addition of 2 mL 33% HCl in portions of 0.4 mL for 1 h, under vigorous stirring. During the reaction, the temperature of the mixture must not exceed $+5^\circ\text{C}$. The obtained diazonium salt was used for the next stage (see below).

Azacoupling: 10 mmol (0.40 g) of NaOH were added to a mixture of 10 mmol (1.77 g) of acetoacetanilide with 30 mL of water-ethanol (1/30, v/v). The solution was cooled in an ice bath, and a suspension of the diazonium salt (prepared according to the procedure described above) was added in two equal portions under rigorous stirring for 1 h. The formed yellow precipitate of NaH_2L was filtered off, recrystallized from methanol and dried in air.

NaH_2L : Yield 77% (based on acetoacetanilide), yellow powder, soluble in water, DMSO, methanol, ethanol and dimethylformamide and insoluble in non-polar solvents. Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_3\text{NaO}_5\text{S}$ ($M_r = 383.35$): C, 50.13; H, 3.68; N, 10.96. Found: C, 50.03; H, 3.72; N, 10.88%. IR (KBr): 3532 (br.) $\nu(\text{H}_2\text{O})$, 3098 and 2925 $\nu(\text{NH})$, 1669 $\nu(\text{C}=\text{O})$, 1601 $\nu(\text{C}=\text{O} \cdots \text{H})$, 1563 $\nu(\text{C}=\text{N})$ cm^{-1} . MS (ESI) (negative ion mode): m/z : 360.3 [$M_r - \text{Na}$] $^-$. ^1H NMR (DMSO- d_6): δ 2.55 (3H, CH_3), 7.14–7.80 (9H, Ar-H), 11.11 (s, 1H, NH), 14.37



Scheme 1. Schematic representation of 1–3.

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