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Short Communication

Water-soluble diphosphadiazacyclooctanes as ligands for aqueous organometallic catalysis

Jérôme Boulanger [a], Hervé Bricout [a], Sébastien Tilloy [a], Aziz Fihri [b], Christophe Len [c], Frédéric Hapiot [a,*], Eric Monflier [a]

[a] Université Lille Nord de France, CNRS UMR 8181, Unité de Catalyse et de Chimie du Solide, UCCS, UArtois, Faculté Jean Perrin, rue Jean Souvraz, SP18, F-62307 Lens Cedex, France
[b] KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology Thuwal 23955, Kingdom of Saudi Arabia
[c] Transformations Intégrées de la Matière Renouvelable - EA 4297 UTC/ESCOM, Université de Technologie de Compiègne, Centre de Recherches de Royallieu, BP 20529, rue Personne de Roberval, F-60205 Compiègne cedex, France

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ABSTRACT

Two new water-soluble diphosphacyclooctanes been synthesized and characterized by NMR and surface tension measurements. Both phosphanes proved to coordinate rhodium in a very selective way as well-defined bidentates were obtained. When used in Rh-catalyzed hydroformylation of terminal alkenes, both ligands positively impacted the reaction chemoselectivity.

1. Introduction

Since the 1970's and the synthesis by E. Kuntz of the benchmark TPPTS ligand, the design of innovative and efficient water-soluble ligands for aqueous organometallic catalysis has always been a challenge [1]. The main role of water-soluble ligands is to stabilize a catalyst into the aqueous phase of a biphasic reaction which results in many benefits [2]. First, the organic products and water-soluble ligand-stabilized catalysts could be easily separated and recovered upon completion of the reaction by simple decantation. Second, the catalytic system could be recycled giving this method a considerable advantage over homogeneous processes. Third, even if alternatives have been developed in other media such as fluorous solvents [3], supercritical CO_2 [4,5] and ionic liquids [6], water remained the best eco-friendly solvent because it is cheap, available in large quantities, non-toxic and non-flammable, to mention only some the main features. Most commonly, the synthesis of water-soluble ligands consists in grafting water-solubilizing groups to known hydrophobic ligands. In this respect, suitable ionic substituents (sulfonate, carboxylate, phosphonate, or ammonium) or nonionic hydrophilic substituents (polyols, carbohydrates, and polyethers) can be used [7–14]. Many water-soluble mono- and polydentate ligands have thus emerged among which phosphanes are the most widely used in catalytic processes. They have been used in various aqueous organometallic reactions, the most studied being hydrogenation, hydroformylation and cross-coupling reactions [2]. Recently, one of us published the synthesis of a 1,5-diphenyl-3,7-dicyclohexyl-1,5-diaza-3,7-diphosphacyclooctane ligand which proved to be effective in a Pd-catalyzed Suzuki-Miyaura cross-coupling reaction [15]. However, the poor water-solubility of the ligand limited its application in aqueous organometallic catalysis and prompted us to develop its water-soluble version. In this context, the sulfonated ligands **1** and **2** (Scheme 1) have been synthesized and their catalytic performance has been evaluated in a Rh-catalyzed hydroformylation of terminal alkenes.

2. Experimental

2.1. General

Organic compounds were purchased from Aldrich Chemicals in their highest purity and used without further purification. All liquid reagents were degassed by bubbling nitrogen for 15 min before each use or by two freeze-pump-thaw cycles before use. Distilled deionized water was used in all experiments. All reactions and workup procedures were performed under an inert atmosphere using conventional vacuum-line and glasswork techniques.

2.2. Mass spectrometry

High-resolution electrospray mass spectra (ESI-HRMS) in the positive ion mode were obtained on a Q-TOF Ultima Global hybrid quadrupole time-of-flight instrument (Waters-Micromass), equipped with a pneumatically assisted electrospray (Z-spray) ionization source and an additional sprayer (Lock Spray) for the reference compound. The

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[*] Corresponding author. Tel.: +33 3 2179 1773; fax: +33 3 2179 1755.
E-mail address: frederic.hapiot@univ-artois.fr (F. Hapiot).

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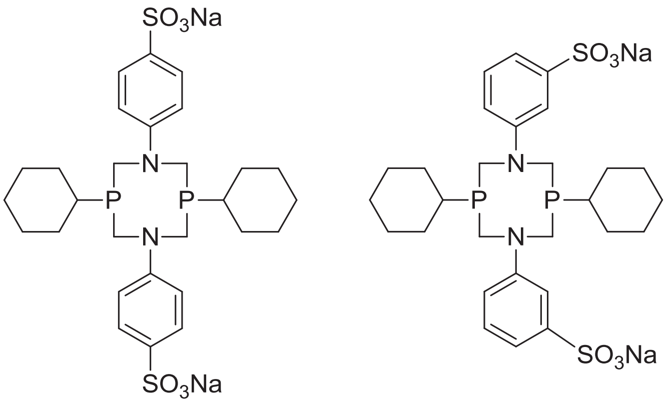


1 **2**

Scheme 1. Water-soluble diphosphadiazacyclooctanes derivatives **1** and **2**.

purified compounds were dissolved in methanol (0.01 mg/mL) and the solutions were directly introduced (5 mL/min) through an integrated syringe pump into the electrospray source. The source and desolvation temperatures were 80 and 150 °C, respectively.

2.3. NMR measurements

NMR spectra were recorded at 25 °C on a Bruker DRX300 spectrometer operating at 300 MHz for ^{1}H nuclei, 75.5 MHz for ^{13}C nuclei and 121.5 MHz for ^{31}P nuclei. $^{31}P\{^{1}H\}$ NMR spectra were recorded with an external reference (85% H_3PO_4). D_2O (99.92% isotopic purity) was purchased from Euriso-Top.

2.4. Phosphanes synthesis

A Schlenk flask was charged with cyclohexylphosphine (10% in hexane, 14.6 mL, 8.3 mmol), degassed aqueous formaldehyde (37%, 1.92 mL, 25.8 mmol) and distillated acetonitrile (25 mL). After 2 h stirring at room temperature, the solvents were removed under vacuum and the resulting oil was combined with sodium 4-aminobenzenesulfonate (1.62 g, 8.3 mmol) in degassed ethanol (20 mL) and was refluxed overnight. The resulting suspension was cooled to room temperature. The precipitate was filtered and washed with copious dry ethanol and vacuum dried to yield phosphane **1** as a white powder (4.6 g, 6.86 mmol, 83%). A similar procedure was used to synthesize phosphane **2** except for the use of sodium 3-aminobenzenesulfonate (1.62 g, 8.3 mmol), which yielded a similar white product (4.8 g, 7.2 mmol, 87%). The NMR analysis of phosphanes **1** and **2** is detailed in Supporting Information.

2.5. Determination of the phosphane basicity

Phosphane selenides were synthesized by refluxing an excess of selenium (10 eq.) with the phosphane (25 mg) in absolute ethanol (1.5 mL) under nitrogen for 15 h [16]. The resulting mixture was directly analyzed by $^{31}P\{^{1}H\}$ NMR without any purification. In all cases, NMR spectra exhibit the presence of phosphane selenides which are characterized by a singlet with two satellites due to only 7.6% of active selenium isotope (^{77}Se) in NMR spectroscopy.

2.6. Surface tension measurements

The surface tension measurements were performed using a KSV Instruments digital tensiometer (Sigma 70) with a platinum plate. The precision of the force transducer of the surface tension apparatus was 0.1 mN m^{-1}. The experiments were performed at 293 K ± 0.5 controlled by a thermostated bath Lauda (RC6 CS).

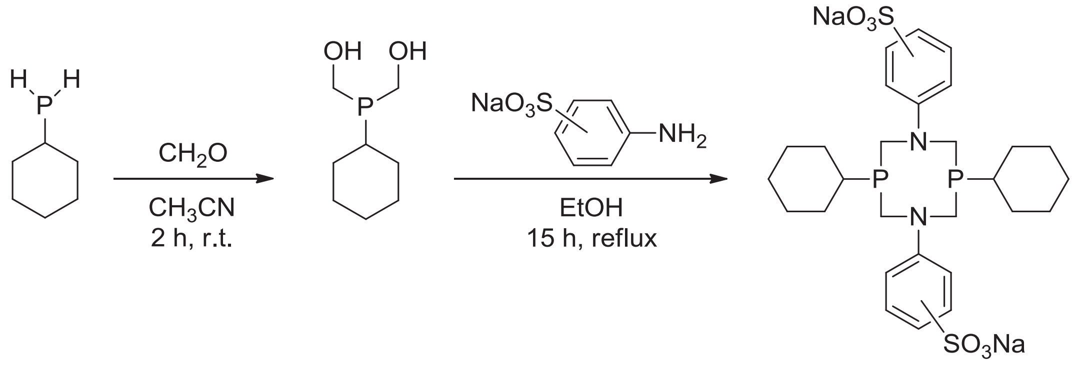
2.7. Typical procedure for the Rh-catalyzed hydroformylation of terminal alkenes

In a typical experiment, $Rh(acac)(CO)_2$ (0.04 mmol) and the water-soluble ligand (0.21 mmol) were dissolved in 11.5 mL of water. The resulting aqueous phase and the olefin (20.35 mmol) were charged into the 50 mL reactor, which was heated at the desired temperature. The mixture was stirred at 1500 rpm and the autoclave was pressurized with 50 atm of CO/H_2 (1:1) from a gas reservoir connected to the reactor through a high-pressure regulator valve allowing to keep constant the pressure in the reactor throughout the whole reaction. Once the reaction was complete, the organic phase was recovered by decantation. Gas chromatographic analyses of the organic phase were carried out on a Shimadzu GC-17 A gas chromatograph equipped with a polydimethylsiloxane capillary column (30 m × 0.32 mm) and a flame ionization detector (GC:FID).

3. Results and discussion

3.1. Synthesis of the water-soluble diphosphadiazacyclooctane derivatives

The synthesis of phosphanes **1** and **2** has been carried out as follows. Once cyclohexylphosphane and aqueous formaldehyde have been mixed to form the dihydroxymethylphosphane intermediate, reaction with sodium anilinesulfonates substituted in *meta-* or *para*-position led to the expected diphosphadiazacyclooctane derivatives



1 (para) or **2** (meta)

Scheme 2. Synthesis of diphosphanes **1** and **2**.