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Short Communication

Water-soluble diphosphadiazacyclooctanes as ligands for aqueous organometallic catalysis

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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.

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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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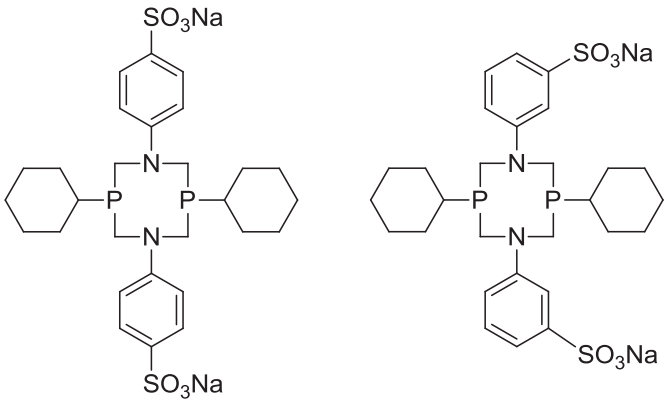


Scheme 1. Water-soluble diphosphadiazacyclooctanes derivatives **1** and **2**.

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).

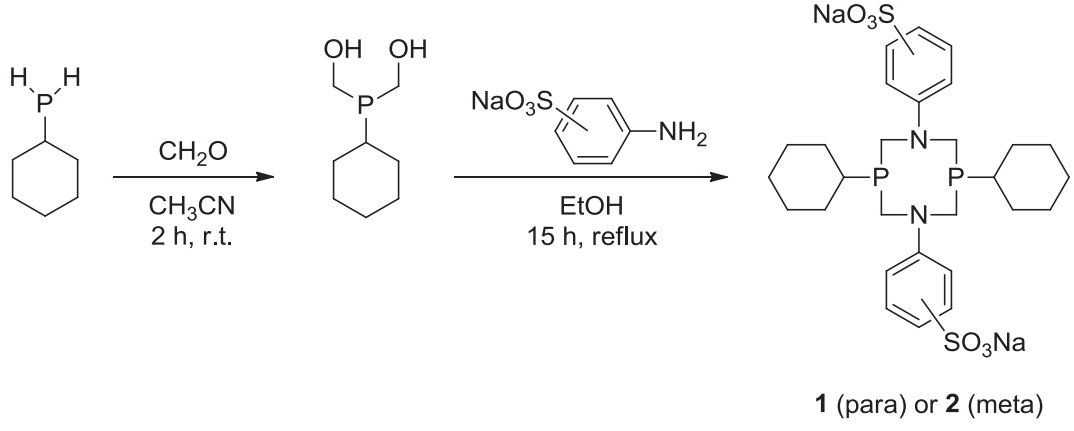
2.7. Typical procedure for the Rh-catalyzed hydroformylation of terminal alkenes

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).

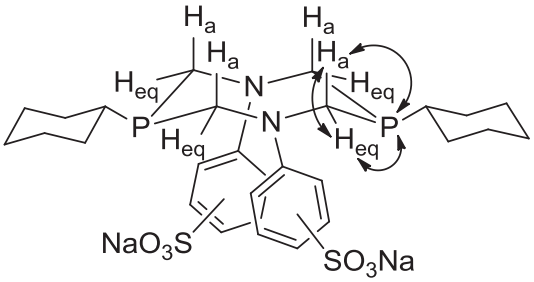
3. Results and discussion

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



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



Scheme 3. Chair–chair conformation of diphosphanes **1** and **2**.

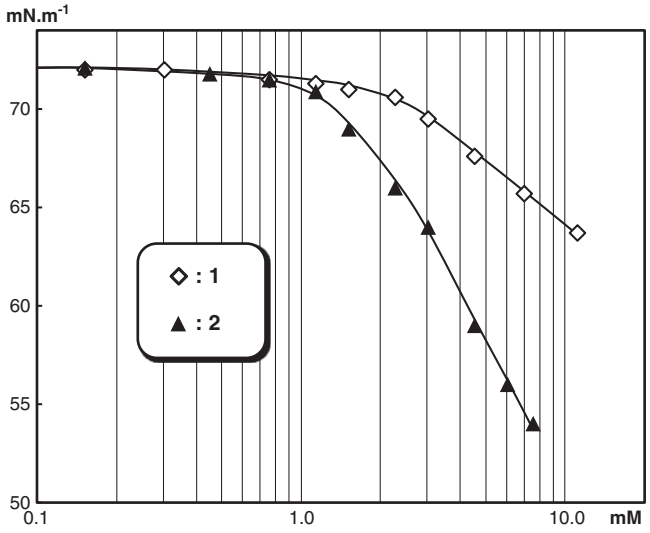


Fig. 1. Tensiometric properties of diphosphanes **1** and **2** as a function of their concentration in water at room temperature.

(Scheme 2). The synthesis of these ligands is quite straightforward with high reaction yields (80–90%) and the water solubility of these phosphanes (about 10 mM at 25 °C) is high enough to make them practically applicable in aqueous catalysis.

Mass spectrometry analyses confirmed the purity of ligands **1** and **2** (ESI). The NMR analyses of the diphosphanes revealed the magnetic inequivalence of the methylene protons located between the nitrogen and the phosphorus atoms. Doublets of doublets were detected characteristic of both a ^2J coupling constant between methylene protons ($^2J_{H,H}=15.4$ Hz and $^2J_{H,H}=15.3$ Hz for **1** and **2**, respectively) and a ^2J coupling constant connecting the methylene protons and the phosphorus atoms ($^2J_{H,P}=5.9$ Hz and $^2J_{H,P}=5.7$ Hz for **1** and **2**, respectively). These NMR data suggest that the phosphanes adopted a chair–chair conformation in which both phosphorus atoms displayed their electron lone pair on the same side of the molecule (Scheme 3). A κ^2-*P,P* coordination mode onto a metal atom is then conceivable.

3.2. Phosphane basicity

The $^1J_{P-Se}$ first order phosphorous selenium coupling constants of the Se=**1** and Se=**2** selenides are 700 and 720 Hz, respectively. The lower $^1J_{P-Se}$ values obtained for Se=**1** and Se=**2** indicate that **1** and **2** are more electron rich and thus more basic than TPPTS ($^1J_{P-Se}=757$ Hz). The results were coherent with the trialkyl nature of the phosphorus atoms in **1** and **2** by comparison with TPPTS [16].

3.3. Tensiometric measurements

Ligands **1** and **2** have been characterized by surface tension measurements in water. Their ability to modify the air–water interface clearly appeared when increasing their concentration. A regular decrease in surface tension γ for each diphosphane was indicative of an interfacial adsorption in the 1–10 mM concentration range. **2** appeared to be more surface active than **1** (Fig. 1). Note that no critical micellar concentration could be observed in the studied concentration range. In fact, **1**

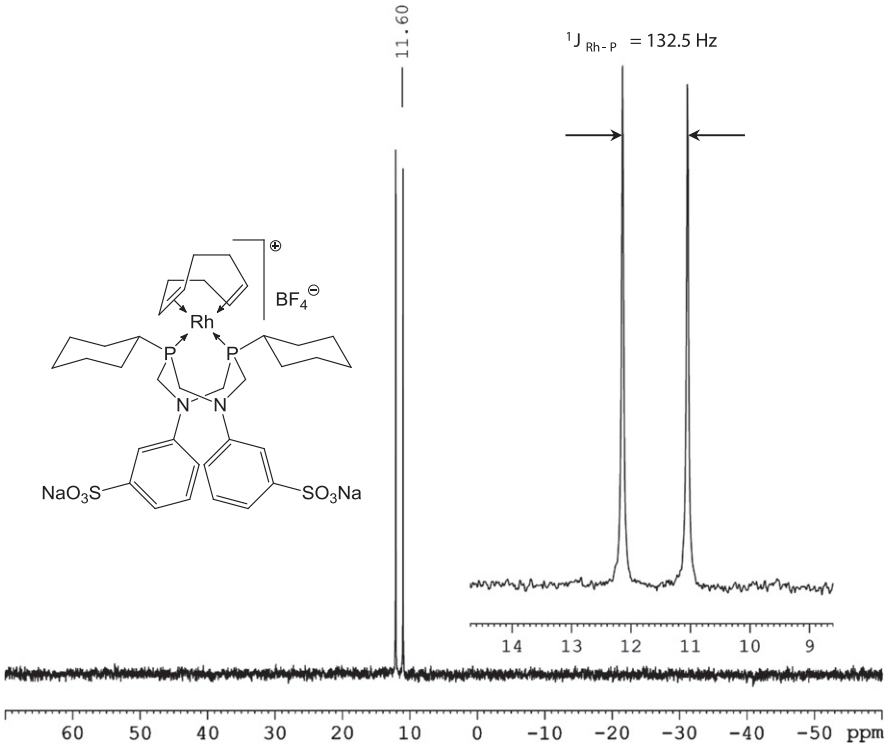


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of a 6 mM solution of [Rh(COD)(**2**)$^+$, BF_4^-] in a D_2O/EtOH (50/50) mixture.

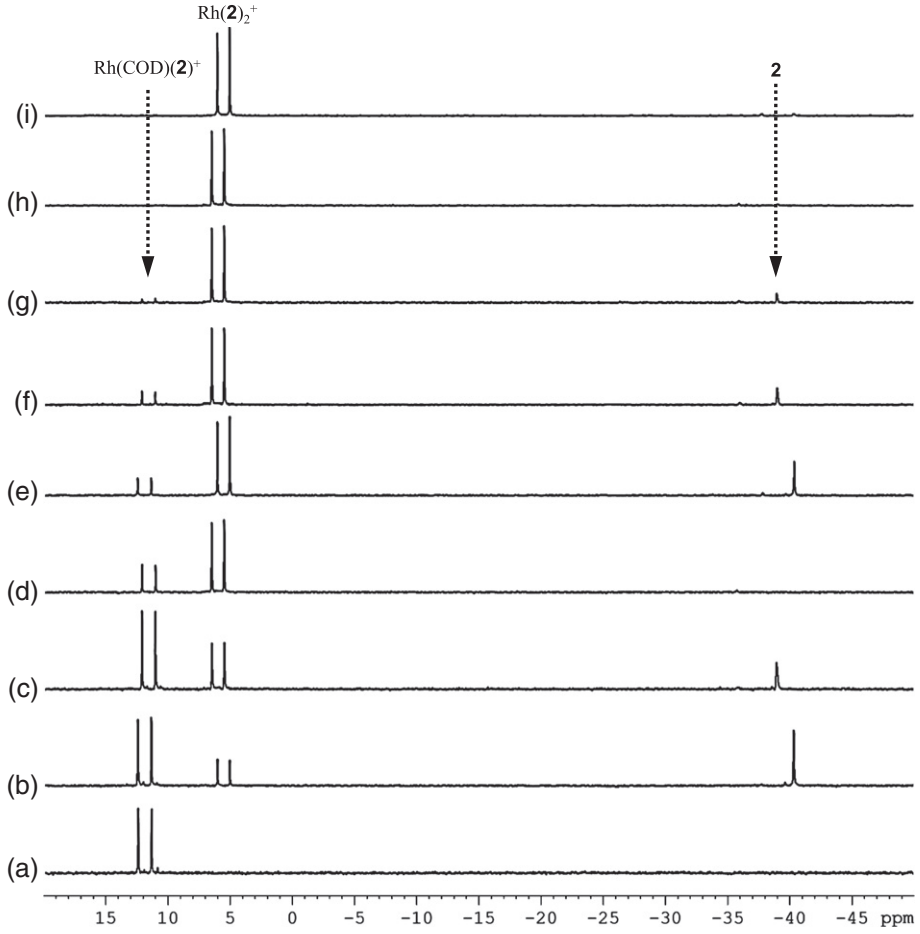


Fig. 3. $^{31}P\{^1H\}$ NMR spectra (121.5 MHz, DMSO-D6) of a mixture of $[Rh(COD)_2^+, BF_4^-]$ (12 mM) and **2**. (a) 1 eq. of **2** (12 mM) after 10 min at 20 °C (recorded at 20 °C), (b) 1.5 eq. of **2** (18 mM) after 10 min at 20 °C (recorded at 20 °C), (c) 1.5 eq. of **2** (18 mM) after 10 min at 60 °C (recorded at 60 °C), (d) 1.5 eq. of **2** (18 mM) after 30 min at 60 °C (recorded at 60 °C), (e) 2 eq. of **2** (24 mM) after 10 min at 20 °C (recorded at 20 °C), (f) 2 eq. of **2** (24 mM) after 10 min at 60 °C (recorded at 60 °C), (g) 2 eq. of **2** (24 mM) after 20 min at 60 °C (recorded at 60 °C), (h) 2 eq. of **2** (24 mM) after 30 min at 60 °C (recorded at 60 °C), i) 2 eq. of **2** (24 mM) after 30 min at 60 °C (recorded at 20 °C).

and **2** could be considered hydrotropic. Over about 10 mM for **1** and 8 mM for **2**, no data could be collected because of solubility limitations.

3.4. Coordination properties

NMR experiments realized in a D_2O/EtOH mixture (50/50) showed that mixing the $Rh(COD)_2BF_4$ cationic precursor and **1** or **2** in stoichiometric proportion gave the expected $[Rh(COD)(\mathbf{1})^+, BF_4^-]$ and $[Rh(COD)(\mathbf{2})^+, BF_4^-]$ complexes. Fig. 2 is illustrative of the $^{31}P\{^1H\}$ spectrum obtained for $[Rh(COD)(\mathbf{2})^+, BF_4^-]$. The well-defined doublet ($^1J_{Rh\text{-}P} = 132.5$ Hz) is characteristic of two phosphorus in a symmetrical environment and coordinated to the rhodium center in a κ^2-*P,P* coordination mode (Fig. 2). No other Rh-complexes could be detected informative of the very selective coordination mode of the ligand onto the metal.

An additional experiment has been carried out in a D_2O/EtOH mixture (50/50) with $Rh(COD)_2BF_4$ as a cationic precursor and 2 equiv. **2**. In these conditions, a new Rh-species could be detected. The ^{31}P NMR signal was upfield shifted (5.54 ppm vs. 11.89 ppm for $[Rh(COD)(\mathbf{2})^+, BF_4^-]$ and revealed a more electron-rich metallic center. Here again, the doublet was characteristic of phosphorus atoms in a symmetrical environment with a $^1J_{Rh\text{-}P}$ coupling constant of 120.8 Hz and could be attributed to the planar $[Rh(\mathbf{2})_2^+, BF_4^-]$ complex (ESI). The proportion of the latter could be varied depending on the ligand amount as depicted in Fig. 3. 100% $[Rh(\mathbf{2})_2^+, BF_4^-]$ could be obtained after heating the solution at 60 °C for 30 min in the presence of 2 eq. of **2**.

3.5. Rh-catalyzed hydroformylation of terminal alkenes

The catalytic performances of **1** and **2** were evaluated in Rh-catalyzed hydroformylation of two different alkenes, namely methyl 4-pentenoate (**3**) and acetoxystyrene (**4**). $Rh(CO)_2(acac)$ (acac = acetylacetonate) was used as catalytic precursor under 50 bar CO/H_2. The first catalytic runs have been carried out using **3**, a partially water-soluble substrate able to react directly in the aqueous bulk. Table 1 showed that the conversion was very dependent upon the ligand proportion.

Using 1 eq. ligand **1** at 80 °C (Table 1, run 1), a total conversion was reached within 150 min along with an excellent 99% chemoselectivity

Table 1
Rh-catalyzed hydroformylation of methyl 4-pentenoate (**3**) and acetoxystyrene (**4**).

Run	Substrate	Phosphane	L/Rh	Temp. (°C)	Conversion (%)	Aldehydes selectivity (%)	l/b
1	**3**	**1**	1	80	100	99	1.1
2	**3**	**1**	2	80	8	90	1.7
3	**3**	**1**	2	100	23	95	1.7
4	**3**	**2**	1	80	95	95	1.2
5	**3**	**2**	2	80	12	98	0.9
6	**3**	**2**	2	100	14	96	0.9
7	**3**	**DPPPTS**	1	80	99	98	1.2
8	**4**	**1**	1	80	83	98	0.5
9	**4**	**2**	1	80	78	98	0.3
10	**4**	**DPPPTS**	1	80	99	90	0.07

Conditions: $n(Rh(CO)_2(acac)) = 3.88$ μmol (1 mg), substrate (1.94 mmol), 12 mL water, reaction time = 150 min, 50 bar CO/H_2, substrate/Rh = 500.

in aldehydes and a poor regioselectivity (l/b = 1.1). Thus, almost no isomerization of the C=C double bond occurred during the catalytic process, thus highlighting the selective ability of the catalyst to orient the reaction towards the hydroformylation process. However, the low l/b ratio clearly indicated that no preference was given to one or the other alkenyl carbon for them to be functionalized by a formyl group. Increasing the amount of **1** at 80 °C (Table 1, run 2) led to a huge decrease in the conversion (from 100% to 8% within 150 min). As clearly established above (see Section 3.4), a high-coordinated rhodium species was probably formed with negative impact on the substrate complexation. The significant drop in conversion was accompanied by a slight decrease in chemoselectivity (90% aldehydes) and an increase in regioselectivity (l/b = 1.7). Increasing the temperature from 80 to 100 °C did not counterbalance the ligand effect as 23% conversion was only reached within 150 min (Table 1, run 3). In that case, the aldehyde proportion was slightly higher (95.0%) and the l/b ratio remained constant (1.7). A similar trend was observed for **2** in terms of catalytic activity. Thus, from 95% with 1 eq. **2** at 80 °C (Table 1, run 4), the conversion dropped to 12 and 14% at 80 and 100 °C, respectively. While the chemoselectivity was hardly impacted by variation of proportions in **2** (in the range 95–98% aldehydes), the regioselectivity suffered from an excess **2** in solution as a very low 0.9 l/b ratio was measured using 2 eq. **2** at any temperature (Table 1, runs 5 and 6). When comparing **1** and **2**, no significant difference in catalytic performances could be noticed. Thus, using a linear terminal alkene as substrate, the *para*- or *meta*-position of the sulfonate groups had no real influence on the coordination sphere. This conclusion was coherent with the geometry of the Rh-complexes when coordinated by **1** or **2**. Indeed, a structural study carried out on non-sulfonated analogues of **1** and **2** showed the phenyl groups to be far from the metallic center [17]. Consequently, the steric hindrance around the metal was not high enough to discriminate the two C=C carbons. To complete this series of experiments, the catalytic behavior of **1** and **2** has been compared to a structurally close water-soluble ligand, namely the well-known DPPPTS (tetra-sulfonated 1,3-bis(diphenylphosphino)propane). DPPPTS has been chosen as its two phosphorus atoms are distant from each other by four covalent bonds, as observed for **1** and **2**. Ligands **1** or **2** appeared to be as effective as DPPPTS, either in terms of conversion or selectivities (run 7), thus highlighting their bidentate nature during the course of the reaction.

The Rh-catalyzed hydroformylation has been widened to acetoxystyrene (Table 1, runs 7 and 8). 83% and 78% of substrate were converted at 80 °C under 50 bar CO/H_2 within 150 min using **1** and **2**, respectively (Table 1, run 1 and 2). As observed for **3**, the chemoselectivity was high (98% aldehydes). Contrary to what was usually observed for terminal alkenes, it is well known that Rh-catalyzed hydroformylation of styrene derivatives mainly led to branched aldehydes because of the formation, during the catalytic cycle, of a pseudo π-allyl intermediate. In this context, it appeared that the Rh-catalyst stabilized by 1 equiv **2** was more regioselective than that stabilized by **1** as higher proportions of branched aldehydes were formed (76% vs. 65%, respectively). As observed above for **3**, conversion of **4** was performed as efficiently using **1** or **2** than using DPPPTS, even if the selectivity in branched aldehyde was somewhat lower with **1** or **2**.

4. Conclusion

In this study, two new water-soluble diphosphadiazacyclooctane derivatives have been synthesized using a straightforward two-step synthetic procedure. They displayed a κ^2-*P,P* coordination mode on rhodium complexes. We demonstrated their potential in rhodium-catalyzed hydroformylation of two terminal alkenes. The conversion proved to be very dependent upon the phosphane/Rh ratio. A stoichiometric proportion was optimized to yield high conversion. The high chemoselectivities attainable in hydroformylation of terminal alkene derivatives constitute without doubt one of the main advantages of these new diphosphanes as water-soluble ligands. Extension of the use of water-soluble diphosphadiazacyclooctane derivatives to other catalytic reactions is currently on-going.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.09.019.

References

[1] E.G. Kuntz, ChemTech (1987) 570.
[2] K.H. Shaughnessy, Chemical Reviews 109 (2009) 643.
[3] D.P. Curran, Angewandte Chemie International Edition 37 (1998) 1174.
[4] W. Leitner, Accounts of Chemistry Research 35 (2002) 746.
[5] D. Prajapati, M. Gohain, Tetrahedron 60 (2004) 815.
[6] M. Haumann, A. Riisager, Chemical Reviews 108 (2008) 1474.
[7] V. Pârvulescu, C. Hardacre, Chemical Reviews 107 (2007) 2615.
[8] C. Machut, J. Patrigeon, S. Tilloy, H. Bricout, F. Hapiot, E. Monflier, Angewandte Chemie International Edition 46 (2007) 3040.
[9] H. Fu, M. Li, J. Chen, R. Zhang, W. Jiang, M. Yuan, H. Chen, X. Li, Journal of Molecular Catalysis A: Chemistry 292 (2008) 21.
[10] M. Ferreira, H. Bricout, A. Sayede, A. Ponchel, S. Fourmentin, S. Tilloy, E. Monflier, Advanced Synthesis and Catalysis 350 (2008) 609.
[11] S. Tilloy, F. Hapiot, D. Landy, S. Fourmentin, V. Michelet, J.P. Genêt, E. Monflier, Advanced Synthesis and Catalysis 348 (2006) 1547.
[12] C. Machut-Binkowski, F.X. Legrand, N. Azaroual, S. Tilloy, E. Monflier, Chemistry–A European Journal (2010) 10195.
[13] H. Bricout, E. Banaszak, C. Len, F. Hapiot, E. Monflier, Chemical Communications 46 (2010) 7813.
[14] D. Ngan Tran, F.X. Legrand, S. Menuel, H. Bricout, S. Tilloy, E. Monflier, Chemical Communications 48 (2012) 753.
[15] A. Fihri, D. Luart, C. Len, A. Solhy, C. Chevrin, V. Polshettiwar, Dalton Transactions 40 (2011) 3116.
[16] M. Ferreria, H. Bricout, A. Sayede, F. Hapiot, S. Tilloy, E. Monflier, ChemSusChem 1 (2008) 631.
[17] S. Otto, A. Ionescu, A. Roodt, Journal of Organometallic Chemistry 690 (2005) 4337.