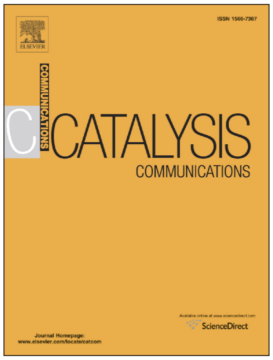

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An effective diphosphoramidite rhodium catalyst for selective hydroformylation of 1-octene

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Abstract

A very efficient and highly selective rhodium catalyst with a C_2-symmetric BINOL-derived diphosphoramidite ligand for hydroformylation of 1-octene has been developed. At mild conditions (50 °C and 10 bar H_2/CO) a very active rhodium catalyst has been obtained which produces over 99% of aldehydes with 98.2% *n*-regioselectivity. The spectroscopic characterization of the hydridorhodium catalytically active species showed that the diphosphoramidite ligand coordinates bis-equatorially in the trigonal bipyramidal rhodium complex, which coupled with its π-acceptor capacity might account for the high catalyst performance.

Keywords: hydroformylation; diphosphoramidite; regioselectivity; rhodium catalyst; homogeneous catalysis

1. Introduction

The hydroformylation of unfunctionalized terminal olefins is an important industrial process for producing aldehydes [1,2].

Rhodium complexes with phosphorus ligands are known to be the most effective homogeneous catalysts for the hydroformylation of unfunctionalized short-medium chain olefins [3].

~~Despite high price of rhodium, P-ligand modified rhodium catalysts are suitable for industrial applications as they predominantly produce the desired linear aldehyde at low syngas pressure [4]. In this context, the electronic [5,6] and steric [7,8,9] properties of the ancillary phosphorus ligands play a critical role on the activity and selectivity of the rhodium catalyst. Hence, many efforts have been done to develop P-ligands that improve the catalyst performance.~~

The electronic [4,5] and steric [6,7,8] properties of the ancillary phosphorus ligands play a critical role on the activity and selectivity of the rhodium catalyst. Hence, despite high price of rhodium, P-ligand modified rhodium catalysts are suitable for industrial applications as they predominantly produce the desired linear aldehyde at low syngas pressure [9]. Therefore, several efforts have been done to develop P-ligands that improve the catalyst performance.

In 1968, Pruett and Smith found that the hydroformylation of terminal olefins catalyzed by rhodium complexes with π-acceptor triaryl phosphite ligands gave very high percentage of linear aldehydes [10]. Since then, several mono [11,12,13] and bidentate [14,15,16,17] phosphite ligands have been explored and their positive effect on both rate and regioselectivity has been proved.

In recent years, phosphoramidites have been the subject of growing interest as π-acceptor ligands for rhodium-catalyzed hydroformylation of olefins [2].

Phosphoramidites are an interesting class of ligands because they are synthesized in two steps from accessible and inexpensive sources [18]. Furthermore, these ligands are quite stable in air and in some cases are resistant to hydrolysis [19].

In 1996, van Leeuwen *et al*. first tested a series of mono- and bidentate phosphoramidites in the rhodium catalyzed hydroformylation of 1-octene [20]. The authors showed that rhodium catalysts with bis-equatorially coordinating bidentate phosphoramidites produced higher quantities of linear aldehyde than ones with monodentate phosphoramidites.

More recently, very high l/b ratios of aldehydes (up to 471) have been obtained using pyrrolyl-based phosphoramidites, although with high percentages of the isomerized product 2-octene [6,21,22,23,24].

For several years, our research group has been interested in the design and development of new bidentate phosphoramidite ligands to be used as auxiliaries in homogeneous catalysis [25,26,27,28].

We have recently prepared the bidentate chiral C_2-symmetric diphosphoroamidite ligand **1** (Fig. 1) having the 1,2-diaminobenzene fragment as the backbone and two (*R*)-1,1'-binaphtalene-2,2'-dioxy (Bino) groups. This ligand was readily synthesized, in high yields, by reaction of 1,2-phenylenediamine with two equivalents of (*R*)-BINOL-phosphorochloridite. It easily formed the chelate rhodium(I) complex $[Rh(cod)(P,P)]BF_4$ (cod = 1,5-cyclooctadiene) useful as pre-catalyst for asymmetric hydrogenation of dimethylitaconate [29].

We then decided to test the BINOL-derived diphosphoroamidite **1** in other catalytic transformations.

During our research on its possible use as chiral auxiliary in asymmetric catalysis, we found that Matt and coworkers achieved a high regioselectivity in the rhodium-catalyzed hydroformylation of 1-octene using C_2-symmetric 1,3-calix[4]diphosphites with a calix[4]arene backbone and two (*S*)-BinoP groups at the lower rim [30,31]. The authors suggested that the steric hindrance of the binaphthyl moieties was relevant for the regioselectivity.

In view of this findings, we have thought that our bidentate C_2-symmetric phosphoramidite ligand **1** suitable featured for application in the rhodium-catalyzed hydroformylation because it contains a flat rigid skeleton and two bulky binaphthyl groups with a defined configuration.

Here we show that the (*S*,*S*)-phosphoramidite **1**/Rh system is a highly selective catalyst for the hydroformylation of 1-octene at very mild conditions. The spectroscopic characterization under atmospheric pressure and room temperature of the trigonal bipyramidal hydridorhodium catalytically active species with bis-equatorially coordinating ligand **1** is also reported.

2. Experimental

2.1 General remarks

All reagents were purchased from Sigma-Aldrich and used without further purification. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques. Solvents were bought in crown cap anhydrous bottles. The nuclear magnetic resonance spectra were recorded with a Bruker AMX R-300 spectrometer equipped with a pulsed field gradient probe. The values of chemical shifts (δ) for ^1H spectra and $^{13}C\{^1H\}$ NMR are measured relative to the solvent peak and are reported in ppm in reference to the value for the tetramethylsilane (TMS δ = 0 ppm). The chemical shifts for the $^{31}P\{^1H\}$ NMR spectra were measured using aqueous H_3PO_4 (85% D_2O) as an external reference (δ = 0 ppm). Hydroformylation experiments were executed in a 100 mL stainless steel autoclave equipped with glass reaction vessel. IR spectra were recorded on a Nicolet iS50 FT-IR spectrometer. Conversion and selectivities was determined by ^1H NMR and GC Fisons 8000 ThermoQuest (using helium as a carrier gas and a flame ionization detector FID) equipped with a OV1 capillary column. (25m x 0.25mm).

2.2 General procedure for the Rh(I)-catalyzed hydroformylation.

All hydroformylations were performed in a glass-lined, 100 mL stainless steel autoclave containing a magnetic stirring bar. In a typical experiment $[Rh(acac)(CO)_2]$ (acac = acetylacetonate) (4×10^{-3} mmol) and the ligand (1×10^{-2} or 6×10^{-3} mmol) were dissolved in 10 mL of toluene under an argon atmosphere in a Schlenk apparatus; 1-octene (10 mmol) was added resulting in a substrate:Rh ratio of 2500:1. The autoclave was placed under vacuum and subsequently purged three times using argon gas. The catalyst solution was introduced via a syringe into the autoclave and was flushed twice with syngas (CO/H_2 1:1 v/v), after which it was pressurized with syngas to the desired pressure and heated to the required temperature. At full conversion, the reactor was cooled and carefully vented and then opened. The reaction mixture was filtered through a short pad of silica and analyzed by ^1H NMR and by GC. The components of the reaction mixture were identified using authentic GC standards (where available).

2.3 In situ preparation of $[HRh(CO)_2(1)]$ complex.

The catalytically active hydride complex was prepared by the reaction of $[Rh(acac)(CO)_2]$ (8 mg, 0.031 mmol) with ligand **1** (25 mg, 0.034 mmol) in benzene-d_6 at 50° C, in autoclave under argon. After half an hour, the autoclave was purged three times using syngas, pressurized to 10 bar H_2/CO and heated at 50°C for 3 hours. Upon cooling to room temperature and depressurization, the red-ruby solution was transferred under an argon atmosphere into a 5 mm NMR tube to be further analyzed. The complex solution remained stable for several days at room temperature

3. Results and discussion

The hydroformylation of 1-octene with the diphosphoramidite ligand (*S*,*S*)-**1** rhodium catalyst system was carried out in toluene solution using an equimolar hydrogen/carbon monoxide mixture and a substrate-to-metal ratio of 2500.

The results obtained with the rhodium catalyst prepared *in situ* by addition of ligand **1** to [Rh(acac)$(CO)_2$] ~~(acac = acetylacetonate)~~ are reported in Table 1.

The first test was conducted at 80° C and 20 bar with a ligand: metal ratio of 2.5:1. A 94.8% conversion of 1-octene was obtained within 6 h. The aldehyde selectivity was very high (99.5%) and the regioselectivity reached 91.7 % (Entry 1).

No marked influence of CO/H_2 pressure on catalyst performance was observed. Lowering syngas pressure to 10 bar caused only small decreases in activity and regioselectivity of the rhodium catalyst (Entry 2).

~~It is well known that the regioselectivity increases with decreasing temperature at the cost of the reaction rate~~. ~~Instead, in our case~~ The conversion remained high (over 90%) when the reaction temperature was decreased from 80 to 60°C and a significant improvement in the regioselectivity (90 to 97.8%) was obtained (Entries 3-4).

Interestingly, the selectivity of (*S*,*S*)-phosphoramidite **1**/Rh catalyst system improved with increasing of conversion of 1-octene (Entries 4-5).

~~The effects of ligand: metal ratio on catalyst performance was also evaluated~~.

Moreover, at a ligand to rhodium ratio of 1.5, the regioselectivity remained high (96.9%) (Entry 6).

Given the above, we decided to test our catalytic system at 50° C under 10 bar of CO/H_2 pressure.

The results obtained were quite surprising. A 96.3% conversion of 1-octene was obtained in 4 h with a regioselectivity of 98.4% (Entry 7). It is noteworthy that a 91.9% conversion was reached within 2 h at the same temperature (Entry 8).

Finally, an improvement of the catalyst performance could be obtained by mixing ligand **1** and [Rh(acac)$(CO)_2$] in toluene at 50° C for 30 min in a Schlenk flask before introducing in the autoclave (Entry 9).

~~Compared with calix[4]arene-based binaphthyl diphosphites modified rhodium catalyst, BINOL-derived diphosphoramidite ligand **1** formed a more effective hydroformylation catalyst at lower pressure and temperature. Moreover, for Matt’s ligands large excesses (L/Rh = 10) were required to attain high regioselectivities.~~

Compared with bidentate phosphoramidites reported by van Leeuwen [20], BINOL-derived diphosphoramidite **1** formed a more effective hydroformylation rhodium catalyst at milder conditions and lower L/Rh ratios. Probably the rigidity of ligand **1** plays a key role in determining the high regioselectivity.

~~In order to get information on the catalytically active hydride complex formed with the diphosphoramidite **1**, we carried out the reaction of [Rh(acac)(CO)$_2$] with ligand **1** in benzene-d$_6$ at 50° C, in autoclave under argon. After half an hour, the autoclave was purged three times using syngas, pressurized to 10 bar H$_2$/CO and heated at 50°C for 3 hours. Upon cooling to room temperature and depressurization, the red-ruby solution was transferred under an argon atmosphere into a 5 mm NMR tube to be further analyzed. The complex solution remained stable for several days at room temperature~~.

In order to get information on the hydridorhodium diphosphoramidite catalyst, we carried out the reaction of [Rh(acac)(CO)$_2$] with ligand **1** under hydroformylation conditions in benzene-d$_6$. The resulting red-ruby solution was immediately analysed by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy under atmospheric conditions.

The corresponding ^{31}P{^{1}H} NMR spectrum showed only a doublet at δ 167.66 ppm with the J_{RhP} coupling constant of 235 Hz (similar value as those found for bidentate phosphite ligands laying in equatorial positions [32]). The ^{1}H NMR signals support the presence in solution of the stable hydridorhodium derivative, showing the expected doublet of triplets at δ -10.24 ($^1J_{RhH}$ = 5 Hz, $^2J_{PH}$ = 5 Hz), due to the coupling of the hydride with two (time-averaged) equivalent phosphorus atoms and the rhodium atom. The small J_{RhH} and J_{PH} coupling constants of 5 Hz are indicative of coordination of both phosphorus atoms in the equatorial plane of the trigonal bipyramidal rhodium complex (Fig. 2) [20]. On the basis of the above, it was performed ^{31}P-^{1}H correlation spectroscopy that has revealed the presence of cross peak between the doublet of phosphorus atoms and the doublet of triplets of the hydride atom confirming the spin-spin coupling between proton and the two phosphorus atoms. The IR spectrum, recorded on the NMR solution, showed two absorption bands for the carbonyl ligands at 2076 and 2023 cm^{-1}. The number and position of the carbonyl frequencies confirm that only the *ee* isomer is present [23]. This results show, as reported by van Leeuwen [20], that the bis-equatorial coordination of the bidentate phosphoramidites ligand is one of the requirements for achieving high l/b ratios.

Although a simple correlation between spectroscopic results and the observed high selectivity is not possible, we believe that the equatorial-equatorial coordination mode coupled to the π-acid character of the bulky diphosphoramidite ligand **1**, determine the outcome of the hydroformylation reaction.

4. Conclusions

In conclusion, we can say that a new effective and highly selective hydroformylation catalyst operating at very mild conditions has been developed. The spectroscopic data obtained for the hydride complex [HRh(CO)$_2$(**1**)] pointed out an equatorial-equatorial coordination of the diphosphoramidite ligand in the trigonal bipyramidal catalytically active species.

To our knowledge this is the first phosphoramidite/Rh system that turned out to be a very efficient catalyst for hydroformylation of 1-octene at low pressure and low temperature.

Finally, we believe that the peculiar steric and electronic properties of the ligand **1** make it promising for application in ~~industrial~~ hydroformylation reactions of a broad range of olefins.

Acknowledgements

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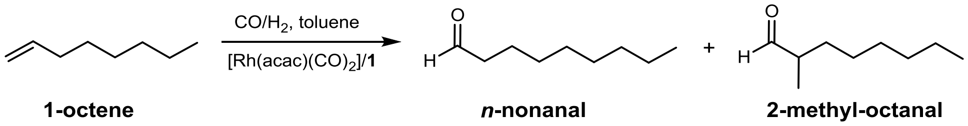
Declarations of Interest

None

Table 1. Hydroformylation of 1-octene catalyzed by [Rh(acac)$(CO)_2$]/**1**.[a]



Entry	L/Rh	T(°C)	P (bar)	t (h)	Conv.[b] (%)	Aldehyde selectivity[c] (%)	*n*-Regioselectivity[d] (%)
1	2.5	80	20	6	94.8	99.5	91.7
2	2.5	80	10	6	93.3	99.3	90.9
3	2.5	70	10	6	94.2	99.5	96.3
4	2.5	60	10	6	93.8	99.4	97.8
5	2.5	60	10	4	91.6	99.2	96.9
6	1.5	60	10	4	94.7	99.5	96.9
7	1.5	50	10	4	96.3	99.6	98.4
8	1.5	50	10	2	91.9	99.2	97.9
9[e]	1.5	50	10	2	93.3	99.3	98.2

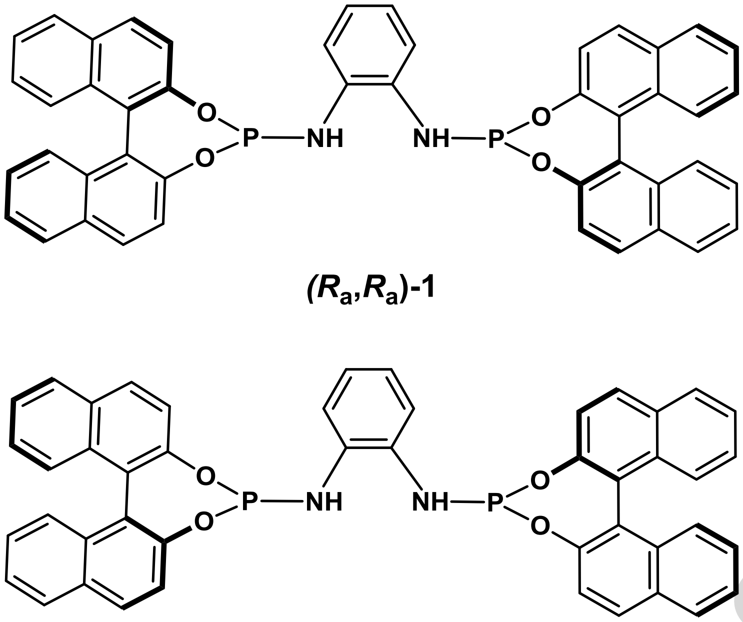
[a] Reaction conditions: toluene (10 ml); CO/H_2 = 1/1; [Rh(acac)$(CO)_2$] (4×10^{-3} mmol); catalyst:1-octene = 1:2500.

[b] Conversion was determined by ^{1}H NMR and by GC 8000 ThermoQuest.

[c] Yield (all aldehydes)/Conv.

[d] Yield (linear aldehyde)/Total Yield (all aldehydes).

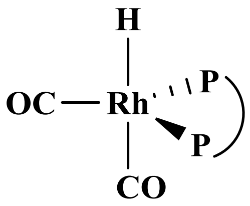
[e] [Rh(acac)$(CO)_2$] and ligand **1** were previously mixed at 50° C for 30 minutes.



(R_a,R_a)-**1**

(S_a,S_a)-**1**

Figure 1.



ee

Figure 2

Figure 1**.** C_2-symmetric diphosphoramidite ligands.

Figure 2. Trigonal bipyramidal hydridorhodium complex (*ee*).

Highlights

- Efficient and highly selective hydroformylation catalyst.
- High chemo- and regioselectivity at low pressure and temperature.
- Use of bulky C_2-symmetric diphosphoramidite ligand for selective hydroformylation.

Graphical abstract