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Preliminary communication

Hydroformylation of some functionalized olefins catalyzed by rhodium(I) complexes with pydiphos and its *P*-oxide ☆

C. Basoli [a], C. Botteghi [b], M.A. Cabras [c], G. Chelucci [c], M. Marchetti [a,*]

[a] *Istituto per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, CNR, Via Vienna 2, I-07100 Sassari, Italy*
[b] *Dipartimento di Chimica, Università di Venezia, Calle Larga Santa Marta 2134, I-30123 Venezia, Italy*
[c] *Dipartimento di Chimica, Università di Sassari, Via Vienna 2, I-07100 Sassari, Italy*

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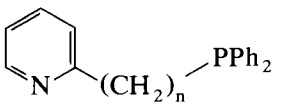
Abstract

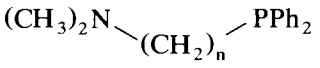
The chiral optically active pyridylphosphines pydiphos (**10**) and its *P*-oxide (**11**) were tested as ligands in rhodium(I) complexes to form catalysts for the enantioselective hydroformylation of some functionalized olefins. These hydroformylation reactions provide in most cases good chemo- and regioselectivity, but unsatisfactory enantioselectivity. In the hydroformylation of styrene, vinyl acetate and phenyl vinyl ether, the $Rh^{(I)}$ complex containing the *P*-oxide **11** is remarkably more active than the catalyst formed with the pyridylphosphine analogue **10**.

Keywords: Hydroformylation; Pyridylphosphines; Catalysis; Rhodium; *N–P* ligands

In recent years there has been an increasing interest in the preparation of mixed bidentate ligands (*P–S*, *P–N*, *N–S*, *N–O*, *P–O*) [1–8] and in the utilization of their metal complexes in various homogeneous catalytic reactions [9–15]. In the hydroformylation reaction an increase in catalytic activity of $Rh^{(I)}$ carbonyl complexes was found when using some structurally simple *P–N* ligands such as diphenylphosphinopyridines [3] and diphenylphosphinoamines [16,17] having the general formulae shown below.



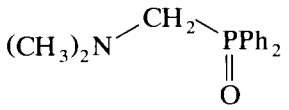
1, n = 0
2, n = 1
3, n = 2



4, n = 0
5, n = 1
6, n = 2

For example, styrene is hydroformylated at a higher reaction rate by the catalytic system formed from $[\{Rh(COD)Cl\}_2]$ (COD = *cis,cis*-1,5-cyclooctadiene) and **3** or **6** than by that formed from the same catalytic precursor and diphosphines [16]. The regioselectivity towards the more useful branched isomer 2-phenylpropanal was also higher than that obtained by using more traditional tertiary phosphines [16].

Furthermore, the catalytic activity of $Rh^{(I)}$ carbonyl complexes with diphenylphosphinoamines such as **5** is significantly less than that of the corresponding *p*-oxide **7** [17].



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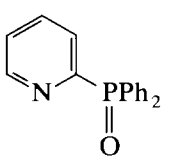
In contrast, pyridylphosphines structurally related to **7** gave the opposite result. For instance, the use of the pyridylphosphine oxide **8** gave no enhancement of activity compared with the pyridylphosphine **1** [17]. Whereas the phosphine oxide **9** resulted less effective than the corresponding pyridylphosphine [17].



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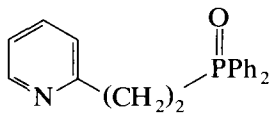

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☆ Dedicated to Professor Fausto Calderazzo in recognition of his important contribution to organometallic chemistry.

* Corresponding author.

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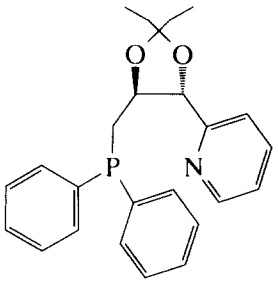
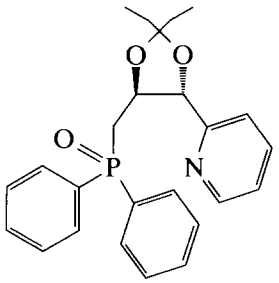
We now report results obtained in the enantioselective hydroformylation of styrene and other functionalized olefins catalyzed by $[Rh(CO)_2(acac)]$ (Hacac = 2,4-pentadione) in the presence of (−)-(4*S*,5*R*)-4-(2-pyridyl)-5-(diphenylphosphino)methyl-2,2-dimethyl-1,3-dioxolane (pydiphos, **10**) and its *P*-oxide derivative (**11**). Compound **10** was prepared according to a published procedure [5], whereas the corresponding *P*-oxide **11** was obtained quantitatively by oxidation of **10** [18].



Pydiphos (**10**)

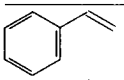
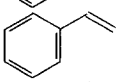
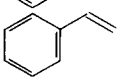


Pydiphos P-oxide (**11**)

The hydroformylation reactions were carried out at 90 atm total pressure ($CO/H_2 = 1:1$), 30–80 °C using a substrate-to-catalytic precursor ratio of 300:1. The catalytic precursor was formed in situ by adding, under inert atmosphere, **10** or **11** (2–2.5 mmol) to a solution of $[Rh(CO)_2(acac)]$ (1 mmol) in benzene (20 ml).

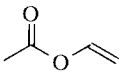
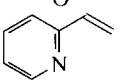
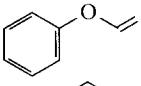
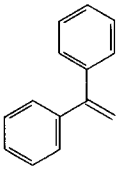
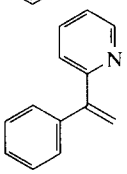
Table 1 shows the results obtained in the hydroformylation of styrene at 30°C with **10** and **11**. A comparative experiment using only $[Rh(CO)_2(acac)]$ is also reported. The data indicate that the pyridylphosphine **10** significantly reduces the catalytic activity of $[Rh(CO)_2(acac)]$, even if the regioselectivity is practically unaffected. The corresponding *P*-oxide **11** considerably enhances the reaction rate giving a very effective catalyst (97% yield in 5 h). The enantioselectivity induced by these chiral ligands was always less than 1%.

Table 1
Hydroformylation of styrene using **10** and **11** in the catalytic precursor [a]

Substrate	Ligand	Reaction time, h	Conversion, %	Yield, %	b/n
	none	16	99	97	97/3
	**10**	20	80	70	95/5
	**11**	5	99	97	95/5

[a] Reaction conditions: the reaction was carried out on 20 ml of a 0.5 M benzene solution of the substrate in a stirred stainless steel vessel at 30°C and at 90 atm of $CO/H_2 = 1:1$, using $[Rh(CO)_2(acac)]$ as catalyst precursor, substrate/catalyst = 300/1; catalyst precursor/chiral ligand = 1/2.5.

Table 2
Hydroformylation of some functionalyzed olefins using **10** in the catalytic precursor [a]

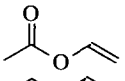
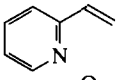
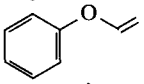
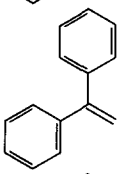
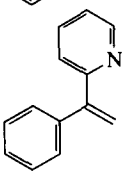
Substrate	Reaction time, h	Conversion, %	Yield, %	b/n
	6	95	90	96/4
	3	97	95	99/1
	5	99	70	80/20
	18	37	21	1/99
	21	47	13 [b]	99/1

[a] Reaction conditions: the reaction was carried out on 20 ml of a 0.5 M benzene solution of the substrate in a stirred stainless steel vessel at 80°C and at 80 atm of $CO/H_2 = 1:1$, using $[Rh(CO)_2(acac)]$ as the catalyst precursor; substrate/catalyst = 300/1; catalyst precursor/chiral ligand = 1/2.5. [b] The low yield is due to the concomitant hydrogenation of the substrate.

Contrasting results were obtained using other functionalized olefins (Tables 2 and 3). Both reaction rate and chemoselectivity of the *oxo*-reaction on vinylacetate and phenyl vinyl ether were improved using the *P*-oxide **11** instead of **10**. Secondary reactions had a negative influence on the catalysis when 1,1-diarylethenes were used together with **11**. Double bond hydrogenation occurred with 1,1-diphenylethene and 1-phenyl-1-(2-pyridyl)ethene.

The percentage enantiomeric excess in all cases was extremely low. Only in the hydroformylation of the phenyl vinyl ether with **10** and of 1-phenyl-1-(2-pyridyl)ethene with **11** a greater enantioselectivity was observed, ca. 10%. However, some chiral aldehydes derived from the asymmetric hydroformylation of vinyl olefins are highly racemizable. For instance, the branched *oxo*-product from 2-vinylpyridine was isolated as a mixture of 70% of enol form and 30% of aldehyde form (^1H NMR and ^{17}O NMR analyses). The enol is stabilized by the formation of a six-membered ring formed by intramolecular hydrogen bonding involving the pyridine nitrogen atom.

Table 3
Hydroformylation of some functionalyzed olefins using **11** in the catalytic precursor [a]

Substrate	Reaction time, h	Conversion, %	Yield, %	b/n
	1	99	95	97/3
	16	70	67	99/1
	2	99	97	87/13
	111	64	61 [b]	1/99
	69	99	60	99/1

[a] Reaction conditions: see footnote of Table 2. [b] Concomitant hydrogenation of the substrate was observed.

Considering also the results for the styrene hydroformylation using **1**, **3–9** reported recently [16,17], rationalization of the activating effect of **11** compared with ligand **10** in the same catalytic reaction appears rather difficult. Amer et al. correlated the catalytic activity of rhodium complexes containing mixed *P–N* chelating ligands or their corresponding *P*-oxide to the relative stability of the different metallocycles formed through coordination [16,17]. Compounds containing five- or six-membered metallocycles produce a very effective catalytic system for styrene hydroformylation. This chelating effect can play an important role in promoting the reductive elimination of the aldehyde products from the intermediate rhodium σ-acyl complex [16].

In our case molecular models show that both **10** and **11** are able to act as chelating ligands, even though the metallocycles formed are seven- and eight-membered respectively. The stiff dioxolane ring in **10** and **11** restrains both the diphenylphosphine and pyridine groups so as to facilitate coordination of the phosphorus and nitrogen (or oxygen) atoms without appreciable distortion of the ligand.

Support for the proposed bidentate coordination of *P*-oxide **11** is given by the comparison of the IR and ^{31}P NMR spectra of the ligand and the complex formed by addition of $[Rh(CO)_2(acac)]$ to **11** in 1:2 ratio in chloroform in situ [17]. A shift of ν(P=O) from 1260 to 1215 cm^{-1} was observed, indicating a small but significant weakening of the P=O bond owing to coordination. A parallel shift of 0.1 ppm downfield was obtained in the ^{31}P NMR spectrum, indicating weak interaction of the P=O group with the rhodium. The presence in **11** of one donor group weakly interacting with the metal might be responsible for the higher activity of the catalyst containing **11** compared with that containing **10**. This produces a vacant coordination site, promoting the oxidative addition of molecular hydrogen.

However, other mechanisms for the enhancement of the catalytic activity of *P*-oxide complexes compared with those containing the corresponding phosphines could play a role. Indeed, it was recently claimed [19] that rhodium carbonyl complexes with triphenylphosphine oxide were more efficient catalysts in hydroformylation of octenes than those containing the triphenylphosphine [19].

As rhodium complexes containing *P*-oxides have interesting catalytic activity in olefin hydroformylation, their behaviour is worth a more extensive investigation.

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[16] C. Abu-Gnim and I. Amer, *J. Mol. Catal., 85* (1993) L275.
[17] C. Abu-Gnim and I. Amer, *J. Chem. Soc., Chem. Commun.*, (1994) 115.
[18] A cooled solution of **10** (500 mg) in CH_2Cl_2 (50 ml) was shaken in a separation funnel with 5% hydrogen peroxide (20 ml). After separation of the organic layer, the solvent was evaporated and the crude residue was characterized by ^{31}P NMR spectroscopy: δ, 30.83 ppm.
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