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Hydroformylation of styrene using thiolato–pyrazolate bridge rhodium catalysts modified with phosphorous ligands

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Abstract

Catalytic precursor systems prepared using $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(COD)_2]$ in the presence of triphenylphosphine and chiral diphosphines are active in styrene hydroformylation. The effect of the pressure and the dependence on the P/Rh ratio are studied. When triphenylphosphine is used as phosphorous ligand complete conversion to aldehydes and regioselectivities as high as 90% in 2-phenylpropanal are obtained at very mild conditions. The use of (+)-(2*R*,4*R*)(−)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane ((+)-BDPP) or (−)-(2*S*,4*S*) ((−)-BDPP) as chiral diphosphine in a P/Rh ratio of 2 provides 95% regioselectivity and enantiomeric excess as high as 50%.

Keywords: Hydroformylation; Enantioselectivity; Rhodium; Diphosphine

1. Introduction

In practically all Pt or Rh hydroformylation catalysts, phosphorous ligands are present in the complex or are added to the catalytic solution. In asymmetric hydroformylation the selectivity has recently been proved to depend on the structure of different modified diphosphines and diphosphites [1–3].

Concerning the asymmetric hydroformylation of styrene, it has recently been shown that the asymmetric induction of a given homochiral ligand can be improved by changing the starting organometallic complex [4,5].

In particular, we have studied the influence on the selectivity in the hydroformylation of styrene of different thiolate and dithiolate bridge rhodium complexes together with BDPP as chiral diphosphine [5]. BDPP had previously been used as a chiral ligand in Pt/Sn catalysed enantioselective hydroformylation of styrene [6–8]. Although the best ee results with BDPP were

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75% [6] and 88% [7], the regioselectivity in 2-phenylpropanal was low (40% and 29%, respectively) [6–8].

The addition of (+)-BDPP to the dinuclear thiolate rhodium complex $[Rh(\mu\text{-}SBu^t)(CO)_2]_2$, first prepared by Kalck et al. [9], provides total conversion into aldehydes with 90% regioselectivity in 2-phenylpropanal and 10% (*R*) enantiomeric excess [5]. Enantiomeric excesses as high as 43% (*S*) with complete conversion into aldehydes and regioselectivities up to 94% in 2-phenylpropanal were reported at 30 bar and 65°C using the dithiolate bridge complexes $[Rh_2(\mu\text{-}S(CH_2)_nS)(COD)_2]$ ($n = 2$, 3 and 4) in the presence of BDPP (P/Rh = 2) [5].

The achiral rhodium precursor system $[Rh(\mu\text{-}OMe)(COD)]_2$ in the presence of phosphorous ligands is known to lead to the mononuclear rhodium hydride carbonyl phosphorous species in hydroformylation conditions [10]. When this complex was used in asymmetric styrene hydroformylation in the presence of different chiral diphosphines, the best results were obtained with BDPP [4]. It should be pointed out that in this system a P/Rh ratio of 4 was required to obtain considerable enantiomeric excesses in the hydroformylation of styrene [4].

We have previously described the preparation and reactivity of complexes of general formulae $[M_2(\mu\text{-}pz)(\mu\text{-}StBu)(L'_2)_2]$ (M = Rh, Ir; pz = pyrazolate; L'_2 = diolefin, $(CO)PR_3$) [11–13]. Reactivity studies showed the marked flexibility of the $M(\mu\text{-}pz)(\mu\text{-}StBu)$ framework. In particular, the complexes $[Rh_2(\mu\text{-}pz)(\mu\text{-}StBu)(CO)_2L_2]$ ($L = PPh_3$, $P(OMe)_3$, $P(OPh)_3$) are active catalysts in the hydroformylation of 1-hexene at very mild conditions, 5 bar and 80°C, providing complete conversion to aldehydes and selectivities in *n*-heptanal of 70% [13].

In this work, we present the hydroformylation of styrene using the complex $[Rh_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(COD)_2]$ as catalyst precursor in the presence of triphenylphosphine and chiral diphosphine ligands. We also study different pressure and temperature conditions, as well as different P/Rh ratios in an attempt to improve the selectivity results.

2. Experimental

2.1. General methods

All syntheses of rhodium complexes were performed using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. The complexes $[Rh_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(COD)_2]$ and $[Rh_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_2(PR_3)_2]$ were prepared using literature methods [13]. Phosphorous reactants and the $[Eu(hfc)_3]$ chiral shift reagent were purchased and used without further purification. Proton NMR spectra were measured on a Varian Gemini 300 MHz spectrometer and referenced in the standard way. Gas chromatography analyses were performed on a Hewlett–Packard Model 5890, a gas chromatograph with a flame ionization detector using a 25 m × 0.2 mm Ø capillary column (Ultra 2). Enantiomeric excesses were measured on the same equipment using a 50 m × 0.25 mm Ø capillary column (FS-cyclodex β-I/P).

2.2. Catalysis

Low-pressure hydroformylation experiments (5 atm) were carried out in a specially designed autoclave with magnetic stirring. The catalytic solution was contained in a glass vessel. Constant temperature was maintained by circulating water through a double jacket. The gas mixture was introduced at constant pressure from a gas ballast. The drop in pressure in the ballast was monitored using a pressure transducer connected to an electronic measurement and printing unit.

High-pressure hydroformylation experiments (30 atm) were carried out in a Berghof autoclave, and the reaction mixtures were magnetically stirred and electrically heated.

2.3. Standard catalysis experiment

A solution of the substrate (20 mmol), the catalyst precursor (0.05 mmol) and the phosphorous compound in 12.5 ml of solvent were introduced into the evacuated autoclave. The gas mixture was introduced and the system was heated. When thermal equilibrium was reached, the gas mixture was introduced until the desired pressure was obtained and stirring was initiated. Small samples of the catalytic solution were taken at various intervals to be analysed. After the reaction time, the autoclave was cooled to room temperature and depressurized. The samples were analysed by gas chromatography.

2.4. Enantiomeric excess measurements

Enantiomeric excesses were measured by three different methods.

2.4.1. ^1H NMR using Eu(hfc)$_3$ as a chiral shift reagent [14,15]

After the catalytic run, 0.2 ml of the catalytic solution was evaporated to dryness and dissolved in C_6D_6. ^1H NMR were recorded after adding portions (10–20 mg) of Eu(hfc)$_3$ until neat splitting of the signal for the formyl proton.

2.4.2. GC using chiral column of the alcohols obtained by reduction of the resulting aldehydes

After the catalytic run, 2 ml of the catalytic solution was added drop by drop to a stirred suspension of lithium aluminium tetrahydride (110 mg) in 5 ml of anhydrous tetrahydrofuran. After 5 min, methanol was added until bubbling stopped. Aluminium salts were removed by filtration through celite. The filtrate was evaporated until dry, dissolved in diethyl ether (30 ml), washed with sulphuric acid (10%) (3×15 ml), dried over magnesium sulfate and analysed by GC.

2.4.3. GC using chiral column of the acids obtained oxidizing the resulting aldehydes [16]

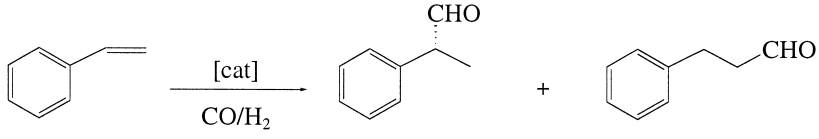
After the catalytic run, 2 ml of the catalytic solution was diluted with an aqueous 1.25 M potassium phosphate buffer solution (10 ml). An aqueous 1 M $KMnO_4$ solution (10 ml) was added to the resulting solution and stirred vigorously during 30 min. The oxidation was quenched by adding a saturated solution of Na_2SO_3 and the resulting pH of the mixture was adjusted to 3 with diluted HCl to dissolve the colloidal MnO_2. The usual extractive work-up provided the carboxylic acids which were analysed by GC after being distilled.

3. Results and discussion

The hydroformylation of styrene (Scheme 1) has been studied using the dinuclear complex [Rh$_2$(μ-pz)(μ-SBu^t)(COD)$_2$] [11,12] as catalyst precursor in the presence of various phosphorous ligands.

In general, carbonyl phosphine complexes [{Rh(μ-SR)(CO)(PR$_3$)}$_2$] are used directly as catalyst precursors [17], or the catalytic systems are prepared in situ by adding phosphorus ligands to [{Rh(μ-SR)(COD)}$_2$] under hydroformylation reaction conditions [18–20].

For comparative purposes, experiments were done using the isolated mixed complex [Rh$_2$(μ-pz)(μ-SBu^t)(CO)$_2$(PR$_3$)$_2$] as catalyst precursor as well as [Rh$_2$(μ-pz)(μ-SBu^t)(COD)$_2$] in the



1 **2** **3**

Scheme 1.

presence of PPh_3. In both cases, the results obtained in styrene hydroformylation were similar. In fact, the mixed carbonyl phosphine complex $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2(PR_3)_2]$ was observed after the hydroformylation reaction in the second case.

Triphenylphosphine and the diphosphines (2*S*,3*S*)-2,3-*O*-isopropiliden-2,3-dihydroxi-1,4-bis(diphenylphosphino)butane ((+)-DIOP) and (+)-(2*R*,4*R*)(−)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane ((+)-BDPP) or (−)-(2*S*,4*S*) ((−)-BDPP) were used as phosphorous ligands. All the reactions were carried out using a 1/1 ratio of CO/H_2. Tables 1 and 2 summarize the reaction conditions and the results of the hydroformylation runs. No hydrogenation or isomerization products were observed in any of the experiments.

Table 1 shows the results obtained in the hydroformylation of styrene when triphenylphosphine was used as ligand. Nearly complete conversion to aldehydes (97%) occurred using a P/Rh ratio of 1 at 5 bar and 80°C although the selectivity for the branched aldehyde was low (entry 1).

Complete conversion into aldehydes and 78% regioselectivity in 2-phenylpropanal was obtained in 5 h by increasing the CO/H_2 pressure to 30 bar (entry 2).

It is generally believed that selectivities increased while reducing temperature [3,21,22]. As expected, when the temperature was decreased to 65°C (entry 3), the regioselectivity increased and 91% of 2-phenylpropanal was obtained.

The use of a P/Rh ratio of 2 decreases the activities and regioselectivities independently on the condition used (entries 4 and 5). Therefore, the excess of phosphorous ligand does not provide better results.

Although pure complexes could not be obtained from the reactivity towards diphosphine, these ligands were used to prepare in situ catalyst precursor systems.

Table 2 shows the results obtained in the asymmetric styrene hydroformylation when the complex $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(COD)_2]$ is used as catalyst precursor in the presence of chiral diphosphines.

The use of the chiral diphosphine (+)-DIOP at 30 bar and 65°C (entry 6) with a P/Rh ratio of 4 gives complete conversion into aldehydes with 62% regioselectivity in 2-phenylpropanal. A 15% (*S*) enantiomeric excess is observed in this case. Similar results are obtained using the same diphosphine but decreasing the pressure from 30 to 5 bar and the P/Rh ratio from 4 to 2 (entry 7).

However, when the chiral diphosphine used is (+)-BDPP at 30 bar and 65°C (entry 8) with a P/Rh ratio of 2, 94% regioselectivity in 2-phenylpropanal is obtained with 51% (*S*) enantiomeric excess.

It is noteworthy that a strong dependence on the P/Rh ratio has been previously observed when $[Rh(\mu\text{-OMe})(COD)]_2$/BDPP is used as catalyst precursor in asymmetric styrene hydroformylation [4,5].

This new mixed thiolate–pyrazolate/BDPP system provides higher enantioselectivity than $[Rh(\mu\text{-OMe})(COD)]_2$/BDPP or $[Rh(\mu\text{-SBu}^t)(CO)_2]_2$/BDPP when the P/Rh ratio used is 2. These systems provided enantiomeric excesses between 5 and 10% in the opposite enantiomer (entries 9 and 10) [4,5]. A higher excess of diphosphine is not required to obtain enantiomeric excesses of almost 50% when the thiolate–pyrazolate/BDPP system is used.

Table 1
Styrene hydroformylation using the $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(COD)_2]/PPh_3$ system as catalyst precursor[a]

Run	P/Rh	*P* (bar)	*T* (°C)	*t* (h)	Conv[b] (%)	2-PP[c] (%)
1	1	5	80	7	97	57
2	1	30	80	5	100	78
3	1	30	65	7	100	91
4	2	5	80	8	80	41
5	2	30	65	8.5	72	89

[a] Reaction conditions: Solvent: tetrahydrofuran, substrate/precursor = 400, $CO/H_2 = 1$.
[b] Aldehyde conversion measured by GC.
[c] 2-Phenylpropanal.

Table 2
Asymmetric styrene hydroformylation using the $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(COD)_2]/PR_3$ system as catalyst precursor[a]

Run	P (bar)	T (°C)	PR_3	P/Rh	Conv[b] (%)	2-PP[c] (%)	ee[d] (%)
6	30	65	(+)-DIOP	4	99	62	15 (S)[e, f]
7	5	65	(+)-DIOP	2	96	62	12 (S)[g]
8	30	65	(+)-BDPP	2	60	94	51 (S)[e, f]
9[h]	30	65	(+)-BDPP	2	98	91	5 (R)[e,f]
10[i]	30	65	(+)-BDPP	2	100	90	10(R)[e,f]
11	5	65	(+)-BDPP	2	36	94	38 (S)[g]
12[j]	5	65	(−)-BDPP + PPh_3	2 + 1	70	95	50 (R)[g]
13	30	65	(+)-BDPP + PPh_3	2 + 1	44	95	46 (S)[g]

[a]Reaction conditions: Solvent: tetrahydrofuran, substrate/precursor = 400, $CO/H_2 = 1$, $t = 24$ h.
[b]Aldehyde conversion measured by GC.
[c]2-Phenylpropanal.
[d](%) ee was measured by chiral gas chromatography and ^1H NMR; see notes e,f,g.
[e]Chiral gas chromatography on the 2-phenylpropanal obtained by reduction of the aldehydes with $LiAlH_4$.
[f]^1H NMR with the addition of $[Eu(hfc)_3]$.
[g]Chiral gas chromatography on the 2-phenylpropanoic acid obtained oxidising the aldehydes with $KMnO_4$.
[h]Catalyst precursor $[Rh(\mu\text{-OMe})(COD)]_2$.
[i]Catalyst precursor $[Rh(\mu\text{-SBu}^t)(CO)_2]_2$.
[j]17 h.

Since reducing the temperature, a better enantioselectivity is generally observed [21,22], a 25°C temperature was used but no activity was observed. At 5 bar and 65°C the activity decreases, as does the enantioselectivity (38% (*S*)), while the regioselectivity in 2-phenylpropanal is maintained (94%) (entry 11).

The use of a mixture of diphosphine and triphenylphosphine has been previously reported to improve selectivities. This effect has been attributed to the intermediate species stabilisation [3,23–25]. In our case, a higher activity resulted when an equimolecular amount of triphenylphosphine was added to the catalytic system (entry 12). The regioselectivity is maintained (95%) and the enantiomeric excess increases to 50% (*R*). The use of a higher pressure does not improve the results (entry 13).

4. Conclusions

Catalytic precursor systems prepared using $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(COD)_2]$ in the presence of PPh_3, DIOP, BDPP and BDPP + PPh_3 are active in styrene hydroformylation.

BDPP provides better enantiomeric excesses than other chiral diphosphines, as it has been previously observed in other rhodium systems. Only a P/Rh ratio of 2 is required to obtain 50% enantiomeric excess.

In general, by increasing the pressure from 5 to 30 bar, better conversion and enantioselectivities are obtained. On the other hand, when the reaction pressure is 5 bar the best conversion and selectivity is obtained using BDPP combined with PPh_3.

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