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Asymmetric hydroformylation of styrene with rhodium complexes of sulfonated diphosphines in aqueous systems

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Abstract

Hydroformylation of styrene has been performed using as catalyst precursor $[Rh(\mu\text{-OMe})(cod)]_2$ (cod = 1,5-cyclooctadiene) associated with the sulfonated diarylphosphines dpppts [tetrasulfonated 1,3-bis(diphenylphosphino)propane], dppbts [tetrasulfonated 1,4-bis(diphenylphosphino)butane], (*R*,*R*)-CBDTS [1,2-bis(diphenylphosphinomethyl)cyclobutane] and (*S*,*S*)-BDPPTS [2,4-bis(diphenylphosphino)pentane] in aqueous solutions. The best results were obtained with the dpppts system using water–methanol as the solvent at 14 atm, a [P]/[Rh] ratio of 4 and a temperature range of 50–80°C. Under these conditions, the rhodium–dpppts catalyst gives regioselectivities up to 93% in 2-phenylpropanal. The rhodium–dppbts system gives higher conversions (up to 91%), but lower regioselectivity in 2-phenylpropanal (89%). The asymmetric hydroformylation of styrene using CBDTS as the ligand provided one of the highest enantioselectivity reported up to now for this reaction using sulfonated diphosphines (17% e.e. in *S*-2-phenylpropanal), although BDPPTS gives a slightly lower enantioselectivity of 14%, but with a very low conversion.

Keywords: Rhodium; Hydroformylation; Sulfonated diphosphines; Aqueous system; Asymmetric catalysis

1. Introduction

One way of solving the problem of separating the reaction products from the catalyst in homogeneous catalysis is to use water-soluble ligands [1,2], the most studied of which are sulfonated phosphines. Since the rhodium–TPPTS [TPPTS = $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$] system was first used in the hydroformylation of propene [3,4] and it was first applied in industry by Rhône-Poulenc/Ruhr-Chemie in 1984 [5,6], many sulfonated ligands have been prepared. Although most of the hydroformylation examples used monophosphines and mononuclear complexes, binuclear thiolate bridged complexes associated with TPPTS [7–9] have also been studied in the hydroformylation of 1-hexene and 1-octene.

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The activities obtained with the rhodium/TPPTS system have been improved using different sulfonated phosphines. Rhodium complexes associated with electron donating trisulfonated tris(ω-phenyl)alkylphosphines, $P[(CH_2)_n\text{-}C_6H_4\text{-}p\text{-}SO_3Na]_3$ ($n = 1$, 2, 3, or 6) had higher activity and lower regioselectivity in the hydroformylation of 1-octene [10] in an aqueous phase at lower [P]/[Rh] ratio. The improvement in conversion and selectivity using $P[C_6H_4\text{-}(CH_2)_m\text{-}C_6H_4\text{-}p\text{-}SO_3Na]_3$ ($m = 3$ and 6) as the ligand in the hydroformylation of 1-octene [11–13] has been attributed to the ability of these phosphines to aggregate in solution. The norbornene monophosphine derivative NORBOS–Na [14] is more active in propene hydroformylation than the rhodium–TPPTS system but n/i selectivities are lower under the same conditions.

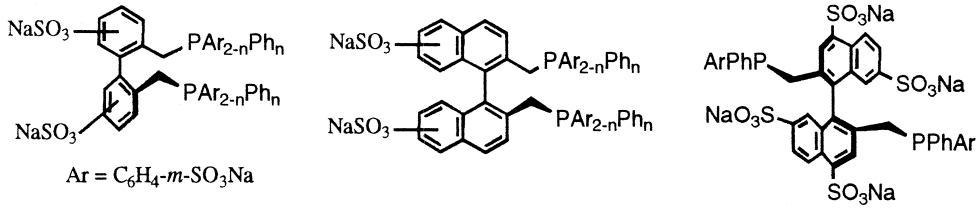
Although diphosphines generally have higher selectivities in hydroformylation in organic media [15,16], the sulfonated diphosphines have scarcely been investigated and this is probably due to the difficulty of preparing pure sulfonated ligands. Improvements in the purification methods of these kind of ligands have only recently been reported [17,18].

The sulfonated biphenyl derivative BISBIS–Na (Fig. 1) [14,18,19] and BINAS–Na [20] associated with the $[Rh(acac)(CO)_2]$ complex have higher activities and selectivities than the rhodium–TPPTS system in the hydroformylation of propene under the same reaction conditions. The BISBIS–Na system is also active in the hydroformylation of higher olefins such as 1-hexene.

Alkyl sulfonated diarylphosphines have scarcely been studied in hydroformylation. The system Rh–dppets [dppets: tetrasulfonated 1,2-bis(diphenylphosphino)ethane] [21] gave a low conversion in the hydroformylation of 1-octene (5–25%). The $[Rh(acac)(CO)_2]$/dppbts system (dppbts: tetrasulfonated 1,4-bis(diphenylphosphino)butane) has also been used in the hydroformylation of methyl acrylate and provides very poor chemo- and regioselectivity [22].

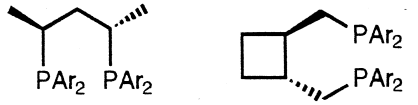
Asymmetric styrene hydroformylation in a two-phase system is still an unresolved problem with few examples being reported in the literature. Chiral sulfonated phosphines such as the monophosphine $P(menthyl)[(CH_2)_8C_6H_4\text{-}p\text{-}SO_3Na]_2$ associated with rhodium complexes [23] gave higher conversion and regioselectivity in the branched aldehyde than the Rh–TPPTS system, but no optical induction was observed in the formation of 2-phenylpropanal. The only reported chiral sulfonated diphosphine giving some optical induction is (*S*)-BINAS6–Na (Fig. 1) [24]. Biphasic hydroformylation of styrene in a methanol/water/toluene solution using the catalytic system rhodium/(*S*)-BINAS6–Na proceeds with good regioselectivity in 2-phenylpropanal (95%) and an enantioselectivity up to 18%.

We also reported [25] that the catalyst precursor based on $[Rh(\mu\text{-}OMe)(cod)]_2$ (cod = 1,5-cyclooctadiene) and (*S,S*)-2,4-bis(diphenylphosphino)pentane or (*S,S*)-BDPP as the chiral ligand, using a [P]/[Rh] ratio of 4, provided enantioselectivities up to 56% in (*S*)-2-phenylpropanal with 96% regioselectivities in the branched product in the hydroformylation of styrene. Some related diphosphites derived from 2,4-pentanediol also provided high enantioselectivities in this reaction [26–28].



BISBIS-Na BINAS-Na BINAS6-Na

Fig. 1. Sulfonated diphosphines.



(S,S)-BDPPTS (R,R)-CBDTS

Fig. 2. Chiral sulfonated diphosphines.

These results prompted us to study the behavior of tetrasulfonated diphosphines (*S,S*)-BDPPTS [29] [(tetrasulfonated 2,4-bis(diphenylphosphino)pentane] and (*R,R*)-CBDTS [tetrasulfonated 1,2-bis(diphenylphosphinomethyl)cyclobutane] [29] (Fig. 2) in the hydroformylation of styrene. These chiral diphosphines have previously been used in the hydrogenation of enamides providing good enantioselectivities [29–31], but they have never been applied in hydroformylation.

We report the results in hydroformylation of the rhodium complex $[Rh(\mu\text{-OMe})(cod)]_2$ associated with the above-mentioned chiral sulfonated diphosphines together with the related achiral tetrasulfonated alkyldiarylphosphines 1,3-bis(diphenylphosphino)propane (dpppts) and 1,4-bis(diphenylphosphino)butane (dppbts) as a model of catalytic behaviour.

2. Experimental

2.1. General methods

All syntheses of the rhodium catalyst precursor were carried out using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. All other reagents were used as supplied. The complex $[Rh(\mu\text{-OMe})(cod)]_2$ [32] and the diphosphines dpppts [33], dppbts [33], (*S,S*)-BDPPTS [29] and (*R,R*)-CBDTS [29] were prepared as previously reported. Gas chromatography analyses were performed in a Hewlett-Packard 5890A in an Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) column (25 m × 0.2 mm Ø) for the separation of the aldehydes and in an FS-cyclodex β-I/P (50 m × 0.25 mm Ø) for the separation of the chiral alcohols and carboxylic acids.

2.2. Catalysis

Hydroformylation experiments were carried out in an autoclave with magnetic stirring. The catalytic solution was contained in a Teflon vessel and the inside of the autoclave's cap was also Teflon-covered to prevent the solution coming into direct contact with the stainless steel. Constant temperature was maintained by an electric heating mantle.

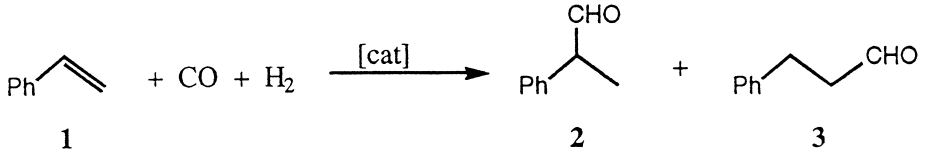
2.3. Standard hydroformylation experiment

The catalyst precursor $[Rh(\mu\text{-OMe})(cod)]_2$ (0.015 mmol) and the sulfonated phosphorus compound in the corresponding ratio was stirred for 1 h in 6 ml of the corresponding solvent until total dissolution. The substrate (15 mmol) was added and the total mixture introduced into the evacuated autoclave. The gas mixture was introduced and the system heated. When thermal equilibrium was reached, more gas mixture was introduced until the desired pressure. After the reaction time, the

autoclave was cooled to room temperature and depressurised. The final mixture was extracted with dichloromethane (3×5 ml), the organic phase was dried over magnesium sulfate and analysed by GC. Enantiomeric excesses were measured by GC using a chiral column after the aldehydes had been transformed into the carboxylic acids [34] or the alcohols [25] following described procedures.

3. Results and discussion

Hydroformylation of styrene **1** yields 2-phenylpropanal **2** and 3-phenylpropanal **3** according to Eq. (1). Different reaction conditions of this hydroformylation reaction were studied using $[Rh(\mu\text{-}OMe)(cod)]_2$/dpppts and dppbts as catalyst precursors. The results are summarised in Table 1.



1 **2** **3**

(1)

The catalyst was initially obtained from $[Rh(\mu\text{-}OMe)(cod)]_2$ and dpppts using a ratio $[P]/[Rh] = 4$. When the solvent was only water (Table 1, entry 1), at 80°C and 14 atm, conversion was 72% after 24 h; however, the selectivity in aldehydes was only 61% and the remaining 39% was 2- and 3-phenylpropanal. The formation of ethylbenzene was not observed.

Adding methanol as a co-solvent (Table 1, entry 2) so as to increase the solubility of styrene in the catalytic phase increased the chemoselectivity of the reaction with the formation of only aldehydes in a **2**/**3** ratio of 93/7; unfortunately the conversion was lower (only 62%).

The same trends were given by decreasing the [P]/[Rh] ratio to 3 at 80°C under 14 atm in a water–methanol mixture (Table 1, entry 3), but 9% the products were unidentified and polymers also formed. At a [P]/[Rh] ratio of 6 (Table 1, entry 4), the conversion was lower (25%) even if the reaction was regiospecific with the formation of the branched product **2** only.

Table 1
Hydroformylation of styrene using $[Rh(\mu\text{-}OMe)(COD)]_2$ with various sulfonated phosphines as catalyst precursor[a]

Entry	Ligand	[P]/[Rh]	p (atm)	T (°C)	Co-solvent[b]	Conversion (%)	Selectivity (%)	
							Aldehydes	**2**/**3**
1[c]	dpppts	4	14	80	–	72	61	81/19
2	dpppts	4	14	80	methanol	62	100	93/7
3[d]	dpppts	3	14	80	methanol	76	88	95/5
4	dpppts	6	14	80	methanol	25	100	100/0
5[d]	dpppts	3	14	120	methanol	98	91	84/16
6[d]	dpppts	3	30	80	methanol	36	83	100/0
7	dpppts	3	14	80	ethanol	29	100	79/21
8[c]	dppbts	4	14	80	–	98	72	80/20
9	dppbts	4	14	80	methanol	91	99	89/11
10	dppbts	4	14	65	methanol	63	100	89/11
11	dppbts	4	14	80	toluene	4	100	88/12

[a] Reaction conditions $[Rh(\mu\text{-}OMe)(COD)]_2 = 5 \times 10^{-3}$ M, [styrene]/[Rh] = 500, solvent 6 ml, $CO/H_2 = 1/1$.
[b] Ratio of water/co-solvent = 1:1.
[c] Alcohols were also formed.
[d] Polymers were also formed.

Table 2
Asymmetric hydroformylation of styrene using $[Rh(\mu\text{-OMe})(cod)]_2$ in the presence of chiral sulfonated ligands CBDTS and BDPPTS as catalyst precursor[a]

Run	Ligand	[P]/[Rh]	T (°C)	Conversion (%)	Selectivity (%)		e.e. (%) (Config)
					Aldeshydes	**2**/**3**	
1	CBDTS	4	50	76	100	70/30	9 (*S*)
2[b]	CBDTS	4	50	67	100	76/24	17 (*S*)
3[c]	CBD	4	50	23	100	73/27	< 1 (*S*)
4	BDPPTS	4	65	48	98	94/6	2 (*R*)
5[b]	BDPPTS	4	65	4	100	90/10	14 (*R*)

[a]Reaction conditions $[Rh(\mu\text{-OMe})(COD)]_2 = 5\times10^{-3}$ M, [styrene]/[Rh] = 500, solvent 6 ml (methanol/water:1/1), total pressure = 14 atm, $CO/H_2 = 1/1$, t = 24 h.
[b]pH = 7.
[c]Solvent THF.

When temperature was increased to 120°C at [P]/[Rh] = 3 at 14 atm (Table 1, entry 5), the conversion increased, but the regioselectivity in **2** was lower. At higher pressure (Table 1, 30 atm for entry 6), conversion was only 36%, and the selectivity in **2** was total, but formation of by-products and polymers was again observed.

Substituting methanol by ethanol as a co-solvent (Table 1, entry 7) gave a lower conversion, with complete chemoselectivity but lower regioselectivity. This is in contrast with previous results reported by Escaffre et al. [7], Kalck et al. [8] and Monteil et al. [9] who observed an increase in conversion using this solvent. Biphasic systems such as water–ethyl acetate, water–methanol–toluene or water–methanol–hexane gave very low conversions (< 5%) after 24 h under the same conditions.

In the case of the rhodium–dppbts system, conversion was very high (98%) when water was the only solvent (Table 1, entry 8), but alcohols were also formed as in the case of dpppts. At 80°C and 14 atm, in water–methanol as the solvent (Table 1, entry 9), an increase in chemoselectivity was observed, with similar selectivity and conversion (91%). Decreasing the temperature to 65°C gave lower conversion (63%) (Table 1, entry 10). Very low activity was observed using a true biphasic water–toluene system (Table 1, entry 11).

Comparing these results with reported data, the regioselectivity observed using the diphosphines dpppts and dppbts is higher than when the monophosphines such as TPPTS and $P(menthyl)[(CH_2)_8C_6H_4\text{-}p\text{-}SO_3Na]_2$ [23] were used, even though the activities are lower in our case. This is in agreement with the results in the literature concerning non-sulfonated phosphines [15,16]. It should be pointed out that the rhodium catalyst associated with the sulfonated diphosphine BINAS6–Na [24] also gave high regioselectivity in 2-phenylpropanal (up to 95%).

Attempts to reuse the catalytic system were unsuccessful probably due to phosphine oxidation. [2] When the aqueous phase of entry 2 (Table 1) was reused, only 2% conversion was observed in the second run.

Taking into account the above study and the previous reported results on using BDPP–rhodium systems [25], we undertook the hydroformylation of styrene using $[Rh(\mu\text{-OMe})(cod)]_2$ associated with the chiral sulfonated diphosphines BDPPTS and CBDTS. The results are summarised in Table 2.

It should be pointed out that the chemoselectivity in aldehydes was complete for both systems; however, the regioselectivity in 2-phenylpropanal was higher when BDPPTS was used as the ligand.

[2] In a preliminary high-pressure NMR study, formation of the phosphine oxide was observed under catalytic conditions.

The 1,4-diphosphine CDBTS provided a higher conversion than BDPPTS, in agreement with the trend observed previously when dpppts was compared to dppbts.

The enantioselectivities of 2-phenylpropanal using these chiral ligands were generally low: 9% with CBDTS and 2% with BDPPTS (Table 2, entries 1 and 4). In order to avoid a possible racemization of the 2-phenylpropanal in the basic medium due to the sulfonated phosphine syntheses, we performed an experiment at initial pH 7 (Table 2, entries 2 and 5) by adding sulfuric acid (0.5 M) and a buffer solution, respectively. The enantiomeric excess increased to 17% and 14% for the CBDTS and the BDPPTS catalyst, respectively. In the case of CBDTS system, the conversion decreased to 67% but very low conversion was obtained with BDPPTS system. The drop in conversion with decreasing pH has also been reported in the hydroformylation of 1-octene using rhodium–TPPTS systems [35].

The homogeneous rhodium–BDPP system at 10 atm, 65°C and a [P]/[Rh] ratio of 4 gave enantioselectivities up to 53% in 2-phenylpropanal in tetrahydrofurane [25]. As previously noticed for other phosphines [24] and also for other reactions [30,31,36], sulfonated chiral phosphines gave lower enantioselectivities. In contrast, the enantiomeric excess obtained using the non-sulfonated CBD system (Table 2, entry 3) in tetrahydrofurane under the same conditions was very low ($< 1\%$).

4. Conclusion

In conclusion, the rhodium–dppbts catalyst generally produces higher conversions of aldehyde, while the rhodium–dpppts catalyst is usually more regioselective in branched aldehyde.

The rhodium–CBDTS catalyst studied here showed an enantioselectivity (17%) as high as the best result reported by Eckl et al. [24] in the hydroformylation of styrene with sulfonated ligands (enantiomeric excess of 18% was reported for BINAS6–Na), while the rhodium–BDPPTS catalyst provided slightly lower but very low conversion.

Work is now in progress to evaluate the influence of the pH on this reaction and to determine the species formed under the catalytic conditions.

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