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Platinum-catalysed enantioselective hydroformylation of styrene. Platinum–diphosphine–tin(II)fluoride catalytic system: a novel asymmetric hydroformylation catalyst

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Abstract

Enantioselective hydroformylation of styrene was carried out in the presence of platinum-containing catalysts. Tin(II) fluoride was used as cocatalyst, giving a catalytic system of unusually high stability. When the optically active diphosphine 2,4-bis(diphenylphosphino)pentane (BDPP) was used the absolute configuration of the 2-phenylpropanal formed varied with the temperature used. In dichloromethane the enantiomeric excess depends strongly on the temperature used. Although the addition of 2-diphenylphosphino-pyridine to the catalytic system strongly reduces the catalytic activity, the BDPP-2-diphenylphosphino-pyridine "mixed-phosphine system" gave 86.7% e.e.

1. Introduction

The asymmetric functionalization of unsaturated prochiral olefins by formation of a formyl group has been investigated by many research groups in the last two decades [1]. Although several phosphines have been found to be effective in platinum- and rhodium-catalysed asymmetric hydroformylation [2], $SnCl_2$ seems to be the only promising cocatalyst in the platinum-phosphine-additive system tested up to now and the hydroformylations were carried out almost exclusively in aromatic solvents [3–4]. The ease of carbene-like insertion of tin(II) chloride into the Pt–Cl bond results in the formation of $PtCl(SnCl_3)(P–P)$ type catalyst containing a strongly *trans*-activating $SnCl_3^-$ ligand [5], which plays a key role in the reactivity of the catalytic species [6–9].

Recently we showed that the enantioselectivity is especially sensitive to temperature when BDPP is used as a ligand in the hydrogenation of Schiff base [10] or hydroformylation of styrene [11] with rhodium- or platinum-based catalytic systems, respectively. We assumed that there was a correlation between the catalyst conformation (achiral chair, chiral δ and λ skew) and the configuration of the major enantiomer in the products. Reactions for which the variation of selectivity with temperature has been recorded have been reviewed by Scharf *et al.* in terms of the isoinversion principle [12].

We also showed previously that the enantioselectivity of hydroformylation can be increased by the use of monophosphine–platinum-tin(II) chloride "mixed-phosphine" systems [13].

In this paper, we present the results of a study of asymmetric hydroformylation of styrene with a number of preformed and "in situ" platinum catalysts under various conditions.

2. Results and discussion

2.1. Enantioselective hydroformylation of styrene in the presence of the platinum–BDPP–tin(II) fluoride "in situ" catalyst

Tin(II) difluoride, SnF_2 was used instead of $SnCl_2$ as cocatalyst in the platinum catalysed asymmetric hydroformylation of styrene. As is well known, the hydroformylation to give branched (2-phenylpropanal, **2**) and

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linear (3-phenylpropanal, **3**) regioisomers is always accompanied by the formation of ethylbenzene (**1**).

$$PhCH{=}CH_2 \xrightarrow[cat.]{CO/H_2} PhC_2H_5 + PhCH(CHO)CH_3 + Ph(CH_2)_2CHO$$

1 **2** **3**

Surprisingly, the $PtCl_2(BDPP) + SnF_2$ system is not only an active enantioselective catalyst, but remains effective up to 220°C (Table 1). Even at this temperature only a small amount of platinum metal separates. Much decomposition was observed previously in the presence of $SnCl_2$ above 120°C, and above 150°C the activity of the catalysts is usually completely lost [11].

Hydroformylation involving long reaction times at low temperature gave the chiral aldehyde (**2**) in moderate to good enantiomeric excess. Although the racemization of the optically active α-phenylpropanal is very fast at high temperatures [14] the hydroformylation is enantioselective even at 200°C. The direction of the change in the predominant configuration with the reaction temperature is the same as that observed previously [11]. The structure of the catalytically active species responsible for the stereochemical outcome of the hydroformylation must be slightly different from that in the earlier cases. In platinum + BDPP + $SnCl_2$-catalysed reaction below 88°C formation of *S*-enantiomer is favoured whereas at higher temperatures the *R*-enantiomer predominates, but in the presence of SnF_2 the inversion takes place at about 110°C (Fig. 1).

There is less hydrogenation (side reaction) with $PtCl_2$(diphosphine) + SnF_2 catalysts than with those containing $SnCl_2$, less than 3% of **1** being obtained below 50°C with the SnF_2 species.

Use of VALPHOS ((+)-(*R*)-1,2-bis(diphenylphosphino)-3-methyl-butane) in place of BDPP markedly affects both catalytic activity and regioselectivity. Although for the extent of conversion much longer times were needed, the ratios of branched to linear aldehyde are favourable with VALPHOS. These results show the effect of variation in the chelate structures. Whereas the BDPP-chelate ring is flexible and shows a skew-

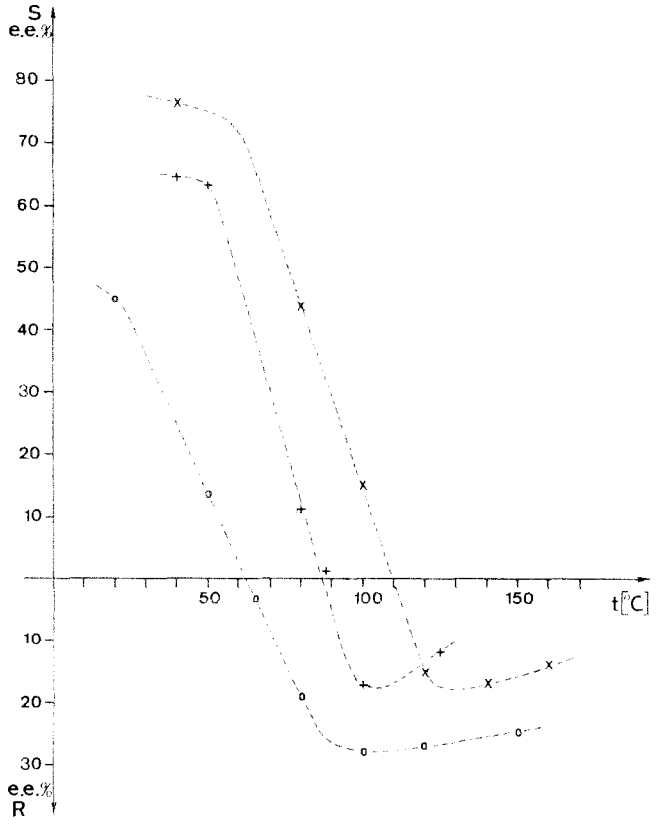

Fig. 1. Asymmetric hydroformylation of styrene in the presence of $PtCl(SnCl_3)$(BDPP) in toluene (+); $PtCl_2$(BDPP) + SnF_2 in toluene (×) and $PtCl_2$(BDPP) + $SnCl_2$ in dichloromethane (○).

TABLE 1. Asymmetric hydroformylation of styrene in the presence of $PtCl_2$(BDPP) + SnF_2 (runs 1–7) (and $PtCl_2$(VALPHOS) + SnF_2 (runs 8,9)) at different temperatures [a]

Run	Temperature (°C)	Reaction time (h)	Conv. [b] (%)	R_C [c] (%)	R_R [d] (%)	e.e. (%); abs. conf.
1	40	240	72	97.6	31.8	76.0; *S*
2	80	120	53	95.2	33.5	44.3; *S*
3	100	5	26	95.0	30.8	15.1; *S*
4	120	5	36	84.7	27.6	15.2; *R*
5	140	5	86	75.0	23.8	16.6; *R*
6	160	2	80	62.9	22.9	14.2; *R*
7	200	1.5	84	37.6	24.1	5.2; *R*
8	160	50	70	66.9	60.3	23.7; *S*
9	200	25	55	48.7	62.6	24.3; *S*

[a] Reaction conditions: 0.025 mmol Pt-complex; 0.05 mmol SnF_2; 100 mmol styrene; solvent toluene; $p(CO) = p(H_2) = 40$ bar. [b] (mmol product/mmol initial substrate) · 100. [c] **(2 + 3)/(1 + 2 + 3)** · 100. [d] **2/(2 + 3)** · 100.

TABLE 2. Asymmetric hydroformylation of styrene in the presence of $PtCl_2(BDPP) + SnCl_2$ in dichloromethane [a]

Run	Temperature (°C)	Reaction time (h)	Conv. [b] (%)	R_C [c] (%)	R_R [d] (%)	e.e. (%); abs. conf.
1	20	72	36	99	50.1	45.0; *S*
2	50	12	25	95	61.6	14.5; *S*
3	65	12	29	94.7	60.7	3.4; *R*
4	80	12	52	93.9	47.5	19.2; *R*
5	100	10	79	92.6	33.5	28.0; *R*
6	120	10	94	85.7	27.3	27.2; *R*

[a] Reaction conditions: 0.025 mmol Pt-complex; 0.05 mmol SnF_2; 100 mmol styrene; solvent toluene; $p(CO) = p(H_2) = 40$ bar. [b] (mmol product/mmol initial substrate) · 100. [c] $(2 + 3)/(1 + 2 + 3) \cdot 100$. [d] $2/(2 + 3) \cdot 100$.

chair equilibrium [11], VALPHOS seems to form a more rigid chelate with a different arrangement of the phenyl group in the PPh_2 fragment.

The need for long reaction times at low temperatures can be accounted for terms of the lower concentration of the complexes containing a direct platinum–tin bond. Tin(II) chloride reacts almost quantitatively with $PtCl_2P_2$ complexes [5], whereas insertion of SnF_2 into the Pt–Cl bond must take place to a lesser extent at low temperature. No signals were observed in the ^{31}P NMR spectrum that could be assigned to a $PtCl(SnClF_2)$(BDPP) complex.

2.2. Enantioselective hydroformylation of styrene in the presence of platinum–BDPP–tin(II) chloride "in situ" catalyst using dichloromethane solvent

For a long time halogenated hydrocarbons have been considered to be inappropriate solvents for asymmetric hydroformylation because of the low e.e-s obtained under the usual reaction conditions. The $SnCl_2$ insertion into Pt–Cl bond is very fast in chloroform or dichloromethane, giving the $SnCl_3^-$-containing complex that is crucial for effective carbonylation. (^{31}P NMR spectroscopy revealed quantitative formation of $PtCl(SnCl_3)$(P–P)-type complexes in dichloromethane).

The selectivity towards aldehyde formation and the regioselectivity were much higher in dichloromethane than in aromatic solvents for a given type of catalyst.

When in the present work the enantioselective hydroformylation of styrene was carried out in dichloromethane the effect of variation of the temperature mentioned above was again observed. Below 63°C the formation of (*S*)-2-phenylpropanal is favoured, but at higher temperatures the *R*-enantiomer of 2-phenylpropanal predominates, with low to moderate e.e-s (Table 2, Figure 1). Although the form of the plot of e.e. against the reaction temperature is similar to those obtained under a variety of reaction conditions, the differing positions of the plots indicates that slightly different transition states are involved.

The strong dependence of the optical yield on reaction temperature shows the importance of making studies over a large range of temperature. The phenomenon could be due to the interplay of kinetic factors and the sterical difference between transition states which contain the prochiral substrate with coordination varying from *si* to *re* enantiosites.

2.3. Asymmetric hydroformylation of styrene in the presence of phosphine–platinum-tin(II) chloride "in situ" catalysts

The use of 2-diphenylphosphinopyridine as the ligand in the rhodium-triphenylphosphine catalytic system has a beneficial effect on the selectivity in hydroformylation [15].

TABLE 3. Asymmetric hydroformylation of styrene in the presence of platinum "*in situ*" catalysts [a]

Run	Catalyst	R. time (h)	R. temp. (°C)	Conv. [b] (%)	R_C [c] (%)	R_R [d] [%]	e.e.; abs. conf.
1	$PtCl_2(PhCN)_2 + 2Ph_3P + 2SnCl_2$	23	100	51	93.6	41.4	–
2	$PtCl_2(PhCN)_2 + 2Ph_3P + Ph_2PyP + 2SnCl_2$	23	100	8	93.3	30.4	–
3	$PtCl_2(PhCN)_2 + 2Ph_2PyP + 2SnCl_2$	23	100	2	84.4	35 [e]	–
4	$PtCl_2(BDPP) + Ph_2PyP + 2SnCl_2$	160	40	30	97.6	31.8	86.7; *S*
5	$PtCl_2(BDPP) + Bu_3P + 2SnCl_2$	240	25	69	91.1	38.6	72.5; *S*
6	$PtCl_2(BDPP) + 2Bu_3P + 2SnCl_2$	240	25	< 2	n.d.	n.d.	n.d.

[a] Reaction conditions: 0.025 mmol Pt-complex; 0.05 mmol SnF_2; 100 mmol styrene; solvent toluene; $p(CO) = p(H_2) = 40$ bar. [b] (mmol product/mmol initial substrate) · 100. [c] $(2 + 3)/(1 + 2 + 3) \cdot 100$. [d] $2/(2 + 3) \cdot 100$.

In platinum-catalysed hydroformylation addition of 2-diphenylphosphino-pyridine strongly reduces the catalytic activity (Table 3). However, use of this monodentate phosphine in the BDPP-containing catalyst resulted in 86.7% e.e. Upon the addition of one equivalent of the basic monodentate phosphine (Bu_3P) to the $PtCl_2$(BDPP) precursor the reaction becomes less enantioselective. When less basic phosphines (*e.g.* Ph_3P) were used [13], the catalytic activity of the system was lower, and two equivalents of Bu_3P completely deactivated the catalytic system. In the first step the [PtCl(diphosphine)(monophosphine)]$^+$ ionic complex was formed [16]. Upon addition of basic monodentate phosphine to the precursor in threefold (or larger) excess the ionic species predominates but partial substitution of the diphosphine takes place. When the reaction is monitored by ^{31}P NMR, a singlet from free BDPP (or PPh_2 noncoordinating) appears at -0.2 ppm and the very weak central lines of a new $[PtP_3Cl]^+$ complex were clearly observed and could be assigned to a Pt-complex containing the diphosphine as a monodentate ligand along with two PBu_3 ligands. This explanation is consistent with the absence of a $[Pt(PBu_3)_3Cl]^+$ cation [17] even in the presence of a six-fold excess of PBu_3. This complex should give two signals at 1.4 and 10.2 ppm.

3. Experimental section

3.1. Reagents

The catalytic precursors $PtCl_2(PhCN)_2$, $PtCl_2$[(*S,S*)-BDPP] and $PtCl_2$[(*R*)-VALPHOS] were prepared by procedures described previously [11,18].

Toluene was distilled under argon from sodium in the presence of benzophenone. Dichloromethane was dried over calcium chloride and distilled. Styrene was freshly distilled under argon before use.

The compositions of the reaction mixtures were determined by GLC with a Hewlett-Packard 5830A Gas Chromatograph fitted with a capillary column coated with SP-2100. The optical rotations of the products were measured for neat liquids with a Schmidt Haensch LM visual polarimeter and with a Polamat (Karl Zeiss, Jena) automatic polarimeter after fractional vacuum distillation of the product mixture. The optical yields were calculated by use of the reported value, $[\alpha]_D^{25} + 238°$, for neat (*S*)-2-phenylpropanal [19].

3.2. Hydroformylation experiments

In a typical experiment a solution of 0.025 mmol (17.5 mg) $PtCl_2$[BDPP], 0.05 mmol (9.5 mg) of $SnCl_2$ in toluene containing 0.1 mol (11.5 ml) of styrene was transferred under argon into a 150 ml stainless steel autoclave. The vessel was pressurized to 80 bar total pressure ($CO/H_2 = 1/1$), placed in a thermostated electric oven, and agitated by an arm shaker. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed, and quickly analysed by GLC, then fractionally distilled to enable determination of the optical purity of the 2-phenylpropanal.

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