

Asymmetric hydroformylation of styrene with $\text{PtCl}_2(\text{atropoisomeric diphosphine})/\text{SnCl}_2$ systems

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Abstract

The new chiral complex $[\text{PtCl}_2\{(S)-(-)\text{-MeOBIPHEP}\}]$, where MeOBIPHEP is the atropoisomeric diphosphine 2,2'-bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl, has been synthesized. In the presence of SnCl_2 this species is an efficient catalyst for the asymmetric hydroformylation of styrene. Asymmetric inductions are higher than those attainable using the system $[\text{PtCl}_2\{(R)-(+)\text{-BINAP}\}]/\text{SnCl}_2$, where BINAP is 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl. The influence of CO and H_2 partial pressures on the catalytic activity of the $[\text{PtCl}_2\{(S)-(-)\text{-MeOBIPHEP}\}]/\text{SnCl}_2$ system has also been studied.

Keywords: Asymmetric hydroformylation; Hydroformylation; Platinum; Styrene

1. Introduction

In recent years there has been much interest in asymmetric hydroformylation of styrene [1,2] since the resulting branched product 2-phenylpropanal can be readily oxidized to the corresponding acid which belongs to the family of 2-arylpropanoic acids. This class of compounds has become commercially important since they are very effective nonsteroidal analgesics [3,4].

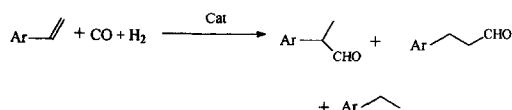
Platinum(II) complexes of the type $[\text{PtCl}_2(\text{chiral diphosphine})]$ promoted by SnCl_2 are widely used as catalysts in the asymmetric hydroformylation of olefins. As a matter of fact, using diphosphines with dibenzophospholyl substituents [5,6] or the atropoisomeric ligand (S)-BINAP [7], these systems give very high asymmetric inductions.

In the present paper we describe the study of the catalytic activity of the $[\text{PtCl}_2\{(S)-(-)\text{-MeOBIPHEP}\}]/\text{SnCl}_2$ system containing the atropoisomeric diphosphine 2,2'-bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl [8]. The catalytic activity of the new MeOBIPHEP containing complex has been compared with that of complex $[\text{PtCl}_2\{(R)-(+)\text{-BINAP}\}]$ under the same conditions.

2. Results and discussion

The synthesis and characterization of the catalyst precursor $[\text{PtCl}_2\{(S)-(-)\text{-MeOBIPHEP}\}]$ 1 are described in the experimental part. Complex 1 in the presence of SnCl_2 efficiently catalyzes the hydroformylation of styrene (Scheme 1). The influence of the temperature on this reaction is reported in Table 1.

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Scheme 1.

The optical purity (o.p.) obtained at 30°C (71.7%) is very high but the reaction rate is disappointing. As usual, an increase in the reaction temperature causes substantial growth of the reaction rate which is adversely accompanied by a decrease in the optical purity of the branched aldehyde, optical purity which at 80°C approaches zero. The branched to straight aldehyde ratio (regioselectivity) is approximately 1 at 30°C and decreases on increasing the reaction temperature, analogous behaviour was previously reported in the case of $[\text{PtCl}_2(\text{SnCl}_3)\{(-)-(2S,4S)\text{-}2,4\text{-bis(diphenylphosphino)pentane}\}]$ [9]. The formation of the by-products, polystyrene and ethylbenzene, is not significant and only slightly increases with temperature. In Table 2, we have reported the data obtained with $[\text{PtCl}_2\{(R)\text{-}(+)\text{-BINAP}\}]$ 2/ SnCl_2 under identical experimental conditions. Comparison of the data in Table 1 and Table 2 indicates that in both cases the branched

aldehyde produced has prevailing absolute configuration equal to that of the asymmetric ligand used. Complex 1 gives higher o.p.. The main difference in the behaviour of the two complexes under examination consists in the opposite dependence of the regiochemistry of the reaction upon temperature.

In the case of catalysts containing atropoisomeric diphosphines, no information is available on the stereochemistry of the addition of formyl group and hydrogen atom to the double bond. The deuteroformylation of norbornene carried out as described by Botteghi [10] indicates that with both 1 and 2 catalysts the addition is *cis*, as previously found with platinum [10,11], rhodium [12] or cobalt [13] complexes.

The influence of the pressure of hydrogen and of carbon monoxide on the catalytic activity of the 1/ SnCl_2 system is reported in Table 3 and Table 4, respectively. The $P(\text{H}_2)$ seems to affect markedly only the reaction rate, even if at the lowest $P(\text{H}_2)$ value a small effect on regioselectivity is also recognizable. Much more interesting are the data relevant to the influence of the $P(\text{CO})$

Table 1

Hydroformylation of styrene in the presence of the catalytic system $[\text{PtCl}_2\{(S)\text{-}(-)\text{-MeOBIPHEP}\}]/\text{SnCl}_2$; influence of temperature

Temperature (°C)	Reaction time (h)	Conversion (%)	Yield (%)		Isomeric ratio branched/straight	Optical purity (%) (absolute configuration)
			Aldehydes	Ethylbenzene		
30	356	56.9	42.3	1.4	1.07	71.7 (S)
50	116	85.1	60.5	2.9	0.99	54.7 (S)
80	16	91.0	70.7	6.5	0.75	0.1 (S)

Styrene: 50 mmol; $[\text{PtCl}_2\{(S)\text{-}(-)\text{-MeOBIPHEP}\}]$: 0.05 mmol; SnCl_2 : 0.05 mmol; substrate/catalyst: 1000/1; toluene: 35 ml; $P(\text{H}_2) = P(\text{CO})$: 50 atm.

Table 2

Hydroformylation of styrene in the presence of the catalytic system $[\text{PtCl}_2\{(R)\text{-}(+)\text{-BINAP}\}]/\text{SnCl}_2$; influence of temperature

Temperature (°C)	Reaction time (h)	Conversion (%)	Yield (%)		Isomeric ratio branched/straight	Optical purity (%) (absolute configuration)
			Aldehydes	Ethylbenzene		
30	570	37.4	25.2	0.8	0.47	60.0 (R)
50	70	57.3	36.4	1.5	0.47	45.3 (R)
80	24	76.2	54.5	4.1	0.67	6.3 (R)

Styrene: 50 mmol; $[\text{PtCl}_2\{(R)\text{-}(+)\text{-BINAP}\}]$: 0.05 mmol; SnCl_2 : 0.05 mmol; substrate/catalyst: 1000/1; toluene: 35 ml; $P(\text{H}_2) = P(\text{CO})$: 50 atm.

Table 3

Hydroformylation of styrene in the presence of the catalytic system $[\text{PtCl}_2\{(S)-(-)\text{-MeOBIPHEP}\}]/\text{SnCl}_2$; influence of $P(\text{H}_2)$

$P(\text{H}_2)$ (bar)	Reaction time (h)	Conversion (%)	Yield (%)		Isomeric ratio branched/straight	Optical purity (%) (absolute configuration)
			Aldehydes	Ethylbenzene		
20	237	57.0	41.4	1.0	0.78	54.3 (S)
50	116	85.1	60.5	2.9	0.99	54.7 (S)
80	72	67.7	46.4	3.5	0.96	58.5 (S)
110	54	68.9	42.7	4.7	0.95	56.2 (S)

Styrene: 50 mmol; $[\text{PtCl}_2\{(S)-(-)\text{-MeOBIPHEP}\}]$: 0.05 mmol; SnCl_2 : 0.05 mmol; substrate/catalyst: 1000/1; toluene: 35 ml; $P(\text{CO})$: 50 atm; T : 50°C.

Table 4

Hydroformylation of styrene in the presence of the catalytic system $[\text{PtCl}_2\{(S)-(-)\text{-MeOBIPHEP}\}]/\text{SnCl}_2$; influence of $P(\text{CO})$

$P(\text{CO})$ (bar)	Reaction time (h)	Conversion (%)	Yield (%)		Isomeric ratio branched/straight	Optical purity (%) (absolute configuration)
			Aldehydes	Ethylbenzene		
20	98	34.2	20.8	2.8	0.91	28.2 (S)
50	116	85.1	60.5	2.9	0.99	54.7 (S)
80	96	61.5	41.4	1.3	0.85	67.4 (S)
110	140	87.2	67.3	1.5	0.96	69.2 (S)

Styrene: 50 mmol; $[\text{PtCl}_2\{(S)-(-)\text{-MeOBIPHEP}\}]$: 0.05 mmol; SnCl_2 : 0.05 mmol; substrate/catalyst: 1000/1; toluene: 35 ml; $P(\text{H}_2)$: 50 atm; T : 50°C.

(Table 4). Low values of this parameter adversely affect both the reaction rate and the optical purity of the branched aldehyde. Increasing the $P(\text{CO})$, the o.p. of the branched aldehyde smoothly increases until an asymptotic value ($\sim 70\%$) is reached (Fig. 1).

Such trend is opposite to that usually found. In fact, many research groups reported that high $P(\text{CO})$ values bring about low reaction rates and low o.p. [14–17]. This latter behaviour and some other peculiar aspects of the hydroformylation carried out in the presence of Pt complexes have been justified by Consiglio et al. [15] invoking the presence of an intricate set of equilibria which involve the CO pressure and the catalytically active species; on the other hand, it has been also surmised [14,16,17] that several different catalysts might be operative, their relative concentrations depending on $P(\text{CO})$ values.

In our opinion, the results above reported are not sufficient to support any mechanistic conclusion even if the particular nature of the atropois-

meric MeOBIPHEP ligand is likely to play a key role.

Owing to the unusual dependence of the o.p. on the $P(\text{CO})$ and the interesting enantioselectivity obtained, further studies of the mechanism of the reaction are in progress.

3. Experimental

The chiral ligand $(S)-(-)\text{-MeOBIPHEP}$ was prepared as described in literature [8]. Complex $[\text{PtCl}_2\{(S)-(-)\text{-MeOBIPHEP}\}]$ **1** was synthesized by adding an equimolecular amount of the atropoisomeric diphosphine to $[\text{PtCl}_2(1,5\text{-cyclooctadiene})]$ [18] in CH_2Cl_2 . The resulting solution was stirred for 3 h under nitrogen. Addition of n-hexane afforded the product as a white powder (75% yield). The IR spectrum (Nicolet 750 FT-IR; Nujol mull between CsI windows) shows two weak absorptions at 317 and 293 cm^{-1} (Pt–Cl stretchings). The ^{31}P -NMR spectrum

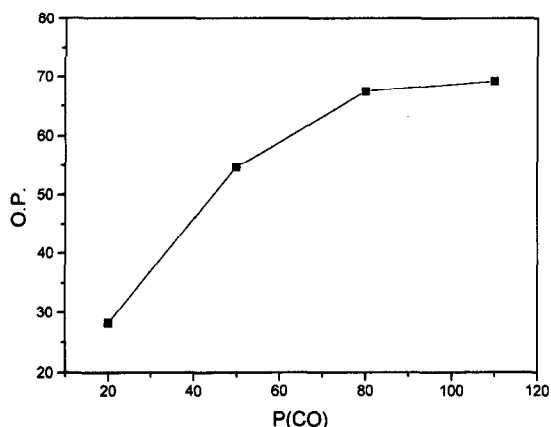


Fig. 1. Optical purity of 2-phenyl propanal obtained by hydroformylation of styrene carried out at various $P(\text{CO})$.

(Bruker 200 AC in CDCl_3) consists of a singlet at 8.54 ppm (downfield with respect to 85% H_3PO_4) flanked by ^{195}Pt satellites [$^1J(\text{Pt}-\text{P}) = 3650 \text{ Hz}$]; the $^1\text{H-NMR}$ spectrum displays a singlet at 3.49 ppm due to the hydrogen atoms of the methoxyl groups and complex multiplets (6.40–7.40 ppm) due to the aromatic hydrogens. Specific optical rotation (Perkin Elmer 241) is $[\alpha]_{\text{D}}^{25} = -238^\circ$ (c 0.495, CH_2Cl_2).

Complex $[\text{PtCl}_2\{(\text{R})-(+)\text{-BINAP}\}]$ was prepared as reported in literature [7] for the (S) - $(-)$ -BINAP analogue.

Catalytic experiments were carried out in a magnetically stirred stainless steel autoclave ($\approx 150 \text{ cm}^3$). The catalytic system was prepared mixing in the reactor equimolecular amounts of the platinum complex and SnCl_2 in toluene. The composition of the crudes was determined by GLC using isopropylbenzene (cumene) as internal standard; this allowed us to quantify both the expected aldehydes and ethylbenzene and the GLC undetectable polystyrene. The formation of the polymer was confirmed by IR spectroscopy. The optical purity of the branched aldehyde was determined by polarimetry (Perkin Elmer 241)

using the specific rotatory power values reported by Consiglio [19]

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