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Temperature dependence of the asymmetric induction in the $PtCl(SnCl_3)[(-)$-(2*S*, 4*S*)-2,4-bis(diphenylphosphino)pentane]-catalyzed enantioselective hydroformylation reaction

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Abstract

Asymmetric hydroformylation of some prochiral olefins has been shown to be catalyzed by a new (preformed) $PtCl(SnCl_3)$[(*S*,*S*)-BDPP] ((*S*,*S*)-BDPP = (−)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane) catalyst. Vinylidene carboxylic esters are hydroformylated regioselectively but with rather moderate enantioselectivity. In hydroformylation of styrene the linear non chiral regioisomer 3-phenylpropanal is the main product, but the enantioselective formation of 2-phenylpropanal is strongly influenced by the reaction temperature, the *S*-enantiomer predominate at lower and the *R*-species at higher temperatures. Appropriate choices of the partial pressure of CO and H_2 led to a relatively high (76.5%) enantiomeric excess.

Introduction

Asymmetric hydroformylation of unsaturated substrates has been intensively studied [1]. Especially high enantioselectivity has been achieved with Pt-diphosphine-chloro catalysts. Simple olefins, not containing functional groups, were hydroformylated with $PtCl(SnCl_3)$[(*R*,*R*)-DIOP] catalyst (DIOP = 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane) to give enantiomeric excesses of up to 47% [2]. In the hydroformylation of styrene about 80% e.e. was achieved with the (*R*,*R*)-DBP-DIOP-$PtCl_2$/$SnCl_2$-H_2O catalytic system (DBP-DIOP = 2,2-dimethyl-4,5-bis(5*H*-dibenzophosphol-5-ylmethyl)-1,3-dioxolane) [3] and with the (*S*,*S*)-BPPM-$PtCl_2$-$SnCl_2$ supported catalyst ((*S*,*S*)-BPPM = (2*S*,4*S*)-*N*-t-butoxycarbonyl-4-(diphenylphosphino)-2-(diphenylphosphino)methylpyrrolidine [4]. Vinylidene esters were hydroformylated regioselectively with the DIOP-containing Pt catalyst to give the "less branched" aldehyde in optical yields strongly dependent on the

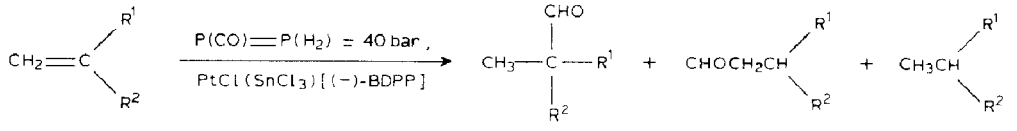
reaction conditions and the nature of the substituents on the olefin. In the hydroformylation of dimethyl itaconate the corresponding aldehyde enantiomer was formed in 83.5% e.e. [5]. Recently various vinyl aromatics, vinyl acetate, and *N*-vinyl phtalimide have been asymmetrically hydroformylated with a $PtCl_2$[(*S*,*S*)-BPPM] + $SnCl_2$ catalyst, with enantioselectivities of up to 82%, when the same substrates were used in triethyl orthoformate as solvent the corresponding diethyl acetals were isolated in e.e.'s of > 96–98% [6].

In view of these excellent catalytic results we decided to study the mechanism of the enantioselective hydroformylation reaction with the new $PtCl(SnCl_3)$[(*S*,*S*)-BDPP] catalyst. Our first studies revealed a strong influence of the reaction temperature in the enantioselectivity and this uncommon behaviour in asymmetric hydroformylation, together with other results is described below.

Results and discussion

For the hydroformylations a new platinum-diphosphine complex, $PtCl(SnCl_3)$-[(*S*,*S*)-BDPP], was used. The chiral phosphine ligand was previously used in rhodium-catalyzed asymmetric hydrogenations [7]. BDPP appears to be unique in the sense that its rhodium(I) complexes serve as effective homogeneous asymmetric catalysts not only for hydrogenation of *Z*-α-amidoacrylic acids but also for the reduction of α-ethylstyrene, acetophenone, and acetophenonebenzylimine. Apart from the high optical yields, a very strong dependence of the e.e. on the reaction temperature and the solvent composition was observed [8].

A similar strong dependence of enantioselectivity on the reaction temperature was observed also for the homogeneous hydroformylation of styrene with $PtCl(SnCl_3)$[(*S*,*S*)-BDPP] as catalyst. At 50 °C a moderate e.e. was detected for the chiral branched formyl product (**2a**) with the *S* enantiomer predominating. Surprisingly, at 100 °C *R* was the major enantiomer. The same phenomenon was found also for formation of the chiral linear formyl product (**3b**) of α-methylstyrene



	R^1	R^2
1a	H	Ph
1b	CH_3	Ph
1c	CH_3	$COOCH_3$
1d	CH_2COOCH_3	$COOCH_3$

Scheme 1

(**1b**) (Table 1, Scheme 1). To our knowledge such a phenomenon has been observed previously only in the hydroformylation of 1-butene, but in that case isomerization of the α-olefin was considered to be the reason for the unexpected results, and at 140 °C decomposition of the catalyst was also detected [2]. For the other functionalized unsaturated esters we studied the predominant enantiomer, which did not change over the temperature interval investigated, but the asymmetric induction was undoubtedly higher at lower temperature. In the hydroformylation of dimethyl itaconate (**1d**) the accompanying hydrogenation is also enantioselective, and the e.e. for **4d** is higher than for **3d**. This is in contrast to earlier results obtained with analogous Pt-DIOP catalysts [5].

Table 1

Asymmetric hydroformylation of **1a-d** with $PtCl(SnCl_3)$[(*S*,*S*)-BDPP] catalyst [a]

Susbstrate	Temperature (°C)	Reaction time (h)	Conversion [b] (%)	**2**		**3**		**4**		Selectivity [c] to aldehyde (%)
				(%)	e.e.(%)	(%)	e.e.(%)	(%)	e.e.(%)	
1a	100	4.5	76	18	17.1 (*R*)	48	–	10	–	87
1a	50	25	60	22	63.1 (*S*)	35	–	3	–	95
1b	120	2.5	46	0		38	1.8 (*R*)	8	–	83
1b	100	4.5	64	0		51	1.3 (*R*)	13	–	80
1b	50	110	35	0		33	9.2	2	–	94
1c	140 [d]	4.5	36	0		25	7.5 (*S*)	11	–	69
1c	100	6.5	61	0		47	8.2 (*S*)	14	–	77
1c	50	18	21	0		17	13.9 (*S*)	4	–	81
1d	100	12	64	0		49	26.7 (*R*)	15	44 (*R*)	77
1d	50	70	36	0		29	39.1 (*R*)	7	58 (*R*)	80

[a] Reaction conditions: 35 ml toluene; 0.1 mol substrate; Pt/substrate = 1/2000; $P(CO) = P(H_2) = 40$ bar. [b] (mol reacted substrate/mol initial substrate)·100. [c] (mol aldehyde/mol reacted substrate)·100. [d] Some catalyst decomposition was observed.

Table 2

Influence of the temperature on the hydroformylation of styrene (**1a**) with $PtCl(SnCl_3)[(S,S)\text{-BDPP}]$ [a] (I) and with $PtCl(SnCl_3)[(S,S)\text{-BDPP}]+2SnCl_2$ (II) catalysts

Reaction temperature (°C)	React. time (h)		Conversion (%) [b]		**2a**				**3a** (%)		**4a** (%)		Selectivity to aldehyde [c] (%)		Regioselectivity [d] (%)	
	I	II	I	II	I		II									
					(%)	e.e. (%)	(%)	e.e. (%)	I	II	I	II	I	II	I	II
40	55	115	76	56	31	64.5 (*S*)	23	75.5 (*S*)	42	32	3	1	96	98	42	42
50	25	60	60	56	22	63.1 (*S*)	22	72.0 (*S*)	35	32	3	2	95	96	38	40
80	6	10	71	65	22	11.1 (*S*)	22	22.0 (*S*)	42	37	7	6	90	91	34	37
88	5		77		21	1.4 (*S*)			49		7		91		32	
100	4.5	3	76	50	18	17.1 (*R*)	14	9.9 (*R*)	48	30	10	6	86	88	27	32
120		1.5		55			13	19.4 (*R*)		32		10		82		29
125	1.5		87		20	12.1 (*R*)			51		16		82		28	
140		1		62			13	18.0 (*R*)		34		15		76		28

[a] Reaction conditions: 35 ml toluene; 0.1 mol substrate; Pt/substrate = 1/2000; $P(CO) = P(H_2) = 40$ bar. [b] (mol reacted substr./mol initial substr.)·100. [c] (mol aldehyde/mol reacted substr.)·100. [d] [**2a**/(**2a**+**3a**)]·100.

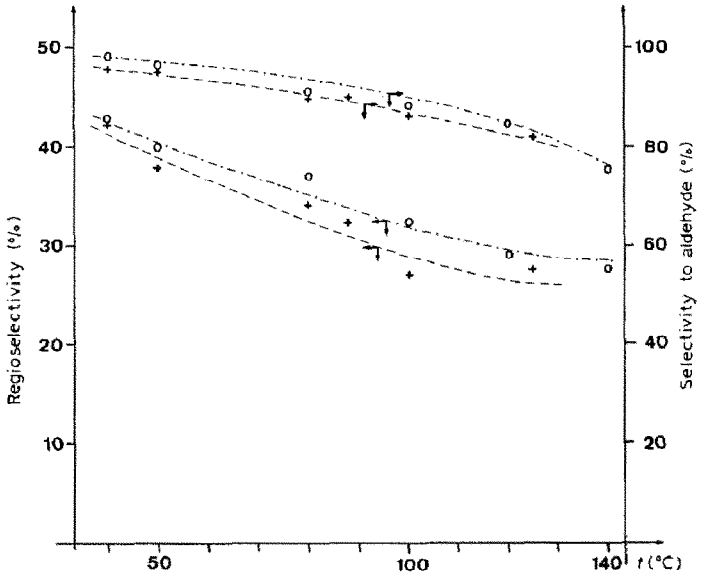


Fig. 1. The temperature dependence of the regioselectivity and the selectivity towards aldehydes in the hydroformylation of styrene with $PtCl(SnCl_3)$ [(*S*,*S*)-BDPP] (+) and $PtCl(SnCl_3)$[(*S*,*S*)-BDPP] + $2SnCl_2$ (○) catalysts.

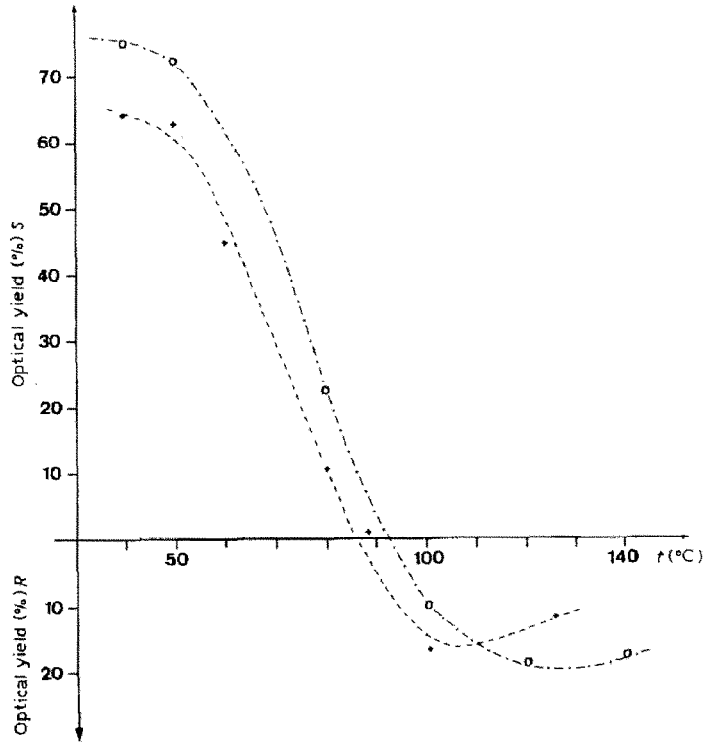


Fig. 2. The temperature dependence of the optical yield in the hydroformylation of styrene with $PtCl(SnCl_3)$[(*S*,*S*)-BDPP] (+) and $PtCl(SnCl_3)$[(*S*,*S*)-BDPP] + $2SnCl_2$ (○) catalysts.

Table 3

The effect of partial pressure of hydrogen and carbon monoxide on the enantioselectivity in the hydroformylation of **1a** [a]

Catalyst	Reaction temperature (°C)	$P(CO)$ (bar)	$P(H_2)$ (bar)	Reaction time (h)	Conversion [b] (%)	e.e. [c] of **2a** (%)	Selectivity to aldehyde [d] (%)
$PtCl(SnCl_3)$-[(*S*,*S*)-BDPP]	40	40	40	55	76	64.5	96
	40	40	160	65	100	73.8	88
	50	40	40	25	60	63.1	95
	50	40	80	16	65	72.8	89
$PtCl(SnCl_3)$-[(*S*,*S*)-BDPP] $+2SnCl_2$	40	40	40	115	56	75.5	99
	40	40	80	72	69	75.9	91
	40	20	80	70	80	76.5	85

[a] Reaction conditions: 35 ml toluene; 0.1 mol substrate; Pt/substrate = 1/2000. [b] (mol reacted substr./mol initial subst.)·100. [c] The prevailing enantiomer is *S* in all cases. [d] (mol aldehyde/mol reacted substr.)·100.

The unusual behaviour of styrene in enantioselective hydroformylation was studied in detail (Table 2). The chemoselectivity towards aldehyde formation with both catalysts is moderately decreased by increasing the reaction temperature. The same trend was observed in regioselectivity; i.e. the proportion of the chiral product (**2a**) decreases with increasing the reaction temperature (Fig. 1). The influence of the temperature is especially strong on the enantioselectivity and asymmetric induction is somewhat higher in the presence of an excess of $SnCl_2$ (Fig. 2). This may be due to the higher concentration of the catalytically active $PtH(SnCl_3)(CO)$[(*S*,*S*)-BDPP] complex that is probably responsible for the asymmetric induction.

The enantioselectivity of the asymmetric hydroformylation with the preformed catalyst is also considerably influenced by the partial pressure of CO and H_2 (Table 3) the e.e. values for the chiral aldehyde (**2a**) rising with increasing $P(H_2)$ and decreasing $P(CO)$. This effect is negligible, however in the presence of an excess of $SnCl_2$.

We have no exact explanation for this unuasual behaviour of the BDPP-containing catalysts in styrene hydroformylation. The strong influence of the reaction temperature on the enantioselectivity may be due to a change in the conformation of the six-membered chelate ring [9], but kinetic effects may also be important [10]. For a better understanding of this phenomenon a detailed investigation of the reaction with various substrates involving changes in the chiral ligand of the catalyst, is in progress.

Experimental

Reagents

$PtCl_2(PhCN)_2$ was prepared from $PtCl_2$ in hot benzonitrile by a standard method [11]. (−)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (BDPP) was prepared as described previously [7].

Toluene was distilled under nitrogen from sodium in the presence of benzophenone.

Dimethyl itaconate was made by esterification of itaconic acid. Methyl methacrylate and styrene were freshly distilled under argon.

The ^1H NMR spectra were recorded for $CDCl_3$ solutions containing TMS as internal standard on a Tesla BS 487C spectrometer at 80 MHz, and the ^{31}P NMR spectra at 32.1 MHz on a Varian CFT-20 spectrometer for solutions in CD_2Cl_2, with 85% phosphoric acid as external reference. The optical rotations of the products were measured for neat liquids, after vacuum distillation from the reaction mixture, on a Schmidt Haensch LM visual polarimeter. The optical yields were calculated by use of reported values for the optical rotations of the pure products [5,3,12].

Preparation of $PtCl_2$[(S,S)-BDPP]

To a refluxing yellow solution of 0.715 g (1.516 mmol) $PtCl_2(PhCN)_2$ in 70 ml of benzene under argon was added a solution of 0.88 g (1.53 mmol)(*S,S*)-BDPP in 20 ml of benzene. After a few minutes fine white crystals separated. The mixture was stirred for one hour then cooled to room temperature to give additional solid. The solid was filtered off, washed with benzene, and dried under reduced pressure, to give 1.016 g (1.44 mmol, 95%) of $PtCl_2$[(*S,S*)-BDPP] as a white powder. Anal. Found: C, 49.39; H, 4.24. $C_{29}H_{30}Cl_2P_2Pt$ calcd.: C, 49.30; H, 4.30%. ^{31}P NMR (CD_2Cl_2): 7.21 ppm, d, J(Pt–P) 3413 Hz.

Preparation of $PtCl(SnCl_3)$[(S,S)-BDPP]

$PtCl_2$[(*S,S*)-BDPP] (0.617 g; 0.874 mmol) and (anhydrous) $SnCl_2$ (0.171 g; 0.9 mmol) were dissolved in 40 ml CH_2Cl_2 under argon. After 2 h the yellow solution was concentrated to 20 ml. Crystallization of the product from the reaction mixture at -5 °C gave colorless crystals. Yield: 0.634 g (0.708 mmol, 81%). Anal. Found: C, 38.78; H, 3.33. $C_{29}H_{30}Cl_4P_2SnPt$ calcd.: C, 38.85; H, 3.36%. ^{31}P NMR (CD_2Cl_2): P^1 (*trans* to $SnCl_3$): 13.79 ppm $J(Pt–P^1)$ 2759 Hz; $J(P^1–P^2)$ 23.7 Hz; P^2 (*cis* to $SnCl_3$): 7.43 ppm $J(Pt–P^2)$ 3348 Hz; $J(P^1–P^2)$ 23.7 Hz.

Hydroformylation experiments

In a typical experiment a suspension of 0.05 mmol (44.8 mg) of $PtCl(SnCl_3)$[(*S,S*)-BDPP] in 35 ml toluene containing 0.10 mol substrate was transferred under argon into a 150 ml stainless steel autoclave. The autoclave 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, the pale yellow solution was removed, quickly analyzed by GC, and fractionally distilled for further characterization of product by ^1H NMR and mass spectroscopy.

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