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Asymmetric hydroformylation with Pt-phosphine-$SnCl_2$ and Pt-bisphosphine-$CuCl_2$ (or CuCl) catalytic systems

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Abstract

A study has been made of asymmetric hydroformylation of styrene with $PtCl_2(PPh_3)_2$ + bisphosphine + $SnCl_2$ (bisphosphine: BDPP = (−)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane or DIOP = (−)-(4*R*,5*R*)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane) and $PtCl_2$(bisphosphine) + PPh_3 + $SnCl_2$ catalysts prepared "in situ". The presence of an excess of the phosphine ligand slightly lowered the reaction rate, but the enantioselectivity of these systems is significantly higher than those involving $PtCl(SnCl_3)$(bisphosphine) catalysts. Under mild reaction conditions 88.8% enantiomeric excess was achieved. Replacing $SnCl_2$ in these catalysts by $CuCl_2$ or CuCl gave a new homogeneous catalytic system which is active at higher reaction temperature ($> 100\,°C$), but has a rather moderate enantioselectivity.

Introduction

The effects of various parameters on the enantioselective hydroformylation with platinum-phosphine-$SnCl_2$ catalysts have been intensively studied in recent years and fairly high asymmetric induction achieved [1]. Thus hydroformylation of styrene with the platinum-BDP-DIOP/$SnCl_2$-H_2O (BDP-DIOP = (−)-(4*R*,5*R*)-2,2-dimethyl-4,5-bis(5*H*-dibenzophosphol-5-ylmethyl)-1,3-dioxolane) catalyst gave about 80% e.e. [2], and that of *p*-substituted styrenes with a platinum catalyst containing BPPM as chiral ligand (BPPM = (2*S*,4*S*)-*N*-t-butoxycarbonyl-4-(diphenylphosphino)methylpyrrolidine) gave 70–95% enantioselectivity [3]. More recently 2-phenylpropanal has been synthesized with 76.5% enantiomeric excess by use of a $PtCl(SnCl_3)$(BDPP) catalyst [4]. In some cases a dramatic decrease in the reaction rate has been observed when the chelating ligand is used in excess.

To clarify the role of various additives on the reaction rate a detailed study of 1-heptene hydroformylation was carried out [5], and the $PtCl_2(PPh_3)_2 + SnCl_2$ system found to be the most promising combination; the $PtCl(SnCl_3)P_2$ is formed in which the $SnCl_3^-$ ligand exerts a strong *trans*-effect [6].

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Table 1

Asymmetric hydroformylation with Pt-diphosphine-PPh_3-$SnCl_2$ catalytic systems [a]

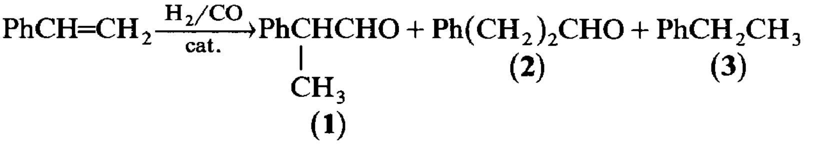
Run	Catalyst [b]	Reaction temperature (°C)	Reaction time (h)	Conversion[c] (%)	**1**		**2** (%)	**3** (%)	Selectivity to aldehydes [d] (%)	R selectivity [e] (%)
					(%)	e.e. (%)				
1	$I+\frac{1}{2}DIOP+2SnCl_2$	120	1.5	70	19	5.1(*S*)	31	20	71	38
2	$I+DIOP+2SnCl_2$	120	2	76	24	5.0(*S*)	42	10	87	36
3	$PtCl(SnCl_3)(DIOP)$	120	2	82	25	2.6(*S*)	42	15	82	37
4	$I+\frac{1}{2}BDPP+2SnCl_2$ [f]	20	210	14	4	88.8(*S*)	10	0.2	98	29
5	$I+\frac{1}{2}BDPP+2SnCl_2$	40	88	37	14	79.4(*S*)	22	1	97	39
6	$I+\frac{1}{2}BDPP+2SnCl_2$ [f]	40	112	45	15	83.1(*S*)	28	2	96	35
7	$I+BDPP+2SnCl_2$	25	168	14	4	85.9(*S*)	10	0.2	99	29
8	$I+\frac{1}{2}BDPP+2SnCl_2$	125	3	34	8	9.0(*R*)	22	4	88	27
9	$II+2PPh_3+2SnCl_2$	125	6	63	14	9.8(*R*)	40	9	86	26
10	$PtCl(SnCl_3)(BDPP)$	40	55	76	31	64.5(*S*)	42	3	96	42
11	$PtCl(SnCl_3)(BDPP)$	80	6	71	22	11.1(*S*)	42	7	90	34
12	$II+2SnCl_4$	80	6	59	17	14.6(*S*)	39	3	95	30
13	$II+2SnCl_4$	110	1.5	76	22	13.5(*R*)	46	8	89	32

[a] Reaction conditions: 35 ml toluene; 0.1 mol styrene; Pt/styrene = 1/2000; $P(CO) = P(H_2) = 40$ bar. [b] $I = PtCl_2(PPh_3)_2$ $II = PtCl_2(BDPP)$. [c] (mol reacted substrate/mol initial substrate) × 100. [d] (mol aldehyde/mol reacted substrate) × 100. [e] **1**/(**1** + **2**) × 100. [f] $P(CO)$ 40 bar; $P(H_2)$ 80 bar.

We discuss here the asymmetric hydroformylation of styrene with platinum-phosphine catalysts prepared "in situ" containing both achiral monodentate and chiral bisphosphines, and describe the unexpected effect of $CuCl_2$ and CuCl.

Results and discussion

Hydroformylation of styrene with $PtCl_2(PPh_3)_2$ + bisphosphine + $SnCl_2$ catalytic systems (bisphosphine = DIOP or BDPP) prepared "in situ" was carried out under different conditions to give a mixture of the chiral 2-phenylpropanal (**1**), the linear non-chiral 3-phenylpropanal (**2**), and ethylbenzene (**3**) (eq. 1). In contrast to earlier results [3], the lowering of the catalytic activity due to the excess of phosphine is relatively small (Table 1), and the enantioselectivities of these catalysts are significantly higher than those achieved with the preformed catalysts of the type $PtCl(SnCl_3)P_2$. In accordance with our earlier observation [4], the optical selectivity with BDPP-containing catalysts is strongly influenced by the reaction temperature, and the opposite enantiomer predominates at higher temperature (run 5 and 8). Under mild reaction conditions, a rather high (88.8%) enantiomeric excess was observed (run 4). In the presence of an excess of PPh_3 the $PtH(SnCl_3)(CO)BDPP$



$$PhCH{=}CH_2 \xrightarrow[cat.]{H_2/CO} \underset{\substack{|\\ CH_3\\ \mathbf{(1)}}}{PhCHCHO} + \underset{\mathbf{(2)}}{Ph(CH_2)_2CHO} + \underset{\mathbf{(3)}}{PhCH_2CH_3} \qquad (1)$$

complex cannot be regarded as the only catalytically active species; e.g. a complex containing both PPh_3 and the bisphosphine acting, as an monodentate ligand cannot be excluded, as suggested by Consiglio for a related hydrocarbalkoxylation reaction [7]. This possibility seems to be supported by the fact, that both $PtCl_2(PPh_3)_2 + \frac{1}{2}$bisphosphine + $SnCl_2$ and the $PtCl_2$(bisphosphine) + $2PPh_3$ + $SnCl_2$ catalytic systems give the same enantiomeric excess (run 8 and 9).

In addition to the generally used $SnCl_2$, $SnCl_4$ is also known to have an activating effect, and under hydroformylation conditions its partial reduction to $SnCl_2$ has been suggested [5]. This is in accordance with our results in enantioselective hydroformylations. The strong influence of the reaction temperature on enantioselectivity in this system is also evident (run 12 and 13).

The $PtCl_2$(bisphosphine) complexes are completely inactive in hydroformylation under the reaction conditions used (see Table 2), but addition of $CuCl_2$ (or CuCl) instead of $SnCl_2$ gave new active catalysts which are effective working at higher (> 100 °C) temperature (Table 2). However in all experiments (even at 125 °C) there is a considerable induction period. The influence of the solvent on enantioselectivity is also detectable (run 2).

In these catalytic systems $PtH(CO)(CuCl_2)BDPP$ (or $PtH(CO)(CuCl_3)BDPP$) is assumed to be the active species of the hydroformylation reaction, as proposed for the analogous $SnCl_2$-containing catalysts, but further investigation is needed.

Experimental

Reagents

The catalytic precursors $PtCl_2[(R,R)$-DIOP] and $PtCl_2[(S,S)$-BDPP] and their $SnCl_3^-$ containing derivatives were prepared as described previously [8,4].

Table 2

Asymmetric hydroformylation with $PtCl_2$(diphosphine) + $CuCl_2$(or CuCl) catalytic systems[a]

Run	Catalyst[b]	Reaction temperature (°C)	Induction time (h)	Reaction time (h)	Conversion[c] (%)	**1**		**2** (%)	**3** (%)	Selectivity to aldehyde[d] (%)	R selectivity[e] (%)
						(%)	e.e. (%)				
1	$PtCl_2$(DIOP) + $CuCl_2$[f]	100	1.5	6.5	32	11	10.6(*S*)	17	4	88	39
2	$PtCl_2$(DIOP) + $CuCl_2$[g]	100	1.5	3	15	5	1.7(*R*)	8	2	87	39
3	$PtCl_2$(DIOP) + $CuCl_2$	125	1	4.5	43	13	5.2(*S*)	22	8	81	37
4	$PtCl_2$(DIOP) + CuCl	100	3	3	22	7	8.9(*S*)	12	3	86	37
5	$PtCl_2$(BDPP) + $CuCl_2$[f]	100	2	10	17	4	12.3(*R*)	12	1	94	25
6	$PtCl_2$(BDPP) + CuCl	120	1.5	8.5	14	3	14.5(*R*)	10	1	93	23

[a] Reaction conditions: 35 ml toluene; 0.1 mol styrene; Pt/styrene 1/2000; $P(CO) = P(H_2) = 40$ bar. [b] For the abbreviations see Table 1. [c] (mol reacted substrate/mol initial substrate) × 100. [d] (mol aldehyde/mol reacted substrate) × 100. [e] **1**/(**1** + **2**) × 100. [f] Without $CuCl_2$ (in 10 h) no reaction; it was started by the addition of $CuCl_2$. [g] Solvent CH_2Cl_2.

Toluene was distilled under argon from sodium in the presence of benzophenone. Styrene (used as a substrate) was freshly distilled under argon.

The compositions of the reaction mixtures were determined by GLC with a Hewlett–Packard 5830A Gas Chromatography 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 after fractional vacuum distillation of the reaction mixture. The optical yields were calculated by use of the reported value, α_D^{25} $+238^0$, for neat (S)-2-phenylpropanal [9].

Hydroformylation experiments

In a typical experiment a solution of 0.05 mmol (38.2 mg) $PtCl_2DIOP$, 0.1 mmol (19 mg) $SnCl_2$ and 0.1 mmol (26.2 mg) of PPh_3 in toluene containing 0.1 mol (11.5 ml) of styrene was transferred under argon to a 150 ml stainless steel autoclave. (In other cases the copper salts were placed into the autoclave.) It 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 and quickly analyzed by GLC, then fractionally distilled for determination of the optical purity of the 2-phenylpropanal.

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