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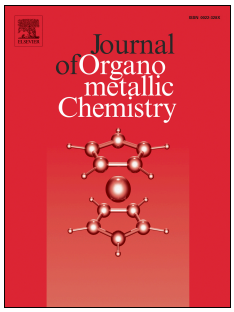

Enantioselective hydroformylation of 2- and 4-substituted styrenes with $PtCl_2$[(*R*)-BINAP] + $SnCl_2$ 'in situ' catalyst

Péter Pongrácz, László Kollár

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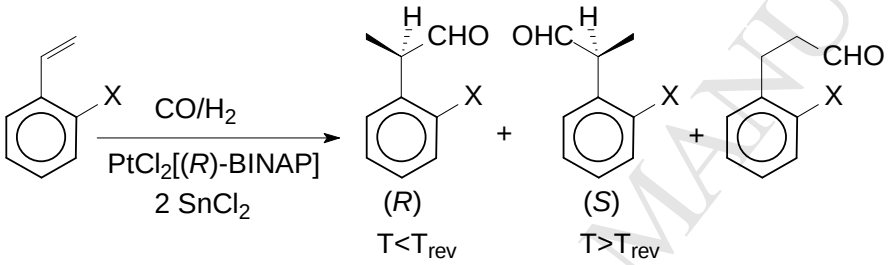
Péter Pongrácz and László Kollár*

Graphical abstract (pictogram)



X = H (**a**), F (**b**), OMe (**c**), Cl (**d**), Br (**e**), CH_3 (**f**), CF_3 (**g**)

Enantioselective Hydroformylation of 2- and 4-Substituted Styrenes with $PtCl_2$[(*R*)-BINAP] + $SnCl_2$ 'in situ' Catalyst.

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Abstract: Two sets of styrenes possessing various substituents either in *ortho* or *para* position were hydroformylated in the presence of 'in situ' catalyst formed from $PtCl_2$[(*R*)-BINAP] and tin(II) chloride. The reversal of the absolute configuration of the preferred enantiomers was observed using both sets of substrates by the variation of the reaction temperature in the range of 40-100 ^oC. In case of the 4-substituted styrenes, the reversal temperature of the enantioselectivity shows correlation with the Hammett substituent constants, *i.e.*, with the electron donor or electron acceptor properties of the *para*-substituents. This phenomenon was explained by the reversible formation of the Pt-branched alkyl intermediates, leading to the corresponding *(R)*- and (*S)*-enantiomers of 2-arylpropanals.

Strong substituent effect on the regioselectivity was observed in the hydroformylation of 2-substituted styrenes: the presence of substituents characterised by larger steric parameter resulted in the highly favoured formation of the linear aldehyde. For instance, regioselectivities of 45%, 22% and 7% towards branched aldehyde were obtained with styrene, 2-fluoro- and 2-bromostyrene, respectively, at 80 ^oC reaction temperature. In addition to the characteristic change of regioselectivity, the reversal of absolute configuration as a function of reaction temperature was also observed.

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Key-words: hydroformylation, platinum, enantioselectivity, substituent effect, temperature effect

1. Introduction

The highly selective hydroformylation of alkenes is one of the oldest success-story of homogeneous catalysis. Its application is widely known for the chemo- and regioselective synthesis of n-butyraldehyde in cobalt- and rhodium-catalysed reaction,[1,2] as well as for the synthesis of 2-arylpropanals in rhodium-catalysed enantioselective hydroformylation of vinyl aromatics.[3] In the latter case, both rhodium- and platinum-catalysts can be used for the synthesis of the precursors of non-steroidal anti-inflammatory drugs (NSAIDs), such as ibuprofen, naproxen or suprofen.[4]. The rhodium-BINAPHOS catalysts, discovered by Takaya,[5] enabled enantioselective hydroformylationst using several types of substrates, therefore, their application has been predominating over the platinum catalysts in enantioselective hydroformylation.

Since the early discovery of the hydroformylation activity of platinum-monophosphine-tin(II)halide type 'in situ' systems,[6] several platinum-chiral diphosphine-tin(II) chloride catalysts were developed and successfully applied not only for the enantioselective hydroformylation of vinylaromatics but also for the highly enantio- and regioselective hydroformylation of 1,1-disubstituted olefins resulting in chiral building blocks (CBBs).[7] Furtherrmore, the relative kinetic inertness and facile NMR investigations still made platinum catalysts a perfect tool for mechanistic studies (*vide infra*).

In addition to the application of dozens of mono- and bidentate phosphorus ligands in platinum-tin(II) halide-catalysed hydroformylation,[8] some examples on the tin(II) halide-free hydroformylation using diphenylphosphinous acid platinum complexes[9] or platinum-alkyl/aryl–BF_3/$B(Ar_F)_3$ boron additive systems[10] were also published.

Regarding the clearing-up of the reaction mechanism, both rhodium-[11,12] and platinum containing systems were investigated. The latter ones were studied by both analytical[13] and computational[14] methods. The importance of the good leaving properties of the trichlorostannato ligand was also proved by high pressure NMR studies.[15]

An unprecedented phenomenon, a strong dependence of the enantioselectivity on the reaction temperature in asymmetric hydroformylation was first observed using styrene as substrate in the presence of $PtCl(SnCl_3)$[(*2S,4S*)-BDPP)][8d,e] and $PtCl_2$[(*S*)-BINAP][8l] catalyst precursors. The temperature dependence of the reversal of enantioselectivity in Pt-BDPP-catalysed hydroformylation of styrene was rationalized in a seminal deuterioformylation work published by Casey *et al.*[16] It was discovered that the step determining the stereochemical outcome of the reaction, *i.e.*, the styrene insertion into the Pt-H bond forming a Pt-alkyl intermediate, can be considered as largely irreversible at low temperature (40 ^oC) but reversible at higher temperature (100 ^oC). In our group, the same Pt-(*2S,4S*)-BDPP-tin(II) chloride system was used in the hydroformylation of 4-substituted styrenes. The electronic effect of the 4-substituents on the reversal temperature was rationalised by the reversibility of of the platinum-alkyl formation step.[17]

This paper describes the asymmetric hydroformylation of two sets of styrenes possessing various substituents either in 2- or in 4-position in the presence of an 'in situ' catalyst formed from $PtCl_2$[(*R*)-BINAP] and tin(II) chloride. It is worth noting that the Pt-BINAP complexes showing a rigid chelate ring is completely diffrent from the abovementioned BDPP-containg ones, forming a chelate ring with several possible conformers. Here we report a systematic study on the influence of the electron donor or electron acceptor properties of the *para*-substituents of styrene, as well as the steric parameters of the *ortho*-substituents on chemo-, regio- and enantioselectivities in Pt-BINAP-catalysed hydroformylation.

2. Materials and Methods

2.1. General procedures

The $PtCl_2(PhCN)_2$[18] and the $PtCl_2$[(*R*)-BINAP][8l] precursors were synthesized as described earlier. Toluene was distilled and purified by standard methods and stored under argon. The substrates, 2- and 4-substituted styrenes and tin(II) chloride (anhydrous) were used as obtained from Sigma-Aldrich without any further purification. All reactions were carried out under argon atmosphere using standard Schlenk technique.

Mass-spectrometry data have been obtained using a GC-MS system consisting of a Perkin Elmer AutoSystem XL gas-chromatograph. The GC and chiral GC measurements were run on a Chrom-Card Trace GC-Focus GC gas-chromatograph. The enantiomeric excesses were determined on a capillary Cyclodex-column, (*S*)-2-arylpropanals were eluted before the (*R*) enantiomers, except **6c** and **6f** derivatives. (In these two cases the (*R*)-enantiomer were eluted first.)

2.2. Hydroformylation experiments

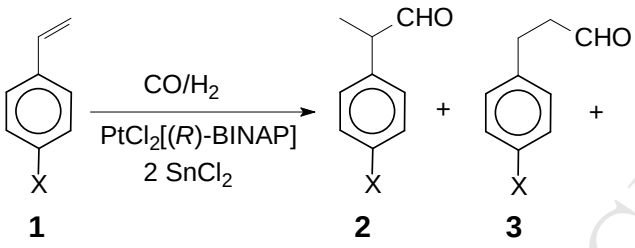
In a typical experiment, a solution of $PtCl_2$[(*R*)-BINAP] (4.5 mg; 0.005 mmol) and tin(II) chloride (1.9 mg; 0.01 mmol) in toluene (5 mL) containing styrene derivatives (**1a-g**, **5a-g**) (1.0 mmol) was transferred under argon into a 100 mL stainless steel autoclave. The reaction vessel was pressurized to 80 bar total pressure (CO/H_2 = 1:1) and placed in an oil bath of constant temperature. The mixture was stirred with a magnetic stirrer for the given reaction time. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analyzed by GC-MS and chiral GC.

3. Results

3.1. Enantioselective hydroformylation of 4-substituted styrenes with $PtCl_2$[(R)-BINAP] + $SnCl_2$ 'in situ' catalyst

An 'in situ' catalyst, formed from $PtCl_2$[(*R*)-BINAP] and tin(II) chloride, was used at various temperatures with 80 bar of CO/H_2 (1:1) mixture (*Scheme 1*) for the hydroformylation of 4-substituted styrenes (**1a-g**). As

generally observed in platinum-catalysed hydroformylation, some catalytic activities were observed at room temperature, however, rather low conversions were obtained even at 40 °C. At higher temperatures, some degradation of the catalyst was observed (typically above *ca.* 120 °C). Therefore, the evaluation of the catalysts was carried out in the temperature range of 60 °C to 100 °C. As expected, two aldehyde regioisomers (**2** and **3**) and a hydrogenation product (**4**) were obtained in all cases (*Scheme 1*).



X = H (**a**), F (**b**), OMe (**c**), Cl (**d**), CH_3 (**f**), CF_3 (**g**)

Scheme 1. Hydroformylation of 4-substituted styrenes in the presence of $PtCl_2$[(*R*)-BINAP] + $SnCl_2$ 'in situ' catalyst

In general, chemoselectivities towards aldehydes higher than 85%, at lower temperatures typically higher than 90% were observed (*Table 1*). The tendency of increasing selectivity towards aldehydes with decreasing reaction temperature was observed with all substrates **1a-g**. For example, 85%, 91% and 94% chemoselectivities were obtained using **1g** as substrate at 100 °C, 80 °C and 60 °C, respectively (*entries 16-18*). The aldehyde selectivities obtained with various substrates at the same temperature show small differences especially at low reaction temperatures (3% difference at 60 °C), while slightly wider range of chemoselectivity (a difference of 5%) was obtained at 100 °C. For example, the chemoselectivities obtained at 60 °C and 100 °C were varied in the range of 93% (**1a**) to 96% (**1c**) (*entries 3, 6, 9, 12, 15*), and 85% (**1g**) to 90% (**1c**) (*entries 1, 4, 7, 10, 13*), respectively (*Table 1*).

Unlike the general trends observed with platinum catalysts, the application of a BINAP-containing catalyst results in a characteristic increase of regioselectivity towards branched aldehyde by increasing temperature. For instance, 48%, 52% and 54% regioselectivity was obtained at 60 °C, 80 °C and 100 °C for 4-methoxystyrene (**1c**) (*entries 7-9*). Much lower regioselectivities towards branched aldehyde regioisomers were shown with **1b**, **1d** and **1g**, containing electron acceptor groups such as 4-fluoro, 4-chloro and 4-trifluoromethyl substituents, respectively. In these cases the preference of the linear aldehyde was observed resulting in a branched to linear aldehyde ratio of *ca.* 1:2.

A strong dependence of e.e. on the reaction temperature was obtained in the enantioselective hydroformylation of all substrates (**1a-g)** (*Figure 1*), reflecting to a same phenomenon as observed previously with the parent styrene (**1a**) in the presence of Pt-BINAP-tin(II) halide catalysts.[8l] That is, the formation of the

(*S*)-enantiomer is favoured at low temperatures, while the (*R*)-enantiomer of 2-arylpropanals (**2a**-**g**) is predominating at higher temperatures. The difference in substrate behaviour is characterised by the temperature of the reversal of the enantioselectivity, *i.e.*, by the temperature of the change of the absolute configuration of the dominating enantiomer. When this 'reversal temperature' is plotted against Hammett-constants (σ_{para}) of the corresponding substituents[19] (*Figure 2*), although the correlation is not strong, an increase of the reversal temperature by increasing electron acceptor properties of the 4-substituents such as F (**b**), Cl (**d**) and CF_3 (**g**) was shown. The reversal of the enantioselectivity occurred at 76 ^{o}C, 80 ^{o}C and 84 ^{o}C with fluoro (σ_{para} = +0.062), chloro (σ_{para} = +0.227) and trifluoromethyl (σ_{para} = +0.540) substituents, respectively. Accordingly, much lower reversal temperatures were observed with electron donor substituents. That is, the reversal of the enantioselectivity occurred at 71 ^{o}C and 70 ^{o}C with methyl (σ_{para} = -0.170) and methoxy (σ_{para} = -0.268) substituents, respectively. (It has to be added that the reversal temperatures might have *ca*. ± 1 ^{o}C error due to the difficulties in their determination, *i.e.*, to provide perfect racemic mixtures *experimentally* under the conditions of the enantioselective hydroformylation above.)

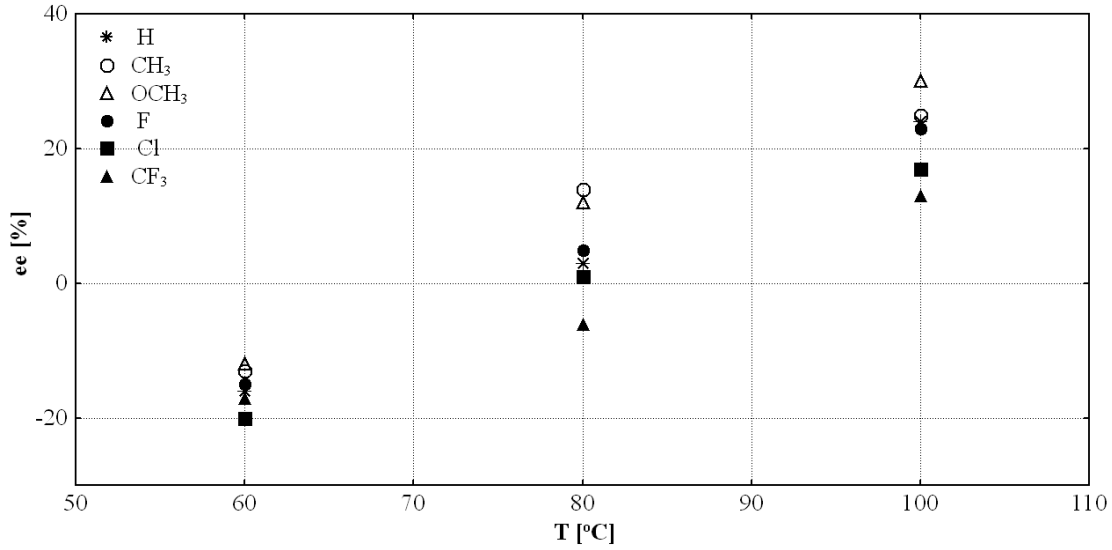


Figure 1. Effect of temperature on the enantioselectivity in the hydroformylation of **1a-g** in the presence of Pt-(*R*)-BINAP catalyst.

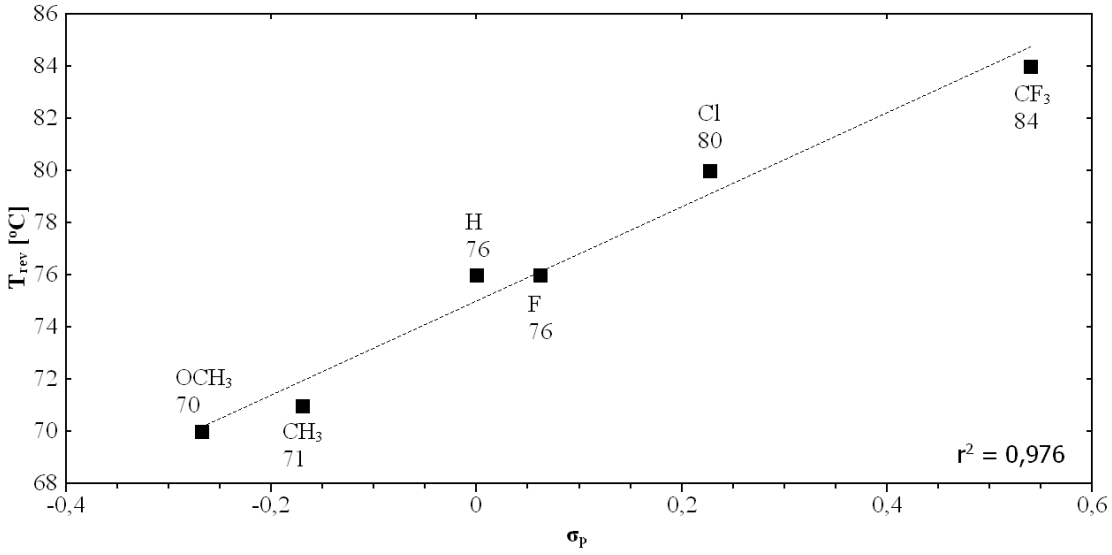


Figure 2. The reversal temperatures of the enantioselectivity (T_{rev}) plotted against the Hammett constants (σ_p) in the hydroformylation of **1a-g** in the presence of Pt-(*R*)-BINAP catalyst.

Table *1*. Hydroformylation of 4-substituted styrenes in the presence of $PtCl_2$[(*R*)-BINAP] + $SnCl_2$ 'in situ' catalyst [a)]

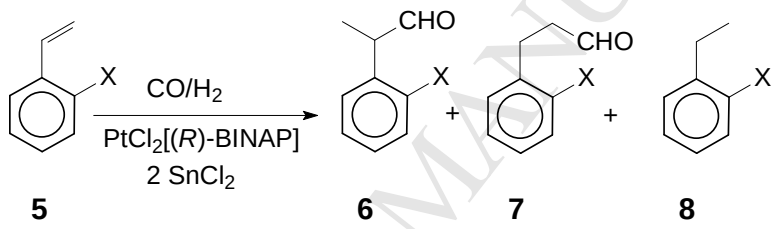
Entry	Substrate	T [^oC]	time [h]	conv.[b)] [%]	R_c [c)] [%]	R_{br} [d)] [%]	e.e. [e)] [%]
1	**1a**	100	23	>99	88	44	24 (*S*)
2	**1a**	80	24	12	86	40	3 (*S*)
3	**1a**	60	120	56	93	36	16 (*R*)
4	**1b**	100	28	80	85	42	23 (*S*)
5	**1b**	80	24	>99	89	40	5 (*S*)
6	**1b**	60	240	>99	95	36	15 (*R*)
7	**1c**	100	25	>99	90	54	30 (*S*)
8	**1c**	80	96	91	94	52	12 (*S*)
9	**1c**	60	166	88	96	48	12 (*R*)
10	**1d**	100	24	88	86	41	17 (*S*)
11	**1d**	80	72	98	93	37	1 (*S*)
12	**1d**	60	140	>99	95	34	20 (*R*)
13	**1f**	100	24	99	90	49	25 (*S*)
14	**1f**	80	48	97	92	46	14 (*S*)
15	**1f**	60	164	19	94	46	13 (*R*)
16	**1g**	100	24	73	85	35	13 (*S*)
17	**1g**	80	48	>99	91	35	6 (*R*)
18	**1g**	60	96	88	94	34	17 (*R*)

a) Reaction conditions (unless otherwise stated): 0.005 mmol of $PtCl_2$[(*R*)-BINAP], 0.01 mmol of $SnCl_2$, 1 mmol of substrate (**1**), $p(CO)=p(H_2)=40$ bar, 5mL of toluene
b) Determined by GC
c) Chemoselectivity towards aldehydes: (**2**+**3**)/(**2**+**3**+**4**)x100
d) Regioselectivity towards branched aldehyde: **2**/(**2**+**3**)x100
e) Determined by chiral GC (dominating enantiomer in brackets)

3.2. Enantioselective hydroformylation of 2-substituted styrenes with $PtCl_2$[(R)-BINAP] + $SnCl_2$ 'in situ' catalyst

Although some sporadic results can be found in the literature on the diastereoselective hydroformylation of chromium-tricarbonyl complexes of 2-substituted styrenes bearing planar element of chirality[20] and the control of stereochemistry by 2-amino groups in anionic polymerization of 2-substituted styrenes is also known[21], there is no precedence for the 'direct' hydroformylation of similar compounds.

Based on earlier findings in the hydroformylation of styrene,[8l] the 'in situ' catalyst, formed from $PtCl_2$[(*R*)-BINAP] and tin(II) chloride seemed to be a good choice of catalyst to study the factors controlling regio- and enantioselectivity in the hydroformylation of 2-substituted styrenes (**5a-g**). The series of 2-substituted styrenes were hydroformylated at various temperatures with 80 bar of CO/H_2 (1:1) mixture in the presence of Pt-BINAP-tin(II) chloride catalyst. Branched and linear aldehyde regioisomers (**6** and **7**, respectively) and a hydrogenation product (**8**) were formed (*Scheme 2*).



X = H (**a**), F (**b**), OMe (**c**), Cl (**d**), Br (**e**), CH_3 (**f**), CF_3 (**g**)

Scheme 2. Hydroformylation of 2-substituted styrenes in the presence of $PtCl_2$[(*R*)-BINAP] + $SnCl_2$ 'in situ' catalyst

The chemoselectivities towards aldehydes (**6** and **7**) are rather similar to those obtained with 4-substituted styrenes bearing the same series of substituents. Chemoselectivities of 90% or higher were observed at low temperatures except to **5g**. For example, the corresponding aldehyde regioisomers were formed with 84%, 89%, 93% and 94% chemodelectivities using **5f** as substrate at 100 ^oC, 80 ^oC, 60 ^oC and 40 ^oC, respectively (*Table 2, entries 21-24*).

As for the regioselectivity towards branched aldehyde (**6**), both increase and decrease of regioselectivity by increasing temperature was shown depending on the 2-substituent. For instance, a slight increase from 25% (40 ^oC) to 29% (100 ^oC) in case of **5c** (*entries 9-12*), and a decrease from 28% (40 ^oC) to 22% (100 ^oC) in case of **5b** (*entries 5-8*) were observed. It has to be noted that in general much lower regioselectivities were observed with 2-substituted styrenes than with the corresponding 4-substituted ones and with the parent styrene (**1a**=**5a**). (It seems to be obvious that the formation of the platinum-branched alkyl catalytic intermediate, leading to **6**, is less favoured due to steric factors.) In three cases (**5e**, **5f**, **5g**) the regioselectivities

were below 10%. In the latter case, the formation of the linear aldehyde (**7g**) is especially highly favoured.

As above, a strong dependence of e.e. on the reaction temperature was obtained in the Pt-(*R*)-BINAP-catalysed enantioselective hydroformylation of all substrates (**5a-g)** (*Figure 3*). As in case of 4-substituted styrenes (**1a-g**) (*Chapter 2.1.*), the formation of the (*S*)-enantiomer is favoured at low temperatures and that of the (*R*)-enantiomer at higher temperatures.[23] It has to be added that due to extremely low branched selectivity, and therefore large errors in the determination of e.e-s, they were not determined in case of **5g**. Furthermore, the temperature dependence of enantioselectivity in case of the 2-fluoro-substituted derivative (**5b**) is quite unexpected. (*Table 2, entries 5-8*).

The reversal temperatures proved to be the lowest when substrates **5f** and **5e** possessing substituents characterised by large steric factors (CH_3 (Es=-1.24), Br ((Es=-1.16), respectively) were hydroformylated. The *ortho*-substituent characterised by small Es (OCH_3 (Es=-0.55) shifted the reversal temperature to higher values.

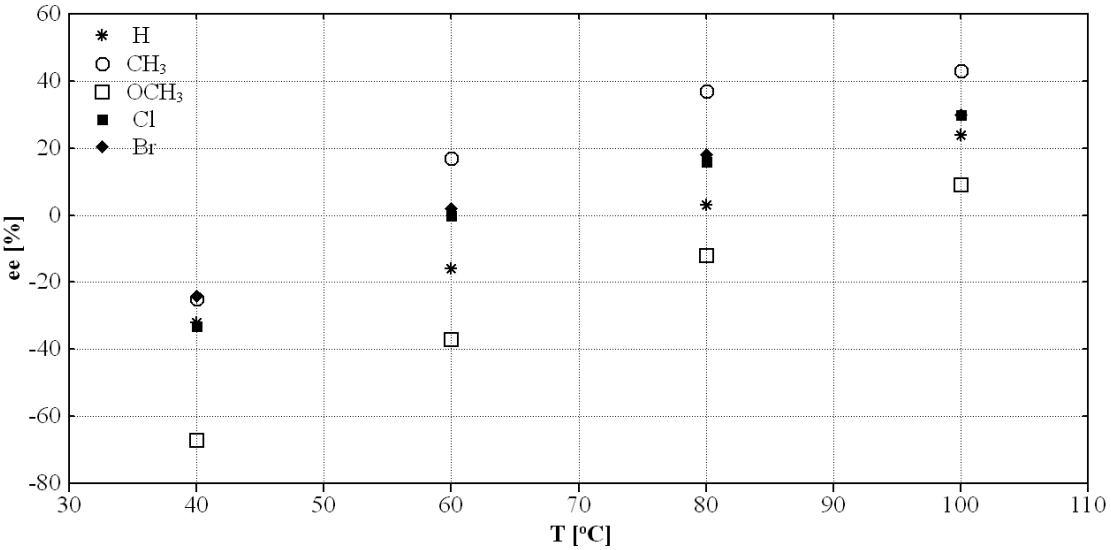


Figure 3. Effect of temperature on the enantioselectivity in the hydroformylation of **5a-g** in the presence of Pt-(*R*)-BINAP catalyst.

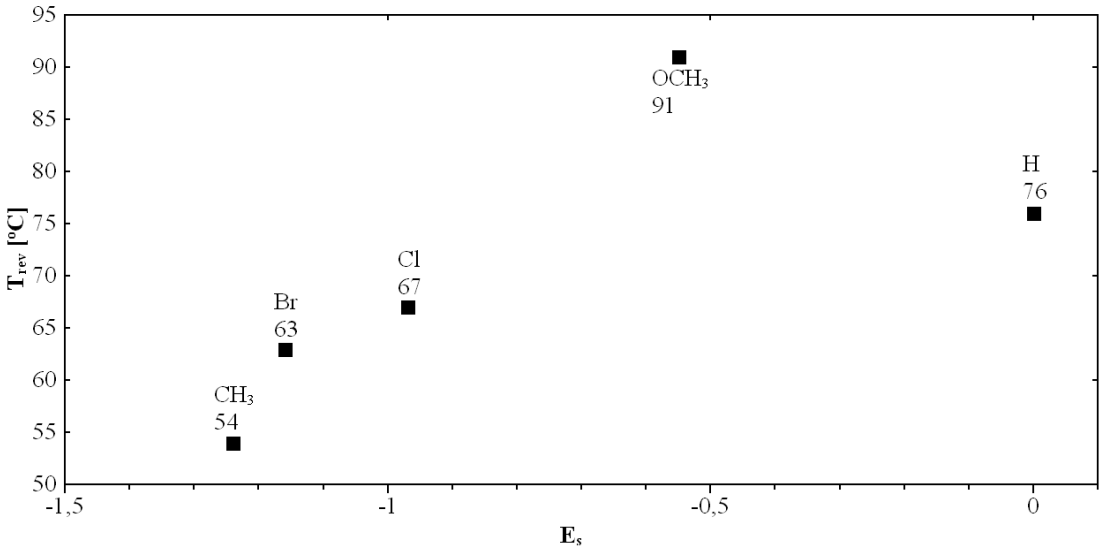


Figure 4. The reversal temperatures of the enantioselectivity (T_{rev}) plotted against the steric constants (Es) in the hydroformylation of **5a-g** in the presence of Pt-(*R*)-BINAP catalyst.

Table 2. Hydroformylation of 2-substituted styrenes in the presence of $PtCl_2$[(*R*)-BINAP] + $SnCl_2$ 'in situ' catalyst [a)]

Entry	Substrate	T [°C]	time [h]	conv. [b)] [%]	R_c [c)] [%]	R_{br} [d)] [%]	e.e. [e)] [%]
1	**5a=1a**	100	23	>99	88	44	24 (S)
2	**5a=1a**	80	24	12	86	40	3 (S)
3	**5a=1a**	60	120	56	93	36	16 (R)
4	**5a=1a**	40	120	16	91	31	32 (R)
5	**5b**	100	24	83	85	22	29 (S)
6	**5b**	80	168	>99	89	22	2 (R)
7	**5b**	60	240	13	87	23	41 (S)
8	**5b**	40	264	28	90	28	60 (S)
9	**5c**	100	23	>99	91	29	9 (S)
10	**5c**	80	72	>99	82	30	12 (R)
11	**5c**	60	144	97	96	25	37 (R)
12	**5c**	40	120	55	96	25	67 (R)
13	**5d**	100	24	97	79	10	30 (S)
14	**5d**	80	72	>99	86	10	16 (S)
15	**5d**	60	168	60	91	9	0
16	**5d**	40	240	31	92	10	33 (R)
17	**5e**	100	24	>99	79	8	30 (S)
18	**5e**	80	72	91	84	7	18 (S)
19	**5e**	60	144	79	90	6	2 (S)
20	**5e**	40	128	8	93	7	24 (R)
21	**5f**	100	24	97	84	8	43 (S)
22	**5f**	80	96	89	89	5	37 (S)
23	**5f**	60	144	93	93	4	17 (S)
24	**5f**	40	240	36	94	2	25 (R)
25	**5g**	100	24	45	77	2	n.d.
26	**5g**	80	168	57	84	3	n.d.
27	**5g**	60	120	0	n.d.	n.d.	n.d.

a) Reaction conditions (unless otherwise stated): 0.005 mmol of $PtCl_2$[(*R*)-BINAP], 0.01 mmol of $SnCl_2$, 1 mmol of substrate, $p(CO)=p(H_2)=40$ bar, 5mL of toluene.
b) Determined by GC.
c) Chemoselectivity towards aldehydes: (**6**+**7**)/(**6**+**7**+**8**)x100
d) Regioselectivity towards branched aldehyde: **6**/(**6**+**7**)x100
e) Determined by chiral GC (favoured enantiomer in brackets)

4. Discussion

Using BINAP as bidentate diphosphine ligand, able to form conformationally rigid chelate ring, (*S*)-2-arylpropanals and the corresponding (*R*)-enantiomers predominate at low and high temperature, respectively, when the hydroformylation of the corresponding 4-substituted styrene (**1a-g**) was carried out in the presence of Pt-*(R)*-BINAP-tin(II) chloride catalytic systems.

Using **1a-g** as substrates, our results have shown that unexpected reversal of the enantioselectivity occurs in a temperature range of 70 ^{o}C to 84 ^{o}C depending on the electron donor/electron acceptor properties of the 4-substituents of the substrate. Since the stereochemical outcome of the reaction is determined in the formation of the platinum-alkyl leading to the formation of (*S*)- and (*R*)-**2a-g**, the electronic properties of the substituents play a crucial role. The weakening of the Pt-carbon bond and increase of the reversal temperature is due to electron acceptor substituents, such as CF_3 or Cl. Based on these results, a facile insertion of carbon monoxide but not a β-hydride elimination resulting in the styrene derivative can be supposed.

The electron donor substituents such as CH_3 or OCH_3 increase electron density on the Pt-carbon bond and therefore, increase reversibility of the Pt-alkyl formation. Consequently, the reversal temperature of enantioselectivity was decreased. In these cases β-hydride elimination is preferred to carbon monoxide insertion. The corresponding styrene derivatives are ‘re-formed’ and are inserted into the Pt-H bond resulting in the favoured formation of the corresponding *(S)*-2-arylpropanals.

It can be stated that using 4-substituted substrates,[17] much lower reversal temperatures (lower by 20-35 ^{o}C!) were observed in the presence of the Pt-BINAP catalysts than with the corresponding Pt-BDPP systems. One of the main differences between Pt-BDPP and Pt-BINAP is the conformational rigidity of chelate ring formed by the latter one. While BDPP forms a 6-membered chelate with transition metals which has several ring conformations and high flexibility of the chelate ring, the 7-membered BINAP-transition metal chelate ring is relatively rigid, *i.e.*, the rotation of the binaphthyl ring around C1-C1’ axis is the only possibility to alter the distance between phosphorus donor atoms. According to NMR[8l] and crystallographic investigations,[22] the chiral arrangement of the phenyl rings of coordinated BINAP, determining the ‘chiral pocket’ available for styrene derivatives for coordination from *re* or *si* enantiosites, can be considered as more crowded. Focusing our attention on the stereodefining step of the hydroformylation, it can be stated that this crowded arrangement leads to the reversibility of the Pt-alkyl formation, and as above, resulted in the decrease the reversal temperature of enantioselectivity.

5. Conclusion

Platinum–(R)-BINAP–tin(II) chloride 'in situ' systems proved to be active catalyst in the hydroformylation of 2- and 4-substituted styrenes. The reversal of the absolute configuration of the branched formyl regioisomer (2-arylpropanal derivatives) can be rationalised explained by the reversible formation of the corresponding Pt-

branched alkyl intermediates. In addition to the unexpected change of absolute configuration, a strong substituent effect on the regioselectivity was observed in the hydroformylation of 2-substituted styrenes: substituents with larger steric parameters, due to steric reasons, favour the formation of the linear aldehyde.

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Captions to Scheme and Figures

Scheme 1. Hydroformylation of 4-substituted styrenes in the presence of $PtCl_2$[(*R*)-BINAP] + $SnCl_2$ 'in situ' catalyst.

Scheme 2. Hydroformylation of 2-substituted styrenes in the presence of $PtCl_2$[(*R*)-BINAP] + $SnCl_2$ 'in situ' catalyst.

Figure 1. Effect of temperature on the enantioselectivity in the hydroformylation of **1a-g** in the presence of Pt-(*R*)-BINAP catalyst.

Figure 2. The reversal temperatures of the enantioselectivity (T_{rev}) plotted against the Hammett constants (σ_p) in the hydroformylation of **1a-g** in the presence of Pt-(*R*)-BINAP catalyst.

Figure 3. Effect of temperature on the enantioselectivity in the hydroformylation of **5a-g** in the presence of Pt-(*R*)-BINAP catalyst.

Figure 4. The reversal temperatures of the enantioselectivity (T_{rev}) plotted against the steric constants (Es) in the hydroformylation of **5a-g** in the presence of Pt-(*R*)-BINAP catalyst.

Highlights

- Platinum-catalysed enantioselective hydroformylation of 2- and 4-substituted styrenes.
- Unusual temperature dependence of the enantioselectivity.
- Explanation on the reversal of the favoured enantiomer..
- Reversal temperature *vs* σ_p, regioselectivity *vs* σ_p correlations.