ELSEVIER

Journal of Molecular Catalysis A: Chemical 122 (1997) 95–101

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

The effect of triflate additives in platinum-catalyzed enantioselective hydroformylation

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Received 1 October 1996; revised 16 December 1996

Abstract

Styrene was hydroformylated in the presence of platinum containing in situ catalysts formed in the reaction of $PtCl_2$(diphosphine), tin(II)chloride, and tin(II)triflate (or silver triflate). The reaction resulted in both linear and branched formyl regioisomers, achiral 3-phenyl-propanal and chiral 2-phenyl-propanal, respectively. Using the optically active Pt–*bdpp* (*bdpp* = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane) systems high ee-s were achieved, which were decreased substantially in the presence of triflate anion. The activity of the catalyst was reduced by the addition of silver triflate and its application in excess resulted in the formation of inactive systems. However, regioselectivity towards chiral branched aldehyde (2-phenylpropanal) was increased both with achiral and chiral bidentate phosphine-containing catalysts upon addition of silver triflate. In the presence of platinum-phosphine–tin(II)chloride in situ systems containing tin(II)triflate consecutive hydrogenation of the aldehyde regioisomers formed in hydroformylation of styrene took also place.

Keywords: Platinum; Hydroformylation; 2-Phenyl-propanal; Triflate anion; Nonsteroidal antiinflammatory agents

1. Introduction

Since in most cases only one enantiomer of a racemic mixture shows the desired biological activity, the demand for enantiomerically pure compounds is steadily increasing [1]. Among these derivatives the nonsteroidal antiinflammatory agents (NSAI), especially 2-arylpropionic acids represent a class of pharmaceuticals of high practical importance [2]. In addition to classical organic synthetic methods [3] the synthesis of 2-arylpropionic acids can be carried out by the following homogeneous catalytic procedures: (i) asymmetric hydrovinylation of vinylaromatics (codimerization of vinylaromatics and ethylene) and subsequent oxidation of the carbon–carbon double bond (Eq. (1)), (ii) enantioselective hydrogenation of 2-aryl-acrylic acids (Eq. (2)), (iii) homogeneous catalytic asymmetric carbonylation reactions such as hydroformylation (X = H) and hydrocarbalkoxylation (X = OR) followed by oxidation and hydrolysis, respectively, or direct hydrocarboxylation (X = OH) Eq. (3)).

$$\mathrm{ArCH{=}CH_2 + CH_2{=}CH_2 \longrightarrow ArC^*H(CH_3)(CH{=}CH_2)} \quad (1)$$

$$\downarrow$$

$$\mathrm{ArC^*H(CH_3)COOH}$$

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PII S1381-1169(97)00021-6

$$Ar(COOH)C{=}CH_2 + H_2 \rightarrow ArC{*}H(CH_3)COOH \quad (2)$$

$$ArCH{=}CH_2 + CO + HX \rightarrow ArC{*}H(CH_3)COX \quad (3)$$

In spite of the good regioselectivities obtained in hydrovinylation [4], and excellent optical yields in homogeneous enantioselective hydrogenation of carbon–carbon double bond [5], the carbonylation reactions, especially rhodium- and platinum-catalyzed hydroformylation gained ground in the last decade [6,7]. Although there are several limitations concerning chemo- and regioselectivities of the hydroformylation reaction, the moderate to good enantioselectivities and the ease of the synthesis of the substrates are promising for future application. (The probable future commercial synthesis of *naproxen* (Fig. 1) employs an electrochemical reduction of the 6-methoxy-2-acetylnaphthalene in the presence of carbon dioxide. The resulting α-hydroxypropionic acid is dehydrated to produce the α-naphtylacrylic acid derivative, the appropriate substrate of enantioselective hydrogenation [8].)

Early work concentrated on rhodium based catalysts being active even at low temperature, since these might be expected to minimize racemization of the formyl products via keto-enol tautomerism. These catalysts yielded mainly the desired branched aldehyde, but the ee-s were rather low until the use of Takaya's chelating *binaphos* ligand possessing two phosphorus atoms of different donor strength [9].

In the last two decades platinum-catalyzed reactions have shown the most promise. The platinum-chiral diphosphine–tin(II)chloride in situ systems and $PtCl(SnCl_3)$(chiral diphosphine) preformed catalysts are well-known active catalysts in enantioselective olefin hydroformylation and proved to be very efficient for the hydroformylation of both vinyl- [10–15] and vinylidene-type olefins [15,16]. They could be considered as efficient catalysts for the synthesis of α-aryl-propionic acids like *ibuprofen*, *naproxen*, or *suprofen* (Fig. 1) [15].

Furthermore, the presence of tin(II)chloride as trichlorostannato ligand or counterion proved to be crucial for the activity of the platinum-containing catalytic system [17]. In the presence of basic amines $HSnCl_3$ abstraction from the $PtH(SnCl_3)P_2$ intermediate takes place and the platinum complexes obtained did not show any catalytic activity [18].

Some platinum-based hydroformylation catalysts containing diphenylphosphinous acid as the ligand, which do not require the presence of $SnCl_2$ have been reported in the literature [19,20] but do not have been developed.

The Pt(0) complexes like $Pt(CH_2{=}CH_2)$(P–P) (where P–P = *diop*, (2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane); 1,2-bis(diphenyl-phosphinomethyl)benzene [21], *dppb* (1,4-bis(diphenylphosphino)-butane [22]) show some catalytic activity by the addition of methanesulfonic acid. Although the alkene conversion is quite high (close to the $SnCl_2$ added system) the chemoselectivity to the formation of aldehydes is much lower since hydroformylation is always accompanied by the consecutive

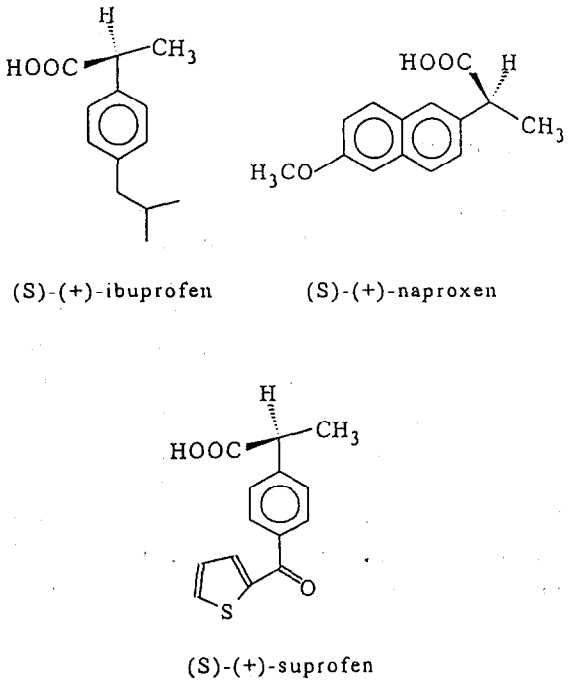

Fig. 1. Nonsteroidal antiinflammatory agents.

reduction of the primarily formed aldehyde and by the formation of high-boiling by-products. The hydrido-complex $PtH(OSO_2CH_3)(P_2)$ as key-intermediate has been recently postulated [22].

The systematic investigation of these preformed and in situ catalysts lead to our study on the effect of triflate anion of low coordinating ability.

In this paper the effect of silver triflate on the tin(II)chloride-containing catalyst, as well as the catalytic features of the hydroformylation of styrene in the presence of tin(II)triflate and tin(II)fluoride cocatalysts will be described.

2. Materials and methods

2.1. Chemicals

The diphosphine ligands (*dppp*, *bdpp*) and tin(II) triflate were purchased from Fluka, Strem and Aldrich, respectively and have been used without further purification. Anhydrous tin(II)chloride was prepared from $SnCl_2 \cdot 2H_2O$ by acetic anhydride and washing with ether. Styrene was distilled under argon before use. Toluene, used as solvent for catalytic experiments, was dried over sodium in the presence of benzophenone and was distilled under argon. $PtCl_2$(diphosphine) complexes were prepared according to the literature [11].

2.2. Instrumentation

^1H and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Varian Unity 300 (Palo Alto, CA) spectrometer at 300 and 121.4 MHz, respectively. Chemical shifts are reported in δ ppm, referred to TMS (tetramethylsilane) as internal standard and to orthophosphoric acid (85%, higher fields refer to lower chemical shifts) as external standard.

Gas-liquid chromatographic (GLC) analyses were performed on a Hewlett-Packard (Palo Alto, CA) 5830 gas chromatograph using a capillary column (25 m × 0.2 mm) coated with OV-1. Argon was used as carrier gas, with a constant flow rate of 1 ml/min and the injector and detector were set at 250°C. Oven temperature was held at 50°C for 2 min and then ramped to 200°C at 10°C/min.

Mass spectra were recorded on a HP-5971A GC-MSD apparatus using a 10 m OV-1 column with the same program.

The optical purities were determined by chiral GC (CP-Cyclodextrin-B-2,3,6-M-19 column, 25 m, film thickness 0.25 μm) on the corresponding 2-phenyl-propionic acid obtained by $KMnO_4$ oxidation of the reaction mixture containing 2-phenylpropanal [23]. Argon was used as carrier gas with a flow rate of 2 ml/min and the injector and detector were set at 250°C. Oven temperature was held at 100°C for 2 min and then ramped to 200°C at 3°C/min. The retention times of (*S*)- and (*R*)-2-phenylpropionic acid were 32.24 and 32.57 min, respectively.

The optical rotations of the products were measured for neat liquids with a Schmidt Haensch LM visual 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-phenyl-propanal [10]. The optical yields were checked by NMR in the presence of chiral shift reagent, Eu(*dcm*)$_3$.

Hydroformylation experiments were carried out in a 100 ml stainless steel autoclave equipped with a magnetic stirrer.

2.3. Hydroformylation experiment

In a typical experiment, 0.025 mmol $PtCl_2$(diphosphine), 9.5 mg (0.05 mmol) $SnCl_2$, 20.8 mg (0.05 mmol) $Sn(OTf)_2$, 11.5 ml (100 mmol) styrene and 30 ml toluene was placed under argon into a 150 ml stainless steel 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

Table 1
Platinum-catalyzed hydroformylation of styrene (**1**) in the presence of silver triflate [a]

Run	Catalyst	Temp. (°C)	p (bar)	Run time (h)	Conv. [b] (%)	R_C [c] (%)	R_{RB} [d] (%)	ee (%)
1	**I** + $2SnCl_2$	100	80	4	76	86	27	–
2	**I** + $2SnCl_2$ + 0.5 AgOTf	100	90	25	86	73	54	–
3	**I** + $2SnCl_2$ + AgOTf	100	90	20	94	75	52	–
4	**I** + $2SnCl_2$ + 2AgOTf	100	110	35	98	70	67	–
5	**I** + $2SnCl_2$ + 3 AgOTf	100	80	25	98	–	–	–
6	**II** + $2SnCl_2$	100	80	3	50	88	32	9.9 (*R*)
7	**II** + $2SnCl_2$ + 2AgOTF	100	80	25	75	88	37	1.6 (*R*)
8	**II** + $2SnCl_2$	60	80	30	60	90	38	63.0 (*S*)
9	**II** + $2SnCl_2$ + 2AgOTf	60	80	100	98	69	44	0.9 (*S*)
10	**II** + $2SnCl_2$	40	80	115	58	98	42	75.5 (*S*)
11	**II** + $2SnF_2$	100	80	5	26	95	31	15.1 (*S*)
12	**I** + $2SnF_2$ + 2AgOTf	100	80	100	60	72	54	–
13	**II** + $2SnF_2$	40	80	240	72	98	32	76.0 (*S*)
14	**II** + SnF_2 + 5AgF	40	80	180	65	97	33	71.3 (*S*)

Catalyst precursors: **I** = $PtCl_2$(dppp); **II** = $PtCl_2$[(*S*,*S*)-(bdpp)].
[a] Reaction conditions: Pt/**1** = 1/4000; solvent toluene.
[b] (mol reacted **1**/mol initial **1**) × 100.
[c] (**2** + **3**)/(**2** + **3** + **4**) × 100.
[d] **2**/(**2** + **3**) × 100.

pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed, and quickly analyzed by GLC, then fractionally distilled to enable determination of the optical purity of 2-phenylpropanal.

3. Results

Hydroformylation of styrene (**1**) as model compound in the presence of platinum catalysts has been carried out. The reaction yields both regioisomers, 2-phenyl-propanal (**2**) and 3-phenyl-propanal (**3**). The reaction is accompanied by the formation of the hydrogenation product of the substrate, ethylbenzene (**4**) (Eq. (4)).

$$\underset{\mathbf{1}}{PhCH{=}CH_2} + CO + H_2 \rightarrow \underset{\mathbf{2}}{PhC{*}H(CH_3)CHO} + \underset{\mathbf{3}}{Ph(CH_2)_2CHO} + \underset{\mathbf{4}}{PhC_2H_5} \quad (4)$$

The data of the catalytic experiments allow the following conclusions:

(i) The addition of AgOTf to Pt(*dppp*)Cl_2 + $SnCl_2$ catalyst (*dppp* = 1,3-bis(diphenylphosphino)propane) in various molar ratio resulted in lower conversion (Table 1). Using the triflate in excess, the catalyst was desactivated completely (Run 5). However, the use of silver triflate in the same amount as $SnCl_2$ (or less) yielded catalytic systems possessing different selectivity features from those without silver triflate additive.

(ii) While chemoselectivities decreased slightly upon addition of silver triflate, the regioselectivities towards branched chiral aldehyde of practical importance increased dramatically by the factor of 2.5 (Run 1–4).

(iii) The platinum complex of chiral bidentate phosphine *bdpp* (*bdpp* = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane), which is able to form six-membered chelate ring like *dppp*, forms active catalyst both at 60 and 100°C. The regioselectivity towards branched aldehyde has been increased upon addition of AgOTf as has been proved for the *dppp*-containing systems. A

Table 2
Hydroformylation of styrene in the presence of $PtCl_2(P_2) + SnCl_2 + Sn(OTf)_2$ in situ catalysts [a]

Catalyst	4 (%)	Aldehydes (%)			Alcohols %		Dimers (%)	Oligomers (%)
		2	ee; abs. conf.	3	2a	3a		
$PtCl_2$(dppp) + 2 $SnCl_2$ + $Sn(OTf)_2$	0.5	16	–	4	7	9.5	35	28
$PtCl_2$(dppp) + 2 $SnCl_2$ + 2 $Sn(OTf)_2$	3.5	–	–	–	1	2	93.5	–
$PtCl_2$(bdpp) + 2 $SnCl_2$ + 2 $Sn(OTf)_2$ [b]	5	39	29.3 (*S*)	57	–	–	–	–
$PtCl_2$(bdpp) + 2 $SnCl_2$ + 2 $Sn(OTf)_2$	17	31	19.3 (*R*)	53	–	–	–	–

[a] Reaction conditions (unless otherwise stated): Pt/styrene = 1/4000, $p(CO) = p(H_2) = 40$ bar; $T = 100$°C; solvent toluene; composition of the reaction mixtures are indicated in the table.
[b] $T = 50$°C.

strong temperature dependence of the asymmetric induction was observed, as described previously [11,12]. At low temperature the formation of (+)-(*S*)-**2**, at higher temperature that of (-)-(*R*)-**2** is favoured.

(iv) The fact that the active catalysts in the presence of additives are different from those without silver triflate can be proved also when SnF_2 is used as tin-containing cocatalyst. The $PtCl_2$(*bdpp*) + $2SnF_2$ catalytic system yields mainly aldehydes in styrene hydroformylation (Run 13). The use of silver fluoride does not cause any significant changes in catalytic properties (Run 14).

v) The addition of tin(II)triflate to the tin(II)chloride-containing system resulted mainly in dimerization of the substrate (Eq. (5); Table 2). The hydrogenation of the dimers yielded diphenylbutane isomers up to 12%.

$$2PhCH{=}CH_2 \rightarrow \begin{cases} PhC{*}H(CH_3)(C(Ph){=}CH_2)\ (2\text{–}5\%) \\ + \\ PhC{*}H(CH_3)(CH{=}CHPh)\ (90\text{–}95\%) \\ + \\ PhCH_2CH_2CH{=}CHPh\ (3\text{–}5\%) \end{cases} \quad (5)$$

While using $SnCl_2/Sn(OTf)_2 = 2/1$ ratio the amount of the aldehyde regioisomers and the corresponding alcohols (chiral 2-phenyl-propanol (**2a**) and achiral 3-phenyl-propanol (**3a**)), formed by subsequent hydrogenation, is nearly the same as the amount of dimers, the use of equal amount of $SnCl_2$ and $Sn(OTf)_2$ resulted in the formation of dimers almost exclusively, when *dppp* was used as ditertiary phosphine (Run 1,2). Surprisingly, side-reactions took place in a negligible extent in the presence of *bdpp* (Run 3,4).

4. Discussion

The phenomenon of changing the prevailing enantiomer of 2-phenyl-propanal by the variation of the temperature is known and has been proved in some cases [11,12,24], when *bdpp* and its analogues have been used as chiral chelating phosphines. The formation of the dominant *S* enantiomer of 2-phenylpropanal at low temperatures can be due to both steric effects (the presence of major δ-skew conformer, which could coordinate the substrate from the *si* enantioface) and kinetic effects (the increased reactivity of the transition states coordinating the substrate from the *si* enantioface).

The difference in optical yields obtained in the absence and in the presence of silver triflate reflects to the presence of different catalytic intermediates. The strong decrease of ee-s could not be explained only by racemization of the branched aldehyde in elevated reaction time, since it must be rather low at 60°C. The difference in catalytic systems is also indicated by the slightly increased regioselectivities, which were obtained upon addition of silver triflate.

The different selectivities from those without

triflate can be rationalized by the formation of ionic species in the catalytic cycle (Fig. 2). The cationic species formed by the addition of one equivalent of silver triflate could easily coordinate the olefin and activate hydrogen by the hydrogenolysis of the Pt–Sn bond. (It must be noted, that $SnCl_3^-$ could also act as counterion [25], and an interplay of $[Pt(P_2)(L)(SnCl_3)]^+$ and $[Pt(P_2)(L)(OTf)]^+$ complex cations may result in the catalytic properties different from the 'basic' system.) The activation of carbon monoxide, the CO insertion and the formation of aldehyde regioisomers are favoured by ionic species [26]. Similar ionic species are supposed when tin(II)chloride has been used in excess ($SnCl_2/AgOTf = 2/1$), but the $Pt(P_2)X(SnCl_3)$-covalent species (X = Cl, OTf) are present in higher concentration.

By the addition of a further equivalent of silver triflate ($SnCl_2/AgOTf = 1/2$) resulted in the formation of $[Pt(P_2)(OTf)_2]$ covalent complexes, which are unable to activate hydrogen in the absence of trichlorostannato ligand. The $Pt(bdpp)(OTf)_2$ precursor was prepared on the basis of analogous procedure [27] and tested in hydroformylation *without showing any catalytic*

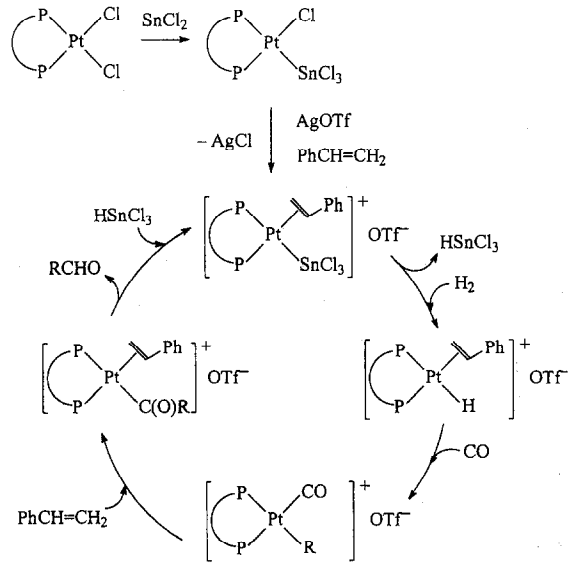

Fig. 2. Proposed mechanism of platinum-catalysed hydroformylation in the presence of silver triflate additive.

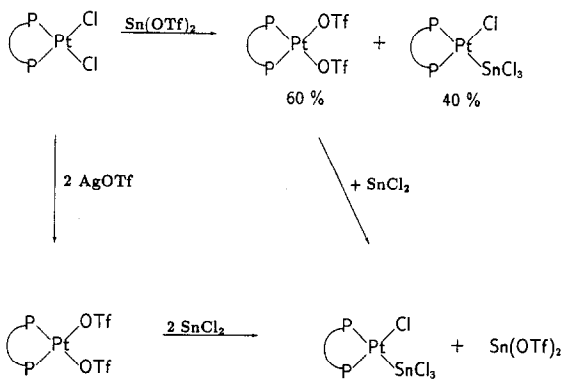

Fig. 3. Reaction of Pt(II) complexes (on the basis of in situ ^{31}P NMR studies)

activity even in long reaction times. Both the in situ NMR experiments and the synthesis have shown the facile formation of covalent $Pt(P_2)(OTf)_2$ complex (when P_2 = bdpp, δ = 10.1 ppm; J(Pt–P) = 3505 Hz) by using two equivalents of silver triflate. However, the addition of tin(II)chloride at the same ratio resulted in nearly quantitative formation of $PtCl(SnCl_3)(P_2)$ (when P_2 = bdpp, δ_1 = 6.9 ppm; J_1(Pt–P) = 3344 Hz; δ_2 = 13.1 ppm; J_2(Pt–P) = 2730 Hz) (Fig. 3).

The catalytic results could be explained by the interplay of $Pt(SnCl_3)(OTf)(P_2)$ complex formed by $SnCl_2$ insertion into the Pt–Cl bond and the above $PtCl(SnCl_3)(P_2)$ complex.

The presence of Pt–$SnCl_3$ moiety seems to be indispensable in the 'first part' of the catalytic cycle under above conditions, that means the catalytic steps before the formation of platinum-alkyl intermediate are favoured by $SnCl_2$.

The addition of tin(II)triflate to the $PtCl_2$(*dppp*) + $SnCl_2$ system leads to the formation of side products of the substrate (mixture of dimers and higher oligomers). In the absence of platinum catalysts similar oligomerization reactions have been observed. The unexpected consecutive hydrogenation of the formyl regioisomers to the corresponding alcohols indicates the formation of platinum catalysts of novel type, because the $PtCl(SnCl_3)(P_2)$-type complexes, unlike many cobalt- and rhodium-

containing catalysts, are reluctant towards hydrogenation of the aldehyde. The chlorine-triflate exchange between Pt–Cl and $Sn(OTf)_2$, as well as between $SnCl_2$ and $Sn(OTf)_2$ resulting in SnCl(OTf) and its insertion into the Pt–Cl bond, may be responsible for the formation of catalytic species, which are effective hydrogenation catalysts of the aldehydes.

The reaction of $Pt(P_2)Cl_2$ with $Sn(OTf)_2$ yields a 60/40 mixture of $Pt(P_2)(OTf)_2$ and $PtCl(SnCl_3)(P_2)$, as well as $SnCl_2$ and unreacted $Sn(OTf)_2$ as was proved by ^{31}P NMR experiments (Fig. 1).

The unexpectedly 'clean' hydroformylation (without formation of alcohol regioisomers) by using $PtCl_2(bdpp) + SnCl_2 + Sn(OTf)_2$ in situ catalyst can be explained by the fast and dominant formation of trichlorostannato–platinum species of high carbonylation activity.

Acknowledgements

The authors thank G. Szalontai and S. Iglewski for NMR measurements. L.K. thanks the Hungarian National Science Foundation (OTKA 2319) and COST Program (ERBCIPECT 926001) for financial support.

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