

Hydroesterification of styrene catalyzed by Montmorillonite–Diphenylphosphinepalladium(II) chloride in the presence of chiral phosphines

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Abstract

The catalyst system, montmorillonite–diphenylphosphinepalladium(II) chloride complex, HCl–NMDPP, afforded the corresponding branched ester quantitatively at 125°C and 45 atm of CO pressure. The high catalytic activity (substrate/Pd = 500) demonstrates its potential use on commercial scale although the enantioselectivity is not satisfactory. In contrast to previous studies, bulky bidentate ligands were also effective because of the higher interlamellar spacings of the catalyst.

Keywords: Styrene; Hydroesterification; Chiral phosphines; Montmorillonite; Palladium complex; Regioselectivity

1. Introduction

Catalytic hydroesterification of olefins with CO and an alcohol has attracted considerable interest for the synthesis of industrially important carboxylic esters [1,2]. Transition metal catalyzed hydroesterification of olefins usually affords a mixture of normal and branched esters [3–5]. The branched acid esters derived from arylethenes are useful precursors for 2-arylpropionic acids such as ibuprofen and naproxen, the non-steroidal anti-inflammatory drugs [6,7].

Palladium complexes have received great attention because they are not only effective at lower CO pressures but also selective to branched esters and acids [4,5,8–15]. There are only few successful reports on asymmetric hydroesterification. One of the best results has been shown by Alper in hydrocarboxylation of arylethenes using PdCl₂–CuCl₂–HCl–(*S*)- or (*R*)-BNPPA (1 atm of CO at room temperature) [16]. The corresponding ester was obtained in 66–89% conv. (*S*/*C* = 4.2–10), 83–91% ee. Consiglio and co-workers [17] and Hayashi et al. [18] reported on asymmetric hydrocarboxylation of α -methylstyrene catalyzed by PdCl₂–DIOP (400 atm of CO at 100°C, ~ 60% ee, *S*/*C* = 200) or PdCl₂(PhCN)₂–chiral dibenzophospholes (240

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atm of CO at 100°C, 23–83% conv., $S/C = 200$, 7.3–44% ee), respectively. Cometti and Chiusoli reported hydroesterification of styrene using a combination of a NMDPP–Pd(dba)₂ complex (NMDPP = neomenthyl-diphenylphosphine) with excess trifluoroacetic acid (1 atm of CO at 50°C, $S/C = 188$, 3% isolated yield, 52% ee) [19].

Heterogeneous catalysts are preferred in industry because of their ease of separation and reusability. Swelling-type smectite clays such as montmorillonite have recently attracted much interest as supports for transition metal complexes. These clays can be functionalized by attachment of organic ligands to which a metal can coordinate [20–22] or via ion exchange with a cationic metal complex [23–25]. In many cases, transition metal complexes immobilized on montmorillonite show enhanced reactivity and selectivity in hydrogenation, hydroformylation and carbonylation [20–27]. The better results are considered to be due to their lamellar swelling structure, large surface area, and availability of both Brønsted and Lewis acidic sites. Recently there are some reports on hydroesterification of olefins by palladium complexes intercalated in smectite clays. Crocker and Herold reported hydroesterification of ethylene using Pd^{II} complexes intercalated in smectite clay by ion exchange [28]. They concluded that acidic forms of montmorillonite have a promoting effect on these reactions. Alper reported that Pd(OAc)₂ immobilized on montmorillonite displays good selectivity in hydroesterification of olefins to give branched esters (45 atm of CO at 125°C, $S/C = 500$, 80% isolated yield) [29]. The remarkably high catalytic activity of palladium complexes immobilized on montmorillonite prompted us to investigate hydroesterification of styrene with these complexes in the presence of chiral phosphines.

We report here hydroesterification of styrene catalyzed by the montmorillonite–diphenylphosphinepalladium(II) chloride anchored complex in the presence of various chiral phosphorous ligands.

2. Experimental

2.1. General procedure, materials, and measurement

All manipulation of oxygen- and moisture-sensitive materials were conducted under purified argon atmosphere (deoxygenated by BASF-Catalyst R3-11 at 80°C). Proton NMR spectra were recorded on a JEOL EX-270 spectrometer using tetramethylsilane as an internal standard. HPLC analyses were carried out on a TOSOH CCPM equipped with CO-8000 injection unit and UV-8000 detector.

All commercially available reagents were used as-received unless otherwise stated. Benzene was distilled under argon after drying over sodium benzophenone ketyl. Methanol was distilled over magnesium methoxide. Montmorillonite–diphenylphosphine–PdCl₂ was prepared according to our earlier literature reported method [21]. (*R,S*)-BINAPHOS [30] and Pd(dba)₂ [31] were prepared by the reported procedures. Preparation of (*R*)-7,7'-bis(diphenylphosphinomethyl)-2,2'-dimethoxy-1,1'-binaphthyl will be reported elsewhere. Carbon monoxide was purchased from Teisan Co.

2.2. Hydroesterification of styrene

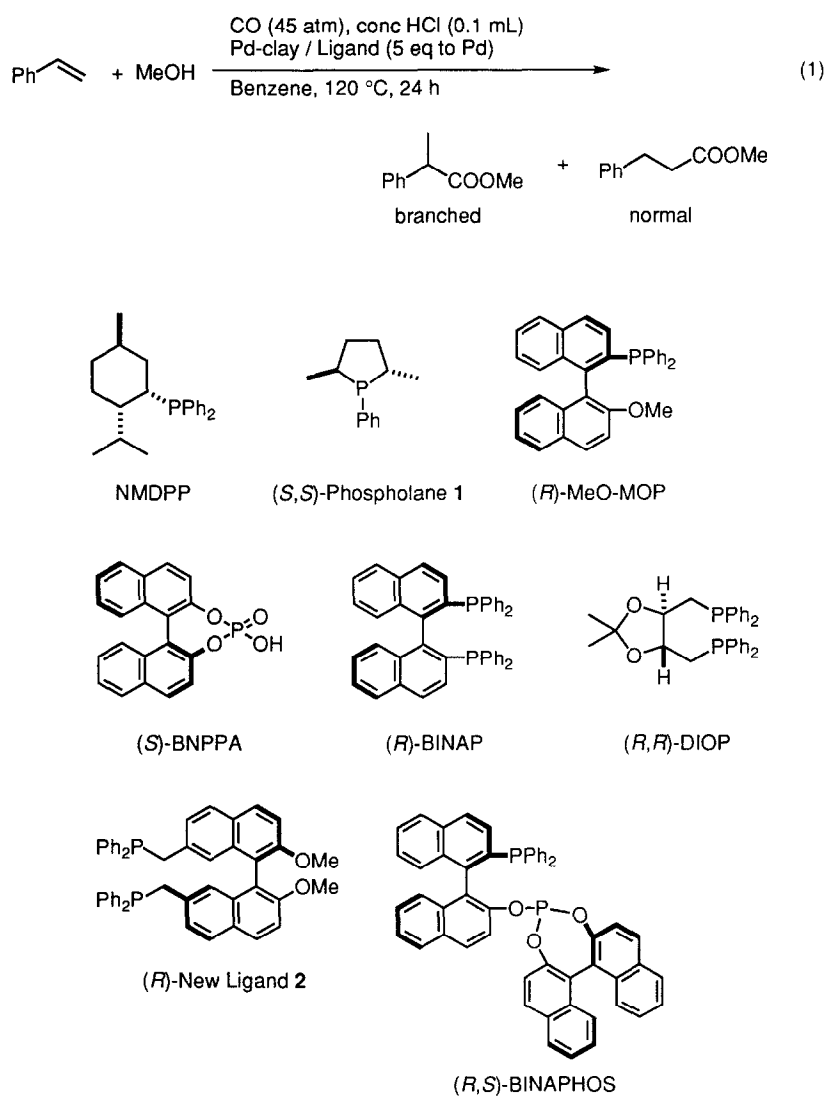
A solution of styrene (0.11 ml, 1.0 mmol) in benzene (10 ml) was prepared in a 20-ml Schlenk tube, and degassed by three freeze-thaw cycles. The solution was transferred into a 50-ml stainless-steel autoclave containing Pd-clay (20.0 mg, 0.0020 mmol of Pd) and ligand (0.010 mmol) under argon. To this was added methanol (0.24 ml, 6.0 mmol), conc. HCl (0.10 ml). The mixture was stirred under 45 atm of CO for 24 h in an oil bath maintained at 125°C. After cooling down to room temperature, CO was released and the reaction mixture was filtered, concentrated with rotary evaporator. Conversion and selectivity were determined by ¹H-NMR. Pure ester was isolated by column chromatography on silica gel using hexane/ethyl

acetate (9/1) as an eluent. The enantiomeric excess was determined by HPLC analysis (Daicel CHIRALCEL OJ, hexane/2-propanol = 99/1, 1 ml min⁻¹).

3. Results and discussion

Hydroesterification of styrene was carried out with montmorillonite–diphenylphosphine–PdCl₂ along with various chiral phosphorous ligands in the presence of concentrated hydro-

chloric acid (Scheme 1). The ligand effect on the reaction is shown in Table 1. No reaction took place in the absence of a ligand (run 1). Monodentate phosphines led to complete selectivity to the branched ester and the product was isolated in high yield, but the enantioselectivities were poor (runs 3–4). Excellent regioselectivity has also been obtained with an (*S,S*)-phospholane **1**, but the catalytic activity was lower (run 5). On the contrary, mixtures of branched and linear esters were obtained with conventional bisphosphine ligands (runs 7–8).



Scheme 1.

Table 1

Hydroesterification of styrene catalyzed by montmorillonite–diphenylphosphinepalladium(II) chloride in the presence of different chiral phosphines ^a

Entry	Ligand	Conv. (%) ^b	Branched/linear	% ee (Config)
1	None	0	–	–
2	PPh ₃	100	100/0	–
3	NMDPP	77 (73)	100/0	1.8 (<i>S</i>)
3A ^c	NMDPP	33	100/0	1.2 (<i>S</i>)
4	(<i>R</i>)-MeO-MOP	78 (72)	100/0	5.0 (<i>R</i>)
5	(<i>S,S</i>)-Phospholane	49	98/2	2.4 (<i>R</i>)
6	(<i>S</i>)-BNPPA	0	–	–
7	(<i>R</i>)-BINAP	22	50/50	ND ^d
8	(<i>R,R</i>)-DIOP	12	< 10/> 90	–
9	(<i>R</i>)-New ligand ^e	23	100/0	12.0 (<i>S</i>)
10	(<i>R,S</i>)-BINAPHOS	52	86/14	6.0 (<i>R</i>)

^a Styrene (0.11 ml, 1.0 mmol) in benzene (10 ml) was treated with methanol (0.24 ml, 6.0 mmol) at 125°C for 24 h under 45 atm of CO in the presence of Pd-clay (20.0 mg, 0.0020 mmol of Pd), ligands (0.010 mmol), and conc. HCl (0.10 ml).

^b Isolated yields are shown in parentheses.

^c Reaction with a used catalyst.

^d Not determined. Complexity of the reaction mixture prevented purification of the product and HPLC analysis.

^e (*R*)-7,7'-bis(diphenylphosphinomethyl)-2,2'-dimethoxy-1,1'-binaphthyl.

Similar regioselectivities with chelating bisphosphines are reported in homogeneous conditions [5]. Nevertheless, it is noteworthy that the reaction proceeded with the bulky bidentate ligands in this Pd-clay system and this is against the observation by Lee and Alper that no reaction has taken place with dppp [1,3-bis(diphenylphosphino)propane] and dppb [1,4-bis(diphenylphosphino)butane] in their Pd(OAc)₂ immobi-

lized on montmorillonite [29]. This may be explained that the basal (001) spacings in the present clay complex is 18 Å [21] which is higher than the clay complex (15 Å) they used. Higher enantioselectivity, 12% ee has been achieved with a new ligand 2 as well as complete regioselectivity (run 9). Larger bite angle of this ligand may be advantageous to this reaction. The phosphine–phosphite ligand BI-

Table 2

Effect of acid additives on the hydroesterification of styrene ^a

Entry	Acid (amount)	Conv. (%) ^b	Branched/linear	% ee (Config)
1	None	0	–	–
2	HCl (0.1 ml)	77 (73)	100/0	1.8 (<i>S</i>)
3	HCl (0.05 ml)	58	100/0	1.8 (<i>S</i>)
4	HCl (0.02 ml)	30	100/0	racemic
5 ^c	HCl (0.1 ml)	50	100/0	3.0 (<i>S</i>)
6	CF ₃ COOH (0.1 ml)	0	–	–
7	CF ₃ COOH (0.02 ml)	0	–	–
8	TsOH ^d (0.02 mmol)	0	–	–
9	HBFB ^e (0.15 ml)	67 ^f	–	–
10	CuCl ₂ (0.01 mmol)	0	–	–

^a Styrene (0.11 ml, 1.0 mmol) in benzene (10 ml) was treated with methanol (0.24 ml, 6.0 mmol) at 125°C for 24 h under 45 atm of CO in the presence of Pd-clay (20.0 mg, 0.0020 mmol of Pd), NMDPP (0.010 mmol), and additives.

^b Isolated yields are shown in parenthesis.

^c Methanol was used as a solvent.

^d *p*-Toluenesulfonic acid.

^e 48 wt% in water.

^f The product was PhCH(CH₃)OCH₃. No ester was obtained.

NAPHOS, which has been shown to be an excellent ligand for enantioselective carbonylation such as hydroformylation and copolymerization with olefins [30,32], was also used as a ligand. In this reaction, BINAPHOS complex showed higher activity than those with other bidentate ligands, but the obtained regio- and enantioselectivity were inferior to the new ligand (run 10). It is possible that BINAPHOS worked as a monodentate ligand because hydrolysis of the phosphite site might have taken place under the acidic reaction condition.

Reusability is an important feature of heterogeneous catalysis. Since no precipitation of palladium metal was observed when the reaction was completed in run 3, the catalyst was recovered, washed, and subjected for the same reaction (run 3A). Reused catalyst maintained the selectivity, albeit with lower activity (run 3A). Loss of palladium at the washing may be the reason for the lower catalytic activity. When water was used instead of methanol in an attempt to produce the acid directly, there is no reaction and the catalyst precursor decomposed to inactive palladium metal.

Table 2 summarizes the effect of various acid additives using neomenthylidiphenylphosphine as the standard chiral ligand. No reaction has occurred without acid (run 1). Among the additives tested, only HCl was found to be effective (run 2). At lower concentration of HCl, the catalyst partially decomposed to palladium metal during the reaction, and the yield was lowered (runs 3–4). Other acid additives caused deposi-

Table 3
Effect of pressure on the hydroesterification of styrene ^a

Entry	Pressure (atm)	Conv. (%)	Branched /linear	% ee (Config)
1	45	77	100/0	1.8 (S)
2	35	100	100/0	racemic
3	5	33 ^b	–	–

^a Styrene (0.11 ml, 1.0 mmol) in benzene (10 ml) was treated with methanol (0.24 ml, 6.0 mmol) at 125°C for 24 h under CO in the presence of Pd-clay (20.0 mg, 0.0020 mmol of Pd), NMDPP (0.010 mmol), and conc. HCl (0.10 ml).

^b The product was ethylbenzene.

Table 4
Effect of ligand/Pd ratio on the hydroesterification of styrene ^a

Entry	Ligand/Pd	Conv. (%)	Branched/linear	% ee (Config)
1	0	0	–	
2	2	24	100/0	3.0 (S)
3	5	77	100/0	1.8 (S)
4	10	100	100/0	racemic

^a Styrene (0.11 ml, 1.0 mmol) in benzene (10 ml) was treated with methanol (0.24 ml, 6.0 mmol) at 125°C for 24 h under 45 atm of CO in the presence of Pd-clay (20.0 mg, 0.0020 mmol of Pd), ligand (NMDPP), and conc. HCl (0.10 ml).

tion of Pd metal, and styrene was recovered quantitatively (runs 6–8). These results form a striking contrast to those with homogeneous catalyst reported by Cometti and Chiusoli, in which CF₃COOH acted as the only effective promoter and the conversion and asymmetric induction were very low with other acids such as CH₃COOH, HCOOH, HCl and HBr [19]. With HBF₄, no CO insertion has occurred and 1-methoxyethylbenzene was obtained (run 9). Addition of CuCl₂ which is reported to be effective in homogeneous condition [14] resulted in no reaction.

It was reported that the CO pressure has a great influence on the catalytic activity and selectivity. Consiglio and coworkers increased the CO pressure from 50 to 700 atm to obtain better optical purity [17] while Cometto and Chiusoli reported that lower pressure around 1 atm resulted in higher ee [19]. We also examined the pressure effect on the reaction and the results are shown in Table 3. When CO pressure was lowered from 45 to 35 atm, higher conversion has been achieved with slight loss of ee (runs 1 and 2). This is in sharp contrast to the observation reported in homogeneous conditions where higher CO pressure afforded better conversions [[9,14]]. On the other hand, only hydrogenation has proceeded to give ethylbenzene at 5 atm of CO (run 3). Methanol is reported to act as a hydrogen donor in the presence of transition metal catalysts [33].

Table 4 shows the effect of ligand/Pd ratios on the catalytic activities. The catalytic activity

Table 5
Hydroesterification of styrene by homogeneous or heterogeneous catalysts^a

Entry	Catalyst	Press (atm)	Conv. (%) ^b	Branched/linear	% ee (Config)
1 ^c	Pd(dba) ₂ /NMDPP	1	20	94/6	12.0 (S)
2	Pd(dba) ₂ /NMDPP	45	40	100/0	racemic
3	Pd-clay/NMDPP	45	77 (73)	100/0	1.8 (S)
4 ^c	Pd(dba) ₂ /(R,S)-BINAPHOS	1	0	–	–
5	Pd(dba) ₂ /(R,S)-BINAPHOS	45	6	60/40	racemic
6	Pd-clay/(R,S)-BINAPHOS	45	52	86/14	6.0 (R)
7 ^c	Pd(dba) ₂ /New ligand	1	trace	0/100	–
8	Pd-clay,/New ligand	45	23	100/0	12.0 (S)

^a Styrene (0.11 ml, 1.0 mmol) in benzene (10 ml) was treated with methanol (0.24 ml, 6.0 mmol) at 125°C for 24 h under 45 atm of CO in the presence of Pd-clay (20.0 mg, 0.0020 mmol of Pd) or Pd(dba)₂ (0.0020 mmol), ligands (0.010 mmol), and conc. HCl (0.10 ml).

^b Isolated yield is shown in parenthesis.

^c The reactions were carried out under the same condition as reported in Ref. [19]. Styrene (0.15 ml, 1.3 mmol) in methanol (10 ml) at 50°C for 5 h under 1 atm of CO in the presence of Pd(dba)₂ (0.00695 mmol), NMDPP (0.020 mmol), and conc CF₃COOH (0.03 ml).

significantly decreased with decreasing concentration of phosphine, but enantioselectivity was slightly improved. In the absence of phosphine ligand, no reaction has taken place. These results show the importance of the excess ligand for stabilizing the Pd complex.

The comparison between homogeneous and heterogeneous catalysts are displayed in Table 5. The products from heterogeneous reaction conditions are clean and easy to separate. On the other hand, homogeneous catalysts were less active and gave mixtures of esters.

Racemization of the product during the reaction may be a possible explanation for the poor enantioselectivities. However, no racemization has taken place when the optically pure ester was treated under the same reaction conditions. Thus it seems that the enantiofacial selection by the catalyst was not sufficient to afford satisfactory ee. The reaction pathway is considered to be similar to that reported by Lee and Alper [29].

4. Conclusion

The Pd anchored clay catalyzed hydroesterification of styrene in the presence of chiral phosphine ligands afforded the branched acid esters with excellent regioselectivity, but the enantioselectivity was not satisfactory. The new

observation in this catalyst system is that the bulky ligands were also effective because of the higher interlamellar spacings of the catalyst. This will allow us for further ligand design to the goal of enantioselectivity.

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