Hydroxycarbonylation of styrene with palladium catalysts
The influence of the mono- and bidentate phosphorus ligand

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Abstract

A systematic study of the hydroxycarbonylation reaction of styrene is described. The effect of the catalytic precursor and the reaction conditions on the results of the reaction was investigated. Several monophosphines (PPh$_3$, P(p-Tol)$_3$, P(p-C$_6$H$_4$OMe)$_3$, P(p-C$_6$H$_4$F)$_3$, PPh$_2$(o-Tol), PMe$_3$, PCy$_3$) and diphosphines (dppe, dppp, dppb, dppf, HomoXantphos, DPEphos, Xantphos, BDPP, BINAP, BPPFA, DIOP) were applied to control the regioselectivity of the reaction. The effect of the bite angle of the diphosphines has also been studied. Catalysts containing monophosphines as ligands give 2-phenylpropanoic acid as the major product and the 3-phenyl propanoic acid is obtained when diphosphines are used. Two catalytic cycles are proposed to explain the influence of the different palladium precursors with mono- and diphosphines. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The palladium-catalysed hydroxycarbonylation of alkenes has attracted considerable interest in recent years as a procedure for obtaining carboxylic acids. In general, using carbon monoxide and an acidic medium, palladium systems in the presence of mono- or bidentate phosphines afford a mixture of linear and branched acids [1]. The regioselective hydroxycarbonylation of 4-methylstyrene has been studied using a homogeneous catalyst system of PdCl$_2$-CuCl$_2$-PPh$_3$ which provided the branched α-(4-methylstyrene) acid [2]. The need for alternative catalysts in the selective hydroxycarbonylation of alkenes has led to the development of other palladium systems. For instance, palladium (II) acetate/oxalic acid systems have been used in the presence of a chelating phosphorus ligand [3,4]. Highly selective hydroxycarbonylation of styrene has been reported using palladium precursors containing amino thiolates [5], cysteine ethyl ester [6] or S,S-thiolate-thioether ligands [7] in the presence of phosphorus ligands. When triphenylphosphine was used as the ligand the main product was branched 2-phenylpropionic acid. Some reports have shown that this reaction also takes place if water is used instead of acid [5,8].

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In recent years, some studies reported the hydroxycarbonylation of alkenes in a two-phase system using water-soluble palladium catalysts. Recoverable palladium systems have been prepared with sodium trisulphonated triphenylphosphine (TPPTS) in the presence of a Brønsted acid as promoter [9–12], the acid form TPPTSH [13], or cyclodextrin in a two-phase system [14]. Recently, it has also been reported that a water-soluble diphosphine with a xanthene type backbone in the biphasic palladium-catalysed hydroxycarbonylation reaction leads to the selective formation of carboxylic acids [15].

The reaction parameters have not been studied systematically. The stability of the catalytic species during the catalytic reaction is crucial, since formation of metallic palladium is often observed. The dependence of the activity and selectivity of the reaction on the auxiliary ligand is another subject of interest. Although it is well established that catalytic efficiency depends on several factors, it has been found in a number of processes using diphosphines as ligands, that the ligand bite angle influences the catalytic results [16,17]. In recent years, a correlation between ligand bite angles and catalytic selectivity has been observed in rhodium catalysed hydroformylation [18–20], nickel hydrocyanation [21,22], palladium catalysed allylic alkylation [23] and cross coupling reactions of Grignard reagents with organic halides [24,25].

Several parts of the carbonylation mechanism have been discussed [26], but a complete catalytic cycle has not been established. The related alkoxycarbonylation reaction has been studied in much more detail [1,27–31], and two major mechanisms have been proposed [32–40]: the 'hydrido-route', which seems to produce mainly linear esters [41], and the 'carboalkoxy' mechanism, which is often invoked for reactions where the major product is the branched one [8]. Using triphenylphosphine as a ligand, the kinetics of styrene carboxylation to methyl 2-phenylpropionate and methyl-3-phenylpropionate have been reported and the activity and selectivity of the catalyst are sensitive to all reaction parameters studied [42]. The asymmetric alkoxycarbonylation of styrene with chiral phosphines as ligands has also been studied [27–30].

This paper describes a systematic study of the hydroxycarbonylation reaction of styrene using modified palladium catalysts. The effect of the reaction conditions and the precursor on the results of the reaction was investigated. Several monophosphines and diphosphines were applied to control the regioselectivity of the reaction.

2. Experimental

2.1. General methods

All palladium complexes were synthesised using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. The catalytic precursors [PdCl$_2$(PhCN)$_2$], [PdCl$_2$(PPh$_3$)$_2$], [PdCl$_2$(dppb)], [Pd$_2$(dba)$_3$] (dba: dibenzylideneacetone) and [Pd(MeCN)$_2$(PPh$_3$)$_2$](ClO$_4$)$_2$ were prepared as previously described [43–47]. The phosphines HomoXantphos, DPEphos and Xantphos were synthesised via published methods [48]. All other reagents were commercial samples and were used as purchased. Gas chromatography analyses were performed on a Hewlett-Packard 5840A, a gas chromatograph with flame ionisation detector using an Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) (25 m × 0.2 mm Ø) capillary column. Enantiomeric excesses were measured by GC on the same equipment using an FS-cyclodex β-I/P (50 m × 0.25 mm Ø) capillary column.

2.2. Catalysis

High-pressure hydroxycarbonylation experiments were carried out in a Berghof autoclave, and the reaction mixtures were magnetically stirred and electrically heated. Experiments at 30 bar or below were performed at constant pressure and the pressure drop in the ballast was monitored using a pressure transducer connected to an electronic measuring device and printing unit. Experiments above 30 bar were not performed at constant pressure, but the pressure drop was never more than 3 bar (i.e. < 10% of the initial pressure).

2.3. Standard catalysis experiment

A Solution of the substrate (2.5 mmol), the catalyst (0.04 mmol), oxalic acid (2.5 mmol) and the phosphine in 10 ml of dimethoxyethane were intro-

duced into the evacuated autoclave. Carbon monoxide was introduced and the system was heated. When thermal equilibrium was reached, stirring was initiated. After the reaction time, the autoclave was cooled to room temperature and depressurised. Conversion and regioselectivities were determined by GC analysis of the crude samples.

3. Results and discussion

Although many palladium systems were reported (see Section 1), the differences in the Pd precursors, co-catalysts and reaction conditions do not allow a systematic comparison of the results obtained.

The system consisting of oxalic acid in 1,2-dimethoxyethane (DME) as solvent allows relatively mild conditions and high regioselectivity in linear acid when 1,4-bis(diphenylphosphine)butane, dppb, is used [3,4]. We used these conditions to compare the activity of several neutral and cationic palladium complexes modified with mono- or diphosphines in the hydroxycarbonylation of styrene (Eq. (1)). We also attempted to optimise the reaction conditions for several catalytic precursor systems.

$$Ph \diagdown \xrightarrow[\text{CO}]{\text{[Pd], } H_2C_2O_4} Ph - \overset{*}{\diagdown} \text{COOH} + Ph \diagdown \text{COOH}$$

2-PP   **3-PP**

$$(1)$$

3.1. Monophosphine ligands

Table 1 shows the conversion to acids and the regioselectivity obtained. The formation of other

Table 1
Hydroxycarbonylation of styrene using palladium complexes in the presence of PPh$_3^a$

Run	Precursor	% Conversion	2-PP/3-PP
1	$[PdCl_2(PPh_3)_2]$	98	84/16
2	$[PdCl_2(PhCN)_2]$	96	84/16
3	$[Pd_2(dba)_3]$	37	87/13
4	$[Pd(OAc)_2]$	24	63/37
5	$[Pd(MeCN)_2(PPh_3)_2](ClO_4)_2$	53	94/6

[a] Reaction conditions: 10 ml DME (dimethoxyethane), 30 bar CO, 100°C, P/Pd = 4/1, 2.5 mmol styrene, 0.04 mmol precursor, 2.5 mmol $H_2C_2O_4$, 20 h.

Table 2
Hydroxycarbonylation of styrene with $[PdCl_2(PhCN)_2]$ at different conditions in the presence of PPh$_3^a$

Run	P/Pd	Subst/Pd	P (bar)	T (°C)	% Conversion	2-PP/3-PP
6	4	200	30	40	73	95/5
7	4	200	30	60	81	98/2
8	4	200	30	80	89	88/12
9	4	200	30	100	98	95/5
10	4	200	20	100	93	61/39
11	4	200	40	100	75	92/8
12	4	62.5	30	100	99	90/10
13	4	400	30	100	75	85/15
14	2	200	30	100	99	60/40
15	3	200	30	100	100	70/30
16	6	200	30	100	99	74/26

[a] Reaction conditions: 10 ml DME (dimethoxyethane), 0.04 mmol precursor, mmol $H_2C_2O_4$ = mmol styrene, 20 h.

products has not been observed. When PPh$_3$ is used as a monophosphine at 30 bar of CO and 100°C, conversions were highest using divalent palladium precursors such as chlorides, $[PdCl_2(PPh_3)_2]$ and $[PdCl_2(PhCN)_2]$ (entries 1, 2). These catalysts provide total conversions in 20 h and regioselectivities up to 84% for the branched 2-phenylpropionic acid. For non-chloride complexes such as $[Pd_2(dba)_3]$ and $[Pd(OAc)_2]$ conversions were lower at the same conditions (entries 3, 4). The cationic complex $[Pd(MeCN)_2(PPh_3)_2](ClO_4)_2$ provided a regioselectivity of 94% for the branched acid, although the conversion was only 53%.

Addition of PPh$_3$ to a solution of $[PdCl_2(PhCN)_2]$ leads to the formation of $[PdCl_2(PPh_3)_2]$ in solution. Entries 1 and 2 in Table 1 show that the same results were obtained for catalyst precursors that were prepared in situ.

The catalyst precursors containing chloride as the anion show the highest conversion in this reaction. During the catalytic cycle HCl forms, which leads to high activity since chloride functions as a coordinating anion, as has been reported [2,49].

In this study, $[PdCl_2(PhCN)_2]$ was used as the catalyst precursor in the presence of triphenylphosphine. The effect of pressure, temperature, P/Pd and substrate/Pd ratios were studied (Table 2). Temperatures were between 40 and 100°C. At higher temperatures the conversion increased and the re-

gioselectivity was slightly affected (entries 6–9). At temperatures higher than 100°C the precursor decomposes to palladium metal in the Pd/PPh$_3$ systems.

The effect of the CO pressure was also studied and it was found that the regioselectivity for 2-PP was highest at 30 bar (entries 9–11). Changing the substrate/Pd ratio from 62.5 to 400 decreases the conversion (entries 9, 12, 13).

Results were best at a P/Pd ratio of 4; at lower or higher ratios the conversion was retained but the regioselectivity decreased (entries 9, 14–16). The fact that the regioselectivity depends on CO pressure and excess of PPh$_3$ may be due to the presence of intermediates in which carbon monoxide and phosphine compete for coordination positions, according to the mechanistic proposal previously reported in the literature [50–52].

We have checked solvents with different polarities. Results were best for 1,2-dimethoxyethane and tetrahydrofuran. Conversions and regioselectivities were lower when toluene was used whereas in 2-butanone the conversion was retained but the regioselectivity decreased.

Taking into account the results in Table 2, we established the following reaction conditions for comparative studies: 30 bar, 100°C, substrate/Pd ratio = 200, P/Pd ratio = 4, 1,2-dimethoxyethane as the solvent and [Pd] = 4 mM.

The use of several monophosphines in the hydroxycarbonylation reaction of styrene in several Pd systems have been previously reported, to lead to mainly branched acid [8,49,53].

In the present study, phosphines with various electronic and steric properties were used under the

Table 3
Hydroxycarbonylation of styrene with [PdCl$_2$(PhCN)$_2$] using monophosphines[a]

Run	Phosphine	θ	% Conversion	2-PP/3-PP
17	PPh$_3$	145	96	84/16
18	P(p-Tol)$_3$	145	98	69/31
19	P(p-C$_6$H$_4$OMe)$_3$	145	79	98/2
20	P(p-C$_6$H$_4$F)$_3$	145	96	79/21
21	PPh$_2$(o-Tol)	161	76	100/0

[a] Reaction conditions: 10 ml DME (dimethoxyethane), 30 bar CO, 100°C, P/Pd = 4/1, 2.5 mmol styrene, 0.04 mmol precursor, 2.5 mmol H$_2$C$_2$O$_4$, 20 h.

Table 4
Hydroxycarbonylation of styrene with [Pd$_2$(dba)$_3$] using monophosphines[a]

Run	Phosphine	θ	% Conversion	2-PP/3-PP
3	PPh$_3$	145	37	87/13
22	P(p-C$_6$H$_4$OMe)$_3$	145	30	85/15
23	PPh$_2$(o-Tol)	161	8	94/6

[a] Reaction conditions: 10 ml DME (dimethoxyethane), 30 bar CO, 100°C, P/Pd = 4/1, 2.5 mmol styrene, 0.04 mmol precursor, 2.5 mmol H$_2$C$_2$O$_4$, 20 h.

conditions described above (Table 3). Basic phosphines such as PMe$_3$, PCy$_3$ show no activity, phosphines with cone angles > 145°, however, increase the regioselectivity of branched acids albeit at reduced conversions. When PPh$_2$(o-Tol) was used as the ligand the regioselectivity for the branched acid was 100% (entry 21).

To compare how the modification of the ligands affected other systems, we used the most efficient monophosphines with a Pd(0) system (Table 4). In all the experiments performed using [Pd$_2$(dba)$_3$] as the precursor, the conversion and the regioselectivity were lower than in the case of Pd(II)-chloride precursors used under the same conditions (entries 19, 21).

3.2. Diphosphine ligands

It has been reported that when diphosphines are used in the Pd/oxalic acid/DME system in the hydroxycarbonylation of styrene the regioselectivity for the linear acid is high [3,4].

We have investigated the reaction conditions for the [PdCl$_2$(PhCN)$_2$]/oxalic/DME system with the diphosphine dppb. When diphosphines are used as ligands more severe conditions are required as compared to monophosphines to obtain similar levels of activity: 75 bar CO, 150°C and P/Pd ratio of 10. Results were the same for the isolated [PdCl$_2$(dppb)] precursor when the catalytic system [PdCl$_2$(Ph-CN)$_2$]/diphosphine was prepared in situ. The conversions to acid (98%) were higher than previously reported for the [Pd(OAc)$_2$] precursor although the regioselectivity was the same [3,4].

The effect of different diphosphines (Scheme 1) was studied under these conditions (Table 5).
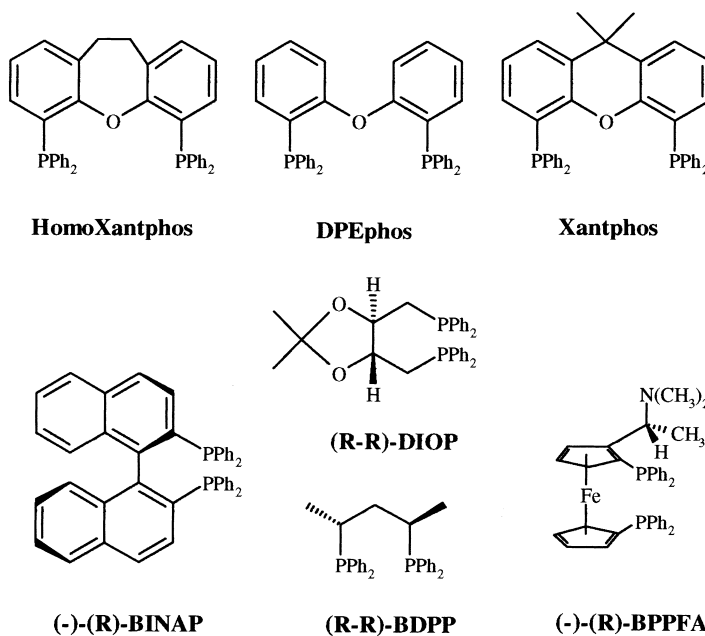
Scheme 1. Diphosphines used in hydroxycarbonylation.

Diphosphines with bite angles smaller than 90° such as dppe and dppp (entries 24, 25), provided only low conversions to acid, and in addition hydrogenation and hydroformylation products were observed. Similar results have been observed when these diphosphines were applied inthe hydroxycarbonylation of styrene using formic acid [3,4]. Taking into account that the catalytic system formed with dppb, which has a wider bite angle than dppe and dppp provides total chemoselectivity in acids

Table 5
Hydroxycarbonylation of styrene with $[PdCl_2(PhCN)_2]$ using diphosphines having different bite angles[a]

Run	Diphosphine	Bite angle (calculated)	% Conversion		2-PP/3-PP
			24 h	2 h	
24	dppe	78	5	–	47/53
25	dppp	86	28	–	23/77
26	dppb	98	95	24	17/83
27	dppf	99	96	39	16/84
28	HomoXantphos	102	98	–	15/85
29	DPEphos	103	99	93	14/86
30	Xantphos	110	99	96	19/81

[a] Reaction conditions: 10 ml DME (dimethoxyethane), 75 bar CO, 150°C, P/Pd = 10/1, 8 mmol styrene, 0.04 mmol precursor, 8 mmol $H_2C_2O_4$.

together with high conversion and regioselectivity in linear acid, we explored other diphosphines with even larger bite angles, such as 1,1′-bis(diphenylphosphino)ferrocene (dppf, 99°), 10,11-dihydro-4,5-bis (diphenylphosphino) dibenzo[b,f]oxepine (Homo Xantphos, 102°), bis(2-(diphenylphosphino)phenyl)ether (DPEphos, 103°) and 9,9-dimethyl-4,6-bis(diphenylphosphine)xanthene (Xantphos, 110°), which were previously shown to give excellent regioselectivities in the rhodium catalysed hydroformylation reaction [48].

Diphosphines with bite angles wider than 98°, all give high conversions to acids increasing with the bite angle and the regioselectivity in linear acid was high, about 85% (entries 26–30). Conversions measured at 2 h lead us to conclude that diphosphines with bite angles > 102° show excellent activities.

The most efficient diphosphines were also explored using a zerovalent Pd precursor (Table 6). The conversions and regioselectivities are similar to those obtained for $[PdCl_2(PhCN)_2]$.

It is important to note that diphosphines behave differently from monophosphines in this respect.

We also tested several diphosphines under the conditions used by Alper [3,4] (20 bar CO, sub-

Table 6
Hydroxycarbonylation of styrene with $[Pd_2(dba)_3]$ using diphosphines[a]

Run	Diphosphine	Bite angle (calculated)	% Conversion	2-PP/3-PP
31	dppb	98	96	17/83
32	dppf	99	96	22/78
33	DPEphos	103	85	19/81
34	Xantphos	110	96	18/82

[a] Reaction conditions: 10 ml DME (dimethoxyethane), 75 bar CO, 150°C, P/Pd = 10/1, 8 mmol styrene, 0.04 mmol precursor, 8 mmol $H_2C_2O_4$, 24 h.

strate/Pd = 62.5, P/Pd = 4), see Table 7. The regioselectivities are similar to those in the systems described above (entries 26–34) although conversions are lower. However, high pressures and high P/Pd ratios provide better conversions as has been shown for dppb.

Asymmetric hydroxycarbonylation has been studied by many groups, but has met with little success and as a result few reports have appeared [54,55]. We initially tested several chiral monophosphines as neomenthyldiphenylphosphine or (−)-(R)-*N*,*N*-dimethyl-1-[(S)-1′,2-bis(diphenylphosphino)-ferrocenyl]ethylamine, which provide branched acid as the major product. However, enantioselectivity was not observed. When chiral diphosphines were used as ligands (Table 8), the experiments were performed at 20 bar of CO because the regioselectivity towards the branched acid can be slightly increased. Only in the case of BINAP 11% ee was obtained together with 30% of regioselectivity in branched acid (entry 41).

Table 7
Hydroxycarbonylation of styrene with $[Pd(OAc)_2]$ using diphosphines[a]

Run	Diphosphine	Bite angle (calculated)	% Conversion	2-PP/3-PP
35	dppb	98	75	17/83
36	dppf	99	96	18/82
37	HomoXantphos	102	96	17/83
38	DPEphos	103	76	12/88
39	Xantphos	110	88	14/86

[a] Reaction conditions: 10 ml DME (dimethoxyethane), 20 bar CO, 150°C, P/Pd = 4/1, 2.5 mmol styrene, 0.04 mmol precursor, 2.5 mmol $H_2C_2O_4$, 24 h.

Table 8
Hydroxycarbonylation of styrene with $[PdCl_2(PhCN)_2]$ using chiral diphosphines[a]

Run	Phosphine	Bite angle[b]	% Conversion	2-PP/3-PP	% ee
40	BDPP	91	35	31/69	3
41	BINAP	93	42	30/70	11
42	BPPFA	99	88	15/85	4
43	DIOP	100	94	14/86	2

[a] Reaction conditions: 10 ml DME (dimethoxyethane), 20 bar CO, 150°C, P/Pd = 10/1, 2.5 mmol styrene, 0.04 mmol precursor, 2.5 mmol $H_2C_2O_4$, 24 h.
[b] Angles taken from crystal structure data [16,17].

Further work using other chiral precursors is in progress.

3.3. Mechanistic considerations

Our results show that the use of either monophosphines or diphosphines as ligands in the palladium-catalysed hydroxycarbonylation of styrene lead to completely different catalysts. This suggests that different intermediates might be involved in the catalytic cycle. Firstly, in the case of monophosphines, only Pd(II) precursors containing chloride give reasonable activity. When diphosphines are used as auxiliary ligands, Pd(O) and Pd(II) precursors afford similar results. Secondly, as far as regioselectivity is concerned, the branched acid is the major product when monophosphines are used as ligands, while linear acid is the major product when diphosphines are the auxiliary ligands. Thirdly, monophosphines give much faster catalysts.

Two mechanisms have been proposed for the alkoxycarbonylation reaction [32–34], the first one involving the formation of a Pd-H intermediate and the second one involving the formation of a Pd-COOH intermediate. Insertion of styrene is likely to be much faster in the hydride species than in the carboxylic acid species. Since insertion of alkenes is usually the slowest step in carbonylation reactions, we would expect the catalytic reaction involving hydrides to be the fastest. On the other hand, it has been reported [56] that insertion of styrene into a metal acyl bond lead to branched products, while insertion into hydrides lead to linear products. In the present examples, the monophosphines give the fastest catalyst and branched product and the diphos-
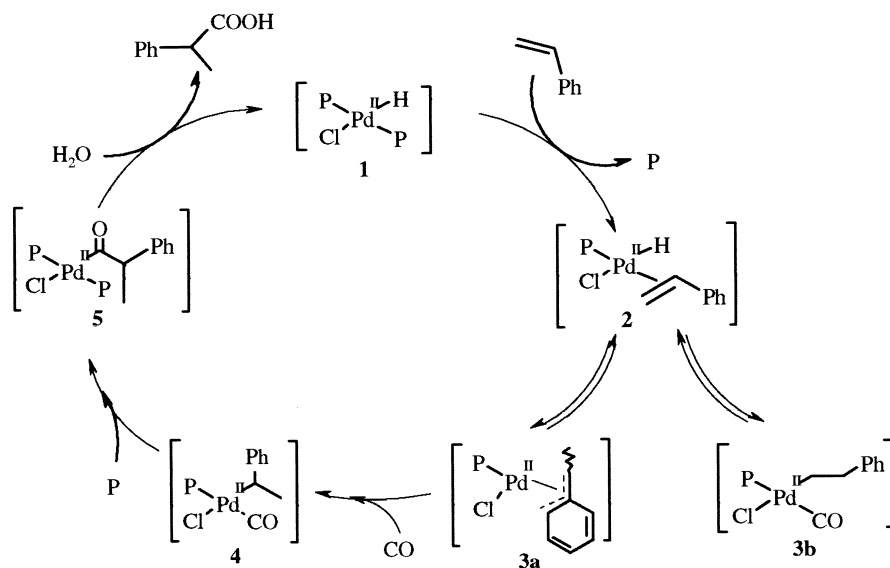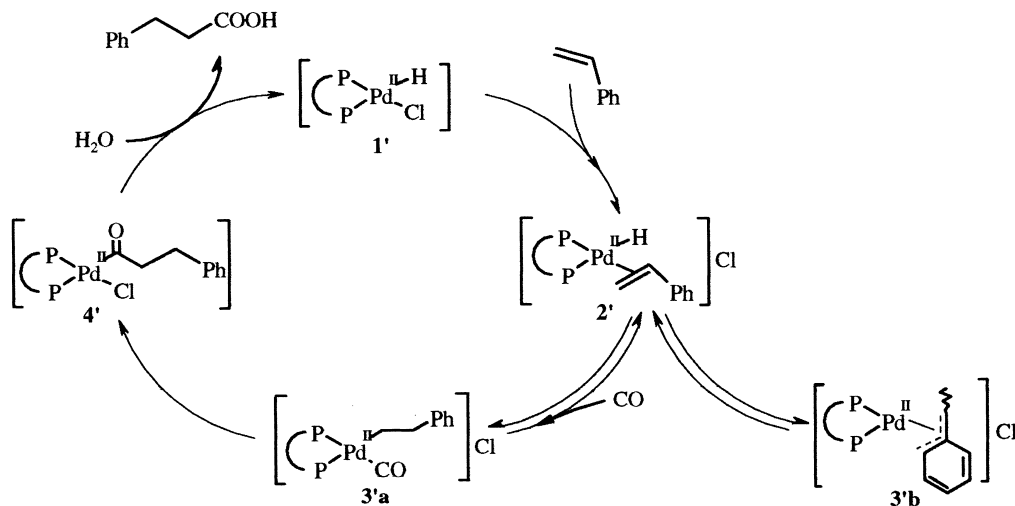
Scheme 2. Proposed catalytic cycle for the hydroxycarbonylation of styrene with monophosphines.

phines give much slower catalysts, and linear product. Thus, the present results contrast the expectations.

We propose, in accord with recent literature [57–60], that palladium hydrides are the key intermediates, both for the monophosphine based systems and for the diphosphine based systems. Moreover, the absence of by-products is in disagreement with the occurrence of metal-carboxylic acid intermediates. The intermediacy of PdCH(Ph)CH$_2$COOH, the putative intermediate formed from styrene insertion in PdCOOH fragments, would lead undoubtedly to unsaturated acids, via beta-hydride elimination, or diacids, via double carbonylation.

To explain our results, two simplified catalytic cycles involving Pd-H intermediates are proposed in

Scheme 3. Proposed catalytic cycle for the hydroxycarbonylation of styrene with diphosphines.

Schemes 2 and 3. The Initial formation of Pd-H intermediates can take place in several ways: (i) via reduction of Pd(II) to Pd(O) with phosphines, followed by oxidative addition of strong acid [61,62]; (ii) via the watergas shift reaction [63]; (iii) through reaction with the oxalic acid as proposed by Alper [3,4].

The insertion of styrene into the palladium hydride bond leads to two alkyl isomers, which can interconvert via β-elimination. Kinetic studies using deuterium in the hydroxycarbonylation of styrene [64,65] have shown that for the branched alkyl intermediate β-elimination is faster than CO insertion, and that for the linear alkyl intermediate, on the other hand, carbonylation is faster than β-elimination. Finally, insertion of carbon monoxide into the Pd-alkyl bond and nucleophilic attack of water leads to the formation of carboxylic acids.

For monodentate phosphines (Scheme 2) a *trans* orientation of the phosphine ligands is preferred for steric and electronic reasons. Displacement of one phosphine ligand will provide a coordination site for the alkene. It is known that *cis–trans* isomerisation is rapid in the presence of excess of ligand [66]. In the alkyl/acyl species, the *trans* orientation also avoids the unfavourable *trans* disposition of phosphine and a hydrocarbyl group. As the key intermediate species **2** containing only one phosphine ligand is proposed, which has little steric hindrance, leading to a stabilised π-benzylic species **3a** and, eventually, the formation of branched acid [67,68] (Scheme 2).

Diphosphine ligands, however, will give stable, *cis*-coordinated complexes. In complex **1′** (Scheme 3), displacement of the chloride ion is required before alkene coordination can take place, giving the cationic species **2′**. This rearrangement may explain the more severe reaction conditions required in comparison with monophosphine ligands.

In addition, the results obtained using diphosphines are the same, irrespective of the palladium precursors used, suggesting that anions are indeed displaced as in **2′** and **3′**. In the case of monophosphines, however, chloride can remain coordinated to the palladium centre, thus bringing about an important difference between the two systems.

It has been argued that the chelate coordination of the diphosphine increases the hydridic character of the Pd-H intermediate promoting the addition of hydrogen to yield linear compounds [69]. The regioselectivity of styrene insertion has also been studied in the palladium catalysed oligomerisation of styrene and carbon monoxide [56]. Using diphosphines the insertion of the first styrene into the palladium hydride complex leads to formation of linear alkyl-palladium species in this reaction. The same happens in the hydroxycarbonylation reported here. The reason for this is in part steric hindrance, since the phenyl group will point away from the bulky diphosphine. Increasing the bite angle will increase the steric hindrance further and indeed a higher linearity is observed.

An alternative explanation for the high linearity for diphosphine catalysts might be found in the higher temperatures used. In rhodium catalysed hydroformylation, the fast β-elimination of branched alkyl intermediates is held responsible for the higher linearities produced at higher temperatures [48,70,71]. However, experiments performed under identical conditions (20 bar CO, 150°C and P/Pd ratio = 4) for PPh_3 as the monophosphine show that the branched/linear ratio is still 73/27, while a ratio of 28/72 was obtained for the diphosphine dppb. Thus, the temperature does not explain the high linearity obtained with diphosphine catalysts.

4. Conclusions

The regioselectivity found in the hydroxycarbonylation of styrene with palladium precursor systems under the appropriate reaction conditions can be high for either the linear or the branched product and can be controlled by modifying the auxiliary phosphorus ligand. When monophosphines are used as ligands the major product is 2-phenylpropanoic acid with practically total regioselectivity. In contrast, the use of diphosphines as auxiliary ligands leads the regioselectivity to the linear product, achieving regioselectivity in the 3-phenylpropanoic acid of 85%.

Diphosphines with bite angles

$\approx 102°$ give the best activities.

Two catalytic cycles have been proposed for the hydroxycarbonylation of styrene in the presence of chlorides with mono- and diphosphines in order to

explain the influence of the different palladium precursors. In both cases, palladium hydrides are the key intermediates and the association/dissociation of chloride ions and phosphines causes the difference between the two systems.

References

[1] A. Höhn, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, VCH, Weinheim, 1996, p. 138.

[2] J.-Y. Yoon, E.J. Jang, K.H. Lee, J.S. Lee, J. Mol. Catal. 118 (1997) 181.

[3] B. El Ali, H. Alper, J. Mol. Catal. 77 (1992) 7.

[4] B. El Ali, H. Alper, J. Mol. Catal. 80 (1993) 377.

[5] D. Kruis, N. Ruiz, M.D. Janssen, J. Boersma, C. Claver, G. van Koten, Inorg. Chem. Commun. 1 (1998) 295.

[6] J. Real, M. Pagès, A. Polo, J.F. Piniella, Á. Álvarez-Larena, Chem. Commun. (1999) 277.

[7] N. Ruiz, I. del Río, J.L. Jiménez, C. Claver, J. Forniés-Cámer, C.C.J. Cardin, S. Gladiali, J. Mol. Catal. 143 (1999) 171.

[8] D.M. Fenton, J. Org. Chem. 38 (1973) 3192.

[9] S. Tilloy, E. Monflier, F. Bertoux, Y. Castanet, A. Mortreux, New J. Chem. 21 (1997) 529.

[10] F. Bertoux, S. Tillol, E. Monflier, Y. Castanet, A. Mortreux, J. Mol. Catal. 138 (1999) 53.

[11] F. Bertoux, E. Monflier, Y. Castanet, A. Mortreux, J. Mol. Catal. 143 (1999) 23.

[12] G. Papadogianakis, G. Verspui, L. Maat, R.A. Sheldon, Catal. Lett. 47 (1997) 43.

[13] B. Xie, Y. Kou, Y. Ying, J. Mol. Catal. (China) 11 (1997) 81.

[14] E. Monflier, S. Tilloy, F. Bertoux, Y. Castanet, A. Mortreux, New J. Chem. 21 (1997) 857.

[15] M. Schroeder Goedheijt, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Commun. (1998) 2431.

[16] P.C.J. Kamer, J.N.H. Reek, P.W.N.M. van Leeuwen, Chemtech 9 (1998) 27.

[17] P. Dierkes, P.W.N.M. van Lecuwen, J. Chem. Soc., Dalton Trans. (1999) 1519.

[18] C.P. Casey, G.T. Whiteker, M.G. Melville, L.M. Petrovich, J.A. Gavney, D.R. Powell, J. Am. Chem. Soc. 114 (1992) 5535, 10680.

[19] M. Kranenburg, Y.E.M. van der Burgt, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje, Organometallics 14 (1995) 3081.

[20] K. Yamamoto, S. Momose, M. Funahashi, S. Ebata, H. Ohmura, H. Komatsu, M. Miyazawa, Chem. Lett. (1994) 189.

[21] W. Goertz, P.C.J. Kamer, P.W.N.M. van Leeuwen, D. Vogt, Chem. Commun. (1997) 1521.

[22] M. Kranenburg, P.C.J. Kamer, P.W.N.M. van Leeuwen, D. Vogt, W. Keim, J. Chem. Soc., Chem. Commun. (1995) 2177.

[23] M. Kranenburg, P.C.J. Kamer, P.W.N.M. van Leeuwen, Eur. J. Inorg. Chem. (1998) 25.

[24] T. Hayashi, M. Konishi, M. Kumada, Tetrahedron Lett. 21 (1979) 1871.

[25] T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, K. Hirotsu, J. Am. Chem. Soc. 106 (1984) 158.

[26] Y.G. Noskov, E.S. Petrov, Kinet. Catal. 38 (1997) 520.

[27] S. Oi, M. Nomura, T. Aiko, Y. Inoue, J. Mol. Catal. 115 (1997) 289.

[28] H. Zhou, J. Hou, J. Cheng, S. Lu, H. Fu, H. Wang, J. Organomet. Chem. 543 (1997) 227.

[29] G. Consiglio, J. Organomet. Chem. 132 (1977) C26.

[30] T. Hayashi, M. Tanaka, I. Ogata, J. Mol. Catal. 26 (1984).

[31] M.C. Bonnet, A.L. Monteiro, I. Tkatchenko, J. Mol. Catal. 143 (1999) 131.

[32] M. Kawana, S. Nakamura, E. Watanabe, H. Urata, J. Organomet. Chem. 542 (1997) 185.

[33] D. Milstein, Acc. Chem. Res. 21 (1988) 428.

[34] T. Fuchikami, K. Ohishi, I. Ojima, J. Org. Chem. 48 (1983) 3803.

[35] P. Pino, F. Piacenti, M. Bianchi, in: I. Wender, P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, Wiley/Interscience, New York, 1977, p. 233.

[36] I. Tkatchenko, in: C. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, UK, 1982, p. 101.

[37] I. Ojima, Chem. Rev. 88 (1988) 1011.

[38] E.S. Petrov, Zh. Fiz. Khim. 62 (1988) 2858.

[39] I. Ojima, M. Eguchi, M. Tzamarioudaki, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Pergamon Press, Oxford, UK, 1995, p. 9.

[40] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, J. Mol. Catal. 104 (1995) 17.

[41] G. Cavinato, L. Toniolo, J. Organomet. Chem. 398 (1990) 187.

[42] A. Seayad, A.A. Kelkar, R. Chaudhari, L. Toniolo, Ind. Eng. Chem. Res. 37 (1998) 2180.

[43] F.R. Hartley, Org. Chem. Rev. A 6 (1970) 119.

[44] R.J. Angelici, Reagents for Transition Metal Complexes and Organometallic Syntheses, Wiley, 1992, p. 61.

[45] W.L. Steffen, G. Palenik, Inorg. Chem. 15 (1976) 2432.
[46] M.F. Rettig, P.M. Maitlis, Inorg. Synth. 28 (1990) 110.
[47] J.A. Davies, F.R. Hartley, S.G. Murray, J. Chem. Soc., Dalton Trans. (1980) 2246.
[48] M. Kranenburg, Y.E.M. van der Burgt, P.C.J. Kamer, P.W.N.M. van Leeuwen, Organometallics 14 (1995) 3081.
[49] E.J. Jang, K.H. Lee, J.S. Lee, Y.G. Kim, J. Mol. Catal. 138 (1999) 25.
[50] Y.G. Noskov, M.I. Terekhova, E.S. Petrov, Kinet. Katal. 34 (1993) 1001.
[51] Y.G. Noskov, E.S. Petrov, Kinet. Katal. 34 (1993) 1005.
[52] E.T. Kron, Y.G. Noskov, M.I. Terekhova, E.S. Petrov, Zh. Fiz. Khim. 70 (1996) 82.
[53] US Patent 5,315,026 (1994).
[54] G.W. Parshall, W.A. Nugent, Chemtech (1988) 184.
[55] H. Alper, N. Hamel, J. Am. Chem. Soc. 112 (1990) 2803.
[56] C. Pisano, A. Mezzetti, G. Consiglio, Organometallics 11 (1992) 20.
[57] R. Naigre, T. Chenal, I. Cipres, P. Kalck, J.-C. Daran, J. Vaissermann, J. Organomet. Chem. 480 (1994) 91.
[58] G. Cavinato, L. Toniolo, J. Mol. Catal. 104 (1996) 221.
[59] M. Kawana, S. Nakamura, F. Watanabe, H. Urata, J. Organomet. Chem. 542 (1997) 185.
[60] S. Oi, M. Nomura, T. Aiko, Y. Inoue, J. Mol. Catal. 115 (1997) 289.
[61] C. Amatore, A. Jutand, M.J. Medeiros, New J. Chem. 20 (1996) 1143.
[62] V.V. Grushin, Chem. Rev. 96 (1996) 2011.
[63] B. Drent, P.H.M. Budzelaar, Chem. Rev. 96 (1996) 663.
[64] Y.G. Noskov, E.S. Petrov, Kinet. Catal. 38 (1997) 520.
[65] C. Benedek, G. Szalontai, A. Gömöry, S. Tõrös, B. Heil, J. Organomet. Chem. 579 (1999) 147.
[66] D.A. Redfield, J.H. Nelson, Inorg. Chem. 12 (1973) 15.
[67] F.C. Rix, M. Brookhart, P.S. White, J. Am. Chem. Soc. 118 (1996) 2436.
[68] G. Gatti, J.A. López, C. Mealli, A. Musco, J. Organomet. Chem. 483 (1994) 77.
[69] Y. Sugi, K. Bando, Chem. Lett. (1976) 727.
[70] R. Lazzaroni, R. Settambolo, A. Raffaelli, S. Pucci, G. Vitulli, J. Organomet. Chem. 339 (1988) 357.
[71] R. Lazzaroni, A. Raffaelli, R. Settambolo, S. Bertozzi, G. Vitulli, J. Mol. Catal. 50 (1989) 1.