



Pergamon

Tetrahedron: Asymmetry 10 (1999) 4463–4467

TETRAHEDRON:  
ASYMMETRY

## Recoverable chiral palladium–sulfonated diphosphine catalysts for the asymmetric hydrocarboxylation of vinyl arenes

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Received 6 October 1999; accepted 18 November 1999

### Abstract

Water-soluble palladium complexes with sulfonated diphosphines dpppts (1,3-bis[di(*m*-sodiumsulfonatophenyl)phosphino]propane), dppbts (1,4-bis[di(*m*-sodiumsulfonatophenyl)phosphino]butane), (*S,S*)-BDPPTS (2,4-bis[di(*m*-sodiumsulfonatophenyl)phosphino]butane) and (*R,R*)-CBDTS (1,2-bis[di(*m*-sodiumsulfonatophenyl)phosphinomethyl]cyclobutane) are active in the hydrocarboxylation of vinyl arenes without addition of acid. The stability of the catalyst systems increases when the reaction is performed in an acidic medium and the catalysts could be recycled twice with no loss in activity or enantioselectivity in the case of the [Pd(OAc)<sub>2</sub>]/BDPPTS system. Enantioselectivities up to 43% are obtained. © 1999 Elsevier Science Ltd. All rights reserved.

Catalytic hydrocarboxylation, providing carboxylic acids from alkenes, is an interesting procedure for transforming organic molecules.<sup>1</sup> Palladium catalysts with phosphorus ligands in the presence of variable amounts of Brønsted acids of different strength, as well as other co-catalysts, are the most used systems for this process.<sup>2</sup> The use of water as a solvent has important environmental and economic effects.<sup>3</sup> Recently, some reports have appeared on hydrocarboxylation reactions which use either recoverable palladium complexes with sodium trisulfonated triphenylphosphine (TPPTS)<sup>4–7</sup> and its acid form TPPTSH<sup>8</sup> or a two phase Pd-modified β-cyclodextrin.<sup>9</sup>

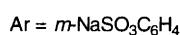
Diphosphine chelate ligands are widely used in homogeneous catalysis and are of particular interest in enantioselective reactions. In our continuing study on the carbonylation of styrene as a model alkene for the preparation of arylpropionic acids, we have recently applied sulfonated diphosphines in the hydroformylation reaction.<sup>10</sup> As far as we know, there are only very few studies on the use of sulfonated diphosphines in the hydrocarboxylation of alkenes. A palladium system with the sulfonated derivative of the xantphos diphosphine (xantphos-s) in addition to TsOH was shown to be very effective in the

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hydrocarboxylation of ethylene, propene and styrene.<sup>11</sup> There are no examples in the literature on the asymmetric hydrocarboxylation of alkenes using chiral sulfonated diphosphines.

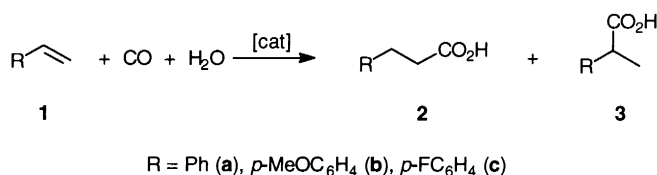
Under the carbonylation conditions, oligomerization and copolymerization of CO/alkenes are competitive reactions with the hydrocarboxylation. Pd/dpppts systems with a ratio of 1:1 have been reported to be active for the alternating copolymerization of ethene and CO, however, at a molar ratio of 1:2 copolymerization has been reported to be inhibited.<sup>12</sup>

Here we describe the use of the sodium salt of the tetrasulfonated alkyl diphenylphosphines 1,3-bis(diphenylphosphino)propane (dpppts), 1,4-bis(diphenylphosphino)butane (dppbts), as a model for the chiral diphosphines (*S,S*)-2,4-bis(diphenylphosphino)pentane ((*S,S*)-BDPPTS) and (*R,R*)-1,2-bis(diphenylphosphinomethyl)cyclobutane ((*R,R*)-CBDTS) (Scheme 1) in the palladium hydrocarboxylation of vinyl arenes at different pH conditions. These phosphines were prepared according to published procedures.<sup>13</sup>



Scheme 1.

The hydrocarboxylation of vinyl arenes **1a–c** yields the corresponding linear **2a–c** and branched (**3a–c**) carboxylic acids (Scheme 2). Catalyst precursors were prepared by adding the corresponding sulfonated diphosphine to a suspension of the compound and Pd(OAc)<sub>2</sub> (ligand/Pd molar ratio of 2) in water.<sup>†</sup>



Scheme 2.

The results of the hydrocarboxylation of vinyl arenes **1a–c** are shown in Table 1. No polymers were detected except in the case of entries 4 and 6 (Table 1).

In general, the hydrocarboxylation reactions reported in the literature are performed in the presence of acid. Nevertheless, when PdCl<sub>2</sub>/TPPTS was used as catalyst precursor, 2 equivalents of HCl per mol of Pd were formed and, in this case, at a styrene/Pd molar ratio of 50, quantitative conversion of styrene to the corresponding carboxylic acids was observed in the absence of any added Brønsted acid.<sup>5</sup> Therefore, using Pd(OAc)<sub>2</sub>, since AcOH is presumably formed, as well as carboxylic acids during the reaction,<sup>14</sup> we studied the activity of palladium diphosphine systems without addition of acid. Using this procedure, the solutions of Pd(OAc)<sub>2</sub>/diphosphines in water have initial pH in the range 10–12 because traces of sodium hydroxide remain from the synthesis of the ligand. The palladium precursor with the

<sup>†</sup> *Experimental procedure:* A mixture of 0.04 mmol of Pd(OAc)<sub>2</sub> with the corresponding amount of sulfonated phosphine in 10 ml of water was stirred for 1 h until total dissolution. The substrate was added and the mixture was placed in an evacuated autoclave and was pressurized with CO at the desired pressure. Final solutions were extracted with 3×5 ml of diethyl ether and analyzed by GC. *Recycling experiments:* After the first run, the aqueous phase was extracted with diethyl ether (3×5 ml) under nitrogen and the corresponding amount of substrate was added. The mixture was placed in the autoclave as described above and the overall recycling procedure was then repeated.

Table 1  
Hydrocarboxylation of styrene derivatives (**1a–c**) using [Pd(OAc)<sub>2</sub>]/L as catalyst precursors<sup>a</sup>

Entry	L	substrate	pH <sup>b</sup>	Conversion (%)	Selectivity (%)	2/3 (%)	%ee <sup>c</sup>
1 <sup>d</sup>	dpppts	<b>1a</b>	11.8	99	99	76/24	-
2	dppbts	<b>1a</b>	13.6	100	100	67/33	-
3	BDPPTS	<b>1a</b>	12.7	57	91	81/19	<1(S)
4 <sup>d,e</sup>	BDPPTS	<b>1b</b>	12.7	81	38	70/30	22(+)
5	BDPPTS	<b>1c</b>	12.7	74	100	71/29	14(-)
6 <sup>e</sup>	CBDBTS	<b>1a</b>	12.1	100	100	71/29	10(S)
7	CBDBTS	<b>1b</b>	12.1	95	100	51/49	14(+)
8	CBDBTS	<b>1c</b>	12.1	97	100	76/24	13(-)
9	dpppts	<b>1a</b>	3.5	98	100	78/22	-
10	dppbts	<b>1a</b>	2.9	100	100	69/31	-
11	BDPPTS	<b>1a</b>	3.4	99	94	66/34	32 (S)
12 <sup>f</sup>	BDPPTS	<b>1b</b>	3.5	98	96	55/45	43 (+)
13 <sup>f</sup>	BDPPTS	<b>1c</b>	3.5	99	92	65/35	36 (+)
14 <sup>f</sup>	CBDBTS	<b>1a</b>	3.2	100	87	71/29	14 (R)
15 <sup>f</sup>	CBDBTS	<b>1b</b>	3.7	98	95	67/33	20 (-)
16 <sup>f</sup>	CBDBTS	<b>1c</b>	3.6	100	99	74/26	17 (-)

<sup>a</sup>Reaction conditions: Pd(OAc)<sub>2</sub> : 0.04 mmol; [substrate]/Pd(OAc)<sub>2</sub>: 62.5; 10 ml H<sub>2</sub>O; pressure 20 bars; temperature 120°C unless otherwise stated; ligand to palladium molar ratio = 2; time = 16 h; <sup>b</sup>initial pH values; <sup>c</sup>enantiomeric excess was determined by published procedures.<sup>15</sup> <sup>d</sup>formation of palladium black. <sup>e</sup> polymers were also found <sup>f</sup> 100° C

sulfonated diphosphines dpppts and dppbts at these conditions (Table 1, entries 1 and 2) give practically total conversion in acids and the percentages of the branched product **3a** are 24% and 33%, respectively. This regioselectivity in **3a** is consistent with non aqueous palladium–diphosphine systems.<sup>2a</sup> The average TOF at 4 h reaction time for this system was low (14 h<sup>-1</sup>) for the Pd–dpppts system. Pd/TPPTS at basic pH in a water/toluene biphasic system has been reported to promote very slow hydrocarboxylation of alkenes.<sup>4</sup>

When the Pd–dpppts catalyst precursor was used in a toluene/water biphasic system, we observed a decrease in chemoselectivity and dimerization of styrene (not reported in Table 1). Unfortunately, in the case of Pd(OAc)<sub>2</sub>–dpppts in water, increasing the [substrate]/Pd(OAc)<sub>2</sub> molar ratio the chemoselectivity decreases substantially and oligomeric materials were detected (not reported in Table 1).

The diphosphines CBDBTS and BDPPTS were used as chiral ligands in the hydrocarboxylation of **1a–c** without addition of acid (Table 1, entries 3–8). In these conditions, the palladium/CBDBTS system is, in general, more active and provides higher percentages of the branched products for the substrates **1a** and **1b** than the palladium/BDPPTS system. The highest value of the branched product is 49% in **3b** for the Pd/CBDBTS system (Table 1, entry 7). The highest enantioselectivity (ee 22%) is obtained in the hydrocarboxylation of **1b** using the palladium/BDPPTS system but in this case the selectivity in the formation of the acids was low and polymers were also found (Table 1, entry 4). The enantioselectivities obtained for the substrates **1a–c** ranged from 10 to 14% when the system Pd/CBDBTS was used (Table 1, entries 6–8).

These results show that palladium–diphosphine systems are active in the hydrocarboxylation of styrene

in water without addition of acid. Nevertheless, the catalytic systems are not stable since a black precipitate, presumably metallic palladium, was observed at the end of the reaction (Table 1, entries 1 and 4). To confirm this, the aqueous phase in the case of entry 1 was recycled after the products had been extracted and a decrease in the catalytic activity was observed (60% conversion in the second run after 16 h).

It has been reported that addition of a Brønsted acid increases the activity of the catalytic systems.<sup>4</sup> The results of the hydrocarboxylation of substrates **1a–c** in acidic media are reported in Table 1 (entries 9–16). The pH of the solution was adjusted to 3.5 by adding dilute sulfuric acid (0.25 M). Sulfuric acid was selected because, for the Pd/TPPTS system, the nature of the anion of the acid has been reported to affect the reaction rate only slightly.<sup>4</sup> In acidic media, practically total conversions and high selectivities in the carboxylic acids were always obtained and no precipitation of black palladium was detected in any case.

The catalyst precursors with the diphosphines dppts and dpbts in acidic media provide similar results as observed without addition of acid (Table 1, entries 9 and 10). The activity of the Pd/dppts in an acidic medium (TOF at 4 h was 14 h<sup>-1</sup>) was similar to that in a basic medium. Although polymerization was observed in the case of substrate **1b** when the reaction was run at 120°C, it was not detected at a temperature of 100°C (Table 1, entry 12).

These diphosphine systems in acidic media proved to be recoverable. In the case of the system Pd–dppts, at the end of the reaction (Table 1, entry 9), after the products had been extracted with ether, the aqueous phase was recycled three times with no loss of activity or selectivity (Fig. 1a). Only after the third run was some precipitation of black palladium observed.

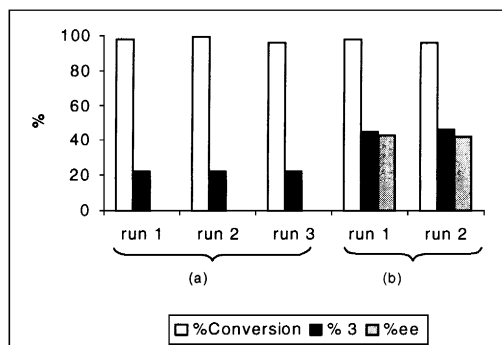


Fig. 1. Results of recycling the aqueous phase of (a) entry 9, (b) entry 12 in Table 1

An increase in the amount of the branched products, **3**, in respect to the basic medium was observed in the case of the Pd/BDPPTS systems in an acidic medium, giving 45% in **3b** (Table 1, entry 12). The percentages of the branched product **3a** obtained are in the same range as for the Pd/xantphos-s/TsOH system for which a maximum of 35% in 2-phenylpropanoic acid was reported.<sup>11</sup>

The enantioselectivity was also higher in acidic media. The best enantioselectivity was obtained with the Pd/BDPPTS system in the case of **3b** with 43% ee (Table 1, entry 12). Furthermore, this system was recycled twice with no loss of activity, regioselectivity or enantioselectivity (Fig. 1b). No palladium black was observed after the second run.

Interestingly, while in basic media BDPPTS and CBDTS systems provided the same enantiomer from the same substrate, in acidic media the absolute configurations of the branched products **3** are (*S*) or (+) for the Pd/BDPPTS system and (*R*) or (–) for the Pd/CBDTS system. This may be due to the formation of different catalytic species depending upon the pH of the medium.

In conclusion, the catalyst precursors obtained from Pd(OAc)<sub>2</sub> associated with sulfonated diphosphines are active in the hydrocarboxylation of styrene in water without addition of acid although the formation of black palladium at the end of the reaction shows that the species involved are not stable. Acidic solutions of the palladium–diphosphines are more stable and can be recycled up to three times in the case of the dpppts system with no loss of activity or regioselectivity. The highest enantioselectivity (43% in **3b**) was obtained with the Pd/BDPPTS catalyst precursor and the aqueous solution was recycled maintaining the activity and enantioselectivity in the second run.

Work is in progress to optimize the enantioselectivity of the reaction and determine the catalytically active species.

## Acknowledgements

We thank the Ministerio de Educación y Ciencia and Generalitat de Catalunya for financial support (PB97-04070C05-01 and ‘Acció integrada’ ACI-96) and Professor P. W. N. M van Leeuwen for interesting discussions.

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