

Highly selective hydrocarboxylation of styrene with oxalic acid or water using palladium *ortho*-amino arenethiolates with intramolecular coordinating nitrogen Lewis bases

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Abstract

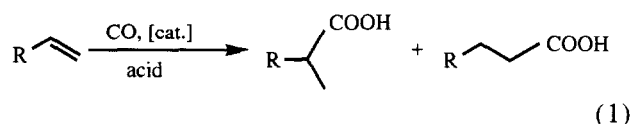
Under mild conditions and in the presence of a catalytic amount of an S,N-chelated palladium *ortho*-amino arenethiolate complex, styrene reacts with carbon monoxide and oxalic acid or water to selectively give 2-phenylpropanoic acid in high yield. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The hydrocarboxylation and alkoxycarbonylation of olefins have been extensively studied using different palladium precursors in combination with acids and alcohols respectively [1,2]. In hydrocarboxylation, the selectivity of linear versus branched products is an important issue because, in general, mixtures of isomeric carboxylic acids are obtained. The reaction with palladium complexes usually requires various promoters to achieve the desired activity, selectivity and stability of the catalyst [3–5]. Palladium systems using copper chloride in acidic media have also been reported and the effects of additives and reaction conditions have been studied [6–8].

Styrene is one of the most studied substrates, since the commercially important 2-arylpropionic acids are representative of higher-value acids. Although research efforts have led to progress in this area [9–12], new methodologies for the catalytic hydrocarboxylation of alkenes (Eq. (1)) are of considerable interest since total control of the regioselectivity and stereoselectivity in carboxylations are still underdeveloped [1,2]. In the case of hydrocarboxylation of 4-methylstyrene, the regioselectivities are high when the PdCl₂–CuCl₂–PPh₃ catalyst system is used [8].

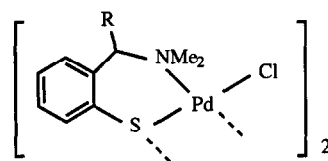


The need for milder reaction conditions in the selective hydrocarboxylation of olefins has led to palladium(II) acetate and oxalic or formic acid being used in the presence of chelating phosphorus ligands as catalysts [3–17]. The hydrocarboxylation of alkenes and alkynes reported by Alper and co-workers using these systems is a methodology of considerable interest [15,16]. Homogeneous catalyst precursors have been prepared using Pd(OAc)₂ in the presence of 1,4-bis(diphenylphosphino)butane (dppb) and used as effective catalysts for hydrocarboxylation of simple and functionalised olefins [17]. These systems are particularly regioselective and, in the case of styrene, the straight chain acid is obtained achieving 86% when the ligand is dppb. The use of dppb + PPh₃ gives the best results, although the presence of PPh₃ increases the yield but does not change the product distribution. The linear isomer is usually the dominant product.

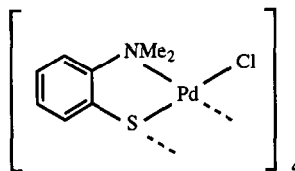
In the last year a water-soluble catalyst system has been reported [18,19]. The Pd(OAc)₂–TPPTSH–HOAc–H₂O system has been used in the hydrocarboxylation of styrene in a weak acidic medium giving a branched product regioselectivity of about 90% [18]. The hydrocarboxylation of alkenes

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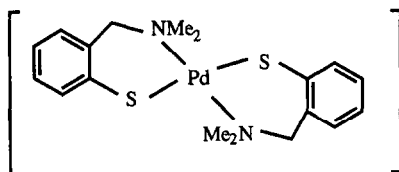
type "RSPdCl"



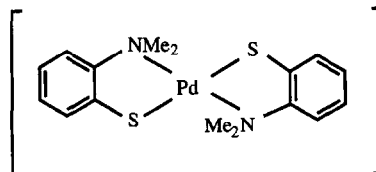
1 (R = H)
1b (R = (R)-Me)



2

type "(RS)₂Pd"

3



4

- 1 [PdCl(SC₆H₄(CH₂NMe₂)-2)]₂
1b (R)-[PdCl(SC₆H₄(C(Me)HNMe₂)-2)]₂
2 [PdCl(SC₆H₄NMe₂-2)]₄
3 [Pd(SC₆H₄(CH₂NMe₂)-2)₂]
4 [Pd(SC₆H₄NMe₂-2)₂]

Fig. 1. Catalyst precursors.

in a two-phase system using a water soluble palladium complex of trisulfonated triphenylphosphine TPPTS as catalyst and a Brönsted acid as promoter has also been reported. In that work, low pH values (1.8–3.0) are required to obtain high activities. The regioselectivity is 65% in linear acid [19].

The regioselectivity has been said to depend on the ligands, if esters are formed, using different phosphorus ligands [1,2,20,21]. The use of different mono- or diphosphine ligands has been reported for both reactions, hydrocarboxylation and alkoxycarbonylation [22]. However, the role of other ligands containing N or S donor atoms in the hydrocarboxylation reaction has been much less studied [23].

In this work we present the use of palladium aminoarene-thiolates with intramolecular coordinating nitrogen Lewis bases as the catalyst precursor in the hydrocarboxylation of styrene with oxalic acid or water. The effect of varying the P and T on the results of the catalytic reaction is also studied.

2. Experimental

The palladium complexes [PdCl(SC₆H₄(C(R)HNMe₂)-2)]₂ (1: R = H; 1b: enantiopure, R = (R)-Me), [PdCl(SC₆H₄NMe₂-2)]₄ (2), [Pd(SC₆H₄(CH₂NMe₂)-2)₂] (3) and [Pd(SC₆H₄NMe₂-2)₂] (4) were synthesised according to the literature [24,25].

2.1. Catalytic experiments

A solution of styrene (2.0 mmol), catalyst (0.04 mmol in palladium), PPh₃ (0.16 or 0.04 mmol) and oxalic or formic acid (2.5 mmol) in 10 ml of dimethoxyethane was introduced into an evacuated autoclave equipped with a magnetic stirrer. Carbon monoxide was also introduced and the system was heated. When thermal equilibrium was reached, stirring was initiated. After 20 h, the autoclave was cooled to room temperature and depressurised. Conversions and regioselectivities were determined by GC analysis of crude samples on a Hewlett-Packard model 5890 chromatograph with flame ionisation detection using a 25 m capillary column (Ultra 2).

3. Results and discussion

We recently reported a new class of Pd(II) complexes containing monoanionic amino arenethiolate ligands that adopt S,N-bidentate coordination at palladium [24,25] (see Fig. 1). We now report the use of palladium arenethiolate complexes of the type 'RSPdCl' ([PdCl(SC₆H₄(C(R)HNMe₂)-2)]₂ (1: R = H; 1b: enantiopure, R = (R)-Me and [PdCl(SC₆H₄NMe₂-2)]₄ (2)) and '(RS)₂Pd' ([Pd(SC₆H₄(CH₂NMe₂)-2)₂] (3) and [Pd(SC₆H₄NMe₂-2)₂] (4)) as catalyst precursors for the highly selective conversion of styrene to branched carboxylic acids. All hydrocarboxylation reactions were performed in 1,2-dimethoxyethane in the presence of oxalic acid with 1.6 mol% of the palladium complex

Table 1
Results of Pd arenethiolate catalysed hydrocarboxylation of styrene using oxalic acid ^a

Entry	Precursor	<i>p</i> (atm)	<i>T</i> (°C)	Conversion (%)	Selectivity 2-PP (%)
Type 'RSPdCl'					
1	1	30	100	98	83
2	1b	30	100	86	91 (4% e.e.)
3	2	30	100	97	94
4 ^b	2	30	100	60	100
5	2	80	100	98	97
6	2	30	150	15	100
7	2	80	150	55	97
Type '(RS) ₂ Pd'					
8	3	30	100	35	100
9	3	80	100	45	100
10	4	30	100	87	100
11	4	80	100	97	98
12	PdCl ₂ (PhCN) ₂	30	100	100	89

^a Reaction conditions: 2.5 mmol styrene, 10 ml DME (1,2-dimethoxyethane), 0.04 mmol precursor, 2.5 mmol H₂C₂O₄ · 2H₂O, P:Pd = 4:1, reaction time: 20 h.

^b P:Pd = 1:1.

and PPh₃ as the additive. The presence of PPh₃ was found to be essential for catalysis. In the absence of this additive, no conversion was detectable when oxalic acid was used and less than 5% was noted in runs with formic acid.

At a temperature of 100°C and a CO pressure of 30 atm (non-S.I. unit: 1 atm = 101325 Nm⁻²) these catalysts provide conversions of 34–98% and regioselectivities of 83–100% for 2-phenylpropanoic acid (2-PP) (Table 1). Under these conditions complexes **1** and **2** give over 97% conversion (entries 1 and 3) with complex **2** providing the best regioselectivity for 2-PP (94%, entry 3). Lowering the P:Pd ratio from 4:1 to 1:1 causes a drop in conversion, although regioselectivity increases (entry 4). When the CO pressure is increased to 80 atm, the conversion is maintained but the regioselectivity is slightly increased (entry 5). With a reaction temperature of 150°C for precursor **2** (entries 6 and 7), conversions are lower but regioselectivities are higher with the concomitant formation of palladium black at the end of the reaction.

In general, higher temperatures lead to decomposition of the palladium arenethiolate catalyst and lower the conversion dramatically, although the regioselectivity improves. Higher pressures, however, increase conversion and have little overall effect on the selectivity.

Conversions using mononuclear complexes **3** and **4** were lower than conversions using complexes **1** and **2**, but the regioselectivity increased to 100% (entries 8 and 10). Increasing the CO pressure to 80 atm also led to an increase in conversion (entries 9 and 11).

In an attempt to obtain chiral induction in the branched isomers, the chiral catalyst precursor **1b** was also tested. Conversion and selectivity were as expected, but enantiomeric excesses did not exceed 4% (entry 2). This may mean that the chiral information is not present in the actual catalytically active species, i.e., the thiolate ligand is cleaved from the

palladium centre. If this is so, then it should be possible to use catalyst precursors that do not have a thiolate moiety. Indeed, when we tested PdCl₂(PhCN)₂ as a catalyst precursor, conversion into acids was complete, although the regioselectivity towards the branched acid was lower (89%, entry 12).

The different regioselectivities of the two systems should be noted because it shows that the amino arenethiolate ligand has a considerable effect on the catalytic cycle.

As has been mentioned in Section 1, most of the studies on the hydrocarboxylation reaction are made in the presence of acidic media. To further our knowledge of these precursors, we carried out the reaction using water in place of acidic media as previously studied for other palladium systems [3]. When catalytic precursors **2** and **4**, as well as PdCl₂(PhCN)₂, were tested in the hydrocarboxylation of styrene using water instead of oxalic acid, we did observe conversion into acids (Table 2). Using **2**, conversion was low when 2 equiv. of water (with respect to styrene) were used, but when the excess of water was increased (20 equiv.) conversion was almost complete and selectivity to 2-PP was high. At low water concentrations, **4** also gave low conversions (entry 3).

Table 2
Results of Pd arenethiolate catalysed hydrocarboxylation of styrene using water ^a

Entry	Precursor	Water (mmol)	Conversion (%)	Selectivity 2-PP (%)
1	2	5	22	100
2	2	50	97	90
3	4	5	13	100
4	PdCl ₂ (PhCN) ₂	50	99	87

^a Reaction conditions: 2.5 mmol styrene, 10 ml DME, 0.04 mmol precursor, 30 atm CO, 100°C, P:Pd = 4:1, reaction time: 20 h.

Like the experiments using oxalic acid shown in Table 1, the regioselectivity obtained with aminothioliolate systems is higher than in the case of the $\text{PdCl}_2(\text{PhCN})_2$ precursor.

The regioselectivity observed in these systems is quite unlike the regioselectivities previously reported for Pd/dppb/formic or oxalic acid (dppb = 1,4-bis(diphenylphosphino)butane) catalytic systems [13,14,17] in which a cationic Pd(II) complex $[\text{PdH}(\text{CO})(\text{dppb})]^+ [\text{HOC}(\text{O})\text{CO}_2]^-$ is proposed as an important intermediate [17].

We are at present carrying out further studies on the intermediate compounds in our system to shed some light on the nature of this unusual selectivity. We are also studying the role of the ancillary ligands NS^- in **1–4** and PhCN in $\text{PdCl}_2(\text{PhCN})_2$.

4. Conclusions

In conclusion, although triphenylphosphine is required as auxiliary ligand, these catalyst precursors lead to the total regioselective formation of branched carboxylic acids, which is not frequently observed in the hydrocarboxylation reaction. Furthermore, neither co-catalysts nor acidic media are required.

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