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Journal of Molecular Catalysis A: Chemical 143 (1999) 171–180

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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High-branched selectivity in the palladium-catalysed alkoxycarbonylation of styrene in the presence of thiol–thioether atropisomeric ligands

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Received 26 May 1998; accepted 28 August 1998

Abstract

New mononuclear and dinuclear palladium complexes containing one neutral and one anionic sulfur donor centre derived from the atropisomeric thiol–thioether derivative **3** (RHbinas) were prepared and characterized both in solution and in the solid state. Crystal structures of $[PdCl(Mebinas)]_2$ (**4**) and $[PdCl(Mebinas)(PPh_3)]$ (**6**) were determined by X-ray diffraction. In the presence of triphenylphosphine and oxalic acid, the new complexes are active catalysts for the hydrocarboxylation of styrene, showing a high regioselectivity towards the branched product under mild conditions (up to 97% of 2-phenylpropanoic acid).

Keywords: Alkoxycarbonylation; Hydrocarboxylation; Thiol–thioether ligands; Palladium complexes; Catalysis

1. Introduction

Palladium(II) complexes are of interest as catalyst precursors for a wide variety of homogeneous processes. Most frequently, these catalysts make use of triarylphosphines or chelating diphosphines as supporting ligands [1,2]. Chiral chelating diphosphines are extensively used in enantioselective catalysis as chiral inducers. Among them, bidentate atropisomeric derivatives such as BINAP [3] or BINAPHOS [4] have shown a remarkable efficiency and provide the best e.e.s in the hydrogenation and hydroformylation of olefins, respectively.

Chiral ligands containing sulfur donor centres are attracting interest as chiral inducers in transition metal catalysed reactions. We have recently shown that rhodium complexes with the atropisomeric dithioethers R_2binas (**1**) [5] and R_2biphes (**2**) [6] (Scheme 1) display a high catalytic activity in the

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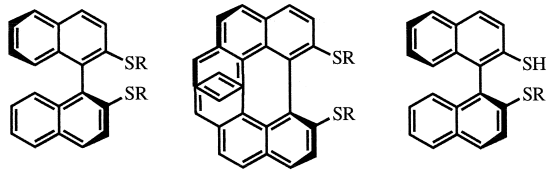
1381-1169/99/$ - see front matter
PII: S1381-1169(98)00383-5



1 R_2**binas** **2** R_2**biphes** **3 RHbinas**

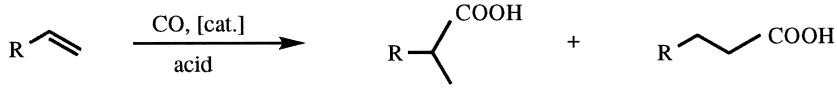
1a R= Me **2a** R= Me **3a** R= Me
1b R= ^{i}Pr **2b** R= ^{i}Pr **3b** R= ^{i}Pr

Scheme 1. R_2binas (**1**) and R_2biphes (**2**), RHbinas (**3**).

hydroformylation of styrene. Quantitative conversion of the substrate with complete chemoselectivity in the formation of the aldehydes are easily obtained under mild conditions together with a high regioselectivity in the branched aldehyde. Recently, we have reported the preparation of Rh(I), Pd(II) and Pt(II) complexes with the chiral C_2-symmetrical dithioether ligands Me_2binas derived from 1,1′-binaphthalene-2,2′-dithiol (H_2binas) [7].

By a suitable modification of the parent substrate, the C_2-symmetry inherent with the structure of 2,2′-disubstituted binaphthyl derivatives can be broken down. According to this strategy, the *S,S*′-heterotopic atropisomeric ligands **3** (RHbinas) which have a thioether and a thiol group as sulfur containing arms, have been prepared [8]. These derivatives are a new type of bidentate ligand where the chelate coordination of the thiolate group to the metal is supported by the proximate sulfide group. They offer a valid alternative to aminothiols, which have been previously reported and used in catalytic reactions [9–11].

The Pd-catalysed hydrocarboxylation of olefins provide a powerful synthetic tool for the preparation of chiral carboxylic acids. Styrene is one of the most studied substrates, since it is converted into 2-arylpropionic acid which is the simplest representative of an important class of non steroidal anti-inflammatory agents. Although research efforts have lead to some progress in this area, [12–16] new methodologies for the catalytic hydrocarboxylation of alkenes (Eq. (1)) which allow a better control of regioselectivity and of the stereoselectivity are of considerable interest.



(1)

In this paper, we report on the preparation and structural characterization of mono- and dinuclear Pd(II)-complexes containing the thiol–thioether ligand **3** and on their use as catalyst precursors in the hydrocarboxylation of styrene.

2. Experimental section

2.1. General methods

All syntheses of palladium complexes were performed using standard Schlenk techniques under a nitrogen atmosphere. The ligands **3** RHbinas (R = Me, **3a**, ^{i}Pr, **3b**) were prepared using a previously

described method [8]. $[PdCl_2(PhCN)_2]$ [17] was prepared according to the literature. Solvents were distilled and deoxygenated before use. Triphenylphosphine was of commercial origin and used without further purification. All other reagents were commercial samples and were used as purchased. Gas chromatography was performed on a Hewlett-Packard 5840A chromatograph with flame ionization detector using an Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) (25 m × 0.2 mm Ø) capillary column (Ultra 2). Elemental analyses were performed on a Carbo Erba microanalyser. Infrared spectra (KBr pellets) were obtained using a Midac Prospect spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 MHz spectrophotometer and chemical shifts are quoted in ppm downfield from internal TMS. ^{31}P NMR spectra were obtained on the same equipment, using external H_3PO_4 as reference. Mass spectra were measured on a VG Autospec spectrometer.

2.2. Preparation of the precursors

*2.2.1. [PdCl(Mebinas)]$_2$ (**4**)*

A solution of $[PdCl_2(PhCN)_2]$ in toluene was prepared (0.28 mmol palladium complex to 10 ml toluene) and (±) MeHbinas, **3a** was added (0.30 mmol). The mixture reaction was vigorously stirred for 40 h and finally heated at 50°C for 4 h. The solution became orange. At room temperature, hexane was added (30 ml) and an orange solid appeared which was filtered off, washed with hexane and vacuum dried. Quantitative yields of the di-[chloro(2-thiol-2′-(methylthioether)-1,1′-binaphthyl)palladium(II)] (**4**) were obtained.

Anal. Calcd. for $C_{42}H_3OS_4Cl_2Pd_2$ (945.8): C, 53.3; H, 3.2; S, 13.5. Found: C, 53.7; H, 3.5; S, 13.0. ^1H NMR ($CDCl_3$), δ (ppm): 2.67 (s, 6H, CH_3), 6.93–9.21 (m, 24H, arom). ^{13}C NMR ($CDCl_3$), δ (ppm): 19.4 (s, CH_3), 122.2–135.8 (arom). IR (KBr): ν_{arom}: 400–1600 (w) and 2950–3100 (vw) cm^{-1}. Mass spectra (m/e): 911 (M^+–Cl), 876 (M^+–2Cl), 544 (M^+–2Cl–Mebinas).

*2.2.2. [PdCl(^{i}Prbinas)]$_2$ (**5**)*

A solution of $[PdCl_2(PhCN)_2]$ in toluene was prepared (0.28 mmol palladium complex to 10 ml toluene) and (±) ^{i}PrHbinas, **3b**, was added (0.30 mmol). The mixture reaction was vigorously stirred for 40 h and finally heated at 50°C for 4 h. The solution became orange. At room temperature, hexane was added (30 ml) and an orange solid appeared which was filtered off, washed with hexane and vacuum dried. Quantitative yields of the di-[chloro(2-thiol-2′-(isopropylthioether)-1,1′-binaphthyl)palladium(II)] (**5**) were obtained.

Anal. Calcd. for $C_{46}H_{38}S_4Cl_2Pd_2$ (1001.8): C, 55.1; H, 3.8; S, 12.7. Found: C, 55.6; H, 3.9; S, 12.1. ^1H NMR ($CDCl_3$), δ (ppm): 1.29 (m, 6H, CH_3), 1.58 (m, 6H, CH_3), 3.80 (m, 2H, CH), 6.80–9.20 (m, 24H, arom). ^{13}C NMR ($CDCl_3$), δ (ppm): 30.1 (s, CH_3), 30.2 (s, CH_3), 42.4 (s, CH), 124.4–134.8 (arom). IR (KBr): ν_{arom}: 400–1600 (w) and 2950–3100 (vw) cm^{-1}. Mass spectra (m/e): 967 (M^+–Cl), 932 (M^+–2Cl).

*2.2.3. [PdCl(Mebinas)(PPh_3)] (**6**)*

A solution of $[PdCl(Mebinas)]_2$ (**4**) in dimethoxyethane was prepared (0.053 mmol palladium complex to 10 ml dimethoxyethane) and PPh_3 was added (0.12 mmol). The mixture reaction was vigorously stirred for 2h and became red. Hexane was added (30 ml) and a red solid appeared which

was filtered off, washed with hexane and vacuum dried. Quantitative yields of the [chloro(2-thiol-2′-(methylthioether)-1,1′-binaphthyl)triphenyl phosphine palladium(II)] (**6**) were obtained.

Anal. Calcd. for $C_{39}H_{30}S_2PClPd$ (734.9): C, 63.7; H, 4.1; S, 8.7. Found: C, 64.2; H, 4.8; S, 8.1. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.63 (s, 3H, CH_3), 6.85–8.05 (m, 27H, arom). ^{13}C NMR ($CDCl_3$), δ (ppm): 18.3 (s, CH_3), 122.1–136.0 (arom). ^{31}P NMR, δ (ppm): 24.02 (s, PPh_3). IR (KBr): ν_{arom}: 400–1600 (w) and 2950–3100 (vw) cm^{-1}. Mass spectra (m/e): 699 (M^+–Cl), 470 (M^+–PPh_3), 401 (M^+–Mebinas), 370 (M^+–Cl–Mebinas).

2.2.4. [PdCl(^{i}Prbinas)(PPh_3)] (7)

A solution of [PdCl(^{i}Prbinas)]$_2$ (**5**) in dimethoxyethane was prepared (0.053 mmol palladium complex to 10 ml dimethoxyethane) and PPh_3 was added (0.12 mmol). The mixture reaction was vigorously stirred for 2 h and became red. Hexane was added (30 ml) and a red solid appeared which was filtered off, washed with hexane and vacuum dried. Quantitative yields of the [chloro(2-thiol-2′-(isopropylthioether)-1,1′-binaphthyl) triphenylphosphine palladium(II)] (**7**) were obtained.

Anal. Calcd. for $C_{41}H_{34}S_2PClPd$ (762.9): C, 64.5; H, 4.5; S, 8.3. Found: C, 65.1; H, 4.8; S, 7.9. ^{1}H NMR ($CDCl_3$), δ (ppm): 1.01 (m, 3H, CH_3), 1.18 (m, 3H, CH_3), 3.35 (m, 1H, CH), 6.80–8.10 (m, 27H, arom). ^{13}C NMR ($CDCl_3$), δ (ppm): 29.9 (s, CH_3), 30.0 (s, CH_3), 38.6 (s, CH), 125.2–135.1 (arom). ^{31}P NMR: δ (ppm): 23.89 (s, PPh_3). IR (KBr): ν_{arom}: 400–1600 (w) and 2950–3100 (vw) cm^{-1}. Mass spectra (m/e): 727 (M^+–Cl), 399 (M^+–bina^{s}Pr).

2.3. Crystal data for the compounds 4 and 6

Suitable crystals of the complexes **4** and **6** were grown by diffusing *n*-hexane into a solution of the above compounds in dichloromethane and mounted on a glass fiber. The data were collected and processed at room temperature on a Mar Research image plate scanner, graphite-monochromated Mo–Kα radiation was used to measure 95/2° frames, 180 s per frame in all cases.

Compound **4**: $Pd_2S_4Cl_2C_{42}H_{30} \cdot 2.5CH_2Cl_2$, $M = 1153.88$, triclinic, $a = 9.513(5)$, $b = 15.374(3)$, $c = 16.451(2)$ Å, $\alpha = 71.29(6)$, $\beta = 82.02(6)$, $\gamma = 79.31(6)$°, $U = 2232.0$ Å^3, space group P-1 (No. 2), $Z = 2$, Dc = 1.717 g cm^{-3}, $F(000) = 1144$. Orange, crystal dimensions $0.13 \times 0.21 \times 0.15$ mm, m(Mo–Kα) = 14.45 cm^{-1}.

Compound **6**: $PdS_2ClC_{39}H_{30}$, $M = 735.57$, monoclinic, $a = 16.745(1)$, $b = 8.829(2)$, $c = 23.133(1)$ Å, $\beta = 106.38(5)$°, $U = 3281.2$ Å^3, space group $P2_1/c$ (No. 14), $Z = 4$, Dc = 1.489 g cm^{-3}, $F(000) = 1496$. Violet, crystal dimensions $0.23 \times 0.15 \times 0.15$ mm, m(Mo–Kα) = 8.51 cm^{-1}.

The XDS [18] package was used to give: 4673 unique reflections [merging $R = 0.0295$] (**3**) and 5830 [merging $R = 0.0182$] (**6**).

The heavy atoms were found from the Patterson map using the SHELX86 [19] program and refined subsequently from successive difference Fourier maps using SHELXL93 [20] by full-matrix least squares of 557 (**4**) and 427 (**6**) variables, to a final *R*-factor of 0.065 (**4**) and 0.037 (**6**) for 4666 (**4**) and 5830 (**6**) reflections with $[F_o] > 4\sigma(F_o)$. All atoms were revealed by the Fourier map difference. Non hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and then refined with fixed isotropic atomic displacement parameters. The weighing scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$, $a = 0.1055$ (**4**), 0.0815 (**6**) and $b =$ 18.70 (**4**), 7.15 (**6**) with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Additional material comprising H-atom coordinates thermal parameters and remaining bond lengths and angles are available from the author upon request.

2.4. Catalysis

High-pressure hydroformylation experiments (30 bar) were carried out in a Berghof autoclave, and the reaction mixtures were magnetically stirred and electrically heated. These experiments were not performed at constant pressure, but for the amount of substrate used the drop in pressure was never more than 3 bar.

2.5. Standard catalysis experiment

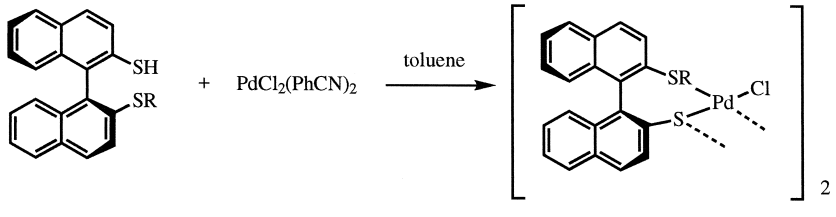
A solution of the substrate (2.5 mmol), the catalyst (0.04 mmol), the oxalic acid (2.5 mmol) and triphenylphosphine in 10 ml of dimethoxyethane were introduced into the evacuated autoclave. Carbon monoxide was introduced and the system was heated. When thermal equilibrium was reached, stirring was initiated. After the reaction time, the autoclave was cooled to room temperature and depressurized. Conversion and regioselectivities were determined by GC analysis of crude samples.

3. Results and discussion

3.1. Preparation of the palladium complexes

Complexes $[PdCl(Rbinas)]_2$, R = Me (**4**), ^{i}Pr (**5**) were obtained by addition of one equivalent of RHbinas, **3a**, to a toluene solution of $[PdCl_2(PhCN)_2]$. Addition of hexane to the reaction mixture results, in both cases, in the precipitation of an orange solid which was separated by filtration (Scheme 2). The ^{1}H NMR spectra of **4** and **5** show the alkyl proton signals of the thioether group of the ligands at $\delta = 2.67$ (s) (**4**) and $\delta = 1.29$ (m) (**5**). The different signals corresponding to the aromatic protons of the coordinated thiol–thioether ligands can be seen at $\delta = 6.8$–9.2. The heaviest ions in the FAB mass spectra of both **4** and **5** suggest the loss of chloride in the molecular ion.

The molecular structure of **4** was established by X-ray crystallography. A view of the molecule is given in Fig. 1 and the most significant bond angles and lengths are listed in Table 1. The crystal contains dinuclear units of **4** in which each thiolate–thioeter acts as a chelate ligand in a seven-membered ring with a distorted twisted chair conformation. The methyl group is located in a pseudoequatorial position giving the structure an overall C_2-symmetry, where both Pd atoms are located on a two-fold axis. Both S-thioeter strereogenic centres display a pyramidal geometry and have the same relative configuration (*S,S* or *R,R*), whereas the binaphthyl moieties have the opposite chiral



3a R= Me
3b R= ^{i}Pr

4 R= Me
5 R= ^{i}Pr

Scheme 2.

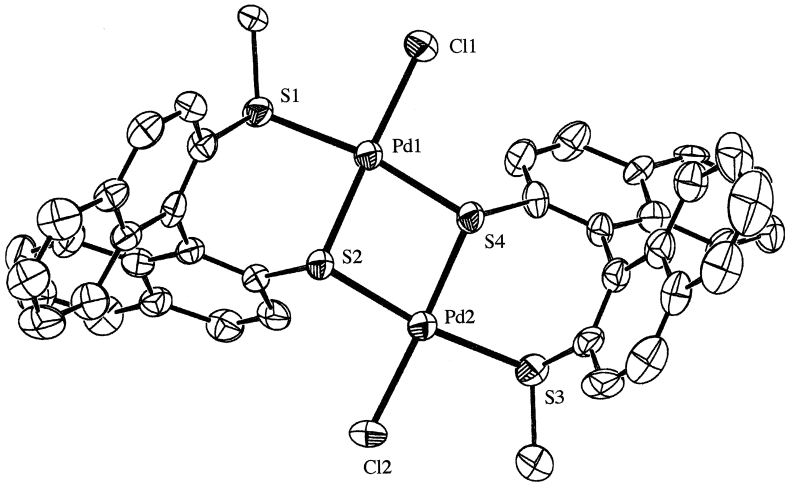


Fig. 1. X-ray structure of $[PdCl(Mebinas)]_2$ (**4**).

notation. The naphthyl rings corresponding to each diaryl substituent are significantly bent and with a dihedral angle of 75° between their planes, which allows the diaryl backbone to be basically free from torsional strain. The coordination around the Pd atom is essentially square planar and angles between metal, sulfurs from the same ligand and chloride are close to 90 and 180° (e.g., S1–Pd1–Cl1 = 93.13°, S1–Pd1–S4 = 171.21°), depending on the case. The dihedral angle between the two coordination planes is 150°. Similar thiolate derivatives show smaller angles between the coordination planes.

Table 1
Selected bond distances (Å) and angles (°) for complexes **4** and **6**

	4	**6**
Pd1–S1	2.344(3)	2.4675(9)
Pd1–S2	2.312(3)	2.3145(8)
Pd1–S4	2.340(3)	–
Pd2–S4	2.316(3)	–
Pd2–S2	2.330(3)	–
Pd2–S3	2.336(3)	–
Pd1–Cl1	2.322(3)	2.3441(10)
Pd2–Cl2	2.332(3)	–
Pd1–P1	–	2.2590(8)
S1–Pd1–Cl1	93.13(11)	88.36(3)
S1–Pd1–S4	171.21(10)	–
S2–Pd1–Cl1	173.54(12)	172.22(4)
S2–Pd1–S4	81.05(9)	–
S2–Pd2–S4	81.19(9)	–
S2–Pd2–S3	170.01(10)	–
S4–Pd2–Cl2	175.36(11)	–
S3–Pd2–Cl2	93.18(10)	–
S1–Pd1–P1	–	174.56(3)
S1–Pd1–S2	–	93.18(3)
P1–Pd1–Cl1	–	93.35(3)
P1–Pd1–S2	–	84.44(3)
φ	150	–

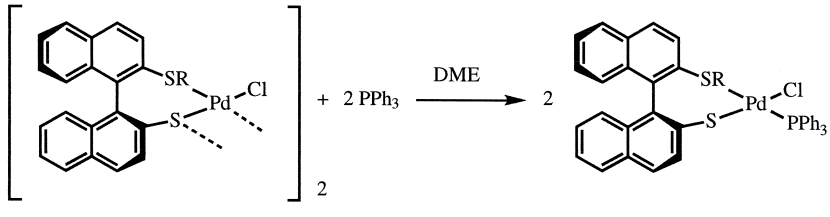
Probably, the binaphthyl ligands do not permit a major bent of the structure. The Pd–S thioether bond distances (2.336 and 2.334 Å) are slightly longer that those observed in other Pd complexes with diaryl [21] or aryl alkyl [22] sulfide ligands (2.293 and 2.288 Å, respectively). The palladium complex with a bis methyl thioether ligand [$PdCl_2$(Me_2binas)] [7] recently reported, shows slightly shorter Pd–S thioether distances (2.297 and 2.316 Å) but they are closer to the distances observed in **4**. This small difference could be attributed to the different *trans* effect of the S-thiolate, in this case, with respect to the chloride in the other complex.

Thiolate groups are in *trans* respect to the chloride atoms and thioether groups from the second ligand. The Pd–S thiolate bond distances (2.316 and 2.340 Å) are comparable with those observed in other Pd complexes with bridged thiolate ligands (2.33 Å) [23] but they are significatively different between them. In particular, the distance between the metal and the thiolate which participates in the chelate ring with the thioether (Pd2–S4) is shorter than the other one (Pd1–S4), so the first bond is stronger than the second one. This difference could be attributed to the weaker *trans* effect of the chloride as compared to the sulfur-thioether. Thus, the dinuclear structure can be imagined as formed by the association of the two equivalent mononuclear fragments which are obtained by cleavage of Pd1–S4 and Pd2–S2.

The Pd–Cl bond lengths (2.327 Å) are slightly longer than the observed in the complex with the dithioether ligand (2.295 Å). This could be attributed to the stronger *trans* effect of the thiolate group. The presence of terminal chloride ligands in polynuclear palladium complexes is not unusual and the examples available include tetranuclear species such as [$PdCl(SC_6H_4NMe_2$-2)]$_4$, [24] as well as dinuclear [*trans*-Pd_2Cl_2(μ-SPh)$_2$(PMe_3)$_2$] [25] and trinuclear species [Pd_3Cl_2(μ-SCy)$_4$)(PMe_3)$_2$] [26]. From these and our examples, it is apparent that anionic S-donor centres display a pronounced aptitude, even higher than chloride anions, to act as bridging ligands. The remaining bond distances and angles within the structure of the thiol–thioether ligand are unexceptional.

Of the possible stereoisomers of complex **4**, which differ either in the conformation of the chelate ring or in the spatial arrangement of the *S*-methyl substituents, this one is expected to be the most stable because both methyl groups are located in equatorial position of the energetically favoured twist-chair conformation [8]. Although its preferential separation in crystalline form from the solution does not necessarily depend from a higher inherent stability, but may only reflect small differences in solubility or in crystal packing energy, NMR evidences are in keeping with the view that this isomer corresponds to the main product present in solution.

Adding two equivalents of triphenylphosphine to dimethoxyethane solutions of **4** and **5** yields mononuclear complexes which are formed by cleavage of the thiolate bridges (Scheme 3). The elemental analyses match the stoichiometry [PdCl(Rbinas)(PPh_3)], R = Me (**6**), ^{i}Pr (**7**). The ^{31}P–{^{1}H} NMR spectrum in $CDCl_3$ show one singlet at $\delta = 24.02$ (**6**) and $\delta = 23.89$ (**7**).



4 R= Me
5 R= ^{i}Pr

6 R= Me
7 R= ^{i}Pr

Scheme 3.

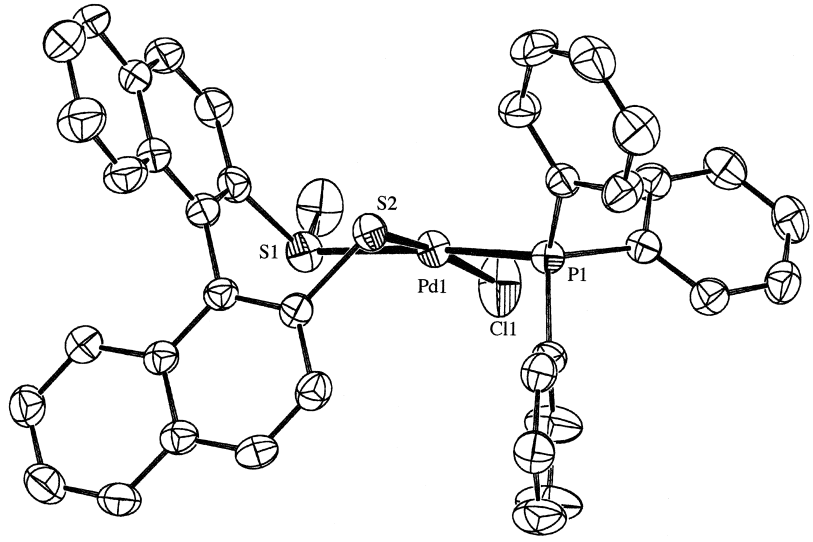


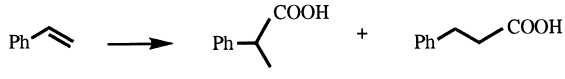
Fig. 2. X-ray structure of [PdCl(Mebinas)(PPh_3)] (**6**).

In the case of **6**, suitable crystals were grown and the structure was established by X-ray crystallography (Fig. 2). Table 1 gives the most significant intramolecular bond distances and angles for **6**. The crystal contains discrete mononuclear units of **6** in which the thiolate–thioether acts as a chelate ligand in a seven-membered ring with a highly distorted twisted chair conformation. The coordination around the Pd is essentially square planar. The Pd–S thiolate bond distance (2.314 Å) are comparable with those observed in **4** but the Pd–S thioether bond distance (2.467 Å) is longer. This difference gives a measure of the weaker *trans* influence of the sulfur as compared to the phosphorus donor.

3.2. Catalytic hydrocarboxylation

All experiments were carried out in 1,2-dimethoxyethane solution and in the presence of oxalic acid at 100°C. In the presence of four equivalents of triphenylphosphine, the complex **4** displayed a high catalytic activity (90% conversion into acids) under 30 atm (Table 2, run 1). No hydrogenation

Table 2
Hydrocarboxylation of styrene using palladium complexes + nPR_3



2-PP 3-PP

Run	Precursor	Pd/P	% C_{acids}	% **2PP**	% **3PP**
1	**4**	4	90	89	11
2	**5**	4	92	74	26
3	**6**	1	25	96	4
4	**7**	1	69	97	3

Reaction conditions: solvent:dimethoxyethane, 30 atm CO, 100°C, 2.5 mmol styrene, 0.04 mmol precursor, 2.5 mmol $H_2C_2O_4$, reaction time: 24 h.

or isomerization were observed and the regioselectivity in 2-phenylpropanoic acid was 89%. Increasing the reaction temperature up to 150°C resulted in an extensive decomposition of the catalyst leading to dramatically lower conversions.

Complex **5** showed a similar behaviour, but the amount of the branched acid was lower (74%). The presence of PPh_3 is essential for the reaction to occur as no carbonylation product could be detected in the absence of this additive.

For a deeper insight into the effect of triphenylphosphine, complexes **6** and **7** were prepared by adding PPh_3 to a solution of **4** and **5**, respectively. They were tested as such without any additional PPh_3 (Table 2, run 3 and 4). Conversions into acids were lower, particularly in the case of precursor **6** (25%), but the shares of 2-phenylpropanoic acid improved substantially (96%). It is worth to note that the regioselectivity observed with these catalysts is quite different from the ones previously reported for Pd/diphosphines catalysts with formic or oxalic acid [27–30].

Under the same conditions, the hydrocarboxylation of styrene using the dithioether complexes $[PdCl_2(MeS(CH_2)_4SMe)]$ and $[PdCl_2(Me_2binas)]$ without any additional PPh_3 as catalyst precursors, did not produced any acid [31]. The reaction takes place if some PPh_3 is added, but in separate experiments we have found that triphenylphosphine completely displaces to dithioether ligands from the above reported complexes, leading to $[PdCl_2(PPh_3)_2]$.

In the case of thiolate–thioether ligands, however, we have found that the reaction of $[PdCl(Rbinas)]_2$ with PPh_3 affords $[PdCl(Rbinas)(PPh_3)]$ and that the chelating S-donor ligand is not released by the metal at any time. We are therefore confident that, although triphenylphosphine is required for these complexes to be catalytically active, the sulfur ligand is not displaced from the metal and that its presence will contribute to obtain enantiometric excesses in the case of using optically pure ligand.

Further studies aimed at intercepting the catalytic intermediates of our system and at exploiting the enantiopure ligands **4**–**7** in the asymmetric hydrocarboxylation are in progress in our laboratories.

Acknowledgements

This work was carried out within the framework of the COST D2 program of the C.E. 'Selective synthesis'. Financial support from the *Spanish CICYT* (Ministerio de Educación y Cultura), *CIRT* (Generalitat de Catalunya), Proj. QFN-95-4725-CO3 and the Italian Ministero dell'Universitá e della Ricerca Scientifica e Technologica (MURST) is gratefully acknowledged.

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