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Journal of Organometallic Chemistry 509 (1996) 9–14

Journal of Organometallic Chemistry

Synthesis of new hydrophilic phosphines by addition of diphenylphosphine on activated alkenes: characterization of their rhodium complexes

L. Lavenot, M.H. Bortoletto, A. Roucoux, C. Larpent, H. Patin *

Laboratoire de Chimie Organique et des Substances Naturelles, associé au CNRS URA 1467, Ecole Nationale Supérieure de Chimie de Rennes, avenue du Général Leclerc, 35700 Rennes-Beaulieu, France

Received 15 March 1995

Abstract

The regioselective addition of diphenylphosphine on conjugated olefins leads to new hydrophilic phosphines. Ligands with various functional groups (carboxylic, sulfonate, trimethylammonium and hydroxy) and their neutral and cationic rhodium complexes have been prepared and characterized.

Keywords: Water soluble phosphines; Rhodium complexes; Michael addition

1. Introduction

Biphasic catalysis consisting of a water-phase containing catalytic species and a non-miscible organic phase continues to attract interest in view of industrial applications [1]. For this purpose, numerous attempts have been made to introduce hydrophilic functional groups, on convenient ligands, mainly phosphines [1–3]. Up to now, sulfonated phosphines have been mostly studied because this highly hydrophilic group affords water solubility to the ligands and to their metal complexes [4,5]. Several catalytic applications have been published [1,5] among which hydroformylation of propene [6] and carbon–carbon coupling [7] have been applied on industrial plants. In our group, we have recently focused on the synthesis of hydrophilic phosphines bearing functional groups other than sulfonates with the objective of a better control of water solubility of the corresponding coordination compounds. We are guided by the conviction that for a specific reaction involving particular substrates the catalyst has to be exactly adapted to the hydrophilic and hydrophobic characters of the partners. In this paper, we describe the preparation and characterization of several new phosphines and of neutral and cationic rhodium coordination compounds.

2. Michael addition of diphenylphosphine on acrylic esters and amides

Addition of secondary phosphines on conjugated olefins is a well-known reaction in organic synthesis [8]. This reaction can be performed without a catalyst [9], under radical conditions [10], in the presence of a Lewis acid [11] or by using strong bases [12]. Moreover, several limitations have been encountered owing to the further oxidation of phosphorus and/or competing polymerization. Recently, a significant improvement have been recorded [8] using an aqueous base under mild conditions [13]. In our case we must take into account other parameters such as the water solubility of the Michael product and an enhanced tendancy to oxidation in a strongly basic aqueous medium. We have found that the addition of a small amount of tetraethylammonium hydroxide into a solution of Ph_2PH and

* Corresponding author.

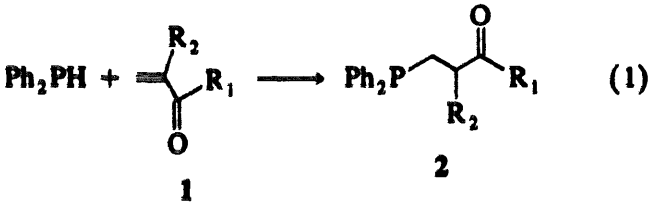
Elsevier Science S.A.
SSDI 0022-328X(95)05790-0

Table 1
Synthesis and characterization of 2

Compound	Reaction time	Isolated yield (%)	$^{31}P\{^1H\}$ NMR, δ (ppm)
2a [a]	30 min	70	−16.5 [b]
2b [a]	16 h	66	−18.3 [c]
2c [a]	4 h 30 min	30 [d]	−20.7 [c]
2d [a]	30 min	69	−21.0 [b]
2e [a]	20 h	47	−17.7 [c]
2f [e]	4 h	60	−16.5 [b]
2g [e]	30 min	93	−19.5 [c]

[a] Solvent, CH_3CN; 83×10^{-3} molar equivalent of NEt_4^+, OH^-.
[b] In CD_3CN with H_3PO_4 external standard.
[c] In CD_3OD with H_3PO_4 external standard.
[d] Moderate yield comes from hydrolysis of the starting material.
[e] Solvent, CH_3CN; 2.5 ml of NaOH (10 N).

activated alkene in acetonitrile leads to the desired phosphines with good yields (Table 1):



(1)

1 2

a: R_1 = -NH-C(CH$_3$)$_2$CH$_2$SO$_3^\ominus$ NEt$_4^\oplus$ R_2 = H

b: R_1 = -O- N$^\oplus$(CH$_3$)$_3$ I$^-$ R_2 = H

c: R_1 = -O- N$^\oplus$(CH$_3$)$_2$ - SO$_3^\ominus$ R_2 = CH$_3$

d: R_1 = OCH$_3$ R_2 = -CH$_2$CO$_2$CH$_3$

e: R_1 = -NH-C(CH$_2$OH)$_3$ R_2 = H

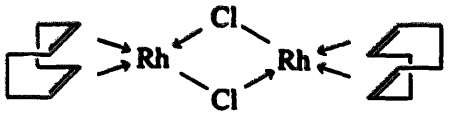
f: R_1 = -O- N(CH$_3$)$_2$ R_2 = H

g: R_1 = OH R_2 = -CH$_2$CO$_2$H

A small quantity of diterbutylphenol was always added to prevent polymerization. Some limitations have been encountered when the hydrolysis of the ester function competes with the nucleophilic addition of Ph_2PH and when the olefin is very hygroscopic. In the latter case, the presence of a larger amount of water seems to favor the production of phosphine oxide. Compound **2g** was obtained in a one-pot reaction with an excess of NaOH or from **2d** by acid hydrolysis.

3. Complexes of phosphines 2 with rhodium(I)

In order to avoid oxidation at phosphorus when complexation occurs in water in the presence of Rh(III) [14] we have used preformed Rh(I) dimer 3 [4]. Complexes 4 and 5 are prepared according to literature methods adapted to the particular case of hydrophilic phosphines. Other hydrosoluble phosphines are known to react similarly, and the ^{31}P NMR spectral parameters (δ, $^1J_{Rh-P}$ and possibly $^2J_{P-P}$) compare well with those of 4 and 5 [14,15]. The neutral complexes 4 are obtained by addition of one equivalent of ligand 2 to the dimer $[RhCl(COD)]_2$ in ethanol or tetrahydrofuran (THF) in the presence of aqueous NaCl to avoid the displacement of the chlorine ligand:



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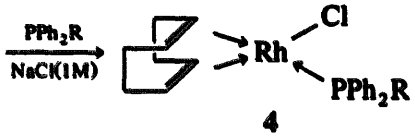


4

(2)

a: R = -C(=O)-NH-C(CH$_3$)$_2$CH$_2$SO$_3^\ominus$ NEt$_4^\oplus$

b: R = -C(=O)-O- N$^\oplus$(CH$_3$)$_3$ I$^\ominus$

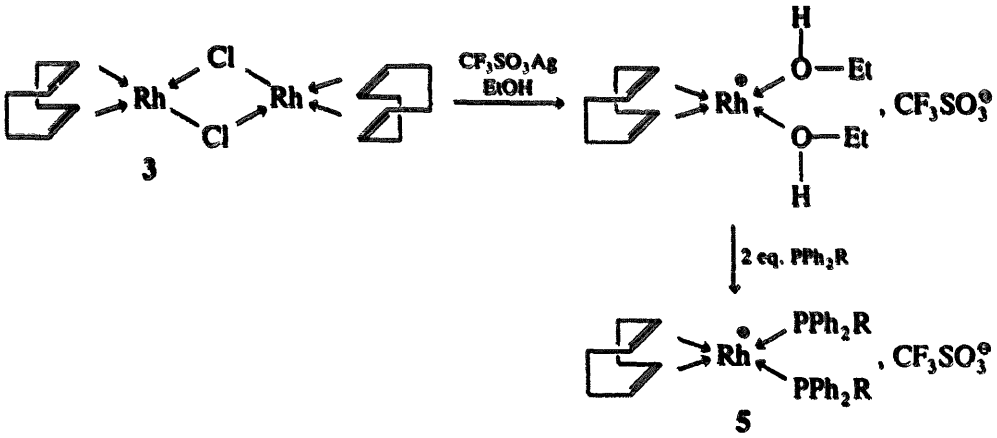
c: R = -C(=O)-O- N$^\oplus$(CH$_3$)$_2$ - SO$_3^\ominus$

e: R = -C(=O)-NH-C(CH$_2$OH)$_3$

f: R = -C(=O)-O- N(CH$_3$)$_2$

g: R = -CH(CO$_2$H)-CH$_2$CO$_2$H

h: R = -C$_6$H$_4$-SO$_3$Na



3 5

(3)

Table 2
^{31}P NMR data of 4

Complex	δ (ppm)	$^{1}J_{Rh-P}$ (Hz)
4a [a]	24.8	154
4b [a]	25.3	156
4c [a]	22.0	149
4e [a]	23.0	149
4f [a]	24.7	154
4g [a]	23.3	149
4h [b]	30.9	152

[a] Solvent mixture of CD_3OD–EtOH–THF–H_2O.
[b] Solvent mixture of H_2O–THF–CD_3OD.

Table 3
^{31}P NMR data of 5

Complex R	δ (ppm)	Multiplicity	$^{1}J_{Rh-P}$ (Hz)	$^{2}J_{P-P}$ (Hz)
5a	24.8	d	154	—
5b [a]	25.3	d	151	—
5c [a]	22.6, 22.9	dd, dd	144	44
5e [a]	23.7	d	149	—
5f [a]	23.3, 24.1	dd, dd	137	34
5g [a]	23.2	d	151	—
5h [b]	26.1	d	149	—

[a] Solvent mixture, EtOH–CD_3OD.
[b] Solvent mixture, H_2O–EtOH–CD_3OD.

Complexes 4 are characterized in solution by their ^{31}P NMR spectra showing a doublet around 25 ppm with $^{1}J_{Rh-P}$ in the range of 150 Hz (Table 2).

For the synthesis of cationic complexes 5, silver triflate is added to a solution of dimer $[RhCl(COD)]_2$ and the addition of two equivalents of ligand 2 in ethanol or THF affords 5 [4].The complexes 5a, 5b, and 5e are characterized in solution by their ^{31}P NMR spectra: one doublet around 25 ppm with $^{1}J_{Rh-P} \approx 150$ Hz. For compounds 5c and 5f the phosphorus ligands are not equivalent. Presumably for stereoelectronic (5c) and/or steric (5f) reasons, there is a loss of symmetry, giving rise to an additional coupling $^{2}J_{P-P}$ (Table 3).

For comparison 4h and 5h have been prepared with (triphenylphosphine monosulfonate sodium salt) and also studied by ^{31}P NMR. Chemical shifts vary significantly in both series certainly owing to cumulated influences of ligand and solvent effect; however, the $^{1}J_{Rh-P}$ values are very close to the values already recorded [14].

4. Conclusion

In conclusion we have described a general method for the synthesis of various hydrophilic phosphines by addition of Ph_2PH on acrylic esters and amides. These compounds possess the expected properties to coordinate on rhodium(I) and lead to new complexes; the ability of these to catalyze hydrogenation and carbon–carbon coupling in biphasic conditions are currently being examined.

5. Experimental section

Preparations and NMR studies of the phosphines and complexes were carried out under anaerobic conditions. All solvents were degassed before use. $^{13}C\{^1H\}$ NMR spectra (22.5 MHz) were recorded on a JEOL FX90Q and $^{31}P\{^1H\}$ NMR spectra (32.38 MHz) were recorded on a Brucker WP 80 MHz (external reference, 85% H_3PO_4). Phosphine oxides (δ) were prepared when necessary for analytical purposes.

5.1. Phosphines (2) and phosphine oxides (6)

5.1.1. Synthesis of 2a

Commercially available 2-acrylamido-1-propane sulfonic acid (621.8 mg, 3×10^{-3} mol) was dissolved in 8 ml of acetonitrile and tetraethylammonium hydroxide (1.08 ml, 3×10^{-3} mol) solution in water (40% by weight) was added to neutralize the acid. Then, a mixture of diterbutylphenol (9 mg, 4.4×10^{-5} mol), tetraethylammonium hydroxide (90 μl, 2.5×10^{-4} mol) and 8 ml of acetonitrile was placed under nitrogen. Diphenylphosphine (519 μl, 3×10^{-3} mol) and the deoxygenated solution of acrylamido propane sulfonic acid prepared before were successively added. The solution was maintained at room temperature for 4 h. The mixture was cooled and the solvent removed to dryness. After addition of 20 ml of 10% NaOH aqueous solution the mixture was washed three times by Et_2O (20 ml). The remaining aqueous phase was extracted ten times by CH_2Cl_2 (10 ml) and all the combined organic phases were dried on $MgSO_4$. After removal of the solvent under vacuum, 1.09 g of phosphine 2a was obtained (70% yields) as a colorless oil.

$R_f = 0.28$ (Ethylacetate:methanol, 2:8).

$^{31}P\{^1H\}$ NMR ($CDCl_3$–$CHCl_3$): δ −17.7 ppm.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.31 (t, 12H, $^{3}J = 7$ Hz); 1.31 (t, 12H, $^{3}J = 7$ Hz); 1.32 (t, 12H, $^{3}J = 7$ Hz); 1.57 (s, 6H); 2.15–2.40 (m, 4H); 2.90 (s, 2H); 3.33 (q, 8H, $^{3}J = 7$ Hz); 7.20–7.75 (m, 10H); 8.03 (s, NH) ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 22.5 MHz): δ 7.2 (s); 22.9 (d, $^{1}J = 12$ Hz); 26.0 (s); 33.4 (d, $^{2}J = 18$ Hz); 51.7 (s), 52.02 (s), 52.1 (s), 52.26 (s); 60.5 (s); 127.94 (s); 128.2 (s); 132.3 (d, $^{2}J = 19$ Hz); 137.8 (d, $^{1}J = 13$ Hz); 171.2 (d, $^{3}J = 15$ Hz) ppm.

5.1.2. Synthesis of 6a

1.47 g (2.8×10^{-3} mol) of phosphine 2a was dissolved in 20 ml of water; 286 μl of H_2O_2 (30%) were added and the reaction was stirred at room temperature for 12 h. A colorless oil is obtained.

^{31}P {^1H} NMR (D_2O): δ 40.3 ppm.

The product purified by column chromatography undergo exchange of NEt_4^+ by H^+ (ethylacetate: methanol, 6:4). The phosphine obtained as a white solid was recrystallized in boiling chloroform (melting point (m.p.), 230°C).

Elemental anal. Found: C, 55.32; H, 5.31; O, 18.83, P, 7.23. $C_{19}H_{24}O_5NSP$ calc.: C, 55.74; H, 5.91; O, 19.54; P, 7.56%.

5.1.3. Synthesis of 2b

Commercially available 2-(dimethylamino)ethylacrylate (3 ml, 1.94×10^{-2} mol) was added dropwise to a solution of iodomethane (1.2 ml, 1.94×10^{-2} mol) in 25 ml of CH_2Cl_2 under nitrogen. The mixture was maintained at room temperature for 16 h. The salt **1b** was filtered and recrystallized in boiled methanol; **1b** was obtained with a 86% yield as a white solid.

^1H NMR (CD_3OD, 89.5 MHz): δ 3.33 (s, 3H); 3.41 (s, 6H); 3.924(m, 2H); 4.70 (m, 2H); 6.01 to 6.46 (m, 3H) ppm.

^{13}C {^1H} NMR (CD_3OD, 22.5 MHz): δ 55.6 (s, CH_3); 55.7 (s, CH_3); 55.8 (s, CH_3); 60.0 (s, CH_2); 66.5 (s, CH_2); 129.5 (s, CH=); 133.9 (s, CH_2=); 167.2 (s, C=O) ppm.

A mixture of diterbutylphenol (3 mg, 1.45×10^{-5} mol) and olefin **1b** (284.9 mg, 10^{-3} mol) in 6 ml of CH_3CN was heated at 80°C under nitrogen. 30 µl (8.3×10^{-5} mol) of tetraethylammonium hydroxide and 173 µl (10^{-3} mol) of diphenylphosphine were successively added. The solution was maintained at 80°C for 16 h. The mixture was cooled and the solvent was removed to dryness. The residue was washed three times with hexane (20 ml); the oil was solubilized in 10 ml of HCl (1 N) and extracted three time with CH_2Cl_2 (20 ml) and all the combined organic phases were washed with water and dried on $MgSO_4$. After removal of the solvent under vacuum phosphine **2b** was obtained with a 66% yield as a white solid. It was recrystallized in boiling ethylacetate: methanol (10: 1) mixture (m.p. 149°C).

^{31}P {^1H} NMR (CD_3CN–CH_3CN): δ −16.5 ppm.

^{13}C {^1H} NMR ($CDCl_3$, 22.5 MHz): δ 22.2 (d, $^1J_{PC}$ = 12 Hz); 30.3 (d, $^2J_{PC}$ = 19 Hz); 54.3 (s); 57.70 (s); 64.7 (s); 128.9 (d, $^3J_{PC}$ = 11 Hz); 128.6 (s); 132.4 (d, $^2J_{PC}$ = 19 Hz); 153.8 (d, $^1J_{PC}$ = 19 Hz); 193.1 (d, $^3J_{PC}$ = 13 Hz) ppm.

Elemental anal. Found: C, 50.76; H, 5.88; O, 6.94; P, 6.69. $C_{20}H_{27}O_2NPI$ calc: C, 50.97; H, 5.77, O, 6.79; P, 6.57%.

5.1.4. Synthesis of 2c

A mixture of diterbutylphenol (60 mg, 2.9×10^{-4} mol) and commercially available betain **1c** (3.35 g, 1.2×10^{-2} mol) in 100 ml of CH_3CN was heated at 70°C under nitrogen. Tetraethylammonium hydroxide (300 µl, 8.3×10^{-4} mol) and diphenylphosphine (173 µl, 10^{-3} mol) were successively added. The solution was maintained at 70°C for $4\frac{1}{2}$ h. The mixture was cooled, hydrochloric acid (1 N) (830 µl; 8.3×10^{-3} mol) was readily added and the solvent removed to dryness. 20 ml of water were added and the mixture was washed three time with Et_2O. Water was removed under vacuum and methanol added to the product. The methanol was removed and the solid dried under vacuum, the phosphine was obtained with a 30% yield as a white solid.

R_f = 0.29 (methanol).

^{31}P {^1H} NMR (CD_3OD–CH_3OH): δ −20.7 ppm.

^{13}C {^1H} NMR (CD_3OD, 22.5 MHz): δ 19.6 (d, ^3J = 10 Hz); 20.8 (s); 34.1 (d, ^1J = 14 Hz); 39.1 (d, ^2J = 17 Hz); 49.5 (s); 52.8 (s); 60.1 (s); 64.6 (s); 65.8 (s); 130.5 (d, ^3J = 9 Hz); 130.8 (d, ^4J = 5 Hz); 134.5 (d, ^2J = 20 Hz); 134.6 (d, ^2J = 20 Hz); 139.9 (d, ^1J = 13 Hz); 140.1 (d, ^1J = 12 Hz); 177.1 (d, ^3J = 6 Hz) ppm.

5.1.5. Synthesis of 6c

1 g (2.15×10^{-3} mol) of phosphine **2c** was dissolved in 10 ml of water, 220 µl of H_2O_2 (30%) were added and the reaction stirred at room temperature for 12 h. The solvent was removed under vacuum and a white solid is obtained. It was recrystallized in boiling dichloromethane.

^{31}P {^1H} NMR (D_2O): δ 37.1 ppm.

Elemental anal. Found: C, 56.83; H, 6.65; O, 19.70; P, 6.51. $C_{23}H_{32}O_6NSP$ calc.: C, 57.37; H, 6.70; O, 19.93; P, 6.43%.

5.1.6. Synthesis of 2d

A mixture of diterbutylphenol (30 mg, 1.47×10^{-4} mol), tetraethylammonium hydroxide (345 µl, 9.6×10^{-4} mol) in 30 ml of CH_3CN was placed under nitrogen. Diphenylphosphine (2 ml, 1.15×10^{-2} mol) and a solution of commercially available dimethylitaconate (1.89 g, 1.15×10^{-2} mol) in 10 ml of CH_3CN were successively added. The mixture was maintained at room temperature for 30 min. The solution was cooled and the solvent removed to dryness. 20 ml of water with 0.96 ml of HCl (1 N) were added and this aqueous layer was extracted three times with 30 ml of Et_2O and all the combined organic layers were washed with water and dried over $MgSO_4$. After removal of the solvent under vacuum, phosphine **2d** was obtained with a 69% yield as colorless oil.

R_f = 0.32 (CH_2Cl_2).

^{31}P {^1H} NMR (CD_3CN–ether): δ −21.0 ppm.

^{13}C {^1H} NMR ($CDCl_3$, 22.5 MHz): δ 30.7 (d, ^1J = 15 Hz); 36.4 (d, ^3J = 10 Hz); 38.8 (d, ^2J = 17 Hz); 51.6 (s); 51.8 (s); 128.5 (d, ^3J = 7 Hz); 128.5 (d, ^3J = 7 Hz); 128.7 (s); 128.89 (s); 132.6 (d, ^2J = 19 Hz); 132.8 (d, ^2J = 20 Hz); 137.3 (d, ^1J = 15 Hz); 137.9 (d, ^1J = 15 Hz); 171.8 (s); 174.5 (d, ^3J = 7 Hz) ppm.

5.1.7. Synthesis of 6d

2.76 g (8.02×10^{-3} mol) of phosphine **2d** was dissolved in 10 ml of water, 820 μl of H_2O_2 (30%) were added and the reaction stirred at room temperature for 12 h. The solvent was removed under vacuum and a colorless oil is obtained. The product is purified by column chromatography with ethylacetate as eluent. A white solid compound was obtained and recrystallized in boiling hexane (m.p. 103°C).

^{31}P {^1H} NMR (D_2O): δ 34.0 ppm.

Elemental anal. Found: C, 63.38%; H, 5.57%; O, 22.11%; P, 8.72. $C_{19}H_{21}O_5P$ calc.: C, 63.33%; H, 5.87%; O, 22.20%; P, 8.10%.

5.1.8. Synthesis of 2e

Tris(hydroxymethyl)acrylamidomethane **1e** was prepared according to a published procedure [16]. It was dried under vacuum at 40°C for 3 days before use. Then, a mixture of diterbutylphenol (3 mg, 1.45×10^{-5} mol) and olefin **1e** (175.2 mg, 10^{-3} mol) in 6 ml of CH_3CN was heated at 80°C under nitrogen. Tetraethylammonium hydroxide (30 μl, 8.3×10^{-5} mol) and diphenylphosphine (173 μl, 10^{-3} mol) were successively added. The solution was maintained at 80°C for 20 h. The mixture was cooled and the solvent removed to dryness. The residue was washed three times with hexane (20 ml). 20 ml of HCl (1 N) was added and this aqueous phase was washed three times with Et_2O (100 ml). The white solid was filtered and washed with Et_2O. Phosphine **2e** was obtained with a 47% yield.

R_f = 0.26 (ethylacetate).

^{31}P {^1H} NMR (CD_3OD–CH_3OH): δ −17.7 ppm.

^{13}C {^1H} NMR (CD_3OD, 22.5 MHz): δ 25.5 (d, ^1J = 11 Hz); 34.6 (d, ^2J = 18 Hz); 63.3 (s); 64.43 (s); 130.5 (d, ^3J = 10 Hz); 130.5 (s); 134.6 (d, ^2J = 18 Hz); 140.2 (d, ^1J = 12 Hz); 177.1 (d, ^3J = 14 Hz).

Elemental anal. Found: C, 63.04; H, 6.82; O, 17.83; P, 8.40. $C_{19}H_{24}O_4NP$ calc.: C, 63.15; H, 6.70; O, 17.71; P, 8.57%.

5.1.9. Synthesis of 2f

A mixture of diterbutylphenol (30 mg, 1.45×10^{-4} mol), tetraethylammonium hydroxide (300 μl, 8.3×10^{-4} mol) and 50 ml of CH_3CN was placed under nitrogen. Diphenylphosphine (1.73 ml, 10^{-2} mol) and commercially available 2-dimethylaminoethylacrylate (1.52 ml, 10^{-2} mol) were successively added. The solution was maintained at room temperature for 4 h. The mixture was cooled and the solvent removed to dryness. 90 ml of water with 10 ml of HCl (12 N) were added and this aqueous layer was washed three times with Et_2O (100 ml). Aqueous NaOH solution (1 N) was added until pH 10 and was extracted three times with Et_2O. All the combined organic layers were washed with water and dried over $MgSO_4$. After removal of the solvent under vacuum, the phosphine **2f** was obtained with a 60% yield as a colorless oil.

R_f = 0.47 (ethylacetate : methanol, 50 : 50).

^{31}P {^1H} NMR (CD_3CN–CH_3CN): δ −16.5 ppm.

^1H NMR ($CDCl_3$, 89.55 MHz): δ 2.16 (s, 6H); 2.27 (t, 2H, ^3J = 5.6 Hz); 2.31 (t, 2H, ^3J = 5.3 Hz); 2.43 (t, 2H, ^3J = 5.8 Hz); 4.05 (t, 2H, ^3J = 5.8 Hz); 7.0–7.5 (m, 10H) ppm.

^{13}C {^1H} NMR ($CDCl_3$, 22.5 MHz): δ 22.6 (d, ^1J = 12 Hz); 30.3 (d, ^2J = 20 Hz); 45.2 (s); 57.3 (s); 61.88 (s); 127.9 (s); 128.27 (s); 132.3 (d, ^2J = 18 Hz); 137.4 (d, ^1J = 12 Hz); 172.5 (d, ^3J = 15 Hz) ppm.

5.1.10. Synthesis of 6f

0.72 g (2.19×10^{-3} mol) of phosphine **2f** was dissolved in a mixture of water (30 ml) and CH_3CN (20 ml), 250 μl of H_2O_2 (30%) were added and the reaction stirred at room temperature for 30 min. The solvent was removed under vacuum and a colorless oil was obtained. The product was purified by column chromatography (ethylacetate : methanol, 1 : 1). 0.61 g of product was obtained as a colorless oil.

^{31}P {^1H} NMR (D_2O): δ 37.5 ppm.

Elemental anal. Found: C, 65.75; H, 6.90; O, 13.95; P, 8.83. $C_{19}H_{21}O_5P$ calc.: C, 66.08; H, 7.01; O, 13.90; P, 8.96.

5.1.11. Synthesis of 2g

A mixture of diterbutylphenol (30 mg, 1.45×10^{-4} mol) with 2.5 ml of NaOH (10 N) in 10 ml of CH_3CN was placed under nitrogen. Diphenylphosphine (1.73 ml, 10^{-2} mol) was added and the mixture was heated at 60°C; a solution of dimethylitaconate (1.58 ml; 10^{-2} mol) in 10 ml of CH_3CN was added dropwise and the mixture was maintained at 60°C for 3 h. The mixture was cooled and the solvent removed to dryness. After addition of 50 ml of 10% NaOH aqueous solution, the mixture was washed four times with Et_2O (40 ml). HCl (1 N) was added until pH 1 and the aqueous layer was extracted six times with Et_2O (40 ml). All the combined organic layers were dried over $MgSO_4$. After removal of the solvent under vacuum, the phosphine **2g** was obtained with a 93% yield as a white solid (m.p., 157°C).

^{31}P {^1H} NMR (CD_3OD–CH_3OH): δ −19.5 ppm.

^1H NMR (D_2O, 89.55 MHz): δ 2.38 (s, 2H); 2.53 (s, 2H); 3.41 (s, 1H); 7.2–7.7 (m, 10H) ppm.

^{13}C {^1H} NMR (CD_3OD, 22.5 MHz): δ 32.3 (d, ^1J = 14 Hz); 38.2 (d, ^3J = 11 Hz); 40.9 (d, ^2J = 17 Hz); 130.3 (d, ^3J = 7 Hz); 130.4 (d, ^3J = 7 Hz); 130.6 (s); 130.8 (s); 134.4 (d, ^2J = 19 Hz); 134.6 (d, ^2J = 20 Hz); 139.6 (d, ^1J = 11 Hz); 140.2 (d, ^1J = 10 Hz); 176.0 (s, C_1); 178.7 (d, ^3J = 7 Hz) ppm.

Elemental anal. Found: C, 64.51; H, 5.32; O, 19.46; P, 9.40. $C_{17}H_{17}O_4P$ calc.: C, 64.55; H, 5.42; O, 20.23; P, 9.79.

5.2. Synthesis of rhodium coordination compounds

5.2.1. (COD)RhCl(PPh$_2$R) (4)

3.6×10^{-4} mol of phosphine 2 in an aqueous solution of NaCl (1 M) was added to 88.7 mg (1.8×10^{-4} mol) of [RhCl(COD)]$_2$ in ethanol (3 ml). Sometimes, it is necessary to improve the solubility by addition of THF (3 ml). After stirring for 1 h a yellow solution is obtained and the complex characterized by ^{31}P NMR.

5.2.2. [(COD)Rh(PPh$_2$R)$_2$]$^+$, $CF_3SO_3^-$ (5)

[RhCl(COD)]$_2$ (88.7 mg, 1.8×10^{-4} mol) and 92.5 mg (3.6×10^{-4} mol) of silver triflate (CF_3SO_3Ag) were dissolved in ethanol (3 ml). After stirring for 15 min the precipitate of silver chloride was filtered and the ethanolic solution was added to 7.2×10^{-4} mol of phosphine 2 in ethanol. The yellow solution was stirred for 15 min at room temperature and the complex characterized by ^{31}P NMR.

Acknowledgments

P. Auvray, M. Guinard, Ph. Charreau and Cl. Chaintron (Rhône-Poulene RPAN) are greatfully aknowledged for helpful discussion and financial support (M.H.B.) and L.L. (BDI, CNRS).

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