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Complexation on rhodium of bidentate and potentially hemilabile phosphorous ligands

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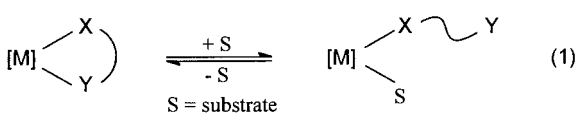
Abstract

Various bifunctional potentially hemilabile ligands bearing phosphorous groups have been prepared and their coordination to rhodium has been studied. Their effect on the hydroformylation of styrene has been assessed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Hemilabile ligand; Rhodium; Phosphonate; Hydroformylation

1. Introduction

Since the introduction of the concept of hemilability in coordination chemistry at the end of the 1970s [1], there has been considerable interest in the use of so-called hemilabile ligands in recent years [2–5]. They have two different coordination centers: one functional group strongly bound to a transition metal and another coordinatively labile. The latter can dissociate from the metal allowing the formation of a free coordination site, which may be important in homogeneous catalysis for incorporation of substrates; whereas the chelate effect of these ligands confers stability on the catalyst precursor in the absence of the substrate [6,7]



(1)

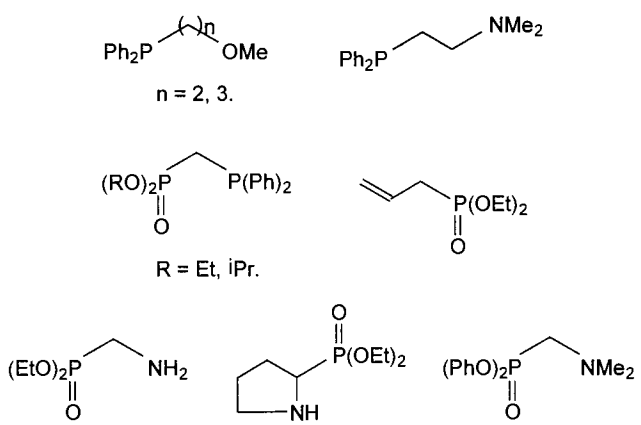
We have used a series of mixed bidentate potentially hemilabile ligands (Scheme 1)—ether-phosphine [3–9] or amine-phosphine [10], and ligands bearing the less studied phosphonate groups like phosphine-phosphonate [11], amine-phosphonate and allyl-phosphonate—to study their complexation on rhodium dimeric compounds: the tetracarbonyl-di-μ-chlorodirhodium(I) $[RhCl(CO)_2]_2$ **1** or the di-μ-chloro-di-(1,5-cyclooctadiene)dirhodium(I) $[RhCl(COD)]_2$ **2**.

Their effect on the hydroformylation of styrene with a rhodium catalyst has been assessed.

2. Results and discussion

2.1. Complexation of phosphine-phosphonate and ether-phosphine ligands

Treatment of $[RhCl(CO)_2]_2$ **1** with two equivalents of phosphine-phosphonate in CH_2Cl_2 at r.t. leads, by cleavage of the chloro-bridges, to mononuclear deriva-



Scheme 1.

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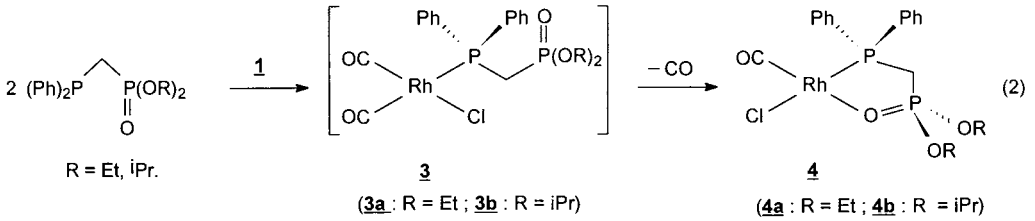
tives whose spectroscopic data show the coordination of the phosphine group [12,13].



R = Et, iPr.

3 (**3a** : R = Et ; **3b** : R = iPr)

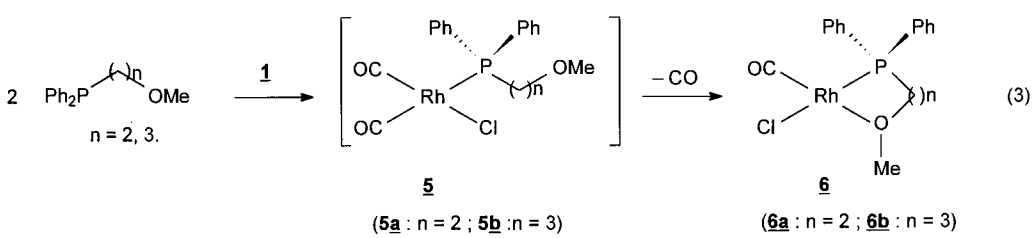
4 (**4a** : R = Et ; **4b** : R = iPr)

(2)

These compounds **3** easily undergo a decarbonylation process to give rise to the chelate complexes **4** [14]. This type of reaction is generally observed in the reaction of dimer **1** with most usual bidentate ligands [16].

This structure has been confirmed by the single crystal structure determination of complex **4b** (reaction 2, R = ^{i}Pr) (Fig. 1). It shows that the phosphine group is *trans* to the chlorine. The coordination of the phosphoryl (P=O) is indicated by a longer bond length (1.490(7) Å) than the P=O bond length of an uncoordinated phosphonate group [17]. Such a coordination of the phosphoryl group is shown on complex *cis*-$RhCl(CO)Ph_2PCH_2P(O)Ph_2$, obtained by reaction of the phosphine-phosphine oxide ligand $Ph_2P–CH_2–P(O)Ph_2$ on dimer **1** [15].

Analogous results are obtained by reaction of dimer **1** with the ether-phosphine ligands. Indeed, the spectroscopic data of the obtained compounds [18] are in accordance with the formation of complexes **5** and **6**.



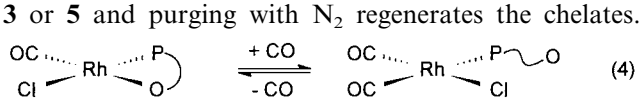
n = 2, 3.

5 (**5a** : n = 2 ; **5b** :n = 3)

6 (**6a** : n = 2 ; **6b** : n = 3)

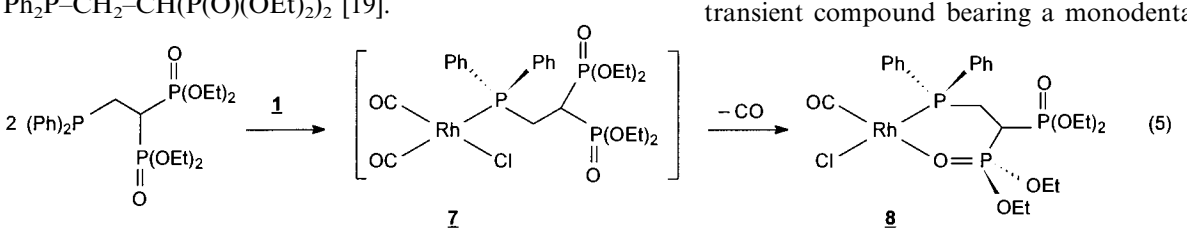
(3)

The hemilabile behaviour of the ligands is illustrated by the reaction of the chelate complexes with carbon monoxide: bubbling CO at r.t. through a dichloromethane solution of **4** or **6** quantitatively affords the complexes **3** or **5** and purging with N_2 regenerates the chelates.



4 or **6** **3** or **5** (4)

The lability of the phosphonate function is also well-established by the ^{31}P-NMR spectroscopic study of complex **8**, similarly obtained by reaction of dimer **1** with two equivalents of the phosphine-diphosphonate ligand $Ph_2P–CH_2–CH(P(O)(OEt)_2)_2$ [19].



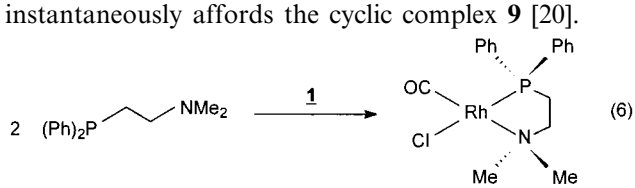
7 **8** (5)

Indeed, at 0°C, the ^{31}P-NMR spectrum of **8** in $CDCl_3$ presents three signals at 42.9, 27.1 and 19.0 ppm, respectively ascribed to the phosphine, the free phosphonate and the coordinated phosphonate groups. An increase in the temperature produces the coalescence of the two later, and only one signal at 22.4 ppm is observed for the phosphonate groups at 60°C, indicating the equivalence of these two functions. This rapid exchange between the phosphonates highlights their great lability.

The addition of the phosphonate-phosphine on dimer **2** has been recently described by Bischoff et al. [11]. The monodentate and bidentate complexation of the ligand have been observed and the hemilability of the ligand has been brought to the fore by reaction with carbon monoxide.

2.2. Complexation of amine-phosphine ligands

Reaction of **1** with two equivalents of $Ph_2P–CH_2–CH_2–NMe_2$ under the precedently described conditions instantaneously affords the cyclic complex **9** [20].



9 (6)

A careful monitoring of the reaction at low temperature has not allowed the spectroscopic observation of a transient compound bearing a monodentate ligand.

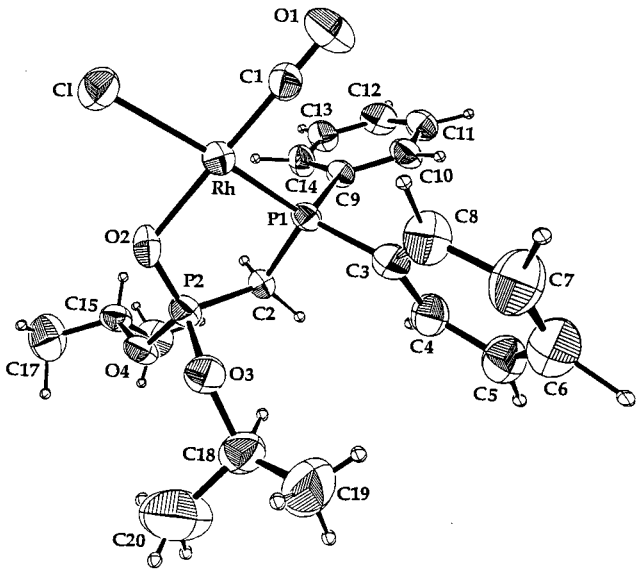
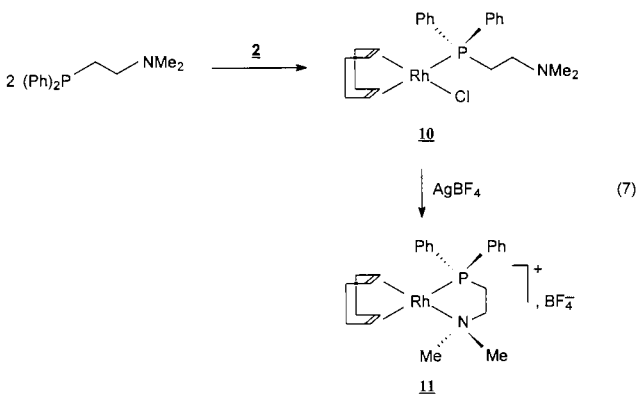


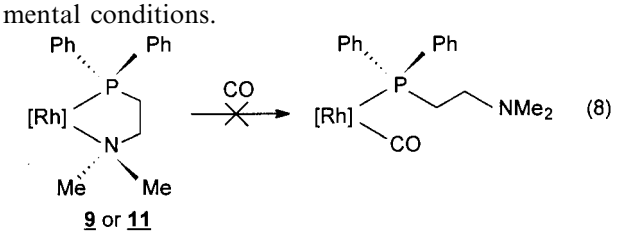
Fig. 1. Molecular structure of **4b**. Selected bond lengths (Å): Rh–Cl, 2.364(2); Rh–P(1), 2.206(2); Rh–O(2), 2.123(7); Rh–C(1), 1.79(1); P(2)–O(2), 1.490(7). Selected bond angles (°): Cl–Rh–O(2), 88.2(2); Cl–Rh–P(1), 174.52(8); Cl–Rh–C(1), 93.9(3); P(1)–Rh–O(2), 88.1(2); Rh–O(2)–P(2), 117.3(3).

On the other hand, reaction of this amine-phosphine with dimer **2** allows the isolation of monodentate complex **10**, with the phosphine group bound to the rhodium centre [21].



Addition of $AgBF_4$ on **10** leads to the chelate cation **11** [21]. A similar cyclic complex has been directly obtained by Anderson and Kumar by reaction of dimer **2** with $Ph_2PCH_2NMe_2$ in the presence of $NaBPh_4$ in acetonitrile [22].

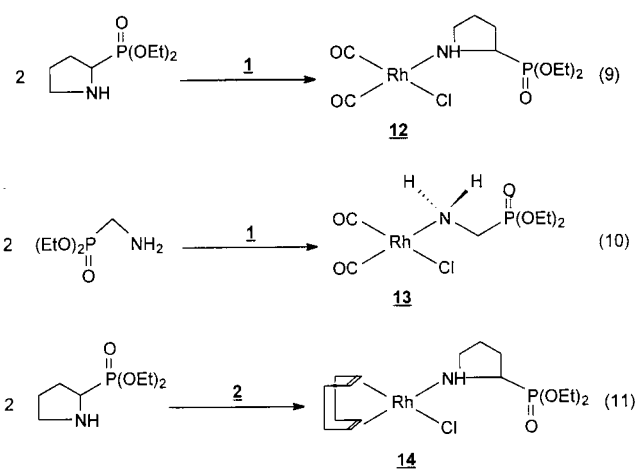
Since the amino group of complexes **9** and **11** remains bound to the metal centre in the presence of carbon monoxide pressure, this amine-phosphine ligand cannot be considered as hemilabile under these experimental conditions.



2.3. Complexation of amine-phosphonate ligands

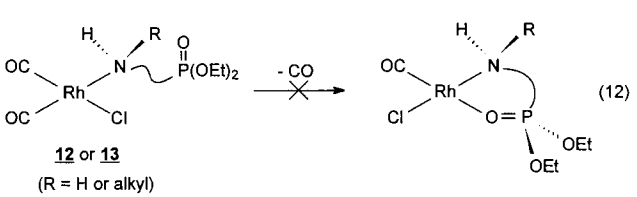
Concerning the amine-phosphonate ligands, the nature of the amino group is of importance. Indeed, when a tertiary amine-phosphonate is used, complexes obtained from reaction with dimer **1** or **2** are found very unstable and cannot be characterised. Similar reaction on **1** has been studied by Abu-Gnim and Amer with the tertiary amino-phosphine oxide ligand $Me_2N–CH_2–P(O)Ph_2$. It allows the characterisation of a compound which seems to be the chelate complex *cis*-$RhCl(CO)Me_2NCH_2P(O)Ph_2$ [23].

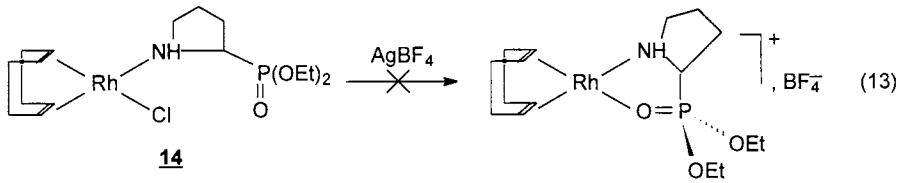
On the other hand, when the amino-phosphonate ligands bears a secondary or a primary amine function, complexes in which the ligand is monodentate and bound by the amino group [24] are isolated from reaction with dimer **1** or **2**.



The single crystal structure for complex **12** confirms this structure (Fig. 2). The P=O bond length (1.438(6) Å) is shorter than the one observed for the coordinated phosphonato group of **4b**. However, this value is identical to the one usually observed for free phosphonates [18].

These complexes, **12**–**14**, are very stable, and whatever the conditions (heating under vacuum or reaction with the CO trap Me_3NO for **12** and **13**, reaction with $AgBF_4$ for **14**), do not evolve toward the formation of the cyclic form with a bidentate ligand. Therefore, the amine-phosphonate compounds cannot be regarded as hemilabile bidentate ligands under the experimental conditions of this work.





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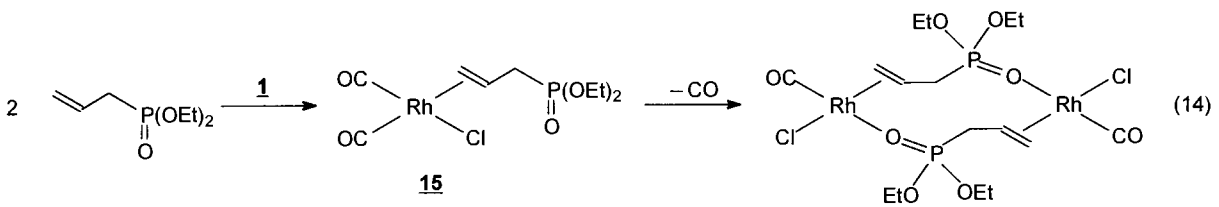
2.4. Complexation of allyl-phosphonate ligands

A more original result is observed in the reaction of the allyl phosphonate CH_2=CH–CH_2–P(O)$(OEt)_2$ with dimer **1** [24].



15

16

Indeed, if the first step is similar: cut of chloro-bridges and allyl coordination, the decarbonylation process does not lead to the chelate mononuclear complex, but to the dimer **16**, in which the two rhodium centres are bridged by two allyl-phosphonate ligands in the *cis* position. The single crystal structure for this original complex **16** has been realised (Fig. 3).

To our knowledge, **16** is the first bimetallic rhodium complex bearing chlorine and carbonyl ligands and two bridging mixed bidentate ligands in the *cis* position. Indeed, if Ph_2P–CH_2–P(S)Ph_2 (dppms) is known to give the cyclic monomer complex [Rh(Cl)(CO)(Ph_2P–CH_2–P(S)Ph_2) by reaction with **1** [25], in particular conditions it leads to the dimeric complex [Rh(Cl)(CO)(μ-dppms)$_2$Rh(Cl)(CO)], with the phosphine *trans* to the thiophosphoryl [26]. Similarly, the reaction of the rhodium carbonyl chloride dimer **1**

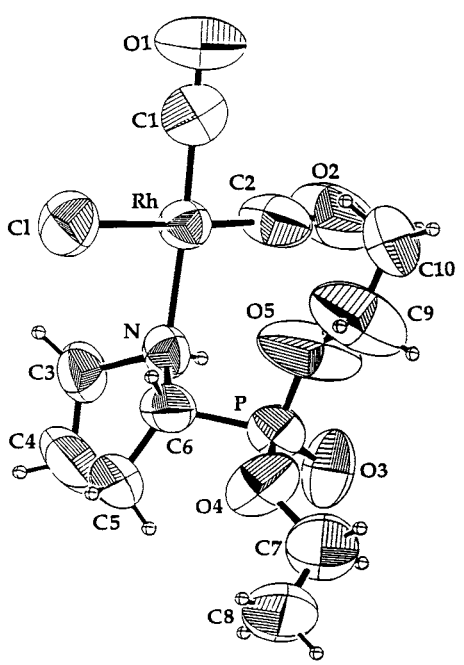


Fig. 2. Molecular structure of **12**. Selected bond lengths (Å): Rh–Cl, 2.335(2); Rh–N, 2.118(2); Rh–C(1), 1.802(9); Rh–C(2), 1.849(8); P–O(3), 1.438(6). Selected bond angles (°): Cl–Rh–N, 89.1(1); Cl–Rh–C(1), 88.4(2); Cl–Rh–C(2), 178.1(3); N–Rh–C(1), 177.1(3); N–Rh–C(2), 92.8(3); C(1)–Rh–C(2), 89.7(4).

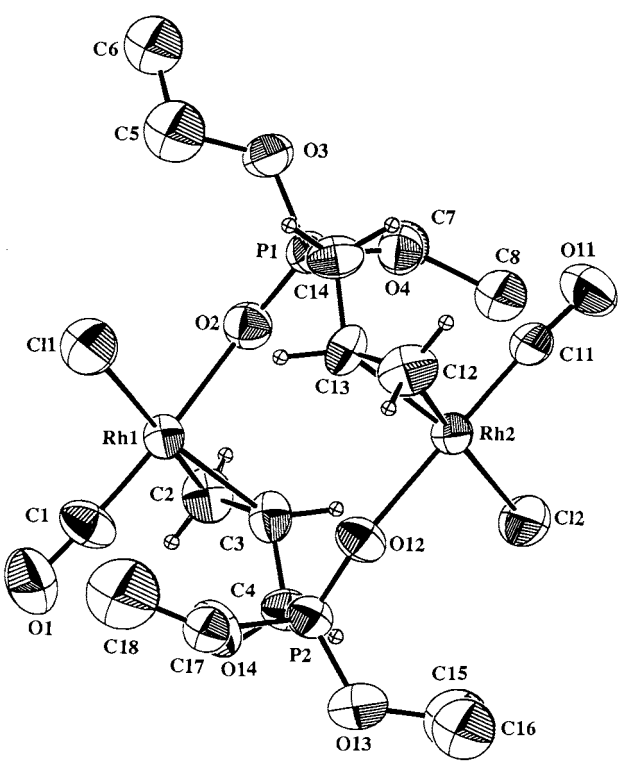
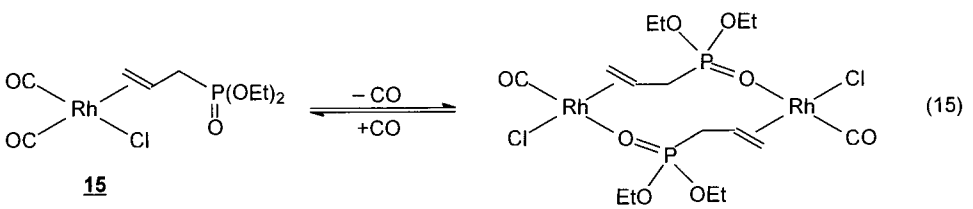


Fig. 3. Molecular structure of **16**. Selected bond lengths (Å): Rh(1)–Cl(1), 2.327(3); Rh(1)–O(2), 2.092(7); Rh(1)–C(1), 1.76(1); Rh(1)–C(2), 2.12(1); Rh(1)–C(3), 2.13(1); O(2)–P(1), 1.482(7). Selected bond angles (°): Cl(1)–Rh(1)–O(2), 90.6(2); Cl(1)–Rh(1)–C(1), 92.0(4); Cl(1)–Rh(1)–C(2), 165.9(3); Cl(1)–Rh(1)–C(3), 155.6(3); O(2)–Rh(1)–C(1), 175.1(4); C(2)–Rh(1)–C(3), 38.1(4); Rh(1)–O(2)–P(1), 145.4(4).

with $Ph_2P–CH_2–SMe$ has been shown to give the binuclear face-to-face complex with the phosphine *trans* to the thioether group [27].

The distance between the allyl and the phosphonate groups does not seem to be responsible for the formation of **16** since the cyclic monomeric complex [Rh(Cl)(L)(CH_2=CH–NHPh)], bearing a shorter bidentate ligand, has been described [28].

The hemilabile behaviour of the allyl-phosphonate ligand in complex **16** is illustrated by its reaction with carbon monoxide (below). Bubbling CO at r.t. through a dichloromethane solution of **16** affords the mononuclear complex **15** bearing the monodentate allyl-phosphonate ligand for which reversible coordination of the oxygen is observed; whereas the metal–olefin bond remains intact. Purging with nitrogen regenerates complex **16** indicating that the reaction is reversible.

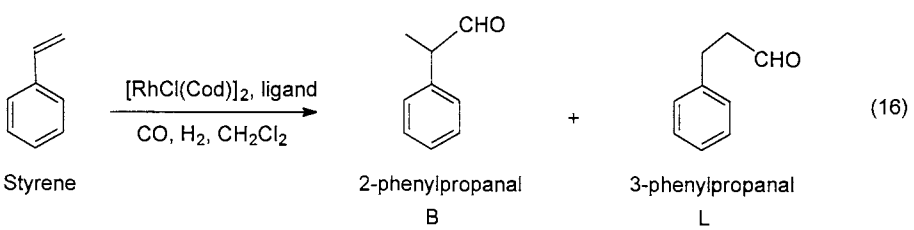


(15)

To our knowledge, this reaction is the first example that shows the hemilability of a mixed bidentate ligand with an allyl moiety. Consequently, this new type of complex represents an interesting potential model for the study of catalytic functionalisation of olefins involving labile ligands.

2.5. Evaluation of the catalytic activity of the bifunctional ligands

We have studied the activity of the above described mixed-donor ligands on the catalytic hydroformylation of styrene. The transformation of styrene under carbon monoxide and dihydrogen pressure with dimer **2** leads to two isomeric aldehydes.



(16)

Under the conditions usually used for the study of this reaction (CH_2Cl_2, 80°C, 1 h, 40 bar), Table 1 shows that if the conversion of styrene into aldehydes is high, the selectivity (B/L) is lower than the one obtained with the reference PPh_3.

More interestingly, Table 2 shows good conversion and excellent selectivity at 25°C for some of our ligands, in particular the amino-phosphine and the amino-phosphonate compounds, whereas PPh_3 remains inactive under the same conditions.

It is noteworthy that the best results are obtained with the tertiary amine-phosphonate ligand, which is the only one to give no stable complex with dimer **1** or **2**. This can show the importance of the lability of the ligands in catalytic reactions.

3. Conclusion

We have studied the coordination to rhodium of various bifunctional potentially hemilabile ligands. Thus, some compounds like amino-phosphonates, exclusively give monodentate complexes. Conversely, the amino-phosphine ligands lead to bidentate complexes. In these model studies, we have seen no evidence for hemilabile behaviour of the ligands.

On the other hand, compounds like ether-phosphine, phosphine-phosphonate and allyl-phosphonate are perfectly hemilabile and the monodentate and bidentate forms of the ligands can be observed by complexation on rhodium. Moreover, this study has allowed the synthesis of original complexes that represent interesting models for the study of catalytic reactions.

Examination of the catalytic activity of the mixed ligands on the hydroformylation of styrene has shown promising results.

4. Experimental

All manipulations were performed under an atmosphere of nitrogen with standard Schlenk techniques, and all solvents were distilled under an inert atmosphere from an appropriate drying agent [29].

IR spectra were recorded in dichloromethane on a Perkin-Elmer 1430 spectrophotometer. The ^{31}P-NMR (121.49MHz) spectra were obtained in $CDCl_3$ on a Bruker AC300 spectrometer using 87% HPO_4 as an external standard.

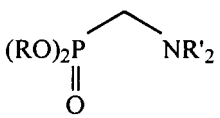
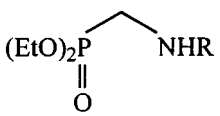
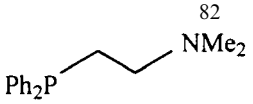
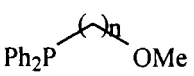
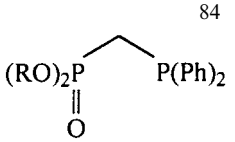
The hydroformylation experiments were conducted in a stainless steel autoclave equipped with a mechanical stirrer. The styrene in dichloromethane was progressively introduce with a HPLC Gilson 307 pump.

GC analysis were made on a HP5890 equipped with a 25×0.25 mm SE30 capillary column. Quantitative measurements used toluene as internal standard.

4.1. General procedure for the preparation of complexes **4**, **6**, **8**, **9**, **12**, **13** and **16**

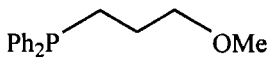
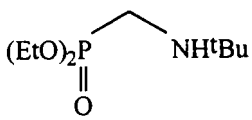
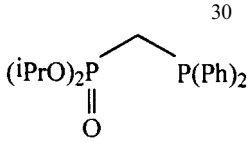
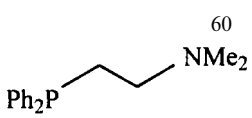
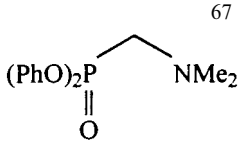
To a solution of $[RhCl(CO)_2]_2$ **1** (0.25 mmol, 97 mg) in 10 ml of dichloromethane, two equivalents of ligand (0.50 mmol) are added at r.t. The reaction is monitored by IR spectroscopy. After 30 min stirring, the two bands ν(CO) of **1** (2080, 2030 cm^{-1}) have disappeared and the solvent is removed under vacuum. The residue is washed with hexane and recrystallised in a mixture of hexane:dichloromethane 2:1.

Table 1
Hydroformylation of styrene at 80°C[a]

Ligand	Conversion (%)	Selectivity (%)
PPh_3	77	92/8
	75	64/36
		
	55	65/35
		
	82	66/34
		
	80	87/13
		
	84	63/37
		

[a] Pressure CO/H_2 (1:1) = 40 atm, 1 h; $[RhCl(COD)_2]$/ligand/styrene = 1:**4**:167, for a monofunctional ligand; $[RhCl(COD)_2]$/ligand/styrene = 1: **2**:167, for a bifunctional ligand.

Table 2
Hydroformylation of styrene at 25°C[a]

Ligand	Conversion (%)	Selectivity (%)
Without ligand	0	—
	0	—
		
PPh_3	1	100/0
	8	100/0
		
	30	99/1
		
	60	99/1
		
	67	99/1
		

Pressure CO/H_2 (1:1) = 40 atm, 15 h; $[RhCl(COD)_2]$/ligand/styrene = 1:**4**:167, for a monofunctional ligand; $[RhCl(COD)_2]$/ligand/styrene = 1:**2**:167, for a bifunctional ligand.

4.2. General procedure for the preparation of complexes **10**, **14** and **15**

Two equivalents of ligands (0.40 mmol) are added in a dichloromethane solution (10 ml) of $[RhCl(COD)]_2$ **2** (100 mg, 0.20 mmol) at r.t. After 1 h stirring, the solvent is removed and the residue washed with hexane. The complexes are recrystallised in a mixture of hexane:dichloromethane 2:1.

Table 3
Crystal data and structure refinement for **4b**

Formula	$RhClP_2C_{20}H_{26}O_4$
Molecular weight	530.73
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.988(6)
b (Å)	11.586(7)
c (Å)	12.621(6)
α (°)	66.16(5)
β (°)	73.14(4)
γ (°)	83.21(5)
V (Å^3)	1150(1)
Z	2
ρ_{calc} (g cm^{-3})	1.532
$F(000)$	270
μ(Mo–K$_\alpha$)	10.057
T (K)	294
Crystal size (mm)	$0.25 \times 0.28 \times 0.30$
Radiation	Mo–K$_\alpha$
Max 2θ (°)	50
Range of hkl	0–10; −13–13; −14–14
No. of reflections measured	4324
no. of reflections observed ($I > \sigma(I)$)	2495 (4σ)
R_{int} (from merging equiv. reflections)	0.024
R (isotropic)	0.088
R (anisotropic)	0.072
N(obs.)/N(var.)	2495/331
R	0.061
R_w	0.053
$w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.004F_o^2)^2]^{-1/2}$	
S_w	2.156
Max residual (e Å^{-3})	1.41
Δ/σ	2.11

Table 4
Crystal data and structure refinement for **12**

Formula	$RhClPC_{10}H_{18}NO_5$
Molecular weight	401.59
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.888(2)
b (Å)	10.547(3)
c (Å)	10.804(4)
α (°)	61.89(3)
β (°)	68.13(3)
γ (°)	74.04(3)
V (Å^3)	822.9(5)
Z	2
ρ_{calc} (g cm^{-3})	1.621
$F(000)$	404
μ(Mo–K$_\alpha$) (cm^{-1})	12.923
T (K)	294
Crystal size (mm)	$0.20 \times 0.30 \times 0.30$
Radiation	Mo–K$_\alpha$
Max 2θ (°)	50
Range of hkl	0–10; −12–12; −12–12
No. of reflections measured	4235
No. of reflections observed ($I > \sigma(I)$)	1873 (3σ)
R_{int} (from merging equiv. reflections)	0.026
R (isotropic)	0.085
R (anisotropic)	0.057
N(obs.)/N(var.)	1873/197
R	0.045
R_w	0.045
$w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.004F_o^2)^2]^{-1/2}$	
S_w	0.785
Max residual (e Å^{-3})	0.66
Δ/σ	0.02

4.3. General procedure for the preparation of complex **11**

To a solution of [RhCl(COD)] **2** (80 mg, 0.16 mmol) in 10 ml of dichloromethane two equivalents of ligand (0. 32 mmol) are added. After 1 h stirring, the solution is cooled to −5°C and $AgBF_4$ (63 mg, 0.32 mmol) in 15 ml of THF is added. After 30 min stirring, the mixture of solvents is removed. The residue is dissolved in 10 ml of dichloromethane and the solution is filtered to eliminate any AgCl formed. The complex is recrystallised in a mixture of hexane:dichloromethane 2:1.

4.4. Crystal structure analysis for complexes **4b**, **12** and **16**

The microcrystals used for the X-ray studies have been obtained by recrystallisation in a mixture of dichloromethane:hexane 1:2.

The data were collected on a CAD-4 Enraf-Nonius difractometer with graphite-monochromated Mo–K$_\alpha$ radiation. Tables 3–5 give the experimental data for the structures of **4b**, **12** and **16**. The unit cell parameters are determined by least-squares fitting of a set of 25 high-θ reflections. After Lorentz and polarisation corrections, the structures were solved with direct methods, scale factor refinement and Fourier differences. The entire structures were refined by full-matrix least-squares techniques. Atomic scattering factors were taken from [30]. All calculations were performed on a digital Microvax 3100 computer with the MolEN package (Enraf-Nonius, 1990). The graphic illustrations have been realised by the ORTEP program.

4.5. General procedure for the hydroformylation reactions

In a typical run, 0.012 mmol of $[RhCl(COD)]_2$ (5.9 mg) and 0.024 mmol of bifunctional ligand (or 0.048 mmol of monofunctional ligand) in 4 ml of dichoromethane were placed in the autoclave under nitrogen atmosphere. The autoclave was pressurised with CO (20 bar) and H_2 (20 bar) and thermostated at the required temperature. The solution of styrene (25.3 mmol, 2.9 ml) and toluene (25.4 mmol, 2.7 ml) in 25 ml of dichloromethane was introduced with the high pres-

Table 5
Crystal data and structure refinement for **16**

Formula	$Rh_2Cl_2P_2C_{16}H_{30}O_8$
Molecular weight	689.08
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	13.289(3)
b (Å)	17.511(9)
c (Å)	22.538(5)
V (Å^3)	5245(3)
Z	8
ρ_{calc} (g cm^{-3})	1.745
$F(000)$	2752
μ(Mo–K$_\alpha$) (cm^{-1})	16.00
T (K)	293
Crystal size (mm)	$0.15 \times 0.30 \times 0.40$
Radiation	Mo–K$_\alpha$
Max 2θ (°)	50
Range of *hkl*	0–15; 0–20; 0–26
No. of reflections measured	5124
No. of reflections observed ($I > \sigma(I)$)	2603 (4.0σ)
R (isotropic)	0.095
R (anisotropic)	0.072
Fourier difference	0.36–0.15
N(obs.)/N(var.)	2603/256
R	0.061
R_w	0.048
$w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.004F_o^2)^2]^{-1/2}$	
S_w	3.37
Max residual (e Å^3)	0.48
Δ/σ	0.02

sure pump. After the reaction time quoted in Tables 1 and 2, the autoclave was cooled and flushed with nitrogen. The reaction products were analysed by GC.

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[12] (a) **3a**: ν(CO): 2085, 2000 cm^{-1}, ν(PO): 1260 cm^{-1}. (b) **3b**: ν(CO): 2090, 2000 cm^{-1}, ν(PO): 1260 cm^{-1}; ^{31}P-NMR, δ: 24.1 ppm (dd, $^1J_{PRh} = 115.9$ Hz, $^3J_{PP(O)} = 47.8$ Hz), 25.5 ppm (d, $^3J_{PP(O)} = 47.8$ Hz). The observation of two almost equally intense bands in the ν(CO) region of the IR spectrum ($\approx$2090, 2000 cm^{-1}, CH_2Cl_2) is in accord with *cis* Rh(Cl)(CO)$_2$(L) complexes [13]. A ^{31}P-NMR shift downfield from the corresponding resonance of uncoordinated phosphine and a $^1J_{PRh}$ of 115–125 Hz are observed.
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[14] (a) **4a**: ν(CO): 1990 cm^{-1}, ν(PO): 1160 cm^{-1}. (b) **4b**: ν(CO): 1990 cm^{-1}, ν(PO): 1160 cm^{-1}; ^{31}P-NMR, δ: 33.3 ppm (d, $^1J_{PRh} = 158$ Hz), 45.7 ppm (s). The observation of one intense band in the ν(CO) region of the IR spectrum ($\approx$1990 cm^{-1}, CH_2Cl_2) is in accord with *cis*-Rh(Cl)(CO)(L)(L′) complexes [15]. The value of the IR frequency ν(P=O) represents an energy decrease of ca. 100 cm^{-1} showing the coordination of the phosphonate group [11]. A ^{31}P-NMR shift downfield from the corresponding resonance of free phosphonate is observed.
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[18] (a) **5a**: ν(CO): 2095, 2000 cm^{-1}; ^{31}P-NMR, δ: 28.0 ppm (d, $^1J_{PRh} = 125.0$Hz). (b) **5b**: ν(CO): 2080, 2000 cm^{-1}; ^{31}P-NMR, δ: 31.3 ppm (d, $^1J_{PRh} = 124.8$Hz). (c) **6a**: ν(CO): 1990 cm^{-1}; ^{31}P-NMR, δ: 38.1 ppm (d, $^1J_{PRh} = 173.7$Hz). (d) **6b**: ν(CO): 1970 cm^{-1}; ^{31}P-NMR, δ: 43.0 ppm (d, $^1J_{PRh} = 173.2$Hz).
[19] **8**: ν(CO): 1990 cm^{-1}; ^{31}P-NMR (273 K), δ: 42.9 ppm (dd, $^1J_{PRh} = 167.7$Hz, $^3J_{PP(O)} = 45.5$Hz), 27.1 ppm (d, $^2J_{P(O)P(O)} = 7.5$Hz), 19.0 ppm (dd, $^3J_{P(O)P} = 45.5$Hz, $^2J_{P(O)P(O)} = 45.5$Hz).
[20] One band is observed in the ν(CO) region of the IR spectrum; the ^{31}P-NMR resonance of the phosphine (60.6 ppm) is shift downfield from the corresponding resonance of free phosphine (-20.0 ppm), $^1J_{PRh} = 172.5$Hz.
[21] (a) **10**: ^{31}P-NMR ($CDCl_3$), δ: 26.3 ppm (d, $J = 149.2$Hz). (b) **11**: ^{31}P-NMR ($CDCl_3$), δ: 41.7 ppm (d, $J = 160.4$Hz).
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