Hydroformylation of styrene and 1-octene catalyzed by binuclear and oligomer rhodium(I) complexes containing the bis-*p*-phosphinito ligands [(*p*-Ph₂POC₆H₄)₂X] (X = O, CMe₂, S)

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Abstract

The reactions of rhodium(I) substrates with the ligands [(*p*-Ph₂POC₆H₄)₂X] (X = O, **1**; X = CMe₂, **2**; X = S, **3**) have been studied with the aim to obtain rhodium(I) complexes to utilize as precatalysts in hydroformylation of olefins. The reactions of [Rh(CO)₂Cl]₂ with ligands **1–3**, in a Rh to ligand 1:1 molar ratio, in toluene, at room temperature afford the products [Rh(CO)(Cl)(μ-L)]₂ (L = **1–3**). The reactions of [Rh(acac)(CO)₂] with **2** are strongly dependent on the ligand nature and experimental conditions. The product formed in a 1:0.5 Rh to ligand molar ratio is dimer with the metal centers held together by the ligand, while the product formed in a 1:1 molar ratio is oligomer. The in situ catalytic systems formed either by [Rh(CO)₂Cl]₂ and ligands **1–3** or by [Rh(acac)(CO)₂] and **2**, at variable ligand-to-metal molar ratio, have been employed in the hydroformylation of styrene and 1-octene. Almost quantitative conversion of styrene was achieved with the catalytic system formed by [Rh(acac)(CO)₂] and **2**, in a 1:0.5 molar ratio, operating at 60°C and 40 atm. The chemoselectivity of the reaction was very high being the linear (L) and the branched (B) aldehydes about 99.9% of the reaction products. The terminal aliphatic olefin 1-octene was hydroformylated with lower conversion in the aldehydes with respect to styrene and isomerization and hydrogenation of the double bond occurred in great extent. Lowering the temperature, the conversion of 1-octene increases but the chemoselectivity drastically decreases owing to the formation of more isomerization products. The results have been explained considering both the flexibility and the number of phosphorus atoms (considering each of them as a monodentate ligand) coordinated to each metal center in the trigonal bipyramidal hydridorhodium intermediates formed, namely {[Rh(H)(CO)₃]₂(μ-**2**)} (1:0.5 [Rh(acac)(CO)₂] to **2** molar ratio) and the oligomer [Rh(H)(CO)₂(μ-**2**)]n (1:1 [Rh(acac)(CO)₂] to **2** molar ratio). In the presence of an excess of ligand **2** the conversion in the aldehydes drastically decreases owing to the rigidity of the intermediate hydridorhodium oligomer species formed. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Hydroformylation; Styrene; 1-Octene

1. Introduction

Recent homogeneous catalysis studies indicate that structural characteristics of coordinated

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diphosphine ligands produce relevant effects on the activity and selectivity induced by the catalyst. Casey et al. [1,2] introduced recently the concepts of 'natural bite angle' and 'flexibility' as steric parameters of diphosphine ligands. The modulation of the 'natural bite angle' and of the 'flexibility' can give rise to metal complexes having a variety of structures. This possibility results of particular relevance in homogeneous catalysis. In the rhodium catalyzed hydroformylation of olefins, the natural bite angle of the chelating diphosphine used for the synthesis of the catalytic system influences the regioselectivity of the catalytic process. Casey et al. [1,2] showed that using the [2,2′-bis(diphenylphosphino)methyl]-1,1′-biphenyl ligand (BISBI), which coordinates to rhodium in the trigonal bipyramidal intermediate species as bis-equatorial ligand (P–Rh–P angle ca. 120°), the regioselectivity in the linear aldehyde is 66:1, while using 1,2-bis(diphenylphosphino)ethane, which coordinates as equatorial–axial ligand (P–Rh–P angle ca. 90°) the regioselectivity results lowered to 2.1:1.

Recently we have synthesized large valence angle bis-p-phosphinito ligands (p-Ph$_2$POC$_6$H$_4$)$_2$X (X = O, **1**; X = CMe$_2$, **2**; X = S; **3**) (Fig. 1) and studied their applications in reactions with [Ru(p-cymene)Cl$_2$]$_2$, [Rh(C$_5$Me$_5$)Cl$_2$]$_2$ and [Rh(C$_5$H$_5$)(CO)$_2$] [3].

Ligands **1–3** have been designed to induce a bridging coordination in transition metal complexes. Their geometry have been most accurately predicted by AMPAC (MOPAC) calculations [4]. It has showed that the P–O bond distances are nearly the same for all the ligands

indicating that the changes in the X-group have only a minor influence on the electronic properties of the phosphorus donor. This result was confirmed by the ^{31}P{^{1}H} NMR chemical shift values found for the ligands. Interestingly the P...P separation ranges from 9.848 Å for **2** to 11.506 Å for **1** indicating that cis or trans chelation to one metal atom is hindered using these ligands. The C–X–C angles range from 100.3° for X = S to 115.9° for X = O; the C–X–C values are not directly related to the P...P separation. This work deals with the synthesis of binuclear rhodium(I) complexes containing the ligands **1–3** and their use, as precatalysts, in the hydroformylation of styrene and 1-octene.

2. Results and discussion

2.1. Synthesis

The reactions of rhodium(I) substrates with the ligands [(p-Ph$_2$POC$_6$H$_4$)$_2$X] (X = O, **1**; X = CMe$_2$, **2**; X = S, **3**) have been studied with the aim to obtain rhodium(I) complexes to utilize as precatalysts in hydroformylation of olefins. The geometry of ligands induce formation of rhodium(I) binuclear or oligomer complexes which have the potential of catalyzing hydroformylation reactions more efficiently. The reactions of [Rh(CO)$_2$Cl]$_2$ with ligands **1–3** in a 1:1 rhodium to ligand molar ratio, in toluene at room temperature, afford the products [Rh(CO)(Cl)(μ-L)]$_2$ (L = **1–3**), as yellow-orange moderate air-stable solids. The compounds have been characterized by analytical data. Their formulation as dimers was supported by the presence of the corresponding molecular peak in the electron impact mass spectra. Spectroscopic data also support the proposed structures. The IR spectra, in nujol mull, show only one ν(CO) band in the range 1985–1990 cm^{-1} as expected for a centrosymmetric binuclear rhodium(I) complex in which two square planar units, con-
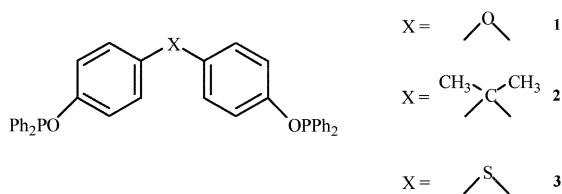
Fig. 1.

taining the CO ligand in trans position to Cl, are held together by two bridging bidentate ligands L. A similar structure was reported for the analogous complexes containing bridging dppm ligands $[Rh(CO)Cl(\mu$-dppm$)]_2$ (dppm = bis(diphenylphosphino)methane) [5]. The $^{31}P\{^1H\}$ NMR spectra, in $CDCl_3$ solution, show for complexes $[Rh(CO)(Cl)(\mu$-L$)]_2$ (L = **1–3**) a doublet centered respectively at δ 125.8 ppm (^1J(RhP) = 145.8 Hz) (for L = **1**), δ 125.5 ppm (^1J(RhP) = 143.5 Hz) (for L = **2**), δ 124.6 ppm (^1J(RhP) = 145.2 Hz) (for L = **3**). The ^1H NMR spectra in $CDCl_3$ exhibit the resonances associated with ligands **1–3** in the correct integration ratio.

The dimeric structure of $[Rh(CO)(Cl)(\mu$-L$)]_2$ (L = **1–3**) is surprising; in fact, starting from $\{[Ru(p$-cymene$)(Cl)(CH_3CN)](\mu$-**1–3**$)\}[PF_6]_2$ and $\{[Rh(\eta^5$-$C_5Me_5)(Cl)(CH_3CN)](\mu$-**1–3**$)\}[PF_6]_2$ were not able [3] to obtain the corresponding compounds in which the metal centers are held together by two bridging phosphinito ligands. Very likely the presence of two bridging ligands induces strong repulsive interactions between the phenyl groups of the phosphinito ligands and the isopropyl moiety of the *p*-cymene or the methyls of the η^5-pentamethylcyclopentadienyl ligand and prevents the formation of these species. It is very likely that the presence of small ligands, as CO and Cl, coordinated to rhodium(I) center and in cis position to the phosphorus atoms allows the formation of binuclear complexes as $[Rh(CO)(Cl)(\mu$-L$)]_2$ (L = **1–3**). For example [6], it is well-known that bridging coordination of 2-(diphenylphosphino)pyridine (Ph_2PPy), because of its rigidity and small bite angle, requires small ligands cis to the phosphorus atom; consequently bimetallic complexes in which two d^8 metal centers are surrounded by two 'head to tail' Ph_2PPy have been synthesized only when CO, halogenides or CNMe are the coordinated ligands cis to phosphorus.

The reactions of $[Rh(acac)(CO)_2]$ with **1–3** are strongly dependent on the ligand nature and experimental conditions. We report in detail the

results of the reaction with ligand **2** because, in this case, the nature of the products was well established. However, the reactions with **1** and **3** proceed similarly. Following the reaction of $[Rh(acac)(CO)_2]$ with **2** by IR and $^{31}P\{^1H\}$ NMR spectra we observed that the addition of **2** to $[Rh(acac)(CO)_2]$ in a 1:0.5 Rh to ligand molar ratio, in toluene, produces two doublets of different intensity in the $^{31}P\{^1H\}$ NMR spectrum, the major product at δ 139.6 ppm (^1J(RhP) = 199.5 Hz) and the minor product at δ 139.84 ppm (^1J(RhP) = 199.5 Hz). A third signal of very low intensity was observed at δ 140.09 ppm (^1J(RhP) = 199.3). In the IR spectrum the ν(CO) bands of $[Rh(acac)(CO)_2]$ have been replaced by a ν(CO) band at 1993 cm^{-1}. Further addition of **2**, until to reach a 1:1 Rh to ligand molar ratio, produces in the $^{31}P\{^1H\}$ NMR spectrum disappearance of the signal centered at δ 139.6 ppm and increase of the signal at δ 139.84 ppm; the ν(CO) in the IR spectrum remains nearly unchanged. In a separate experiment, the product formed in the reaction between $[Rh(acac)(CO)_2]$ and **2**, in a 1:0.5 Rh to ligand molar ratio was isolated as a red-orange solid, soluble in benzene and chlorinated solvents. Analytical and spectroscopic data support its formulation as the dimer $\{[Rh(acac)(CO)]_2$-$(\mu$-**2**$)\}$, with the metal centers hold together by the ligand **2** (Fig. 2).

In accordance the IR spectrum, nujol mull, showed a ν(CO) band at 1992 cm^{-1} and in the $^{31}P\{^1H\}$ NMR spectrum, in C_6D_6 solution, a
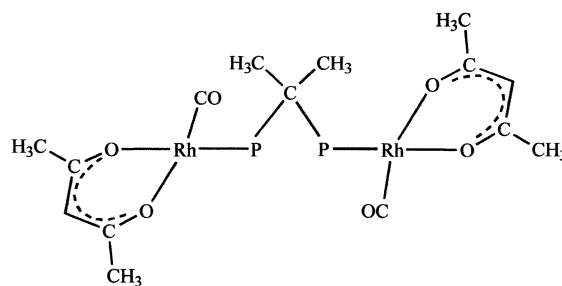

Fig. 2.

doublet centered at δ 139.63 ppm (^1J(RhP) = 199.2 Hz) appeared.

Experimental data indicated that the product formed in the reaction of [Rh(acac)(CO)$_2$] with **2** in a 1:1 Rh to ligand molar ratio, was the oligomer [Rh(acac)(CO)(μ-**2**)]$_n$. Considering the acac ligand as chelate, a structure in which the rhodium(I) is five-coordinate and the trigonal bipyramidal units are held together by bridging ligands **2** seems very likely. The presence of a single resonance in the ^{31}P{^{1}H} NMR spectrum in C$_6$D$_6$, supports a structure with the phosphorus atoms of **2** both coordinate to different rhodium centers either in the equatorial plane or in the axial position. The unchanged value of the ν(CO) with respect to {[Rh(acac)(CO)]$_2$(μ-**2**)} supports the trans arrangement of the CO to carbon atom of the acac. Moreover, in the trigonal bipyramidal structures, the preferred configuration seems that with bulky ligands in the equatorial position [7]. However a structure in which square planar units, formed by coordination of the acac as monodentate anionic ligand, are held together by bridging ligands **2** does not ruled out.

2.2. Catalytic runs

The catalytic systems based on [Rh(acac)(CO)$_2$] or [Rh(CO)$_2$Cl]$_2$ and the ligand [(p-Ph$_2$POC$_6$H$_4$)$_2$CMe$_2$], **2**, have been used in the hydroformylation reactions. However more important results have been compared with those obtained using the catalytic systems [Rh(acac)(CO)$_2$] and **1** or **3**. Styrene and 1-octene have been chosen as reference substrates to test the activity of these new catalytic systems. The hydroformylation reactions were carried out in toluene solution under a hydrogen–carbon monoxide 1:1 pressure. Either the preformed precatalyst or the in situ systems formed by [Rh(acac)(CO)$_2$] or [Rh(CO)$_2$Cl]$_2$ and ligands **1–3**, at variable ligand-to-metal molar ratio, have been employed as catalysts. Preliminary was ascertained that in catalytic conditions the

[HRh(CO)$_4$], [Rh$_4$(CO)$_{12}$] and [Rh$_6$(CO)$_{16}$] species were not formed.

The results obtained in the hydroformylation of styrene are reported in Table 1. The reactions have been carried out at temperatures of 40 and 60°C under 20 and 40 atm of CO and H$_2$ (1:1). It is evident that the catalytic system formed by [Rh(acac)(CO)$_2$] and **2**, in a 1:0.5 or 1:1 Rh to ligand molar ratio, displays a catalytic activity, in the hydroformylation of styrene, more than that formed by [Rh(CO)$_2$Cl]$_2$ and **2**. Almost quantitative conversion of styrene has been achieved operating at 60°C and 40 atm (conversion 99.9%) (entry 8) or at 60°C and 20 atm (conversion 92%) (entry 4) for 6 h, at a styrene-to-catalyst ratio of 500. The chemoselectivity of the reaction was very high being the linear (L) and the branched (B) aldehydes about 99.9% of the reaction products. The molar ratio between [Rh(acac)(CO)$_2$] and **2** drastically influences the conversion of styrene; operating at 40°C and 20 atm and using 1:0.5, 1:1, and 1:2 [Rh(acac)(CO)$_2$] to ligand molar ratios the conversion values are 56.2, 46.7 and 2.9, respectively (entries **1–3**). The CO–H$_2$ pressure influences the rate of the reaction; operating at 40°C the conversion raises from 56.2 to 76.8% (entries 1 and 6) increasing the pressure from 20 to 40 atm. As expected for the rhodium-catalyzed hydroformylation of styrene, the branched aldehyde was formed in more extent than the linear one [8]. The regioselectivity, expressed as the ratio B/L, is high and in all experiments at 40°C, independently from the pressure, its value reaches about 26.

A comparison of the data obtained with [Rh(acac)(CO)$_2$] and **2**, in a 1:0.5 molar ratio, with the corresponding ones using ligands 1 and 3 do not evidence significant changes in the conversion, chemoselectivity and regioselectivity values (entries 8, 9, 10).

The catalytic system based on [Rh(CO)$_2$Cl]$_2$ and **2** resulted less efficient than [Rh(acac)(CO)$_2$] and **2**. In fact, operating at 60°C and 20 atm the conversion of styrene was of 30.1% and at 40°C only of 5.4% (entries 12, 11). Also the

Table 1
Hydroformylation of styrene[a]

Entry	[L]/[Rh]	P (atm)	T (°C)	Conversion (%)	Hydr.[b]	Aldehydes		L/B[d]	TOF[e]
						Branched[c]	Linear[c]		
1	0.5	20	40	56.2	2.7	92.3	5	5/95	47
2	1	20	40	46.7	4.5	91.9	3.6	4/96	39
3	2	20	40	2.9	6.9	31	–	0/100	2.4
4	0.5	20	60	92.0	–	84	16	16/84	76.7
5	1	20	60	95.1	3.3	85.6	11.1	12/88	79.2
6	0.5	40	40	76.8	2.5	93.7	3.8	4/96	64
7	1	40	40	65.1	4.7	91.8	3.5	4/96	54.2
8	0.5	40	60	99.9	–	82	18	18/82	83.2
9[f]	0.5	40	60	99	–	82	18	18/82	82.5
10[g]	0.5	40	60	99.1	–	82	18	18/82	82.6
11[h]	1	20	40	5.4	29.6	57.4	13.0	19/81	4.5
12[h]	1	20	60	30.1	25.0	61.1	13.9	19/81	25.1

[a]Reaction conditions: solvent toluene (10 ml); $CO/H_2 = 1$; catalyst = $[Rh(acac)(CO)_2]/[(p\text{-}Ph_2POC_6H_4)_2CMe_2]$; catalyst:styrene = 1:500.
[b]Ethylbenzene.
[c]Branched aldehyde 2-phenylpropionaldehyde, linear aldehyde 3-phenylpropionaldehyde.
[d]L/B = linear/branched.
[e]TOF = [moles of product/moles of catalyst × reaction time].
[f]L = $[(p\text{-}Ph_2POC_6H_4)_2O]$.
[g]L = $[(p\text{-}Ph_2POC_6H_4)_2S]$.
[h]Catalyst = $[Rh(CO)_2Cl]_2/[(p\text{-}Ph_2POC_6H_4)_2CMe_2]$.

chemo- and regioselectivity result lower than those observed with the catalytic system [Rh(acac)(CO)$_2$] and **2**.

The results obtained in the hydroformylation of 1-octene are reported in Table 2. In the presence of the catalytic systems formed by [Rh(acac)(CO)$_2$] or [Rh(CO)$_2$Cl]$_2$ and **2** the terminal aliphatic olefin 1-octene was hydroformylated with lower conversion in the aldehydes with respect to styrene. With 1-octene, isomer-

Table 2
Hydroformylation of 1-octene[a]

Entry	[L]/[Rh]	P (atm)	T (°C)	Conversion (%)	Isomeriz	Hydr.[b]	Aldehydes		L/B[d]	TOF[e]
							Branched[c]	Linear[c]		
13	0.5	20	40	71.2	35.3	2.8	25.4	36.5	59/41	37
14	1	20	40	88.2	12.1	17.9	28.7	41.3	59/41	73.5
15	10	20	40	78.8	95.7	4.3	–	–	–	5.5
16	0.5	20	60	62.5	13.6	6.1	33.4	46.9	58/42	52
17	1	20	60	60.9	11	5.7	34.8	48.5	58/42	50.7
18	0.5	40	40	91.6	5.1	1.5	42.7	50.7	54/46	76.3
19	1	40	40	81.2	13.1	1.9	37.0	48.0	56/44	67.7
20[f]	1	20	40	72.5	91.6	–	4.7	3.7	56/44	60.4
21[g]	1	20	60	73.8	42.0	13.3	13.2	31.5	70/30	61.5

[a]Reaction conditions: solvent toluene (10 ml); $CO/H_2 = 1$; catalyst = $[Rh(acac)(CO)_2]/[(p\text{-}Ph_2POC_6H_4)_2CMe_2]$; catalyst:styrene = 1:500.
[b]Octane.
[c]Branched aldehyde 2-methyloctanal, linear aldehyde *n*-nonal.
[d]L/B = linear/branched.
[e]TOF = [moles of product/moles of catalyst × reaction time].
[f,g]Catalyst = $[Rh(CO)_2Cl]_2/[(p\text{-}Ph_2POC_6H_4)_2CMe_2]$.

ization and hydrogenation of the double bond occurred in great extent during the reaction and the aldehydes 1-nonanal and 2-methyloctanal have been obtained together with octane and isomerization products. Surprisingly, lowering the temperature, the conversion of 1-octene increases but the chemoselectivity drastically decreases owing to the formation of more isomerization products. In the rhodium-catalyzed hydroformylation the reduction of the pressure induces decrease in the aldehydes because the σ-acyl derivative is formed in minor yield. This was observed also in the hydroformylation of 1-octene with $[Rh(acac)(CO)_2]$ and **2** and is evident when we consider the amount of aldehydes formed. The trend of the conversion is pointing in opposite direction with respect to the aldehydes formed and indicates that lowering the pressure increases the isomerization products. It is noteworthy that the isomerization products are more than the hydrogenation one.

3. Conclusion

In the rhodium catalyzed hydroformylation of terminal aliphatic alkene, as 1-octene, isomerization normally occurs together the hydroformylation process and the amount of isomerized product is high. Moasser and Gladfelter, operating under mass transfer limiting conditions, reported high isomerization rates in the hydroformylation of 1-octene [9]. Recently, von Rooy et al. have found that the rhodium catalyzed hydroformylation of 1-octene using bulky diphosphites, occurs with very high selectivity for the linear aldehyde although the isomerization products reach a 26.5% value; interestingly, hydrogenation of 1-octene was not observed [10]. The results of van Leeuwen study are consistent with a kinetic scheme in which the addition of alkene is the rate-determining step of the process [10]; however by other studies emerges that experimental conditions determinate the rate-determining step of the process [11–13]. Ziòlkowski and coworkers [14–18]

studied 1-hexene hydroformylation in the presence of catalytic systems formed by $[Rh(acac)(CO)_2]$ or $[Rh(acac)(CO)L]$ (L = tertiary phosphine or phosphite) and PR_3 or clelating bidentate modifying ligands; using as catalyst $[Rh(acac)(CO)(PPh_3)]$ (at 1 MPa and 353 K), the presence of an excess of free PPh_3 increases the yield of aldehydes from 20 to 80% while the isomerization product 2-hexene drastically decreases [14]. The authors assumed that the formation of non-substituted rhodium carbonyls, namely $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$, were responsible of the isomerization of 1-hexene to 2-hexene. Using $[Rh(acac)(CO)(PPh_3)]$ as precatalyst, the species active in the hydroformylation process was assumed to be $[Rh(H)(CO)(PPh_3)_3]$; high selectivity to aldehydes was achieved in the presence of excess of free ligand because it is necessary to maintain in solution rhodium complexes with two or more PPh_3 ligands.

It is generally assumed that tertiary phosphine and diphosphine ligands form trigonal bipyramidal hydridorhodium complexes, which are the active catalysts in the hydroformylation reaction [1,2,19]. It appeared that structures either with the diphosphine ligand in equatorial–equatorial or in equatorial–axial position are stabilized depending on the distance between the phosphorus atoms and the flexibility of the bridge. In the case of two monodentate phosphine ligands, they might occupy two equatorial, two axial, or one equatorial and one axial sites in the trigonal bipyramidal intermediate. For L = PPh_3, Brown and Kent [7] showed by NMR studies that a 85:15 of equatorial–equatorial:equatorial–axial mixture of isomers of $[RhH(CO)_2(PPh_3)_2]$ is present in solution, in rapid equilibrium at room temperature. It is noteworthy that the isomer with the phosphine ligands both in axial position was not detected. Bulky ligands show preferential equatorial–equatorial coordination because of less steric congestion in the equatorial plane of trigonal bipyramidal rhodium complexes [7]. The behavior of a bridging diphosphine (or bridging bis-

phosphinito ligands as **1–3**) can be assimilated to that of a monodentate tertiary phosphine. An important question arising from this study is the influence of the nature of the trigonal bipyramidal hydridorhodium on the catalytic process, being the ligands **1–3** able to induce only bridging coordination in transition metal complexes.

Very likely, the rigidity of the backbone of ligands **1–3** makes the formation of the trigonal bipyramidal rhodium(I) complexes intermediate very difficult, particularly when the metal centers are held together by two bridging ligands, as well as for the precatalysts $[Rh(CO)(Cl)(\mu$-L)$]_2$ (L = **1–3**) ($[Rh(CO)_2Cl]_2$ + **1–3** in Rh to ligand molar ratio 1:2). Sanger [20] showed that A-frame complexes, in which the two rhodium atoms are bridged by two bis(diphenylphosphino)methane ligands, present a low catalytic activity probably owing to the rigidity of the catalytic system.

From data of Tables 1 and 2 emerges that the catalytic system formed by $[Rh(acac)(CO)_2]$ and **2** in the rhodium to ligand molar ratio 1:0.5 exhibits a capability to convert the styrene in the corresponding aldehydes comparable to that of the catalytic system formed by $[Rh(acac)-(CO)_2]$ and **2** in the rhodium to ligand molar ratio 1:1; in the hydroformylation of 1-octene, at 20 atm, the aldehydes formed with the catalytic system formed by $[Rh(acac)(CO)_2]$ and **2** in the rhodium to ligand molar ratio 1:1 results significantly more than that obtained with the catalytic system formed by $[Rh(acac)(CO)_2]$ and **2** in the rhodium to ligand molar ratio 1:0.5. It is noteworthy that in the hydroformylation either of styrene or of 1-octene an rhodium to

ligand molar ratio more than 1:1 (entries 3 and 15) drastically reduces the aldehydes formed. These results can be explained considering both the flexibility and the number of phosphorus atoms (considering each of them as a monodentate ligand) coordinated to metal center in the trigonal bipyramidal hydridorhodium (I) intermediate. Kalck [21] successfully explored dirhodium complexes bridged by two thiolato ligands in the hydroformylation of 1-hexene; the high catalytic activity has been ascribed to the good flexibility around the two sulphur atoms which maintains the binuclear framework and allows synergistic effects between the hydride–metal centers. In our study cooperative effects can be excluded being the metal centers at a distance more than 9.0 Å [3]. Still acceptable results in the hydroformylation of styrene and 1-octene have been obtained when the trigonal bipyramidal hydridorhodium intermediates formed, namely $\{[Rh(H)(CO)_3]_2(\mu$-**2**)$\}$ (Fig. 3a) and the oligomer $[Rh(H)(CO)_2(\mu$-**2**)]n (Fig. 3b), show some flexibility; the presence in the intermediate $[Rh(H)(CO)_2(\mu$-**2**)$]_n$ of two coordinated P-atoms for each rhodium center increases its catalytic activity with respect to $\{[Rh(H)-(CO)_3]_2(\mu$-**2**)$\}$ in the aldehydes formation.

Very likely the presence of an excess of ligand **2** affords, as intermediate, a very rigid hydridorhodium oligomer species containing three phosphorus ligands in the equatorial plane of the trigonal bipyramid, bridged each to a different rhodium atom. Unfortunately, all the attempts to characterize the hydridorhodium intermediates failed owing to the instability of these species at 1 atm of CO–H_2 (1:1).
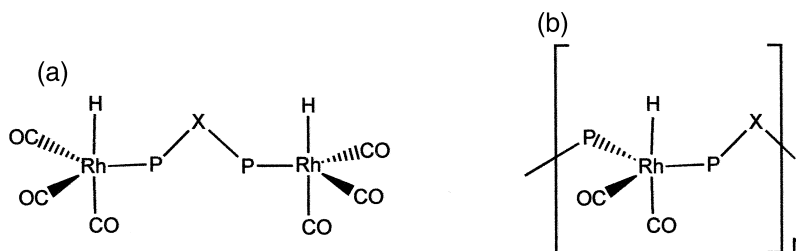

Fig. 3.

Isomerization, hydrogenation and hydro-formylation catalytic processes require an σ-alkyl intermediate; thus the ratio of the octene-isomerization products is dependent on the relative rate of subsequent steps, reductive elimination, CO migration and β-hydrogen elimination. Under our reaction conditions, for high temperatures and CO pressure a faster CO addition, and subsequent migration with formation of σ-acyl derivative, compared to β-hydrogen elimination occurs. Low CO pressures and high temperatures facilitate β-hydrogen elimination; in these conditions the formation of isomerized products dominates the hydroformylation of 1-octene.

4. Experimental

4.1. Materials

Styrene and 1-octene were purchased (Aldrich) and distilled before use. All other reagents were used as supplied.

Solvents were dried by standard procedures. All experiments were performed under an atmosphere of purified nitrogen. IR spectra were obtained as Nujol mulls on KBr plates using a Perkin-Elmer FTIR 1720 spectrophotometer. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AMX R300. ^{1}H NMR spectra were referenced to internal standard tetramethylsilane and ^{31}P{^{1}H} spectra to external 85% H_3PO_4; positive chemical shifts are for all nuclei to higher frequency. Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano, Italy.

4.2. Hydroformylation procedure

All high pressure experiments were performed in a 100 ml Berghoff stainless-steel autoclave equipped with gas and liquid inlets, a heating device, and magnetic stirring. The reactions were carried out in a Teflon vessel fitted to the internal wall of the autoclave, thus preventing undesirable effects due to the metal of the reactor. The autoclave was closed and de-gassed through three vacuum-nitrogen cycles. A solution of starting catalyst and of the olefin (in a typical experiment 5 mmol of substrate and 0.01 mmol of rhodium catalyst), in toluene (10 ml, was introduced under nitrogen, and gases (H_2/CO 1:1) were admitted up to the desired pressure. At the end of each catalytic run, the autoclave was cooled in a cold water bath and slowly vented. The conversion and the composition of the reaction products were determined by GLC with a Carlo Erba HRGC 5160 Mega Series apparatus (split/splitless injector, MEGA OV1 25 m column, film thickness 2 μm, carrier gas He, FID detector).

4.3. Syntheses {Rh(CO)Cl[μ-(p-Ph$_2$POC$_6$-H$_4$)$_2$O]}$_2$

A toluene solution (5 ml) of **1** (0.234 g, 0.41 mmol) was added to a stirring solution of [Rh(CO)$_2$Cl]$_2$ (0.08 g, 0.205 mmol) in the same solvent (15 ml). After about 1 h, the reaction mixture was reduced to ca. 3 ml and hexane (20 ml) was added. The yellow-orange solid obtained was filtered, washed with hexane (3 × 10 ml) and dried. Yield: 80% Anal. Calcd. for $C_{74}H_{56}Cl_2O_8P_4Rh_2$: C, 60.31;H 3.83; Cl, 4.81. Found: C, 60.43; H 4.11, Cl, 5.02. IR (KBr, Nujol) ν(CO) 1985 cm^{-1}. ^{1}H NMR (CDCl$_3$) 6.7–6.9 (m, CH, 16H) 7.29–7.50 (m, CH, 24H), 7.73–7.9 (m, CH, 16H). ^{31}P{^{1}H} NMR (CDCl$_3$) δ 125.8 (d, ^1J(RhP) = 145.8 Hz).

4.4. {Rh(CO)Cl[μ-(p-Ph$_2$POC$_6$H$_4$)$_2$CMe$_2$]}$_2$

This compound was obtained similarly to **4**, as yellow-orange solid, by starting from **2** (0.230 g, 0.386 mmol) and [Rh(CO)$_2$Cl]$_2$ (0.75 g, 0.193 mmol). Yield: 87%. Anal. Calcd for $C_{80}H_{68}Cl_2O_6P_4Rh_2$: C, 62.97; H 4.49; Cl, 4.65. Found: C, 63.17; H 4.66, Cl, 4.44. IR (KBr, Nujol) ν(CO) 1990 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 1.60 (s, CH$_3$, 12H) 6.5–6.8 (m, CH, 16H) 7.25–7.48

(m, CH, 24H), 7.70–7.88 (m, CH, 16H). $^{31}P\{^1H\}$ NMR (CDCl$_3$) δ 125.5 (d, ^1J(RhP) = 143.5 Hz).

4.5. $\{Rh(CO)Cl[\mu\text{-}(p\text{-}Ph_2POC_6H_4)_2S]\}_2$

This compound was obtained similarly to **4**, as yellow-orange solid, by starting from **3** (0.256 g, 0.437 mmol) and [Rh(CO)$_2$Cl]$_2$ (0.85 g, 0.218 mmol). Yield: 81%. Anal. Calcd. for C$_{74}$H$_{56}$-Cl$_2$O$_6$P$_2$S$_2$Rh$_2$: C, 59.02; H 3.75; Cl, 4.71. Found: C, 59.27; H 4.05, Cl, 4.94. IR (KBr, Nujol) ν(CO) 1990 cm^{-1}. ^1H NMR (CDCl$_3$) 6.66–6.85 (m, CH, 8H) 7.18–7.45 (m, CH, 12H), 7.69–7.88 (m, CH, 8H). $^{31}P\{^1H\}$ NMR (CDCl$_3$) δ 124.6 (d, ^1J(RhP) = 145.2 Hz).

4.6. $\{[Rh(acac)(CO)]_2[\mu\text{-}(p\text{-}Ph_2POC_6H_4)_2\text{-}CMe_2]\}_2$

A toluene solution (5 ml) of **2** (0.095 g, 0.16 mmol) was added to a stirring solution of [Rh(acac)(CO)$_2$ (0.082 g, 0.32 mmol) in the same solvent (15 ml). Immediately the solution color turned from yellow to red-orange. Then reaction mixture was reduced to ca. 3 ml and hexane (20 ml) was added. The yellow-orange solid obtained was filtered, washed with diethyl ether (3 × 10 ml) and dried in vacuo. Yield: 78%. Anal. Calcd. for C$_{51}$H$_{48}$O$_8$P$_2$Rh$_2$: C, 57.97; H 4.58. Found: C, 57.78; H 4.31. IR (KBr, Nujol) ν(CO) 1992 cm^{-1}. ^1H NMR (C$_6$D$_6$) δ 1.2 (s, CH$_3$, 12H), 1.6 (s, CH$_3$, 6H), 5.06 (s, CH, 2H), 6.7–6.9 (m, CH, 8H), 7.28–7.51 (m, CH, 12H), 7.74–7.8 (m, CH, 8H). $^{31}P\{^1H\}$ NMR (C$_6$D$_6$) δ 139.63 (d, ^1J(RhP) = 199.2 Hz).

4.7. $\{Rh(acac)(CO)[\mu\text{-}(p\text{-}Ph_2POC_6H_4)_2\text{-}CMe_2]_n\}$

A toluene solution (5 ml) of **2** (0.190 g, 0.16 mmol) was added to a stirring solution of [Rh(acac)(CO)$_2$ (0.082 g, 0.32 mmol) in the same solvent (15 ml). Immediately the solution color turned from yellow to red. Then the reac-

tion mixture was reduced to ca. 3 ml and hexane (20 ml) was added. The orange solid obtained was filtered, washed with diethyl ether (3 × 10 ml) and dried in vacuo. Yield: 75%. Calcd for C$_{44}$H$_{41}$O$_5$P$_2$Rh: C, 64.87; H 5.07. Found: C, 64.61; H 4.75 IR (KBr, Nujol) ν(CO) 1995 cm^{-1}. ^1H NMR (C$_6$D$_6$) δ 1.3 (s, CH$_3$, 12H), 1.59 (s, CH$_3$, 6H), 5.08 (s, CH, 2H), 6.7–6.9 (m, CH, 8H), 7.28–7.51 (m, CH, 12H), 7.74–7.8 (m, CH, 8H). $^{31}P\{^1H\}$ NMR (C$_6$D$_6$) δ 139.2 (d, ^1J(RhP) = 199.4 Hz).

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