Chapter 4

New ligands for the hydroformylation of 1-octene in supercritical carbon dioxide.

New P-donor ligands $PPh_{3-n}(OC_9H_{19})_n$ (n = 3, 2, 1) containing branched alkyl chains were synthesised and their coordination to Rh(I) and Pd(II) complexes was studied. The X-ray structure of $[Rh\{PPh_2(OC_9H_{19})\}_4]PF_6$ was determined. The reaction of the $[Rh(acac)(CO)_2]/PPh_{3-n}(OC_9H_{19})_n$ systems with CO/H_2 at 5 atm and 80 ºC in methyltetrahydrofurane led to the formation of $[RhH(CO)\{PPh_{3-n}(OC_9H_{19})_n)\}_3]$ as a main species. The Rh-catalysed hydroformylation of 1-octene with these ligands was investigated using supercritical carbon dioxide and toluene as solvents. Although the catalytic systems are not soluble in $scCO_2$, they are active. The activities were similar in toluene than in $scCO_2$ but the selectivities in aldehydes in the case of the phosphonite derivative were higher in the supercritical medium than in toluene.

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4.1 Introduction

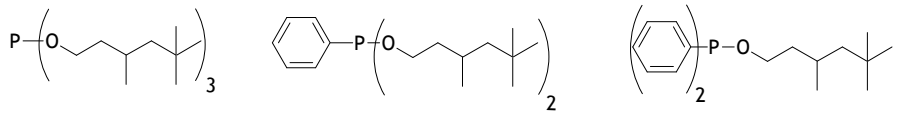
In the last few years, supercritical carbon dioxide ($scCO_2$) has received growing attention as an alternative reaction medium for homogeneous catalysis [1]. Supercritical carbon dioxide is an environmentally friendly and cheap solvent. More important, however, are its gas-like proprieties, especially in reactions in which the reactants are gases. $ScCO_2$ is highly miscible with gases such as hydrogen and carbon monoxide (it can therefore avoid the gas-liquid mass transfer) and is highly compressible. It also has low viscosity and therefore has high diffusivity. Moreover, its ability as an extraction solvent has proved useful for separating the products from the catalysts without the need for harder conditions such us those used for the distillation of higher alkenes [2].

The catalytic hydroformylation of long chain alkenes is an interesting reaction for transforming alkenes into aldehydes using carbon monoxide and hydrogen [3]. The aldehydes obtained allow the synthesis of oxo-alcohols used in the detergent industry and as plasticizers in the polymer industry. Rhodium catalysts associated with P-donor ligands are the most successful system for the hydroformylation of alkenes in mild conditions. Water is used as a green solvent in this reaction, but this process is limited to short chain alkenes (propene and 1-butene) because a certain solubility of the alkene in water is required [4]. $ScCO_2$ is a non-polar solvent in which alkenes are soluble, but ligand modification is needed to increase the solubility of the catalytic systems. The most successful approach is to introduce perfluoralkyl chains in the ligand [5]. However, the synthesis of perfluorinated ligands is difficult and expensive.

Cole-Hamilton and co-workers obtained good activities when they used alkylated phosphines such as $[Rh_2(OAc)_4]/PEt_3$ systems, which are soluble in $scCO_2$, in the hydroformylation of 1-hexene, but the n/i ratios were modest (2.1-2.6) [6]. Ligands containing alkylic groups, preferably branched, with a

chain length of eight carbons, have reportedly showed high solubility in supercritical carbon dioxide [7]. In the case of alkylic phosphines, when $P(C_8H_{17})_3$ were used, the Rh-systems were not soluble at the conditions studied and the turn over frequency (TOF) were low (3-7 h^{-1}, 8-20 % conversion in 2 h), though n/i ratios were higher (up to 3.9) [6]. When linear alkylated groups were introduced into the aromatic rings ($P(C_6H_4C_6H_{13})_3$, $P(C_6H_4C_{10}H_{21})_3$, and $P(C_6H_4C_{16}H_{33})_3$), the corresponding rhodium systems, which are partially soluble in $scCO_2$, afforded activities in the hydroformylation of 1-hexadecene with average TOF (h^{-1}) of 150, 350 and 20, respectively. This correlated with a maximum solubility of the $C_{10}H_{21}$ derivative [5c]. Other $scCO_2$ insoluble systems, such as $P(OPh)_3$, P-(*p*-OC_6H_4-$C_9H_{19})_3$ and $PPh_2(CH_2CH(CO_2C_{16}H_{33})CH_2CO_2C_{16}H_{33})$, are reported to show good activity in the hydroformylation of 1-hexene. The advantage of insoluble systems is that the products can be flushed away from the insoluble catalyst system using the excellent extraction ability of $scCO_2$ [8].

The incorporation of *tert*-butyl substituents in alkyl chains of P-donor ligands is reported to increase solubility in $scCO_2$ [7, 9]. Introducing branched chains in surfactants derived from sodium bis-2-ethyl-1-hexylsulfosuccinate increases their solubility in $scCO_2$ [10]. In this paper we present the synthesis of three new P-donor ligands with nine carbon-branched alkyl substituents (Fig. 1) and their application to the rhodium-catalysed hydroformylation of 1-octene in $scCO_2$ and in toluene as solvents. Phosphite (**1**), phosphonite (**2**) and phosphinite (**3**) ligands were selected because the introduction of oxy groups has a positive effect on activity and regioselectivity [3b,11]. Bulky monophosphonite ligands have had very high activities in the isomerization/hydroformylation of octene [11]. We also studied the coordination of the new ligands to rhodium(I) and palladium(II) complexes.



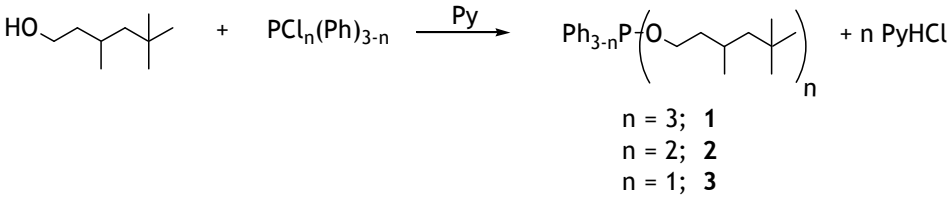
1 **2** **3**

Figure 1. P-donor ligands

4.2. Results and Discussion

4.2.1. Synthesis of ligands

Ligands **1**-**3** were prepared from the commercially available alcohol, 3,5,5-trimethylhexanol, by reaction with phosphorus trichloride or the corresponding chlorophenylphosphine in diethylether in the presence of pyridine (Scheme 1). The ligands were purified by flash chromatography under inert atmosphere and obtained as air- and moisture-sensitive colourless oils in good yields (56-80 %). The ^{1}H NMR spectra show the methylenic signals (-OCH_2-) at δ 3.8 ppm, the methylenic and methynic signals between δ 1.6-1.0, and the methylic doublet and singlet from the *tert*-butyl group at δ 0.9 ppm. The signals were assigned by means of COSY and HETCOR experiments. The ^{31}P-{^{1}H} NMR singlet signals appeared at 139.9, 156.6 and 112.5 ppm for **1**-**3** respectively, which are typical values for this kind of phosphorus compounds [12].



n = 3; **1**
n = 2; **2**
n = 1; **3**

Scheme 1. Synthesis of 1-3

4.2.2. Synthesis of complexes

To explore the coordination chemistry of the P-donor ligands (**1**-**3**), we decided to study their reactivity with rhodium(I) and palladium(II) complexes. We chose complex [Rh(cod)$_2$]PF$_6$ (cod = C_8H_{12}, 1,5-cyclooctadiene) as a model for cationic complexes (scheme 2). The reaction of the ligands **1**-**3** with [Rh(cod)$_2$]PF$_6$, in anhydrous dichloromethane at room temperature should proceed by a displacement of the ligand 1,5-cyclooctadiene, followed by a coordination of two P-donor ligands (**1**-**3**). Using 3,5,5-trimethylhexyl phosphite **1** in a P:Rh molar ratio 2:1, the complex [Rh(cod)(**1**)$_2$]PF$_6$ (**4**) was obtained as a relatively air stable yellow oil in high yield. Several attempts to solidify the complex were unsuccessful. The ^{31}P-{^{1}H} NMR showed a doublet at 116.1 ppm (J_{PRh} = 244.0 Hz), which corresponded to the coordinated phosphite ligand and the characteristic septuplet of the counteranion PF_6^- at –143.2 ppm (J_{PF} = 711.5 Hz). The presence of coordinated cyclooctadiene was confirmed by ^{1}H NMR with the signals at δ 4.05 ppm (HC=CH) and 2.57 and 2.36 ppm (-CH_2-). The ^{1}H NMR signals corresponding to the coordinated ligand shifted slightly with respect to those of the free ligand. The mass spectra show a signal at m/z = 1129.5 corresponding to the [Rh(cod)(**1**)$_2$]$^+$ fragment.

However, if the same precursor complex [Rh(cod)$_2$]PF$_6$ is treated with the same molar ratio P:Rh 2:1 using phosphonite **2**, the ^{31}P-{^{1}H} NMR spectrum shows two doublets in the region of coordinated phosphorus at δ 146.0 (J_{PRh} =

165.9 Hz), and 138.5 ppm (J_{PRh} = 170.8 Hz) and the ^{1}H NMR spectrum show signals corresponding to coordinated cyclooctadiene (at δ 4.0 and 2.5-2.7 ppm). When the P:Rh molar ratio was 4:1, the ^{31}P-{^{1}H} NMR spectrum showed only the signal at δ 146.0 ppm. There was no evidence of coordinated cod in the ^{1}H NMR spectrum, and only signals attributed to the coordinated ligand were detected. In this case, a relatively air stable yellow oily solid was obtained in 76% yield. The mass spectra of the isolated product had a signal m/z 1679.7 corresponding to the cationic fragment [Rh(**2**)$_4$]$^+$. We propose that, at a P:Rh ratio of 2:1, a mixture of [Rh(cod)(**2**)$_2$]PF$_6$ and [Rh(**2**)$_4$]PF$_6$ (**5**) was formed and the total substituted species **5** was formed at P:Rh 4. Similar species [RhL$_4$]$^+$ formed for L = PPh(OCH$_3$)$_2$ [13], which had similar ^{31}P NMR data (δ = 148 ppm, J_{PRh} = 170 Hz) [14].

$$[Rh(cod)_2]PF_6 + 2\ P(OC_9H_9)_3 \longrightarrow [Rh(cod)(\mathbf{1})_2]PF_6 + cod$$
1 **4**

$$[Rh(cod)_2]PF_6 + 4\ PPh(OC_9H_9)_2 \longrightarrow [Rh(\mathbf{2})_4]PF_6 + 2\ cod$$
2 **5**

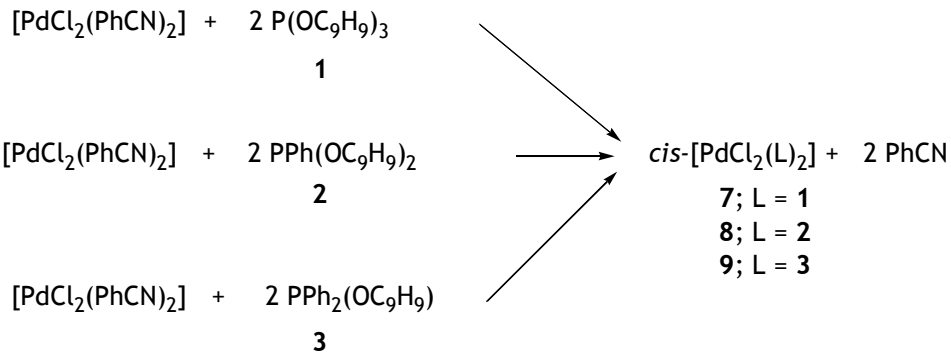
$$[Rh(cod)_2]PF_6 + 4\ PPh_2(OC_9H_9) \longrightarrow [Rh(\mathbf{3})_4]PF_6 + 2\ cod$$
3 **6**

Scheme 2. Synthesis of 4-6.

In the reaction of [Rh(cod)$_2$]PF$_6$ with ligand **3**, only one doublet was observed in the ^{31}P-{^{1}H} NMR spectrum at P:Rh 2:1 and P:Rh 4:1 at δ 132.3 (J_{PRh} = 162.2 Hz), which agrees with the data reported for [Rh{PPh$_2$(OR)}$_4$]$^+$ (R = Me: δ 132.2 ppm, J_{PRh} = 159 Hz; R = Et: δ 130.5 ppm, J_{PRh} = 156 Hz) [15], and a septuplet signal of PF$_6^-$ at δ –143.1 ppm (J_{FP} = 712.6 Hz). In the ^{1}H NMR spectrum, there were only signals corresponding to the coordinated ligand **3**.

A relatively air-stable yellow solid was isolated in 73 % yield. The X-ray analysis (discussed below) showed that [Rh(**3**)$_4$]PF$_6$ (**6**) was formed.

To prepare palladium neutral complexes we chose [PdCl$_2$(PhCN)$_2$] as a model precursor. The reaction of ligands **1**-**3** with [PdCl$_2$(PhCN)$_2$] in anhydrous dichloromethane at room temperature proceeded by the displacement of two molecules of PhCN followed by the coordination of two P-ligands to afford [PdCl$_2$(**1**-**3**)$_2$] (**7**-**9**, Scheme 3), which were obtained as a relatively air-stable yellow oils in good yields with mass spectra in agreement with a mononuclear formulation. The ^{1}H NMR spectra of **7**-**9** showed the signals corresponding to the coordinated ligands. The ^{31}P-{^{1}H} NMR spectra showed only one singlet signals at δ 94.2 (**7**), 122.2 (**8**) and 110.2 (**9**) ppm, which indicates that only one of the two possible isomers (*cis* or *trans*) were formed. The difference between the ^{31}P NMR signal in the complex and that of the free ligand defined as the coordination chemical shift Δ (δ_{coord}-$\delta_{free\ ligand}$) for similar palladium(II) complexes is indicative of the stereochemistry of these complexes. The lowest (negative) values of Δ are related with *cis*-isomers containing ligands with Tolman angles Θ less than 140° and high values (positive) of Δ are related with *trans*-isomers containing ligands with Tolman angles Θ higher than 140° [16]. Based on this observation, since the values of Δ for complexes **7** and **8** are –45.7 and -34.4 ppm respectively, we propose that the *cis* isomers were formed in these complexes. In the case of complex **9** the value of Δ was –2.3 ppm. Taking in account that the estimated value of the Tolman's angle Θ from the X-ray structure is 128°, we also propose the formation of the *cis* isomer for complex **9**.



Scheme 3. Synthesis of 7-9

*4.2.3. X-ray structure of **6***

The crystal structure of complex **6** was obtained by slow diffusion of diethylether into a dichloromethane solution of the complex. The X-ray structure is shown in Figure 2 and selected bond distances and angles are given in Table 1.

The cationic rhodium complex contains four coordinated phosphinite ligands **3** as observed in solution. The Rh-P bond lengths (2.2848(6) Å) are in the range reported for other Rh(I) complexes with phosphinite ligands [17]. The cation complex has a slightly tetragonal distorted square-planar geometry (*trans* P-Rh-P angles 166.64(3)º) due to intramolecular ligand repulsion. Similar distortion, but to a greater extent, has been reported for $[Rh(PMe_3)_4]^+$ (*trans* P-Rh-P angles 148.29º and 151.46º) [18]. The C-P-Rh angles (115.75(8) and 118.97(8)º) deviated form the ideal tetrahedral value, as observed in coordinated P-donor ligands. The estimated Tolman angle Θ for **3**, calculated in accordance with the reported method [19], was 128º. The alkoxy chains are in a staggered arrangement up and down the coordination plane in order to minimise repulsion. There is a disorder in the *t*-Bu fragments. The PF_6^- anions

are located in the cavities formed with the four *t*-Bu groups from two different cationic units.

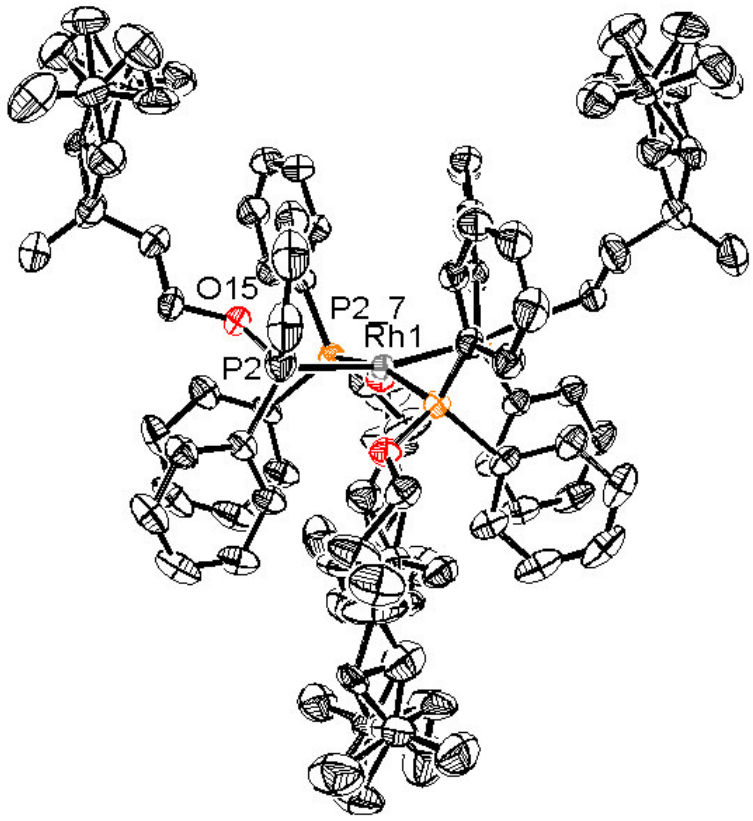


Figure 2. ORTEP drawing of complex **6**. PF_6^- and hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) of complex **6**.[a]

Bond lengths		*Bond angles*	
Rh1-P2	2.2848(6)	P2^{i}-Rh1-P2^{iii}	90.776(3)
P2-C3	1.8222(25)	P2^{i}-Rh1-P2^{ii}	166.64(3)
P2-C9	1.815(2)	C3-P2-Rh1	115.75(8)
P2-O15	1.6170(17)	C9-P2-Rh1	118.97(8)
O15-C16	1.447(3)	O15-P2-Rh1	107.03(6)
		C9-P2-C3	105.14(11)

[a] Estimated standard deviations are given in parentheses

4.2.4. Reactivity of [Rh(acac)(CO)$_2$]/1-3 with CO and H$_2$

The reactivity of the systems [Rh(acac)(CO)$_2$]/**1**-**3** with CO and H_2 was analysed using high pressure NMR (HPNMR) and IR (HPIR). The $^{31}P\{^1H\}$ and ^1H NMR spectra were performed on the complex [Rh(acac)(CO)$_2$] associated with 4 equivalents of ligand **1-3** in toluene-d_6 ([Rh] = 2.10^{-2} M) and stepwise adding H_2 and CO pressure. As the IR technique is more sensitive, the IR spectra could be done at concentrations closer to the catalytic ($2\text{-}5.10^{-3}$ M) in methyltetrahydrofuran at the same conditions. The list of identified species is given in Table 2.

When we added 4 moles of **1** to [Rh(acac)(CO)$_2$] in toluene, the $^{31}P\text{-}\{^1H\}$ spectrum shows a major wide signal at δ 140 ppm, a small multiplet at δ 80 ppm along with a singlet at δ 0 ppm due to decomposed ligand (Figure 3a). The wide signal at δ 140 ppm is attributed to a mixture of the species [Rh(acac)(CO)$_n$(**1**)$_{(2-n)}$]. Adding 2.5 atm of H_2 to this solution (Figure 3b), two new doublet signals were observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum at δ 158.9 ppm (J = 212.3 Hz) and δ 157.9 ppm (J = 207.8 Hz). Two new signals appeared also in the hydride region of the ^1H NMR spectrum at δ –10.7 ppm (quintet, J = 7.8 Hz) and δ–11.8 ppm (double quintet, J = 33.7 Hz, J = 9.4 Hz). After further

addition of 2.5 atm of CO (5 atm total pressure) and heating the system for 1h at 80 ºC the doublet signal in the ^{31}P-{^{1}H} NMR spectrum at δ 157.9 ppm, the hydride at δ –11.8 ppm and the multiplet signal at δ 80 ppm disappeared, and new signals were observed: δ (ppm) 154.6 (d, J_{RhP} = 194.6 Hz), 140.8 (dd, J = 273.6 Hz, J = 164.7 Hz), 138.1 (s, free **1**), 70.2 (dt, J = 273.4, J = 94.3 Hz) (Figure 3c). We assigned the signals at δ 157.9 ppm and the hydride double quintet δ –11.8 ppm to the species [RhH(**1**)$_4$] (**10**) by comparison with published data for the analogous species [RhH{P(OPh)$_3$}$_4$] (δ_P: 129.7, J_{RhP} = 232.8 Hz; δ_H(hydride): - 10.6 J_{RhH} = 44 J_{PH} = 7 Hz) [20]. The ^{31}P-{^{1}H} major doublet signal at δ 158.9 ppm together with the hydrido quintet at δ −10.7 of the ^{1}H NMR was attributed to [RhH(CO)(**1**)$_3$] (**11**). The reported data for [RhH(CO){P(OPh)$_3$}$_3$] (δ_P: 141.1, J_{RhP} = 240 Hz; δ_H(hydride): - 10.9, J_{RhH} = J_{PH} = 3 Hz) [20] are in agreement with the values observed for **11**. The minor signal at δ 154.6 ppm (J_{RhP} = 194.6 Hz) is attributed to the dicarbonyl species [RhH(CO)$_2$(**1**)$_2$] (**12**), whose hydrido signal is not detected in the ^{1}H NMR due to the low concentration. The signals at δ 140.8 and 70.2 could correspond to mixed complexes with phosphito/phosphonate ligands formed by the partially decomposed ligand. Coordination of phosphonates to rhodium complexes is described in the literature [21] and the chemical shifts observed correlate the ones reported for mixed species. At the end of the experiment, the pressure was released and water was added to decompose the remaining ligand. The signals at δ 140.8 and 70.2 disappeared and a new doublet at δ 132.4 ppm which could correspond to a species with only phosphonate ligands (Figure 4).

The HPIR spectra of [Rh(acac)(CO)$_2$]/**1** at 5 atm CO/H$_2$ (1/1) in the ν(CO) region initially showed signals at 2049, 2025, 1980 and 2005 and 1960 cm^{-1} (Figure 5). By comparison with published data for [RhH(CO){P(OPh)$_3$}$_3$] (ν(CO) = 2060m 2010w 1960w cm^{-1}) [22], the band at 2025 cm^{-1} was assigned to **11**. The absorptions at 2049 and 1980 could correspond to the equatorial equatorial isomer of **ee-12** and the ones at 2005 and 1960 could correspond to

the equatorial axial isomer **ea-12**. The data reported for the ee-$[RhH(CO)_2\{P(OPh)_3\}_2]$ were 2053, 2018 cm^{-1} and for the isomer ea-$[RhH(CO)_2\{P(OPh)_3\}_2]$ they were 2034 and 1992 cm^{-1} [23]. After 1h at 80 ºC bands appeared at 1991 and 1828 cm^{-1} attributed to rhodium species with bridged carbonyl ligands.

Table 2. Identified species for $[Rh(acac)(CO)_2]$/**1**-**3** (P/Rh = 4) systems at 5 atm CO/H_2 (1/1) after 1h at 80 ºC.

Complex	^{31}P (J_{RhP}, Hz)	^{1}H (hydride) (J_{PH}, J_{RhH} Hz)	ν(CO) (cm^{-1})
$[RhH(\mathbf{1})_4]$ (**10**)	157.9 d (207.8)	-11.8 dq (33.7, 9.4)	-
$[RhH(CO)(\mathbf{1})_3]$ (**11**)	158.9d (212.3)	-10.7 qi (7.8, 7.8)	2025
$[RhH(CO)_2(\mathbf{1})_2]$ (**12**)	154.6d (194.6)	n.d	2049,2005, 1980,1960
$[RhH(CO)(\mathbf{2})_3]$ (**13**)	169.8d (189.0)	-10.0 qi (7.7, 7.7)	2065
$[RhH(CO)_2(\mathbf{2})_2]$ (**14**)	168.2d (145.7)	n.d.	2073, 2042, 2029, 1991
$[RhH(CO)(\mathbf{3})_3]$ (**15**)	138.1d (163.3)	-9.4 dq (12.3, 4.7)	2025
$[RhH(CO)_2(\mathbf{3})_2]$ (**16**)	136.8d (147.2)	-9.1 dt (11.7, 6.3)	2044, 2006, 1996, 1918

n.d. = not detected

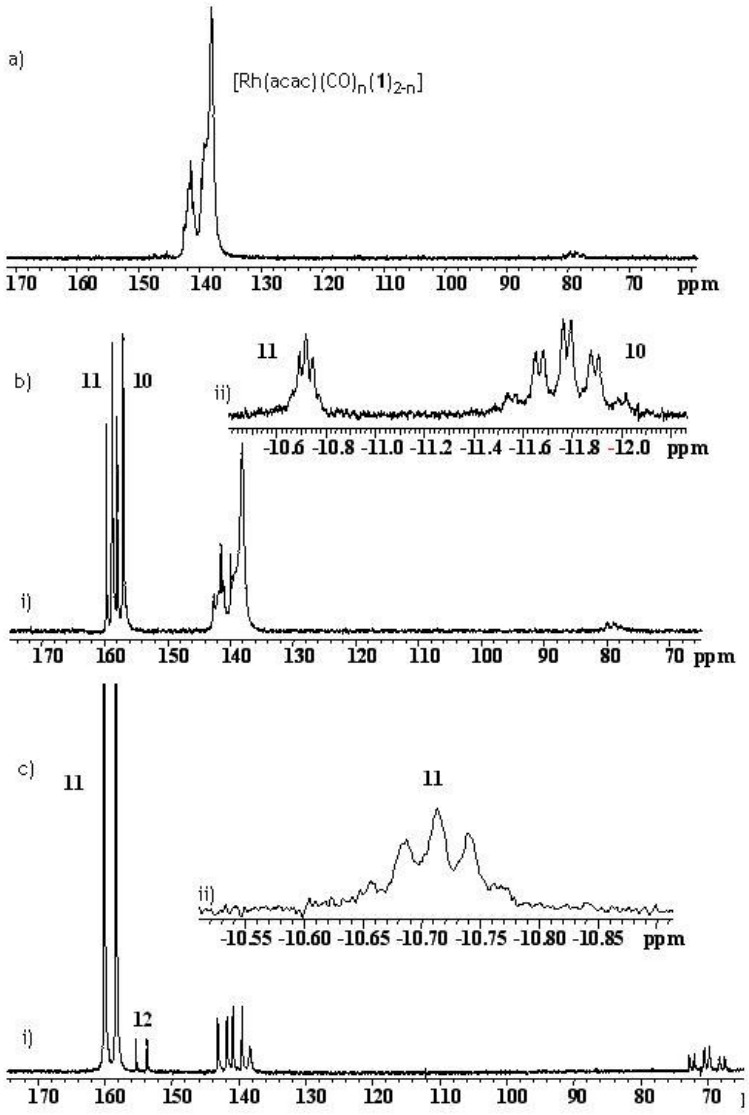


Figure 3. NMR spectra at 20 ºC of [Rh(acac)(CO)$_2$]/**1** (P/Rh = 4) in toluene- d$_6$: **a**) $^{31}P\{^1H\}$ under nitrogen; **b**) (i) $^{31}P\{^1H\}$ NMR under 2.5 bar of H_2; (ii) Hydride region of the ^1H NMR; **c**) (i) $^{31}P\{^1H\}$ NMR under 5 bar of CO/H_2 (1:1); (ii) Hydride region of the ^1H NMR.

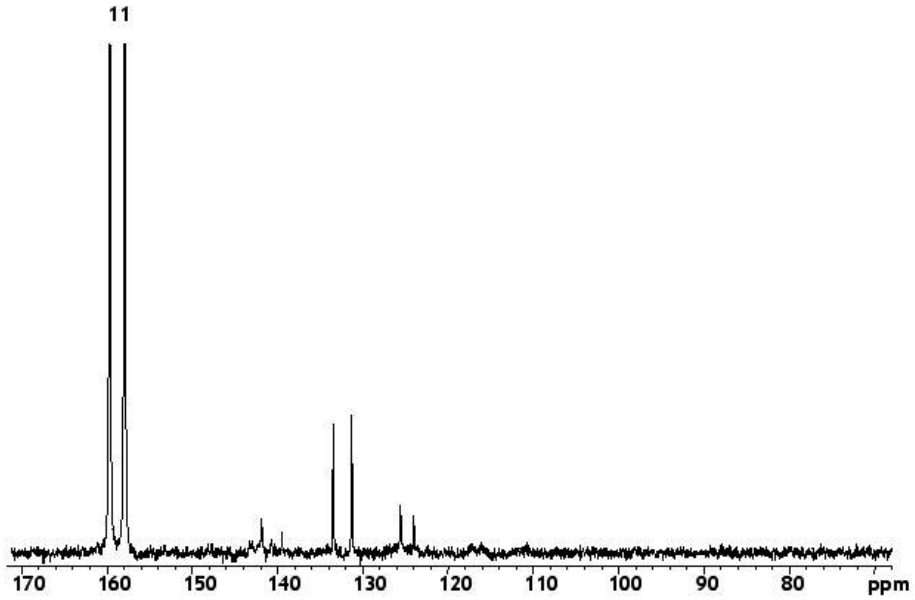


Figure 4. $^{31}P\{^{1}H\}$ NMR spectrum at 20 ºC of $[Rh(acac)(CO)_2]$/**1** (P/Rh = 4) in toluene- d_6 after release the pressure and add water to the system

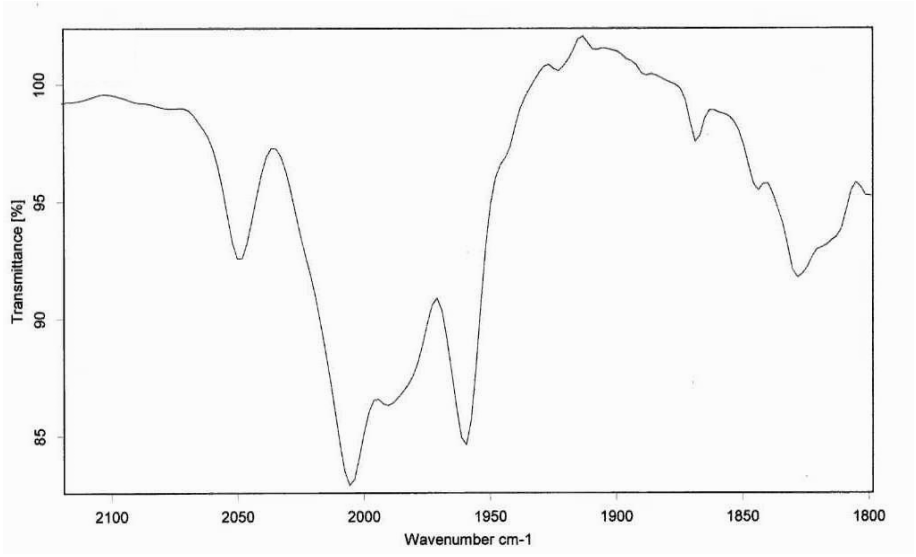


Figure 5. HPIR spectrum of the system $[Rh(acac)(CO)_2]$/**1** (P/Rh = 4) at 5 atm CO/H_2 (1/1) in methyltetrahydrofurane after 1h stirring at 80ºC.

The ^{31}P-{^{1}H} NMR spectrum of the [Rh(acac)(CO)$_2$]/**2** system (P/Rh = 4) in toluene showed broad signals at δ 161.7, 156.4 and 87.9 ppm (Figure 6a). The signals at low field are attributed to the species formed by direct substitution of CO by ligand **2** [Rh(acac)(CO)$_n$(**2**)$_{(2-n)}$]. Adding 5 atm of CO/H$_2$ (1/1) to this solution and heating for 1h at 80 ºC, the ^{31}P{^{1}H} NMR at room temperature showed a well-resolved major doublet signal at δ 169.8 (J_{RhP} = 189.0 Hz), which correlated with a hydride quintet signal at δ -10.0 (J_{PH} = J_{RhH} = 7.7 Hz) and was attributed to the species [RhH(CO)(**2**)$_3$] (**13**) (Figure 6b). At δ 168.2 there was a minor, partly overlapped, doublet (J_{RhP} = 145.7 Hz) that was attributed to the dicarbonyl species [RhH(CO)$_2$(**2**)$_2$] (**14**), though the hydride signal in the ^{1}H NMR was not detected. At δ 156 ppm there was the remaining signal of the non reacted species [Rh(acac)(CO)$_n$(**2**)$_{(2-n)}$]. The slow reaction rate with CO/H$_2$ of similar precursors containing phosphite ligands has been reported [24]. The broad doublet at δ 144.1 (J_{RhP} = 168.7 Hz) was resolved at –70 ºC and could correspond to dimeric Rh(0) complexes [Rh$_2$(CO)$_6$(**2**)$_2$] or [Rh$_2$(CO)$_4$(**2**)$_4$], which has been observed for other P-donor rhodium systems [25]. At δ 120 and 82 ppm, there were broad multiplet signals attributed to mixed phosphonite/phosphonate species.

The HPIR spectrum after 1 h at the reaction conditions showed several absorption in the 2200-1800 cm^{-1} region that were difficult to assign (Figure 7). The band at 2065 could correspond to compound **13** and the ones at 2073 and 2029 cm^{-1} and 2042 and 1991 cm^{-1} could correspond to the **ee**- and **ea**-isomers of **14**, respectively. The absorptions around 1800 cm^{-1} could correspond to the Rh(0) dimeric species.

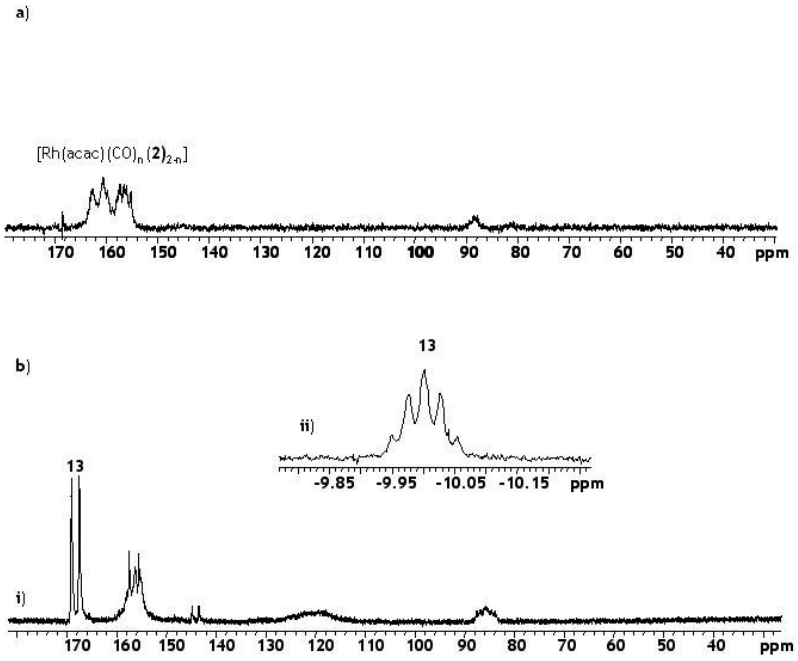


Figure 6. NMR spectra at 20 ºC of $[Rh(acac)(CO)_2]$/**2** (P/Rh = 4) in toluene- d_6: a) $^{31}P\{^1H\}$ under nitrogen; b) (i)$^{31}P\{^1H\}$ NMR at 70 ºC of $[Rh(acac)(CO)_2]$/**2** under 5 bar of CO/H_2 (1:1); (ii) Hydride region of the ^1H NMR.

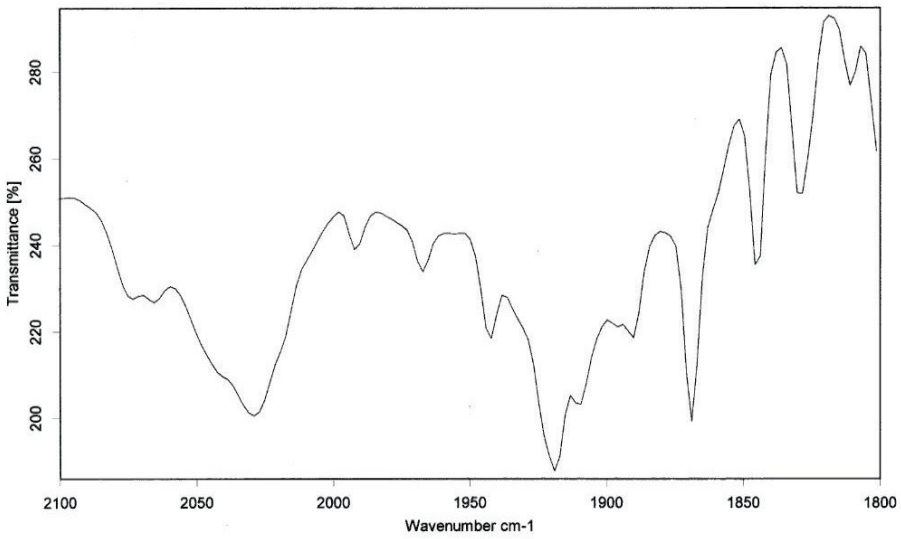


Figure 7. HPIR spectra of the system [Rh(acac)(CO)$_2$]/**2** (P/Rh = 4) at 5 atm CO/H$_2$ (1/1) in methyltetrahydrofurane after 1h stirring at 80ºC.

When we added 2 moles of **3** to [Rh(acac)(CO)$_2$] in toluene- d$_6$, the ^{31}P-{^{1}H} spectrum shows a small doublet signal at δ 133.3 ppm and a wide singlet at δ 123.8 ppm (Figure 8a). These signals were attributed to a mixture of the species [Rh(acac)(CO)$_n$(**3**)$_{(2-n)}$]. Adding 2.5 atm of H$_2$ to this solution after 1h at 80 ºC the ^{31}P-{^{1}H} NMR spectrum showed five signals at δ(ppm): 138.1 (d, *J* = 163.3 Hz), 136.8, minor partially overlapped doublet (J_{PRh} = 147.2 Hz), 133.0 (*J* = 192.0 Hz) and a not resolved minor signals at 117.7 and 94.1 (Figure 8b). The ^{1}H NMR in the hydride region showed a double quartet signal at -9.4 ppm (J_{HP} = 12.3 Hz, J_{HRh} = 4.7 Hz). By comparison with published data [26], the doublet at δ 138.1 ppm together with the hydride signal at δ −9.4 ppm were attributed to the species [RhH(CO)(**3**)$_3$] (**15**), the minor partially overlapped doublet at δ 136.8 ppm was attributed to species [RhH(CO)$_2$(**3**)$_2$] (**16**) and the major doublet at 133.0 (*J* = 192.0 Hz) could correspond to [Rh(acac)(**3**)$_2$] . The complex [RhH(CO){PPh$_2$(OPh)}$_3$] show signals at δ_P 142 (J_{PRh} = 169 Hz) and

δ_H –9.4 dq (J_{HP} = 13 Hz, J_{HRh} = 3 Hz) and [$RhH(CO)_2\{PPh_2(OPh)\}_2$] show signals at δ_P 145 (J_{PRh} = 165 Hz) and δ_H –9.5 [27]. The signals at 117.7 and 94.1 ppm in the $^{31}P\{^1H\}$ spectrum may correspond to mixed phosphinite/phosphonate species. At P/Rh = 4 the $^{31}P\{^1H\}$ NMR spectrum of [$Rh(acac)(CO)_2$]/**3** at 5 atm CO/H_2 (1/1) after 1h at 80 ºC showed five signals (Figure 8c) a major doublet at 138.1 ppm (J_{PRh} = 163.3 Hz), which together with the hydride signal at -9.4 (dq, J_{HP} = 12.3 Hz, J_{HRh} = 4.7 Hz) were assigned to specie **15**, a partially minor overlapped doublet at 136.8 ppm (J_{PRh} = 147.2 Hz),which together with the hydride signal at δ –9.1 (dt, J_{HP} = 11.7 Hz, J_{HRh} = 6.3 Hz) were assigned to **16**, a double triplet at 130.8 (J = 122.6 Hz, J =94.5 Hz,), a singlet at 111.7 (free **3**), and a double doublet 84.9 (J = 122.0 Hz, J = 101.7 Hz). The signals at 130.8 and 84.9 ppm could correspond to mixed phosphinite/phosphonate species as proposed for the other systems.

The IR spectrum of [$Rh(acac)(CO)_2$]/**3** at the same conditions initially showed only one band at 1987 cm^{-1} in the 2200-1800 cm^{-1} region. After 1h stirring at 80 ºC, five absorptions were detected at 2044, 2025, 2006, 1966, 1918 cm^{-1} (Figure 9). The band at 2025 cm^{-1} was assigned to **15**. The absorptions at 2044 and 1966 cm^{-1} were attributed to isomer **ee-16**, since they were similar to ones reported for the equatorial-equatorial isomer of [$RhH(CO)_2(PPh_2(OPh))_2$] (2045, 1970 cm^{-1}) [27]. The ones at 2006 and 1918 cm^{-1} could correspond to the **ea-15** isomer.

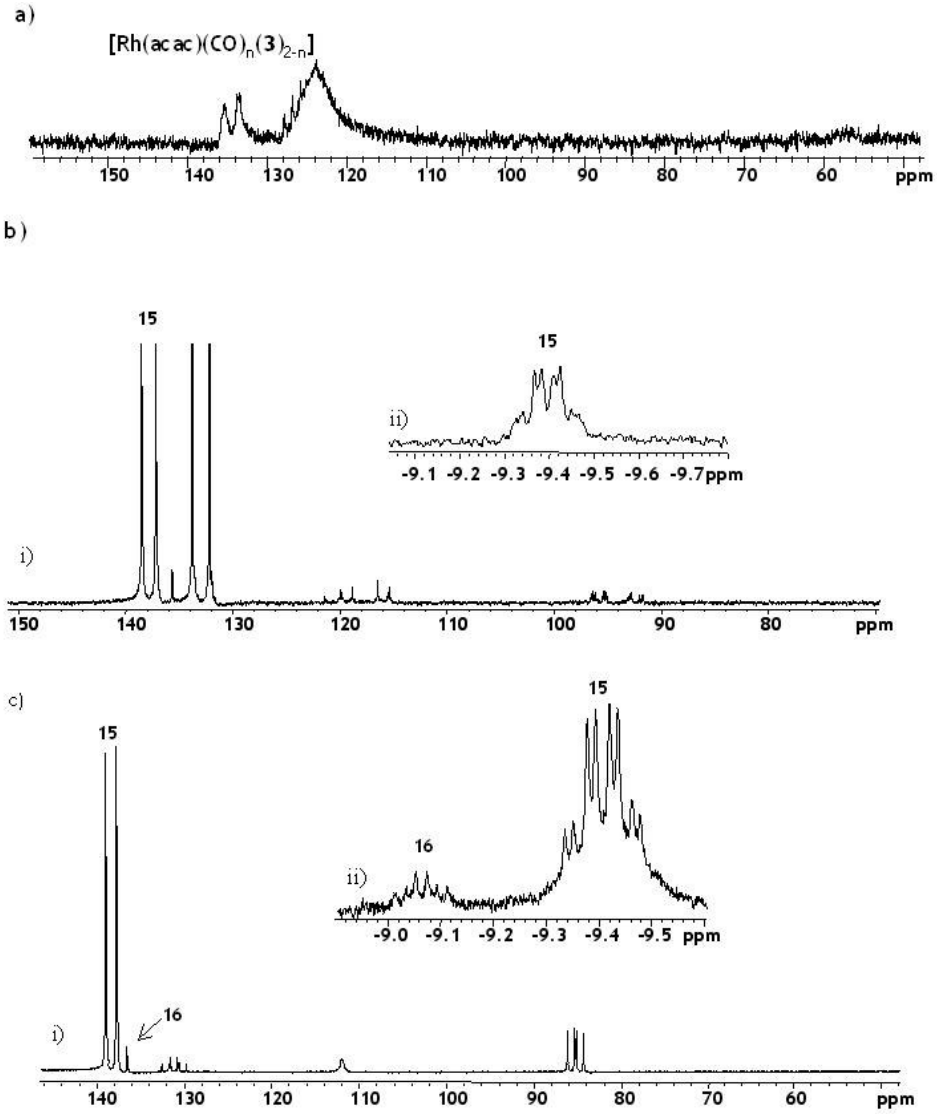


Figure 8. NMR spectra at 20 ◦C of [Rh(acac)(CO)$_2$]/**3** (P/Rh = 2) in toluene- d$_6$; (a) ^{31}P{^{1}H} under nitrogen ;**b**) (i) ^{31}P{^{1}H} under 2,5 bar of H_2; (ii) Hydride region of the ^{1}H NMR **c**) (i) ^{31}P{^{1}H} (P/Rh = 4) under 5 bar of CO/H_2 (1:1); (ii) Hydride region of the ^{1}H NMR.

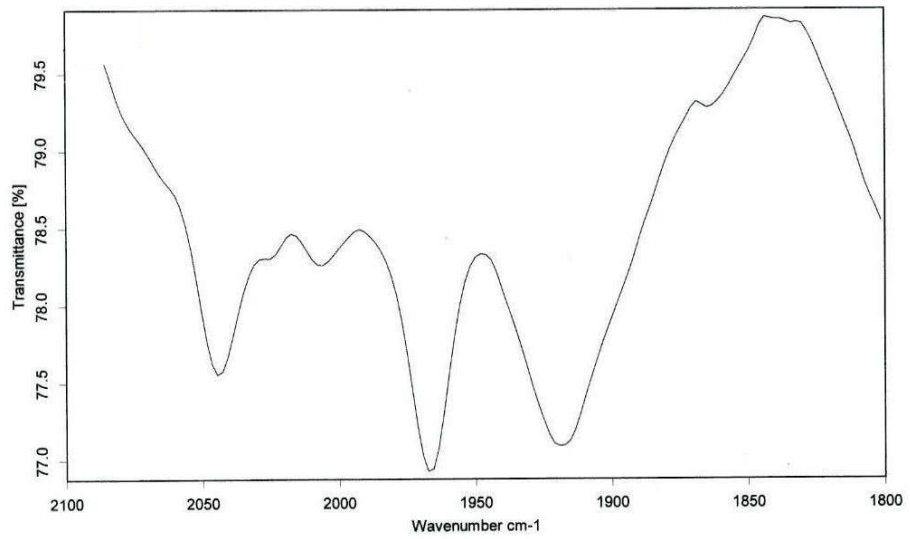
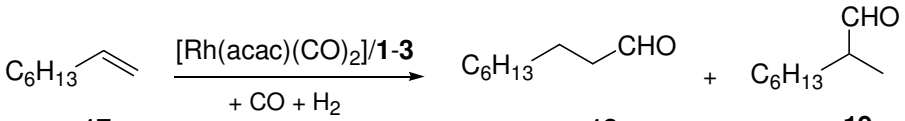


Figure 9. HPIR spectrum of [Rh(acac)(CO)$_2$]/**3** (P/Rh = 4) at 5 atm CO/H$_2$ (1/1) in methyltetrahydrofurane after 1h stirring at 80ºC.

In summary, the study of the reactivity of [Rh(acac)(CO)$_2$]/**1**-**3** with CO and H$_2$ at 5 atm (CO/H$_2$ = 1/1) and 80ºC shows that in all cases the precursors [RhH(CO)(**1**-**3**)$_3$] are formed as the main species.

4.2.5. Hydroformylation of 1-octene

We studied the hydroformylation of 1-octene (**17**) to obtain the corresponding linear (**18**) and branched (**19**) aldehydes (scheme 4) in toluene as a model solvent and in scCO$_2$.



17 **18** **19**

Scheme 4. Hydroformylation of 1-octene using different [Rh(acac)(CO)$_2$]/**1**-**3** systems

Hydroformylation of 1-octene in toluene

Table 3 (entries 1–7) shows the results of 1-octene hydroformylation in toluene using [Rh(acac)(CO)$_2$]/**1**-**3** as catalysts precursors. In the conditions we studied, the products obtained were the isomeric aldehydes n-nonanal (**18**), iso-nonanal (**19**) and the isomerised products 2-octene (*cis* and *trans*), 3-*trans*-octene and 4-*trans*-octene. No hydrogenated products were observed. The selectivity in isomerised products is also listed.

Hydroformylation using [Rh(acac)(CO)$_2$]/**1** in toluene (entry 1, table 3) shows high activity (Conv % = 98) and high selectivity in aldehydes at a molar ratio P/Rh of 4, though isomerised octenes were also formed . The n/iso ratio was relatively high (3.5), as is observed for other Rh-phosphite systems [3b]. When the P/Rh ratio dropped to 2, conversion, and especially selectivity, decreased (entry 2, table 3).

Catalyst precursors with ligands **2** and **3** provided very low selectivity in the aldehydes and produced octene isomers as the main products (entries 3-7, table 3). Since these poor donor ligands tend to form rhodium species with a high number of coordinated ligands per rhodium (see section 4.2.2), which can inhibit hydroformylation [28], we performed an experiment with a lower P/Rh ratio (entries 6, table 3) but the selectivity in aldehydes decreased dramatically.

Low selectivity in aldehydes has been attributed to the non-formation of the active species [RhH(CO)(Ligand)$_3$]. Our HPIR experiments showed that, in the case of systems with **2** and **3**, an activation time was needed before these species were detected. System [Rh(acac)(CO)$_2$]/**2** was therefore preactivated for 1h at 5 atm (CO/H$_2$=1) at 80 ºC in toluene. Then, 1-octene was added, the system was pressurised and again heated to 80ºC, and the reaction started. The conversion was slightly higher and the selectivity in aldehydes increased from 21 to 47 % (entry 4, table 3). However, similar results were obtained when the preactivated catalyst precursor with ligand **3** was used (entry 7, table 3).

Rhodium catalysts with phosphonite ligands have shown very high activity in the isomerization/hydroformylation of internal alkenes [11]. When we used [Rh(acac)(CO)$_2$]/**2** at the same conditions in the hydroformylation of *trans*-2-hexene, 17 % total conversion was obtained with a selectivity of 45 % of aldehydes and a 1-heptanal/2-methylhexanal/3-ethylpentanal ratio of 24/54/22, which indicates that the isomerization rate was slower than the hydroformylation rate for these systems.

Hydroformylation of 1-octene in supercritical CO$_2$

The solubility of the catalyst precursors in scCO$_2$ was studied using a Thar autoclave equipped with sapphire windows. The purged autoclave was charged with [Rh(acac)(CO)$_2$]/**1**-**3** (P/Rh = 4), filled with CO/H$_2$ at 5 bar (CO/H$_2$ = 1/1) and pressurised with CO$_2$ up to 240 bar at 80 ºC. Visual inspection through the windows showed that the supercritical phase was colourless, which indicates that there was no apparent solubility of these systems.

The catalytic experiments using scCO$_2$ of systems [Rh(acac)(CO)$_2$]/**1**-**3** are summarised in Table 3 (entries 9-19). A reference experiment with the system [Rh(acac)(CO)$_2$]/**1** without solvent provided lower conversion and selectivity than when toluene was used as a solvent (entry 8, Table 3).

As expected due to the low solubility of the catalyst precursors, the conversions using scCO$_2$ were lower than for the toluene systems at similar conditions. However, conversion was good with the catalyst system [Rh(acac)(CO)$_2$]/**1** (entry 9, table 3), though the selectivity in aldehydes fell to 25 %. This led the linear/branched ratio to increase to 4.2. We optimised the conditions with this system by modifying the P/Rh ratio (entry 10, table 3), partial CO/H$_2$ pressure (entry 11, table 3), temperature (entry 12, table 3) and total pressure (entry 13, table 3).

Table 3. Hydroformylation of 1-octene using $[Rh(acac)(CO)_2]$/**1**-**3** catalyst precursors in $scCO_2$.[a]

Entry	L	Solvent	L/Rh	T (ºC)	$P(H_2)$ (bar)	P(CO) (bar)	P_{tot}[b] (bar)	Conv[c] (%)	S_a[d] (%)	18/19 (%)	S_i[e] (%)
1	1	**toluene**	**4**	**80**	**2.5**	**2.5**	**5**	**98**	**86**	78/22	**10**
2	1	**toluene**	**2**	**80**	**2.5**	**2.5**	**5**	**85**	**24**	74/26	**75**
3	2	**toluene**	**4**	**80**	**2.5**	**2.5**	**5**	**89**	**21**	77/23	**79**
4[f]	2	**toluene**	**4**	**80**	**2.5**	**2.5**	**5**	**95**	**47**	53/47[h]	**53**
5	3	**toluene**	**4**	**80**	**2.5**	**2.5**	**5**	**95**	**38**	71/29	**58**
6	3	**toluene**	**2**	**80**	**2.5**	**2.5**	**5**	**95**	**6**	57/37[h]	**93**
7[f]	3	**toluene**	**4**	**80**	**2.5**	**2.5**	**5**	**98**	**36**	63/27	**64**
8	1	**-**	**4**	**80**	**2.5**	**2.5**	**5**	**88**	**80**	74/24[h]	**20**
9	1	**$scCO_2$**	**4**	**80**	**2.5**	**2.5**	**167**	**57**	**25**	81/19	**74**
10	1	**$scCO_2$**	**6**	**80**	**2.5**	**2.5**	**167**	**20**	**68**	85/15	**30**
11	1	**scCO2**	**6**	**80**	**10**	**10**	**167**	**6**	**86**	**81/19**	**14**
12	1	**scCO2**	**6**	**100**	**10**	**10**	**167**	**49**	**90**	**80/20**	**10**
13	1	**$scCO_2$**	**6**	**100**	**10**	**10**	**250**	**82**	**89**	**78/22**	**11**
14	2	**$scCO_2$**	**4**	**80**	**2.5**	**2.5**	**167**	**40**	**76**	76/24	**24**
15[g]	2	**$scCO_2$**	**4**	**80**	**2.5**	**2.5**	**167**	**15**	**12**	**45/55**[h]	**79**
16	2	**$scCO_2$**	**6**	**100**	**10**	**10**	**250**	**70**	**94**	**77/23**	**6**
17	3	**$scCO_2$**	**4**	**80**	**2.5**	**2.5**	**167**	**13**	**41**	**85/15**	**59**
18	3	**$scCO_2$**	**2**	**80**	**2.5**	**2.5**	**167**	**35**	**9**	**77/23**	**91**
19	3	**$scCO_2$**	**6**	**100**	**10**	**10**	**250**	**24**	**79**	**75/25**	**19**

[a]Reaction conditions: toluene: $[Rh(acac)(CO)_2]$: 0.024 mmol, alkene: 4.8 mmol, alkene/Rh= 200, V=10 ml, t:3h. $scCO_2$: $[Rh(acac)(CO)_2]$: 0.06 mmol, alkene: 12 mmol, alkene/Rh= 200, V=25 ml, t:3h, n.d. = not detected; [b] Total pressure; [c] Total conversion measured by GC; [d] Selectivity in aldehydes; [e] Selectivity in isomerized products (internal octenes). [f] preactivated system at 5 atm (CO/H_2: 1), T = 80 ºC for 1h; [g] preactivated system at 5 atm (CO/H_2: 1), T = 80 ºC for 1h in diethylether. [h] 2-ethylheptanal was also detected

At the best conditions (P/Rh = 6, CO/H_2 = 5 atm, T = 100ºC, total pressure 250 atm), we achieved high conversion (82 %) and high selectivity in aldehydes (89 %) (entry 13, table 3) probably because of the greater solubility of the system in $scCO_2$. At these conditions, the l/b ratio was similar to that of the toluene system.

When the system [Rh(acac)$(CO)_2$]/**2** in $scCO_2$ was used, the selectivity in aldehydes increased from 47 % to 76 %, though conversion was lower (entry 14 vs entry 4, Table 3). To favour the formation of the active species in one of the experiments (entry 15, Table 3), the system was preactivated for 1h at 5 atm (CO/H_2=1) at 80 ºC in diethylether. The solvent was then evaporated and 1-octene was added. The system was pressurised and heated again to 80ºC and the reaction started. In this case, the conversion and selectivity decreased considerably and decomposition of the catalyst was observed at the end of the reaction. At the optimised conditions, we obtained high selectivity in aldehydes (94 %) and a conversion of 70 %. When the system [Rh(acac)$(CO)_2$]/**3** (entries 17-19, table 3) was used, the best results were also obtained at the optimised conditions (selectivity in aldehydes 79 % and conversion 24 %).

In summary, the catalyst precursors formed with [Rh(acac)$(CO)_2$]/**1**-**3** are active in the hydroformylation of 1-octene in $scCO_2$. In the catalyst system with the phosphite **1**, similar conversion and selectivities to those of the toluene reaction can be achieved by optimising the reaction conditions. The selectivity in aldehyde of the rhodium catalyst precursors with ligands **2** and **3** increases, especially with ligand **2,** when $scCO_2$ is used as the reaction medium instead of toluene.

4.3. Conclusions

We have synthesised new P-donor ligands **1**-**3** with branched substituents and studied their coordination to Rh(I) and Pd(II) complexes. We have characterised complexes $[Rh(cod)(\mathbf{1})_2]PF_6$, $[Rh(\mathbf{2}\text{-}\mathbf{3})_4]PF_6$ and $[PdCl_2(\mathbf{1}\text{-}\mathbf{3})_2]$. We have determined the X-ray structure of $[Rh(\mathbf{3})_4]PF_6$ and confirmed the formation of the tetrakis(phosphite) complex. The reactivity of $[Rh(acac)(CO)_2]$/**1**-**3** with CO/H_2 at 5 atm (CO/H_2=1) and 80 ºC indicated that $[RhH(CO)(\mathbf{1}\text{-}\mathbf{3})_3]$ is the main species formed in solution. The solubility of the catalyst precursors $[Rh(acac)(CO)_2]$/**1**-**3** in $scCO_2$ is low but they are active in the hydroformylation of 1-octene in $scCO_2$. When $scCO_2$ was used, the catalyst precursor with ligand **1** gave similar activities and selectivities to those in toluene. Also using scCO2, catalyst precursors with ligands **2** and **3** gave lower conversions but the aldehyde selectivity was high.

4.4. Experimental

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled and degassed prior to use. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and NMR spectra were recorded on a Varian Gemini spectrometer operating at ^{1}H (300 or 400 MHz), ^{13}C (75.43 or 100.57 MHz), ^{31}P (121.44 or 161.92 MHz) ^{19}F (376.3 Hz). Chemical shifts were reported relative to tetramethylsilane for ^{1}H and $^{13}C\{^{1}H\}$ as internal reference, H_3PO_4 85% for $^{31}P\{^{1}H\}$. Mass spectrometry was performed in an AUTOSPEC spectrometer (EI-HR) and AUTOFLEX spectrometer (MALDI-TOF). High-pressure NMR experiments (HPNMR) were carried out in a 10 mm diameter sapphire tube with a titanium cap [29]. High-pressure IR experiments were performed in an in situ infrared autoclave [30]. Gas chromatography analyses were performed in a Hewlett-Packard 5890A in an HP-5 (5% diphenylsilicone/95%

dimethylsilicone) column (25 m x 0.2 mm Ø) for the separation of the products.

Catalysis

Hydroformylation experiments were carried out in a Parr autoclave (25 cm^3) with magnetic stirring. The autoclave was equipped with a liquid inlet, a gas inlet, a CO_2 inlet and a thermocouple. An electric heating mantle kept the temperature constant.

Standard hydroformylation experiment in toluene. The reactions in toluene were carried out in the same Paar autoclave. The complex [Rh(acac)$(CO)_2$] (0.024 mmol) and the ligand (0.096 mmol) in toluene (10 ml) were stirred for 1 h at room temperature. The substrate (4.8 mmol) was added and the resulting solution was introduced into the evacuated autoclave. The system was pressurised and heated. When thermal equilibrium was reached, more gas mixture was introduced until the desired pressure was attained. After the reaction time, the autoclave was cooled to room temperature and depressurised. The products were identified by GC-mass spectrometry.

Standard hydroformylation experiment in $scCO_2$. The complex [Rh(acac)$(CO)_2$] (0.06 mmol) and the ligand (0.24 mmol) in ether (2 ml) were stirred for 30 minutes at room temperature. The resulting solution was introduced into the evacuated autoclave, and the solvent was removed in vacuum. The substrate, 1-octene (12mmol) was then added. The system was pressurised with 5 bar of CO/H_2 (1:1), and liquid CO_2 was introduced until a total pressure of 60 bar. The autoclave was heated to the desired temperature. When thermal equilibrium was reached, the total pressure was adjusted with a Thar syringe pump. After the reaction time, the autoclave was cooled down to –10ºC and depressurised. The final mixture was analysed by GC. The products were identified by GC-mass spectrometry.

Solubility studies

The solubility studies were carried out in a Thar reactor (100 cm^3) equipped with sapphire windows and magnetic stirring. The autoclave was charged with a solution in diethyl ether of the ligand (0.220 mmol) and [Rh(acac)$(CO)_2$] (0.055 mmol). The solvent was removed in vacuum, the reactor was pressurised with syn-gas and CO_2, the system was heated to 80ºC, and the total pressure was adjusted to 240 bar. Solubility was monitored by visual inspection.

HP-spectroscopic measurements

HPNMR

In a typical experiment, the NMR tube was filled under N_2 with a solution of [Rh(acac)$(CO)_2$] (0.04 mmol), the ligand **1**-**3** (0.16 mmol) and toluene-d_8 (2 ml). The tube was pressurised to 5 atm CO/H_2 (1/1) and left for 1 h under agitation at 80ºC, and the NMR spectra were recorded.

HPIR

In a typical experiment, the HPIR cell was filled under N_2 with a solution of [Rh(acac)$(CO)_2$] (0.036 mmol), the ligand **1**-**3** (0.144 mmol) and methytetrahydrofurane (15 ml). The cell was pressurised to 5 atm CO/H_2 (1/1) and left for 1 h under agitation at 80ºC, and the IR spectra were recorded.

*Preparation of ligands **1**-**3***

*Preparation of tri(3,5,5-trimethylhexyl) phosphite (**1**).* To a solution of 3,5,5-trymethylhexanol (2.74 g, 0.019 mol) and pyridine (1.50 g, 0.019 mol) in 12 ml of diethylether at –10ºC, a solution of phosphorous trichloride (0.87 g, 6.3 mmol) in 6.5 ml of diethylether was added dropwise. The solution was stirred

at room temperature for 2h. The solution was filtered off and the solvent was removed. The resulting colourless oil was purified by flash chromatography on basic alumina eluting with hexane. Yield: 80 % (colourless oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (q, 6H, POC*H*$_2$, J_{HP} = 7.1 Hz, J_{HH} = 7.1 Hz), 1.57 (m, 6H, POCH$_2$C*H*H- + -C*H*CH$_3$-) 1.36 (m, 3H, POCH$_2$CH*H*-), 1.15 (dd, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 3.4 Hz, 3H, -CH(CH$_3$)C*H*H-), 1.00 (dd, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 6.0 Hz, 3H, -CH(CH$_3$)CH*H*-,), 0.86 (d, $^3J_{HH}$ = 6.4 Hz, 9H, -CH(C*H*$_3$)), 0.82 (s, 27H, C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$): δ 60.49 (d, $^2J_{PC}$ = 10.6 Hz, PO*C*H$_2$), 51.21 (s, -CH(CH$_3$)*C*H$_2$-), 40.52 (d, $^3J_{PC}$ = 4.6 Hz, POCH$_2$*C*H$_2$-), 31.11 (s, -*C*(CH$_3$)$_3$-), 29.99 (s, -C(*C*H$_3$)$_3$-), 25.91 (s, -*C*H(CH$_3$)-), 22.53 (s, -CH(*C*H$_3$)-). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 139.9. EIMS m/z: 461 $[M + H]^{+\cdot}$. High resolution EIMS: 461.4120, $C_{27}H_{58}O_3P$.

*Preparation of bis(3,5,5-trimethylhexyl) phenylphosphonite (**2**).* To a solution of 3,5,5-trymethylhexanol (2.88 g, 0.02 mol) and pyridine (1.58 g, 0.02 mol) in 12 ml of diethylether at –10ºC, a solution of diclorophenyl phosphine (1.79 g, 0.010 mol) in 6.5 ml of diethylether was added dropwise. The solution was stirred at room temperature for 7 h. The solution was filtered off. After all the solvent was removed under reduced pressure, the resulting colourless oil was purified by flash chromatography on basic alumina eluting with hexane. Yield: 56 % (colourless oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (m, 2H, Ph), 7.38 (m, 3H, Ph), 3.87 (m, 2H, -POC*H*H-), 3.75 (m, 2H, -POCH*H*-), 1.64 (m, 4H, POCH$_2$C*H*H- + -C*H*CH$_3$-), 1.43 (m, 2H, POCH$_2$CH*H*-), 1.19 (m, 2H, -CH(CH$_3$)C*H*H-), 1.05 (m, 2H, -CH(CH$_3$)CH*H*-), 0.91 (d, $^3J_{HH}$ = 8.4 Hz, 6H, -CH(C*H*$_3$)-,), 0.87 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$): δ 141.25 (d, $^1J_{PC}$ = 19.2 Hz, C$_i$ Ph), 129.84 (s, C$_p$ Ph), 129.65 (d, $^3J_{PC}$ = 2.3 Hz, C$_m$ Ph), 128.08 (d, J^2_{CP} = 4.5 Hz, C$_o$ Ph), 65.04 (d, $^2J_{PC}$ = 9.2 Hz, PO*C*H$_2$), 64.99 (d, $^2J_{PC}$ = 8.4 Hz, PO*C*H$_2$), 51.26 (s,-CH(CH$_3$)*C*H$_2$-), 51.22 (s,-CH(CH$_3$)*C*H$_2$-), 40.77 (d, $^3J_{CP}$ = 4.6 Hz, POCH$_2$*C*H$_2$-), 40.72 (d, $^3J_{CP}$ = 4.3 Hz, POCH$_2$*C*H$_2$-), 31.1 (s, -*C*(CH$_3$)$_3$-), 29.97 (s, -C(*C*H$_3$)$_3$-), 25.92 (s, -*C*H(CH$_3$)-), 22.54 (s, -CH(*C*H$_3$)-), 22.48 (s, -CH(*C*H$_3$)-). ^{31}P-{^{1}H} NMR

($CDCl_3$): δ 156.6. EIMS m/z: 394.3 $[M]^{+\cdot}$. High resolution EIMS: 394.2991, $C_{24}H_{43}O_2P$.

*Synthesis of (3,5,5-trimethylhexyl) diphenylphosphinite (**3**).* To a solution of 3,5,5-trymethylhexanol (0.66 g, 4.6 mmol) and of pyridine (0.36 g, 4.6 mmol) in 12 ml of diethylether at –10ºC, a solution of chlorodiphenyl phosphine (1.00 g, 4.6 mmol) in 6.5 ml of diethylether was added dropwise. The solution was stirred at room temperature for 2h. The solution was filtered off. After all the solvent was removed under reduced pressure, the resulting colourless oil was purified by chromatography on basic alumina eluting with hexane. Yield: 67 % (colourless oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 4H, Ph), 7.22 (m 6H, Ph), 3.78, (m, 2H, POC*H*$_2$), 1.64 (m, 1H, $POCH_2CHH$-), 1.55 (m, 1H, -C*H*(CH_3)-), 1.40 (m, 1H,- $POCH_2CHH$-), 1.13 (dd, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 3.8 Hz, 1H, -$CH(CH_3)CHH$-), 0.96 (dd, $^2J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 6.8 Hz, 1H,-$CH(CH_3)CHH$-), 0.82 (d, $^3J_{HH}$ = 6.2 Hz, 3H, -$CH(CH_3)_3$-), 0.77 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 142.28 (d, $^2J_{PC}$ = 18.8 Hz, C_i Ph), 130.54 (d, $^2J_{PC}$ = 7.6 Hz, C_o Ph), 130.33 (d, $^2J_{PC}$ = 7.6 Hz, C_o Ph), 129.12 (d, $^3J_{PC}$ = 5.3 Hz, C_m Ph), 128.26 (s, C_p Ph), 128.19 (s, C_p Ph), 68.50 (d, $^2J_{PC}$ = 19,1 Hz, $POCH_2$-), 51.21 (s, -$CH(CH_3)CH_2$-), 40.83 (d, $^3J_{PC}$ = 7.6 Hz, $POCH_2CH_2$-) 31.08 (s, -$C(CH_3)_3$-), 29.99 (s, -$C(CH_3)_3$-) 29.95 (s , -$C(CH_3)_3$-), 25.92 (s, -$CH(CH_3)$), 22.50 (s, -$CH(CH_3)$-). ^{31}P-{1H} NMR ($CDCl_3$): 112.5. EIMS m/z: 328.2 $[M]^{+\cdot}$. High resolution EIMS: 328.1961, $C_{21}H_{29}OP$.

*Preparation of complexes **4**-**9***

*Preparation of $[Rh(C_8H_{12})(\mathbf{1})_2]PF_6$ (**4**).* Ligand **1** (221 mg, 0.48 mmol) was added to a solution of the complex $[Rh(cod)_2]PF_6$ (93 mg, 0.20 mmol) in 2 ml of anhydrous dichloromethane. The solution turned yellow immediately and was stirred for 1 hour. The solvent was evaporated in vacuum and the product was washed with cold methanol. The product was obtained as a yellow oil. Yield: 86 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.05 (m, 16H, $POCH_2$ + CH= cod), 2.57

(m, 4H, CH_2 cod), 2.36 (m, 4H, CH_2 cod), 1.60 (m, 18H, $POCH_2CH_2$- + -$CH$$CH_3$-), 1.22 (dd, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 3.6 Hz, 6H, -$CH(CH_3)CH$*H*-), 1.14 (dd, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 6.0 Hz, 6H, -$CH(CH_3)CH$*H*-), 0.97 (d, $^3J_{HH}$ = 6.4 Hz, 18H, -$CH(CH_3)$-,), 0.90 (s, 54H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 106.2 (m, CH= cod), 65.2 (d, J_{CP} = 6.1 Hz, $POCH_2$), 51.3 (s, -$CH(CH_3)CH_2$-), 39.8 (d, $POCH_2CH_2$-), 31.1 (s, -$C(CH_3)_3$-), 29.9 (s, -$C(CH_3)_3$-) 26.1 (s, (-$CH(CH_3)$-), 22.5 (s, -$CH(CH_3)$-). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 116.1 (d, J_{RhP} = 244.0 Hz), -143.2 (sept., J_{FP} = 711.5 Hz). ^{19}F NMR ($CDCl_3$): δ -73,11 (d, J_{PF} = 715.4 Hz). MS (MALDI-TOF) *m/z*: 1129.54 [M-PF_6-3H]$^+$, 1003.45 [M-PF_6-C_9H_{20}-H]$^+$

*Preparation of [Rh(**2**)$_4$]PF$_6$ (**5**)*. Ligand **2** (316 mg, 0.80 mmol) was added to a solution of the complex [Rh(cod)$_2$]PF_6 (46.5 mg, 0.20 mmol) in 2 ml of anhydrous dichloromethane. The solution turned yellow immediately and was stirred for 1 hour. The solvent was evaporated, washed with cold methanol and dried in vacuum overnight. The product was obtained as a yellow oily solid. Yield: 76 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.5 (m, 20H, Ph), 3.47 (br m, 8H, -POC*H*H-), 3.16 (br, 8H, -POCH*H*-), 1.38 (m br, 24H, $POCH_2CH_2$- + -$CH$$CH_3$-), 1.02 (br m, 16H, -$CH(CH_3)CH_2$-), 0.85 (d, $^3J_{HH}$ = 5.6 Hz, 24H, -$CH(CH_3)$), 0.87 (s, 72H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 137.74 (br, C_i Ph), 131.47 (s, C_o Ph), 130.33 (s, C_m Ph) 128.34 (s, C_p Ph), 66.00 (br, $POCH_2$-) 51.19 (s, -$CH(CH_3)CH_2$-), 39.91 (s, $POCH_2CH_2$-), 31.01 (s, -$C(CH_3)_3$-), 29.90 (s, -$C(CH_3)_3$-), 26.21 (s, -$CH(CH_3)$-), 22.65 (s, -$CH(CH_3)$-). ^{31}P-{^{1}H} δ NMR ($CDCl_3$): 146.0 (d, J_{PRh} = 169.7 Hz), -143.2 (sept., J_{PF} = 711.5 Hz). ^{19}F NMR ($CDCl_3$): δ -74.32 (d, J_{FP} = 710.8 Hz). MS (MALDI-TOF) *m/z*: 1679.7 [M-PF_6-2H]$^+$ 1285.56 [M-PF_6-4H]$^+$

*Preparation of [Rh(**3**)$_4$]PF$_6$ (**6**)*. The ligand **3** (158 mg, 0.47 mmol) was added to a solution of the complex [Rh(cod)$_2$]PF_6 (80 mg, 0.20 mmol) in 2 ml of anhydrous dichloromethane. The solution turned yellow immediately and was stirred for 1 hour. Diethyl ether was then added to the solution to afford a

yellow solid. Yield: **73** %. ^{1}H NMR ($CDCl_3$): δ 7.2-7.3 (m, 40H, Ph), 2.78 (br m, 8H, POC*H*$_2$); 0.80 (m, 12H, $POCH_2CH_2CH(CH_3)$), 0.67 (dd, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 5.6 Hz, 4H, -CH(CH3)CH*H*-), 0.60 (s, 36H, $C(CH_3)_3$), 0,54 (dd, $^2J_{HH}$ = 14. Hz, $^3J_{HH}$ = 3 Hz, 4H, $-CH(CH_3)CHH$-), 0.42 (d, $^3J_{HH}$ = 6.4 Hz, 12H, $-CH(CH_3)$-). ^{13}C NMR ($CDCl_3$): δ 133.25 (br, C_i Ph), 133.01 (s, C_o Ph), 131.06 (s, C_m Ph), 128.27 (s, C_p Ph), 66.53 (s, $POCH_2$), 51.08 (s,$-CH(CH_3)CH_2$-), 37.85 (s, $POCH_2CH_2$), 31.06 (s, $-C(CH_3)_3$-), 29.83 (s, $-C(CH_3)_3$), 26.02 (s, -*C*H(CH3), 22.86 (s, $-CH(CH_3)$). ^{31}P-{^{1}H} NMR ($CDCl_3$): 132.3 d, (J_{PRh} = 162.2 Hz); -143.1 sept. ($J_{P\text{-}F}$ = 712.6Hz).

*Preparation of [PdCl$_2$(**1**)$_2$] (**7**)*. Ligand **1** (120 mg, 0.26 mmol) was added to a solution of the complex [$PdCl_2(PhCN)_2$] (50 mg, 0.13 mmol) in 2 ml of anhydrous dichloromethane. The solution was stirred for 1 hour, the solvent was evaporated in vacuum, and the product was washed with cold methanol and dried under vacuum overnight. The product was obtained as a light yellow oil. Yield: 87 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.15 (m, 12H, POC*H*$_2$) 1.64 (m, 6H, $POCH_2CH$-), 1.55 (m, 6H, $-CHCH_3$-), 1.46 (m, 6H, $POCH_2CH$*H*-), 1.44 (dd, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 3.6 Hz, 6H, $-CH(CH_3)CHH$-), 1.03 (dd, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 6.4 Hz, 6H, $-CH(CH_3)CH$*H*-,), 0.88 (d, $^3J_{HH}$ = 3.2 Hz, 18H, $-CH(CH_3)$-,), 0.83 (s, 54H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 66.60 (s, $POCH_2$), 51.35 (s, $-CH(CH_3)CH_2$-), 39.77 (s, $POCH_2CH_2$-), 31.29 (s, $-C(CH_3)_3$-), 30.18 (s, $-C(CH_3)_3$-), 26.15 (s, $-CH(CH_3)$-) 22.67 (s, $-CH(CH_3)$-). ^{31}P-{^{1}H} NMR ($CDCl_3$): 94.2 s. MS (MALDI-TOF) *m/z*: 1063.7 $[M\text{-}Cl]^+$, 1026.7 $[M\text{-}2Cl]^+$

*Preparation of [PdCl$_2$(**2**)$_2$] (**8**)*. Ligand **2** (51 mg, 0.12 mmol) was added to a solution of the complex [$PdCl_2(PhCN)_2$] (25 mg, 0.06 mmol) in 2 ml of anhydrous dichloromethane. The solution was stirred for 1 hour, the solvent was evaporated in vacuum, and the product was washed with cold methanol and dried under vacuum overnight. The product was obtained as a yellow oil. Yield: 81 %. ^{1}H NMR ($CDCl_3$): δ 7.75 (m, 4H, Ph), 7.45 (m, 6H, Ph), 4.20 (br m,

4H, -POC*H*H-), 3.95 (br m, 4H, -POCH*H*-), 1.71 (m br, 4H, $POCH_2CH$*H*), 1.54 (m br, 8H, *POCH$_2$CH*H + -*CH*CH$_3$-), 1.13 (br m, 8H, -CH(CH$_3$)C*H$_2$*-), 0.90 (d, $^3J_{HH}$ = 6.4 Hz, 12H, -CH(C*H$_3$*)-,) 0.87 (s, 36H, C(C*H$_3$*)$_3$). ^{13}C NMR ($CDCl_3$): δ 140.70 (br, C_i Ph), 132.55 (s, C_o Ph), 131.74 (s, C_m Ph), 129.07, (s, C_p Ph), 67.83 (s, PO*C*H$_2$-), 50.93 (s,-CH(CH$_3$)*C*H$_2$-), 39.22 (s, POCH$_2$*C*H$_2$-), 30.88 (s, -*C*(CH$_3$)$_3$-), 29.77 (s, -C(*C*H$_3$)$_3$-), 25.82 (s, -*C*H(CH$_3$)-), 22.26 (s, -CH(*C*H$_3$)-). ^{31}P-{^{1}H} δ NMR ($CDCl_3$): 122.2 s. MS (MALDI-TOF) *m/z*: 929.4 $[M\text{-}Cl]^+$, 894.4 $[M\text{-}2Cl]^+$

*Preparation of [PdCl$_2$(**3**)$_2$] (**9**)*. Ligand **3** (85.63 mg, 0.26 mmol) was added to a solution of the complex [PdCl$_2$(PhCN)$_2$] (50mg, 0.13 mmol) in 2 ml of anhydrous dichloromethane. The solution was stirred for 1 hour, the solvent was evaporated in vacuum and the residue was washed with methanol. The product was obtained as a yellow oil. Yield: 91 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (m, 8H, Ph), 7.46 (m 12H, Ph), 3.63 (m, 4H, POC*H$_2$*), 1.31-1.19 (m, 6H, POCH$_2$C*H$_2$*- + -*CH*(CH$_3$)- + -CH(CH$_3$)C*H$_2$*-), 0.92 (d, $^3J_{HH}$ = 4.4 Hz, 6H, -CH(C*H$_3$*)-), 0.78 (s, -C(C*H$_3$*)$_3$). ^{13}C NMR ($CDCl_3$): δ 140.4 (br C_i Ph), 132.58 (d, $^2J_{PC}$ = 6.1 Hz, C_o Ph), 132.52 (d, $^2J_{PC}$ = 6.1 Hz, C_o Ph), 131.75 (br, C_m Ph), 128.20 (br, C_p Ph), 67.86 (s, PO*C*H$_2$-), 50.93 (s, -CH(CH$_3$)*C*H$_2$-), 39.22 (POCH$_2$*C*H$_2$-), 30.87 (s, -*C*(CH$_3$)$_3$-), 29.76 (s, -C(*C*H$_3$)$_3$-), 25.81 s, -*C*H(CH$_3$)-), 22.26 (s, -CH(*C*H$_3$)-). ^{31}P ($CDCl_3$): 110.206 s. MS (MALDI-TOF) *m/z*: 796.9 $[M\text{-}Cl]^+$, 762.0 $[M\text{-}2Cl]^+$

Crystal data for complex **6**. Suitable crystals of complex **6** were grown by slow diffusion of diethyl ether into a solution of the complex in dichloromethane and mounted on a glass fibber. The measurements were taken at 120 K in a Brucker SMART CCD1000 diffractometer, with a graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Data collection and processing were carried out using BRUKER Smart and BRUCKER saint. Complex **6** $C_{84}H_{112}O_4P_4Rh.F_6P$ crystallised in a tetragonal *P4/n* space group, with *a* = 18.021 (2) Å, *c* = 13.431 (3) Å, *V* = 4361.8 (12) Å^3, *M* = 1557.50, *Z* = 2, ρ_{calcd} =

1.186 mg m^{-3}, μ = 0.345 mm^{-1}. The yellow crystal was prismatic and of dimensions 0.6 x 0.52 x 0.48 mm. The θ range for measurement was 1.52 to 26.37° and 4471 unique reflections were measured at 393 (2) K (R_{int} = 0.0381). The structure was solved by direct methods (SHELXS-97) [31] and refined on F^2 by full-matrix lest-squares (SHELXL-97) [32] of 278 parameters. All non-hydrogen atoms were refined anisotropically. The data were corrected for absorption effects with SADABS [33]. The final parameters were $R = \sum||Fo| - |Fc|| / \sum|F_o^2|$ = 0.0393 for 3571 reflections with $F_o^2 > 2\sigma(F_o^2)$ and $wR_2 = [\sum w(Fo^2 - Fc^2)/\sum w(Fo^2)^2)]^{1/2}$ = 0.1178, Goodness-of-fit = 1.1. The ORTEP diagram was generated using ORTEP-3 [34]. CCDC-270199 contained the supplementary crystallographic data for this structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

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4.5 References

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