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# New Ligands for Rh-Catalysed Hydroformylation of 1-Octene in Supercritical Carbon Dioxide – X-ray Structure of $[Rh\{PPh_2(OC_9H_{19})\}_4]PF_6$

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The 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 $Pd^{II}$ studied. The X-ray structure of $[Rh\{PPh_2(OC_9H_{19})\}_4]PF_6$ was determined. Reaction of the $[Rh(acac)(CO)_2]/PPh_{3-n}(OC_9H_{19})_n$ systems with $CO/H_2$ at 5 atm and 80 °C in toluene led to the formation of $[RhH(CO)\{PPh_{3-n}(OC_9H_{19})_n\}_3]$ as the main species. The Rh-catalysed hydroformylation of 1-octene with these ligands was investigated in supercritical carbon dioxide ($scCO_2$) and toluene as solvents. Although the catalytic systems are not soluble in $scCO_2$, they are active. The activities are higher in toluene than in $scCO_2$ but the selectivities for aldehydes in the case of the phosphonite derivative are higher in the supercritical medium than in toluene.


## Introduction

In the last few years supercritical carbon dioxide ($scCO_2$) has received growing attention as an alternative reaction medium for homogeneous catalysis[1] as it is an environmentally friendly and cheap solvent. More important, however, are its gas-like properties, 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 a low viscosity and therefore a high diffusivity. Moreover, its ability as an extraction solvent has proved useful for separating the products from the catalysts without the need for harsher conditions such as 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 under mild conditions. Water can be used as a "green" solvent in this reaction, but this process is limited to short-chain alkenes (propene and 1-butene) because a certain degree of 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 often needed to increase the solubility of the catalytic systems. The most successful approach is to introduce perfluoroalkyl 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 phosphanes such as $[Rh_2(OAc)_4]/PEt_3$ systems, which are soluble in $scCO_2$, in the hydroformylation of 1-hexene, but the *n*/*iso* ratios were modest (2.1–2.6).[6] Ligands containing alkyl groups, preferably branched, with a chain length of eight carbon atoms have reportedly shown high solubility in supercritical carbon dioxide.[7] In the case of alkylphosphanes, such as $P(C_8H_{17})_3$, the Rh systems were not soluble under the conditions studied and the turnover frequency (TOF) was low (3–7 $h^{-1}$, 8–20% conversion in 2 h), although the *n*/*iso* ratios were high (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 $scCO_2$, showed activities in the hydroformylation of 1-hexadecene with average TOFs of 150, 350 and 20 $h^{-1}$, respectively. This correlated with a maximum solubility of the $C_{10}H_{21}$ derivative.[5c] Other $scCO_2$-insoluble systems, such as $P(OPh)_3$, $P(p\text{-}OC_6H_4\text{-}C_9H_{19})_3$ and $PPh_2[CH_2CH(CO_2C_{16}H_{33})CH_2\text{-}CO_2C_{16}H_{33}]$, have been 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 by taking advantage of the excellent extraction ability of $scCO_2$.[8]

The incorporation of *tert*-butyl substituents into the alkyl chains of P-donor ligands has been reported to increase their solubility in $scCO_2$.[7,9] Introducing branched chains in surfactants derived from sodium bis(2-ethyl-1-hexyl)sulfosuccinate increases their solubility in $scCO_2$.[10]

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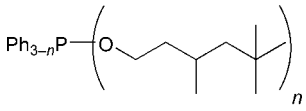
In this paper we present the synthesis of three new P-donor ligands with nine-carbon, branched alkyl substituents (Figure 1) and their application to the rhodium-catalysed hydroformylation of 1-octene in $scCO_2$ and in toluene as solvents. Phosphite (**1**), phosphonite (**2**) and phosphinite (**3**) ligands were selected because the introduction of oxy groups has a positive effect on activity and regioselectivity.[3b,11] Bulky monophosphonite ligands have shown very high activities in the isomerisation/hydroformylation of octene.[11] We also studied the coordination of the new ligands to rhodium(I) and palladium(II).



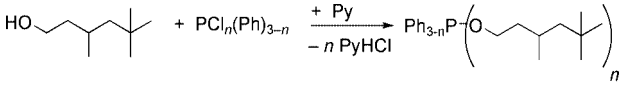

**1**: $n = 3$
**2**: $n = 2$
**3**: $n = 1$

Figure 1. P-donor ligands.

## Results and Discussion

### 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 chlorophenylphosphane in diethyl ether in the presence of pyridine (Scheme 1). The ligands were purified by flash chromatography on basic alumina eluting with hexane under an inert gas and obtained as air- and moisture-sensitive colourless oils in good yields (56–80%). The $^1H$ NNMR spectra show the methylene (-$OCH_2$-) signals at $\delta = 3.8$ ppm, the methylene and methine signals between $\delta = 1.6$ and 1.0 ppm, and the methyl doublet and singlet from the *tert*-butyl group at $\delta = 0.9$ ppm. The signals were assigned by means of COSY and HETCOR experiments. The $^{31}P\{^1H\}$ NMR singlet signals appear at $\delta = 139.9$, 156.6 and 112.5 ppm for **1**–**3**, respectively, which are typical values for this kind of phosphorus compounds.[12]

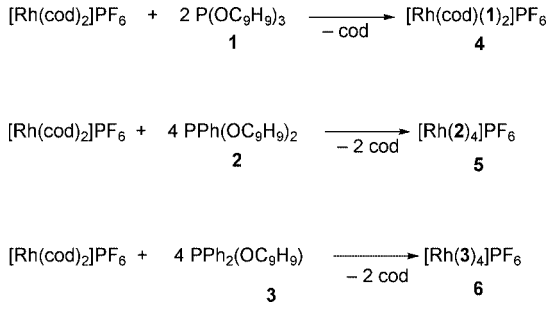



**1**: $n = 3$
**2**: $n = 2$
**3**: $n = 1$

Scheme 1. Synthesis of **1**–**3**.

### 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 $[Rh(cod)_2]PF_6$ (cod = 1,5-cyclooctadiene) as a model for cationic complexes (Scheme 2). The reaction of ligands **1**–**3** with $[Rh(cod)_2]PF_6$ in anhydrous dichloromethane at room temperature should proceed by displacement of the 1,5-cyclooctadiene ligand, followed by coordination of two P-donor ligands. With tris(3,5,5-trimethylhexyl) phosphite (**1**) in a P/Rh molar ratio of 2:1, the complex $[Rh(cod)(\mathbf{1})_2]PF_6$ (**4**) was obtained as a relatively air-stable, yellow oil in high yield. Several attempts to solidify the complex were unsuccessful. Its $^{31}P\{^1H\}$ NMR spectrum shows a doublet at $\delta = 116.1$ ppm ($J_{P,Rh} = 244.0$ Hz), which corresponds to the coordinated phosphite ligand, and the characteristic septuplet of the $PF_6^-$ counteranion at $\delta = -143.2$ ppm ($J_{P,F} = 711.5$ Hz). The presence of coordinated cyclooctadiene was confirmed by the $^1H$ NMR spectrum, which shows signals at $\delta = 4.05$ ppm (HC=CH) and 2.57 and 2.36 ppm (-$CH_2$-). The $^1H$ NMR signals corresponding to the coordinated ligand are shifted slightly with respect to those of the free ligand. The mass spectrum shows a signal at $m/z = 1129.5$ corresponding to the $[Rh(cod)(\mathbf{1})_2]^+$ fragment.




Scheme 2. Syntheses of **4**–**6**.

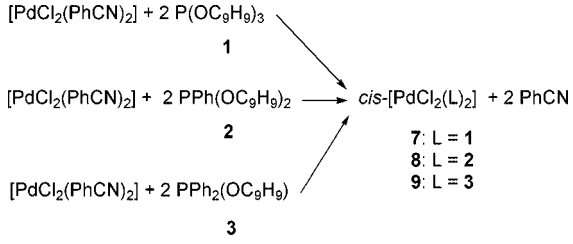
However, upon treatment of the same precursor complex $[Rh(cod)_2]PF_6$ with the same P/Rh molar ratio but using phosphonite **2**, the $^{31}P\{^1H\}$ NMR spectrum shows two doublets in the region of coordinated phosphorus atoms at $\delta = 146.0$ ($J_{P,Rh} = 165.9$ Hz) and 138.5 ($J_{P,Rh} = 170.8$ Hz) ppm and the $^1H$ NMR spectrum shows signals corresponding to coordinated cyclooctadiene (at $\delta = 4.0$ and 2.5–2.7 ppm). When the P/Rh molar ratio is 4:1, the $^{31}P\{^1H\}$ NMR spectrum shows only the signal at $\delta = 146.0$ ppm. There was no evidence of coordinated COD in the $^1H$ NMR spectrum, and only signals attributable to the coordinated ligand were detected. In this case, a relatively air-stable, yellow, oily solid was obtained in 76% yield. The mass spectrum of the isolated product has a signal $m/z = 1679.7$ corresponding to the cationic fragment $[Rh(\mathbf{2})_4]^+$. We propose that, at a P/Rh ratio of 2:1, a mixture of $[Rh(cod)(\mathbf{2})_2]PF_6$ and $[Rh(\mathbf{2})_4]PF_6$ (**5**) is formed and the totally substituted species **5** is formed at a P/Rh ratio of 4. Similar $[RhL_4]^+$ species have been obtained with $PPh(OCH_3)_2$,[13] with similar $^{31}P$ NMR spectroscopic data ($\delta = 148$ ppm, $J_{P,Rh} = 170$ Hz).[14]

In the reaction of $[Rh(cod)_2]PF_6$ with ligand **3** only one doublet is observed in the $^{31}P\{^1H\}$ NMR spectrum at P/Rh ratios of 2:1 and 4:1 [$\delta = 132.3$ ppm ($J_{P,Rh} = 162.2$ Hz)], which agrees with the data reported for $[Rh\{PPh_2(OR)\}_4]^+$ (R = Me: $\delta = 132.2$ ppm, $J_{P,Rh} = 159$ Hz; R = Et: $\delta = 130.5$ ppm, $J_{P,Rh} = 156$ Hz),[15] along with a septuplet signal for $PF_6^-$ at $\delta = -143.1$ ppm ($J_{F,P} = 712.6$ Hz). In the $^1H$

NMR spectrum there are only signals corresponding to the coordinated ligand **3**. A relatively air-stable, yellow solid was isolated in 73% yield. The X-ray crystal structure (see below) shows that this complex is $[Rh(\mathbf{3})_4]PF_6$ (**6**).

To prepare neutral palladium 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 proceeds by the displacement of two molecules of PhCN followed by the coordination of two P ligands to afford $[PdCl_2(\mathbf{1}–\mathbf{3})_2]$ (**7**–**9**, Scheme 3), which were obtained as relatively air-stable, yellow oils in good yields, with mass spectra in agreement with a mononuclear formulation. The $^1H$ NMR spectra of **7**–**9** show signals corresponding to the coordinated ligands. The $^{31}P\{^1H\}$ NMR spectra show only one singlet at $\delta$ = 94.2 (**7**), 122.2 (**8**) and 110.2 ppm (**9**), which indicates that only one of the two possible isomers (*cis* or *trans*) is formed. The difference between the $^{31}P$ NMR signal of the complex and that of the free ligand, known as the coordination chemical shift, $\Delta$ (= $\delta_{coord} - \delta_{free}$), for similar palladium(II) complexes is indicative of the stereochemistry of these complexes. The lowest (negative) values of $\Delta$ are found for *cis* isomers containing ligands with Tolman angles, $\Theta$, of less than 140°, and high values (positive) of $\Delta$ are found for *trans* isomers containing ligands with Tolman angles higher than 140°.[16] Based on this observation, since the values of $\Delta$ for complexes **7** and **8** are –45.7 and –34.4 ppm, respectively, we propose that the *cis* isomers are present in these complexes. In the case of complex **9** the value of $\Delta$ is –2.3 ppm. Taking into account that the estimated value of $\Theta$ from the X-ray structure is 128° (see below), we also propose the formation of the *cis* isomer for complex **9**.




Scheme 3. Syntheses of **7**–**9**.

### X-ray Structure of 6

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

This 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 has a slightly tetrahedrally distorted square-planar geometry [*trans* P–Rh–P angles of 166.64(3)°] due to intramolecular ligand repulsion. A similar distortion, but to a greater extent, has been reported for $[Rh(PMe_3)_4]^+$ (*trans* P–Rh–P angles of 148.29 and 151.46°).[18] The C–P–Rh angles [115.75(8) and 118.97(8)°] deviate from the ideal tetrahedral value, as observed in coordinated P-donor ligands. The estimated Tolman angle for **3**, calculated in accordance with the reported method,[19] is 128°. The alkoxy chains are in a staggered arrangement above and below 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 between the four *t*Bu groups from two different cationic units.

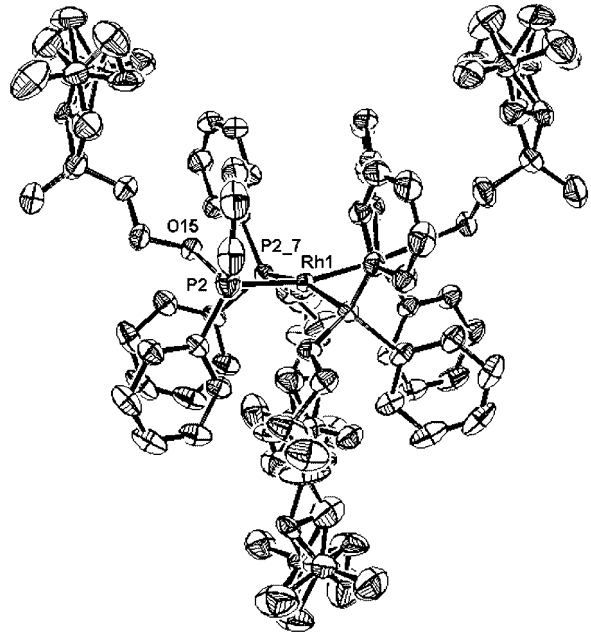



Figure 2. ORTEP drawing of complex **6**. $PF_6^-$ and hydrogen atoms have been omitted for clarity.

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

| | | | |
|---|---|---|---|
| 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. $P2^i$, $P2^{iii}$: phosphorus atoms located in *cis* position; $P2^i$, $P2^{ii}$: phosphorus atoms located in *trans* position.

### 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 by high-pressure NMR (HPNMR) and IR (HPIR) spectroscopy. The $^{31}P\{^1H\}$ and $^1H$ NMR spectra were recorded for the complex $[Rh(acac)(CO)_2]$ in the presence of 4 equiv. of ligand **1**–**3** in $[D_6]$toluene ($[Rh] = 2\times10^{-2}$ M) with stepwise addition of $H_2$ and CO. As the IR technique is more sensitive, the IR spectra could be recorded at concentrations closer to the catalytic value ($2–5\times10^{-3}$ M) in methyltetrahydrofuran under

the same conditions. A list of identified species is given in Table 2.

Table 2. Identified species for [Rh(acac)(CO)$_2$]/**1**–**3** (P/Rh = 4) systems at 5 atm CO/H$_2$ (1:1) after 1 h at 80 °C.

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

[a] n.d. = not detected.

Upon addition of 4 mol-equiv. of **1** to [Rh(acac)(CO)$_2$] in toluene, the $^{31}$P{$^1$H} spectrum shows a major, broad doublet signal at $\delta$ = 140 ppm, attributed to a mixture of the species [Rh(acac)(CO)$_n$(**1**)$_{2-n}$], along with a small multiplet at $\delta$ = 80 ppm and a singlet at $\delta$ = 0 ppm due to decomposed ligand. Addition of 2.5 atm of H$_2$ to this solution caused two new doublet signals to appear in the $^{31}$P{$^1$H} NMR spectrum at $\delta$ = 158.9 ppm ($J$ = 212.3 Hz) and $\delta$ = 157.9 ppm ($J$ = 207.8 Hz). Two new signals also appear in the hydride region of the $^1$H NMR spectrum at $\delta$ = –10.7 ppm (quint, $J$ = 7.8 Hz) and $\delta$ = –11.8 ppm (dq, $J$ = 33.7, 9.4 Hz). After further addition of 2.5 atm of CO (5 atm total pressure) and heating of the system at 80 °C for 1 h, the doublet signal in the $^{31}$P{$^1$H} NMR spectrum at $\delta$ = 157.9 ppm, the multiplet signal at $\delta$ = 80 ppm and the hydride signal at $\delta$ = –11.8 ppm in the $^1$H NMR spectrum disappear and new signals are observed at $\delta$ =154.6 (d, $J_{Rh,P}$ = 194.6 Hz), 140.8 (dd, $J$ = 273.6, 164.7 Hz), 138.1 (s, free **1**) and 70.2 (dt, $J$ = 273.4, 94.3 Hz) ppm. We assigned the signals at $\delta$ = 157.9 ppm and the hydride doublet of quintuplets at $\delta$ = –11.8 ppm to the species [RhH(**1**)$_4$] (**10**) by comparison with published data for the analogous species [RhH{P(OPh)$_3$}$_4$] [$\delta_P$ = 129.7 ($J_{Rh,P}$ = 232.8 Hz) ppm; $\delta_H$(hydride) = –10.6 ($J_{Rh,H}$ = 44, $J_{P,H}$ = 7 Hz) ppm].[20] We assigned the major doublet signal at $\delta$ = 158.9 ppm in the $^{31}$P{$^1$H} NMR spectrum together with the quintuplet at $\delta$ = –10.7 ppm in the $^1$H NMR spectrum to [RhH(CO)(**1**)$_3$] (**11**). The multiplicity of the hydride signal (quintuplet) is explained by the accidentally identical values of $^1J_{Rh,H}$ and $^2J_{P,H}$, as was also reported for [RhH(CO){P(OPh)$_3$}$_3$] [$\delta_P$ = 141.1 ($J_{Rh,P}$ = 240 Hz) ppm; $\delta_H$(hydride) = –10.9 ($J_{Rh,H}$ = $J_{P,H}$ = 3 Hz) ppm].[20] The minor signal at $\delta$ = 154.6 ($J_{Rh,P}$ = 194.6 Hz) ppm is attributed to the dicarbonyl species [RhH(CO)$_2$(**1**)$_2$] (**12**), whose hydride signal is not detected in the $^1$H NMR spectrum due to its low concentration. The signals at $\delta$ = 140.8 and 70.2 ppm could correspond to mixed complexes with phosphite/phosphonate and carbon monoxide ligands formed by the partially decomposed ligand. Coordination of phosphonates to rhodium complexes has been described in the literature[21] and the chemical shifts observed here correlate with those 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 $\delta$ = 140.8 and 70.2 ppm disappeared and new signals appeared, which could correspond to species with only phosphonate ligands.

The HPIR spectra of [Rh(acac)(CO)$_2$]/**1** at 5 atm CO/H$_2$ (1:1) in the ν(CO) region initially show signals at 2049, 2025, 2005, 1980 and 1960 cm$^{-1}$. By comparison with published data for [RhH(CO){P(OPh)$_3$}$_3$] [ν(CO) = 2060 (m) cm$^{-1}$],[22] the band at 2025 cm$^{-1}$ was assigned to **11**. The absorptions at 2049 and 1980 cm$^{-1}$ could correspond to the equatorial/equatorial isomer **ee-12** and those at 2005 and 1960 cm$^{-1}$ could correspond to the equatorial/axial isomer **ea-12**. The bands reported for ee-[RhH(CO)$_2${P(OPh)$_3$}$_2$] appear at 2053 and 2018 cm$^{-1}$ and for the isomer ea-[RhH(CO)$_2${P(OPh)$_3$}$_2$] at 2034 and 1992 cm$^{-1}$.[23] After 2 h at 80 °C, bands appeared at 1991 and 1828 cm$^{-1}$ attributed to rhodium species with bridging carbonyl ligands.

The $^{31}$P{$^1$H} and $^1$H NMR spectra of the [Rh(acac)(CO)$_2$]/**2** system (P/Rh = 4) in toluene under 5 atm of CO/H$_2$ (1:1), after heating at 80 °C for 1 h, show signals assigned to [RhH(CO)(**2**)$_3$] (**13**) and [RhH(CO)$_2$(**2**)$_2$] (**14**; Table 2); the hydride signals could not be detected in the $^1$H NMR spectrum. The signal of the remaining unreacted species [Rh(acac)(CO)$_n$(**2**)$_{2-n}$] appears at $\delta$ = 156 ppm. The slow reaction rate of similar precursors containing phosphite ligands with CO/H$_2$ has been reported.[24] The broad doublet at $\delta$ = 144.1 ($J_{Rh,P}$ = 168.7 Hz) ppm is better resolved at –60 °C and could correspond to dimeric Rh$^0$ complexes [Rh$_2$(CO)$_6$(**2**)$_2$] or [Rh$_2$(CO)$_4$(**2**)$_4$], as has been observed for other P-donor–rhodium systems.[25] The broad multiplets at $\delta$ = 120 and 82 ppm were attributed to mixed phosphonite/phosphonate species.

The HPIR spectrum, after 1 h under these reaction conditions, shows several absorptions in the 2200–1800 cm$^{-1}$ region that were difficult to assign. 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.

The $^{31}$P{$^1$H} NMR spectrum of [Rh(acac)(CO)$_2$]/**3** (P/Rh = 4) at 5 atm CO/H$_2$ (1:1), after 1 h at 80 °C, shows a major signal at $\delta$ = 138.1 ppm, which, together with a hydride signal at $\delta$ = –9.4 ppm, was attributed to the species [RhH(CO)(**3**)$_3$] (**15**) by comparison with published data.[26] A minor, partially overlapped doublet at $\delta$ = 136.8 ppm, together with a hydride doublet of triplets at $\delta$ = –9.1 ppm,

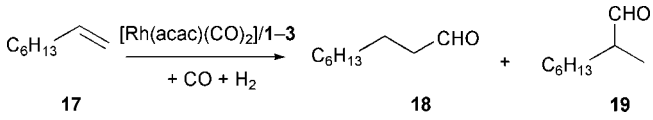
was attributed to the species $[RhH(CO)_2(\mathbf{3})_2]$ (**16**). In comparison, $[RhH(CO)\{PPh_2(OPh)\}_3]$ shows signals at $\delta_P$ = 142 ($J_{P,Rh}$ = 169 Hz) ppm and $\delta_H$ = –9.4 (dq, $J_{H,P}$ = 13, $J_{H,Rh}$ = 3 Hz) ppm and $[RhH(CO)_2\{PPh_2(OPh)\}_2]$ shows signals at $\delta_P$ = 145 ($J_{P,Rh}$ = 165 Hz) ppm and $\delta_H$ = –9.5 ppm.[27] The signals at $\delta$ = 130.8 and 84.9 ppm in the $^{31}P\{^1H\}$ spectrum may correspond to mixed phosphinite/phosphonate species, as proposed for the other systems.

The IR spectrum of $[Rh(acac)(CO)_2]$/**3**, under the same conditions, initially shows only one band at 1987 $cm^{-1}$ in the 2200–1800 $cm^{-1}$ region. After 1 h of stirring at 80 °C, five absorptions are present at 2044, 2025, 2006, 1966 and 1918 $cm^{-1}$. 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 are 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 isomer **ea-16**.

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 80 °C has shown that the precursors $[RhH(CO)(\mathbf{1}–\mathbf{3})_3]$ are formed as the main species in all cases.

## 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 the catalyst precursor. The products obtained were the isomeric aldehydes *n*-nonanal (**18**) and isononanal (**19**) and the isomerised products 2-octene [(*E*) and (*Z*)], (3*E*)-3-octene and (4*E*)-4-octene. No hydrogenated products were observed. The selectivity towards isomerised products is also listed.

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

The catalyst precursors with ligands **2** and **3** provided very low selectivity for 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 atom (see synthesis section above), which can inhibit hydroformylation,[28] we performed an experiment with a lower

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* [°C] | $P(H_2)$ [atm] | *P*(CO) [atm] | $P_{tot}$[b] [atm] | 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 | 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 | 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* = 3 h; $scCO_2$: $[Rh(acac)(CO)_2]$ = 0.06 mmol, alkene = 12 mmol, alkene/Rh = 200, *V* = 25 mL, *t* = 3 h. [b] Total pressure. [c] Total conversion measured by GC. [d] Selectivity for aldehydes. [e] Selectivity for isomerized products (internal octenes). [f] Preactivated system at 5 atm ($CO/H_2$ = 1), *T* = 80 °C for 1 h. [g] Preactivated system at 5 atm ($CO/H_2$ = 1), *T* = 80 °C for 1 h in diethyl ether. [h] 2-Ethylheptanal was also detected.

P/Rh ratio (Entry 6, Table 3); the selectivity for aldehydes decreased dramatically.

The low selectivity for aldehydes has been attributed to the nonformation of the active species $[RhH(CO)(L)_3]$. Our HPIR experiments showed that, in the case of systems with **2** and **3**, an activation time is needed before these species are detected. The system $[Rh(acac)(CO)_2]$/**2** was therefore preactivated in toluene at 5 atm ($CO/H_2$ = 1) and 80 °C for 1 h. 1-Octene was then added, the system was pressurised and again heated to 80 °C, and the reaction started. The conversion was slightly higher and the selectivity for aldehydes increased from 21 to 47% (Entry 4, Table 3). Similar results were obtained when the preactivated catalyst precursor with ligand **3** was used (Entry 7, Table 3).

Rhodium catalysts with phosphonite ligands have been shown to have very high activity in the isomerisation/hydroformylation of internal alkenes.[11] When we used $[Rh(acac)(CO)_2]$/**2** under the same conditions as for the hydroformylation of (2*E*)-2-hexene, 17% total conversion was obtained with a selectivity of 45% for aldehydes and a 1-heptanal/2-methylhexanal/3-ethylpentanal ratio of 24:54:22, which indicates that the isomerisation rate is 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 atm ($CO/H_2$ = 1:1) and pressurised with $CO_2$ up to 240 atm at 80 °C. Visual inspection through the windows showed that the supercritical phase is colourless, which indicates that there is no apparent solubility of these systems.

The catalytic experiments using $scCO_2$ with 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 with $scCO_2$ were lower than for the toluene systems under similar conditions. However, conversion was good with the catalyst system $[Rh(acac)(CO)_2]$/**1** (Entry 9, Table 3), although the selectivity for 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). Under the best conditions (P/Rh = 6, $CO/H_2$ = 20 atm, $T$ = 100 °C, total pressure 250 atm), we achieved high conversion (82%) and high selectivity for aldehydes (89%; Entry 13, Table 3) probably because of the greater solubility of this system in $scCO_2$. Under these conditions, the linear/branched ratio was similar to that of the toluene system.

When the system $[Rh(acac)(CO)_2]$/**2** was used in $scCO_2$, the selectivity for aldehydes increased from 47% to 76%, although the 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 in diethyl ether at 5 atm ($CO/H_2$ = 1) at 80 °C for 1 h. The solvent was then evaporated and 1-octene was added. The system was pressurised and heated again to 80 °C 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. Under the optimised conditions, we obtained high selectivity for 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 under the optimised conditions (selectivity for aldehydes 79% and conversion of 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 for 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.

## Conclusions

We have synthesised new P-donor ligands **1**–**3** with branched substituents and studied their coordination to $Rh^I$ and $Pd^{II}$. We have characterised complexes $[Rh(cod)(\mathbf{1})_2]PF_6$, $[Rh(\mathbf{2},\mathbf{3})_4]PF_6$ and $[PdCl_2(\mathbf{1}–\mathbf{3})_2]$. 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 °C indicates that $[RhH(CO)(\mathbf{1}–\mathbf{3})_3]$ 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 $scCO_2$. In this solvent, the catalyst precursor with ligand **1** gives similar activities and selectivities to those in toluene. Catalyst precursors with ligands **2** and **3** give lower conversions than in toluene but the aldehyde selectivity is higher.

## Experimental Section

**General:** All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were distilled and degassed prior to use. $^1H$, $^{13}C\{^1H\}$, $^{19}F$ and $^{31}P\{^1H\}$ NMR spectra were recorded with Varian Gemini spectrometers operating at 300 or 400 MHz ($^1H$), 75.43 or 100.57 MHz ($^{13}C$), 376.3 MHz ($^{19}F$) or 121.44 or 161.92 MHz ($^{31}P$). Chemical shifts are reported relative to tetramethylsilane for $^1H$ and $^{13}C\{^1H\}$ as internal reference, 85% $H_3PO_4$ for $^{31}P\{^1H\}$ and $CFCl_3$ for $^{19}F$. Mass spectrometry was performed with either an AUTOSPEC (EI-HR) or an AUTOFLEX spectrometer (MALDI-TOF). High-pressure NMR experiments (HPNMR) were carried out in a 10-mm-diameter sapphire tube with a titanium cap equipped with a Teflon/polycarbonate protection.[29] High-pressure IR experiments were performed in situ with an infrared autoclave.[30] Gas chromatography analyses were per-

formed with a Hewlett–Packard 5890A apparatus in an HP-5 (5% diphenylsilicone/95% dimethylsilicone) column (25 m × 0.2 mm) for the separation of the products.

**Catalysis:** Hydroformylation experiments were carried out in a Parr autoclave (25 mL) 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 Parr autoclave. The complex [Rh(acac)(CO)$_2$] (0.024 mmol) and the ligand (0.096 mmol) in toluene (10 mL) were stirred at room temperature for 1 h. The substrate (4.8 mmol) was then 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 required reaction time, the autoclave was cooled to room temperature and depressurised. The products were identified by GC/MS.

**Standard Hydroformylation Experiment in scCO$_2$:** The complex [Rh(acac)(CO)$_2$] (0.06 mmol) and the ligand (0.24 mmol) in diethyl ether (2 mL) were stirred at room temperature for 30 min. The resulting solution was introduced into the evacuated autoclave, and the solvent was removed in vacuo. 1-Octene (12 mmol) was then added. The system was pressurised with 5 atm of CO/H$_2$ (1:1), and liquid $CO_2$ was introduced until a total pressure of 60 bar was reached. 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 –10 °C and depressurised. The final mixture was analysed by GC. The products were identified by GC/MS.

**Solubility Studies:** The solubility studies were carried out in a Thar reactor (100 mL) equipped with sapphire windows and magnetic stirring. The autoclave was charged with a solution of the ligand (0.220 mmol) and [Rh(acac)(CO)$_2$] (0.055 mmol) in diethyl ether. The solvent was removed in vacuo, the reactor was pressurised with syn-gas and $CO_2$, the system was heated to 80 °C, and the total pressure was adjusted to 240 atm. Solubility was monitored by visual inspection through the sapphire windows with a mirror due to safety requirements.

**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 [D$_8$]toluene (2 mL). The tube was pressurised to 5 atm of CO/H$_2$ (1:1) and left at 80 °C for 1 h. The NMR spectra were then 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 methyltetrahydrofuran (15 mL). The cell was pressurised to 5 atm of CO/H$_2$ (1:1) and left at 80 °C for 1 h. The IR spectra were then recorded.

**Preparation of Tris(3,5,5-trimethylhexyl) Phosphite (1):** A solution of phosphorus trichloride (0.87 g, 6.3 mmol) in 6.5 mL of diethyl ether was added dropwise to a solution of 3,5,5-trimethylhexanol (2.74 g, 0.019 mol) and pyridine (1.50 g, 0.019 mol) in 12 mL of diethyl ether at –10 °C. The solution was stirred at room temperature for 2 h. The solution was filtered and the solvent was removed. The resulting colourless oil was purified by flash chromatography on basic alumina eluting with hexane. Yield: 2.33 g (80%) (colourless oil). $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$ = 3.74 (q, $J_{H,P}$ = $J_{H,H}$ = 7.1 Hz, 6 H, POC$H_2$), 1.57 (m, 6 H, POCH$_2$C*H*H + C*H*CH$_3$) 1.36 (m, 3 H, POCH$_2$CH*H*), 1.15 [dd, $^2J_{H,H}$ = 14.0 Hz, $^3J_{H,H}$ = 3.4 Hz, 3 H, CH(CH$_3$)C*H*H], 1.00 [dd, $^2J_{H,H}$ = 14.0 Hz, $^3J_{H,H}$ = 6.0 Hz, 3 H, CH(CH$_3$)CH*H*], 0.86 [d, $^3J_{H,H}$ = 6.4 Hz, 9 H, CH(C*H*$_3$)], 0.82 [s, 27 H, C(C*H*$_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 20 °C): $\delta$ = 60.49 (d, $^2J_{P,C}$ = 10.6 Hz, PO*C*H$_2$), 51.21 [s, CH(CH$_3$)*C*H$_2$], 40.52 (d, $^3J_{P,C}$ = 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$_3$)] ppm. $^{31}$P{$^1$H} NMR (161.9 MHz, $CDCl_3$, 20 °C): $\delta$ = 139.9 ppm. EIMS: *m*/*z* = 461 [M + H]$^+$. High-resolution EIMS: 461.4120 ($C_{27}H_{58}O_3P$).

**Preparation of Bis(3,5,5-trimethylhexyl) Phenylphosphonite (2):** A solution of dichloro(phenyl)phosphane (1.79 g, 0.010 mol) in 6.5 mL of diethyl ether was added dropwise to a solution of 3,5,5-trimethylhexanol (2.88 g, 0.02 mol) and pyridine (1.58 g, 0.02 mol) in 12 mL of diethyl ether at –10 °C. The solution was stirred at room temperature for 7 h and then filtered. After all the solvent had been removed under reduced pressure, the resulting colourless oil was purified by flash chromatography on basic alumina eluting with hexane. Yield: 2.21 g (56%) (colourless oil). $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$ = 7.59 (m, 2 H, Ph), 7.38 (m, 3 H, Ph), 3.87 (m, 2 H, POC*H*H), 3.75 (m, 2 H, POCH*H*), 1.64 (m, 4 H, POCH$_2$C*H*H + C*H*CH$_3$), 1.43 (m, 2 H, POCH$_2$CH*H*), 1.19 [m, 2 H, CH(CH$_3$)C*H*H], 1.05 [m, 2 H, CH(CH$_3$)CH*H*], 0.91 [d, $^3J_{H,H}$ = 8.4 Hz, 6 H, CH(C*H*$_3$)], 0.87 [s, 18 H, C(C*H*$_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 20 °C): $\delta$ = 141.25 (d, $^1J_{P,C}$ = 19.2 Hz, C$_i$ Ph), 129.84 (s, C$_p$ Ph), 129.65 (d, $^3J_{P,C}$ = 2.3 Hz, C$_m$ Ph), 128.08 (d, $^2J_{C,P}$ = 4.5 Hz, C$_o$ Ph), 65.04 (d, $^2J_{P,C}$ = 9.2 Hz, PO*C*H$_2$), 64.99 (d, $^2J_{P,C}$ = 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, $^3J_{C,P}$ = 4.6 Hz, POCH$_2$*C*H$_2$), 40.72 (d, $^3J_{C,P}$ = 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$_3$)] ppm. $^{31}$P{$^1$H} NMR (161.9 MHz, $CDCl_3$, 20 °C): $\delta$ = 156.6 ppm. EIMS: *m*/*z* = 394.3 [M]$^+$. High-resolution EIMS: 394.2991 ($C_{24}H_{43}O_2P$).

**Synthesis of 3,5,5-Trimethylhexyl Diphenylphosphinite (3):** A solution of chlorodiphenylphosphane (1.00 g, 4.6 mmol) in 6.5 mL of diethyl ether was added dropwise to a solution of 3,5,5-trimethylhexanol (0.66 g, 4.6 mmol) and pyridine (0.36 g, 4.6 mmol) in 12 mL of diethyl ether at –10 °C. The solution was stirred at room temperature for 2 h and then filtered. After all the solvent had been removed under reduced pressure, the resulting colourless oil was purified by chromatography on basic alumina eluting with hexane. Yield: 1.01 g (67%) (colourless oil). $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$ = 7.40 (m, 4 H, Ph), 7.22 (m, 6 H, Ph), 3.78, (m, 2 H, POC$H_2$), 1.64 (m, 1 H, POCH$_2$C*H*H), 1.55 [m, 1 H, C*H*(CH$_3$)], 1.40 (m, 1 H, POCH$_2$CH*H*), 1.13 [dd, $^2J_{H,H}$ = 13.8 Hz, $^3J_{H,H}$ = 3.8 Hz, 1 H, CH(CH$_3$)CH*H*], 0.96 [dd, $^2J_{H,H}$ = 14.2 Hz, $^3J_{H,H}$ = 6.8 Hz, 1 H, CH(CH$_3$)C*H*H], 0.82 [d, $^3J_{H,H}$ = 6.2 Hz, 3 H, CH(C*H*$_3$)], 0.77 [s, 9 H, C(C*H*$_3$)$_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 20 °C): $\delta$ = 142.28 (d, $^2J_{P,C}$ = 18.8 Hz, C$_i$ Ph), 130.54 (d, $^2J_{P,C}$ = 7.6 Hz, C$_o$ Ph), 130.33 (d, $^2J_{P,C}$ = 7.6 Hz, C$_o$ Ph), 129.12 (d, $^3J_{P,C}$ = 5.3 Hz, C$_m$ Ph), 128.26 (s, C$_p$ Ph), 128.19 (s, C$_p$ Ph), 68.50 (d, $^2J_{P,C}$ = 19,1 Hz, PO*C*H$_2$), 51.21 [s, CH(CH$_3$)*C*H$_2$], 40.83 (d, $^3J_{P,C}$ = 7.6 Hz, POCH$_2$*C*H$_2$) 31.08 [s, *C*(CH$_3$)$_3$], 29.99 [s, C(*C*H$_3$)$_3$] 29.95 [s, C(*C*H$_3$)$_3$], 25.92 [s, *C*H(CH$_3$)], 22.50 [s, CH(*C*H$_3$)] ppm. $^{31}$P{$^1$H} NMR (161.9 MHz, $CDCl_3$, 20 °C): $\delta$ = 112.5 ppm. EIMS: *m*/*z* = 328.2 [M]$^+$. High-resolution EIMS: 328.1961 ($C_{21}H_{29}OP$).

**Preparation of [Rh(C$_8$H$_{12}$)(1)$_2$]PF$_6$ (4):** Ligand **1** (221 mg, 0.48 mmol) was added to a solution of [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 h. The solvent was then evaporated in vacuo and the product washed with cold methanol. The product was obtained as a yellow oil. Yield: 219 mg (86%). $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$ = 4.05 (m, 16 H,

$POCH_2$ + CH= cod), 2.57 (m, 4 H, $CH_2$ cod), 2.36 (m, 4 H, $CH_2$ cod), 1.60 (m, 18 H, $POCH_2CH_2$ + $CHCH_3$), 1.22 [dd, $^2J_{H,H}$ = 14.0 Hz, $^3J_{H,H}$ = 3.6 Hz, 6 H, $CH(CH_3)CHH$], 1.14 [dd, $^2J_{H,H}$ = 14.0 Hz, $^3J_{H,H}$ = 6.0 Hz, 6 H, $CH(CH_3)CHH$], 0.97 [d, $^3J_{H,H}$ = 6.4 Hz, 18 H, $CH(CH_3)$], 0.90 [s, 54 H, $C(CH_3)_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 20 °C): $\delta$ = 106.2 (m, CH= cod), 65.2 (d, $J_{C,P}$ = 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, $CH(CH_3)$] ppm. $^{19}$F NMR (376.3 MHz, $CDCl_3$, 20 °C): $\delta$ = –73.11 (d, $J_{P,F}$ = 715.4 Hz) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 20 °C): $\delta$ = 116.1 (d, $J_{Rh,P}$ = 244.0 Hz), –143.2 [sept, $J_{F,P}$ = 711.5 Hz] ppm. MS (MALDI-TOF): *m*/*z* = 1129.54 [M – $PF_6$ – 3 H]$^+$, 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 $[Rh(cod)_2]PF_6$ (46.5 mg, 0.20 mmol) in 2 mL of anhydrous dichloromethane. The solution turned yellow immediately and was stirred for 1 h. The solvent was evaporated and the residue washed with cold methanol and dried in vacuo overnight to give the product as a yellow oily solid. Yield: 277 mg (76%). $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$ = 7.5 (m, 20 H, Ph), 3.47 (br. m, 8 H, POC*H*H), 3.16 (br., 8 H, POCH*H*), 1.38 (br. m, 24 H, $POCH_2CH_2$ + $CHCH_3$), 1.02 [br. m, 16 H, $CH(CH_3)CH_2$], 0.85 [d, $^3J_{H,H}$ = 5.6 Hz, 24 H, $CH(CH_3)$], 0.87 [s, 72 H, $C(CH_3)_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 20 °C): $\delta$ = 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, $CH(CH_3)$] ppm. $^{19}$F NMR (376.3 MHz, $CDCl_3$, 20 °C): $\delta$ = –74.32 (d, $J_{F,P}$ = 710.8 Hz) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 20 °C): $\delta$ = 146.0 (d, $J_{P,Rh}$ = 169.7 Hz), –143.2 (sept, $J_{P,F}$ = 711.5 Hz) ppm. MS (MALDI-TOF): *m*/*z* = 1679.7 [M – $PF_6$ – 2 H]$^+$ 1285.56 [M – $PF_6$ – 4 H]$^+$.

**Preparation of [Rh(3)$_4$]PF$_6$ (6):** Ligand **3** (158 mg, 0.47 mmol) was added to a solution of $[Rh(cod)_2]PF_6$ (80 mg, 0.20 mmol) in 2 mL of anhydrous dichloromethane. The solution turned yellow immediately and was stirred for 1 h. Diethyl ether was then added to the solution to afford a yellow solid. Yield: 228 mg (73%). $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$ = 7.2–7.3 (m, 40 H, Ph), 2.78 (br. m, 8 H, $POCH_2$), 0.80 [m, 12 H, $POCH_2CH_2CH(CH_3)$], 0.67 [dd, $^2J_{H,H}$ = 13.8 Hz, $^3J_{H,H}$ = 5.6 Hz, 4 H, $CH(CH_3)CHH$], 0.60 [s, 36 H, $C(CH_3)_3$], 0.54 [dd, $^2J_{H,H}$ = 14.0 Hz, $^3J_{H,H}$ = 3 Hz, 4 H, $CH(CH_3)CHH$], 0.42 [d, $^3J_{H,H}$ = 6.4 Hz, 12 H, $CH(CH_3)$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 20 °C): $\delta$ = 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, $CH(CH_3)$], 22.86 [s, $CH(CH_3)$] ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 20 °C): $\delta$ = 132.3 (d, $J_{P,Rh}$ = 162.2 Hz), –143.1 (sept. $J_{P,F}$ = 712.6 Hz) ppm.

**Preparation of [PdCl$_2$(1)$_2$] (7):** Ligand **1** (120 mg, 0.26 mmol) was added to a solution of $[PdCl_2(PhCN)_2]$ (50 mg, 0.13 mmol) in 2 mL of anhydrous dichloromethane. The solution was stirred for 1 h, then the solvent was evaporated in vacuo and the product was washed with cold methanol and dried under vacuum overnight. The product was obtained as a light-yellow oil. Yield: 124 mg (87%). $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$ = 4.15 (m, 12 H, $POCH_2$) 1.64 (m, 6 H, $POCH_2CHH$), 1.55 (m, 6 H, $CHCH_3$), 1.46 (m, 6 H, $POCH_2CHH$), 1.44 [dd, $^2J_{H,H}$ = 14.0 Hz, $^3J_{H,H}$ = 3.6 Hz, 6 H, $CH(CH_3)CHH$], 1.03 [dd, $^2J_{H,H}$ = 14.0 Hz, $^3J_{H,H}$ = 6.4 Hz, 6 H, $CH(CH_3)CHH$], 0.88 [d, $^3J_{H,H}$ = 3.2 Hz, 18 H, $CH(CH_3)$], 0.83 [s, 54 H, $C(CH_3)_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 20 °C): $\delta$ = 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, $CH(CH_3)$] ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 20 °C): $\delta$ = 94.2 (s) ppm. MS (MALDI-TOF): *m*/*z* = 1063.7 [M – Cl]$^+$, 1026.7 [M – 2 Cl]$^+$.

**Preparation of [PdCl$_2$(2)$_2$] (8):** Ligand **2** (51 mg, 0.12 mmol) was added to a solution of $[PdCl_2(PhCN)_2]$ (25 mg, 0.06 mmol) in 2 mL of anhydrous dichloromethane. The solution was stirred for 1 h, then the solvent was evaporated in vacuo and the product was washed with cold methanol and dried under vacuum overnight. The product was obtained as a yellow oil. Yield: 47 mg (81%). $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$ = 7.75 (m, 4 H, Ph), 7.45 (m, 6 H, Ph), 4.20 (br. m, 4 H, POC*H*H), 3.95 (br. m, 4 H, POCH*H*), 1.71 (br. m, 4 H, $POCH_2CHH$), 1.54 (br. m, 8 H, $POCH_2CH$H + $CHCH_3$), 1.13 [br. m, 8 H, $CH(CH_3)CH_2$], 0.90 [d, $^3J_{H,H}$ = 6.4 Hz, 12 H, $CH(CH_3)$] 0.87 [s, 36 H, $C(CH_3)_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 20 °C): $\delta$ = 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, $POCH_2$), 50.93 [s, $CH(CH_3)CH_2$], 39.22 (s, $POCH_2CH_2$), 30.88 [s, $C(CH_3)_3$], 29.77 [s, $C(CH_3)_3$], 25.82 [s, $CH(CH_3)$], 22.26 [s, $CH(CH_3)$] ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 20 °C): $\delta$ = 122.2 (s) ppm. MS (MALDI-TOF): *m*/*z* = 929.4 [M – Cl]$^+$, 894.4 [M – 2 Cl]$^+$.

**Preparation of [PdCl$_2$(3)$_2$] (9):** Ligand **3** (85.63 mg, 0.26 mmol) was added to a solution of $[PdCl_2(PhCN)_2]$ (50 mg, 0.13 mmol) in 2 mL of anhydrous dichloromethane. The solution was stirred for 1 h, the solvent was evaporated in vacuo and the residue was washed with methanol. The product was obtained as a yellow oil. Yield: 98 mg (91%). $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$ = 7.81 (m, 8 H, Ph), 7.46 (m, 12 H, Ph), 3.63 (m, 4 H, $POCH_2$), 1.31–1.19 [m, 6 H, $POCH_2CH_2$ + $CH(CH_3)$ + $CH(CH_3)CH_2$], 0.92 [d, $^3J_{H,H}$ = 4.4 Hz, 6 H, $CH(CH_3)$], 0.78 [s, $C(CH_3)_3$] ppm. $^{13}$C NMR (100.5 MHz, $CDCl_3$, 20 °C): $\delta$ = 140.4 (br. $C_i$ Ph), 132.58 (d, $^2J_{P,C}$ = 6.1 Hz, $C_o$ Ph), 132.52 (d, $^2J_{P,C}$ = 6.1 Hz, $C_o$ Ph), 131.75 (br., $C_m$ Ph), 128.20 (br., $C_p$ Ph), 67.86 (s, $POCH_2$), 50.93 [s, $CH(CH_3)CH_2$], 39.22 ($POCH_2CH_2$), 30.87 [s, $C(CH_3)_3$], 29.76 [s, $C(CH_3)_3$], 25.81 [s, $CH(CH_3)$], 22.26 [s, $CH(CH_3)$] ppm. $^{31}$P NMR (161.9 MHz, $CDCl_3$, 20 °C): $\delta$ = 110.21 (s) ppm. MS (MALDI-TOF): *m*/*z* = 796.9 [M – Cl]$^+$, 762.0 [M – 2 Cl]$^+$.

**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 fibre. The measurements were taken at 120 K with a Bruker SMART CCD1000 diffractometer equipped with a graphite-monochromated Mo-$K_\alpha$ radiation source ($\lambda$ = 0.71073 Å). Data collection and processing were carried out with Smart and Saint from Bruker. Complex **6** ($C_{84}H_{112}O_4P_4Rh{\cdot}PF_6$) crystallised in a tetragonal *P*4/*n* space group with *a* = 18.021 (2), *c* = 13.431 (3) Å, *V* = 4361.8 (12) Å$^3$, *M* = 1557.50, *Z* = 2, $\rho_{calcd.}$ = 1.186 mg m$^{-3}$, $\mu$ = 0.345 mm$^{-1}$. The yellow crystal was prismatic and of dimensions 0.6 × 0.52 × 0.48 mm. The $\theta$ range for measurement was 1.52–26.37° and 4471 unique reflections were measured at 120 K ($R_{int}$ = 0.0381). The structure was solved by direct methods (SHELXS-97)[31] and refined on $F^2$ by full-matrix least 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 $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.0393 for 3571 reflections with $F_o^2 > 2\sigma(F_o^2)$ and $wR_2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$ = 0.1178. Goodness-of-fit = 1.1. The ORTEP diagram was generated with ORTEP-3.[34] CCDC-270199 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see footnote on the first page of this article): HPNMR and HPIR spectra of systems [Rh(acac)(CO)$_2$]/**1**–**3**.

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