New Rhodium(I) Complexes with Hemilabile Amphiphilic Phosphanes

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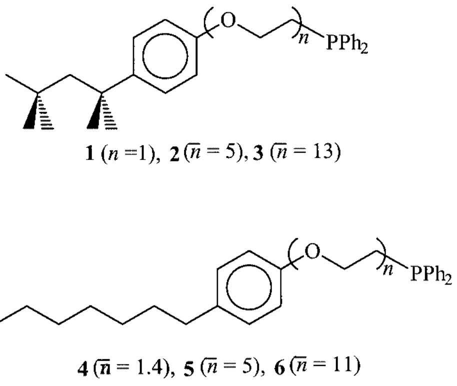
A series of Rh^I complexes was prepared and characterised with the following hemilabile amphiphilic phosphanes: R–(C_6H_4)–(OCH_2CH_2)$_n$–PPh_2 [**1** (R = *tert*-octyl, n = 1), **2** (R = *tert*-octyl, $\bar{n}$ = 5), **3** (R = *tert*-octyl, $\bar{n}$ = 13), **4** (R = *n*-nonyl, $\bar{n}$ = 1.4), **5** (R = *n*-nonyl, $\bar{n}$ = 5), **6** (R = *n*-nonyl, $\bar{n}$ = 11)]. The reactions between **1–6** and $[Rh(COD)(THF)_2]^+$, and the subsequent reaction with CO were studied by ^{31}P NMR and IR spectroscopy. The data are consistent with the formation of P-coordinated and chelated (P,O) species for ligands **2–6**, in agreement with the hemilabile character of these ligands. In the case of ligand **1**, the complex *trans*-$[Rh(\mathbf{1})_2(CO)_2]^+$ has been isolated and the *cis*-$[Rh(\mathbf{1})_2(CO)_2]^+$ compound has been detected. $[Rh(\mathbf{1})_2(CO)]^+$ was prepared by decarbonylation of *trans*-$[Rh(\mathbf{1})_2(CO)_2]^+$, and low-temperature NMR spectroscopic studies have shown the hemilabile character of **1** with a very weak P–O interaction. The molecular structure of *trans*-$Rh(CO)(\mathbf{1})_2Cl$ was determined by X-ray crystallography and shows that the conformation of the *tert*-octylphenoxyethyl chains is nearly identical to that previously reported in the complex *trans*-$PdCl_2(\mathbf{1})_2$.

Introduction

The preparation of new functionalised ligands is a central strategy for improving certain properties in transition metal complexes. Phosphanes are among the most versatile ligands, since they allow the introduction of very different functionalities by means of the different groups bound to the phosphorus atom. In this way, phosphane ligands have become water-soluble,[1] asymmetric,[2] hemilabile[3] and, more recently, amphiphilic.[4] The amphiphilic ligands contain hydrophilic and hydrophobic groups in the same molecule, and their metal complexes may aggregate forming supramolecular arrangements, such as micelles and vesicles.[5] Such micro-heterogeneous systems are attractive for improving catalytic processes, especially those that present phase-transfer limitations, such as those occurring under biphasic conditions.[6] This approach has been utilised in the study of a catalytic reaction accelerated by vesicle formation.[7]

In previous papers, we described the synthesis of neutral amphiphilic phosphanes with hemilabile properties,[8] and anionic water-soluble amphiphilic phosphanes.[9] Ligands were prepared in a straightforward manner from polyethylene glycol monoalkyl ethers, which are common starting compounds as they are used extensively as non-ionic surfactants. In subsequent papers, we have reported on the complexing properties of the neutral ligands **1−6** (Scheme 1) towards Ru^{II},[8] Pd^{II},[10] and hydridorhodium(I) complexes.[11] Hemilabile properties were clearly observed with the Ru^{II} complexes.[8] Here, we present a study of the reactivity of the neutral ligands **1−6** (Scheme 1) towards Rh^I.



Scheme 1

Results and Discussion

1. Ligands

Ligands **1−6** were synthesised from commercial non-ionic Igepal® surfactants.[12] In agreement with the nature of these starting non-ionic surfactants, the ligands were obtained as mixtures of compounds with the same structure but with different ethoxylation grades (Scheme 1). The only exception is **1**, which was obtained as a single compound

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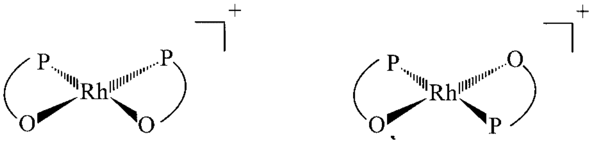
because it crystallised from the reaction mixture as a white solid.

2. Reactivity of Ligands 1−6 towards [Rh(COD)(THF)$_2$][ClO$_4$]

Two equivalents of the ligand (**1−6**) in THF were added to a solution of [Rh(COD)(THF)$_2$][ClO$_4$] prepared by the usual reaction between Rh(COD)(acac) and HClO$_4$ in THF. Complexation was evidenced by the change in the colour of the solution, which became darker, and by the ^{31}P{^{1}H} NMR spectroscopic data. Although several attempts were made, no solid compounds could be obtained. Difficulties in the isolation of solid compounds were also observed in previous complexation studies of ligands **1−6** with Ru^{II} [8] and Pd^{II}.[10]

The ^{31}P{^{1}H} NMR spectra of solutions obtained after the reactions of **1−6** with [Rh(COD)(THF)$_2$][ClO$_4$] show the complete absence of the corresponding free ligand, and display several doublets with coupling constants in the range 121 to 153 Hz. This result agrees with the formation of Rh−P bonds for all the ligands studied. Significant differences are also observed between the spectra for the different ligands. A comparison of the ^{31}P NMR spectroscopic data obtained from the resulting reaction mixtures with published data reporting the reactivity of related hemilabile phosphanes $Ph_2PCH_2CH_2OCH_3$[13] and $Ph_2P(CH_2CH_2O)_2CH_3$[14] is very helpful in the interpretation of our results. The spectrum of the complex obtained with ligand **1** only displays a doublet at $\delta = 17.6$ ppm ($^1J_{PRh} = 144$ Hz). This is in good agreement with the presence of a sole [Rh(COD)(PO)$_2$]$^+$ species (PO = P-coordinated ether−phosphane ligand). The spectra of the complexes obtained with ligands **2−6** also show a doublet with similar characteristics at 17−18 ppm, however, other doublets are also observed in the $\delta = 28$ ppm region. In these spectra, as the polyether chain length increases (i.e. more oxygen atoms are added), the signal that appears at 17−18 ppm is smaller. At the same time, the signals at around $\delta = 28$ ppm become more significant. These results agree with the simultaneous formation of the above-mentioned P-coordinated species [Rh(COD)(PO)$_2$]$^+$ (δ = 17−18 ppm region), and the chelated (P,O) complexes [Rh(COD)(P∩O)]$^+$ (δ = 28 ppm region)[14] (P∩O = chelated ligand). The absence of the signal in the δ = 28 ppm region in the spectrum with ligand **1** is consistent with the unfavourable bidentate coordination of this ligand, since it is hindered by electronic and steric effects of the aryl group bonded to the oxygen atom.[10] Finally, some observations can be made from the spectra of the complexes with ligands **4** and **6**. The spectrum of the complex with ligand **4** shows two doublets at δ = 17.5 and 17.8 ppm that can be assigned to a mixture of [Rh(COD)(PO)$_2$]$^+$ complexes, since this ligand is a mixture that contains a molecule similar to **1** and another species with a longer polyether chain. In the spectrum of the complex with ligand **6**, other signals are also observed at δ = 32.4 and 39.5 ppm. These signals could be justified by the presence of species in which the labile COD ligand could have been replaced by oxygen atoms of the polyether chain,[15] as represented in Scheme 2.

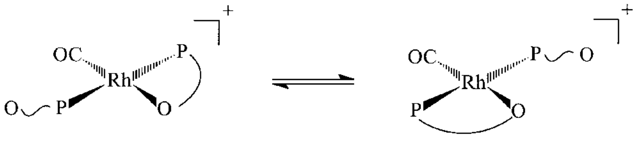


Scheme 2

3. Reaction of [Rh(COD)(L)$_2$]$^+$ Complexes with CO

a) Case where L = Ligands 2−6

After CO was bubbled into THF solutions of the Rh^I complexes described above, the colour turned from orange to yellow. After solvent evaporation, the reaction products were studied by IR and ^{31}P NMR spectroscopy, since, as in the previous section, no solids could be obtained. The ^{31}P{^{1}H} NMR spectra show that the previously observed signals are now absent and a new main signal at δ = 22−25 ppm, with the characteristic shape of a doublet ($J_{Rh\text{-}P}$ = 110−130 Hz) is observed for all the complexes studied. The IR spectra in the ν_{CO} region display a strong ν_{CO} band at around 1980 cm^{-1}. The position of this band is very similar to that reported for related complexes with the [Rh(CO)(P∩O)(PO)]$^+$ structure as *trans*-[Rh(CO)(Ph$_2$PCH$_2$CH$_2$OMe)$_2$]$^+$ (ν_{CO} = 1982 cm^{-1}).[13] For these last complexes, equilibrium between the κ^1 and κ^2 modes of bonding for the two ligands has been suggested (Scheme 3).[13] The $J_{Rh\text{-}P}$ coupling constant observed at room temperature in the ^{31}P{^{1}H} NMR spectra for our complexes is also consistent with this formulation.



Scheme 3

b) Case where L = Ligand 1

As in previously reported studies,[8,10] more detailed work was performed with ligand **1** since it is the only compound that it is not a mixture of polyether ligands,[12] and therefore, the solid compounds can be expected to be isolated. With this aim, the COD complex with the tetrafluoroborate anion was synthesised by reaction of the [Rh(COD)Cl]$_2$ complex with two equivalents of AgBF$_4$ and four equivalents of ligand **1** in THF. A solid complex was isolated by subsequent reaction with CO, followed by crystallisation in diethyl ether. This complex displays an IR ν_{CO} band at 2040 cm^{-1}, and a broad doublet in the ^{31}P{^{1}H} NMR spectrum at δ = 21.0 ppm (J = 104.8 Hz). These spectroscopic parameters are in accordance with published data for *trans*-[Rh(CO)$_2$L$_2$]$^+$ complexes with related hemilabile ether ligands $Cy_2PCH_2CH_2OCH_3$[16] and $Ph_2PCH_2CH_2OPh$.[17] Although other published data indicate that formation of the *trans*-$[Rh(PPh_3)_2(CO)_2]^+$ is uncertain,[18] its existence has been unequivocally demonstrated with the ether ligand $Ph_2PCH_2CH_2OPh$, using ^{31}P NMR spectroscopy of ^{13}CO labelled complexes.[17] The low-temperature $^{31}P\{^1H\}$ NMR spectrum of the dichloromethane solution of the *trans*-$[Rh(\mathbf{1})_2(CO)_2]^+$ complex shows that the broad doublet becomes sharp at a temperature lower than 233 K. A plausible explanation of this could be the restricted rotation around the phosphorus−metal bond at lower temperatures as a result of hydrophobic interactions between the two *tert*-octyl chains. The two reported crystal structures of metallic complexes with this ligand (see reference[10] and section 4 of Results and Discussion) have shown that these hydrophobic interactions could be related to the configuration of the molecules in solid state. The IR spectrum of the mother solution after crystallisation of the *trans*-$[Rh(\mathbf{1})_2(CO)_2]^+$ complex shows two signals at 2040 and 1990 cm^{-1}, and suggests the existence of the kinetically favoured *cis*-$[Rh(\mathbf{1})_2(CO)_2]^+$ complex in solution.[16]

The formation of the monocarbonyl complex *trans*-$[Rh(CO)(P\cap O)(PO)]^+$ with ligands **2**−**6** and the dicarbonyl complex *trans*-$[Rh(\mathbf{1})_2(CO)_2]^+$ can be justified by the propensity of ligand **1** to avoid the P,O chelation because of electronic and steric effects.[10] To force the coordination of the oxygen atom in ligand **1**, the synthesis of the monocarbonyl complex was undertaken by refluxing a dichloromethane solution of the *trans*-$[Rh(\mathbf{1})_2(CO)_2]^+$ complex. This reaction was monitored by IR spectroscopy, which showed the quick formation of a new complex with a ν_{CO} band at 1990 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum at room temperature shows a broad doublet at $\delta = 29.5$ ppm ($J = 120.1$ Hz). The low-temperature $^{31}P\{^1H\}$ NMR spectroscopic measurements (Figure 1) show the evolution of the broad doublet to a broad band at 253 K and a very broad band (22−37 ppm) at 233 K. At lower temperatures, a sharp doublet is formed at $\delta = 23.8$ ppm ($J = 134.3$ Hz) and a broad doublet at $\delta = 34.8$ ppm ($J = 110$ Hz) in a 1:1 ratio. These data are consistent with the existence of a κ^1(P)-coordinated ligand (doublet at $\delta = 23.8$ ppm) and a κ^2 (P,O)-coordinated ligand (doublet at $\delta = 34.8$ ppm). The fact that the κ^2 (P,O) resonance remains broad at this temperature illustrates the previously mentioned unfavourable κ^2 (P,O) coordination mode for **1**. Reported studies with the $Ph_2PCH_2CH_2OPh$ ligand have shown the existence of coordinated arene complexes, and the κ^2 (P,O) coordination of this ligand has been postulated in reaction intermediates.[17] The low-temperature ^1H NMR spectra show the splitting of the signal for the two methylene groups of **1** at 193 K. Furthermore, the arene protons of the phenoxy groups show two sharp doublets at room temperature at $\delta = 6.63$ and 7.16 ppm, which are assigned to the *ortho*- and *meta* arene hydrogen atoms of the phenoxy group, respectively. At low temperatures, the signal for the *meta* hydrogen atom shows insignificant changes. In contrast, the signal for the *ortho*-hydrogen atom shows a broad band at 213 K, which splits into two signals: a sharp band at $\delta = 6.38$ ppm and a broad signal at $\delta = 6.65$ ppm. All these observations − the splitting of the signal for the methylene groups that shows the existence of two different $CH_2CH_2O(C_6H_4)C_8H_{17}$ fragments and the splitting of the signal for the *ortho* hydrogen atoms of the phenoxy groups − are consistent with the co-existence of a κ^1 (P) and a κ^2 (P,O)-coordinated ligand and corroborate the $^{31}P\{^1H\}$ NMR spectroscopic data. It should be emphasised that a η^6-coordination of the arene group is not favourable for electronic reasons and a η^2-coordination of the arene is not supported by the ^1H NMR spectroscopic data.

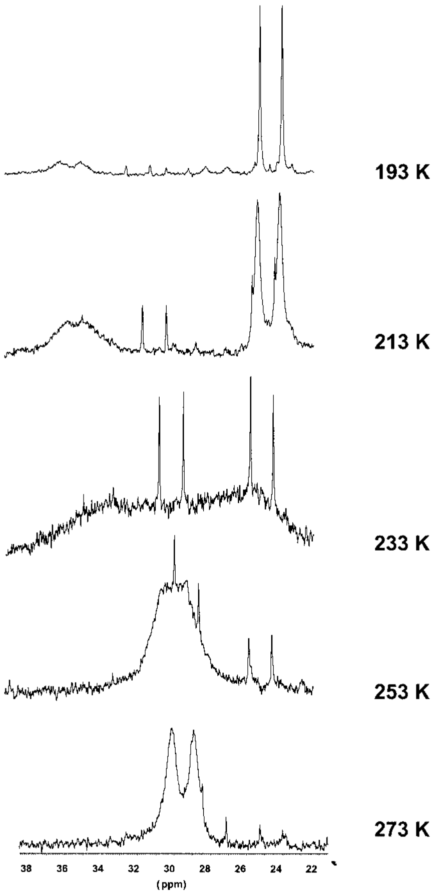
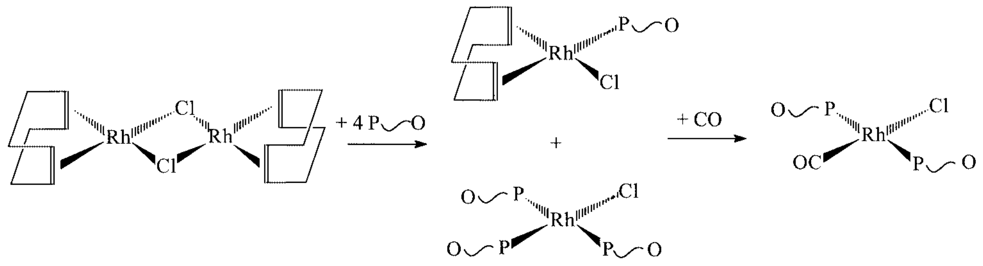


Figure 1. Low-temperature $^{31}P\{^1H\}$ NMR spectra of $[Rh(CO)(\mathbf{1})_2][BF_4]$

Finally, the attracting properties of this ligand should be noted because it can be considered as an hemilabile (P,O) ligand with a very weak, but possible, interaction between the oxygen atom and the metal atom. This observation is supported by our previous studies with Ru^{II} and Pd^{II} complexes. Those studies show the prevailing trend of this ligand to coordinate only by means of the phosphorus atom.[8,10] Finally, further support is available from the published reports on the ligand $Ph_2PCH_2CH_2OPh$, where the P,O coordination was only postulated in the reaction intermediates.[17]

4. Synthesis and X-ray Structure of *trans*-[Rh(CO)(1)₂Cl]

As it was not possible to get single crystals of the cationic complexes of ligand **1**, another attempt was made with neutral chloro rhodium complexes. The reaction of



Scheme 4

$[Rh(COD)(\mu\text{-}Cl)]_2$ with four equivalents of ligand **1** leads to a mixture of two species, according to the $^{31}P\{^1H\}$ NMR spectrum of the reaction medium (Scheme 4). The first is observed as a doublet at $\delta = 28.2$ ppm ($^1J_{PRh} = 150$ Hz) and is assigned to the species [Rh(COD)(**1**)Cl]. The second complex displays a set of signals consisting of a doublet of doublets at $\delta = 22.3$ ppm ($^1J_{PRh} = 137$ Hz; $^2J_{P,P} = 39$ Hz) and a doublet of triplets centred at $\delta = 37.3$ ppm ($^1J_{PRh} = 187$ Hz; $^2J_{P,P} = 39$ Hz), and is assigned to the $[Rh(\mathbf{1})_3Cl]$ species. After bubbling CO into the previous reaction mixture, only one doublet at $\delta = 21.3$ ppm ($^1J_{PRh} = 124$ Hz) is observed. This signal and the presence of an IR band at 1975 cm^{-1} are in good agreement with the formation of a *trans*-$[Rh(CO)(\mathbf{1})_2Cl]$ species. Single crystals of this complex were obtained by crystallisation from an acetone/methanol solution, and the structure of complex was determined by X-ray methods. A perspective view of the molecule with the labelling scheme is shown in Figure 2. The rhodium atom displays a square-planar geometry with phosphane ligands in the *trans* positions, confirming previous assignment from NMR spectroscopic data. Bond lengths and angles around the metal centre are similar to other *trans*-$[Rh(CO)L_2Cl]$ complexes with monodentate phosphane ligands.[19] Note, however, that the most interesting information is attained on comparing the structure of *trans*-$[Rh(CO)(\mathbf{1})_2Cl]$ (Figure 2) with that of the previously reported *trans*-$[PdCl_2(\mathbf{1})_2]$ (Figure 3).[10] Indeed, on comparing both figures, the great similarity between the conformations of the two *tert*-octylphenoxyethyl chains in both complexes can be seen. In both complexes, the phenyl groups bonded to the phosphorus atoms are nearly eclipsed, and the values of the C2−P1−P2−C4 torsion angle in both complexes are very similar {*trans*-$[Rh(CO)(\mathbf{1})_2Cl]$ = 22(1)°; *trans*-$[PdCl_2(\mathbf{1})_2]$ = 24.0(2)°}. This implies that the two *tert*-octylphenoxyethyl chains are close to each other, an arrangement that could be explained by the tendency of the more hydrophobic parts of the molecule to be close together. The analysis of the structure of the $[PdCl_2(\mathbf{1})_2]$ complex led us to consider, jointly with the proposed hydrophobic interactions, that other factors should also be taken into account. Thus, hydrogen bonds between the Cl atom and the hydrogen atoms of the methylene groups bonded to the oxygen atom, or between one oxygen atom and one phenyl group were considered.[10] The noteworthy similarity between the conformation of the hydrophobic groups in the structures of these metal complexes with the two different metal fragments, $PdCl_2$ and Rh(CO)Cl, suggests that the interaction between the *tert*-octylphenoxyethyl chains can play a central role in the conformation of these complexes. It should be emphasised that in the homologous *trans*-$[PdCl_2L_2]$[20] and *trans*-$[Rh(CO)ClL_2]$[19b] complexes with the ligand PPh_2Me, which cannot lead to significant hydrophobic interactions between the methyl groups, the conformation of the two complexes is different (Figure 4). Thus, the phenyl groups

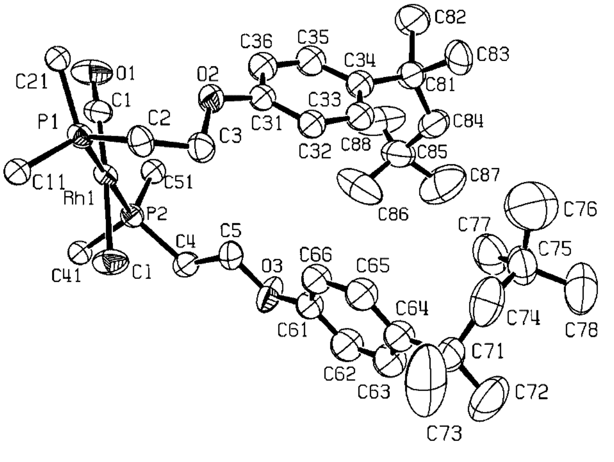


Figure 2. ORTEP diagram of *trans*-$[Rh(CO)(\mathbf{1})_2Cl]$ showing the atom numbering scheme. The phenyl rings bonded to phosphorus have been omitted

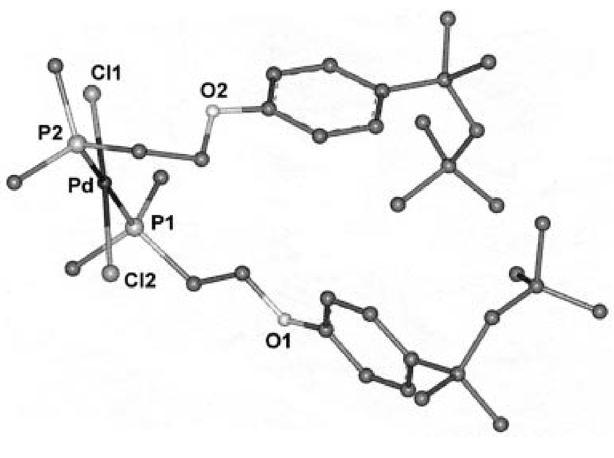


Figure 3. View of the molecular structure of *trans*-$[PdCl_2(\mathbf{1})_2]$. The phenyl rings bonded to phosphorus have been omitted

Figure 4. Molecular structures of *trans*-[Rh(CO)$(PPh_2Me)_2$Cl][19b] (left) and *trans*-[$PdCl_2(PPh_2Me)_2$][10] (right) showing the different conformations of the coordinated phosphane ligands

are nearly eclipsed in the rhodium complex and the methyl groups are closer, whereas in the palladium complex the two methyl groups are located as far apart as possible.

Experimental Section

General Remarks: All reactions were performed under nitrogen by standard Schlenk tube techniques. The NMR spectra were recorded by the *Servei de Ressonància Magnètica Nuclear de la Universitat Autònoma de Barcelona* on a Bruker AC250 instrument. All chemical shift values are given in ppm and are referenced with respect to residual protons in the deuterated solvents for ^1H spectra, to solvent signals for ^{13}C spectra and to external phosphoric acid for $^{31}P\{^1H\}$ spectra. Coupling constants, in parentheses, are expressed in Hz. Infrared spectra were recorded on a Perkin−Elmer FT-2000.

Compounds **1**−**6** were prepared by published procedures.[8b] Microanalyses were performed in the Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona.

Reactivity of 1−6 toward [Rh(COD)(THF)$_2$]$^+$: In a representative procedure 70% $HClO_4$ (0.16 mmol) was added to a yellow solution of [Rh(COD)(acac)] (0.16 mmol) in 10 mL of THF. The solution turned slightly orange. After stirring for several minutes, the corresponding phosphane ligand (0.32 mmol) in 5 mL of THF was added. The orange colour became more intense. The reaction mixture was stirred for over one hour at room temperature. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture was recorded by adding [D$_6$]acetone to the THF solutions. **1**: 17.6 d (J = 144 Hz). **2**: 17.6 (d, J = 142 Hz), 23.8 (d, J = 122 Hz), 28.7 (d, J = 139 Hz). **3**: 17.0 (b), 28.8 (d, J = 139 Hz). **4**: 17.5 (d, J = 150 Hz), 17.8 (d, J = 142 Hz). **5**: 17.7 (d, J = 142 Hz), 26.8 (b). **6**: 17.6 (d, J = 144 Hz), 28.5 (d, J = 153 Hz), 32.4 (d, J = 121 Hz), 39.5 ppm (d, J = 130 Hz).

Reactivity of 2−6 toward [Rh(COD)(THF)$_2$]$^+$ and CO: When CO was bubbled into the previous reaction mixture its colour rapidly turned pale yellow. Bubbling was maintained for one hour after which the reaction solvents were evaporated to dryness. The $^{31}P\{^1H\}$ NMR and IR spectra of the resulting oily products were recorded by adding [D$_6$]acetone to the dichloromethane solutions. $^{31}P\{^1H\}$ NMR spectroscopic data: **2**: 22.0 (d, J = 130 Hz), 23.6 (d, J = 127 Hz). **3**: 21.8 (d, J = 124 Hz). **4**: 25.4 (broad d, $J \approx 110$ Hz). **5**: 23.8 (d, J = 110 Hz), 30.7 (d, J = 113 Hz). **6**: 23.2 (d, J = 113 Hz), 32.5 ppm (d, J = 118 Hz). IR data (νCO, CH_2Cl_2 solution): **2**, 1980; **3**, 1972; **4**, 1980; **5**, 1979; **6**, 1983 cm^{-1}.

Reactivity of 1 toward [Rh(COD)(THF)$_2$][BF$_4$] and CO: Synthesis of *trans*-[Rh(CO)$_2$(1)$_2$][BF$_4$]: [Rh(COD)(μ-Cl)]$_2$ (100 mg, 0.2 mmol) was dissolved in 10 mL of THF and $AgBF_4$ (80 mg, 0.41 mmol) was added to the solution. The solution was stirred for 1 h. Precipitated AgCl was eliminated by filtration through a small pad of Celite. **1** (340 mg, 0.81 mmol) was added to the resulting yellow solution and the solution was stirred for 1 h. CO was bubbled into the solution for 1 h and during this time the solution lightened. THF was then evaporated under vacuum and the residue was dissolved in 5 mL of CH_2Cl_2. 15 mL of diethyl ether was added to this solution and the resulting mixture was cooled to −20 °C. 250 mg of *trans*-[Rh(CO)$_2$(**1**)$_2$][BF$_4$] was isolated as a white powder (57% yield). IR (νCO): 2041 cm^{-1} (CH_2Cl_2 solution); $^{31}P\{^1H\}$ NMR ($CDCl_3$): (293 K) 20.9 (bd, J = 104.8 Hz); (233 K) 20.1 ppm, (d, J = 107.1 Hz). (^1H) NMR (CD_2Cl_2): (293 K) 0.66 (s, 9 H), 1.31 (s, 6 H), 1.69 (s, 2 H), 3.16 (m, 2 H), 4.27 (m, 2 H), 6.57 (d, J = 8.7 Hz, 2 H), 7.21 (d, J = 8.7 Hz, 2 H), 7.44−7.65 ppm (m, 10 H). $C_{58}H_{70}BF_4O_4P_2Rh$ (1082.8): calcd. C 64.3, H 6.5; found C 63.9, H 7.0.

Synthesis of [Rh(CO)(1)$_2$][BF$_4$]: *trans*-[Rh(CO)$_2$(**1**)$_2$][BF$_4$] (250 mg) was dissolved in 15 mL of CH_2Cl_2 and the solution was refluxed for 5 h. The solution was evaporated to dryness and the residue was crystallised in a CH_2Cl_2/hexane mixture at −20 °C. 200 mg of [Rh(CO)(**1**)$_2$][BF$_4$] was isolated (82%). IR (νCO): 1990 cm^{-1} (CH_2Cl_2 solution); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): (293 K) 29.5 (bd, J = 120.1 Hz); (193 K) 23.8, (d, J = 134.3 Hz), 34.8 ppm, (bd, J = 110 Hz). (^1H) NMR (CD_2Cl_2): (293 K) 0.69 (s, 9 H), 1.31 (s, 6 H), 1.69 (s, 2 H), 2.83 (m, 2 H), 4.21 (m, 2 H), 6.63 (d, J = 8.7 Hz, 2 H), 7.16 (d, J = 8.7 Hz, 2 H), 7.47−7.70 ppm (m, 10 H). (193 K) 0.56 (bs, 18 H), 1.23 (bs, 12 H), 1.62 (s, 4 H), 2.57 (b, 2 H), 3.01 (b, 2 H), 3.92 (b, 2 H), 4.22 (m, 2 H), 6.38 (2 H), 6.66 (2 H), 7.05 (b, 4 H), 7.41−7.63 ppm (m, 20 H). $C_{57}H_{70}BF_4O_3P_2Rh$ (1054.8): calcd. C 64.9, H 6.7; found C, 65.0, H 6.5.

Synthesis of *trans*-Rh(CO)(1)$_2$Cl: Ligand **1** (0.27 mmol) and [Rh(COD)(μ-Cl)]$_2$ (0.06 mmol) were dissolved in 25 mL of CH_2Cl_2. The yellow reaction mixture was stirred for one hour. The $^{31}P\{^1H\}$ NMR spectrum of this reaction mixture was recorded by adding [D$_6$]acetone: 22.3 (dd, $^1J_{RhP}$ = 137, $^2J_{P,P}$ = 39 Hz); 28.2 (d, $^1J_{RhP}$ = 150 Hz); 37.3 ppm (dt, $^1J_{RhP}$ = 187, $^2J_{P,P}$ = 39 Hz).

CO was bubbled into the reaction mixture for one hour and during this time the colour changed to pale yellow. The solution was evaporated to dryness and the residue was crystallised in a acetone/methanol mixture at −20 °C. 75 mg of *trans*-[Rh(CO)(**1**)$_2$Cl] was isolated (62%). IR (νCO): 1975 cm^{-1} (CH_2Cl_2 solution). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 21.3 ppm d ($^1J_{RhP}$ = 124 Hz). $C_{57}H_{70}O_3ClP_2Rh$: calcd. C 68.2, H 7.0; found C, 67.5, H 7.4.

X-ray Crystallographic Study: Data were collected on an Enraf−Nonius CAD4 diffractometer at room temperature. Full crystallographic data for *trans*-[Rh(CO)(**1**)$_2$Cl] are gathered in Table 1. All calculations were performed on a PC-compatible computer using the WinGX system.[21] The structures were solved by direct methods, using the SIR92 program,[22] which revealed in each instance the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses using the SHELXS-97 program.[23] One *tert*-octyl group showed structural disorder and it was split; final s.o.f. was 0.5/0.5. The phenyl rings have been refined as rigid groups (D_{6h} symmetry; C−C = 1.39 Å; C−H = 0.93 Å). Atomic scattering factors were taken from the usual tabulations.[24] Anomalous dispersion terms for Rh, P, and Cl were included in F_c.[25] All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms were set in idealised positions (R_3CH, C−H = 0.96 Å; R_2CH_2 = 0.97 Å; C(sp^2)−H = 0.93 Å; U_{iso} 1.2 times greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached) and held fixed during refinements. Final atomic coordinates for all atoms, anisotropic thermal parameters, lists of structure factor amplitude for compounds for the X-ray study are available from the authors upon request.

Table 1. Crystal data and structure refinement for *trans*-[Rh(CO)(**1**)$_2$Cl]

Empirical formula	$C_{57}H_{70}ClO_3P_2Rh$
Molecular mass	1003.43
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$ (#2)
Unit cell dimensions	a = 16.2300(10) Å, α = 101.98(2)° b = 17.057(2) Å, β = 96.83(2)° c = 10.0310(10) Å, γ = 77.830(10)°
Volume	2647.2(4) Å^3
Z	1.259 Mg/m^3
Absorption coefficient	0.475 mm^{-1}
F(000)	1056
Theta range for data collection	1.24 to 21.98°
Index ranges	$0 \leq h \leq 17$, $-17 \leq k \leq 17$, $-10 \leq l \leq 10$
Independent reflections	6462
Completeness to theta = 21.98°	99.8%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6462/11/544
Goodness-of-fit on F^2	1.054
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0420, $wR2$ = 0.1064

CCDC-203524 contains the supplementary crystallographic data for this paper. 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 CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] B. Cornils, W. A. Herrmann (Eds.), *Aqueous-Phase Organometallic Catalysis*, Wiley-VCH, Weinheim, **1998**, chapter 3.2.

[2] [2a] H. B. Kagan, in: *Asymmetric Synthesis* (Ed.: J. D. Morrison), vol. 5, Academic Press, Orlando, **1985**, chapter 1. [2b] H. Brunner, W. Zettlmeier, *Handbook of Enantioselective Catalysis with Transition Metal Compounds*, vol. II, VCH, Weinheim, **1993**. [2c] J. Holz, M. Quirmbach, A. Börner, *Synthesis* **1997**, *9*, 983.

[3] [3a] E. Lindner, S. Pautz, M. Haustein, *Coord. Chem. Rev.* **1996**, *155*, 145. [3b] H. Yang, M. Alvarez-Gressier, N. Lugan, R. Mathieu, *Organometallics* **1997**, *16*, 1401. [3c] E. Lindner, S. Pautz, R. Fawzi, M. Steimann, *J. Organomet. Chem.* **1998**, *555*, 247. [3d] I. Le Gall, P. Laurent, E. Soulier, J. Salaün, H. Abbayes, *J. Organomet Chem.* **1998**, *567*, 13. [3e] S. Borns, R. Kadyrov, D. Heller, W. Baumann, A. Spannenberg, R. Kempe, J. Holz, A. Börner, *Eur. J. Inorg. Chem.* **1998**, *9*, 1291. [3f] C. S. Slone, D. A. Weinberger, C. A. Mirkin, in: *Progress in Inorganic Chemistry* (Ed.: K. D, Karlin), Vol. 48, John Wiley & Sons, New York, **1999**, p. 233. [3g] J. L. Ruiz, T. Flor, J. C. Bayon, *Inorg. Chem. Commun.* **1999**, *2*, 484. [3h] H. Werner, J. Bank, P. Steinert, W. Wolfsberger, *Z. Anorg. Allg. Chem.* **1999**, *625*, 2178. [3i] M. Nandi, J. Jin, T. V. RajanBabu, *J. Am. Chem. Soc.* **1999**, *121*, 9899.

[4] G. Papadogiannakis, R. A. Sheldon, in ref.[1] chapter 3.2.4.

[5] [5a] J. H. Van Esch, A. L. H. Stols, R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.* **1990**, 1658. [5b] G. Ghirlanda, P. Scrimin, P. Tecilla, A. Toffoletti, *Langmuir* **1998**, *14*, 1646. [5c] F. Hampl, F. Liska, F. Mancin, P. Tecilla, U. Tonellato, *Langmuir* **1999**, *15*, 405. [5d] R. Resendes, J. Massey, H. Dorn, M. A. Winnik, I. A. Manners, *Macromolecules* **2000**, *33*, 8.

[6] [6a] B. E. Hanson, H. Ding, C. W. Kohlpaintner, *Catalysis Today* **1998**, 421. [6b] G. Oehme, I. Grassert, S. Ziegler, R. Meisel, H. Fuhrman, *Catalysis Today* **1998**, *42*, 459. [6c] R. Selke, J. Holz, A. Riepe, A. Börner, *Chem. Eur. J.* **1998**, *4*, 769.

[7] M. S. Goedheijt, B. H. Hanson, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2000**, *122*, 1650.

[8] [8a] E. Valls, J. Suades, B. Donadieu, R. Mathieu, *Chem. Commun.* **1996**, 771. [8b] E. Valls, J. Suades, R. Mathieu, *Organometallics* **1999**, *18*, 5475.

[9] E. Valls, A. Solsona, J. Suades, R. Mathieu, F. Comelles, C. López-Iglesias, *Organometallics* **2002**, *21*, 2473.

[10] E. Valls, J. Suades, R. Mathieu, J. F. Piniella, A. Alvarez-Larena, *J. Organomet. Chem.* **2001**, *626*, 139.

[11] A. Solsona, J. Suades, R. Mathieu, *J. Organomet. Chem.* **2003**, *669*, 172.

[12] These products are ethoxylated alkylphenols with different ethoxylation grades.

[13] E. Lindner, H. Norz, *Chem. Ber.* **1990**, *123*, 459.

[14] V. V. S. Reddy, A. Varshney, G. M. Gray, *J. Organomet. Chem.* **1990**, *391*, 259.

[15] E. Lindner, Q. Wang, H. A. Mayer, A. Bader, *J. Organomet. Chem.* **1993**, *458*, 229.

[16] E. Lindner, Q. Wang, H. A. Mayer, R. Fawzi, M. Steimann, *Organometallics* **1993**, *12*, 1865.

[17] E. T. Singewald, X. Shi, C. A. Mirkin, S. J. Schofer, C. L. Stern, *Organometallics* **1996**, *15*, 3062.

[18] R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1971**, *93*, 2397.

[19] [19a] D. C. Smith Junior, E. D. Stevens, S. P. Nolan, *Inorg. Chem.* **1999**, *38*, 5277. [19b] F. Dahan, R. Choukroun, *Acta Crystallogr., Sect. C* **1985**, *41*, 704.

[20] I. Y. Guzman-Jimenez, K. H. Whitmire, *Acta Crystallogr., Sect. C* **1999**, *55*, 9900028.

[21] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

[22] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343.

[23] G. M. Sheldrick, *SHELXS-97, SHELXL-97, CIFTAB − Programs for Crystal Structure Analysis* (Release 97−2), Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, 3400 Göttingen, Germany, **1998**.

[24] [24a] D. T. Cromer, J. T. Waber, *International Tables for X-ray*

Crystallography; Kynoch Press: Birmingham, England, vol. 4, **1974**, Table 22B. [24b] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175. [24c] T. Hahn (Ed.), *International Tables for Crystallography*, Volume A, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1995**.

[25] D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham, England, vol. 4, **1975**, Table 2.3.1.

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