



Departament de Química Física i Inorgànica

**TOWARDS GREEN CHEMISTRY:  
ALTERNATIVE SOLVENTS FOR CATALYSED  
CARBONYLATION REACTIONS**

Memòria presentada per

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Tarragona, Octubre 2005



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CERTIFICA:

Que la memòria que porta per títol "TOWARDS GREEN CHEMISTRY: ALTERNATIVE SOLVENTS FOR CATALYSED CARBONYLATION REACTIONS", que presenta Marta Giménez Pedrós per a obtenir el grau de Doctora en Química, ha estat realitzada sota la meva direcció en el Departament de Química Física i Inorgànica de la Universitat Rovira i Virgili.

Tarragona, Octubre de 2005

Dra. Anna Maria Masdeu i Bultó



## Agraïments

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"The important thing is to not stop questioning"

Albert Einstein



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# Chapter 1

## General introduction

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*The field of homogeneous catalysis has grown dramatically over the past decade, boasting many new applications in the chemical, fine chemical, and pharmaceutical industries. Separating and recycling the catalyst, and to avoid the use of toxic and hazardous solvents are some of the main challenges in this field. Therefore, in recent years a great deal of research has been made in an attempt to solve these problems. Alternative green solvents have been used for catalysis, which also make it possible to recycle the catalyst.*

*The present chapter introduces the concept of homogeneous catalysis and discusses the importance of using alternative reaction media for catalysis. Water and supercritical carbon dioxide are environmentally friendly solvents, which also make it possible sometimes to recycle the catalyst. This first chapter also presents the hydroformylation reaction studied in the first part of the present thesis.*

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# 1

### 1.1. Homogeneous Catalysis

The concept of catalyst was first introduced by Berzelius in the 19th century [1]. Subsequently, Ostwald came up with the definition that we still use today: A *catalyst is a substance that increases the rate of a chemical reaction, without being consumed or produced by the reaction* [2].

The catalyst only has a kinetic effect: it accelerates a reaction that is thermodynamically possible. A catalyst increases the reaction rates because it generates new reaction routes, which have lower activation energies (Figure 1). However, it may sometimes have an influence on the distribution of the reaction products by modifying the rates of the competitive reactions.

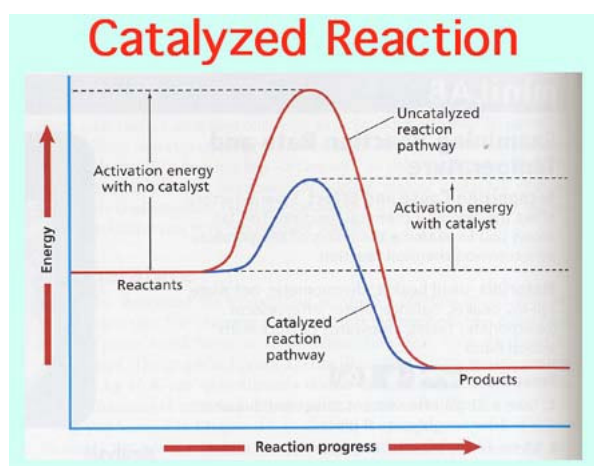


Figure 1. Effect of the catalyst on the reaction rate

Catalysts can be either *homogeneous* or *heterogeneous*. A *homogeneous catalyst* is in the same phase, normally liquid, as the reactants and products. A *heterogeneous catalyst* is in a different phase to that of the reactants, usually the solid phase, and the reactants are in the liquid or gas phase. Although, this general concept not comprises all the catalytic systems, the combination of both types of catalyst is also described. In recent years one of

the approaches that has been developed is the immobilization of the homogeneous catalyst on either solid or liquid supports, which converts the catalytic systems into multiphase systems.

Before 1938, when “oxo-synthesis” was discovered by Otto Roelen, homogeneous catalysis received only little attention [3]. Catalysis was linked to large-volume industrial chemical synthesis (ammonia synthesis, coal hydrogenation or Fischer-Tropsch synthesis). In general, catalysis was synonymous of heterogeneously catalysed reactions. Except in rare cases, such as Grignard reactants or the Mond process, organometallic compounds had no technical or commercial application. In comparison with heterogeneous catalyst, homogeneous catalysis has many advantages:

- The activity and selectivity are high.
- Reactions can be carried out in mild reaction conditions.
- Its sensitivity to catalyst poisons is low.
- There are no diffusion problems.
- The steric and electronic properties of the catalysts can be varied.
- It makes it possible to understand the reaction mechanism.

Despite of all these advantages, homogeneous catalysis has one major disadvantage: is very difficult to separate and reuse the catalytic system. Therefore, in recent years a great deal of research has been carried out to solve this problem. The most successful approach is to convert the homogeneous systems into multiphase systems. The first method was the “heterogenization” of the homogeneous catalyst immobilizing it on the surface of an organic or inorganic support [4-7]. In most cases, the activity of the immobilized system is lower than that of the homogeneous system and the supported catalyst is not as stable as expected, due to the leaching of the catalyst.

A more successful solution is to immobilize the system in a “liquid support”, from where the concept of biphasic catalysis arises. The basic principle of

biphasic catalysis is, therefore, that homogeneous catalysis is in solution in one of the phases while the reaction products are in a second phase, which is immiscible with the catalyst phase and can thus easily be separated [8].

The most developed biphasic system is probably the aqueous/organic solvent biphasic system. The catalyst is usually solubilized in water whereas the substrate and the products remain in the organic phase (Figure 2) [9]. However, the opposite approach has also been studied for water-soluble substrates [10].

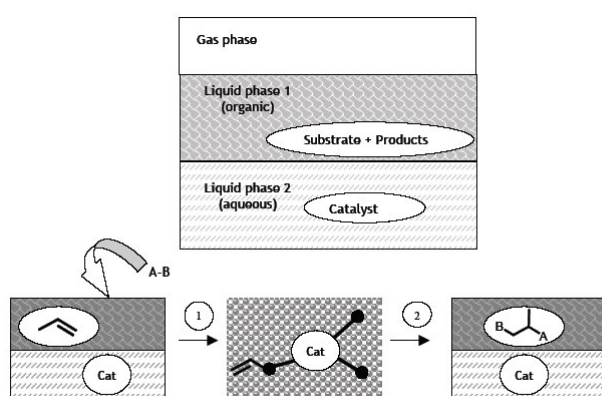


Figure 2. Schematic representation of an aqueous biphasic system.

Water is rarely used as a solvent for organic chemistry because organic compounds are not very soluble in it while some reaction intermediates are extremely reactive in it. It was rediscovered in 1980, when Breslow [11] showed that the rate of the cycloaddition of cyclopentadiene with methyl vinyl ketone in water was enhanced by a factor of more than 700 compared to the reaction in isooctane. Since then interest in the use of water as a solvent



has been growing, not only in attempt to improve reaction rates but also to improve selectivities or facilitate the separation of the catalyst.

The main advantages of using water as a solvent are the following: it is cheap, and more importantly, non-toxic; water-soluble compounds such as carbohydrates can be used directly with no need for the tedious protection-deprotection process; and water-soluble catalysts can be recycled by filtration, decantation or extraction of the other products that are insoluble in water.

Aqueous biphasic catalysis therefore requires a water-soluble catalyst to be used. The solubility of the catalysts in water is determined by their overall hydrophilic nature which may be a consequence of the charge of the complex ion as a whole, or of the good solubility of the ligands [12]. As in organometallic catalysis, phosphines also play a leading role in aqueous organometallic catalysis. Some of the neutral ligands are water soluble because of their ability to form hydrogen bonds with the surrounding water molecules. These ligands usually contains several N or O atoms, such as the 1,3,5-triaza-7-phosphaadamantane (PTA, Figure 3) tris(hydroxymethyl) phosphines,  $(\text{P}(\text{CH}_2\text{OH})_3)$  or several phosphines containing long polyether chains. But the most frequently used ligands in aqueous biphasic catalysis are derived by attaching to water-insoluble tertiary phosphines ionic or polar groups, such as sulfonate, sulphate, phosphonate, carboxylate, phenolate, quaternary ammonium and phosphonium, hydroxylic, polyether, guanidino or polyamide substituents or any combination of them. Figure 3 shows some water-soluble ligands. Sulfonated phosphines are the most important ligands in aqueous organometallic catalysis since they dissolve well throughout the pH-range and are insoluble in common non-polar organic solvents. These ligands can be prepared with straightforward methods. The sulfonate group is deprotonated in a wide pH-range so its coordination to the metal need not be considered, and they are sufficiently stable under most catalysis conditions.

For these reasons the most important ligands used in aqueous catalysis in both academia and industry are the sulfonated monodentate phosphines TPPMS [13] and TPPTS [14], and sulfonated bidentate tertiary phosphines such as BINAPS [15], BISBIS [16] and BINAS [17] (Figure 3).

Apart from aqueous systems there are other possibilities of biphasic systems:

- Organic polar liquid/ Non polar organic liquid
- Ionic liquid/ Organic Liquid
- Organic perfluorinated solvent/ Organic liquid

The first of these systems is based on the immiscibility of liquids that have different polarities and it is applied by Shell in the industrial process SHOP for oligomerization of ethylene to obtain high molecular weight olefins [18]. A nickel-based catalyst is solubilized in butane-1,4-diol. The high molecular weight alkenes formed in the reaction are not soluble in the catalyst phase. Therefore, the catalyst and the products can be separated easily.

The second system uses ionic salts, which have a low melting point. They are usually known as ionic liquids and they form biphasic systems with numerous organic solvents. The system has mainly been used by academia in several organometallic-catalysed reactions [19-21].

Finally, fluorous biphasic catalysis (FBS), was introduced by Horváth and Rabai in 1994 [22]. It is based on the fact that perfluorinated alkanes, ethers and tertiary amines are not very soluble in such organic solvents as aromatic, aliphatic alcohols, acetone, tetrahydrofuran, etc. The catalyst should be soluble in the perfluorinated phase, so the catalyst should be modified increasing the affinity of it for the solvent. The most effective way of doing so is to introduce perfluorinated groups into the ligand structure. Gases are also highly soluble in perfluorinated solvents, especially oxygen, so perfluorinated solvents are particularly attractive for the oxidation processes.

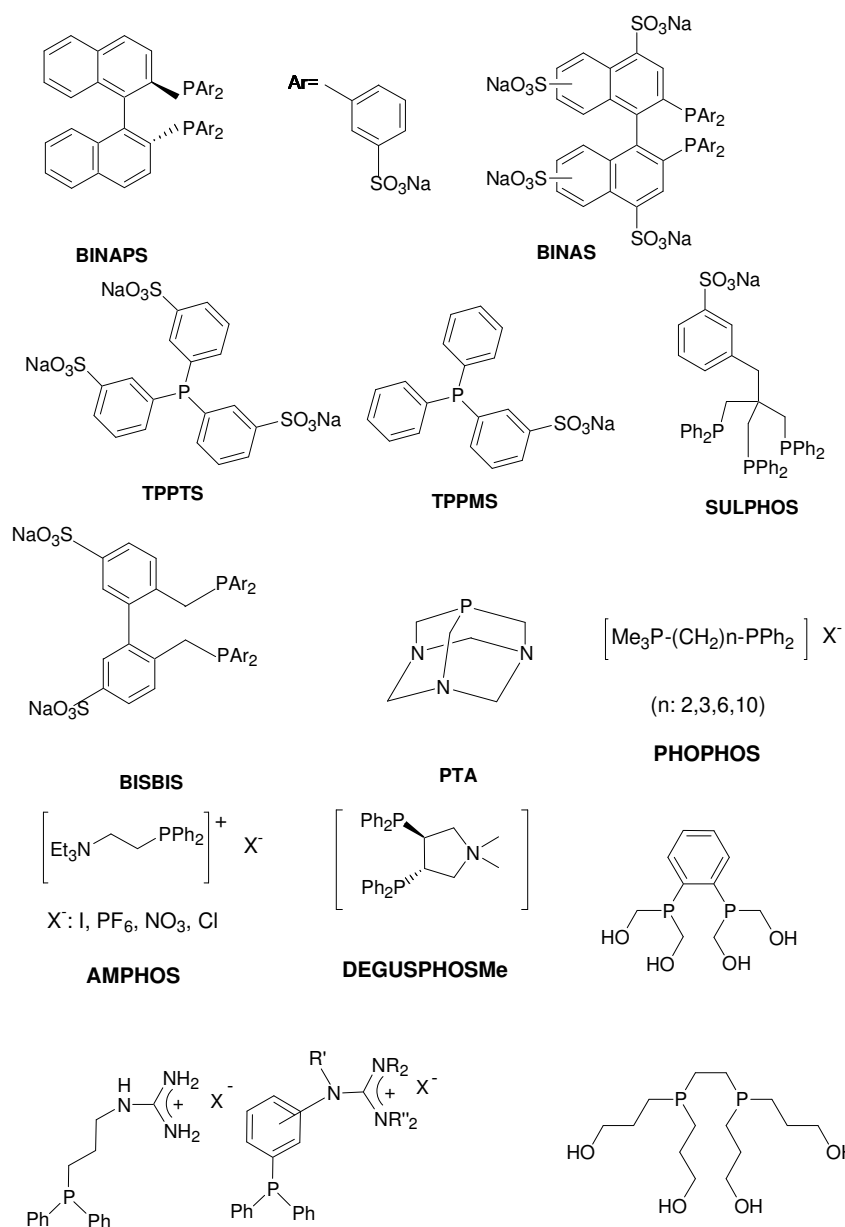


Figure 3. Water-soluble ligands

Hydroformylation is the largest volume homogeneous catalytic process that uses organometallic catalysis in industry [3]. Hydroformylation (Scheme 1) is the reaction of an alkene with carbon monoxide and hydrogen to obtain linear (n) and branched aldehydes (iso).



Hydroformylation (the oxo-process) was discovered by Otto Roelen in 1938 in Ruhrchemie AG. The original process used cobalt carbonyl catalyst as a catalyst. The conditions were harsh, as the reactivity of cobalt was low [24, 25]. Subsequently, cobalt catalyst was modified with tertiary phosphines, such as  $\text{PBU}_3$  (Shell, 1964). The process proceeded at lower temperatures and pressures but still suffered from low n/iso selectivity [26]. The second generation processes use rhodium catalysts associated with arylphosphines. The first industrial process came on stream in 1974 in Celanese [27], followed by Union Carbide (1976) [28] and the Mitsubishi Chemical Corporation (1978) [29], all of which used triphenylphosphine as a ligand.

### Mechanism

The common accepted mechanism for hydroformylation using  $\text{PPh}_3$  as a ligand is depicted in Figure 4. This is the so-called dissociative mechanism, based on the mechanism proposed by Heck and Breslow [30] for cobalt-catalysed hydroformylation [23].

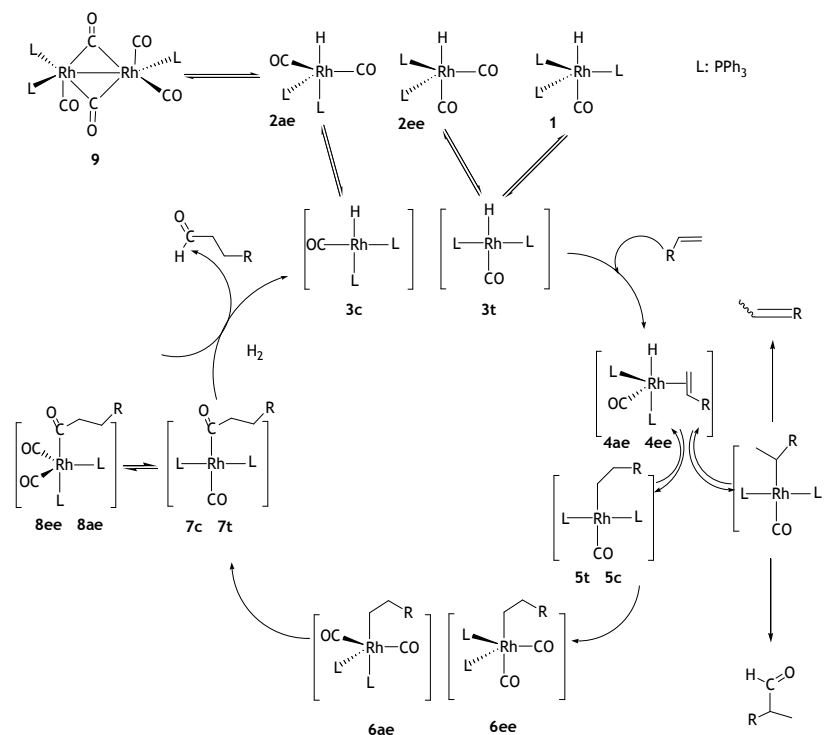


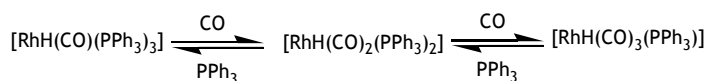
Figure 4. Simplified catalytic cycle for hydroformylation of propene  $\text{L} = \text{PPh}_3$  [23].

The starting complex is  $[\text{RhH}(\text{L})_3\text{CO}]$  (**1**) which under pressure of carbon monoxide forms the complexes **2ae** and **2ee**, containing the phosphine ligands in equatorial positions (ee) or axial-equatorial positions (ae). The dissociation of one phosphine ligand leads either to the square-planar complex **3c** or **3t**, which have phosphines on *cis* or *trans*, respectively. Coordination of the

alkene gives the species **4ae** or **4ee**. The migratory insertion of the hydride into the alkene gives the square-planar complexes **5** is the step that determines the regioselectivity of the system. A  $\beta$ -elimination of hydride in species **5** leads to isomerization when higher alkenes are used, or it can react with carbon monoxide to form trigonal bipyramidal complexes **6**. A second migratory insertion of CO into complexes **6** leads to the formation of acyl complexes **7**, and the reaction of these species with CO forms the saturated acyl intermediates **8**. Reaction of **7** with  $H_2$  gives the aldehyde product and regenerates the unsaturated species **3**. The reaction with  $H_2$  involves an oxidative addition and a reductive elimination.

### Regioselectivity

In the hydroformylation of 1-alkenes two regioisomers can be obtained. The regioselectivity of the catalyst based on  $PPh_3$  varies from 70 to 92 % to linear aldehyde [23]. Selectivity is highest at high concentrations of  $PPh_3$  and low CO pressures. This can be easily explained if the species formed under syn gas pressure and at room temperature (Scheme 2, Figure 4) are taken into account. Species with more coordinated phosphine ligands create more steric hindrance around the metal, which favours the formation of linear alkyl intermediate **5**. Moreover, an increase in the partial pressure of CO favours the dissociation of phosphines and the formation of branched alkyl intermediates.



Scheme 2

Brown and Kent studied the different intermediates formed with  $[RhH(CO)_2(PPh_3)_2]$  by NMR [31]. They observed that the major specie  $[RhH(CO)_2(PPh_3)_2]$  is a mixture of two isomers, the equatorial-equatorial (ee) and the axial-equatorial (ae) with a ratio of 85% and 15%, respectively (Figure 5).

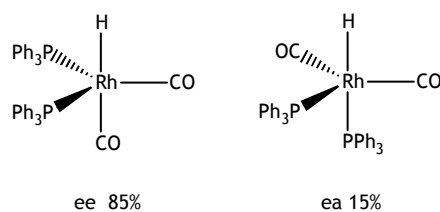


Figure 5

The reaction of these two isomers with styrene leads to the formation of the intermediates  $[\text{Rh}(\text{acyl-branched})(\text{CO})(\text{PPh}_3)_2]$  major (Figure 6a) and  $[\text{Rh}(\text{acyl-linear})(\text{CO})_2(\text{PPh}_3)_2]$  minor (figure 6b). As the time progresses the major acyl specie is depleted partly by isomerization of  $[\text{Rh}(\text{acyl-branched})(\text{CO})(\text{PPh}_3)_2]$  to linear-acyl and partly by an increase in the concentration of the iso-aldehyde. The isomerization occurs slowly so that it is unlikely to contribute to the product isomer distribution. Using 1-octene and 1-decene as a substrates only the isomers  $[\text{Rh}(\text{acyl-linear})(\text{CO})_2(\text{PPh}_3)_2]$  were detected.

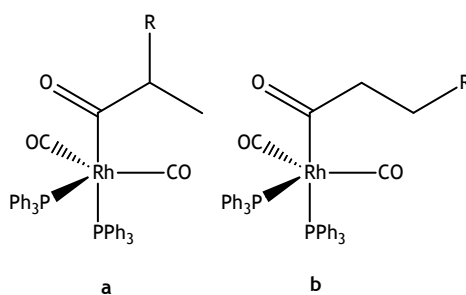


Figure 6

Other important aspects in the rate and selectivity of hydroformylation are the steric and electronic properties of the ligands. The electronic properties of phosphorus ligands have been studied by looking at the stretching frequencies of the coordinated carbon monoxide ligands in complexes such as  $[\text{NiL}(\text{CO})_3]$  or  $[\text{CrL}(\text{CO})_5]$  in which L is the phosphorous ligand [32]. The electronic parameter for phosphorous ligands ( $\chi$ ) was defined by Tolman as

the difference in IR stretching frequencies between the complex  $[\text{NiL}(\text{CO})_3]$  and the reference complex  $[\text{Ni}\{\text{P}(t\text{-Bu})_3\}(\text{CO})_3]$ .

The cone angle,  $\theta$ , introduced by Tolman classifies the phosphorous monodentate ligands by their steric hindrance. The cone angle is defined as the apex angle of a cylindrical cone centred 2.28 Å from the centre of the P atom and just touching the van der Waals radii of the outermost atoms of the molecule (Figure 7).

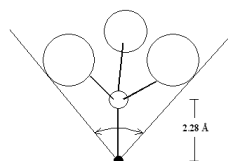
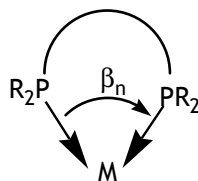


Figure 7. Diagrammatic representation of the Tolman cone angle,  $\theta$

In rhodium-catalysed hydroformylation of lineal alkenes with monophosphines  $\text{PR}_3$  it has been observed that an increase in the cone angle induces better linear aldehyde selectivities. On the other hand, when the ligand has a very large cone angle linear aldehyde regioselectivity decreases, because the steric hindrance only allows species with one coordinated ligand to form.

Bidentate phosphorous ligands provide greater control of regioselectivity because the stability of the bidentate coordination means that much fewer species are formed than with monodentate ligands [33]. The steric effect of bidentate ligands is defined by the bite angle ( $\beta_n$ ) which Casey and Whiteker [34] defined as the preferred ligand-metal-ligand angle formed when a bidentate ligand coordinates to a metal centre (Figure 8).



Figure 8. Bite angle,  $\beta_n$ .

Casey et al. studied how the bite angle affected the hydroformylation of 1-hexene catalysed by rhodium complexes. They observed that the bite angle in the intermediate  $[\text{RhH}(\text{CO})_2(\text{P-P})]$  has considerable influence on the selectivity of the reaction. When BISBI, which has a bite angle of  $113^\circ$  and coordinates in a bis-equatorial fashion, was used as a ligand (Figure 9) the *n*/*iso* ratio obtained was 66, whereas using dppe (Figure 9) (bite angle =  $90^\circ$ ), which coordinates in a axial-equatorial fashion, gave a *n*/*iso* ratio of 2.1. But, it is not only steric effects that lead to this high *n*/*iso* observed for diequatorial chelates. Electronic effects also play a role. The electronic interaction between two equatorial ligands is stronger than between axial-equatorial ligands. For example, back bonding from the rhodium to the alkene ligand in the equatorial plane may be stronger for bisequatorial complexes because of the strong donor phosphines in the equatorial plane. Moreover, the hydride is *trans* to CO in a bisequatorial complex so it may be more acidic than the hydride formed with dppe as a ligand since this is *trans* to a phosphine (Figure 9).

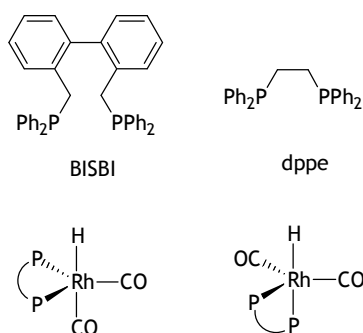


Figure 9

### Phosphites

Phosphites were considered as a ligands for rhodium-catalysed hydroformylation in the late sixties, but triphenylphosphine turned out to be the ligand of choice [33]. Interest in phosphites began anew in the eighties after van Leeuwen and co-workers discovered that bulky monophosphites gave very high rates [35, 36]. Phosphites are easier to prepare than phosphines although they are more sensitive to side-reactions such as hydrolysis, alcoholysis or the Arbuzov reaction. The first example of phosphites being used in rhodium-catalysed hydroformylation was reported by Pruett and Smith of the Union Carbide Corporation, in the hydroformylation of 1-octene and methyl methacrylate [37]. Their results showed a high tendency to form the linear aldehyde.

Ligands with electron-withdrawing substituents increase the reaction rates because of a facile CO dissociation and strong alkene association. Although steric effects generally determine the relative stability of the primary and secondary alkyl complexes, electronic effects also play an important role in the regioselectivity. For diphosphine ligands electron-withdrawing substituents resulted in an increased preference for bisequatorial coordination of the phosphorous donors [38, 39]. Since phosphites have a much higher  $\chi$  value than phosphines, a high preference for bisequatorial coordination is anticipated.

Because of phosphorous ligands are large, phosphites and phosphines creates more steric bulk in the rhodium complex and, the steric hindrance hamper the alkene addition. Therefore, in general, one would expect low reaction rates increasing the steric hindrance around the metal. However, van Leeuwen and Roobeek reported the use of the very bulky tris(ortho *tert*-butylphenylphosphite) as ligand and found high reaction rates in the hydroformylation of so-called unreactive alkenes such as 1,2- and 2,2-dialkylalkenes [35]. The high reactivity of these systems is explained by the exclusively formation of monoligated rhodium phosphite complexes confirmed

by *in-situ* IR and NMR studies [40]. The mechanism proposed for rhodium-catalysed hydroformylation using bulky phosphites is depicted in Figure 10.

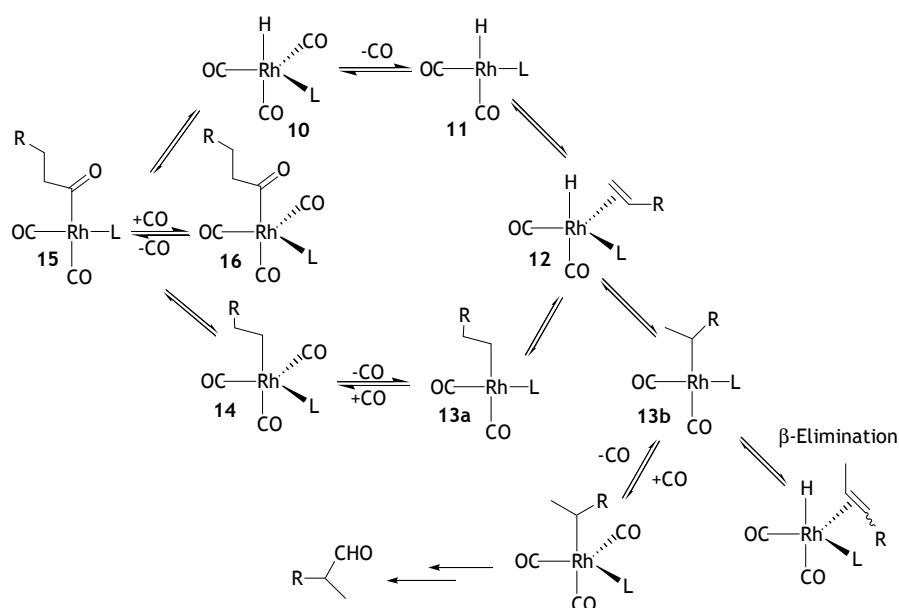


Figure 10. Mechanism proposed for hydroformylation using bulky monophosphites

As a consequence of the large cone angle of tris(ortho *tert*-butylphenyl)phosphite, the species **10** is formed under hydroformylation conditions. Since this species is electronically poor due to the presence of only one weak phosphite donor and strongly electron withdrawing carbonyls, this species easily loses CO, which leads to **11**. Alkene addition leads to species **12**, and the hydride migration results in the formation of the linear (**13a**) or branched (**13b**) alkyl intermediate. By migratory insertion these complexes give the acyl complex. However if a  $\beta$ -hydride elimination occurs in complex **13b** generates the isomerised alkenes. The  $\beta$ -elimination is faster for the

secondary alkyl intermediate than for the primary alkyl intermediate. Therefore, high isomerization rates will reduce the formation of branched acyl but not the formation of linear acyl, so high isomerization rates will reduce the formation of the branched aldehyde. As a consequence, n/iso ratios are high when the isomerization rate increases.

### 1.3. Hydroformylation in aqueous systems

In all homogeneous processes, the catalyst precursor is dissolved in an organic liquid phase together with the substrate and the products. The catalyst has to be recovered with special procedures, such as oxidizing the catalyst and extracting it into an aqueous phase as a salt metal. Moreover, the reaction products have to be separated from the unreacted substrate and phosphines by distillation, which may lead to further side reactions [41].

The first example in hydroformylation of recovering the catalyst without using distillation processes was in 1973, using a cobalt-modified catalyst [42]. Tris(aminoalkyl)phosphine complexes, which can be extracted from the product by an aqueous acid wash, and reextracted to the organic phase after neutralization. The economic advantages of recovering the catalyst, however, were insufficient for a low-cost metal such as cobalt. It was not until 1975 that Rhône Poulenc industries [43] patented the aqueous/organic biphasic hydroformylation of olefins, which used the trisulfonated triphenylphosphine ligand (TPPTS) (Figure 3). The first plant came on stream in 1984 in Oberhausen (Germany) and had a capacity of 100,000 t/year. Its capacity was expanded with a plant in South Korea. The Ruhrchemie- Rhône Poulenc process produces around 600,000 tones of butyraldehyde per year.

In the recent years, new hydrophilic catalysts for aqueous biphasic hydroformylation have been developed [8, 12]. Of the various ligands synthesized, the sulfonated diphosphines BISBIS, NAPHOS and BINAS (Figure 3) and the monophosphine NORBOS (Figure 11) deserve special mention. In all

cases, both activity and regioselectivity (with the exception of NORBOS) are better than for the Rh/TPPTS system (Figure 11). It is also important to notice that P:Rh ratios can be low. For all these reasons, chelating ligands are attracting more attention for future industrial use.

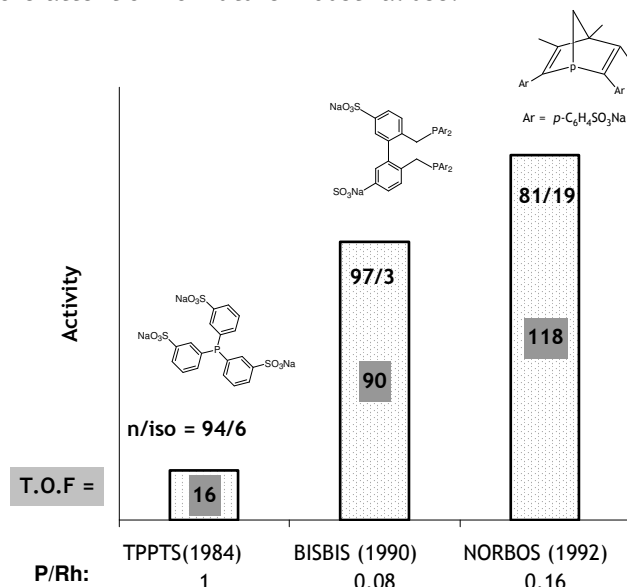


Figure 11. Results of catalysis with water-soluble rhodium-phosphine complexes.  $\text{T.O.F.} = n(\text{aldehyde})n(\text{Rh})^{-1}\text{h}^{-1}$

### Mechanism

The main differences between  $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$  and  $[\text{RhH}(\text{CO})(\text{TPPTS})_3]$  catalysts are basically that the water-soluble catalyst has lower activity and higher selectivity. The activity is lower because the solubility of alkene in water determines the rate of biphasic aqueous hydroformylation [44]. The reason for this is that the hydroformylation takes place in the aqueous phase. The higher selectivity towards the linear aldehydes may be due to the species formed. High pressure  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR showed that the activation energy of phosphine exchange was higher for TPPTS than  $\text{PPh}_3$  [45]. Presumably species such as  $[\text{RhH}(\text{CO})_2\text{L}]$  are responsible for the formation of branched aldehydes. Looking at the general proposed mechanism for hydroformylation the

formation of these species requires the dissociation of a phosphine ligand and considering that the activation energy for phosphine exchange is higher when TPPTS is used, this results in a low concentration of  $[\text{RhH}(\text{CO})_2(\text{TPPTS})]$  species. Another factor that plays a role in the selectivity of a biphasic aqueous system is the ionic strength of the aqueous phase [46]. The high excess of TPPTS used in industrial hydroformylation favours the formation of species with high content of  $[\text{RhH}(\text{CO})(\text{TPPTS})_3]$  which increases the ionic strength of the media. Dissociation of TPPTS in water should be promoted due to the electronic repulsion among the sulfonate groups. Therefore, both effects should favour the formation of  $[\text{RhH}(\text{CO})(\text{TPPTS})_2]$  and hence the regioselectivity towards linear aldehydes [12].

#### *Effect of pH*

The pH of the media also plays an important role in aqueous biphasic hydroformylation. In the Ruhrchemie-Rhône Poulenc process for propene hydroformylation, the pH is kept around neutral values in order to avoid acid- and base-catalysed reactions, and phosphine degradation. On the other hand it has been reported that other sulfonated phosphines can give optimal results in terms of activity at high pH values [47]. Desphande et al. found that the hydroformylation of 1-octene with TPPTS was pH-dependent and that the reaction rates were better between pH values of 10-7 [48]. It has also been shown that reaction rates of the asymmetric hydroformylation of styrene are higher at high pH values [49]. Joó et al. studied the effect of pH on Rh(I) complexes in aqueous solution [50] and investigated the reaction of  $[\text{RhCl}(\text{TPPMS})_3]$  with hydrogen and carbon monoxide. At basic pHs the concentration of the complex  $[\text{RhH}(\text{CO})(\text{TPPMS})_3]$ , which is the precursor of the active catalytic species, were higher. At pHs lower than 5 no reaction of the complex  $[\text{RhCl}(\text{TPPMS})_3]$  with hydrogen was observed. This observation may explain the high activity of these systems observed at basic pH.

### Higher olefins

In spite of the success of the biphasic aqueous process in the hydroformylation of low olefins, the hydroformylation of long chain alkenes in aqueous systems is not economically viable since the low solubility of the alkene in water dramatically reduces the reaction rate. For this reason, various strategies have been developed to increase the solubility of the alkene in water.

The first strategy was to add co-solvents to the system. Adding an organic water miscible-solvent to an aqueous solution increases the mass transfer of the substrate in the aqueous phase. It has been shown that co-solvents such as ethanol, acetonitrile, methanol, ethylene glycol and acetone can enhance the rate of the hydroformylation [48, 51]. Monteil et al. [51] studied the effect of adding various co-solvents when dinuclear rhodium complexes associated with TPPTS in the hydroformylation of 1-octene were used. Ethanol was found to be the best in terms of activity although the selectivity towards linear aldehyde decreased. The addition of lower alcohols was also studied by Barhmann and Bogdanovic [52], and they found that methanol led to the highest rate increase. Similar results were found in the hydroformylation of styrene using methanol as co-solvent [49].

Adding surfactants to the system is another way of increasing the solubility of the substrate in the aqueous phase. A surfactant is a molecule that consists of two parts with opposite character. One part is hydrophilic and the other hydrophobic (Figure 12).

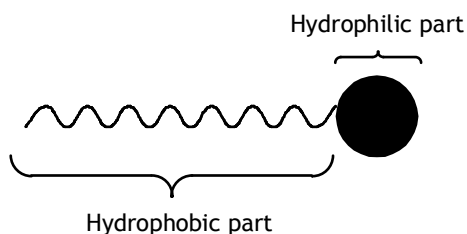


Figure 12. Schematic structure of a surfactant

Surfactants dramatically lower the surface tension of water and form aggregates like micelles in aqueous media [53]. There are many kinds of hydrophilic and hydrophobic groups of surfactants or ambiphilic compounds. Hydrocarbon chains are the most popular hydrophobic groups, fluorocarbon chains and silicon chains are also common. Surfactants are classified by their hydrophilic group. Anionic, cationic, amphoteric and neutral surfactants contain anion, cation, amphoteric ion, and nonion hydrophilic group respectively. Figure 13 shows the typical hydrophobic and hydrophilic groups of surfactants.

Depending on the concentration of the surfactants the molecules are organised in different ways. At low concentrations, surfactants will favour a surface arrangement. At higher concentrations, the surface becomes completely loaded with surfactant and any further addition must aggregate forming micelles or vesicles (Figure 14). This concentration is called the critical micelle concentration (c.m.c). It is a constant for each surfactant and depends on the solvent and temperature. In a polar solvent such as water, the hydrophilic groups are in the external part of the micelle and the hydrophobic groups will be orientated inside the micelle. These micelles are called regular micelles. In non-polar solvents, the distribution is just the opposite and these kinds of micelles are called reverse micelles.

Micelles can solubilize organic or inorganic compounds and affect their reactivity [41]. As a consequence of a gradient of polarity between the surface and the core of the micelle, a substrate can be enclosed in an appropriate environment.



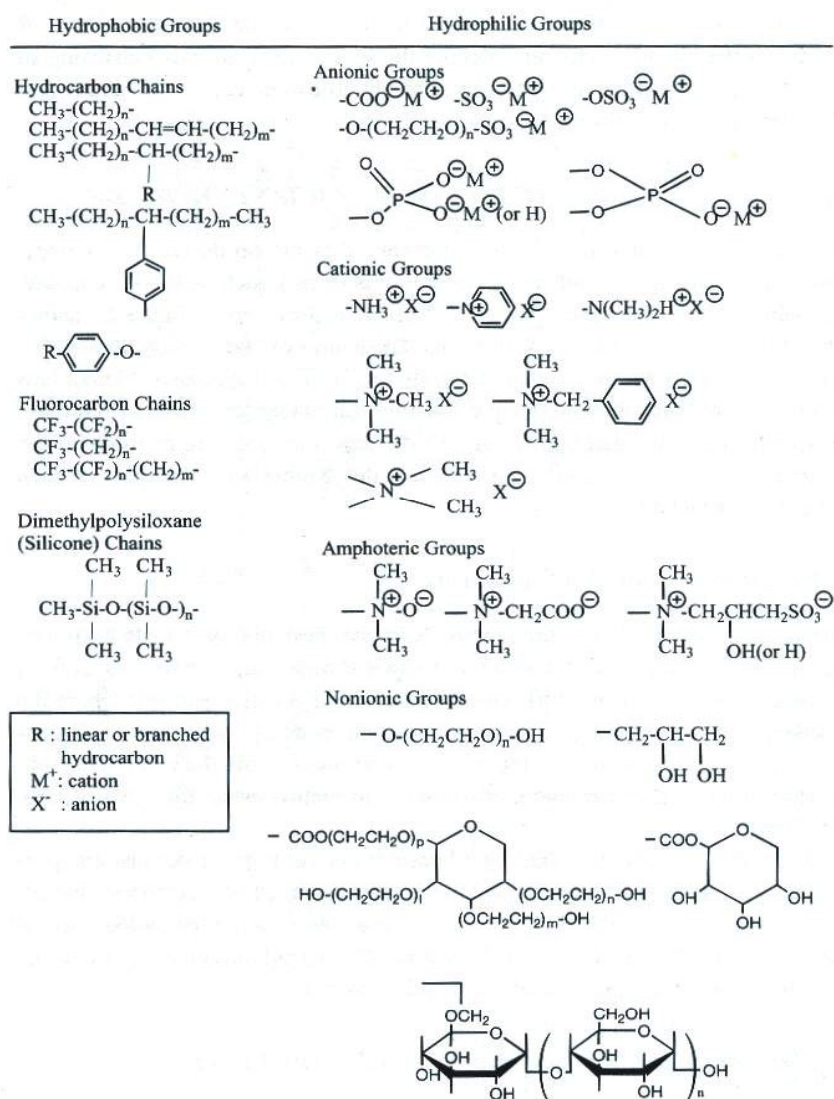


Figure 13. Typical hydrophobic and hydrophilic groups of surfactants

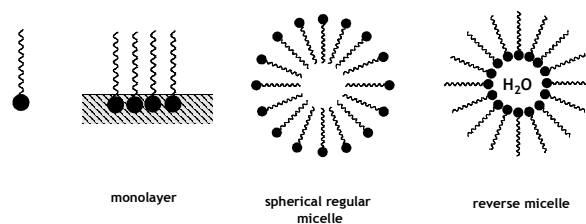


Figure 14. Self-organization of surfactants in water

Surfactants have been long used in aqueous biphasic catalysis and applied mainly to the hydrogenation and hydroformylation of alkenes. In the asymmetric hydrogenation of unsaturated amino acid derivatives catalysed by Rh(I) complexes, various studies have been made of the addition of different surfactants [54, 55, 56]. In all cases, both activity and enantioselectivity increased. It should be also pointed out that results were best when the concentration of the surfactant was above c.m.c.

Surfactants were also used in the hydroformylation of high olefins [57-61]. The hydroformylation of 1-dodecene catalysed by  $[\text{RhCl}(\text{CO})(\text{TPPTS})_2]$  in water using surfactants was studied by Chen et al. [62]. They showed that conversion and regioselectivity increased when cationic surfactants were used. The influence that surfactants have on the rate of hydroformylation may depend on a combination of different factors. The addition of surfactants decreases the surface tension at the boundary of the aqueous phase and organic phase, thus producing a larger interphase area. Also, in the water-phase, the insoluble olefin is efficiently solubilized into the hydrophobic core of the micelles formed, thus favouring contact with the catalyst (Figure 15).

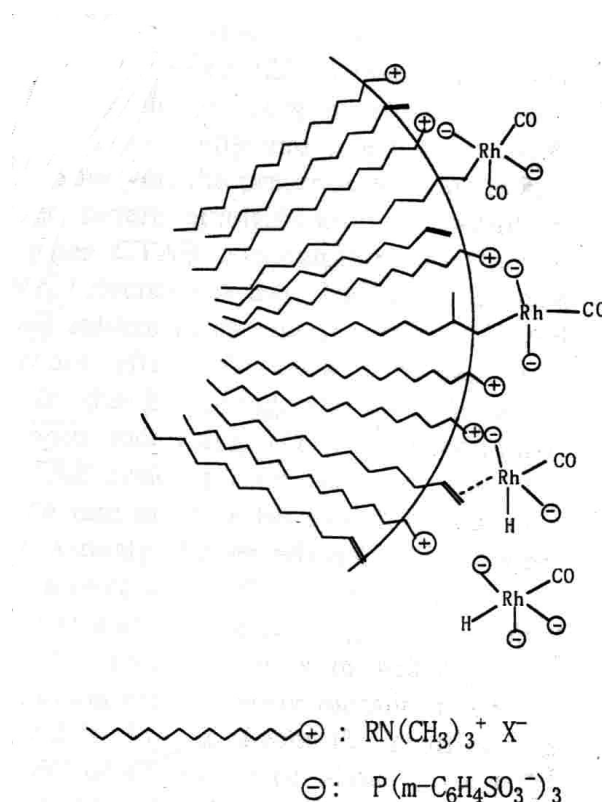


Figure 15. Interaction between the substrate and the catalyst in a micelle [62].

Cyclodextrins have also been used as mass transfer agents to biphasic reactions using water-soluble complexes [41]. Cyclodextrins are cyclic oligosaccharides composed of 6, 7 or 8 glucose units linked by a  $\alpha$ -(1-4) glucosidic bond. As a result of their molecular structure and shape, they possess a unique ability to act as molecular containers by entrapping hydrophobic guest molecules in their internal cavity (Figure 16). The cyclodextrins have been applied to hydroformylation [63, 64], hydrocarbonylation [65] and Wacker oxidations [66].

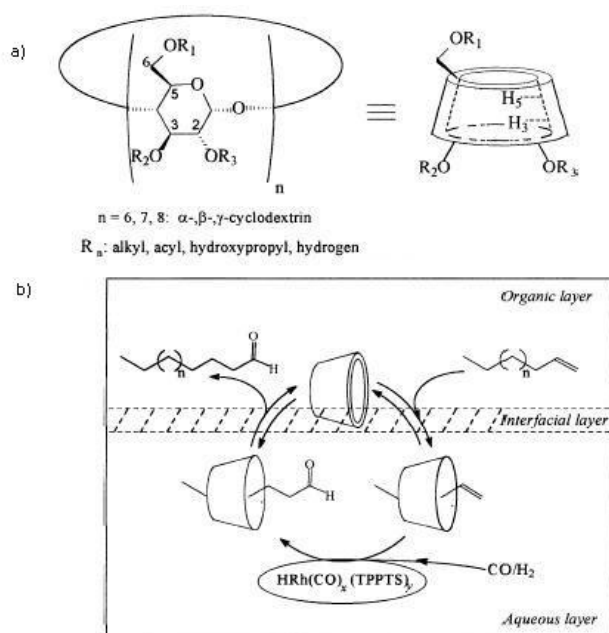


Figure 16. a) Schematic representation of the shape of cyclodextrins; b) Rhodium-catalysed hydroformylation of water-insoluble olefins in presence of cyclodextrin [63].

### Dendrimers

Dendrimers (derived from the Greek words *dendron* (tree) and *meros* (part)) are highly branched macromolecules. The main difference between the linear polymers and dendrimers is that linear polymer consists of long chain molecules, like coils, crisscrossing each other. A dendrimer consists of long chains of molecules that branch out from a common center, and there is no entanglement between the individual dendrimer molecules [67].

Dendrimers have a globular configuration with monomer units branching out from the central core. The structure is highly defined and organized. The branches increase exponentially from the core to periphery (Figure 17) [68].

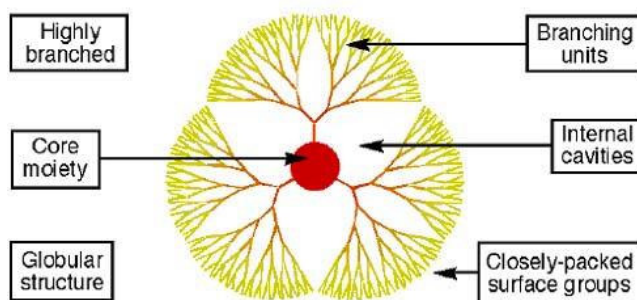


Figure 17. Dendritic structure.

The extremely regular structure of a dendrimer contributes to its nearly perfect spherical shape. Amphiphilic dendrimers have unique solution characteristics. Some amphiphilic dendrimers with ionic peripheral groups that have with hydrophobic interior structures show behaviour characteristic of unimolecular micelles [69].

Two synthetic general methods can be used to prepare dendrimers: the divergent growth method, which starts from the core and builds layers around it (inside-outwards), and the convergent growth method, which makes wedges that can be connected to a core in the last step of the synthesis (outside-inwards) (Figure 18) [70].

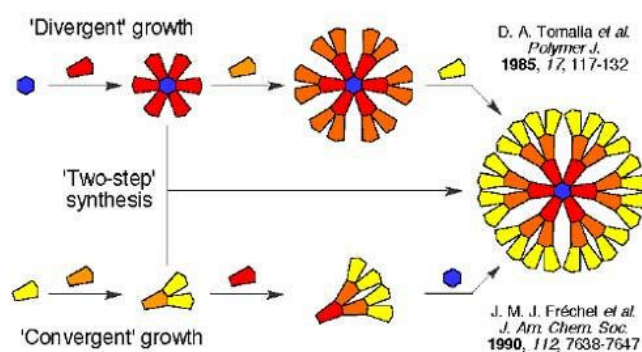


Figure 18

Dendrimers have numerous applications. For example, unsymmetrical dendrimers can form monolayers at gas-liquid interfaces or aqueous-organic interphases [67]. Amphiphilic dendrimers are useful in forming interfacial liquid membranes for stabilizing aqueous-organic emulsions. Dendrimers with carboxylate chain ends can form micelles in water. Their hydrophobic interior dissolves organic molecules that are insoluble in water.

Dendrimers with peripheral catalytic sites have been applied to transition-metal catalysis as a soluble supported catalysis [71].

#### 1.4. Supercritical Fluids (SCF)

A supercritical fluid (SCF) is defined as a substance that is above its critical temperature ( $T_c$ ) and critical pressure ( $P_c$ ). The critical point represents the highest temperature and pressure at which the substance can exist as a vapour and liquid in equilibrium [72]. In the supercritical region there is only one phase, which has properties that are between those of a gas and a liquid. Figure 19 illustrates the transition from the liquid-gas region to the supercritical region (an orange “CO<sub>2</sub>-philic” rhodium complex was added for better contrast) [73].

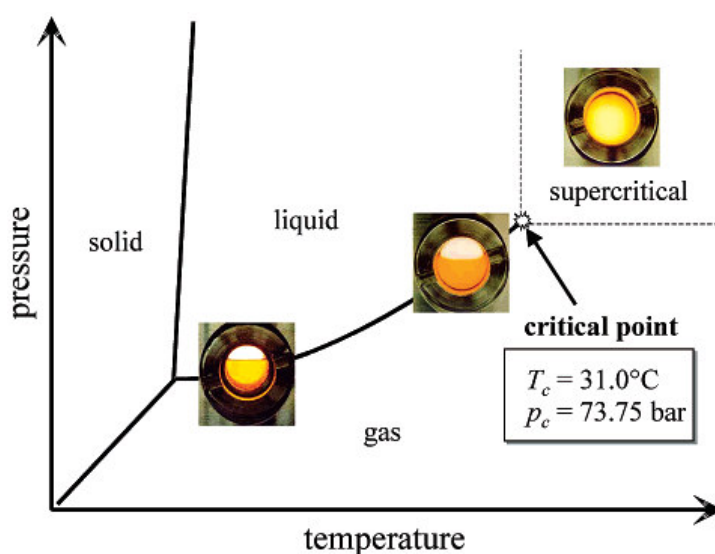


Figure 19. Schematic phase diagram of CO<sub>2</sub>.

Supercritical fluids, especially supercritical carbon dioxide (scCO<sub>2</sub>) has been used for decades as an extraction solvent to produce decaffeinated coffee beans, a large number of aroma products from plants and in the food industry [74, 75]. More recently, supercritical carbon dioxide has been used in other

commercial applications such as dry cleaning, metal degreasing, polymer modification and pharmaceuticals [74].

In the last decade supercritical fluids have emerged as alternative solvents for catalysis since they can replace conventional and hazardous solvents in a wide range of processes [76]. Among the different SCFs, supercritical carbon dioxide is one of the most attractive for alternative reaction media. Carbon dioxide has mild critical data ( $T_c = 31^\circ\text{C}$ ,  $P_c = 73.7$  bar), and is also truly benign and low cost. However, other SCFs such as water ( $T_c = 374^\circ\text{C}$ ,  $P_c = 217.8$  bar), hydrocarbons or fluorocarbons are also good alternative solvents for chemical synthesis [73].

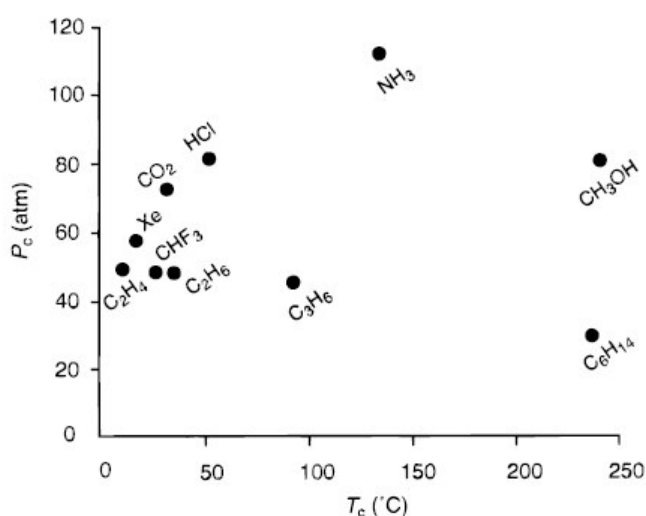


Figure 20. Critical point for selected solvents [77].

But probably the most important advantage of using SCFs is the high miscibility of gases in these media compared to very limited solubility of gases in liquid solvents [77]. This is of considerable interest for homogeneous catalysis and in particular for those reactions in which the reactants are gases. Furthermore, the research made into SCFs extraction and purification of compounds from mixtures can be used in the separation of transition metal



complexes from the reaction products because it solves the problem of recovering the catalyst at the end of the reaction. Controlled pressure reduction can be used to precipitate the catalyst selectively, assuming that these species are less soluble than the products in the supercritical fluid at lower densities.

Homogeneous catalysis in  $\text{scCO}_2$  first became an object of research during the last decade probably due to the low solubilizing power of carbon dioxide.  $\text{ScCO}_2$  is a non-polar solvent so it can only be used as a solvent in a narrow range of non-polar, non-ionic and low molecular weight catalysts, reagents and substrates. This limitation can be countered by using surfactants, co-solvents or other reagents, which increase the solubility of polar or ionic compounds in  $\text{scCO}_2$  [77].

To work with supercritical fluids is important to take into consideration experimental parameters such as temperature and pressure because they affect the density of the system. Figure 21 shows density of  $\text{CO}_2$  as a function of pressure and temperature. For a particular temperature, an increase in the pressure leads to an increase in the density, which can range from 0.05 g/ml to 0.80g/ml. On the other hand for a particular pressure, an increase in the temperature leads to a decrease in the density. It should to be pointed out that the biggest changes in the density values are produced around the critical point. These changes in density affect the ability of the fluid to dissolve substances, thus, changing pressure and temperature the solubility in SCF can be tuned. As an example, the solubility of a polar solute such as benzoic acid in  $\text{scCO}_2$  as a function of pressure and temperature is represented in Figure 22. The isotherms intersect within a restricted region of pressure named crossover pressure, which divides the graph in two regions. Between these two regions, there is a change in the temperature dependency of the solubility.

Below the crossover pressure, an increase in the temperature decreases the solubility of compounds (Figure 22) because the SCF density decreases. Above the crossover pressure, an increase in the temperature increases the solubility of the solute because the volatility of the solute increases.

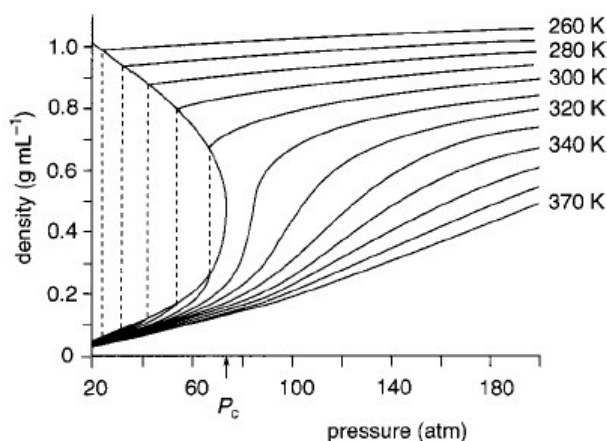


Figure 21. The density of pure CO<sub>2</sub> as a function of pressure and temperature [77].

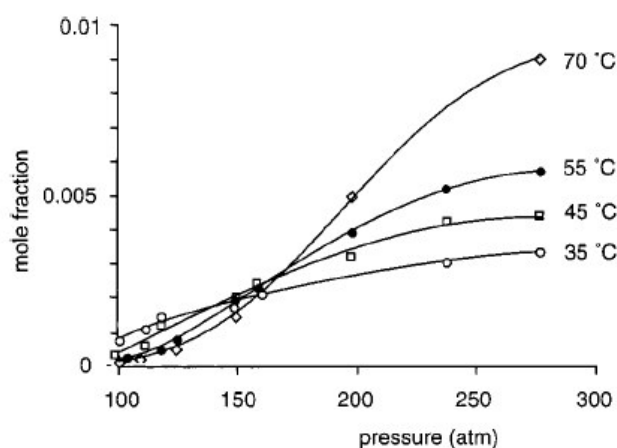


Figure 22. Mole fraction solubility of benzoic acid in scCO<sub>2</sub> as a function of pressure and temperature. The crossover pressure is approximately 160 atm [77].

It is also important to take into account the other density-dependent variables, such as viscosity, and the dielectric constant ( $\epsilon$ ). Since density depends on the pressure, these variables are also pressure-dependent. The absolute values of the variation in  $\epsilon$  depend on the nature of the SCFs. For  $\text{CO}_2$  variation of  $\epsilon$  and viscosity are low (Figure 23), from 1.3 at  $d_r = 1$  to 1.6 at  $d_r = 2$  (reduced density ( $d_r$ ) = value of density at actual point ( $d$ )/Density at the critical point ( $d_c$ )), which means that carbon dioxide remains a very non-polar solvent even for relatively large changes in pressure and temperature. For other more polar fluids, such as fluoroform and water, the same changes in density leads to drastic variations of the dielectric constant [72]

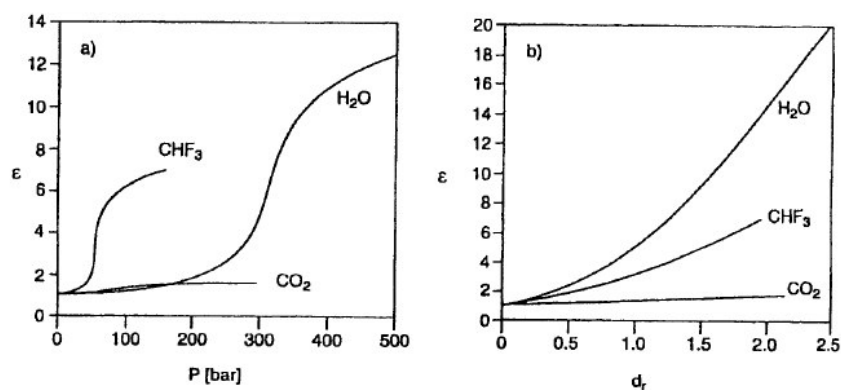


Figure 23. Variation of the dielectric constant of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CHF}_3$  as function of pressure and reduced density [72].

Viscosity is generally lower and diffusivity higher in SCFs than in common liquid solvents. Compounds diffuse in SCFs at faster rates than in liquid solvents. However, this does not mean that SCFs do not have limitations of mass transfer.

Another important parameter is the reactivity of SCFs since they are not always inert under reaction conditions. This can be useful for some activation

processes but hazardous for uncontrolled reactions. Some of the hazardous SCFs are ethyne or 1,1-difluoro-ethene, which can polymerise under pressurization or can be explosive. Even alkanes become thermodynamically unstable at higher temperatures. But sometimes the reactivity of SCFs can be beneficial: the controlled polymerization of  $\text{scC}_2\text{H}_4$ , for example, is an important industrial process.  $\text{ScCO}_2$  can be quite reactive and it inserts readily into M-H, M-R, M-OR or M-NR<sub>2</sub> bonds in transition metal complexes and reacts with secondary and primary amines to form carbamate salts [77].

#### *Solubility of catalyst precursors*

Supercritical carbon dioxide is a non-polar solvent so only non-polar catalysts will be soluble in it. It is known that some transition metal complexes are soluble in  $\text{scCO}_2$  but there is no data for complexes that contain ligands such as phosphines, porphyrines or carbonyls. Polar complexes, ionic complexes or even non-polar complexes containing aryl groups are not soluble in  $\text{scCO}_2$  [77]. Therefore, a great deal of research has been done in recent years to increase the solubility of the catalytic system. One of the first approaches was ligand modification. Ligands with aryl groups were substituted by alkyl or perfluoroalkyl groups [78, 79]. Alkyl phosphines with low molecular masses such as  $\text{PMe}_3$  or  $\text{PEt}_3$  are soluble in  $\text{scCO}_2$  and provide active catalysts in hydroformylation [78, 80, 81]. Smart et al. [82] studied the effect of alkyl chains on the solubility of phosphorous compounds in supercritical carbon dioxide and reported that ligands with an approximate chain length of eight carbons, preferably branched, have the properties that will most likely lead to high solubility (Figure 24). Branched chains were also inserted into surfactants derived from sodium bis-2-ethyl-1-hexyl sulfosuccinate (AOT) and it has shown that a high degree of chain tip methylation increases solubility in supercritical carbon dioxide (Figure 24) [83]. The introduction of alkyl chains between six and sixteen carbons long into aryl phosphines was also studied by

Banet Osuna et al. [84] who showed that the effect is not so pronounced for aryl phosphines. The solubility of the ligands was low and decreased when the number of carbons in the alkyl chain increased. The addition of other CO<sub>2</sub>-philic groups such as silyl or carbonyl, as substituents for aryl groups, provided often soluble systems [81,85].

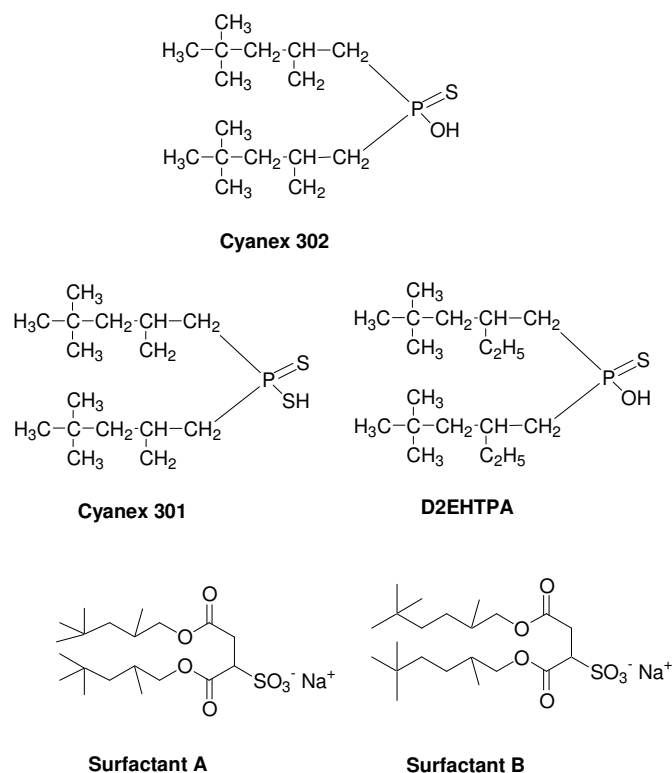


Figure 24. CO<sub>2</sub>-philic compounds containing alkyl-branched groups

However, the most successful approach is to insert perfluorinated chains into aryl phosphines. Leitner and co-workers introduced this concept, by attaching perfluorinated alkyl chains to the ligand. These ligands contain methylene groups in the first two carbons of the aryl substituent (ponytail). The effect of this was to reduce the electrowithdrawing effect [79, 86]. Other groups [84,

87-91] have reported the use of ligands containing perfluorinated chains (Figure 25).

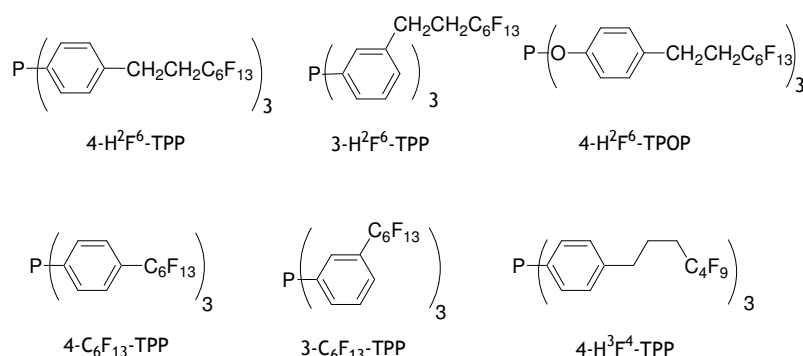


Figure 25. Perfluorinated ligands

The use of co-solvents increases also the solubility of catalyst precursors in supercritical carbon dioxide. Adding polar solvents increases the solubility of polar compounds in  $\text{scCO}_2$ . For example, the addition of 5-10% of methanol increases the solubility of transition metal complexes, which are insoluble without methanol [77]. The use of selected counterions, such as BARF (tetrakis(3,5-bis(trifluoromethyl))phenylborate) or  $\text{CF}_3\text{SO}_3^-$ , also enhanced the solubility of transition metal complexes [92]. Finally, the use of surfactants that form reverse micelles in  $\text{scCO}_2$  and solubilize hydrophilic compounds is another strategy that has been developed. These surfactants contain polar hydrophilic heads and  $\text{CO}_2$ -philic tails such as siloxane or fluorinated groups to increase the solubility in  $\text{scCO}_2$  [93, 94].

Because  $\text{CO}_2$ -philic organometallic complexes are more readily available, carbon dioxide has increasingly been used as an alternative reaction medium in homogenous catalysis. The complete miscibility of gases in carbon dioxide makes it an ideal medium for catalysed reactions in which the reactants are gases. For this reason, one of the most widely studied catalysed reactions in  $\text{scCO}_2$  is hydrogenation. The hydrogenation of carbon dioxide to obtain formic

acid was described by Jessop et al. [78]. Burk et al. [92] used BARF and  $\text{CF}_3\text{SO}_3^-$  as counteranions in their study of asymmetric hydrogenation of  $\alpha$ -enamides with cationic rhodium complexes. They found that the catalytic systems are soluble and obtained enantioselectivities similar to the ones obtained in conventional organic solvents. Other successful examples of asymmetric hydrogenation in  $\text{scCO}_2$  of  $\alpha,\beta$ -unsaturated carboxylic acids [95] or hydrogenation of imines [96] have also been reported.

Hydroformylation has also been widely studied with  $\text{scCO}_2$  as the reaction medium. The first example, was reported by Rathke et al. [97] for the hydroformylation of propylene with  $[\text{Co}(\text{CO})_8]$  as catalyst. However, this process suffered from the drawbacks of cobalt catalysts (high pressures and temperatures). Leitner et al. [79] studied the hydroformylation of various alkenes with  $[\text{Rh}(\text{cod})(\text{hfacac})]$  ( $\text{hfacac}$  = 1,1,1,6,6,6-hexafluoropentane-2,4-dionate) either associated with perfluorinated phosphine ligands or as unmodified complex. The results showed that hydroformylation with the unmodified catalysts is faster in  $\text{scCO}_2$  than in conventional solvents. The results of using  $\text{CO}_2$ -philic ligands were similar to the ones obtained in conventional solvents with triphenylphosphine as the ligand. Furthermore, the extractive properties of carbon dioxide made it possible to extract the products of hydroformylation 1-octene from the catalyst. The aldehydes contained less than 1 ppm of rhodium and the catalyst was reused in five catalytic runs with no loss of activity and selectivity. The use of perfluorinated ligands in rhodium-catalysed hydroformylation was also studied by several groups [84, 88, 89].

Cole-Hamilton et al. [80,81] reported the use of trialkylphosphines such as  $\text{PEt}_3$  as ligands for the rhodium-catalysed hydroformylation of 1-hexene. This kind of ligands are readily available, cheap, soluble in  $\text{scCO}_2$  and do not involve synthesizing perfluorinated ligands, which are difficult to prepare. Ligands containing trimethylsilyl groups,  $\text{P}(4\text{-C}_6\text{H}_4\text{SiMe}_3)_3$  and  $\text{Ph}_2\text{P}(4\text{-C}_6\text{H}_4\text{SiMe}_3)$ , were also investigated in the hydroformylation of 1-octene. Although the

complexes are not totally soluble, the activity and regioselectivity were high (80 and 82.4%, n/iso = 4.0 and 3.0, respectively) [81]. Cole-Hamilton et al. also reported the use of insoluble metal rhodium complexes in the hydroformylation of 1-hexene and 1-nonene [98]. They managed to recycle the catalyst by flushing the products formed into a second autoclave. The products contained undetectable amounts of rhodium. Recently, Leitner et al. [99] reported a cartridge catalyst that used a poly(ethyleneglycol) (PEG) modified phosphine ligand, MeOPEG<sub>750</sub>-PPh<sub>2</sub>. In a scCO<sub>2</sub> regulated reaction separation sequence they tested within other reactions the hydroformylation of 1-octene with the catalyst formed in situ from MeOPEG<sub>750</sub>-PPh<sub>2</sub> and [Rh(acac)(CO)<sub>2</sub>]. The catalyst was insoluble in scCO<sub>2</sub> but its activity was high and conversion reached 99% in two hours. After the reaction time, the products were separated from the catalyst by extraction with scCO<sub>2</sub>. The products contained less than 5 ppm of rhodium and the catalyst was reused six times with no significant changes in activity and selectivity.

Supercritical carbon dioxide has also been successfully applied in carbon-carbon coupling reactions, which occur at high rates and selectivities in scCO<sub>2</sub> [100]. The first example was reported by Tumas et al. [101]. They studied the Heck and Stille couplings using palladium complexes associated with different phosphines. The best results were obtained with fluorinated phosphines. Couplings carried out on a solid support are of particular interest [102], reactions that use polymer supports require solvents that can swell the polymer and expose the active reaction sites. The ability of scCO<sub>2</sub> to plasticise polymers has been exploited in a number of applications, including polymer impregnation, formation of blends and particle formation [103]. For all these reasons, scCO<sub>2</sub> is an interesting alternative solvent for polymer-supported reactions.

Polymerisation reactions have also been studied in scCO<sub>2</sub>. Amorphous low melting point fluoropolymers can be synthesized in carbon dioxide either by free radical or cationic methods. They are not very soluble in common organic



solvents, which makes it difficult for them to be synthesized. In fact, they are only soluble in chlorofluorocarbons (CFCs) and CO<sub>2</sub>. Due to the environmental problems associated with the use of CFCs, CO<sub>2</sub> is an environmentally friendly option for the synthesis of these types of highly fluorinated monomers [104]. Polymerisations catalysed by metal transition complexes have also been studied in scCO<sub>2</sub>. De Vries et al. [105] showed that the polymerisation of ethylene and 1-hexene catalysed by cationic palladium complexes in scCO<sub>2</sub> gave polymers with properties similar to those obtained in dichloromethane. Few studies have been made of the copolymerization of carbon monoxide with olefins in scCO<sub>2</sub> [106-108].

Finally, in the recent years many examples of multiphasic systems that use scCO<sub>2</sub> have been described. The combination of ionic liquids and scCO<sub>2</sub> has emerged as a new biphasic system for homogeneous catalysis. ScCO<sub>2</sub> is soluble in ionic liquids, and decreases their viscosity and therefore, enhances the mass transfer. Ionic liquids are not soluble in scCO<sub>2</sub>. Hence, non-volatile compounds can be extracted quantitatively from ionic liquids with scCO<sub>2</sub> [109]. The biphasic system ionic liquids/scCO<sub>2</sub> has been applied successfully in many homogeneous catalysed reactions [110-114].

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## Aim and scope

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*The development of environmentally friendly chemical processes and catalysis that use benign solvents as a reaction media and can recover and reuse the catalyst is one of the main challenges of the current research. The aim of the present thesis is to apply alternative solvents, water and supercritical carbon dioxide, in such important catalytic processes as the hydroformylation of long chain alkenes and the copolymerization of carbon monoxide and tert-butylstyrene. Various strategies have been used to achieve these goals.*



**Chapter 3** focusses on the hydroformylation of 1-octene and 1-decene in water biphasic systems catalysed by rhodium complexes associated with sulfonated diphosphines, 1,3-bis(diphenylphosphino)propane (dpppts) and 1,4-bis(diphenylphosphino)butane (dppbts) (Figure 1). The aim is to study the effect on activity and selectivity of the addition to the catalytic system of cationic (CTAHSO<sub>4</sub>) and anionic (SDS) surfactants and a dendrimer (Figure 2) in order to improve the mass transfer.

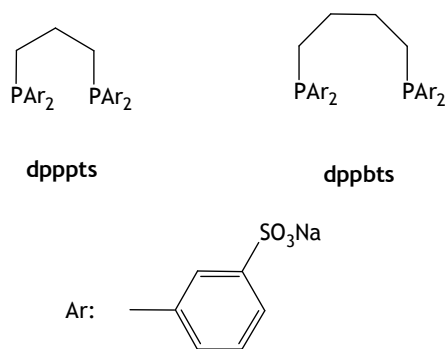


Figure 1

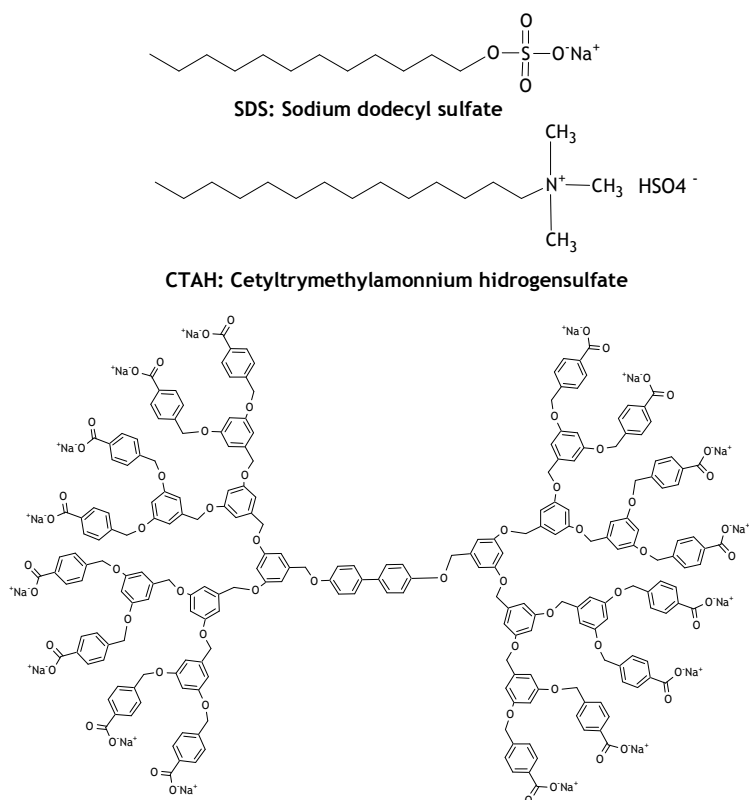


Figure 2

- The objective of **Chapter 4** is to synthesize three new P-donor ligands (Figure 3) with alkyl-branched chains in order to apply them in the hydroformylation of 1-octene in supercritical carbon dioxide. The coordination chemistry of these ligands to rhodium and palladium will be also studied

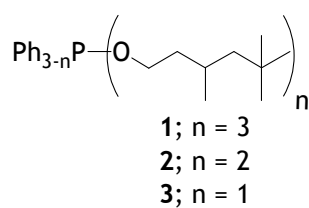


Figure 3

- **Chapter 5** deals with the application of a previously described fluorinated phosphine (Figure 4) in the hydroformylation of alkenes in supercritical carbon dioxide.

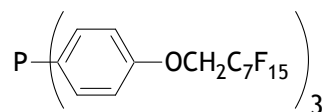


Figure 4

- The aim of **Chapter 6** is to synthesize N-donor fluorinated ligands (Figure 5), coordinate them to palladium and apply them as catalysts precursors for the alternating copolymerization of carbon monoxide and *tert*-butylstyrene using supercritical carbon dioxide as a reaction medium.

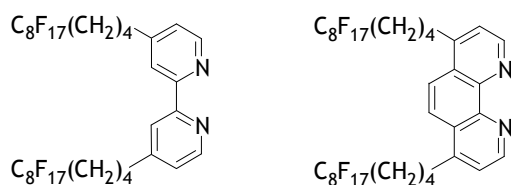


Figure 5

## Micellar effect in rhodium catalysed hydroformylation of high olefin in water

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*High linear alkenes (1-octene and 1-decene) have been hydroformylated using water-soluble rhodium complexes associated with sulfonated diphosphines in the presence of ionic surfactants, a dendrimer or methanol. In all cases, the hydroformylation activities were higher than in experiments without additives. The selectivity in aldehydes was higher when we used cetyltrimethylammoniumhydrogensulfate (CTAHSO<sub>4</sub>) as the surfactant or methanol as the co-solvent.*



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### 3.1. Introduction

The catalytic hydroformylation of long chain alkenes is an interesting reaction for transforming alkenes into aldehydes using carbon monoxide and hydrogen [1, 2]. The hydroformylation of linear olefins is a well-known industrial process and a key step in the manufacture of oxo alcohols.

Hydroformylation can be carried out in biphasic aqueous systems using a rhodium catalyst associated with the water-soluble ligand sodium trisulfonated triphenylphosphine (TPPTS =  $\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})_3$ ) [3]. Since this system was first used in 1984 by Rhône-Poulenc/Ruhr-Chemie in the industrial hydroformylation of propene [4, 5, 6], research into biphasic catalysis has become very active [7]. However, this process is limited to short-chain alkenes (propene and 1-butene) because a certain solubility of the alkene in water is required [8]. This process is therefore not economically viable for long-chain alkenes, which are not very soluble in water. One way to increase the solubility of the substrates in water is to add surfactants to the system [7]. The amphiphilic nature of these substances drastically lowers the surface tension of water because aggregates such as micelles or vesicles form above the critical micelle concentration (c.m.c) [9]. These aggregates increase the solubility of hydrophobic substances thus improving the mass transfer [10, 11]. This strategy has been used in the hydroformylation of alkenes with Rh-TPPTS systems [12, 13, 14]. In the hydroformylation of 1-dodecene, the activity increases in the presence of cationic surfactants such as cetyltrimethylammonium bromide (CTAB). In hydroformylation of  $\omega$ -alkene carboxylic acids methyl esters up to  $\omega$ -decene, cationic tensids were the best systems. The hydroformylation of alkenes between  $\text{C}_6$ - $\text{C}_{16}$  in reverse micellar systems has been studied by Vyve and Renken using sodium dodecylsulfate (SDS) in association with butanol as a co-solvent [15]. Reaction rates were

high in the hydroformylation of 1-dodecene with Rh-TPPTS in a microemulsion using nonionic surfactants of alkylpolyglycoether [16].

Dendrimers are perfect monodisperse macromolecules with a regular and highly branched three-dimensional architecture [17]. Dendritic macromolecules contain a large number of symmetrically arranged branches that result in a three-dimensional globular shape. At high molecular weights these structures may approximate spheres. Functionalising dendrimers with hydrophilic groups on the periphery, they adopt structures that resemble micelles. These micelles are a new class of dendritic macromolecules where an interior hydrophobic is surrounded by a hydrophilic surface. Dendrimers with carboxylate chain ends act as micelles in water since their hydrophobic interior dissolves organic molecules that are insoluble in water. Therefore, these macromolecules may act as surfactants. Fréchet et al [18] reported the synthesis of a “*unimolecular micelle*” based on a polyether structure that contained carboxylate groups on the surface and they tested its solubilization properties in water using pyrene as model. They found that polyether dendrimers were powerful solubilizers, and showed that the dendrimer can solubilize pyrene in water at concentrations ( $5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ) lower than the ones needed for sodium dodecylsulfate (SDS) ( $8.1 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ).

Another way to increase the solubility of alkenes in water is to add a co-solvent to the system. This was widely studied in catalytic systems using water-soluble rhodium complexes and TPPTS as a ligand. For example, the hydroformylation of 1-octene was studied in the presence of co-solvents such as ethanol, methanol, acetonitrile and acetone [19]. The co-solvents increase the concentration of alkene in water. The best result was obtained when

ethanol was used as the co-solvent. Adding alcohols as co-solvents was also studied by Bahrmann and Bogdanovic [20], who found that the reaction rate was enhanced when MeOH was added.

Diphosphines generally provide higher selectivities in hydroformylation in organic media [21, 22], but the sulfonated diphosphines have hardly been investigated. This is probably because it is difficult to prepare pure sulfonated ligands.

The sulfonated biphenyl derivative BISBIS [8, 23, 24] and BINAS [25] associated with the  $[\text{Rh}(\text{acac})(\text{CO})_2]$  complex (acac = acetylacetonate) has higher activities and selectivities than the rhodium-TPPTS system in the hydroformylation of propene under the same reaction conditions. The BISBIS-Na system is also active in the hydroformylation of higher olefins such as 1-hexene.

Alkyl sulfonated diarylphosphines have hardly been studied in hydroformylation. The system Rh-dppets (dppets:  $(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})_2$ ) [26] gave a low conversion in the hydroformylation of 1-octene. The  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{dppbts}$  system (dppbts:  $(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})\text{P}(\text{CH}_2)_4\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})_2$ ) has also been studied in the hydroformylation of methyl acrylate but this provided very poor chemo- and regioselectivity [27].

We recently studied the use of chiral sulfonated diphosphines as ligands in the rhodium asymmetric hydroformylation of styrene in a biphasic aqueous system. The conversions in water were low but the enantiomeric excesses were quite similar to those reported for organic solvents [28, 29].

In this paper, we describe how adding anionic and cationic surfactants, sodium dodecylsulfate (SDS) and cetyl trimethylammonium hydrogensulfate (CTAHSO<sub>4</sub>), and a polyether dendritic molecule (dendrimer **12**) respectively,



affects the hydroformylation of long-chain alkenes (1-octene and 1-decene) in the presence of the rhodium complexes  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2$  (cod = 1,5-cyclooctadiene) associated with sulfonated diphosphines.

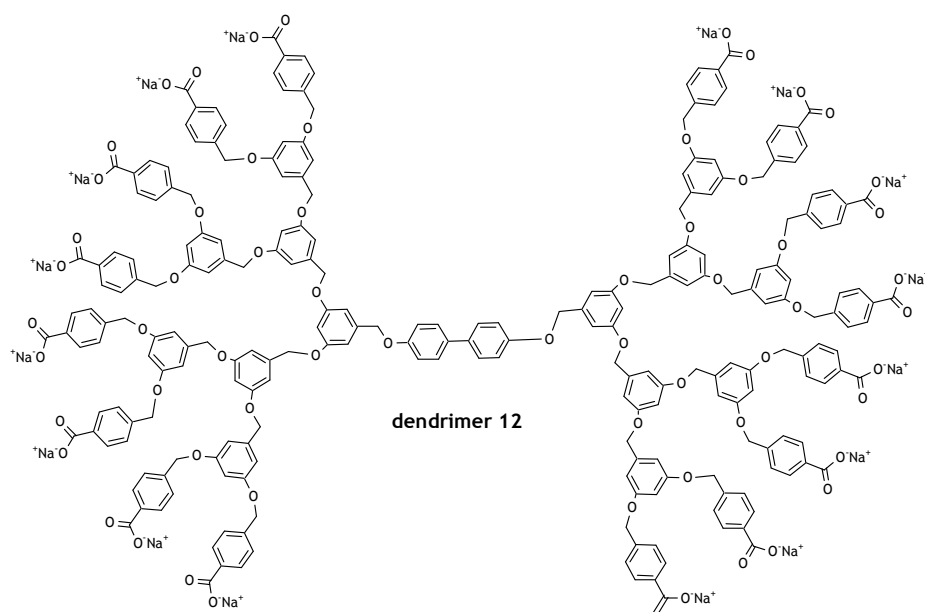


Figure 1.

### 3.2. Experimental

#### General methods

The rhodium catalyst precursors were synthesised using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. All other reagents were used as supplied.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and NMR spectra were recorded on a Varian Gemini spectrometer operating at  $^1\text{H}$  (300 or 400 MHz),  $^{13}\text{C}$  (75.43 or 100.57 MHz). Chemical shifts were reported relative to tetramethylsilane for  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  as internal

reference. Mass spectrometry was performed in an Voyager- DP RP spectrometer (EI-HR). The complex  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2$  [30] and the diphosphines dpppts and dppbts were prepared as previously reported [31, 32]. Dendrimer 12 was prepared by a modified previously reported procedure [18]. Gas chromatography analyses were performed using a Hewlett-Packard 5890A chromatograph in an Ultra-2 (5 % diphenylsilicone/95% dimethylsilicone) column (25 m x 0.2 mm Ø) to separate the products. The pH's were measured with a pH-meter Crison micro pH 2001.

#### *Synthesis of dendrimer 12 (Schemes 1 and 2)*

##### *Procedure I: synthesis of dendritic benzyl alcohols. (3, 5, 7)*

A mixture of the dendritic benzyl bromide (2.05 equiv), 3,5-dihydroxybenzylalcohol **2** (1.00 equiv.), potassium carbonate (2.50 equiv) and 18-crown-6 (0.2 equiv) in acetone was heated at reflux and stirred under nitrogen for 24 h. After this reaction time, the mixture was evaporated under reduced pressure, and the residue was washed with water and dichloromethane. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 50 ml). The combined extracts were dried with  $\text{MgSO}_4$ , evaporated under reduced pressure and purified by flash chromatography.

##### *Procedure II: synthesis of dendritic benzyl bromides (4, 6, 8)*

Triphenylphosphine (1.25 equiv.) and carbon tetrabromide (1.25 equiv) were added to a solution of dendritic benzyl alcohol (1.00 equiv.) dissolved in the minimum amount of tetrahydrofuran and stirred at room temperature under nitrogen. The reaction was monitored by TLC and additional aliquots of  $\text{CBr}_4$  and  $\text{PPh}_3$  were added at *ca.* 15 min. intervals, if it was necessary to force

completion of reaction. The reaction mixture was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 50 ml). The combined extracts were dried with  $\text{MgSO}_4$ , evaporated under reduced pressure and purified by flash chromatography.

#### *Synthesis of $(\text{MeO}_2\text{C})_2\text{-[G-1]-OH}$ (3)*

Procedure I was used to prepare this compound from methyl- 4-bromomethylbenzoate **1** (6 g, 0.026 mol), 3,5-dihydroxybenzyl alcohol **2** (1.78 g, 0.037 mol), potassium carbonate (1.65 g, 0.037 mmol) and 18-crown-6 (0.25 g, 0.25 mmol). The product was purified by flash chromatography eluting with  $\text{CH}_2\text{Cl}_2$  and then with gradually increasing proportions of ether (up to 1:9 ether: $\text{CH}_2\text{Cl}_2$ ) to give **3** as a white crystalline solid. 4.46 g (81%).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 3.55 (t, 1H, OH), 3.92 (s, 6H,  $\text{OCH}_3$ ), 4.58 (d, 2H,  $J$  = 5.2 Hz,  $\text{CH}_2\text{OH}$ ), 5.08 (s, 4H,  $\text{OCH}_2$ ), 6.42 (t, 1H,  $J$  = 2.8 Hz, ArH), 6.55 (d, 2H,  $J$  = 1.6 Hz, ArH), 7.42 and 8.03 ( $\text{AB}_q$ , 8H,  $J$  = 8.4 Hz, PhH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ (ppm): 52.39, 65.26, 69.55, 101.43, 106.01, 127.17, 129.89, 130.096, 142.23, 144.01, 160.03, 167.06.

#### *Synthesis of $(\text{MeO}_2\text{C})_2\text{-[G-1]-Br}$ (4)*

Procedure II was used to prepare this compound from  $(\text{MeO}_2\text{C})_2\text{-[G-1]-OH}$  **3** (4.46 g, 0.011 mol), triphenylphosphine (3.35 g, 0.013 mol) and carbon tetrabromide (4.23 g, 0.013 mol). The product was purified by flash chromatography eluting with hexane:  $\text{CH}_2\text{Cl}_2$  (1:1) and then with gradually increasing proportions of  $\text{CH}_2\text{Cl}_2$  (up to pure  $\text{CH}_2\text{Cl}_2$ ) to give **4** as a crystalline white solid. 4.10 g (80%).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 3.91 (s, 6H,  $\text{OCH}_3$ ), 4.39 (d, 2H,  $\text{CH}_2\text{Br}$ ), 5.08 (s, 4H,  $\text{OCH}_2$ ), 6.51 (t, 1H,  $J$  = 2.4 Hz, ArH), 6.63 (d, 2H,  $J$  = 2.4 Hz, ArH), 7.48 and 8.05 ( $\text{AB}_q$ , 8H,  $J$  = 8.0 Hz, PhH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

$\delta$ (ppm): 33.58, 52.42, 69.68, 102.39, 108.53, 127.23, 130.02, 130.15, 141.93, 159.99, 167.50.

*Synthesis of (MeO<sub>2</sub>C)<sub>4</sub>-[G-2]-OH (5)*

Procedure I was used to prepare this compound from (MeO<sub>2</sub>C)<sub>2</sub>-[G-1]-Br 4 (4.10 g, 8.21 mmol), 3,5-dihydroxybenzyl alcohol 2 (0.56 g, 4.1 mmol), potassium carbonate (1.41 g, 0.010 mol) and 18-crown-6 (0.21 g, 0.82 mmol). The product was purified by flash chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> and then with gradually increasing proportions of ether (up to 1:9 ether:CH<sub>2</sub>Cl<sub>2</sub>) to give 5 as a white crystalline solid. 2.90 g (74%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 2.20 (1t, 1H, *J* = 1.4 Hz, OH), 3.92 (s, 12H, OCH<sub>3</sub>), 4.61 (d, 2H, *J* = 5.4 Hz, CH<sub>2</sub>OH), 4.97 and 5.10 (each s, 12H, OCH<sub>2</sub>), 6.45 and 6.53 (each t, 3H, *J* = 2.0 Hz, ArH), 6.55 and 6.64 (each d, 6H, *J* = 2.0 Hz, ArH), 7.42 and 8.03 (AB<sub>q</sub>, 16H, *J* = 8.0 Hz, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 52.17, 65.17, 69.39, 60.72, 101.36, 101.60, 105.64, 106.34, 126.97, 129.68, 129.87, 141.88, 143.52, 159.82, 159.89, 166.84.

*Synthesis of (MeO<sub>2</sub>C)<sub>4</sub>-[G-2]-Br (6)*

Procedure II was used to prepare this compound from (MeO<sub>2</sub>C)<sub>4</sub>-[G-2]-OH 5 (2.90 g, 2.96 mmol), triphenylphosphine (0.97 g, 3.71 mmol) and carbon tetrabromide (1.23 g, 3.71 mmol). Aliquots were added up to 3 equiv. of PPh<sub>3</sub>/CBr<sub>4</sub> to force the completion of the reaction. The product was purified by flash chromatography eluting with hexane: CH<sub>2</sub>Cl<sub>2</sub> (1:2) and then with gradually increasing proportions of CH<sub>2</sub>Cl<sub>2</sub> (up to pure CH<sub>2</sub>Cl<sub>2</sub>) to give 6 as a crystalline white solid. 2.20 g (71%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 3.92 (s, 12H, OCH<sub>3</sub>), 4.39 (s, 2H, CH<sub>2</sub>Br), 4.95 and 5.09 (each s, 12H, OCH<sub>2</sub>), 6.47 and 6.53 (each t, 3H, *J* = 2.2 Hz, ArH), 6.59 and 6.65 (each d, 6H, *J* = 2.2 Hz, ArH),

7.46 and 8.03 (AB<sub>q</sub>, 16H,  $J = 8.7$  Hz, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm): 31.16, 52.33, 69.53, 101.18, 101.73, 105.79, 106.54, 108.56, 127.13, 128.75, 128.91, 129.81, 130.83, 142.07, 159.97, 166.98.

*Synthesis of (MeO<sub>2</sub>C)<sub>8</sub>-[G-3]-OH (7)*

Procedure I was used to prepare this compound from (MeO<sub>2</sub>C)<sub>4</sub>-[G-2]-Br **6** (2.20 g, 2.11 mmol), 3,5-dihydroxybenzyl alcohol **2** (0.14 g, 1.03 mmol), potassium carbonate (0.39 g, 2.80 mmol) and 18-crown-6 (0.05 g, 0.20 mmol). The product was purified by flash chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> and then with gradually increasing proportions of ether (up to 1:9 ether:CH<sub>2</sub>Cl<sub>2</sub>) to give **7** as a white crystalline solid. 2.00 g (94%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): 2.17 (s, 1H, OH), 3.89 (s, 24H, OCH<sub>3</sub>), 4.59 (d, 2H,  $J = 6.0$  Hz, CH<sub>2</sub>OH), 4.93 and 5.05 (each s, 28H, OCH<sub>2</sub>), 6.45-6.62 (m, 21H, ArH), 7.42 and 8.03 (AB<sub>q</sub>, 16H,  $J = 8.0$  Hz, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm): 52.41, 64.90, 69.60, 69.94, 101.24, 101.80, 105.83, 106.55, 127.20, 129.88, 130.10, 130.72, 142.09, 160.02, 160.10, 167.05.

*Synthesis of (MeO<sub>2</sub>C)<sub>8</sub>-[G-3]-Br (8)*

Procedure II was used to prepare this compound from (MeO<sub>2</sub>C)<sub>8</sub>-[G-3]-OH **7** (2.00 g, 1.03 mmol), triphenylphosphine (0.32 g, 1.21 mmol) and carbon tetrabromide (0.40 g, 1.21 mmol). Aliquots were added up to 6 equiv. of PPh<sub>3</sub>/CBr<sub>4</sub> to force the completion of the reaction. The product was purified by flash chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> and then with gradually increasing proportions of ether (up to 3% ether-CH<sub>2</sub>Cl<sub>2</sub>) to give **8** as a white solid. 0.88g (43%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ(ppm): 3.92 (s, 24H, OCH<sub>3</sub>), 4.36 (d, 2H, CH<sub>2</sub>Br), 4.94 and 5.05 (each s, 28H, OCH<sub>2</sub>), 6.50-6.51 and 6.60-6.63 (each m, 21H, ArH) and 7.43-8.00 (AB<sub>q</sub>, 32H,  $J = 8.0$ Hz, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>)

$\delta(\text{ppm})$ : 33.70, 52.31, 69.54, 69.86, 69.99, 101.73, 102.26, 106.52, 108.32, 127.13, 130.03, 130.48, 139.41, 142.01, 160.00, 166.97.

*Synthesis of  $\{(\text{MeO}_2\text{C})_8\text{-[G-3]}\}_2\text{-[C]}$  (10)*

A mixture of  $(\text{MeO}_2\text{C})_8\text{-[G-3]}\text{-Br}$  **8** (0.88 g, 0.41 mmol), 4-4'-dihydroxybiphenyl **9** (0.035 g, 0.19 mmol), potassium carbonate (0.32 g, 2.32 mmol) and 18-crown-6 (8.00 mg, 0.03 mmol) dissolved in 100 ml of dry tetrahydrofuran was heated at reflux and stirred under nitrogen for 48 h. After the reaction had completed, an excess of **9** (0.35 g, 10 equiv) was added. The mixture was then evaporated under reduced pressure and dissolved into 100 ml of dichloromethane and 100 ml of water. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 50 ml). The combined extracts were dried with  $\text{MgSO}_4$  and evaporated under reduced pressure. The product was purified by flash chromatography eluting with 10% ether- $\text{CH}_2\text{Cl}_2$  and then with gradually increasing proportions of ether (up to 15% ether- $\text{CH}_2\text{Cl}_2$ ). The product was obtained as a white solid 0.51 g (89%).  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ )  $\delta(\text{ppm})$ : 3.88 (s, 48H,  $\text{OCH}_3$ ), 4.94 and 5.06 (s, 60H,  $\text{OCH}_2$ ), 6.51-6.65 (m, 42H, ArH), 6.90 (A,  $\text{AB}_q$ , 4H,  $J = 8.1$  Hz, core), 7.36 (B,  $\text{AB}_q$ , 4H,  $J = 8.1$  Hz, core) 7.45 and 7.99 ( $\text{AB}_q$ , 64 H,  $J = 8.0$  Hz, PhH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta(\text{ppm})$ : 52.34, 69.54, 69.99, 101.73, 106.61, 127.15, 129.87, 130.05, 139.58, 142.02, 160.01, 166.96.

*Synthesis of  $\{(\text{HO}_2\text{C})_8\text{-[G-3]}\}_2\text{-[C]}$  (11)*

To a solution of  $\{(\text{MeO}_2\text{C})_8\text{-[G-3]}\}_2\text{-[C]}$  **10** (0.51 g, 0.12 mmol) in 14 ml of tetrahydrofuran was added potassium hydroxide (2.00 g, 36 mmol) dissolved in 3 ml of water. Methanol (6 ml) was added to this two-phase system to give a homogeneous solution. The solution was heated at reflux for 6 h during which time a precipitate formed. The reaction mixture was evaporated to

dryness and the residue was redissolved in water and the mixture was heated at reflux for 12 h. After cooling to room temperature, the reaction mixture was added dropwise to stirred mixture of water (300 ml) and glacial acetic acid (10 ml). The precipitate was filtered off and dried to give **11** as a brown solid. 0.44 g (90%).

$^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ )  $\delta(\text{ppm})$ : 4.99 and 5.14 (s, 60H,  $\text{OCH}_2$ ), 6.51-6.70 (m, 42H, ArH), 6.80 (A,  $\text{AB}_q$ , 4H,  $J = 8.4$  Hz, core), 7.38 (B,  $\text{AB}_q$ , 4H,  $J = 8.4$  Hz, core) 7.51 and 7.94 ( $\text{AB}_q$ , 64 H,  $J = 8.0$  Hz, PhH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta(\text{ppm})$ : 68.77, 69.16, 101.20, 106.70, 115.18, 115.70, 127.41, 129.55, 130.59, 139.58, 141.78, 159.454, 167.29.

MS FAB:  $m/z$ : 4038.56  $[\text{M-H}]^+$ , 2112.39  $[\text{M-H-C}_{113}\text{H}_{91}\text{O}_{30}]^+$ , 1944.47  $[\text{M-H-C}_{125}\text{H}_{99}\text{O}_{31}]$ .

### Catalysis

Hydroformylation experiments were carried out in an autoclave with magnetic stirring. The catalytic solution was kept in a Teflon vessel. The inside of the cap of the autoclave was also Teflon-covered to prevent the solution from coming into direct contact with the stainless steel. An electric heating mantle kept the temperature constant.

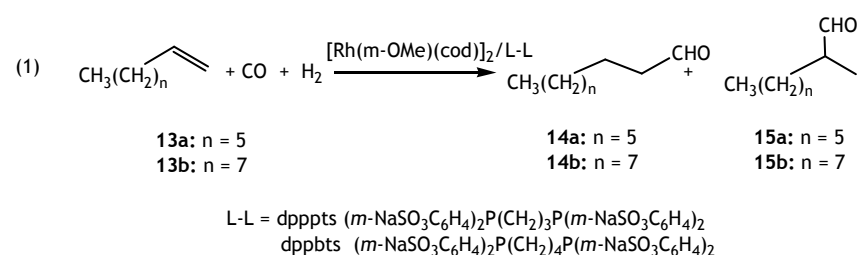
*Standard hydroformylation experiment.* The complex  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2$  (0.05 mmol) and the ligand (0.12 mmol) in water (6 ml) or water/methanol (3ml/3ml) were stirred for 1h at room temperature. NaOH (0.25 M) was then added to adjust the pH to the desired value. The surfactant in the corresponding concentration and the substrate (15 mmol) were 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 reaction mixture was extracted with dichloromethane (3 × 5 mL). In some cases using the anionic surfactant SDS, the final two phases system formed emulsions that were eliminated by addition of sodium chloride. The organic phase was dried over magnesium sulfate and analysed by GC. The products were identified by GC-mass spectrometry.

**Recycling experiments.** In the case of the recycling experiments, the separation was performed under nitrogen. The pH of the aqueous solution was readjusted to the desired value. Fresh substrate was added and the mixture was introduced again into the autoclave following the standard procedure.

### 3.3. Results and Discussion

We studied the hydroformylation of 1-octene (**13a**) and 1-decene (**13b**) to obtain the corresponding linear (**14**) and branched aldehydes (**15**) (equation 1) in aqueous systems. We prepared the catalyst precursors *in situ* by adding the sulfonated diphosphines dppbts (dppbts: tetrasulfonated 1,4-bis(diphenylphosphinobutane) (**16**) or dpppts (dpppts: tetrasulfonated 1,3-bis(diphenylphosphinopropane) (**17**) to the rhodium complex  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2$ .





We adjusted the initial pH of the aqueous phase to 11 because in the literature, activity was reported to be higher in basic medium than in neutral medium in the hydroformylation of 1-octene catalysed by  $[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2/\text{TPPTS}$  [33]. At the end of the reaction generally the pH decreased. In this study we chose an anionic surfactant, sodium dodecyl sulfate (SDS), and a cationic surfactant, cetyltrimethylammonium hydrogensulfate ( $\text{CTAHSO}_4$ ). The c.m.c values for these surfactants in water at 25°C are  $8 \cdot 10^{-3}$  M (SDS) and  $9.2 \cdot 10^{-4}$  M ( $\text{CTAHSO}_4$ ), respectively. To test how the concentration of the surfactants affect the conversion, we used three concentrations of surfactants ( $C_1 = 6.3 \cdot 10^{-3}$  M,  $C_2 = 1.8 \cdot 10^{-2}$  M, and  $C_3 = 3.0 \cdot 10^{-2}$  M). We also test the effect of a dendritic molecule as a surfactant, the polyether dendrimer **11** (scheme 2) ( $C_4 = 8 \cdot 10^{-4}$  M) insoluble in water was added to the catalytic solution and the pH was adjusted to 11 with a NaOH (0.25 M) solution in order to form the dendritic salt **12** (Figure 1).

#### *Synthesis of dendrimer 12*

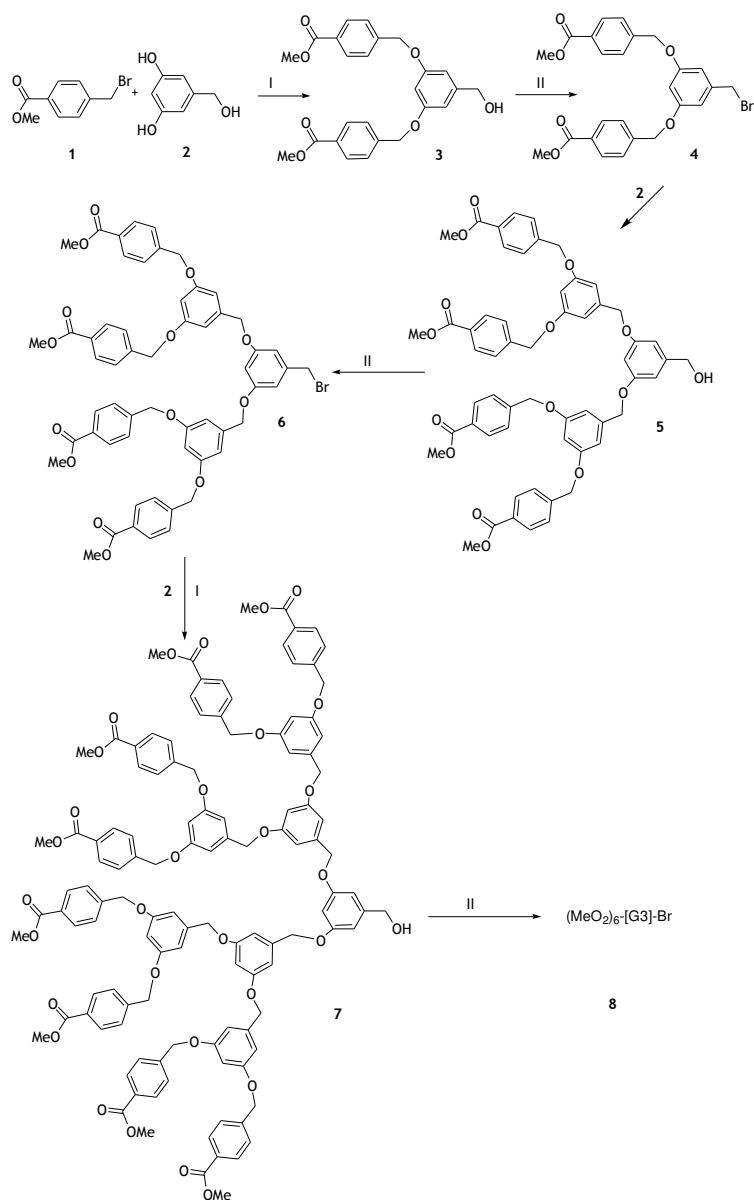
The procedure described by Fréchet et al. (Schemes 1 and 2) [18] was used to prepare dendrimer **12**. To obtain a “*unimolecular micelle*” using a convergent growth synthesis, the starting material, which will become the chain ends, must contain potentially hydrophilic functional groups. The monomer used was the 3,5-dihydroxybenzyl alcohol (**2**). The growth process basically consists of two steps: activation by bromination and coupling by alkylation (Scheme 1 and 2).

The chain ends of the final macromolecule had to be carboxylate groups. However, they could not be present in the starting material because they are unstable in the intermediate alkylation and bromination steps. Therefore, the

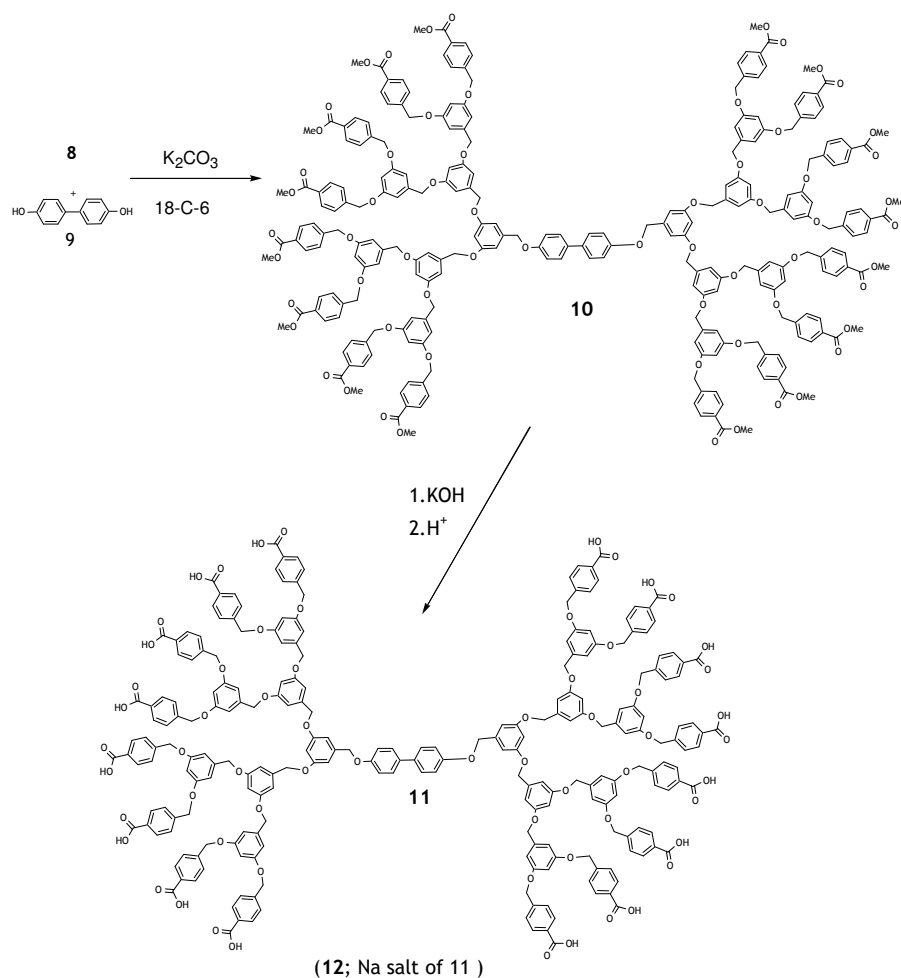
carboxylate group had to be protected with methyl esters. The starting material chosen for the synthesis was methyl *p*-bromomethylbenzoate (**1**). Two molecules of **1**, which will become the chain ends, coupled readily with the monomer 3,5-dihydroxybenzyl alcohol (**2**) in the presence of potassium carbonate and 18-crown-6 in acetone at reflux. These gave the first generation alcohol  $(\text{MeO}_2\text{C})_2\text{-[G1]-Br}$  (**3**) in 81% yield. The activation of **3** with carbontetrabromide/triphenylphosphine proceeded smoothly to give  $(\text{MeO}_2\text{C})_2\text{-[G1]-Br}$  (**4**) in 80% yield. The reaction of 2.05 equiv. of **4** with **2**, in the same conditions as those described above, gave the next generation alcohol  $(\text{MeO}_2\text{C})_4\text{-[G2]-OH}$  (**5**) in 74% yield. The bromination of **5** with  $\text{CBr}_4/\text{PPh}_3$  gave  $(\text{MeO}_2\text{C})_4\text{-[G2]-Br}$  (**6**) in 71% yield. The third generation alcohol  $(\text{MeO}_2\text{C})_8\text{-[G3]-OH}$  (**7**) was accomplished in 94% yield. The activation of **7** with  $\text{CBr}_4/\text{PPh}_3$  gave  $(\text{MeO}_2\text{C})_8\text{-[G3]-Br}$  (**8**) in 43% yield. The yield observed in this step is low because the reactivity of the alcohol decreases increasing the generation number. Finally, the coupling of **8** with the bifunctional core 4,4'-dihydroxyphenyl (**9**) (Scheme 2) in the same conditions as the alkylation steps gave the polyether  $(\text{MeO}_2\text{C})_{16}\text{-[G3]}_2\text{-C}$  (**10**) in 89% yield. The methylester groups were deprotected by alkaline hydrolysis. To overcome the problems of the solubility of **10** in water and potassium hydroxide in organic solvents the reaction was carried out in a mixture of tetrahydrofuran/water/methanol. The acidification of this reaction mixture gave  $(\text{HO}_2\text{C})_8\text{-[G3]}_2\text{-OH}$  (**11**) in 90% yield and the complete desprotection of the methylester groups was confirmed by  $^1\text{H}$  NMR. The polyacid **11** is insoluble in water and, when it was titrated with sodium hydroxide, it gave the sodium salt **12**.

The dendritic species were characterised with  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The characteristic resonances, which made it possible to identify the dendritic species, are the ones due to terminal phenyl ring, which is *p*-substituted with

methylesters, that gave an AB quartet between 7.40 and 8.00 ppm, and the resonance of the methylesters groups that appears around 3.80 ppm. The resonance corresponding to the aromatic intern protons appears between 6.70 - 6.63 ppm while all benzylic protons resonate between 4.91- 5.01 ppm, except the protons corresponding to the group CH<sub>2</sub>OH or CH<sub>2</sub>Br, depending on the dendritic specie, which appear as a singlet between 4.3 - 4.6 ppm. By integrating and comparing the signals, the generation number and the structure were confirmed.



Scheme 1. Reagents I:  $\text{K}_2\text{CO}_3$ , 18-crown-6, II:  $\text{CBr}_4$ ,  $\text{PPh}_3$ . Reaction scheme for preparation of dendritic fragments



Scheme 2. Reaction scheme for preparation of carboxy-terminated dendritic macromolecule  $\{(\text{HO}_2\text{C})_8\text{-[G-3]}\}_2\text{-[C]}$

#### Hydroformylation of 1-octene in aqueous systems

Table 1 shows the results of 1-octene hydroformylation in water using  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2/\text{dppbts}$  as the precursor (entries 1-7). For comparison purposes, the results without surfactant are also given. In the conditions we studied, the

products formed were the isomeric aldehydes *n*-nonanal and *iso*-nonanal, and the isomerization products 2-*trans*-octene, 2-*cis*-octene, and 3-*trans*-octene. No hydrogenation product was observed. Table 1 also shows, therefore, the selectivity in isomerization products.

Table 1. Hydroformylation of 1-octene (**13a**) in aqueous systems using [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/L (L = dppbts (**16**) and dpppts (**17**)) as the catalyst precursors <sup>a</sup>

Entry	Ligand	[Surfactant] <sup>b</sup>	P (bar) H <sub>2</sub> /CO	T (°C)	Conv(%) <sup>c</sup>	S <sub>ald</sub> (%) <sup>d</sup>	n/i	S <sub>isom</sub> (%) <sup>e</sup>
1	16	-	7/7	80	5	40	72/28	55
2	16	SDS (C <sub>2</sub> )	7/7	80	8	38	72/28	50
3	16	SDS (C <sub>3</sub> )	7/7	80	98	31	65/35	62
4	16	SDS (C <sub>3</sub> )	7/7	65	5	55	72/28	45
5	16	CTAHSO <sub>4</sub> (C <sub>1</sub> )	7/7	80	24	96	79/21	1
6	16	CTAHSO <sub>4</sub> (C <sub>3</sub> )	7/7	80	95	79	75/25	12
7	16	12 (C <sub>4</sub> )	7/7	80	4	24	66/34	67
8	17	-	7/7	80	5	80	75/25	< 1
9	17	SDS (C <sub>2</sub> )	7/7	80	33	25	73/27	73
10	17	SDS (C <sub>3</sub> )	7/7	80	66	12	75/25	79
11	17	SDS (C <sub>2</sub> )	25/25	80	30	60	69/31	30
12	17	SDS (C <sub>2</sub> )	17/33	80	13	62	71/29	31
13	17	CTAHSO <sub>4</sub> (C <sub>1</sub> )	7/7	80	17	82	58/42	12

<sup>a</sup> Reaction conditions: substrate = 15 mmol, [Rh( $\mu$ -OMe)(cod)]<sub>2</sub> =  $5 \times 10^{-3}$  M, substrate/precursor = 500, solvent = H<sub>2</sub>O (6ml), P/Rh ratio = 4 (L/[Rh( $\mu$ -OMe)(cod)]<sub>2</sub> molar ratio = 4), time = 24 h, pH 11.

<sup>b</sup> Concentration: C<sub>1</sub> =  $6.3 \times 10^{-3}$  M, C<sub>2</sub> =  $1.8 \times 10^{-2}$  M, C<sub>3</sub> =  $3.0 \times 10^{-2}$  M, C<sub>4</sub> =  $8.0 \times 10^{-4}$  M.

<sup>c</sup> Aldehyde conversion measured by gas chromatography.

<sup>d</sup> Selectivity in aldehydes defined as percent aldehyde conversion/percent total conversion.

<sup>e</sup> Selectivity in isomerised products defined as percent isomerization products/percent total conversion.

<sup>f</sup> Loss of catalyst in the organic layer

The aldehyde conversion and selectivity in aldehydes of the catalyst  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2/\text{dppbts}$  were very low both without any additive (Table 1, entry 1) and with the addition of SDS at low concentration (Table 1, entry 2). Adding anionic surfactant SDS at a higher concentration (Table 1, entry 3) increased the activity (complete conversion was observed at the same reaction time). However, the selectivity was low and similar to the one obtained without additive. Regioselectivity was the same in water as at a low concentration of SDS (Table 1, entry 2), but a higher concentration of surfactant increased the amount of *iso*-nonanal.

To prevent the formation of isomerization products by  $\beta$ -elimination, we performed one experiment at 65 °C. Decreasing the temperature of the reaction effectively enhanced the selectivity in aldehydes; unfortunately the conversion was very low (Table 1, entry 4).

Using dendrimer 12 (Table, entry 7) as a surfactant low conversion was observed, similar to the one obtained with the system without additive (Table 1, entry 7 vs. entry 1). Unfortunately a decrease in aldehydes selectivity and in the regioselectivity was observed obtaining mainly isomers as reaction products.

Adding cationic surfactant  $\text{CTAHSO}_4$  increased the conversion and selectivity in aldehydes (Table 1, entries 5 and 6). This could be due to two factors: the substrate is efficiently dissolved in the micellar system, or the cationic micelle has a positive charged surface that attracts the catalytic rhodium species to the micelle surface through the sulfonated groups, which are negatively charged [12]. This promotes the contact between the substrate and catalyst. However, high concentrations of surfactant can lead to a loss of

catalyst in the organic phase. This can be easily observed because the organic phase became coloured.

In fact, when we used the highest concentration of cationic surfactant, which was above c.m.c. (Table 1, entry 6), there was a loss of catalyst in the organic phase. At concentrations above c.m.c., there is an equilibrium between the free surfactant and the micellar species. Electrostatic interaction between anionic species of the rhodium complex and cationic-surfactant-free species may have been responsible for the loss of catalyst in the organic phase. At a lower concentration of surfactant (Table 1, entry 5), which is closer to c.m.c, this phenomenon did not occur and there was a slight increase in conversion and a higher selectivity. The regioselectivity was better than that of the system without additive: with cationic surfactant, regioselectivity in nonanal was around 80 %.

Table 1 shows the results when the precursor  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2/\text{dpppts}$  was used (entries 8-13). If we compare the different systems, we can see that the Rh/dpppts system was more selective in aldehydes than the Rh/dppbts system when no additive was added (Table 1, entry 8 vs. entry 1).

Adding SDS to the Rh/dpppts system had the same effect as in the Rh/dppbts system. Conversion increased but selectivity decreased when we raised the concentration of the surfactant. To improve the selectivity, we increased the pressure to 50 bar (Table 1, entries 11 and 12). When the hydrogen:carbon monoxide ratio was 1:1, selectivity improved but conversion remained the same (Table 1, entry 11 vs. entry 9). On the other hand, when the  $\text{H}_2:\text{CO}$  ratio was changed to 1:2, there was a drop in conversion (Table 1, entry 12). The regioselectivities obtained in the presence of SDS were similar to those obtained without additive.



Adding CTAHSO<sub>4</sub> had the same effect as the system that used dppbts as the ligand (Table 1, entry 13) i.e. both the activity and the selectivity increased. Note that regioselectivity in nonanal was lower than that of the system that used dppbts as the ligand (Table 1, entry 13 vs. entry 5).

If we compare the two systems [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dppbts and [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dpppts, we can conclude that the system with dpppts is more selective in aldehydes with no additive. Adding SDS enhanced the total conversion, but not the selectivity in aldehydes. On the other hand, adding CTAHSO<sub>4</sub> enhanced both total conversion and selectivity but conversion was still low. Finally, regioselectivities in nonanal were higher when dppbts was used as the ligand and CTAHSO<sub>4</sub> was used as the surfactant.

#### *Hydroformylation of 1-decene in aqueous systems*

Table 2 shows the results of the hydroformylation of 1-decene. Interestingly, when [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dppbts was used as the precursor (Table 2, entries 14-19), the conversion observed in the hydroformylation of 1-decene was higher than that of 1-octene in water (Table 1, entry 1). However, the selectivity in aldehydes was low, and the main products obtained were isomerization products.

Adding SDS to the system [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dppbts (Table 2, entries 15 and 16, vs. Table 1, entries 2 and 3) has the same effect than in the case of 1-octene. The conversion increased with increasing amount of surfactant, but the selectivity in aldehydes and the regioselectivity in nonanal decreased.

Table 2

Hydroformylation of 1-decene (**13b**) in aqueous systems using  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2/\text{L}$  (L = dppbts (**16**) and dpppts (**17**)) as the catalyst precursors<sup>a</sup>

Entry	Run	Ligand	[Surfactant] <sup>b</sup>	Conv(%) <sup>c</sup>	$S_{\text{ald}}$ (%) <sup>d</sup>	n/i	$S_{\text{isom}}$ (%) <sup>e</sup>
14	1	16	-	15	20	73/27	80
15	1	16	SDS ( $C_2$ )	48	31	75/25	69
16	1	16	SDS ( $C_3$ )	88	25	65/35	75
17	1	16	CTAHSO <sub>4</sub> ( $C_1$ )	63	97	78/22	3
18	2	16	CTAHSO <sub>4</sub> ( $C_1$ )	72	96	69/31	4
19	1	16	-	-	-	-	-
20	1	17	SDS ( $C_2$ )	-	-	-	-
21	1	17	SDS ( $C_3$ )	68	21	74/26	76
22	1	17	CTAHSO <sub>4</sub> ( $C_1$ )	3	86	55/45	13

<sup>a</sup> Reaction conditions: substrate = 15 mmol,  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2 = 5 \times 10^{-3}$  M, substrate/precursor = 500, solvent = H<sub>2</sub>O (6ml), P/Rh ratio = 4,  $P = 14$  atm, H<sub>2</sub>/CO = 7/7,  $T = 80^\circ \text{C}$ , time = 24 h, pH 11.

<sup>b</sup> Concentration:  $C_1 = 6.3 \times 10^{-3}$  M,  $C_2 = 1.8 \times 10^{-2}$  M,  $C_3 = 3.0 \times 10^{-2}$  M.

<sup>c</sup> Aldehyde conversion measured by gas chromatography.

<sup>d</sup> Selectivity in aldehydes.

<sup>e</sup> Selectivity in isomerised products.

Adding CTAHSO<sub>4</sub> (Table 2, entry 17) improves both the conversion and the selectivity; it is to be noted that they are even higher than those obtained in the case of 1-octene. A conversion of 63 % with selectivity in aldehydes of up to 97 % was achieved. Additionally, we were able to recycle the system, the conversion and selectivity in aldehydes being maintained (Table 2, entry 18).

When the system Rh-dpppts was used no conversion was detected. Adding SDS resulted in a high increase of the conversion in the highest concentration

studied. However the selectivity was low and the main products were isomerized products (Table 2, entry 21).

Adding CTAHSO<sub>4</sub> improved the activity only very slightly (Table 2, entry 22). If we compare this result with those from the same system in the hydroformylation of 1-octene (Table 1, entry 13, vs. Table 2, entry 22) we can see that the regioselectivity in nonanal was very low when dpppts was used as the ligand.

#### *Hydroformylation in aqueous-methanolic systems*

To compare the strategies for improving the mass transfer between the two phases, we also studied the effect of a co-solvent such as methanol. When methanol was used as the co-solvent, [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dppbts or [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dpppts as the catalyst precursor, and 1-octene as the substrate (Table 3, entries 22 and 23), activities were higher than those obtained in water (Table 1, entries 1 and 7), while the regioselectivities in nonanal were lower. When Rh-dppbts was used as the ligand (Table 3, entry 22), selectivity in aldehydes was 90 %. When 1-octene was used as the substrate, the results for both total conversion and selectivity in aldehydes were highest when methanol was used as the co-solvent. However, regioselectivity in nonanal was low with this system.

Table 3

Hydroformylation of 1-octene (**13a**) and 1-decene (**13b**) in aqueous-methanolic systems using  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2/\text{L}$  (L = dppbts (**16**) and dpppts (**17**) as catalyst precursors.<sup>a</sup>

Entry	Ligands	Substrate	Conversion (%) <sup>b</sup>	$S_{\text{ald}}$ (%) <sup>c</sup>	n/iso	$S_{\text{isom}}$ <sup>d</sup>
23	16	13a	60	90	58/42	3
24	17	13a	67	57	68/32	42
25	16	13b	14	79	74/26	11
26	17	13b	60	23	71/29	60

<sup>a</sup> Reaction conditions: substrate = 15 mmol,  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2 = 5 \cdot 10^{-3}$  M, substrate/precursor = 500, solvent =  $\text{H}_2\text{O}/\text{MeOH}$  (3/3 mL), P/Rh ratio = 4, time = 24 h, pH = 11, T = 80 °C, pressure = 14 atm ( $\text{CO}/\text{H}_2 = 1/1$ )

<sup>b</sup> Aldehyde conversion measured by gas chromatography.

<sup>c</sup> Selectivity in aldehydes.

In the hydroformylation of 1-decene, adding methanol considerably increased conversion when the Rh-dpppts system was used (Table 3, entry 26). When dppbts was used as the ligand (Table 3, entry 25), activity did not improve and only selectivity in aldehydes improved. Regioselectivities with both ligands dppbts and dpppts were similar to those obtained when water was the only solvent.

### **3.4. Conclusions**

In the Rh-sulphonated diphosphine hydroformylation of 1-octene and 1-decene, selectivities and total conversions are modified when surfactants are added or a co-solvent is used.

In the hydroformylation of 1-octene, the results for conversion and selectivity in aldehydes were best when methanol was the co-solvent and dppbts was the ligand, but regioselectivities in nonanal were lower. Adding surfactants increased the conversion with the systems Rh-dpppts and Rh-dppbts. However, selectivity in aldehydes did not improve when SDS was added. The addition of dendrimer **12** did not improve the results, obtaining low conversion and low aldehydes selectivity. Adding CTAHSO<sub>4</sub> increased both the total conversion and the selectivity, and there was a slight improvement in regioselectivity in nonanal. However, a high concentration of surfactant led to a loss of the catalyst in the organic phase.

For 1-decene hydroformylation, the results were best when CTAHSO<sub>4</sub> was used as the surfactant and dppbts was used as the ligand: conversion was 63 % and selectivity in aldehydes was 97 %. Moreover, we could recycle the system maintaining the same activity and selectivity in aldehydes. Adding SDS increased activity, but unfortunately selectivity in aldehydes did not improve. When methanol was used as the co-solvent with the system Rh-dppbts, selectivity increased but the activity was similar to the activity in water.

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

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*New P-donor ligands  $\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$  ( $n = 3, 2, 1$ ) containing branched alkyl chains were synthesised and their coordination to Rh(I) and Pd(II) complexes was studied. The X-ray structure of  $[\text{Rh}\{\text{PPh}_2(\text{OC}_9\text{H}_{19})\}_4]\text{PF}_6$  was determined. The reaction of the  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$  systems with  $\text{CO}/\text{H}_2$  at 5 atm and 80 °C in methyltetrahydrofuran led to the formation of  $[\text{RhH}(\text{CO})\{\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n\}_3]$  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  $\text{scCO}_2$ , they are active. The activities were similar in toluene than in  $\text{scCO}_2$  but the selectivities in aldehydes in the case of the phosphonite derivative were higher in the supercritical medium than in toluene.*



#### 4.1 Introduction

In the last few years, supercritical carbon dioxide (scCO<sub>2</sub>) 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 properties, especially in reactions in which the reactants are gases. ScCO<sub>2</sub> 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 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 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<sub>2</sub> 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<sub>2</sub>(OAc)<sub>4</sub>]/PEt<sub>3</sub> systems, which are soluble in scCO<sub>2</sub>, in the hydroformylation of 1-hexene, but the n/i ratios were modest (2.1-2.6) [6]. Ligands containing alkyl 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.

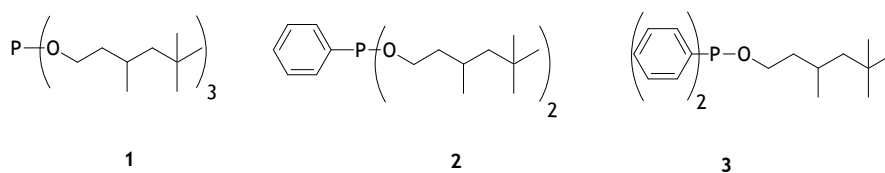
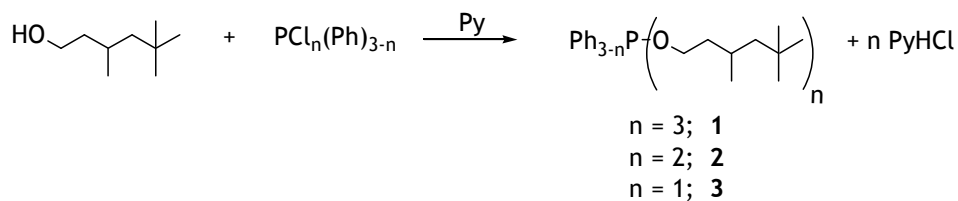


Figure 1. P-donor ligands

## 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  $^1H$  NMR spectra show the methylenic signals ( $-OCH_2-$ ) at  $\delta$  3.8 ppm, the methylenic and methynic signals between  $\delta$  1.6-1.0, and the methylic 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 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].



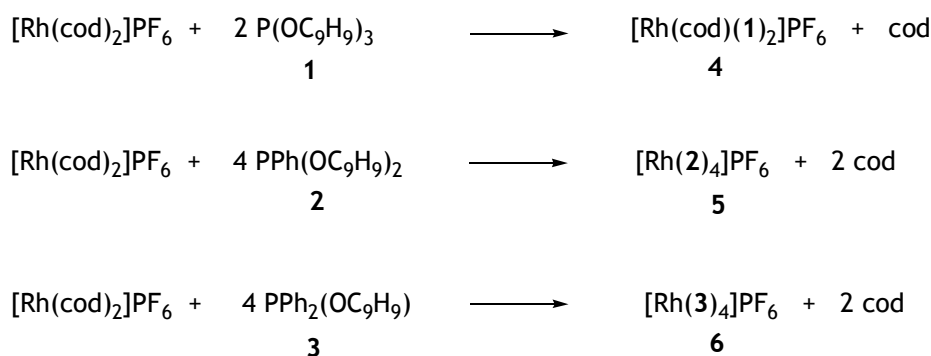
Scheme 1. Synthesis of 1-3

#### 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  $[\text{Rh}(\text{cod})_2]\text{PF}_6$  (cod =  $\text{C}_8\text{H}_{12}$ , 1,5-cyclooctadiene) as a model for cationic complexes (scheme 2). The reaction of the ligands **1-3** with  $[\text{Rh}(\text{cod})_2]\text{PF}_6$ , 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  $[\text{Rh}(\text{cod})(\mathbf{1})_2]\text{PF}_6$  (**4**) was obtained as a relatively air stable yellow oil in high yield. Several attempts to solidify the complex were unsuccessful. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR showed a doublet at 116.1 ppm ( $J_{\text{PRh}} = 244.0$  Hz), which corresponded to the coordinated phosphite ligand and the characteristic septuplet of the counteranion  $\text{PF}_6^-$  at -143.2 ppm ( $J_{\text{PF}} = 711.5$  Hz). The presence of coordinated cyclooctadiene was confirmed by  $^1\text{H}$  NMR with the signals at  $\delta$  4.05 ppm (HC=CH) and 2.57 and 2.36 ppm ( $-\text{CH}_2-$ ). The  $^1\text{H}$  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  $[\text{Rh}(\text{cod})(\mathbf{1})_2]^+$  fragment.

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

165.9 Hz), and 138.5 ppm ( $J_{PRh} = 170.8$  Hz) and the  $^1H$  NMR spectrum show signals corresponding to coordinated cyclooctadiene (at  $\delta$  4.0 and 2.5-2.7 ppm). When the P:Rh molar ratio was 4:1, the  $^{31}P\{-^1H\}$  NMR spectrum showed only the signal at  $\delta$  146.0 ppm. There was no evidence of coordinated cod in the  $^1H$  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 ( $\delta = 148$  ppm,  $J_{PRh} = 170$  Hz) [**14**].

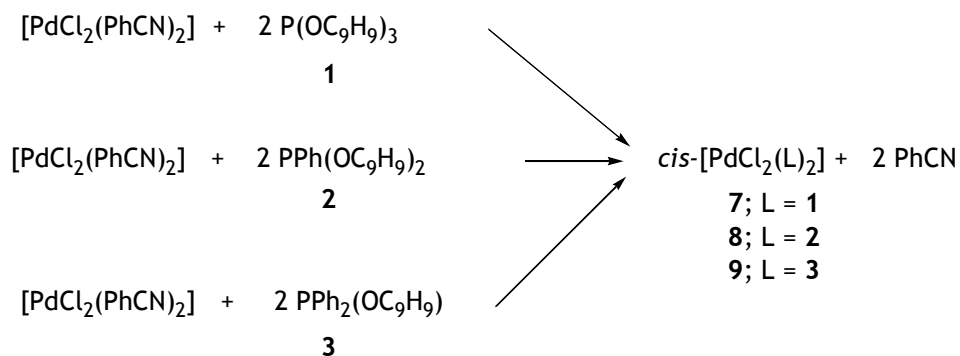


Scheme 2. Synthesis of 4-6.

In the reaction of  $[Rh(cod)_2]PF_6$  with ligand **3**, only one doublet was observed in the  $^{31}P\{-^1H\}$  NMR spectrum at P:Rh 2:1 and P:Rh 4:1 at  $\delta$  132.3 ( $J_{PRh} = 162.2$  Hz), which agrees with the data reported for  $[Rh\{PPh_2(OR)\}_4]^+$  (  $R = Me$ :  $\delta$  132.2 ppm,  $J_{PRh} = 159$  Hz;  $R = Et$ :  $\delta$  130.5 ppm,  $J_{PRh} = 156$  Hz ) [**15**], and a septuplet signal of  $PF_6^-$  at  $\delta$  -143.1 ppm ( $J_{FP} = 712.6$  Hz). In the  $^1H$  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  $[Rh(\mathbf{3})_4]PF_6$  (**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  $[PdCl_2(\mathbf{1-3})_2]$  (**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  $^1H$  NMR spectra of **7-9** showed the signals corresponding to the coordinated ligands. The  $^{31}P\{-^1H\}$  NMR spectra showed only one singlet signals at  $\delta$  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  $\Delta$  ( $\delta_{coord} - \delta_{free\ ligand}$ ) for similar palladium(II) complexes is indicative of the stereochemistry of these complexes. The lowest (negative) values of  $\Delta$  are related with *cis*-isomers containing ligands with Tolman angles  $\Theta$  less than  $140^\circ$  and high values (positive) of  $\Delta$  are related with *trans*-isomers containing ligands with Tolman angles  $\Theta$  higher than  $140^\circ$  [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 were formed in these complexes. In the case of complex **9** the value of  $\Delta$  was -2.3 ppm. Taking in account that the estimated value of the Tolman's angle  $\Theta$  from the X-ray structure is  $128^\circ$ , 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)°) due to intramolecular ligand repulsion. Similar distortion, but to a greater extent, has been reported for  $[\text{Rh}(\text{PMe}_3)_4]^+$  (*trans* P-Rh-P angles 148.29° and 151.46°) [18]. The C-P-Rh angles (115.75(8) and 118.97(8)°) deviated from the ideal tetrahedral value, as observed in coordinated P-donor ligands. The estimated Tolman angle  $\Theta$  for **3**, calculated in accordance with the reported method [19], was 128°. 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  $\text{PF}_6^-$  anions



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

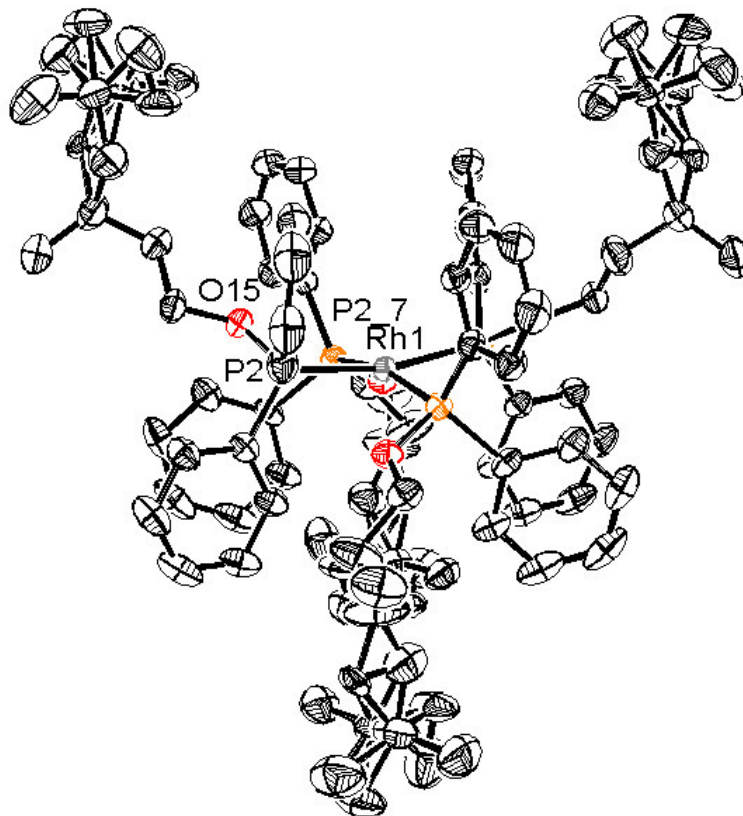


Figure 2. ORTEP drawing of complex 6.  $PF_6^-$  and hydrogen atoms are omitted for clarity.

Table 1  
Selected bond lengths (Å) and angles (°) of complex **6**.<sup>a</sup>

<i>Bond lengths</i>		<i>Bond angles</i>	
Rh1-P2	2.2848(6)	P2 <sup>i</sup> -Rh1-P2 <sup>iii</sup>	90.776(3)
P2-C3	1.8222(25)	P2 <sup>i</sup> -Rh1-P2 <sup>ii</sup>	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)

<sup>a</sup> 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- $d_6$  ( $[Rh] = 2 \cdot 10^{-2}$  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 ( $2-5 \cdot 10^{-3}$  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  $^{31}P\{^1H\}$  spectrum shows a major wide signal at  $\delta$  140 ppm, a small multiplet at  $\delta$  80 ppm along with a singlet at  $\delta$  0 ppm due to decomposed ligand (Figure 3a). The wide signal at  $\delta$  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  $^{31}P\{^1H\}$  NMR spectrum at  $\delta$  158.9 ppm ( $J = 212.3$  Hz) and  $\delta$  157.9 ppm ( $J = 207.8$  Hz). Two new signals appeared also in the hydride region of the  $^1H$  NMR spectrum at  $\delta$  -10.7 ppm (quintet,  $J = 7.8$  Hz) and  $\delta$  -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 1 h at 80 °C the doublet signal in the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum at  $\delta$  157.9 ppm, the hydride at  $\delta$  -11.8 ppm and the multiplet signal at  $\delta$  80 ppm disappeared, and new signals were observed:  $\delta$  (ppm) 154.6 (d,  $J_{\text{RhP}} = 194.6$  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  $\delta$  157.9 ppm and the hydride doublet  $\delta$  -11.8 ppm to the species  $[\text{RhH}(\text{1})_4]$  (**10**) by comparison with published data for the analogous species  $[\text{RhH}\{\text{P}(\text{OPh})_3\}_4]$  ( $\delta_{\text{P}}$ : 129.7,  $J_{\text{RhP}} = 232.8$  Hz;  $\delta_{\text{H}}(\text{hydride})$ : - 10.6  $J_{\text{RhH}} = 44$   $J_{\text{PH}} = 7$  Hz) [20]. The  $^{31}\text{P}\{-^1\text{H}\}$  major doublet signal at  $\delta$  158.9 ppm together with the hydrido quintet at  $\delta$  -10.7 of the  $^1\text{H}$  NMR was attributed to  $[\text{RhH}(\text{CO})(\text{1})_3]$  (**11**). The reported data for  $[\text{RhH}(\text{CO})\{\text{P}(\text{OPh})_3\}_3]$  ( $\delta_{\text{P}}$ : 141.1,  $J_{\text{RhP}} = 240$  Hz;  $\delta_{\text{H}}(\text{hydride})$ : - 10.9,  $J_{\text{RhH}} = J_{\text{PH}} = 3$  Hz) [20] are in agreement with the values observed for **11**. The minor signal at  $\delta$  154.6 ppm ( $J_{\text{RhP}} = 194.6$  Hz) is attributed to the dicarbonyl species  $[\text{RhH}(\text{CO})_2(\text{1})_2]$  (**12**), whose hydrido signal is not detected in the  $^1\text{H}$  NMR due to the low concentration. The signals at  $\delta$  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  $\delta$  140.8 and 70.2 disappeared and a new doublet at  $\delta$  132.4 ppm which could correspond to a species with only phosphonate ligands (Figure 4). The HPIR spectra of  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{1}$  at 5 atm  $\text{CO}/\text{H}_2$  (1/1) in the  $\nu(\text{CO})$  region initially showed signals at 2049, 2025, 1980 and 2005 and 1960  $\text{cm}^{-1}$  (Figure 5). By comparison with published data for  $[\text{RhH}(\text{CO})\{\text{P}(\text{OPh})_3\}_3]$  ( $\nu(\text{CO}) = 2060\text{m } 2010\text{w } 1960\text{w } \text{cm}^{-1}$ ) [22], the band at 2025  $\text{cm}^{-1}$  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 °C 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 °C.

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

n.d. = not detected

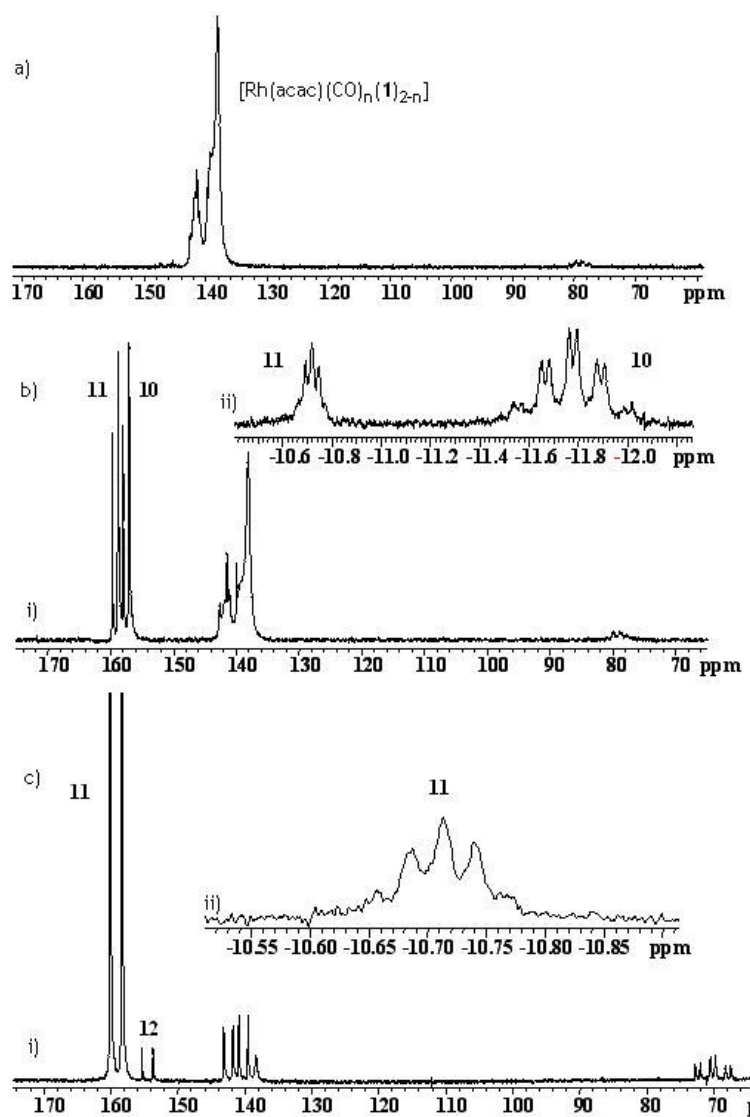


Figure 3. NMR spectra at 20 °C of  $[Rh(acac)(CO)_2]/1$  (P/Rh = 4) in  $toluene-d_6$ : **a)**  $^{31}P\{^1H\}$  under nitrogen; **b)** (i)  $^{31}P\{^1H\}$  NMR under 2.5 bar of  $H_2$ ; (ii) Hydride region of the  $^1H$  NMR; **c)** (i)  $^{31}P\{^1H\}$  NMR under 5 bar of  $CO/H_2$  (1:1); (ii) Hydride region of the  $^1H$  NMR.

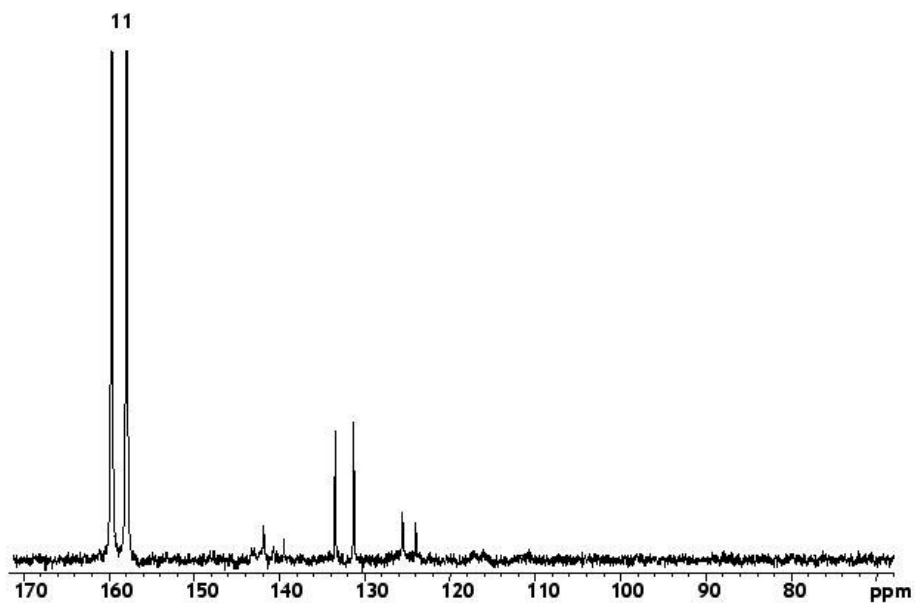


Figure 4.  $^{31}P\{^1H\}$  NMR spectrum at 20 °C of  $[Rh(acac)(CO)_2]/1$  ( $P/Rh = 4$ ) in toluene-  $d_6$  after release the pressure and add water to the system

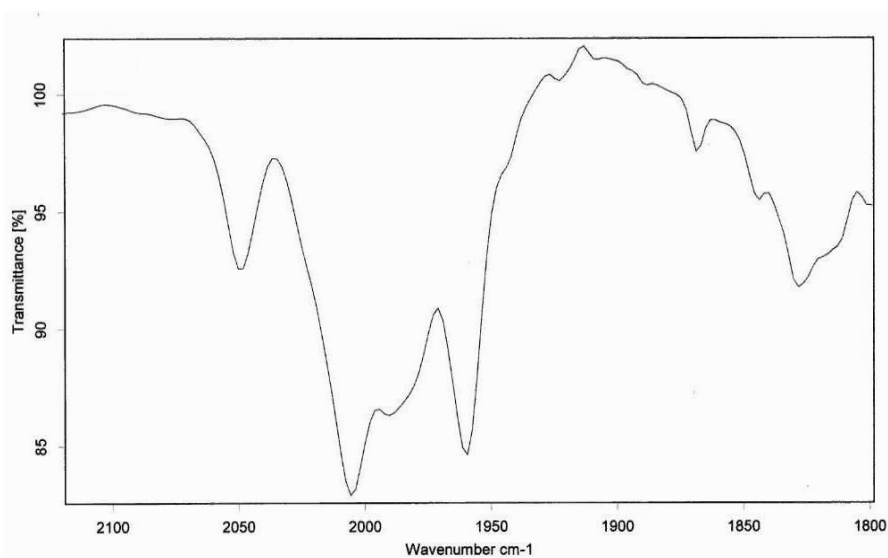


Figure 5. HPIR spectrum of the system  $[Rh(acac)(CO)_2]/1$  ( $P/Rh = 4$ ) at 5 atm  $CO/H_2$  (1/1) in methyltetrahydrofurane after 1h stirring at 80°C.

The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of the  $[\text{Rh}(\text{acac})(\text{CO})_2]/2$  system ( $\text{P/Rh} = 4$ ) in toluene showed broad signals at  $\delta$  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**  $[\text{Rh}(\text{acac})(\text{CO})_n(\text{2})_{(2-n)}]$ . Adding 5 atm of  $\text{CO}/\text{H}_2$  (1/1) to this solution and heating for 1 h at 80 °C, the  $^{31}\text{P}\{-^1\text{H}\}$  NMR at room temperature showed a well-resolved major doublet signal at  $\delta$  169.8 ( $J_{\text{RhP}} = 189.0$  Hz), which correlated with a hydride quintet signal at  $\delta$  -10.0 ( $J_{\text{PH}} = J_{\text{RhH}} = 7.7$  Hz) and was attributed to the species  $[\text{RhH}(\text{CO})(\text{2})_3]$  (**13**) (Figure 6b). At  $\delta$  168.2 there was a minor, partly overlapped, doublet ( $J_{\text{RhP}} = 145.7$  Hz) that was attributed to the dicarbonyl species  $[\text{RhH}(\text{CO})_2(\text{2})_2]$  (**14**), though the hydride signal in the  $^1\text{H}$  NMR was not detected. At  $\delta$  156 ppm there was the remaining signal of the non reacted species  $[\text{Rh}(\text{acac})(\text{CO})_n(\text{2})_{(2-n)}]$ . The slow reaction rate with  $\text{CO}/\text{H}_2$  of similar precursors containing phosphite ligands has been reported [24]. The broad doublet at  $\delta$  144.1 ( $J_{\text{RhP}} = 168.7$  Hz) was resolved at -70 °C and could correspond to dimeric Rh(0) complexes  $[\text{Rh}_2(\text{CO})_6(\text{2})_2]$  or  $[\text{Rh}_2(\text{CO})_4(\text{2})_4]$ , which has been observed for other P-donor rhodium systems [25]. At  $\delta$  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  $\text{cm}^{-1}$  region that were difficult to assign (Figure 7). The band at 2065 could correspond to compound **13** and the ones at 2073 and 2029  $\text{cm}^{-1}$  and 2042 and 1991  $\text{cm}^{-1}$  could correspond to the *ee*- and *ea*-isomers of **14**, respectively. The absorptions around 1800  $\text{cm}^{-1}$  could correspond to the Rh(0) dimeric species.

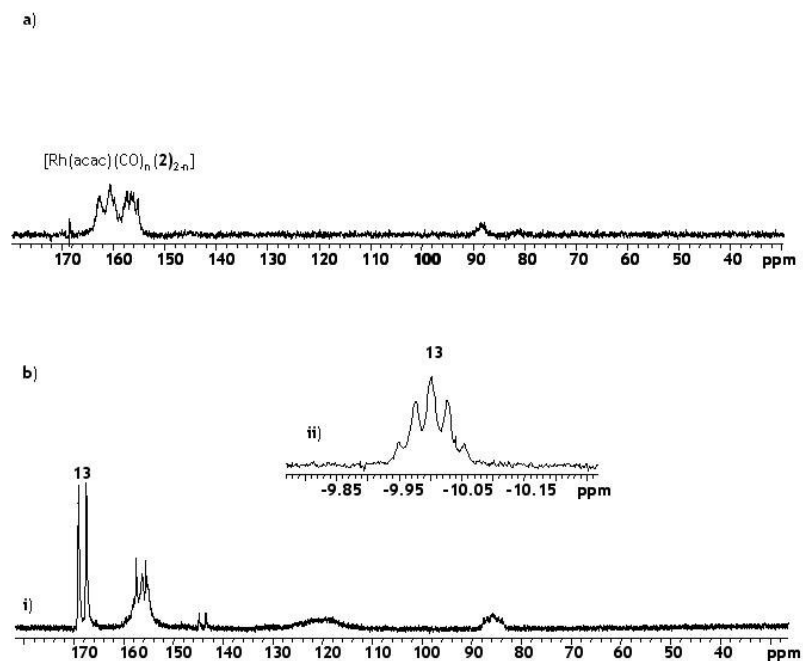


Figure 6. NMR spectra at 20 °C of  $[Rh(acac)(CO)_2]_2$  (P/Rh = 4) in toluene-  $d_6$ : a)  $^{31}P\{^1H\}$  under nitrogen; b) (i)  $^{31}P\{^1H\}$  NMR at 70 °C of  $[Rh(acac)(CO)_2]_2$  under 5 bar of  $CO/H_2$  (1:1); (ii) Hydride region of the  $^1H$  NMR.



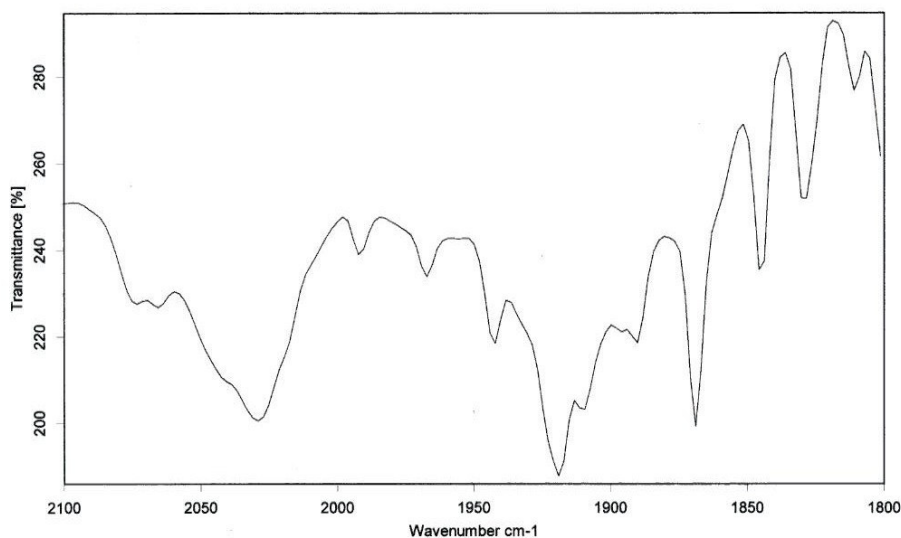


Figure 7. HPIR spectra of the system  $[Rh(acac)(CO)_2]/2$  ( $P/Rh = 4$ ) at 5 atm  $CO/H_2$  (1/1) in methyltetrahydrofuran after 1h stirring at  $80^\circ C$ .

When we added 2 moles of **3** to  $[Rh(acac)(CO)_2]$  in toluene- $d_6$ , the  $^{31}P\{-^1H\}$  spectrum shows a small doublet signal at  $\delta$  133.3 ppm and a wide singlet at  $\delta$  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  $80^\circ C$  the  $^{31}P\{-^1H\}$  NMR spectrum showed five signals at  $\delta$ (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  $^1H$  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  $\delta$  138.1 ppm together with the hydride signal at  $\delta$  -9.4 ppm were attributed to the species  $[RhH(CO)(3)_3]$  (**15**), the minor partially overlapped doublet at  $\delta$  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  $\delta_p$  142 ( $J_{PRh} = 169$  Hz) and

$\delta_H$  -9.4 dq ( $J_{HP} = 13$  Hz,  $J_{HRh} = 3$  Hz) and  $[RhH(CO)_2\{PPh_2(OPh)\}_2]$  show signals at  $\delta_P$  145 ( $J_{PRh} = 165$  Hz) and  $\delta_H$  -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  $[Rh(acac)(CO)_2]/\mathbf{3}$  at 5 atm  $CO/H_2$  (1/1) after 1h at 80 °C 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  $\delta$  -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  $[Rh(acac)(CO)_2]/\mathbf{3}$  at the same conditions initially showed only one band at  $1987\text{ cm}^{-1}$  in the  $2200\text{-}1800\text{ cm}^{-1}$  region. After 1h stirring at 80 °C, five absorptions were detected at 2044, 2025, 2006, 1966,  $1918\text{ cm}^{-1}$  (Figure 9). The band at  $2025\text{ cm}^{-1}$  was assigned to **15**. The absorptions at 2044 and  $1966\text{ cm}^{-1}$  were attributed to isomer **ee-16**, since they were similar to ones reported for the equatorial-equatorial isomer of  $[RhH(CO)_2(PPh_2(OPh))_2]$  ( $2045, 1970\text{ cm}^{-1}$ ) [27]. The ones at 2006 and  $1918\text{ cm}^{-1}$  could correspond to the **ea-15** isomer.

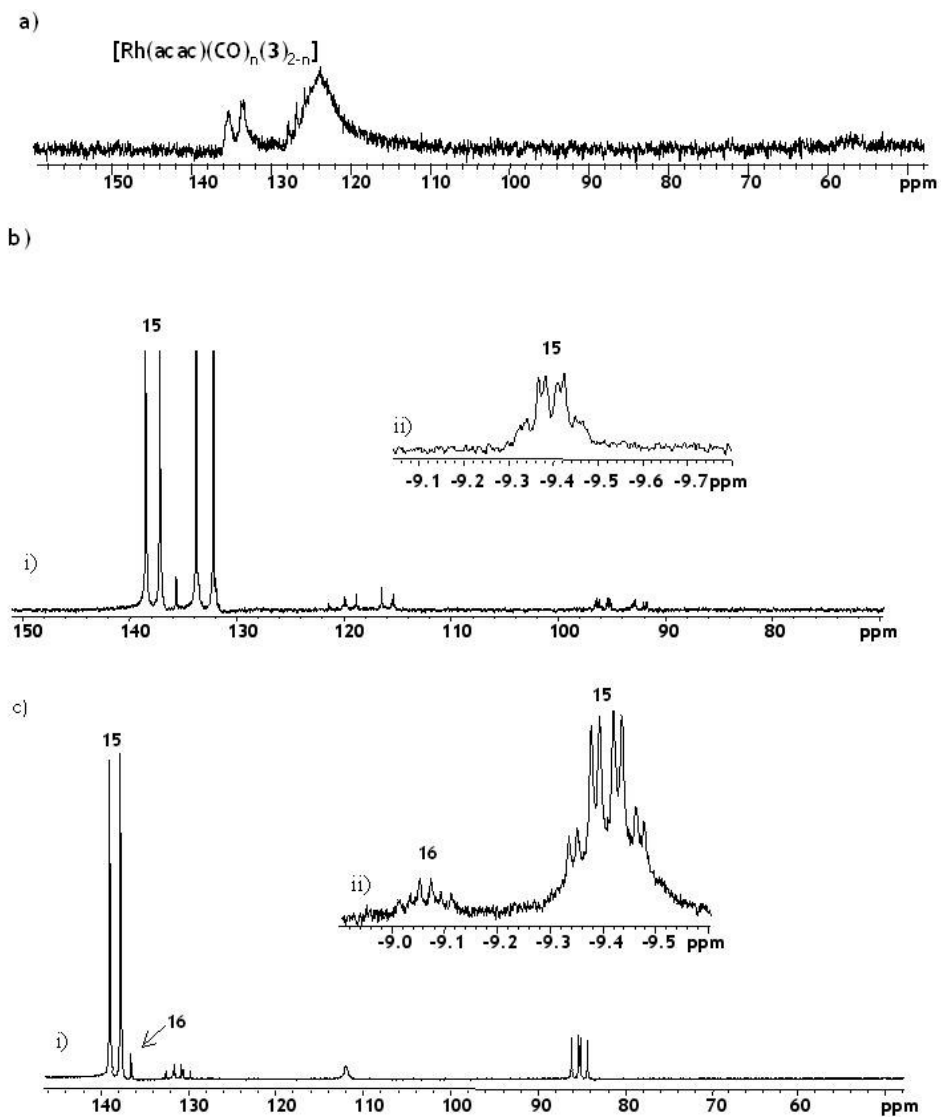


Figure 8. NMR spectra at 20 °C of  $[Rh(acac)(CO)_2]/3$  (P/Rh = 2) in toluene- $d_6$ ; (a)  $^{31}P\{^1H\}$  under nitrogen ; b) (i)  $^{31}P\{^1H\}$  under 2,5 bar of  $H_2$ ; (ii) Hydride region of the  $^1H$  NMR c) (i)  $^{31}P\{^1H\}$  (P/Rh = 4) under 5 bar of  $CO/H_2$  (1:1); (ii) Hydride region of the  $^1H$  NMR.

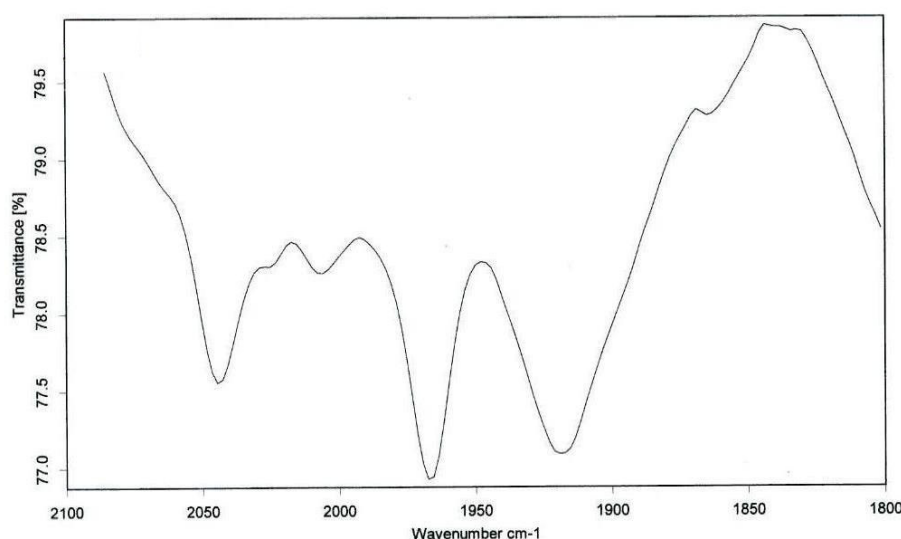
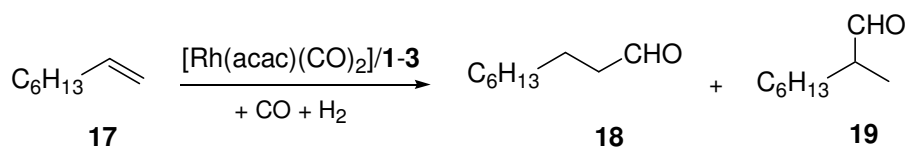


Figure 9. HPIR spectrum of  $[Rh(acac)(CO)_2]/3$  ( $P/Rh = 4$ ) at 5 atm  $CO/H_2$  (1/1) in methyltetrahydrofuran after 1h stirring at 80°C.

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 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  $scCO_2$ .



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 °C in toluene. Then, 1-octene was added, the system was pressurised and again heated to 80°C, 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 °C. 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)<sub>2</sub>]/1-3 catalyst precursors in scCO<sub>2</sub>.<sup>a</sup>

Entry	L	Solvent	L/Rh	T (°C)	P(H <sub>2</sub> ) (bar)	P(CO) (bar)	P <sub>tot</sub> <sup>b</sup> (bar)	Conv <sup>c</sup> (%)	S <sub>a</sub> <sup>d</sup> (%)	18/19 (%)	S <sub>i</sub> <sup>e</sup> (%)
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 <sup>f</sup>	2	toluene	4	80	2.5	2.5	5	95	47	53/47 <sup>h</sup>	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 <sup>h</sup>	93
7 <sup>f</sup>	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 <sup>h</sup>	20
9	1	scCO <sub>2</sub>	4	80	2.5	2.5	167	57	25	81/19	74
10	1	scCO <sub>2</sub>	6	80	2.5	2.5	167	20	68	85/15	30
11	1	scCO <sub>2</sub>	6	80	10	10	167	6	86	81/19	14
12	1	scCO <sub>2</sub>	6	100	10	10	167	49	90	80/20	10
13	1	scCO <sub>2</sub>	6	100	10	10	250	82	89	78/22	11
14	2	scCO <sub>2</sub>	4	80	2.5	2.5	167	40	76	76/24	24
15 <sup>g</sup>	2	scCO <sub>2</sub>	4	80	2.5	2.5	167	15	12	45/55 <sup>h</sup>	79
16	2	scCO <sub>2</sub>	6	100	10	10	250	70	94	77/23	6
17	3	scCO <sub>2</sub>	4	80	2.5	2.5	167	13	41	85/15	59
18	3	scCO <sub>2</sub>	2	80	2.5	2.5	167	35	9	77/23	91
19	3	scCO <sub>2</sub>	6	100	10	10	250	24	79	75/25	19

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

At the best conditions ( $P/Rh = 6$ ,  $CO/H_2 = 5$  atm,  $T = 100^\circ C$ , 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  $80^\circ C$  in diethylether. The solvent was then evaporated and 1-octene was added. The system was pressurised and heated again to  $80^\circ C$  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. 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  $[Rh(cod)(1)_2]PF_6$ ,  $[Rh(2-3)_4]PF_6$  and  $[PdCl_2(1-3)_2]$ . We have determined the X-ray structure of  $[Rh(3)_4]PF_6$  and confirmed the formation of the tetrakis(phosphite) complex. The reactivity of  $[Rh(acac)(CO)_2]/1-3$  with CO/H<sub>2</sub> at 5 atm (CO/H<sub>2</sub>=1) and 80 °C indicated that  $[RhH(CO)(1-3)_3]$  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  $scCO_2$ , 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.  $^1H$ ,  $^{13}C\{^1H\}$ ,  $^{31}P\{^1H\}$  and NMR spectra were recorded on a Varian Gemini spectrometer operating at  $^1H$  (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  $^1H$  and  $^{13}C\{^1H\}$  as internal reference, H<sub>3</sub>PO<sub>4</sub> 85% for  $^{31}P\{^1H\}$ . 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<sup>3</sup>) with magnetic stirring. The autoclave was equipped with a liquid inlet, a gas inlet, a CO<sub>2</sub> 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)<sub>2</sub>] (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)<sub>2</sub>] (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<sub>2</sub> (1:1), and liquid CO<sub>2</sub> 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 -10°C 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<sup>3</sup>) 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)<sub>2</sub>] (0.055 mmol). The solvent was removed in vacuum, the reactor was pressurised with syn-gas and CO<sub>2</sub>, the system was heated to 80°C, 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<sub>2</sub> with a solution of [Rh(acac)(CO)<sub>2</sub>] (0.04 mmol), the ligand 1-3 (0.16 mmol) and toluene-d<sub>8</sub> (2 ml). The tube was pressurised to 5 atm CO/H<sub>2</sub> (1/1) and left for 1 h under agitation at 80°C, and the NMR spectra were recorded.

#### *HPIR*

In a typical experiment, the HPIR cell was filled under N<sub>2</sub> with a solution of [Rh(acac)(CO)<sub>2</sub>] (0.036 mmol), the ligand 1-3 (0.144 mmol) and methyrtetrahydrofurane (15 ml). The cell was pressurised to 5 atm CO/H<sub>2</sub> (1/1) and left for 1 h under agitation at 80°C, 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-trimethylhexanol (2.74 g, 0.019 mol) and pyridine (1.50 g, 0.019 mol) in 12 ml of diethylether at -10°C, 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).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  3.74 (q, 6H,  $POCH_2$ ,  $J_{HP} = 7.1$  Hz,  $J_{HH} = 7.1$  Hz), 1.57 (m, 6H,  $POCH_2CHH-$  +  $-CHCH_3-$ ), 1.36 (m, 3H,  $POCH_2CHH-$ ), 1.15 (dd,  $^2J_{HH} = 14.0$  Hz,  $^3J_{HH} = 3.4$  Hz, 3H,  $-CH(CH_3)CHH-$ ), 1.00 (dd,  $^2J_{HH} = 14.0$  Hz,  $^3J_{HH} = 6.0$  Hz, 3H,  $-CH(CH_3)CHH-$ ), 0.86 (d,  $^3J_{HH} = 6.4$  Hz, 9H,  $-CH(CH_3)$ ), 0.82 (s, 27H,  $C(CH_3)_3$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  60.49 (d,  $^2J_{PC} = 10.6$  Hz,  $POCH_2$ ), 51.21 (s,  $-CH(CH_3)CH_2-$ ), 40.52 (d,  $^3J_{PC} = 4.6$  Hz,  $POCH_2CH_2-$ ), 31.11 (s,  $-C(CH_3)_3-$ ), 29.99 (s,  $-C(CH_3)_3-$ ), 25.91 (s,  $-CH(CH_3)-$ ), 22.53 (s,  $-CH(CH_3)-$ ).  $^{31}P\{-^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  139.9. 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).* 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 diethylether at  $-10^\circ C$ , 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).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.59 (m, 2H, Ph), 7.38 (m, 3H, Ph), 3.87 (m, 2H,  $-POCHH-$ ), 3.75 (m, 2H,  $-POCHH-$ ), 1.64 (m, 4H,  $POCH_2CHH-$  +  $-CHCH_3-$ ), 1.43 (m, 2H,  $POCH_2CHH-$ ), 1.19 (m, 2H,  $-CH(CH_3)CHH-$ ), 1.05 (m, 2H,  $-CH(CH_3)CHH-$ ), 0.91 (d,  $^3J_{HH} = 8.4$  Hz, 6H,  $-CH(CH_3)-$ ), 0.87 (s, 18H,  $C(CH_3)_3$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  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,  $J_{CP}^2 = 4.5$  Hz,  $C_o$  Ph), 65.04 (d,  $^2J_{PC} = 9.2$  Hz,  $POCH_2$ ), 64.99 (d,  $^2J_{PC} = 8.4$  Hz,  $POCH_2$ ), 51.26 (s,  $-CH(CH_3)CH_2-$ ), 51.22 (s,  $-CH(CH_3)CH_2-$ ), 40.77 (d,  $^3J_{CP} = 4.6$  Hz,  $POCH_2CH_2-$ ), 40.72 (d,  $^3J_{CP} = 4.3$  Hz,  $POCH_2CH_2-$ ), 31.1 (s,  $-C(CH_3)_3-$ ), 29.97 (s,  $-C(CH_3)_3-$ ), 25.92 (s,  $-CH(CH_3)-$ ), 22.54 (s,  $-CH(CH_3)-$ ), 22.48 (s,  $-CH(CH_3)-$ ).  $^{31}P\{-^1H\}$  NMR

( $CDCl_3$ ):  $\delta$  156.6. 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).** To a solution of 3,5,5-trimethylhexanol (0.66 g, 4.6 mmol) and of pyridine (0.36 g, 4.6 mmol) in 12 ml of diethylether at  $-10^\circ C$ , 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).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.40 (m, 4H, Ph), 7.22 (m 6H, Ph), 3.78, (m, 2H,  $POCH_2$ ), 1.64 (m, 1H,  $POCH_2CHH$ -), 1.55 (m, 1H,  $-CH(CH_3)$ -), 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,  $-CH(CH_3)$ -), 0.77 (s, 9H,  $C(CH_3)_3$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  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  $[M]^+$ . High resolution EIMS: 328.1961,  $C_{21}H_{29}OP$ .

#### Preparation of complexes 4-9

**Preparation of  $[Rh(C_8H_{12})(1)_2]PF_6$  (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 %.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  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,  $POCH_2CH_2^- + -CHCH_3^-$ ), 1.22 (dd,  $^2J_{HH} = 14.0$  Hz,  $^3J_{HH} = 3.6$  Hz, 6H,  $-CH(CH_3)CHH^-$ ), 1.14 (dd,  $^2J_{HH} = 14.0$  Hz,  $^3J_{HH} = 6.0$  Hz, 6H,  $-CH(CH_3)CHH^-$ ), 0.97 (d,  $^3J_{HH} = 6.4$  Hz, 18H,  $-CH(CH_3)^-$ ), 0.90 (s, 54H,  $C(CH_3)_3$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  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,  $-CH(CH_3)^-$ ).  $^{31}P\{-^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  116.1 (d,  $J_{RHP} = 244.0$  Hz), -143.2 (sept.,  $J_{FP} = 711.5$  Hz).  $^{19}F$  NMR ( $CDCl_3$ ):  $\delta$  -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 %.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.5 (m, 20H, Ph), 3.47 (br m, 8H,  $-POCHH^-$ ), 3.16 (br, 8H,  $-POCHH^-$ ), 1.38 (m br, 24H,  $POCH_2CH_2^- + -CHCH_3^-$ ), 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 ( $CDCl_3$ ):  $\delta$  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,  $-CH(CH_3)^-$ ).  $^{31}P\{-^1H\}$   $\delta$  NMR ( $CDCl_3$ ): 146.0 (d,  $J_{PRh} = 169.7$  Hz), -143.2 (sept.,  $J_{PF} = 711.5$  Hz).  $^{19}F$  NMR ( $CDCl_3$ ):  $\delta$  -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 %**.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.2-7.3 (m, 40H, Ph), 2.78 (br m, 8H,  $POCH_2$ ); 0.80 (m, 12H,  $POCH_2CH_2CH(CH_3)$ ), 0.67 (dd,  $^2J_{HH} = 13.8$  Hz,  $^3J_{HH} = 5.6$  Hz, 4H,  $-CH(CH_3)CHH-$ ), 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 ( $CDCl_3$ ):  $\delta$  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,  $-CH(CH_3)$ ).  $^{31}P\{-^1H\}$  NMR ( $CDCl_3$ ): 132.3 d, ( $J_{PRh} = 162.2$  Hz); -143.1 sept. ( $J_{P-F} = 712.6$ Hz).

**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 %**.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  4.15 (m, 12H,  $POCH_2$ ) 1.64 (m, 6H,  $POCH_2CHH-$ ), 1.55 (m, 6H,  $-CHCH_3-$ ), 1.46 (m, 6H,  $POCH_2CHH-$ ), 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,  $-CH(CH_3)CHH-$ ), 0.88 (d,  $^3J_{HH} = 3.2$  Hz, 18H,  $-CH(CH_3)-$ ), 0.83 (s, 54H,  $C(CH_3)_3$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  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,  $-CH(CH_3)-$ ).  $^{31}P\{-^1H\}$  NMR ( $CDCl_3$ ): 94.2 s. MS (MALDI-TOF)  $m/z$ : 1063.7  $[M-Cl]^+$ , 1026.7  $[M-2Cl]^+$

**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 %**.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.75 (m, 4H, Ph), 7.45 (m, 6H, Ph), 4.20 (br m,

4H, -POCHH-), 3.95 (br m, 4H, -POCHH-), 1.71 (m br, 4H, POCH<sub>2</sub>CHH), 1.54 (m br, 8H, POCH<sub>2</sub>CHH + -CHCH<sub>3</sub>-), 1.13 (br m, 8H, -CH(CH<sub>3</sub>)CH<sub>2</sub>-), 0.90 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 12H, -CH(CH<sub>3</sub>)-), 0.87 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 140.70 (br, C<sub>i</sub> Ph), 132.55 (s, C<sub>o</sub> Ph), 131.74 (s, C<sub>m</sub> Ph), 129.07, (s, C<sub>p</sub> Ph), 67.83 (s, POCH<sub>2</sub>-), 50.93 (s, -CH(CH<sub>3</sub>)CH<sub>2</sub>-), 39.22 (s, POCH<sub>2</sub>CH<sub>2</sub>-), 30.88 (s, -C(CH<sub>3</sub>)<sub>3</sub>-), 29.77 (s, -C(CH<sub>3</sub>)<sub>3</sub>-), 25.82 (s, -CH(CH<sub>3</sub>)-), 22.26 (s, -CH(CH<sub>3</sub>)-). <sup>31</sup>P-{<sup>1</sup>H} δ NMR (CDCl<sub>3</sub>): 122.2 s. MS (MALDI-TOF) *m/z*: 929.4 [M-Cl]<sup>+</sup>, 894.4 [M-2Cl]<sup>+</sup>

*Preparation of [PdCl<sub>2</sub>(3)<sub>2</sub>] (9).* Ligand **3** (85.63 mg, 0.26 mmol) was added to a solution of the complex [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (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 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.81 (m, 8H, Ph), 7.46 (m 12H, Ph), 3.63 (m, 4H, POCH<sub>2</sub>), 1.31-1.19 (m, 6H, POCH<sub>2</sub>CH<sub>2</sub>- + -CH(CH<sub>3</sub>)- + -CH(CH<sub>3</sub>)CH<sub>2</sub>-), 0.92 (d, <sup>3</sup>J<sub>HH</sub> = 4.4 Hz, 6H, -CH(CH<sub>3</sub>)-), 0.78 (s, -C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 140.4 (br C<sub>i</sub> Ph), 132.58 (d, <sup>2</sup>J<sub>PC</sub> = 6.1 Hz, C<sub>o</sub> Ph), 132.52 (d, <sup>2</sup>J<sub>PC</sub> = 6.1 Hz, C<sub>o</sub> Ph), 131.75 (br, C<sub>m</sub> Ph), 128.20 (br, C<sub>p</sub> Ph), 67.86 (s, POCH<sub>2</sub>-), 50.93 (s, -CH(CH<sub>3</sub>)CH<sub>2</sub>-), 39.22 (POCH<sub>2</sub>CH<sub>2</sub>-), 30.87 (s, -C(CH<sub>3</sub>)<sub>3</sub>-), 29.76 (s, -C(CH<sub>3</sub>)<sub>3</sub>-), 25.81 s, -CH(CH<sub>3</sub>)-), 22.26 (s, -CH(CH<sub>3</sub>)-). <sup>31</sup>P (CDCl<sub>3</sub>): 110.206 s. MS (MALDI-TOF) *m/z*: 796.9 [M-Cl]<sup>+</sup>, 762.0 [M-2Cl]<sup>+</sup>

*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 fiber. The measurements were taken at 120 K in a Bruker SMART CCD1000 diffractometer, with a graphite-monochromated Mo<sub>Kα</sub> radiation (λ = 0.71073 Å). Data collection and processing were carried out using BRUKER Smart and BRUCKER saint. Complex **6** C<sub>84</sub>H<sub>112</sub>O<sub>4</sub>P<sub>4</sub>Rh.F<sub>6</sub>P crystallised in a tetragonal *P4/n* space group, with *a* = 18.021 (2) Å, *c* = 13.431 (3) Å, *V* = 4361.8 (12) Å<sup>3</sup>, *M* = 1557.50, *Z* = 2, ρ<sub>calcd</sub> =



1.186 mg m<sup>-3</sup>,  $\mu$  = 0.345 mm<sup>-1</sup>. The yellow crystal was prismatic and of dimensions 0.6 x 0.52 x 0.48 mm. The  $\theta$  range for measurement was 1.52 to 26.37° and 4471 unique reflections were measured at 393 (2) K ( $R_{\text{int}}$  = 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  $R = \sum ||F_o| - |F_c|| / \sum |F_o|^2 = 0.0393$  for 3571 reflections with  $F_o^2 > 2\sigma(F_o^2)$  and  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.1178$ , 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](http://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.ac.uk).

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# Chapter 5

## Hydroformylation of Alkenes with Rhodium Catalyst in Supercritical Carbon Dioxide

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*1-Octene, 1-decene and styrene have been hydroformylated using a CO<sub>2</sub>-philic fluororous ligand associated with a rhodium catalyst. The effect of P/Rh molar ratio, partial pressure of CO/H<sub>2</sub> and total pressure of carbon dioxide were studied. When 1-octene was used as a substrate, high conversion and selectivity in aldehydes were observed using low rhodium concentration and low P/Rh ratios.*

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5

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## 5.1. Introduction

The hydroformylation of long chain alkenes is an important industrial process. The aldehydes obtained can be converted into plasticizer alcohols and biodegradable detergents [1]. The main disadvantage of this reaction is the difficult separation of the reaction products from the catalyst at the end of the reaction due to the high boiling points of the aldehydes. Several strategies have been developed to solve this problem. The most successful one is to use a multiphase system, consisting of two or more immiscible liquid phases. The catalyst is immobilized in liquid phase while the substrate and the product(s) of the catalysed reaction are in the rest of one of the other phases [2].

In 1984, Rhône-Poulenc/Ruhr-Chemie industries initiated the first commercial process for the biphasic aqueous hydroformylation of propene [3-5]. This process produces 300.000 tones of butanal per year but it is not viable for long chain alkenes because certain solubility of the alkene in water is needed in order to obtain a high conversion [6].

In 1994, the concept of the fluorous biphase system (FBS) was introduced by Horváth and Rábai and applied to the hydroformylation of 1-decene [7-9]. The FBS is based on the properties of fluorous solvents, which have a low affinity for non-fluorinated compounds. The catalyst, which contains ligands with fluorous chains, is therefore dissolved in the fluorous phase and the products can be separated by a simple decantation. Since then there has been an increasing interest in the development of catalysts that have high affinities for fluorous phase. Although the FBS has many advantages, it has not been applied at industrial level, due to the high cost of the fluorous solvents.

Supercritical carbon dioxide (scCO<sub>2</sub>) is an attractive green solvent alternative to conventional organic solvents. It is used successfully in industrial extraction processes [10]. ScCO<sub>2</sub> can be used as a solvent in homogeneous catalysis [11]. Carbon dioxide has mild critical data ( $T_c = 31^\circ\text{C}$ ,  $P_c = 73.8$  bar), is both environmentally friendly and relatively inexpensive. Supercritical carbon

dioxide has gas-like properties, and gases such as H<sub>2</sub> and CO are highly soluble in it. For this reason, it is a good alternative solvent, especially in reactions in which reagents are gases. ScCO<sub>2</sub> is a non-polar solvent so modifications in catalytic systems are required to increase the solubility of the catalyst in the reaction media. The best results in terms of solubility have been achieved introducing fluoruous chains into the ligands [12]. Due to the tuneable properties of carbon dioxide, changing the pressure or the temperature of the system could induce the selective precipitation of the catalyst system. The products and the substrate could then be separated from the catalyst extracting with supercritical carbon dioxide [12, 13].

We recently reported the successful application of Rh catalysts using the fluoruous ligand **1** (Figure 1) in the hydrogenation [14] and hydroformylation of [15] alkenes using the FBS concept. The selectivity in aldehydes obtained in the hydroformylation of 1-octene using perfluoromethylcyclohexane was high (96 %) and the activity was up to 1040 h<sup>-1</sup>. When a biphasic perfluoromethylcyclohexane/toluene system was used, the system could be effectively recycled for two consecutive runs. In this study we report the use of this fluoruous monophosphine P(C<sub>6</sub>H<sub>4</sub>-4-OCH<sub>2</sub>C<sub>7</sub>F<sub>15</sub>)<sub>3</sub> (**1**) in rhodium catalytic hydroformylation of model alkenes using supercritical carbon dioxide as solvent.

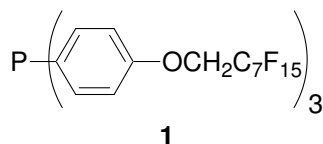


Figure 1. Ligand **1**

## 5.2. Results and Discussion

### *Solubility studies*

We studied the solubility of the catalytic system Rh/1 in supercritical carbon dioxide. The solubility studies were performed in a Thar 100 ml autoclave equipped with sapphire windows and the solubility was established by visual inspection. The catalytic precursor  $[\text{Rh}(\text{acac})(\text{CO})_2]$  ( $0.48 \cdot 10^{-3} \text{ M}$ ), the phosphine 1 ( $\text{P/Rh} = 3$ ) and 1-octene (24mmol) were placed in the autoclave, which was then pressurised with  $\text{CO}/\text{H}_2$ , 10 bar (1:1) and finally with carbon dioxide. The solubility behaviour was studied by increasing the temperature and the total pressure of carbon dioxide progressively using a syringe pump. The mixture became a solubilized one-phase transparent yellow system at  $80^\circ\text{C}$  and 200 bar of total pressure at density of approximately  $0.6 \text{ g}\cdot\text{ml}^{-1}$  (Fig. 2a). When the autoclave was cooled down the two phases were recovered without apparent decomposition (Fig. 2b).

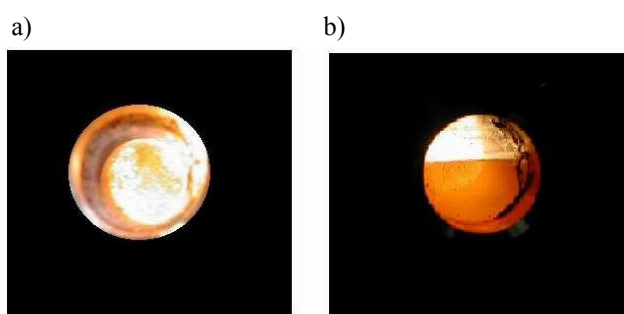


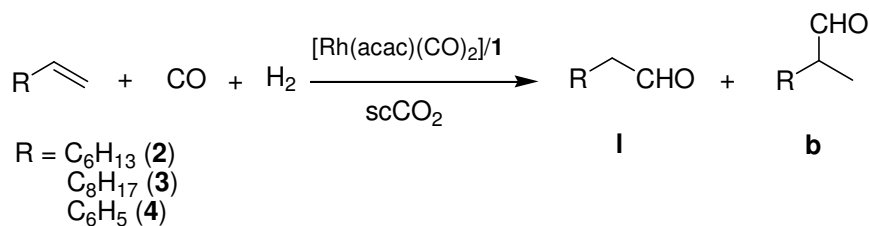
Figure 2. a) Soluble catalyst precursor in one phase system at  $80^\circ\text{C}$  and 200 bar b) Precipitation of catalyst precursor at  $50^\circ\text{C}$  and 135 bar.

### *Hydroformylation reactions*

To investigate the efficiency of the fluororous phosphine 1 in rhodium catalysed hydroformylation, we choose 1-octene (2), 1-decene (3) and styrene (4) as



model substrates for the hydroformylation of 1-alkenes (Scheme 1) in supercritical carbon dioxide.



Scheme 1.

Hydroformylation reactions were carried out using the *in situ* formed catalyst precursor  $[\text{Rh}(\text{acac})(\text{CO})_2]/1$  at 0.48 mM concentration. Using 1-octene (2) as the substrate, we studied the influence of P/Rh ratio, temperature, partial pressure of  $\text{CO}/\text{H}_2$  and total pressure on the activity of the reaction. The results are summarized in Table 1.

At 10 bar of  $\text{CO}/\text{H}_2$ , 200 bar of total pressure, 80 °C and with a P/Rh molar ratio of 3 (entry 1, Table 1), conversion was very low, though the system was soluble under these conditions. The selectivity in aldehydes was also very low and the major products obtained were 2-octene isomers. This low conversion may be due to the lack of formation of the active species, since a period of induction, as reported for low donor phosphite systems, was probably needed [16]. Therefore, to form the active species in the supercritical solvent, we decided to conduct an experiment by heating the system at 80 °C, 10 bar of  $\text{CO}/\text{H}_2$  and  $\text{scCO}_2$  up to 200 bar of total pressure for 1h (entry 2, Table 1). The autoclave was cooled down to -50 °C, depressurised, and the substrate was introduced.  $\text{CO}/\text{H}_2$  and carbon dioxide were again charged, and the reaction was allowed to proceed for 1h. Conversion and aldehydes selectivity increased by up to 49 % and 74 %, respectively.

Increasing the P/Rh molar ratio to 5 (entry 3, Table 1) increased total conversion, but also decreased both aldehydes selectivity and regioselectivity. To prevent the formation of isomerisation products by  $\beta$ -elimination, we decreased the temperature to 60 °C while maintaining the P/Rh ratio at 5 (entry 4, Table 1). We observed a decrease in conversion, a lower selectivity in aldehydes, and no further improvement in the l/b ratio.

Table 1. Hydroformylation of 2-4 using  $[\text{Rh}(\text{acac})(\text{CO})_2]/1$  in  $\text{scCO}_2$ <sup>a</sup>

Entry	Alkene	P/Rh	t(h)	P(CO/H <sub>2</sub> ) (atm)	T °C	P <sub>tot</sub> (atm)	Conv (%) <sup>b</sup>	S <sub>ald</sub> (%) <sup>c</sup>	l/b	S <sub>i</sub> (%) <sup>d</sup>
1	2	3	1	5/5	80	200	4	50	70/30	41
2 <sup>e</sup>	2	3	1	5/5	80	200	49	74	76/24	26
3 <sup>e</sup>	2	5	1	5/5	80	200	66	64	68/32	36
4 <sup>e</sup>	2	5	1	5/5	60	200	29	57	66/34	43
5 <sup>e</sup>	2	3	1	10/10	80	200	66	86	76/24	14
6 <sup>e</sup>	2	3	1	10/10	100	200	47	60	77/23	40
7 <sup>e</sup>	2	3	1	10/10	80	250	40	72	73/27	28
8 <sup>e</sup>	2	3	1	10/10	100	250	73	74	76/23 <sup>f</sup>	26
9 <sup>e</sup>	2	3	1	20/20	80	200	76	74	72/23	26
10 <sup>g,h</sup>	2	5	1	20/20	80	40	68	96	74/26	4
11 <sup>e,h</sup>	2	5	1	20/20	80	200	32	38	64/36	61
12 <sup>i</sup>	2	5	1	20/20	80	40	97	98	73/23	2
13 <sup>e</sup>	3	3	3	10/10	80	200	94	60	71/29	40
14 <sup>e,j</sup>	4	3	3	10/10	80	200	31	87	28/62	-

<sup>a</sup> Reaction conditions: V= 25 ml,  $[\text{Rh}(\text{acac})(\text{CO})_2] = 0.48 \cdot 10^{-3}$  M, 1-octene:Rh = 500. <sup>b</sup> % Conv = total conversion of alkene; <sup>c</sup> % S<sub>ald</sub> = selectivity in aldehydes; <sup>d</sup> % S<sub>i</sub> = selectivity in isomerized products; <sup>e</sup> Preactivation of catalyst; <sup>f</sup> less than 0.5% of ethylhexanal was detected; <sup>g</sup> solvent = C<sub>7</sub>F<sub>14</sub> see reference [15]; <sup>h</sup>  $[\text{Rh}(\text{acac})(\text{CO})_2] = 1,6 \cdot 10^{-3}$  M, S:Rh = 2000. <sup>i</sup> solvent = toluene, ligand = PPh<sub>3</sub>, see reference [15]; <sup>j</sup> 13 % ethylbenzene was also formed.

We studied the effect of partial pressure of CO/H<sub>2</sub> at P/Rh ratio of 3. Increasing the partial pressure to 20 bar (1:1) increased the selectivity in aldehydes (86%) and conversion (66 %) (entry 5 vs entry 2 , Table 1). When we increased the temperature to 100 °C (entry 6, Table 1) while keeping the other parameters constant, we observed a drop in both conversion and aldehydes selectivity.

The total pressure of carbon dioxide and the temperature can also affect the reactivity of the system, since these parameters also affect the density [11, 17]. At the same partial pressure of 20 bar of CO/H<sub>2</sub>, and by increasing the total pressure of carbon dioxide to 250 bar at 80 °C (entry 7 vs entry 5, Table 1), we observed a decrease in conversion and in aldehydes selectivity. Increasing the temperature to 100 °C (entry 8 vs entry 6, Table 1) and applying a higher pressure of carbon dioxide led to better conversion (73 %) and aldehydes selectivity (74 %). The approximate calculated density of the system at 250 bar and 100 °C (entry 8, Table 1) was 0.6 g·ml<sup>-1</sup>, whereas the density at 200 bar and 100 °C (entry 6, Table 1) was 0.5 g·ml<sup>-1</sup>. When we compared these densities with those calculated for the system at 200 bar and 80 °C ( $d = 0.6 \text{ g}\cdot\text{ml}^{-1}$ ) (entry 5, Table 1) and at 250 bar and 80 °C ( $d = 0.7 \text{ g}\cdot\text{ml}^{-1}$ ) (entry 7, Table 1), we found that the best conversions and aldehydes selectivity were obtained when the density of the system was around 0.6 g·ml<sup>-1</sup>.

Increasing the partial pressure of CO/H<sub>2</sub> up to 40 bar (1:1) (entry 9, Table 1) gave higher conversion but slightly decreased aldehydes selectivity.

Optimisation of the conditions therefore showed that the best results (66 % conversion and 86 % selectivity in aldehydes) were obtained at P/Rh molar ratio of 3, 20 bar of CO/H<sub>2</sub> and 200 bar total pressure.

The system Rh/1 was also used in the rhodium catalysed hydroformylation of 1-octene (2) in fluorous systems [15]. The best results in FBS were obtained at P/Rh ratio of 5 and a rhodium concentration of  $1.6\cdot 10^{-3} \text{ M}$  (entry 10, Table 1). To compare both solvents as reaction media, we performed a catalytic

experiment in  $\text{scCO}_2$  using the same conditions than as those in FBS. Under the same conditions, the fluorous system provided better results. However, when we compared the best results for both systems (entry 5 vs entry 10, Table 1), we noticed that similar conversion and regioselectivity can be obtained using  $\text{scCO}_2$  but with the added advantage that the catalyst concentration, P/Rh molar ratio and  $\text{CO}/\text{H}_2$  partial pressure can be much lower. The selectivity in  $\text{scCO}_2$  was about 10 % lower. When we compared the results obtained using the catalyst precursor  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_3$  in toluene (entry 12, Table 1), though conversion and selectivity were lower in  $\text{scCO}_2$ , we found that under suitable conditions this solvent can replace toluene.

The catalytic system Rh/**1** was also applied to the hydroformylation of 1-decene (**3**) and styrene (**4**) (entries 13 and 14, Table 1). When 1-decene (**3**) was used as the alkene, conversion was high but selectivity in aldehydes was moderate. The n/iso ratios were similar to those obtained with 1-octene (**2**) under the same reaction conditions. Styrene (**4**) was also hydroformylated with low conversion (31 %) although aldehydes selectivity was high (87 %) and the l/b ratio was moderate.

### 5.3. Conclusions

Ligand **1** associated with  $[\text{Rh}(\text{acac})(\text{CO})_2]$  afforded an active catalyst in the hydroformylation of olefins in  $\text{scCO}_2$ . The results showed that the system was more active at low rhodium concentrations with low P/Rh ratios. At low  $\text{CO}/\text{H}_2$  pressure, conversions were low. However, increasing the partial pressure up to 20 bar led to high conversion. Higher partial pressures slightly decreased the aldehydes selectivity. The density of the system clearly influences the conversion and selectivity in aldehydes. The best results were obtained at density values close to  $0.6 \text{ g}\cdot\text{ml}^{-1}$ . Comparative results showed that  $\text{scCO}_2$  can replace fluorous systems and, though conversion and

selectivity were lower than when  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_3$ , this system could be also used as a catalyst precursor.

#### 5.4. Experimental

##### *Solubility studies*

The solubility studies were carried out in a Thar reactor (100 cm<sup>3</sup>) equipped with sapphire windows and magnetic stirring. The autoclave was charged with ligand **1** (0.144 mmol),  $[\text{Rh}(\text{acac})(\text{CO})_2]$  (0.048 mmol) and 1-octene (24 mmol). The reactor was pressurised with syn-gas and CO<sub>2</sub>, the system was heated and the total pressure was increased using a syringe pump. Solubility was monitored by visual inspection.

##### *Catalysis in supercritical carbon dioxide*

Hydroformylation experiments were carried out in a Parr autoclave (25 cm<sup>3</sup>) with magnetic stirring. The autoclave was equipped with a liquid inlet, a gas inlet, a CO<sub>2</sub> inlet and a thermocouple. An electric heating mantle kept the temperature constant. The complex  $[\text{Rh}(\text{acac})(\text{CO})_2]$  (0.012 mmol) and the ligand (0.036 or 0.06 mmol) were placed in the autoclave. The autoclave was then evacuated, and the substrate 1-octene (6 mmol) was then added. The system was pressurised with CO/H<sub>2</sub> (1:1), and liquid CO<sub>2</sub> 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 -50 °C and carefully vented. The final mixture was analysed by GC. The products were identified by GC-mass spectrometry.

To preactivate the catalyst,  $[\text{Rh}(\text{acac})(\text{CO})_2]$  and the ligand **1** were placed in the autoclave, the system was evacuated and pressurized with syn gas and carbon dioxide, the system was heated to the desired value, and then more carbon dioxide was added. The system was stirred for 1h, cooled down to -50

°C and depressurised. The substrate was then added and the system was pressurized again. All preactivations were carried out under the same reactions conditions.

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.

### Acknowledgements

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## 5.5. References

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## Chapter 6

### New palladium complexes for alternating CO/*tert*-butylstyrene copolymerisation in supercritical carbon dioxide

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*The activity of new cationic palladium complexes with perfluorinated bipyridine and phenantroline ligands has been studied in the copolymerisation of 4-*tert*-butylstyrene with carbon monoxide in supercritical carbon dioxide. Highly syndiotactic polyketones were obtained. The molecular weight and polydispersity obtained for the polyketones in supercritical carbon dioxide are better than in conventional solvents.*

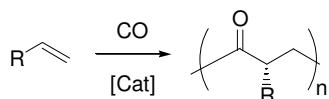
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*Manuscript in preparation: Marta Giménez-Pedrés, Anna M. Masdeu-Bultó, Maurizio Solinas and Walter Leitner, 2005*

### 6.1. Introduction

In the past few years interest has been a growing in synthesizing alternating polyketones of general formula  $[\text{C}(\text{O})\text{CH}(\text{R})\text{CH}_2]_n$  from carbon monoxide and olefins (Scheme 1) [1, 2, 3]. These polyketones are a class of low-cost thermoplastics whose synthesis, properties and applications are still the object of intense fundamental and applied research.

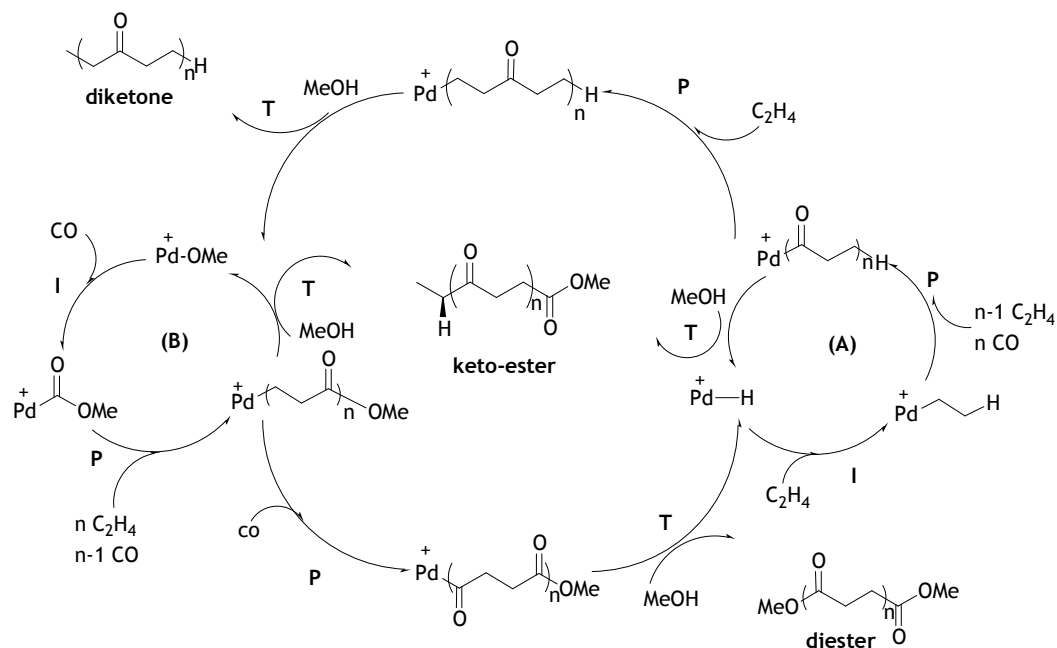


Scheme 1

The first example of metal-catalysed copolymerisation of ethene and carbon monoxide was based on nickel. In the late 1940s, Reppe and Magin showed that  $\text{K}_2[\text{Ni}(\text{CN})_4]$  in water catalysed the production of low-melting polyketone oligomers in addition to diethylketone and propionic acid [4]. Palladium (II) dichloride complexes with monophosphines were first studied by Gough (ICI), and they showed moderate activity in harsh reaction conditions [5]. In the early 1980s Sen reported that cationic palladium (II) complexes containing monodentate phosphines and non-coordinating counteranions such as tetrafluoroborate produces polyketones in mild conditions but at low reaction rates [6, 7]. It was in 1982, that Drent (Shell) discovered that using bidentate phosphines as ligands and weak coordination counteranions in palladium (II) based catalyst obtained high molecular weight polyketones in relatively mild reaction conditions [8, 9].

In 1991, Drent et al. [9] made a careful study of the end groups and presented the first mechanistic interpretation of the copolymerisation of ethene and carbon monoxide in alcoholic solvents [3]. Since then several studies have been made in an attempt to understand this mechanism. In 1996, Drent and

Budzelaar [2] proposed the complete mechanism, which is applicable to other alkenes, for the copolymerisation of ethene and carbon monoxide (Scheme 2).

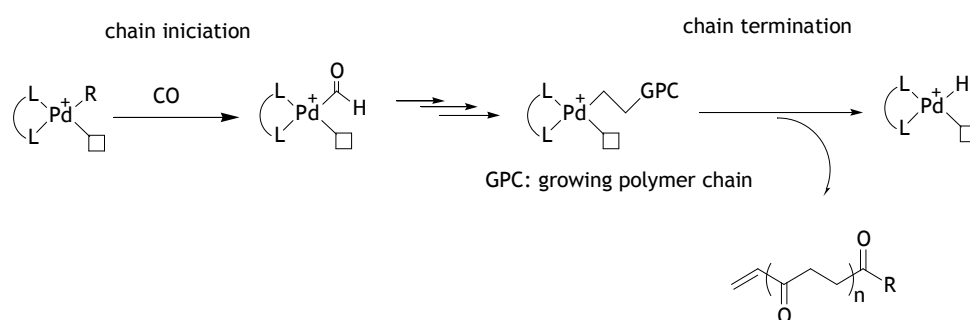


Scheme 2. Proposed mechanism for the copolymerisation of CO/ethene in methanol

Two competing cycles, connected by cross termination steps, would be simultaneously producing polyketones in methanol. The prevalence of either cycle is depending on the experimental conditions. Cycle A is initiated (I) with the insertion of ethene in the palladium hydride bond. The palladium hydride species can be generated in a variety of ways: by a  $\beta$ -hydrogen elimination from a palladium methoxide, a water-gas-shift reaction, a Wacker-type oxidation of ethene or a hydrogen activation (in the presence of hydrogen). Propagation (P) occurs by migratory reversible insertion of CO into the ethyl complex followed by the irreversible migratory insertion of ethene into the palladium acyl bond leading to perfect alternating polyketones. No

propagation errors (double CO or olefin sequences) are observed in this kind of copolymers. Double CO insertion will not occur for thermodynamic reasons, while double ethene insertion is kinetically hampered because palladium (II) centers have a greater affinity for CO than for ethene [10, 11]. The copolymer formed by this cycle has either keto-ester or diketone end groups. The terminal structure depends on the termination path (T). The keto-ester structure is obtained by methanolysis of a Pd-acyl bond, and the diketone structure is obtained if a protonolysis occurs in a Pd-acyl bond.

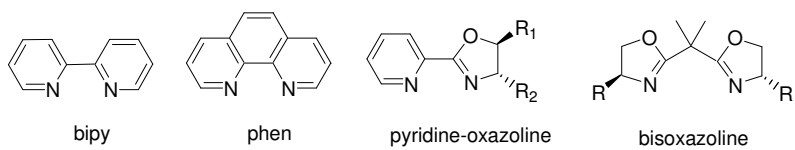
Cycle (B) starts with the palladium carbomethoxy species, which are formed either by a CO insertion into a palladium methoxide or by a methanol direct attacking on coordinated CO. The propagation steps enable the chain to grown. This cycle also shows two different end groups: keto-ester, formed via protonolysis in a Pd-alkyl bond, or diester via methanolysis of a Pd-acyl bond. When the copolymerisation reaction is preformed in non-protic solvents, an alkylpalladium species is necessary so that the first monomer can be inserted (Scheme 3). Termination occurs in this case by  $\beta$ -elimination, which forms Pd-H species and unsaturated-end groups. This pathway is also the main termination step in such alkenes as propene and styrene.



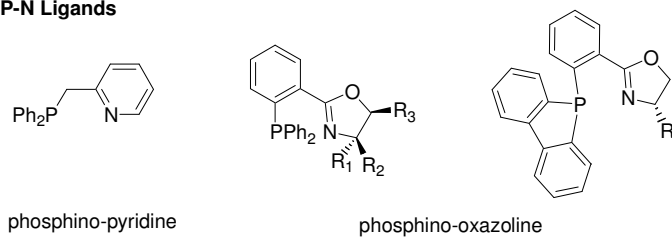
Scheme 3. Initiation and termination steps using an alkylpalladium catalyst in a non-protic solvent

Unlike CO/ethene or CO/propene copolymerisation, catalysts containing diphosphine ligands are not active in the copolymerisation of styrene and their derivatives with carbon monoxide, since low molecular weight oligomers are obtained [2, 12]. This is because  $\beta$ -H elimination is favoured rather than polymer chain growth because the electron density around the metal is higher when a phosphine is coordinated to palladium than to nitrogen ligands [2, 3]. Moreover, the palladium styryl intermediates are strongly stabilized by  $\pi$ -benzylic coordination and so CO insertion is inhibited [13]. However, the unsymmetrical bidentate phosphine-phosphite ligand, (R,S)-BINAPHOS (Figure 1) has been applied to *tert*-butylstyrene/CO copolymerisation [14]. But in general, the most effective system for copolymerising styrene and its derivatives with CO is to use preformed cationic palladium catalyst associated with N-N chelating ligands (Figure 1) such as bipyridine, phenantroline, pyridine-oxazoline or bisoxazoline and weakly coordinating anions [15-18]. Chelating P-N ligands have been also applied to catalysed copolymerisation, although severe reaction conditions are needed to obtain polyketones [19,20]. In the copolymerisation of styrene with carbon monoxide, two additional aspects must be considered: the regioselectivity and the stereoselectivity. Styrene can be inserted into palladium-acyl intermediates either in primary (1,2-insertion) or secondary mode (2,1-insertion) (Scheme 4). Three different arrangements in the polymer structure are possible: tail-to-tail, head-to-tail or head-to head. The styrene is inserted only in secondary mode when bisnitrogen donor ligands are used and head-to tail polymers are obtained. However, the insertion is in primary mode when (R, S)-BINAPHOS is used as a ligand. This mode of insertion also prevents  $\beta$ -H elimination and might explain the activity of this ligand in CO/styrene copolymerisation [21]. A mixture of both insertion modes is observed when P-N ligands are used [20].

**N-N Ligands**



**P-N Ligands**



**P-P Ligands**

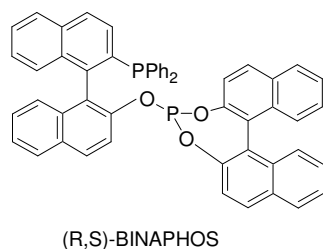
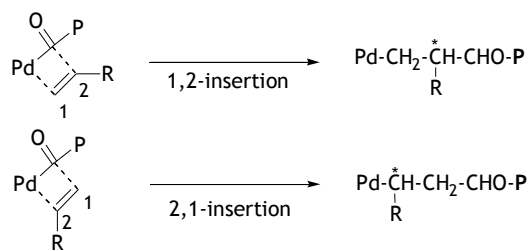


Figure 1. Ligands reported in CO/styrene copolymerisation



Scheme 4

The stereochemistry of the alkene insertion along the chain determines the copolymer tacticity: atactic (stereoirregular), syndiotactic (RSRSRS sequence) or isotactic (RRRRR or SSSSSS sequence) copolymers can be obtained (Figure 2).

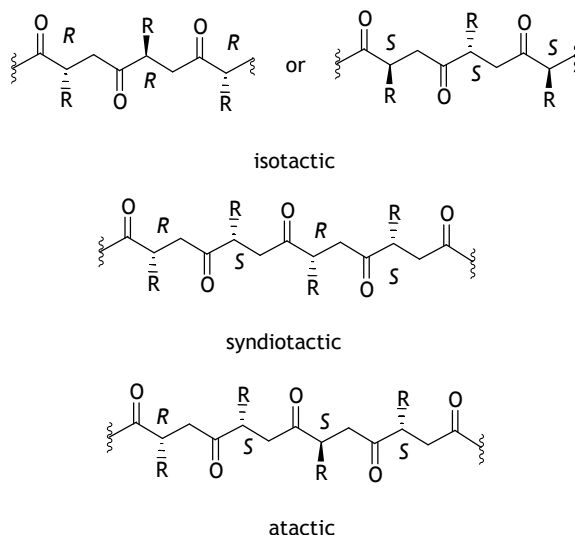
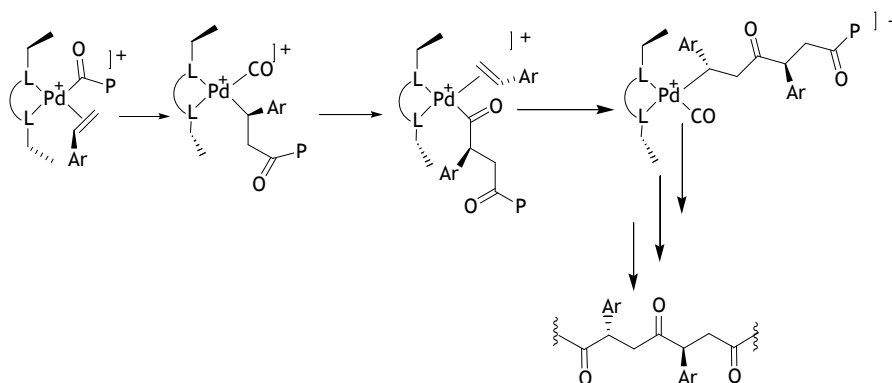


Figure 2. Tacticity of CO/alkene copolymers

Two different mechanisms provide stereoregular copolymers (syndiotactic or isotactic). When a chiral ligand is used, the enantiomeric environment created by the ligand will control the stereoregularity of the styrene insertion. This mechanism is known as *site control* and provides isotactic polymers. When non-chiral ligands are used, the growing polymer chain, which is chiral, controls the stereoregularity of styrene insertion and leads this case to syndiotactic polymers. This mechanism is known as *chain-end control* (Figure 3).

## Site Control



## Chain Control

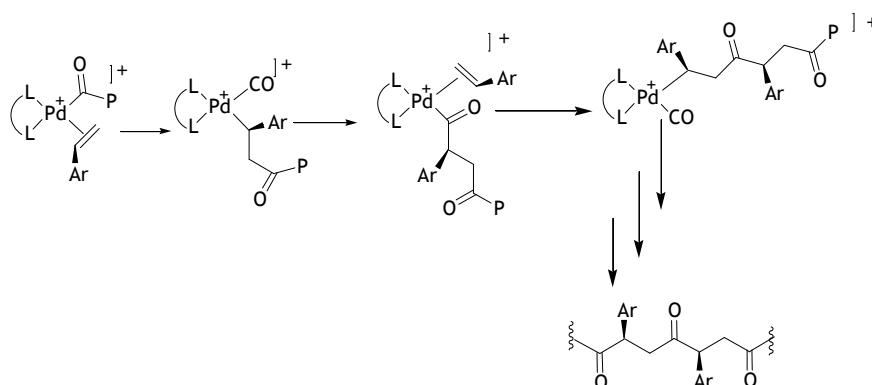


Figure 3

Normally, copolymerisation reactions are carried out with conventional organic solvents, such as methanol, trifluoroethanol or chlorobenzene. During the last years, supercritical carbon dioxide has emerged as an alternative solvent for polymerization reactions [22]. As well as the environmental advantages already discussed, the separation of the solvent from the reaction product is simpler since CO<sub>2</sub> reverts to the gaseous state upon depressurisation, and this results in a dry polymer product. This feature eliminates the energy intensive drying steps required to remove the solvent in polymer manufacturing and may save both money and energy. ScCO<sub>2</sub> can also



be used in polymer processing techniques such as plasticisation, impregnation or polymer extraction and purification [23].

Solubility plays an important role in polymerisation reactions in scCO<sub>2</sub>. While carbon dioxide is a good solvent for non-polar low molecular weight molecules, it is a poor solvent for high molecular weight polymers. In fact, the only polymers that are highly soluble in scCO<sub>2</sub> are fluoropolymers and silicones [24]. This makes it possible to synthesize of high molecular weight fluoropolymers by homogeneous solution polymerisation in scCO<sub>2</sub> [25].

The use of transition metal catalysis for precipitation polymerisations has been studied in supercritical carbon dioxide. DeSimone et al. studied [26] the ring-opening metathesis polymerisation (ROMP) of norbornene in scCO<sub>2</sub> with a [Ru(H<sub>2</sub>O)<sub>6</sub>](*p*-O<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>Me)<sub>2</sub> catalyst which, although insoluble in scCO<sub>2</sub>, was solubilized by adding methanol as a co-solvent. The molecular weights and polydispersities were similar to those obtained without methanol but the yields increased when methanol was used as co-solvent. The presence of methanol had a considerable effect on the microstructure of the polymer. Fürstner et al. [27] reported even higher activities in the polymerisation of norbornene, when they used ruthenium and molybdenum catalysts (Figure 4). The ruthenium catalyst was also used to polymerise cis-cyclooctadiene. Both catalysts produced high molecular weight polymers (10<sup>5</sup>-10<sup>6</sup> g·mol<sup>-1</sup>) in good yields up to 94 %.

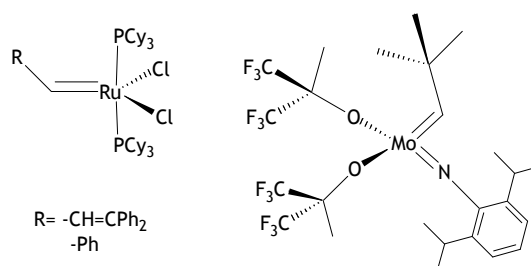


Figure 4.

De Vries et al. [28] studied the polymerisation of 1-hexene and ethene in  $\text{scCO}_2$  with cationic palladium catalyst (Figure 5a). The catalyst was soluble in  $\text{scCO}_2$  probably because BARF was used as counteranion and the polymer precipitated in the reaction media. The results showed that the activities and molecular weight distributions were similar to those obtained when dichloromethane was used as a solvent.

The synthesis of polyketones has hardly been studied in supercritical carbon dioxide. The first example was reported by Kläui and co-workers [29] for the copolymerisation of CO/ethene with a nickel catalyst (Figure 5b). The results showed the formation of a strictly alternating copolymer in  $\text{scCO}_2$ .

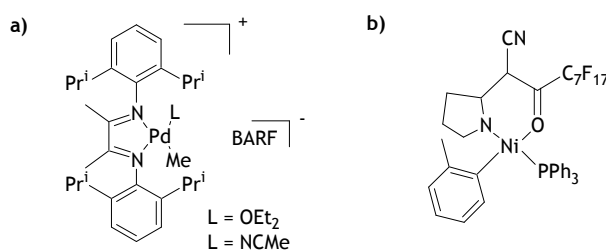


Figure 5.

Nozaki et al. [30] reported the copolymerisation of  $\omega$ -perfluoroalkyl alkenes with CO in  $\text{scCO}_2$  catalyzed by  $\text{Pd(II)-(R,S)-BINAPHOS}$ . When the ligand was not modified, no conversion was observed. Inserting a perfluorinated chain into the ligand makes the catalyst soluble in  $\text{scCO}_2$ , but the reported yield is only 3%.

The present chapter describes the first example known to date of the copolymerisation of *tert*-butylstyrene with CO in supercritical carbon dioxide as a reaction media catalysed by cationic palladium complexes, which contain the bipyridine and phenantroline ligands with perfluorinated chains, **1** and **2** (Figure 6).

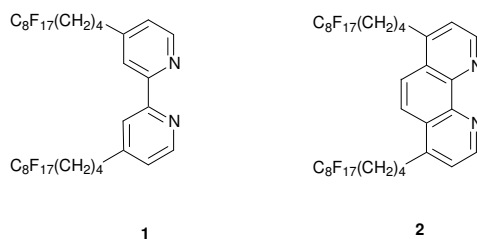
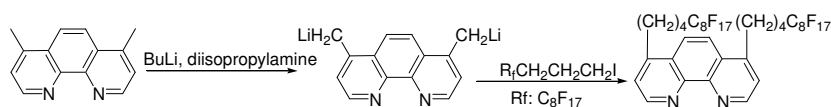


Figure 6. Ligands 1 and 2

## 6.2. Results and discussion

### *Synthesis of ligands*

In an attempt to obtain a catalyst that was both active and soluble in supercritical carbon dioxide we decided to synthesize ligands containing perfluorinated chains. The synthesis of perfluorinated ligand **1** was described by Pozzi et al. [31]. Ligand **2** was prepared with a similar procedure by reaction of 4,7'-dimethylphenanthroline with butyllithium and diisopropylamine and then reaction with 3-perfluorooctyl-1-iodopropane (Scheme 5). Ligand **2** was obtained as a brown solid in a moderate yield (32%).

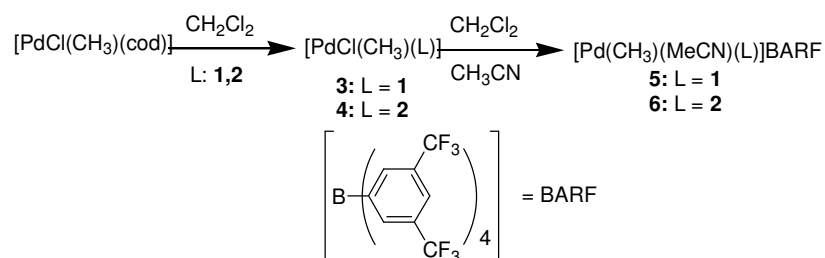
Scheme 5. Synthesis of **2**

The <sup>1</sup>H NMR spectrum of **2** shows the three different methylenic signals at δ 1.78 ppm (-CH<sub>2</sub>-CH<sub>2</sub>-), δ 2.08 ppm (-CH<sub>2</sub>-R<sub>f</sub>) and δ 3.14 ppm (Phen-CH<sub>2</sub>). The signals corresponding to the aromatic protons of the phenanthroline appear at δ 7.38, 7.98 and 9.02 ppm. The <sup>19</sup>F NMR spectra show the signal of the CF<sub>3</sub> at δ -81.17 and the signals of CF<sub>2</sub> appear between δ -114.14 and -126.57 ppm.

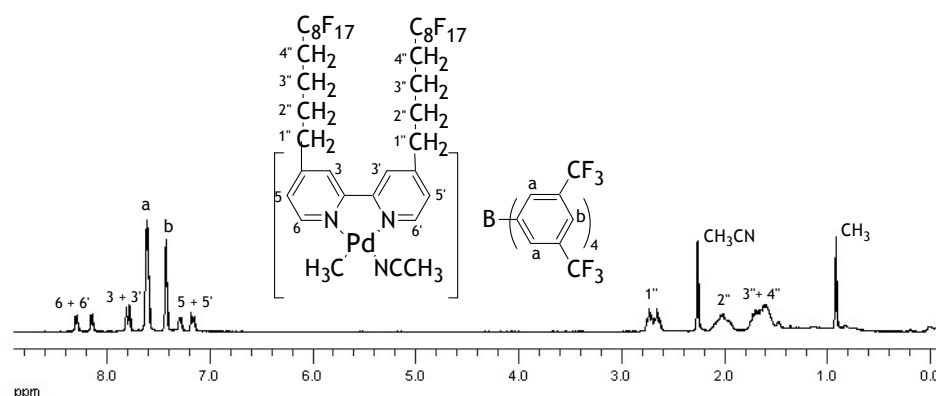
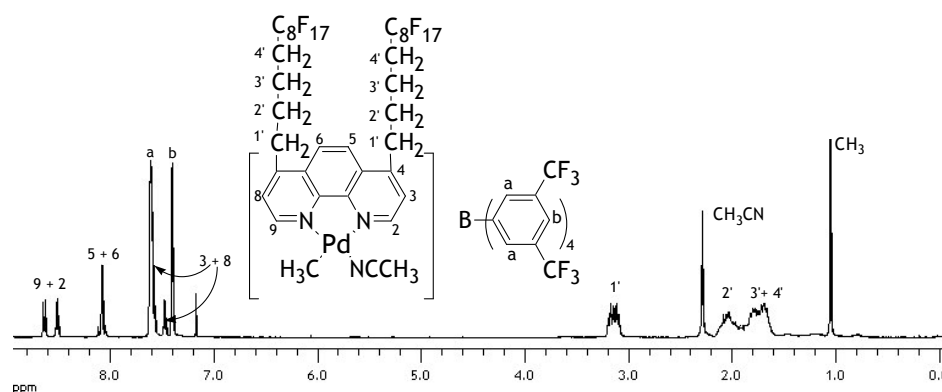
*Synthesis of palladium complexes*

The neutral palladium complexes  $[\text{PdCl}(\text{CH}_3)(\text{L})]$  (3:  $\text{L} = 1$  and 4:  $\text{L} = 2$ ) were prepared by stoichiometric reaction of  $[\text{PdCl}(\text{CH}_3)(\text{cod})]$  ( $\text{cod} = 1,5$ -cyclooctadiene) with the corresponding ligand in anhydrous dichloromethane (Scheme 6). The neutral palladium complexes were not soluble in common deuterated solvents, so the structure was confirmed by mass spectrometry (EI). Complex 3 shows the signal at  $m/z = 1210.0$ , corresponding to  $[\text{M}-\text{Cl}-\text{CH}_3]^+$ , and complex 4 shows the signal at  $m/z = 1234.9$  corresponding to  $[\text{M}+\text{H}-\text{Cl}-\text{CH}_3]^+$ .

Cationic palladium complexes  $[\text{Pd}(\text{CH}_3)(\text{NCCH}_3)(\text{L})]\text{BARF}$  (5:  $\text{L} = 1$  and 6:  $\text{L} = 2$ ,  $\text{BARF} = \text{B}(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4^-$ ) were prepared by reaction of NaBARF in the presence of  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  (Scheme 6). The  $^1\text{H}$  NMR spectra of complexes 5 and 6 (Figure 7 and 8 respectively) show the signal corresponding to the coordinated methyl around  $\delta$  1 ppm and the signal of coordinated acetonitrile ca.  $\delta$  2.32 ppm. The aromatic region shows the signals corresponding to the counteranion at  $\delta$  7.0 and 7.7, and the six signals corresponding to non-equivalent protons of the bipyridine or phenantroline ring between 7.4-8.4 ppm. The  $^{19}\text{F}$  NMR spectra show the signals corresponding to the perfluorinated chain and the signal corresponding to the counteranion around  $\delta$  -63 ppm.



Scheme 6 Synthesis of complexes 3-6.

Figure 7.  $^1H$  NMR spectra of **5**Figure 8.  $^1H$  NMR spectra and **6**

#### Solubility of catalyst precursors in $scCO_2$

The solubility of catalyst precursors **5** and **6** was studied using a 10 ml window-equipped-stainless steel autoclave. The autoclave was charged under argon with 0.0125 mmol of the preformed catalyst **5** or **6**, and then *tert*-butylstyrene (7.75 mmol) was added. The autoclave was filled with CO (1-5 bar), pressurised with carbon dioxide (150- 250 bar) and heated at 37°C.

Visual inspection through the windows showed a homogeneous orange solution even in liquid carbon dioxide. (Figure 9a)

*Copolymerisation of 4-tert-butylstyrene with CO in  $\text{scCO}_2$*

The catalysis was performed using the preformed cationic complexes 5 and 6 in a 10 ml window equipped stainless steel autoclave. The solubility of the palladium complexes in supercritical carbon dioxide was monitored by visual inspection. Both catalyst precursors were soluble in both liquid and supercritical carbon dioxide. As expected, the polyketone was not soluble in  $\text{scCO}_2$  and precipitates during the reaction (Figure 9b).

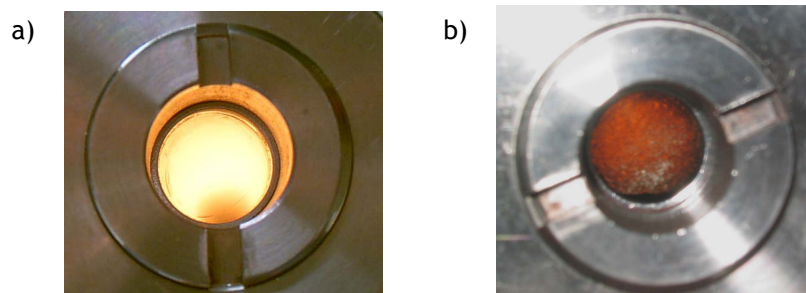


Figure 9.a) Complex 6 solubilized in reaction conditions (5 bar, 250 bar  $\text{CO}_2$ )  
b) during the polymerisation using complex 5. The white solid on the windows is the precipitated polymer.

We also tested the solubility and the activity of the unmodified  $[\text{Pd}(\text{CH}_3)(\text{NCCH}_3)(\text{L})]\text{BARF}$ , (L: 4-4'-dimethylbipyridine). The catalyst was not soluble in the conditions studied (3.4 bar of CO and 145 bar of  $\text{CO}_2$ ), and no polyketone was produced. This clearly showed that a soluble catalyst is required if the activity for copolymerisation in  $\text{scCO}_2$  is to be acceptable.

The results of copolymerising 4-*tert*-butylstyrene with CO/ using complexes **5** and **6** are listed in Table 1. Some experiments using dichloromethane as solvent were carried out to compare the activity in homogeneous catalysis. Partial pressures of carbon monoxide between 1-5 bar were tested. The effect of carbon dioxide pressure on the activity and the molecular weight was also studied. The polymers obtained were characterised by <sup>1</sup>H and <sup>31</sup>C NMR. Figure 10 shows the <sup>13</sup>C NMR spectra of the methylene carbon atom corresponding to different experiments are shown. As a reference an epimerized sample of copolymer is shown. These spectra are consistent with a high syndiotactic copolymer structure (81-90 uu% diads).

Using 1 bar pressure of carbon monoxide (entry 1 and 2, Table 1), productivities were low for both dichloromethane and supercritical carbon dioxide as solvents, although molecular weights were higher in scCO<sub>2</sub>. When the partial pressure of carbon monoxide was increased, both activity and molecular weight were enhanced (entries 2, 3 and 5, Table 1).

Table 1 Copolymerization of CO/TBS in supercritical carbon dioxide using **5** or **6** as catalyst precursor<sup>a</sup>

Entry	Precursor	Time(h)	Productivity [g CP/(g Pd x h)]	P(CO) bar	P(CO <sub>2</sub> ) bar	Mw (Mw/Mn) <sup>d</sup>
1 <sup>b</sup>	<b>5</b>	24	1.79	1	-	6328(1.3)
2	<b>5</b>	24	2.18	1	150	8863 (1.0)
3	<b>5</b>	24	5.79	3.5	170	11130 (1.8)
4 <sup>b</sup>	<b>5</b>	24	12.14	5	-	43740 (5.3)
5	<b>5</b>	24	11.21	5	170	56130 (1.5)
6	<b>5</b>	16	15.25	5	200	63000 (1.8)
7	<b>5</b>	24	9.75	5	250	87820 (1.2)
8 <sup>c</sup>	<b>5</b>	24	10.69	5	250	39740 (1.3)
9	<b>6</b>	24	8.55	5	250	28078 (1.5)

<sup>a</sup> Reaction Conditions: 0.0125 mmol catalyst, substrate/cat = 620, T=37°C <sup>b</sup> CH<sub>2</sub>Cl<sub>2</sub> was used as a solvent, T= 25 °C; <sup>c</sup> no stirring <sup>d</sup> Mw: Molecular weight, Mw/Mn: polydispersity

At 5 bar of CO, when the total pressure of scCO<sub>2</sub> was increased from 170 to 250 bar the molecular weight ( $M_w$ ) increased up to twice the value obtained in dichloromethane with the same catalyst precursor (entry 7 vs 4, Table 1). Moreover, the distribution of molecular weight was very narrow in scCO<sub>2</sub>. The polydispersity decreased from 5.3 in dichloromethane to 1.2 in scCO<sub>2</sub>. This positive effect was attributed to the high miscibility of CO in scCO<sub>2</sub>. The CO is efficiently dissolved and then the gas-liquid mass transfer disappears so the growing chain step could be favoured and  $\beta$ -elimination avoided. Also, the polydispersity is decreased because the polymer precipitates from solution. Taking advantage of the high diffusivity of supercritical carbon dioxide, we decided to perform one test without stirring. The productivity was similar but the molecular weight decreased by half (entry 8, Table 1).



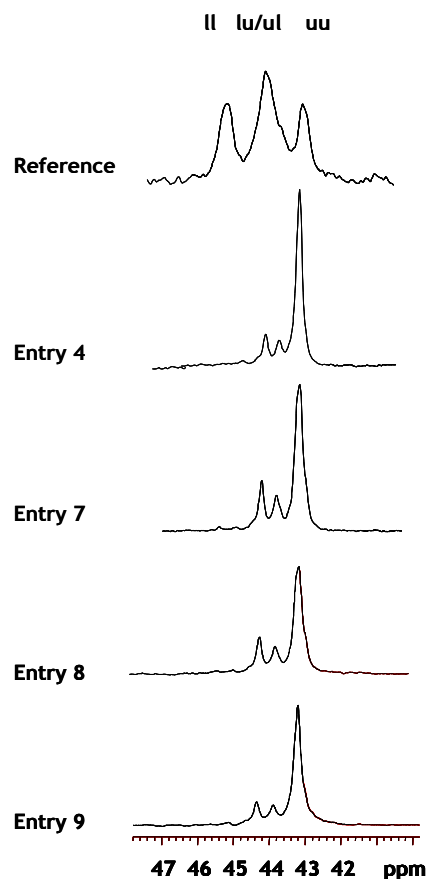


Figure 10. <sup>13</sup>C NMR spectrum in the region of methylene carbon atom corresponding to the copolymer obtained (Table 1)

We also explored the possibility of using supercritical carbon dioxide to extract the catalyst and the unreacted substrate from the polyketone. The extraction was performed by flushing supercritical carbon dioxide between (180-200 bar) through the autoclave for 1h and 15 minutes. The catalyst and the unreacted substrate were collected in two cold traps at -78°C (Figure 11). At the end of the extraction the cold traps contain a mixture not quantified of catalyst and *tert*-butylstyrene.

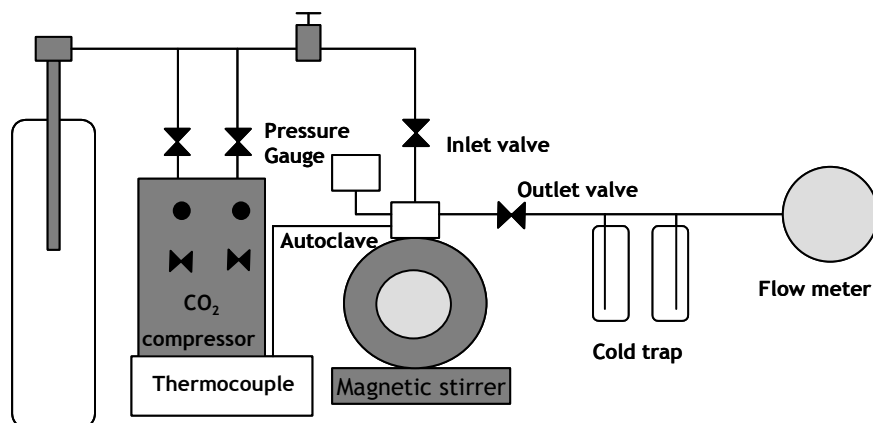


Figure 11. Schematic representation of the extraction of catalyst and unreacted substrate

### 6.3. Conclusions

In conclusion, we showed that CO/TBS could be copolymerised using supercritical carbon dioxide and that there is no need to use toxic organic solvents. Moreover, the polyketones obtained are highly syndiotactic and have higher molecular weights and improved polydispersities. Preliminary experiments suggest that the catalyst can be separated by extraction with supercritical CO<sub>2</sub>.

### 6.4. Experimental part

All reactions were carried out in a nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were distilled and deoxygenated prior to use. The salt  $\text{NaBAR}'_4$  ( $\text{Ar}'=3, 5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$ ) was prepared according to reported methods [32]. Ligand **1** was prepared according to a published method [31].

NMR spectra were recorded on a Varian Gemini spectrometer operating at  $^1\text{H}$  (300 or 400 MHz),  $^{13}\text{C}$  (75.43 or 100.57 MHz),  $^{19}\text{F}$  (376.3 Hz). Chemical shifts were reported relative to tetramethylsilane for  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  as internal

reference. Mass spectrometry was performed in an AUTOSPEC spectrometer (EI-HR) and AUTOFLEX spectrometer (MALDI-TOF).

The molecular weight of the copolymers and molecular weight distributions were determined by gel permeation chromatography (GPC -MALLS). The measurements were made in THF on an Agilent 1100 series using a four-serial column system MZ Gel DVB gel-permeation chromatography device with a Wyatt DAWN Light Scattering and an Optilab (Wyatt Technology) refractive index detector or by gel permeation chromatography (GPC) in CHCl<sub>3</sub> on a Waters 515-GPC device using a linear Waters Ultrastayragel column with a Waters 2410 refractive index detector and polystyrene standards.

*Synthesis of 4,7'-bis[4''-(F-octyl)-butyl]-1,10'-phenantroline (2)*

A solution of n-butyllithium 1.6 M in hexane (10.5 ml, 16.8 mmol) was added, via a syringe, to a solution of diisopropylamine (2.7 ml, 19.2 mmol) in tetrahydrofuran (5 ml) at -78°C. The solution was stirred for 20 min. at -78°C and 4,7'-dimethylphenantroline (1g, 4.8 mmol) in 75 ml of tetrahydrofuran was then added dropwise. The dark brown solution was stirred at -78°C for 1h. Then, 3-perfluorooctyl-1-iodopropane (6.77 g, 11.52 mmol) in 50 ml of tetrahydrofuran was added slowly via a syringe at -78°C. The violet solution was stirred for 5h at -78°C and at room temperature overnight. The solvent was removed under reduced pressure. Then, 60 ml of water were added and the mixture was extracted (2 x 75 ml) of diethylether, and with dichloromethane (2 x 75 ml). The organic extracts were collected and dried over Mg<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was recrystallized from dichloromethane/pentane. The product was obtained as a brown solid. 1.76 g, (Yield = 32 %).

<sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): δ 1.78 (dm, 8H; (H<sub>2</sub>C)<sub>3'-4'</sub>), 2.08 (m, 4H, (H<sub>2</sub>C)<sub>2'</sub>), 3.14 (t, 4H, (H<sub>2</sub>C)<sub>1''</sub>, <sup>2</sup>J = 7.6); 7.38 (d, 2H, H<sub>3,8</sub>, <sup>3</sup>J = 4.5 Hz), 7.98 (s, 2H, H<sub>5,6</sub>), 9.02 (d, <sup>3</sup>J = 4.8 Hz, 2H, H<sub>2,9</sub>); <sup>19</sup>F NMR (CDCl<sub>3</sub>) : δ -81.17 (CF<sub>3</sub>), -114.15 (CF<sub>2</sub>), -122.39 (CF<sub>2</sub>), -123.17 (CF<sub>2</sub>), -123.85 (CF<sub>2</sub>), -126.57 (CF<sub>2</sub>).

EIMS  $m/z$ : 1129.3  $[\text{M} + \text{H}]^{+}$ . High resolution EIMS: 1129.13,  $\text{C}_{36}\text{H}_{23}\text{F}_{34}\text{N}_2$

*Synthesis of [PdClMe(1)] (3).*

A solution of 4,4'-bis[4''-(F-octyl)-butyl]-2,2'-bipyridine (250 mg, 0.2265 mmol) in 10 ml of dichloromethane was added to a solution of [PdClMe(cod)] (50 mg, 0.1887 mmol) in 1 ml of dichloromethane. The yellow mixture was stirred at room temperature for 3.5 h. The complex was filtered off and washed with dichloromethane. This complex was not soluble enough in common deuterated solvents to allow its NMR spectra to be recorded. 0.27 g, (Yield = 96 %)

EIMS  $m/z$ : 1210.0  $[\text{M}-\text{Cl}-\text{CH}_3]^+$ , 1105.2  $[1+1]$

*Synthesis of [PdClMe(2)](4).*

A solution of 4,7'-bis[4''-(F-octyl)-butyl]-1,10-phenantroline (300 mg, 0.2659 mmol) in 10 ml of dichloromethane, was added to a solution of [PdClMe(cod)] (70 mg, 0.2642 mmol) in 5 ml of dichloromethane. The mixture was stirred at room temperature for 3.5h. The product was filtered off and washed with dichloromethane. This complex was not soluble enough in common deuterated solvents to allow its NMR spectra to be recorded. 0.30 g, (Yield = 87 %)

EIMS  $m/z$ : 1234.9  $[\text{M} + \text{H}-\text{Cl}-\text{CH}_3]^{+}$ .

*Synthesis of [PdMe(NCMe)(1)][BARF] (5).*

To a suspension of [4,4'-di-[4''-(F-octyl)-butyl]-2,2'-bipyridyl]chloromethyl-palladium (II) (61 mg, 0.048 mmol) in 5 ml of dichloromethane, sodium tetrakis 3,5-bis-(trifluoromethyl)phenyl borate (40.5 mg, 0.048mmol) and 0.3 ml of acetonitril were added. The mixture was heated for 1h at 40 C. The product was filtered off over celite and the solvent was removed under reduced pressure. The product was obtained as an oil. 77.7 mg (Yield = 78 %)

<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 0.97 (s, 3H, CH<sub>3</sub>) 1.71 (2m, 8H, (CH<sub>2</sub>)<sub>3''-4''</sub>), 2.10 (m, 4H, (CH<sub>2</sub>)<sub>2''</sub>), 2.32 (s, 3H, CH<sub>3</sub>CN), 2.74 (dt, 4H, (CH<sub>2</sub>)<sub>1''</sub>, <sup>2</sup>J = 7.6 Hz), 7.23 (d, 1H, J = 5.2 Hz), 7.34 (d, 1H, J = 5.2 Hz), 7.50 (s, 4H, BAR'), 7.68 (s, 8H, BAR'), 7.85 (s, 1H), 7.87 (s, 1H), 8.23 (d, J = 5.2 Hz, 1H), 8.36 (d, J = 5.6 Hz, 1H); <sup>19</sup>F NMR (CDCl<sub>3</sub>) : δ -62.95 (CF<sub>3</sub>, BARF), -81.43 (CF<sub>3</sub>), -114.93 (CF<sub>2</sub>), -122.51 (CF<sub>2</sub>), -123.31 (CF<sub>2</sub>), -124.15 (CF<sub>2</sub>), -126.73 (CF<sub>2</sub>).

#### Synthesis of [PdMe(NCMe)(2)][BARF] (6)

To a suspension of 4,7'-bis[4''-(F-octyl)-butyl]-1,10'-phenantroline (62.2 mg, 0.048 mmol) in 5 ml of dichloromethane, sodium tetrakis 3,5-bis-(trifluoromethyl)phenyl borate (40.5 mg, 0.048mmol) and 0.3 ml of acetonitril were added. The mixture was heated for 1h at 40 C. The product was filtered off over celite and the solvent was removed under reduced pressure. The product was obtained as an oil. 97.1 mg (Yield= 95 %)

δ <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): 1.05 (s, 3H, CH<sub>3</sub>), 1.74 (2m, 8H; (CH<sub>2</sub>)<sub>3'-4'</sub>), 2.05 (m, 4H, (CH<sub>2</sub>)<sub>2'</sub>), 2.29 (s, 3H, CH<sub>3</sub>CN), 3.12 (t, 2H, (CH<sub>2</sub>)<sub>1'</sub>, <sup>2</sup>J = 7.8 Hz), 3.17 (t, 2H, (CH<sub>2</sub>)<sub>1'</sub>, <sup>2</sup>J = 7.2 Hz), 7.04 (s, 4H, BAR'), 7.48 (d, 1H, J = 5,1 Hz), 7.57 (d overlapped, 1H), 7.61 (s, 8H, BAR'), 8.08 (d, 2H, J = 2,4 Hz), 8.51 (d, 1H, J = 5,1 Hz), 8.64 (d, J = 5.7 Hz, 1H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -62.95 (CF<sub>3</sub>, BARF), -81.28 (CF<sub>3</sub>), -114.74 (CF<sub>2</sub>), -122.43 (CF<sub>2</sub>), -123.22 (CF<sub>2</sub>), -124.04 (CF<sub>2</sub>), -126.65 (CF<sub>2</sub>).

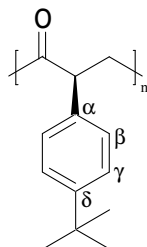
#### CO/TBS copolymerisation experiments

In standard catalytic experiment, a stainless steel high pressure reactor (V = 10 ml) equipped with thick-wall glass windows was filled under argon with a solution of catalyst precursor 5 or 6 (0.0125 mmol) in 2 ml of CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed in vacuum and then *tert*-butylstyrene (1.24 g, 7.75 mmol) was introduced into the reactor under argon. The reactor was charged with CO and CO<sub>2</sub> up to the desired pressure. The reactor was heated to 37 °C and stirred throughout the reaction. After the reaction, the autoclave was

cooled to room temperature and was carefully vented. The copolymer obtained was dissolved in  $\text{CH}_2\text{Cl}_2$  and precipitated by pouring the solution into 800 ml of rapidly stirred methanol. The product was filtered off, washed with methanol and vacuum dried.

#### Copolymer characterization

$\delta$   $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  7.02 (d,  $^3J = 8.0\text{Hz}$ , 2H,  $\text{H}_\beta$  or  $\text{H}_\gamma$ ), 6.62 (d,  $^3J = 8.0\text{Hz}$ , 2H,  $\text{H}_\gamma$  or  $\text{H}_\beta$ ), 4.14 (t,  $^3J = 6.0\text{Hz}$ , 1H, CH), 3.03 (dd,  $^2J = 17.6\text{Hz}$ ,  $^3J = 6.4\text{Hz}$ , 1H,  $\text{CH}_2$ ), 2.64 (dd,  $^2J = 17.6\text{Hz}$ ,  $^3J = 6.4\text{Hz}$ , 1H,  $\text{CH}_2$ ), 1.25 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  206.86 ( $-\text{C}(\text{O})-$ ), 149.76 ( $\text{C}_\delta$ ), 134.26 ( $\text{C}_\alpha$ ), 128.20 ( $\text{C}_\gamma$ ), 125.61 ( $\text{C}_\beta$ ), 52.86 (CH), 43.21 ( $\text{CH}_2$ ), 34.48 ( $\text{C}(\text{CH}_3)_3$ ), 31.48 ( $\text{C}(\text{CH}_3)_3$ ).



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## ***Chapter 7. Concluding Remarks***

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## Concluding Remarks

The main objective of this thesis was to study the use of alternative reaction media water and supercritical carbon dioxide for catalysed carbonylation reactions.

Rhodium-catalysed hydroformylation of 1-octene and 1-decene in biphasic aqueous systems was studied using such strategies to increase the mass transfer as adding cationic and anionic surfactants, methanol co-solvents and a dendrimeric molecule. The following conclusions were drawn:

- Adding an anionic surfactant to both systems increases the conversion to 98% (1-octene, Rh/dppbts) and 88% (1-decene, Rh/dppbts). But the selectivity to aldehydes decreases to 31% and 25%, respectively, and the reaction products are mainly isomers.
- Adding cationic surfactants to the systems increases both the activity and selectivity to aldehydes. However, high concentrations of cationic surfactants led to a loss of catalyst in the organic phase. When 1-octene was used as substrate, the regioselectivity to nonanal increased slightly (n/iso = 79/21). Using 1-decene and dppbts as a ligand the selectivity to aldehydes was as high as 97% and conversion was 63%. The system could also be recycled without affecting the conversion and selectivity.
- Adding methanol as a co-solvent increases the conversion of the hydroformylation of 1-octene when both ligands dppbts and dpppts (60 and 67 %, respectively) are used. When dppbts was used as a ligand, aldehyde selectivity increased to 90%.
- The use of dendrimer **12** did not improve the results.

The following conclusions were drawn about the hydroformylation of 1-octene in supercritical carbon dioxide:

- New P-donor ligands  $\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$  ( $n = 1, 2, 3$ ) containing branched alkyl chains were prepared.
- The cationic rhodium (I) complexes:  $[\text{Rh}(\text{cod})(\text{P}(\text{OC}_9\text{H}_{19})_3)_2]\text{PF}_6$ ,  $[\text{Rh}(\text{PPh}(\text{OC}_9\text{H}_{19})_2)_4]\text{PF}_6$  and  $[\text{Rh}(\text{PPh}_2(\text{OC}_9\text{H}_{19}))_4]\text{PF}_6$ , and palladium neutral complexes: *cis*- $[\text{PdCl}_2(\text{P}(\text{OC}_9\text{H}_{19})_3)_2]$ , *cis*- $[\text{PdCl}_2(\text{PPh}(\text{OC}_9\text{H}_{19})_2)_2]$  and *cis*- $[\text{PdCl}_2(\text{PPh}_2(\text{OC}_9\text{H}_{19}))_2]$  were synthesised.
- The X-ray structure of complex  $[\text{Rh}(\text{PPh}_2(\text{OC}_9\text{H}_{19}))_4]\text{PF}_6$  was determined.
- In hydroformylation conditions, the catalytic systems  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$  ( $n = 1, 2, 3$ ) in toluene mainly formed the species  $[\text{RhH}(\text{CO})\{\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n\}_3]$ . Minor amounts of  $[\text{RhH}(\text{CO})_2\{\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n\}_2]$  were also detected.
- Catalyst precursors  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$  ( $n = 1, 2, 3$ ) were not soluble in  $\text{scCO}_2$ .
- The catalytic systems  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$  ( $n = 1, 2, 3$ ) were active in the hydroformylation of 1-octene in supercritical carbon dioxide and in toluene.
- System  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{P}(\text{OC}_9\text{H}_{19})_3$  led to a total conversion of 98% and 86% of aldehyde selectivity in toluene.

- System  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{P}(\text{OC}_9\text{H}_{19})_3$  at 20 bar of syn gas 1:1, 250 bar of  $\text{CO}_2$  at  $100^\circ\text{C}$  provided conversion as high as 82% with a selectivity of 89%.
- Systems  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$  ( $n = 2, 3$ ) in toluene led to conversions as high as 89% and 95% but low aldehyde selectivities of 21% and 38%, respectively. When  $\text{scCO}_2$  was used, both systems improved aldehyde selectivity. The system  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}(\text{OC}_9\text{H}_{19})_2$  led to an aldehyde selectivity of 94% and a conversion of 70% in optimised reaction conditions.
- The catalytic system  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OCH}_2\text{C}_7\text{F}_{15})_3$  was found to be soluble in  $\text{scCO}_2$  at 10 bar of syn gas (1:1), 200 bar of  $\text{CO}_2$ , and  $80^\circ\text{C}$  of temperature.
- Activities (49-76% of conversion) and selectivities (74-86%) were good when the catalytic system  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OCH}_2\text{C}_7\text{F}_{15})_3$  was used in  $\text{scCO}_2$  at very low rhodium concentrations,  $0.48 \cdot 10^{-3} \text{ M}$ , and low P:Rh = 3 ratios.
- The system  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OCH}_2\text{C}_7\text{F}_{15})_3$  also proved to be active in the hydroformylation of 1-decene and styrene.

The copolymerisation of 4-*tert*-butylstyrene with CO in supercritical carbon dioxide was studied:

- N-donor ligands, bipyridine ( $\text{bipyR}_f$ ) and phenantroline ( $\text{phenR}_f$ ) with perfluorinated chains were synthesised.

- The neutral palladium complexes  $[\text{PdCl}(\text{CH}_3)(\text{BipyR}_f)]$  and  $[\text{PdCl}(\text{CH}_3)(\text{PhenR}_f)]$ , and the cationic palladium  $[\text{Pd}(\text{CH}_3)(\text{NCCH}_3)(\text{Bipy}_f)]\text{BARF}$  and  $[\text{Pd}(\text{CH}_3)(\text{NCCH}_3)(\text{Phen}_f)]\text{BARF}$  were prepared.
- The cationic palladium catalyst precursors were very soluble in supercritical carbon dioxide.
- The application of these cationic complexes to the copolymerisation of *tert*-butylstyrene with CO in  $\text{scCO}_2$  and in dichloromethane was studied. The productivities in both solvents are in the range of 10-15 g CP/g Pd but the molecular weight in  $\text{scCO}_2$  was twice ( $\approx 87000$  g/mol) the value obtained in  $\text{CH}_2\text{Cl}_2$  at the same conditions. The polydispersity in  $\text{scCO}_2$  was 1.2 in front of 5.3 obtained in  $\text{CH}_2\text{Cl}_2$ , indicating a narrow distribution of molecular weights in the supercritical solvent.

*Resum*

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## Resum

Durant aquests últims anys s'ha donat un interès creixent en el desenvolupament de processos químics que siguin respectuosos amb el medi ambient. El disseny de mètodes sintètics que maximitzin la incorporació dels materials utilitzats en el producte final, la minimització de residus i l'ús de catalitzadors són alguns dels principis de la Química Verda. En aquest context, la catàlisi homogènia ha aportat molts avenços, generant nous sistemes catalítics elevadament actius i selectius. Per altra banda, un dels majors problemes que presenta l'ús de catalitzadors homogenis és la separació i reciclatge del catalitzador.

L'objectiu d'aquest treball ha estat l'estudi de l'ús de dissolvents alternatius no tòxics, com l'aigua i el diòxid de carboni supercrític, en les reaccions catalitzades d'hidroformilació i copolimerització. L'ús de dissolvents alternatius en catàlisi homogènia implica fer modificacions en els catalitzadors convencionals per tal d'augmentar la solubilitat d'aquests en el medi. Per tant per tal d'assolir aquests objectius en aquest treball es va plantejar l'obtenció de nous sistemes catalítics que es poguessin utilitzar en els dissolvents aigua i diòxid de carboni.

La hidroformilació d'olefines lineals té un gran interès des del punt de vista industrial, ja que permet la síntesi de alcohols  $C_8$ - $C_{12}$  que s'utilitzen com a plastificants en la indústria dels polímers i també en la preparació de detergents. La hidroformilació del propè en medi aquós utilitzant sistemes de rodi associats a lligands hidrosolubles és un procés que es realitza a escala industrial i permet el reciclatge del catalitzador. No obstant, aquest procés està limitat a olefines de baix pes molecular, ja que es requereix una mínima solubilitat d'aquestes en aigua. En el capítol 3 s'estudia la hidroformilació de 1-octè i 1-decè en medi aquós utilitzant catalitzadors de rodi associats a les difosfines sulfonades hidrosolubles dpppts i dppbts. Com s'ha comentat la

problemàtica d'aquesta reacció radica en la poca solubilitat d'aquestes olefines en aigua, la qual cosa implica una baixa conversió de la reacció. Per tal d'augmentar la solubilitat d'aquestes olefines en l'aigua es van utilitzar diferents estratègies com van ser l'ús de co-solvents, tensioactius i una macromolècula dendrimerica, com a agents de transferència de fase. L'addició de un co-solvent orgànic que sigui miscible en aigua a una solució aquosa augmenta la transferència de massa del substrat en la fase aquosa. Els tensioactius són molècules, que consisteixen en dos parts de polaritat oposada: una part hidrofílica i una part hidrofòbica. El tensioactius disminueixen la tensió superficial de l'aigua i per sobre de una concentració determinada, anomenada concentració micel·lar crítica (cmc), formen en ella agregats com micel·les o vesícules. Aquestes micel·les tenen un exterior hidrofílic i un interior hidrofòbic i poden solubilitzar en el seu interior substàncies orgàniques com les olefines facilitant així el contacte entre el catalitzador i el substrat. En aquest estudi es van utilitzar dos tensioactius, un aniònic i un catiònic, en diferents concentracions. Finalment, els dendrimers són macromolècules que contenen un elevat número de ramificacions, degut a aquesta estructura ramificada els dendrimers tenen una forma tridimensional globular. Els dendrimers ambifílics, que tenen en el seu exterior grups iònics i un interior hidrofòbic, actuen com a micel·les unimoleculars. Per tant es va plantejar la síntesi d'un dendrímer que tingues grups iònics en la superfície i es va utilitzar com agent de transferència de fase. D'aquest estudi se'n van extreure les següents conclusions:

- ✓ l'addició de tensioactius aniònics al sistema augmenta la conversió del sistema en ambdós substrats fins a 98% (1-octè, Rh/dppbts) i 88% (1-decè, Rh/dppbts), malauradament la selectivitat en aldehids va ser baixa (31% i 25% respectivament), obtenint bàsicament isòmers com a productes de reacció.
- ✓ l'addició del tensioactiu catiònic va augmentar tant la conversió com la selectivitat en aldehids. Es destacable però, que a concentracions

elevades de tensioactiu catiònic es produeix una pèrdua de catalitzador en la fase orgànica. Emprant 1-octè com a substrat es va observar també un augment de la regioselectivitat del sistema (n/iso = 79/21). Amb el sistema Rh/dppbts- tensioactiu catiònic i 1-decè com a substrat, es va obtenir una elevada selectivitat en aldehids de 97% amb una conversió de 63%, aquest sistema va poder ésser reciclat mantenint l'activitat i la selectivitat en aldehids.

- ✓ l'addició de metanol com a co-solvent al sistema i 1-octè com a substrat va resultar en un augment de conversió tant amb la difosfina dppbts com amb la dpppts (60 i 67% respectivament). Utilitzant dppbts com a lligand es va observar també una elevada selectivitat en aldehids del 90%.
- ✓ L'addició del dendrimer al sistema no va millorar els resultats obtinguts.

El diòxid de carboni supercrític ( $\text{scCO}_2$ ) també s'ha estudiat com a medi de reacció. Un fluid supercrític és qualsevol substància que es troba per sobre de la seva temperatura i pressió crítica. En la regió supercrítica només existeix una sola fase que posseeix propietats entre un líquid i un gas. L'ús de diòxid de carboni supercrític com a dissolvent en catàlisi presenta moltes avantatges: no és tòxic, no és inflamable i presenta una elevada miscibilitat amb els reactius gasosos, la qual cosa el fa molt interessant ja que moltes reaccions catalitzades són de primer ordre respecte a un reactiu gasos. El diòxid de carboni supercrític és un dels fluids supercrítics més estudiats ja que té una temperatura i pressió crítiques accessibles ( $T_c = 31^\circ\text{C}$ ,  $P_c = 73 \text{ atm}$ ). El  $\text{scCO}_2$  és un dissolvent apolar, per tant en ell es poden dissoldre catalitzadors apolars. La modificació de lligands per obtenir catalitzadors solubles en  $\text{scCO}_2$  és un camp de recerca que s'ha desenvolupat molt en els últims anys. Les principals modificacions que s'han realitzat són la introducció de grups alquil o perfluoroalquil en substitució dels grups aril per tal de fer el lligands més apolars. S'ha descrit també que la introducció de cadenes

ramificades alquílques en el lligand augmenta la solubilitat d'aquest en el diòxid de carboni supercrític, per aquest motiu en el capítol 4 es descriu la síntesis de tres lligands fòsfor-dadors nous que contenen cadenes ramificades,  $\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})$  ( $n = 1, 2, 3$ ), amb l'objectiu d'utilitzar-los en la reacció d'hidroformilació de 1-octè utilitzant com a dissolvent  $\text{scCO}_2$ . Per tal d'estudiar la química de coordinació d'aquests lligands es van sintetitzar els complexos catiónics de Rh(I):  $[\text{Rh}(\text{cod})(\text{P}(\text{OC}_9\text{H}_{19})_3)_2]\text{PF}_6$ ,  $[\text{Rh}(\text{PPh}(\text{OC}_9\text{H}_{19})_2)_4]\text{PF}_6$  i  $[\text{Rh}(\text{PPh}_2(\text{OC}_9\text{H}_{19}))_4]\text{PF}_6$ , i els complexos neutres de pal·ladi (II): *cis*- $[\text{PdCl}_2(\text{P}(\text{OC}_9\text{H}_{19})_3)_2]$ , *cis*- $[\text{PdCl}_2(\text{PPh}(\text{OC}_9\text{H}_{19})_2)_2]$  i *cis*- $[\text{PdCl}_2(\text{PPh}_2(\text{OC}_9\text{H}_{19}))_2]$  i es va determinar la estructura de raig X del complex  $[\text{Rh}(\text{PPh}_2(\text{OC}_9\text{H}_{19}))_4]\text{PF}_6$ . Per mitjà d'estudis de ressonància magnètica i espectroscòpia infraroja a pressió es va determinar que en les condicions d'hidroformilació, els sistemes catalítics Rh/ $\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$  ( $n = 1, 2, 3$ ) emprant toluè com a dissolvent formen majoritàriament les espècies  $[\text{RhH}(\text{CO})\{\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n\}_3]$ . Els lligands  $\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})$  ( $n = 1, 2, 3$ ) no van donar lloc a sistemes catalítics solubles en  $\text{scCO}_2$  en les condicions estudiades. Malgrat això aquests sistemes van ser actius per la reacció d'hidroformilació de 1-octè en  $\text{scCO}_2$  i toluè. Amb el sistema Rh/ $\text{P}(\text{OC}_9\text{H}_{19})_3$  i toluè com a dissolvent, es va obtenir una conversió del 98% i una selectivitat en aldehids del 86%. Tot i que aquest sistema no és soluble en  $\text{scCO}_2$ , emprant les condicions apropiades de reacció (20 bar de gas de síntesi 1:1, 250 bar de  $\text{CO}_2$  i 100°C), es va poder obtenir una conversió del 82% i una elevada selectivitat en aldehids (89%). Amb els sistemes Rh/ $\text{PPh}_{3-n}(\text{OC}_9\text{H}_{19})_n$  ( $n = 2, 3$ ) en toluè, es van obtenir elevades conversions de 89% i 95% respectivament, però la selectivitat en aldehids va ser baixa (21% i 38%). Quan es va utilitzar  $\text{scCO}_2$  com a dissolvent es va poder obtenir una millora de la selectivitat en aldehids. Amb el sistema Rh/ $\text{PPh}(\text{OC}_9\text{H}_{19})_2$ , i les condicions de reacció optimitzades es va obtenir fins a un 94% de selectivitat en aldehids amb una conversió del 70%.

Els lligands que contenen cadenes perfluorades han resultat ser molt efectius per a la solubilització de sistemes catalítics en  $\text{scCO}_2$ . En el capítol 5 es descriu l'aplicació del lligand  $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OCH}_2\text{C}_7\text{F}_{15})_3$  a la reacció d'hidroformilació de 1-octè, 1-decè i estirè catalitzada per rodi. Aquest sistema va resultar soluble en  $\text{scCO}_2$  a les següents condicions de reacció: 10 bar de gas de síntesi (1:1), 200 bar de  $\text{CO}_2$  i  $80^\circ\text{C}$  de temperatura. Emprant concentracions molt baixes de rodi ( $0.48 \cdot 10^{-3} \text{ M}$ ) i una relació P:Rh = 3, es van observar bones activitats (conversió entre 49 i 76%) i selectivitats en aldehyds (74-86%) per a la hidroformilació d'1-octè. El sistema també va resultar actiu per la hidroformilació d'1-decè i estirè.

La reacció de copolimerització d'alquens i monòxid de carboni catalitzada per pal·ladi permet la síntesi de policetones. Aquests copolímers tenen elevat interès industrial ja que són termoplàstics bio- i fotodegradables. Aquesta reacció ha estat molt estudiada en dissolvents orgànics convencionals, com diclorbenzè o metanol. Els sistemes més efectius per a la copolimerització d'olefines i CO es basen en complexos catiónics de pal·ladi que continguin lligands bidentats nitrogen- o fòsfor-dadors. Per a la copolimerització de *tert*-butilestirè i CO, un dels sistemes més actius està basat en l'ús de catalitzadors de pal·ladi amb lligands N-dadors: bipyridina i fenantrolina. En el capítol 6 d'aquesta tesi es descriu el primer exemple de copolimerització de *tert*-butilestirè i monòxid de carboni catalitzada per sistemes de pal·ladi emprant com a medi de reacció el diòxid de carboni supercrític. Per assolir aquest objectiu es van sintetitzar lligands bipyridina i fenantrolina amb cadenes perfluorades per tal d'augmentar la solubilitat del sistema catalític en  $\text{scCO}_2$ . Es van sintetitzar els complexos neutres de pal·ladi  $[\text{PdCl}(\text{CH}_3)(\text{Bipir})]$  i  $[\text{PdCl}(\text{CH}_3)(\text{Phen})]$ , i els complexos catiónics de pal·ladi  $[\text{Pd}(\text{CH}_3)(\text{NCCH}_3)(\text{Bipir})]\text{BARF}$  i  $[\text{Pd}(\text{CH}_3)(\text{NCCH}_3)(\text{Phen})]\text{BARF}$ . Els complexos catiónics de pal·ladi van mostrar una elevada solubilitat en  $\text{scCO}_2$ . La reacció de copolimerització de *tert*-butilestirè i monòxid de carboni es va estudiar tant en  $\text{scCO}_2$  com en diclorometà com a dissolvents. Els resultats van mostrar

que el sistema catalític presenta una activitat similar en diòxid de carboni supercrític a la que s'observa amb diclormetà però en el medi supercrític els copolímers tenen pesos moleculars que arriben a ser el doble del que s'obté en el dissolvent orgànic i amb polidispersitats molt més baixes.