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UNIVERSITAT ROVIRA I VIRGILI
Departament de Química Física i Inorgànica

CARBONYLATION REACTIONS IN SUPERCRITICAL CARBON DIOXIDE

Memòria presentada per

Clara Tortosa Estorach

Tarragona, Desembre 2007

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La Dra. ANNA MARIA MASDEU I BULTÓ, Professora Titular del Departament de Química Física i Inorgànica de la Facultat de Química de la Universitat Rovira i Virgili

CERTIFICA:

Que la memòria que porta per títol "CARBONYLATION REACTIONS IN SUPERCRITICAL CARBON DIOXIDE", que presenta Clara Tortosa Estorach per a obtenir el grau de Doctor en Química, ha estat realitzada sota la meva direcció en el Departament de Química Física i Inorgànica de la Universitat Rovira i Virgili.

Tarragona, Novembre de 2007

Dra. Anna Maria Masdeu i Bultó

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Agraïments

Un cop ha arribat este moment on l'escriptura d'esta tesi ja està finalitzada, és l'hora d'agrair a totes aquelles persones que han fet que tot això sigui possible.

En primer lloc he de donar les gràcies de tot cor a la meva directora de tesi, la Dra. Anna Maria Masdeu i Bultó. Anna, moltes gràcies pel suport que m'has donat, la confiança que has ficat en mi i la dedicació que has tingut durant estos anys. Gràcies per ajudar-me dintre i fora del laboratori, per donar-me l'oportunitat de realitzar estades a l'estranger i assistir a molts congressos i sobretot per animar-me a tirar endavant aquesta tesi.

A la Dra. Carmen Claver, per acceptar-me al grup i per comptar amb mi quan ha fet falta. I com no per tots els soparets tan divertits a casa teva.

També agrair a la resta de professores del grup d'Homogènia, Núria, Elena, Aurora i Montse i a les professores del grup d'Heterogènia Pilar i Yolanda per tenir sempre la porta del despatx oberta i ajudar-me quan ha fet falta. I un agraïment especial per a Arantxa, per l'ajuda al laboratori i també a fora, te dec uns quants litres de gasolina, jeje.

Durant tots aquests anys, he conegut a molta gent que també han aportat el seu granet d'arena per tenir ara aquesta tesi a les mans. La llista és una mica llarga, espero no deixar-me a ningú. Primer als meus

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companys de batalla, Jesús i Bianca, que hem estat lluitant els 4 anys colze amb colze, al final tenim la victòria (esperem, jeje). Jesús, moltes gràcies per tot, sempre animant-me, fent-me riure i ajudant-me en tot el que has pogut. Té desitjo molt bona sort en aquesta nova etapa. Bianca, m'ha costat resumir en dues línies tot el que volia agrair-te. Gràcies per tenir sempre la teva casa oberta, per estar disposada a ajudar-me al labo, per totes les cervesetes, etc... que hem passat juntes. Bé, *Superstar* te desitjo lo millor per estes europes. Marta, a tu també moltes gràcies per ensenyar-me el món supercrític, jeje, i estar sempre disposada a ajudar-me. Dra. Yvette, en un ritme o un altre al final tots anem arribant,jeje. Vanesa, a vore si el Nàstic torna a 1era., molts d'ànims, ja queda molt poquet, una miqueta de paciència i l'últim esforcet. Espero que tot et vagi molt bé i tingues molta sort. Aitor, cantautor, quines rises m'has fet passar, segueix així tio, ets el millor, espero que et vagi bé i que trobes a la teva "jipa". Eva, sort, ja et queda poc, paciència. Als superdoctors del grup, Cyril, Anna, Ali, gràcies per intentar organitzar el caos i estar sempre disposats a ajudar-me. Als que ja no estan, Rosa, quin mes que vam passar a Toulouse, merci. Dr. Eduardo, és un tràmite, no? jeje. Te deseo lo mejor en tu nueva etapa en tu tierra, mucha suerte. Amaia, encara que no vam compartir laboratori, hem compartit feina aquest últim any, gràcies per ajudar-me en el món de la "copo" i en estar sempre disposada a discutir de química, espero que et vagi tot molt bé. Gràcies també a les heterogènies, Olga i Isa, compartint molts dinars a l'office i al seminari durant estos anys. I als més nous, Martha i Ariadna, les meves companyes del labo 218, molta sort en el món del CO_2 supercrític i ànims. A Angélica, Carolina, Verònica, Javi, Dolores que us

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vagi tot molt bé. També als companys del 3r pis, els orgànics, als polimèrics que m'han ajudat quan he rondat per dalt en la caracterització dels copolímers, a la Mercè que hem compartit molts quilòmetres juntes. Als azucarillos, en especial a la Patricia que a part d'una gran companya de laboratori i d'estudi, també és una gran amiga.

També vull donar les gràcies a la Maria José perquè a part de facilitar-me la feina al laboratori i ajudar-me en tot, hem compartit laboratori i moltes xerrades durant aquests anys a la facultat nova. També, al Ramon, moltes gràcies per la paciència que sempre has tingut i la teva dedicació en resoldre tots els problemes de ressonància.

I would like to thank Prof. Joó and Prof. Monflier to accept review this thesis. Specially, Prof. Monflier to send me cyclodextrines to perform part of this work.

During my Ph-D I have been two times in Lausanne (Switzerland) that I have a great memory of my stays there and people which worked there, specially Andy and Celine. I would like to thank Dr. Gabor Lawrenczy for his patients teaching me the techniques for HPNMR and thanks for the nice time I spent in EPFL. El segon any de tesis, vaig estar un mes a Toulouse (França) amb la Prof. Montserrat Gómez, gràcies per ensenyar-me el món de les nanopartícules, que encara que no estigui reflectit en aquesta tesi espero que aquest projecte tiri endavant. Finally, the last year I have been two months in Aachen (Germany) working in the group of Prof. Leitner, working in $scCO_2$, trying to get kilograms of

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polymer. I have to thank Dr. Franciò to make it possible and Prof. Leitner to accept me in his group and for the nice time I spent in Aachen.

També voldria agrair a la gent de fora del laboratori, a tots els amics que m'heu fet passar molts bons moments i sempre heu tingut la paciència d'aguantar-me i ensenyar-me que la vida es molt més que química.
Per acabar, voldria agrair a la meva família, sobretot a vatros: papa, mama i Blanca per ajudar-me a arribar fins aquí, perquè mai vos heu cansat d'animar-me a tirar endavant. Sense vatros no podria estar escrivint estes línies. Moltes gràcies. I als meus iaios que des d'algun lloc han fet força per que arribi fins aquí.

I, un GRÀCIES per tu Edu, que durant tot aquest temps m'has "apoiat" en totes les decisions i m'has animat a mirar cap endavant tot i l'esforç que també suposava per tu.

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Investigar es ver lo que todo el mundo ha
visto, y pensar lo que nadie más ha pensado

Albert Szent-Györgi (1893-1986)

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Chapter 1

General Introduction

Homogeneous catalysis has achieved an important role in chemical industries in the last decades. A recent aspect of this role that is receiving increasing attention is the use of alternative reaction media that solve the environmental problems associated with many of the traditional volatile organic solvents. The use of non-conventional reaction media also provides opportunities for facilitating the recovery and recycling of the catalyst. Among these reaction media, supercritical carbon dioxide is an interesting solvent in the context of green chemistry and catalysis in several mono- and biphasic systems.

This introductory chapter reviews the previous literature on carbonylation reactions of hydrocarboxylation, hydroesterification, copolymerisation and hydroformylation of alkenes in organic solvents. The use of supercritical carbon dioxide as an alternative solvent to perform these carbonylation reactions is also discussed.

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1.1. Homogeneous catalysis

A catalyst is a substance that increases the rate at which a reaction obtains equilibrium, without being consumed with the reagents. The catalyst is combined with the reagents to generate intermediates species, facilitating their transformation into the products by the step reaction of the catalytic cycle (Figure 1).

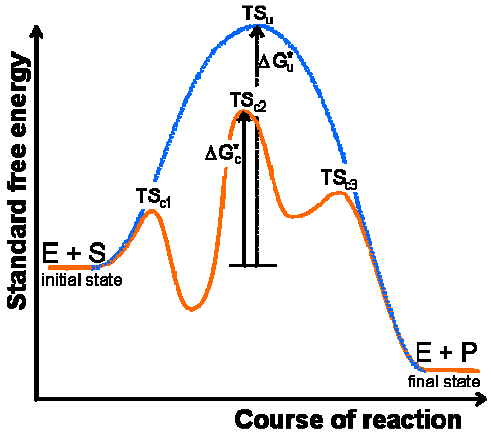

Figure 1. Effect of the catalyst on the reaction.

Homogeneous catalysts, which are in the same phase as the reagents and products, have many advantages compared with heterogeneous catalysts. For example, they have higher activity and selectivity, they are active at milder reaction conditions, they do not have diffusion or mass transfer problems, they can be easily sterically and electronically modified and they present lower sensitivity to catalyst poisons [1]. However, the primary drawback of homogeneous catalysis is the separation and recycling of the catalyst. Within the past few decades, methods and techniques in homogeneous catalysis have

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achieved remarkable progresses on catalyst separation and recycling. One example is the immobilisation of the catalyst on liquid or solid supports, which converts catalytic systems into multiphase systems [2]. In 1972, Manassen and Joó were the first to systematise the idea of multiphase catalysis [3]. Manassen suggested the use of two immiscible liquid phases, one containing the catalyst and the other containing the substrate, and hence the general form of a biphasic catalyst [4].

The immobilisation of the catalyst on the surface of an organic or inorganic support has been largely studied [5-8]. Another growing application is the use of environmental solvents such as water or carbon dioxide, which enable the recycling of the catalyst [9]. Specifically, supercritical carbon dioxide has been proposed as an environmental media for catalytic reactions as well as in the extraction processes, which allows recycling the catalyst from the reaction products [10,11].

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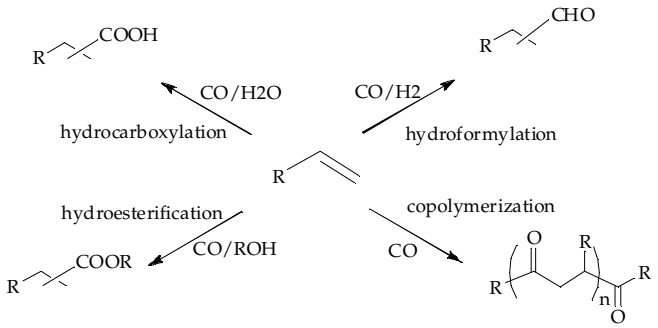
1.2. Carbonylation reactions

Carbonylation reactions involve the introduction of a molecule of carbon monoxide (CO) into substrates such as olefins, alkynes and alkylic, vinylic and arylic species. Additionally, the carbonylation of alcohols, halides and amines have been studied. The carbonylation processes studied in this work are hydroformylation, hydrocarboxylation, hydroesterification and copolymerisation (Scheme 1), all of which are useful methods for generating C-C bonds and obtaining aldehydes, carboxylic acids, esters and polyketones. Rhodium, platinum, nickel, cobalt, palladium and ruthenium-based complexes have been used as catalysts for these processes and are usually combined with different ligands [12,13,1a]. Several ligands have been applied in metal-catalyzed carbonylation reactions and the chemoselectivity and regioselectivity has been determined for these processes. An overview of all the useful ligands in carbonylation reactions is an impossible task. Here, we will very briefly mention the most common ligands in the carbonylation reactions, P- and N- donor ligands.



Scheme 1. Carbonylation of olefins.

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1.2.1. Phosphorus-donor ligands

Phosphorus donor ligands are used in many metal-catalysed carbonylations. Ligands such as phosphines (**1**), phosphites (**2**), phosphorus amides (**3**), phosphoramidites (**4**), phospholes (**5**) and pyrrolylphosphines (**6**) have different electronic and steric hindrance properties, thus changing the substituents of the phosphorus atom (Figure 2). Phosphine and phosphite ligands can be either strong σ-donors with ^{t}Bu substituents for example, or strong π-acceptors, with fluroalkoxy substituents for instance. Using mixtures of all possible groups can provide intermediate properties. Instead of carbon or oxygen, nitrogen substituents can also be used as the connecting atom leading to amide or amidites formation. The advantage of nitrogen substituents as compared to those of oxygen is the possibility for the modification of the steric hindrance near the metal centre, since the nitrogen atom has an extra linkage [14]. A special type of phosphine is the phosphole (**5**), which has been used as a group similar to diphenylphosphine, although it behaves as a slightly bulkier group due its rigidity. However, it has different electronic properties since it has a higher χ-value. The χ-value is an electronic parameter that measures the sum effects of electron donating and accepting properties of the phosphorus ligands [15].

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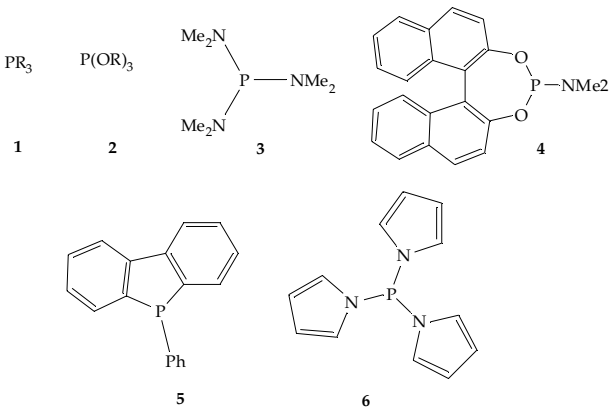

Figure 2. Phosphorus ligands used in carbonylation.

The steric bulk effect of the monophosphines is measured by the Tolman's cone angle (θ) [15]. It is defined according to Figure 3 and includes all the atoms that are in the ligand environment.

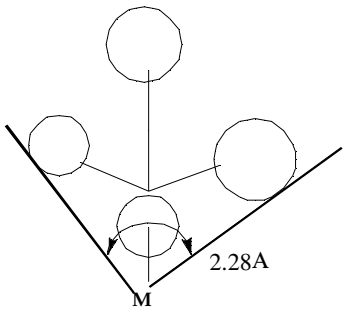

Figure 3. Tolman's cone angle.

The major difference between mono- and bidentate ligands is the ligand backbone, which keeps two phosphorus donor atoms at a specific distance (Figure 4). This distance is specific and characteristic for each

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ligand just like the flexibility of the backbone. The bite angle defines the preferred angle between the metal and two phosphorus atoms [16].

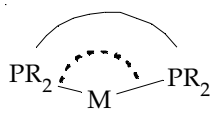

Figure 4. Bite angle.

The effect of the bite angle can be both electronic and steric. The steric effect is related to steric interactions (L-L or L-substrate) generated when the bite angle is modified by changing the backbone. These interactions can change the transition state's energy and the resting states, thus modifying the activity or selectivity of the catalytic system [17]. The electronic component of bite angle is associated with electronic changes in the catalytic centre due to the determination of the metal hybridisation by the bite angle, and thus is also associated with metal orbital energies and reactivity. This can affect the initial, transition or final state of the reaction [17].

1.2.2. Nitrogen-donor ligands

Nitrogen-donor ligands are also very common in homogeneous catalysis. Nitrogen-donor ligands (Figure 5), especially pyridine (**7**) and bisoxazolines (**8**), are much more stable than phosphines, and are therefore preferred for oxidation catalysis. The bonding characteristics of pyridine (sp^2 hybridised nitrogen-centred ligand) and phosphorus

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donor ligand are very different. Both are good σ-donors and poor π–acceptors ligands, . but the π–acceptor ability of P-donor ligands can be easily changed. Diimines (**9**) are also used for polymerisation of alkenes with palladium catalysts [18, 19]. Bipyridine (**10)** or phenantroline (**11**) palladium complexes have also been used in copolymerisation of alkenes with carbon monoxide [20]. Asymmetric nitrogen ligands such as bisoxazolines (**8**) have been afforded an important role in the carbonylation catalysis [20,21]. Pyridine-imidazoline ligands (**12**) have also been used in the Pd-copolymerisation of CO and arenes, and have the possibility of electronic variation by substitution at the amine-nitrogen atom [22,23] (Figure 5).

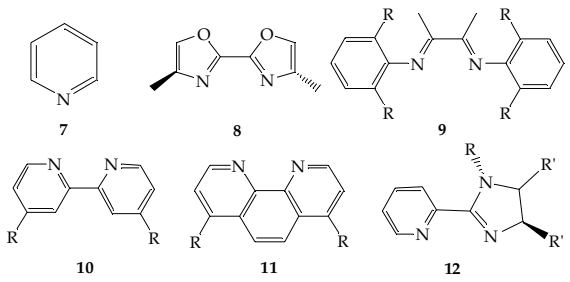

Figure 5. Nitrogen donor ligands.

Mixed nitrogen- and phosphorus-donor ligands such as oxazoline-phosphines also have wide application in catalysis [24].

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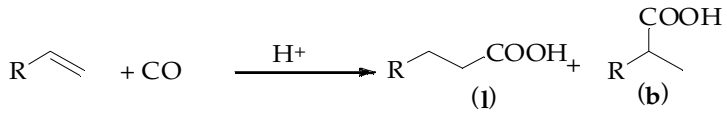
1.3. Hydrocarboxylation

Hydrocarboxylation or hydroxycarbonylation of alkenes to generate acids involves a single insertion of a molecule of carbon monoxide and a molecule of water to an alkene. The main products of the reaction in the absence of isomerisation are the linear (l) and branched (b) carboxylic acids (Scheme 2).



Scheme 2. Hydrocarboxylation reaction.

The hydrocarboxylation has important applications in industrial processes. In the mid-1950s, Reppe (BASF) developed the synthesis of propionic acid from ethylene and water, using a nickel precursor [25]. Another relevant application is the carbonylation of vinyl arenes to obtain 2-phenylpropionic acid derivatives, which are used as anti-inflammatory drugs [12,26].

Among all the metal precursors, the most used catalytic system has historically been palladium associated with phosphorus ligands and halides, although there are other studies using catalyst precursors such as cobalt, nickel, rhodium, iridium, copper, iron or platinum-based complexes [27].

In the last few decades, different palladium systems have been developed to improve the selectivity on the hydrocarboxylation of alkenes. In several studies it has been observed that the regioselectivity

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depends on many reaction parameters including ligand properties (electronic and steric), counterion, co-catalyst addition or substrate. For example, the branched acids of different substrates were regioselectively obtained in the absence of phosphines with a $PdCl_2/CuCl_2/HCl/O_2$ catalytic system [28]. In the hydrocarboxylation of 1-octene with Pd(II)/monophosphine systems, the reported l/b ratio ranged from 0.5 to 3.6 [29]. It was also observed that the phosphines with higher cone angle (θ) had an increased regioselectivity in the branched regioisomer. Similar behaviour was also observed for the hydrocarboxylation of styrene using as a Pd(II) catalyst precursor $[PdCl_2(PhCN)_2]$ and Pd(0) $[Pd_2(dba)_3]$ with different monophosphines (**13-17**, Figure 6). The absence of chloride anions in the metal precursor leads to a decreased conversion and regioselectivity, and phosphines with basic properties did not present catalytic activity [30]. Later, high selectivities in the branched acid was obtained for 4-methylstyrene and α-(4-methylphenyl)propionic acid using $PdCl_2$-$CuCl_2$-PPh_3 system [31].

Regarding palladium catalytic systems with diphosphines, Alper *et al.* reported up to 86% selectivity on the linear acid in the hydrocarboxylation of styrene using palladium acetate with bis(phenylphosphino)butane (dppb) as the catalyst precursor and oxalic or formic acid as the proton transfer agent [32].

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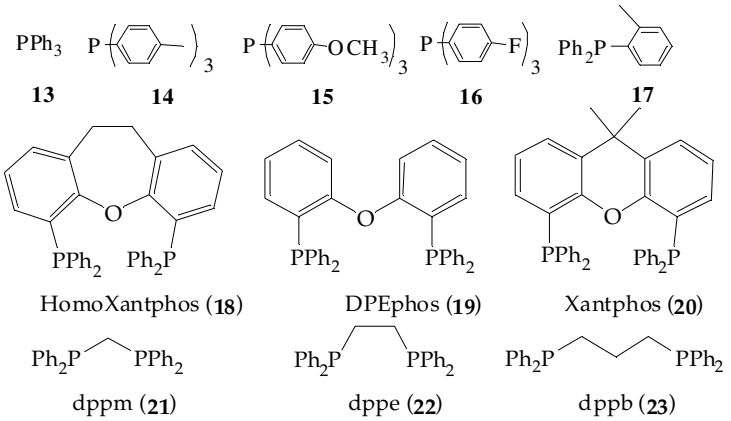

Figure 6. Phosphines ligands used in styrene hydrocarboxylation.

The *bite angle* effect of different diphosphines (**18-23**, Figure 6) were studied using palladium(II) and palladium(0) catalytic precursors [30]. As was observed previously, bidentate ligands favour the linear acid [32].

Diphosphines with less than 90º bite angle showed low conversion and by-products were formed. Ligands with higher bite angle increased the chemoselectivity to the acids and provided good activities. Unlike monophosphines, Pd(0) precursor gives similar results as those obtained with Pd(II).

High selectivities have been obtained using other types of ligands such as arenethiolates with palladium-based complexes [33]. S, S-thiolate-thioether palladium complexes were also used in this reaction associated with triphenylphosphine to obtain activities up to 90% and

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regioselectivities to the branched isomer up to 89% for the hydroxycarbonylation of styrene [34].

The counter anion has an important role on the regioselectivity [35]. This counterion may come from the metal precursor, such as [$PdCl_2L_2$], or from the added acid. Del Río *et al.* have studied this effect on the hydrocarboxylation of styrene using [$Pd_2(dba)_3$] and PPh_3. When the reaction was performed without acid and only with water, the reaction did not take place. Using HCl, HBr and HI the conversion and regioselectivity on the branched isomer decreased in the order $Cl^->Br^->I^-$. When oxalic acid was used, high regioselectivity in the branched acid was obtained (83%), although the activity was low (36%). When we changed the acid to another with weak coordination anions such as *p*-toluenesulphonic acid (*p*-$CH_3C_6H_4SO_3H$), the regioselectivity was inverted to the linear acid (75%). Changing the mono- to diphosphine ligands, the best results were obtained with oxalic acid or water.

Two possible mechanisms were proposed to explain the regioselectivity that was observed when the chloride anion was used. With monophosphines, a neutral species [$PdHCl(PPh_3)$(styrene)] is formed, which favours the branched isomer; when using diphosphine ligands, the cationic intermediate formed [PdH(P-P)(styrene)]Cl favours the linear isomer.

One interesting aspect of the regioselectivity is the substrate properties effect. In vinylarenes, the effect is more relevant due the π-benzyl stabilization, which favours the formation of the branched acid (Scheme 3). For simple alkenes, the steric effect is provided by the

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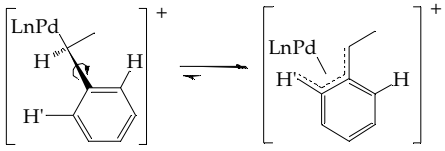
substituents on the alkene [32]. As these have a much bulkier structure, the linear acid is favoured.



Scheme 3. Equilibrium between $^{1}\eta$-benzyl species and $^{3}\eta$-benzyl species.

The electronic properties of the substrate do not affect the regioselectivity. The hydrocarboxylation of 3,3,3-trifluoropropene and pentafluorostyrene substrates with mono- and diphosphines was studied and the expected results were obtained. In Pd-monophosphine systems the major product was the branched isomer, while the linear isomer was the dominant species when Pd-diphosphines were used [36].

In summary, the regioselectivity is dependent upon the ligand used, the counteranion and the bulky structure of the substrate. Thus, lead to suggest a mechanism for the reaction to explain the final products obtained.

The mechanism proposed for the hydrocarboxylation of styrene with Pd-monophosphine systems involves the formation of active Pd-hydride species, the insertion of carbon monoxide and alkene to lead to the Pd-alkyl and Pd-acyl species and nucleophilic attack of the water produces the corresponding acids (Scheme 4) [37,38].

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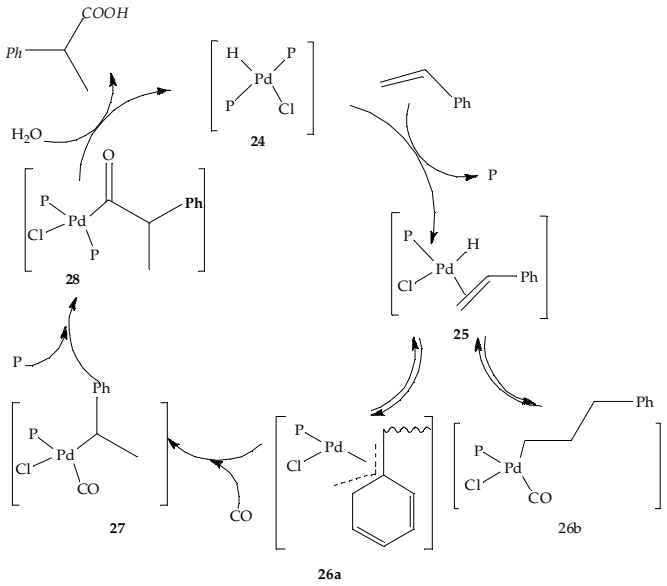

Scheme 4. Catalytic cycle proposed for the hydrocarboxylation of styrene with palladium- monophosphines complexes.

For the system with monophosphines, the steric effect favours the *trans* position of the ligands. Substitution of the ligand by the substrate forming the species **25** (Scheme 4) results in π-benzyl stabilization and the formation of the branched alkyl species **27** to obtain the branched acid. In the case of linear alkenes, the steric requirements of the substrate will favour the formation of the linear acid. In the case of diphosphines, the species will be *cis* and, therefore, favour the formation of the linear product.

Del Río *et al.* studied the mechanism by high pressure NMR spectroscopy (HPNMR) [39]. Hydride species have been detected by HPNMR despite their very unstable intermediates. They are efficient

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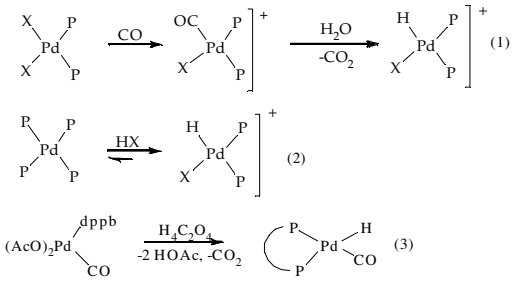
initiators despite their instability since their insertion reaction with alkenes is extremely fast. The formation of hydride species in the hydrocarboxylation conditions can occur by different ways (Scheme 5): (1) By elimination of carbon dioxide of a Pd-COOH species formed by water attack to a coordinated carbon monoxide [40]; (2) By oxidative addition of a strong acid over a zero palladium species; (3) The attack of the oxalic acid as was proposed by Alper *et al.* in 1992. In this case, the hydride species is formed from the palladium(II) by attack of the acid to form the hydride and yield carbonate and carbon dioxide (3) [32].



Scheme 5. Palladium hydride formation.

The ligand used in the complexes is important for the stabilization of the hydride. Diphosphines do not stabilize these hydride complexes and tend to form a binuclear species $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)(P\text{-}P)_2]$, which has been isolated and characterised (Scheme 6). However, a basic monophosphine such as PEt_3, PCy_3 or PBu_3 can stabilize the hydride species.

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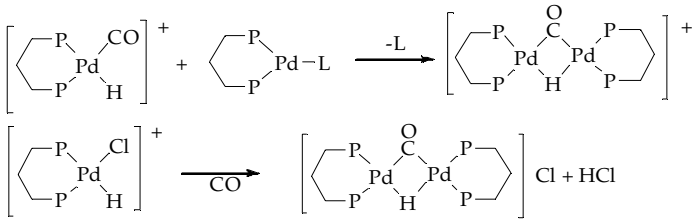

Scheme 6. Formation of the palladium (I) dimer.

The alkyl species $[Pd(CH_2Ph)Cl(PPh_3)_2]$ has also been synthesised and characterised by the oxidative addition of benzyl chloride on the palladium zero species $[Pd(PPh_3)_4]$ [41,42].

The acyl species is formed by 1,1-insertion of a carbon monoxide molecule into the metal-alkyl bond. In 1993, Petrov *et al.* detected the species $[Pd(COEt)(PPh_3)_2]$ in the hydrocarboxylation of 1-etene [43]. Concurrently, Elsevier *et al.* identified the species $[Pd(COMe)(CO)(bdpp)]BF_4$, an acyl species formed with the diphosphine ligand 2,4-bis(diphenylphosphino)pentane (bdpp) [44].

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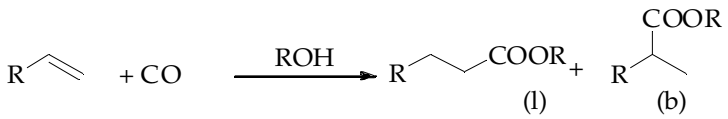
1.4 Hydroesterification

The hydroesterification or alcoxycarbonylation reaction is the formation of carboxylic esters from alkenes by reaction with carbon monoxide and alcohol. The main products obtained are the linear (l) and the branched (b) esters (Scheme 7).



Scheme 7. Hydroesterification of 1-alkenes.

The hydroesterification is industrially important for the synthesis of methylmetacrilate and other intermediates in its synthesis such as methylpropanoate [45,46]. Another relevant application is the hydroesterification of vinyl alkenes for the synthesis of 2-phenylpropionic acids, which are used as anti-inflammatory drugs [26].

As well as in hydrocarboxylation, the regioselectivity is an important parameter of the reaction, as is the enantioselectivity of the chiral center in the branched isomer. Two mechanisms have been proposed for this reaction, which imply essentially the same steps as in hydrocarboxylation. One involves the metal-hydride species (**a**, Scheme 8) and was proposed for the fist time by Knifton in 1976 [47]. The other mechanism occurs through the carboalkoxy species (**b**, Scheme 8) and was proposed by Milstein in 1988 [48].

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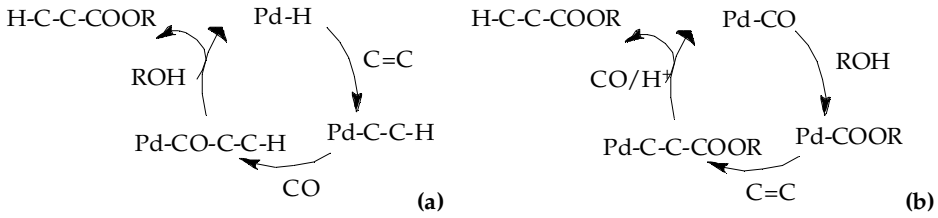
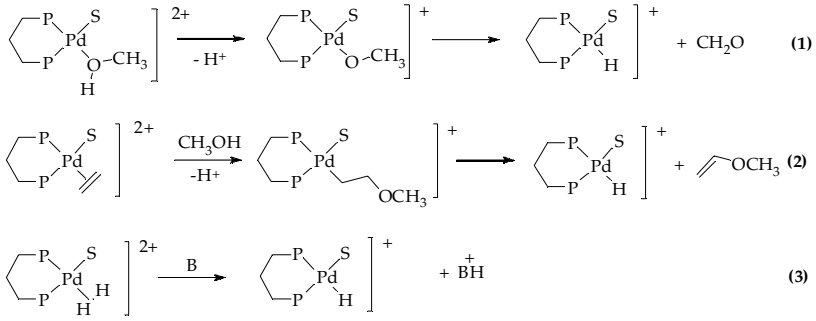


Scheme 8. Schematic mechanism for hydroesterification of alkenes: (**a**) hydride mechanism; (**b**) carboalkoxy mechanism.

The palladium hydride species can be generated in the same ways as in the hydrocarboxylation reaction (Scheme 5), but also by β-hydrogen elimination from a palladium methoxide (1), a Wacker-type oxidation of ethene (with methanol) (2) or a hydrogen activation (in the presence of hydrogen) (3) (Scheme 9) [1c].



Scheme 9. Palladium hydride formation as initiation reaction.

Generally, the hydride mechanism occurs faster than the alkoxy mechanism. In the hydride mechanism, the ester is formed from the attack of the alcohol to the acyl intermediate species. This termination step may occur in different ways (Scheme 10). One possible mechanism

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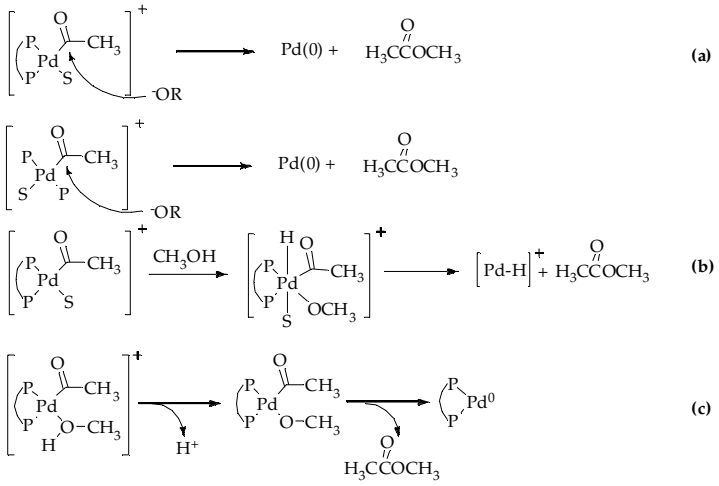
is the direct out-sphere attack of an alcohol or alkoxy to the acyl carbon atom (Scheme 10a), which is accessible for both *cis* and *trans* phosphine complexes. After the reaction, the formed palladium(0) complex must undergo oxidative addition of acid to regenerate the hydride active species. Very often, under the reaction conditions, palladium(0) bears an oxidative addition and dimerisation to form the very stable dimer (Scheme 6) [1c].



Scheme 10. Ester formation mechanism.

The second mechanism involves the oxidative addition of methanol to the divalent acylpalladium complex (Scheme 10b). This has the advantage that the hydride initiator is formed in one step [49,50]. The last possibility for ester formation is through reductive elimination from acyl-alcoxy-palladium complexes, formed by deprotonation of the

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alcohol adducts (Scheme 10c). This step requires the *cis* position of the alkoxide and acyl fragment (Scheme 10c).

It has been shown that the ligand plays a relevant role in the catalytic cycle. Depending on the ligand there are different chemoselectivities and the reaction proceeds to the formation of esters, oligomers or polyketones. Initial studies by Drent and Budzelaar showed that using monophosphine ligands favoured the formation of esters, however diphosphines favoured the chain growing to form polyketones [51].

Later, it was demonstrated that the diphosphine structure is also very important to selectivity. On one hand, if the diphoshine is coordinated to the metal complex in *cis* position, the formation of polyketones is favoured. However, if the diphosphine could be coordinated in *trans* due to a large chain skeleton or high bite angle, then the formation of ester is preferred. The steric hindrance of a diphosphine could also lead to ester formation due to the fact that a bulky diphosphine favours the termination step when the acyl and alcohol are in the *cis* position [44,52].

Different authors have studied the mechanism of the reaction to understand all the experimental results obtained [53,54,55]. Finally, Seayed *et al.* proposed a mechanism for the hydroesterification of styrene with $Pd(OAc)_2$ and PPh_3 shown in Scheme 11 [54].

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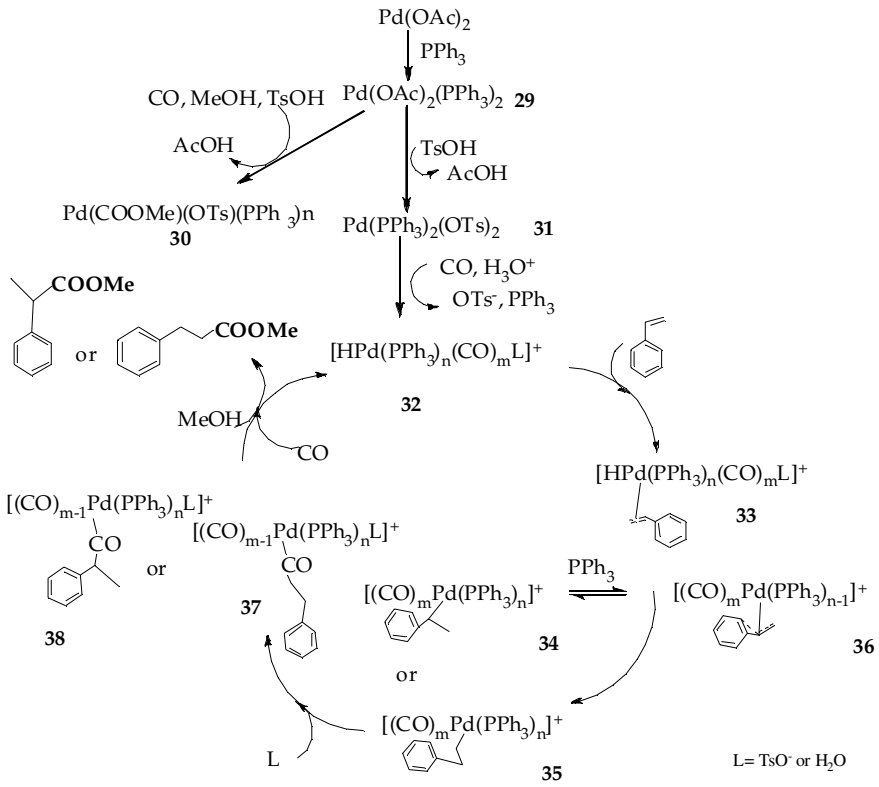

Scheme 11. Hydride mechanism for hydroesterification of styrene.

The catalytic precursor $Pd(OAc)_2$ reacts with the ligand to form the Pd(II) complex $[Pd(OAc)_2(PPh_3)_2]$ (**29**), which is converted into the hydride cationic species (**32**) by reacting with acid, CO or methanol [56]. Part of this catalyst could be transformed into the inactive species (**30**) depending on the methanol concentration. Depending on the CO pressure, the hydride species (**32**) can contain one or two molecules of carbon monoxide. The styrene, which has nucleophilic character, is easily π-coordinated to the cationic species (**33**) and then by 1,2-insertion

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the alkylic species are formed. Depending on the properties on the palladium centre environment and the reaction media, the system will form linear alkyl species **35** or the branched species **34**. Next, the linear (**37**) or the branched (**38**) acyl are formed by migration of CO to the metal alkyl bond. Finally, the corresponding esters are obtained by reaction with the alcohol and the hydride complex is regenerated.

The regioselectivity is determined in the step of the insertion of the alkene. Temperature and CO pressure are important because the linear alkyl intermediate is favoured at high temperatures; otherwise, at high CO pressure a dicarbonyl species is formed, which favours the branched isomer. Ligands strongly influence the regioselectivity, as Seayad *et al.* performed the methoxicarbonylation of styrene with different phosphines [57]. This group studied Pd catalyst with phosphines containing substituents in the aromatic ring and observed that the activity decreased drastically depending on the ligand. This may be related to the modified ability of the metal to coordinate styrene and carbon monoxide. For example, with more basic phosphines, the styrene coordination was not favoured due to its nucleophilic character, while less basic phosphines the styrene coordination would be stronger. In phosphines with electron-withdrawing groups, the phosphorus atom is a good π-acceptor and decreases the electronic density on the metal favouring the branched alkyl-palladium intermediate (**34)**. Otherwise, ligands with electron-donor groups provide higher electron density over the palladium and the linear alkyl species (**35)** is favoured. [58].

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The acid acts to reactivate the palladium(0) formed during the cycle to the hydride species. Studying different acids, Seayed *et al.* observed that the stronger coordination ability of the acid counteranion decreased the activity [57]. Unlike hydrocarboxylation reaction, oxalic and formic acid (see 1.2.) are not active in this reaction due to formation of stable complexes.

The solvent is another important parameter. Non-polar solvents decrease the activity because the association of cationic species with the counteranion is favoured. Coordinating solvents such as ketones occupy a coordinating position on the metal and substitute the coordinated CO; this increases the steric effect and favours the formation of the branched ester. More polar solvents increase the activity and favour the linear ester. In general, increasing the dielectric constant increases the activity.
The substrates with electron-withdrawing groups lead to low activity and branched esters [1c].

Finally, the alcohol used is important in the regioselectivity. Increasing the carbonated chain, the bulky effect increases and the attack to the acyl species is slower, subsequently decreasing the conversion [1c].

In recent years, Iggo *et al.* and van Leeuwen *et al.* have performed different HPNMR of palladium diphosphines ligands to study the alcoxycarbonylation mechanism vs. CO/ethene copolymerisation in detail [59,60]. They studied the effect of the ligand in each pathway of the reaction at each step.

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Although the hydride and carboalkoxy mechanism could operate, many authors only considered that the hydride cycle operates in the alcoxycarbonylation [17,35,54,57], because the alkene insertion into the Pd-carbomethoxy bond is extremely low [61,53]. Iggo *et al.* showed all the intermediates in the initiation and propagation for the hydride mechanism and the propagation for the carboalkoxy mechanism. In contrast with previous publications, they concluded that alkene insertion into Pd-carboalkoxy bond occurs at a similar rate as insertion of alkene into Pd-hydride bond. In general trends, the catalytic system that favours the carboalkoxy mechanism will provide a copolymer, and systems that favour the hydride cycle are a potential mechanism for hydroesterification products [59]. Recently, van Leeuwen *et al.* have reported the theoretical studies of the steric and the bite angle effect of the diphosphines ligand in the methanolysis and the propagation pathway. They concluded that the rate-determining step is the alkene insertion to Pd-carboalkoxy bond. Assuming that the diphosphine should be in *cis* fashion, increasing the bite angle, this increases the rate of methanolysis; the steric bulk of the diphosphine favours the reductive elimination pathway, therefore leading to low-molecular weight products or esters [60].

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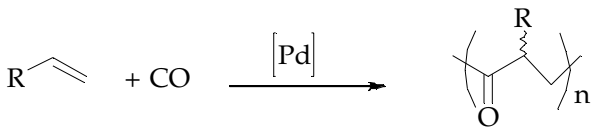
1.5. Copolymerisation CO/alkene

The CO/olefin copolymerisation to obtain polyketones in homogeneous catalysis is of great industrial interest due the low cost of the reactants and the characteristics of the material obtained [62] (Scheme 12).



Scheme 12. CO/alkenes copolymerisation.

The polyketones are low-cost thermoplastic polymers, which can be easily functionalized at the carbonyl groups, and are photo- and biodegradable. The aliphatic polyketones are resistant to high temperatures, non-rigid and have high chemical resistance. From 1995 to 2000 this process was of important industrial interest, mainly by Shell that developed the commercial terpolymer Carilon® (CO/ethylene/propylene).

The most used catalysts for this reaction are palladium(II) complexes that have high activity, and the obtained polyketones are perfectly alternated and have high molecular weight.

The first palladium catalyst used for CO/ethene copolymerisation, $PdCl_2/PR_3$ was published by Gough in 1967 [63]. With this system, polymers with high molecular weights and melting points were obtained, although they were still not pure crystalline and there was

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some amount of palladium metallic. In 1982, Sen *et al.* discovered the first cationic catalyst with the formula $[Pd(PPh_3)_n(NCMe)_{4-n}][BF_4]_2$ which was active for the copolymerisation CO/ethene [64]. In 1984, Drent reported the first well-defined palladium catalyst for the CO/ethene copolymerisation formed by a cationic palladium(II) complex with bidentate ligands and weaker coordinated anions [65,66]. With this system, an activity of 100% and selectivity to perfectly alternated polymer of high molecular weight was obtained.

Hydroesterification and CO-alkene copolymerisation are two closely related reactions. For this reason, the mechanistic results and conclusions obtained in CO-alkene copolymerisation directly relate to hydroesterification.

This reaction was deeply revised by Drent and Budzelaar in 1996 when they proposed the reaction mechanism depicted in Scheme 13. The mechanism consisted of 3 main steps: the initiation of the polymeric chain (**I**), the propagation with a perfect alternation of the monomers (**P**), and finally the termination step by chain transfer (**T**) [51].

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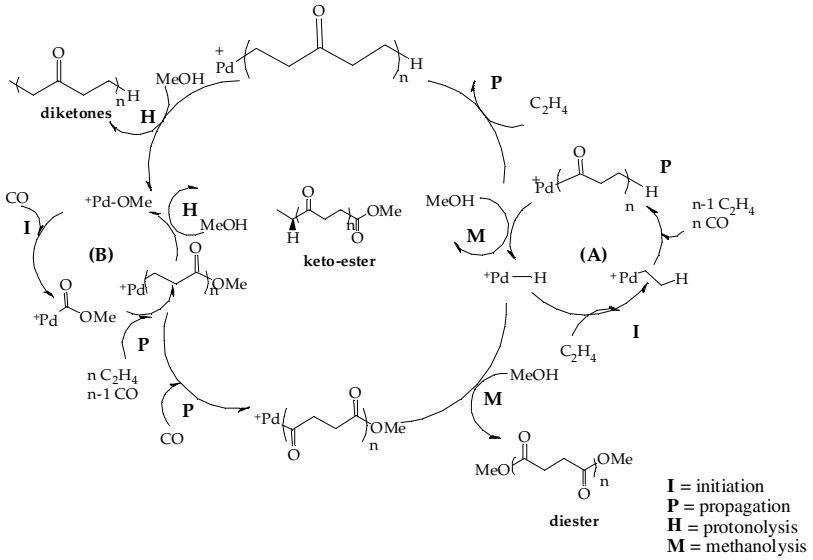

Scheme 13. Mechanism proposed for the copolymerisation of CO/ethene in methanol.

As in the hydroesterification, the catalytic cycle can initiate through a Pd-H (cycle **A**, Scheme 13) or a Pd-COOMe (cycle **B**, Scheme 13) species. Both cycles **A** and **B** produce keto-ester molecules, but the cycles are connected by the two "cross" termination steps that give diester and diketone products. At high temperatures, the formation of appreciable amounts of diesters and diketones was observed, suggesting that the transfer between the cycles is rapid and both cycles contributed with comparable rates. At low temperatures, the "crossover"of products was almost nonexistent, so that only one termination mechanism dominated.

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For cycle **A** the initiation step takes place through ethene 1,2-insertion into the palladium hydride bond. The propagation step (**P**) occurs by reversible migratory 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 [67]. No alternation errors (double insertion of CO or ethene) were observed in this kind of polymer. Double CO insertion will not take place for thermodynamic reasons, while double ethene insertion is kinetically unfavoured since palladium(II) centres have a greater affinity for CO than for ethene [67,68]. The termination step depends on the conditions used on the termination path (**T**). The copolymer formed has either a keto-ester or diketone end group. When the termination step occurs by methanolysis of a Pd-acyl bond a keto-ester structure is obtained, while the aa diketone structure is obtained if protonolysis occurs in the Pd-alkyl bond.

Cycle **B** starts with the palladium carbomethoxy species, which are formed by insertion of carbon monoxide into a Pd-alcoxy bond or insertion of methanol attack directly on coordinated CO. The propagation steps enable the chain to grow. The termination steps also lead to the formation of two groups: keto-esters, formed by protonolysis of the Pd-alkyl bond, or diesters formed via methanolysis of a Pd-acyl bond. When the copolymerisation reaction is performed in aprotic solvents, the synthesis of palladium alkyl (or aryl) species is another method for making an initiating palladium complex. This alkyl complex is only the initiator and is not regenerated during the polymerisation

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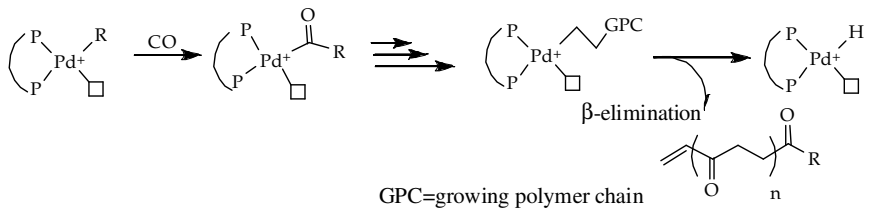
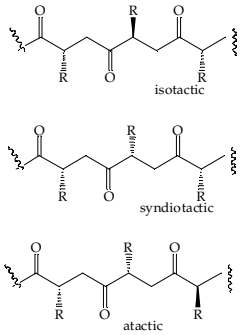
process. After making the first polymer molecule, a chain transfer agent should take over the role of the initiator (Scheme 14).



Scheme 14. Initiation and termination steps in copolymerisation with aprotic solvents using an alkyl-palladium initiator.

The stereochemistry of the alkene insertion along the chain determines the copolymer tacticity. There are three possibilities: atactic (stereoirregular), syndiotactic (RSRSRS sequence) or isotactic (RRRR or SSSSS sequence) copolymers (Scheme 15).



Scheme 15. Tacticity of CO/alkene copolymer.

Stereoregularity can be induced by two different mechanisms. When a chiral ligand with a C_2 symmetry is used, the environment

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created by the ligand will control the stereoregularity of the alkene insertion and will provide isotactic polymers (*site control*). When a non-chiral ligand is used, the growing polymer chain generates stereogenic carbon centers, which will provide stereoregularity of the alkene insertion and lead to syndiotactic polymers (*chain-end control*) (Figure 7) [62].

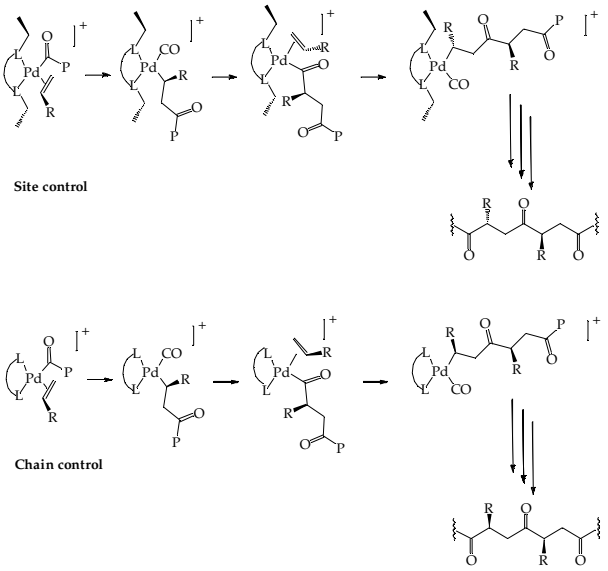

Figure 7. Site control and chain-end control mechanism.

Unlike CO/propene or CO/ethene copolymerisation (alkylic alkenes), in which the diphosphine ligands provide high activity, catalysts containing diphosphine ligands are not active and the best catalytic systems for aromatic olefins are with N-donor ligands [68]. This is because β-hydrogen elimination is favoured rather than polymer chain growth, since the electron density on the metal is higher when phosphorus is coordinated to palladium instead of nitrogen ligands [69].

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However, Nozaky applied an unsymmetrical bidentate phosphine-phosphite ligand, (R, S)-BINAPHOS (Figure 8), for CO/tert-butylstyrene copolymerisation with good activity [70].

The most effective system for copolymerisation of aromatic olefins with carbon monoxide are cationic palladium systems associated with nitrogen-chelating ligands (Figures 5 and 8) such as bipyridines, phenantrolines, pyridine-oxazoline or bisoxazolines and weakly coordinating anions [20,71-74,62].

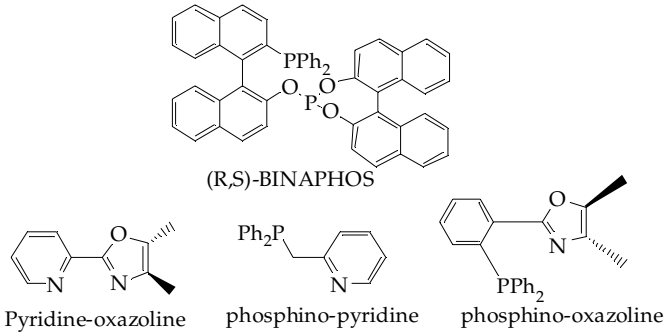

Figure 8. P-P and P-N reported ligands in CO/styrene copolymerisation.

The use of 2,2'-bipyridine (Figure 5, **10**) and 1,10-phenantroline (Figure 5, **11**) was reported for the first time by Shell, using a palladium catalytic system for CO/styrene [75]. It was not until 1992 when Brookhart *et al.* reported the first well-defined precatalyst, a monocationic, organometallic complex [Pd(Me)(MeCN)(N-N)][BArF] (BArF = $B[3,5\text{-}(CF_3)_2C_6H_3]_4$) [76]. Since then, most of the reported precursors in the CO/styrene copolymerisation have been monocationic or dicationic [77,78] palladium species that contain bipyridines or

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phenantrolines such as N-N ligands as well as other N-N ligands such as pyridine-pyrazole,[79] pyridine-oxazoline [80] and pyridine-imidazoline [81,22]. The main problem with this kind of catalyst is the low stability in the reaction media (dichloromethane or methanol). Milani *et al.* have performed a study using trifluoroethanol (TFE) to avoid the decomposition to inactive palladium [82,83]. The ability of the TFE to stabilize the active species due to its lower nucleophilicity allows the synthesis of polyketones in high yield, even in the absence of benzoquinone. Van Leeuwen *et al.* also studied this and observed that the alcohol has an effect on the ratio of growth rates to termination rates. Therefore, the molecular weight of the polymers or oligomers obtained increase in the order: MeOH< EtOH< i-PrOH< t-BuOH< TFE [61].

The presence of an oxidant such as benzoquinone is often required in this reaction. The role of benzoquinone is explained in Figure 9. The benzoquinone is an oxidant reagent that is coordinated to the inactive palladium(0) species, resulting in an electron rich palladium that can be protonated to give hydroquinone and palladium(II), capable of starting a new catalytic cycle [62].

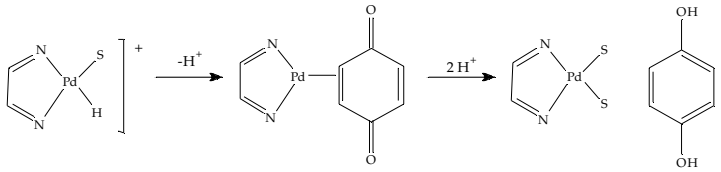

Figure 9. The role of benzoquinone.

Apart from the stereoselectivity provided by chiral ligands or polymeric chains, the regioselectivity should be also considered in the copolymerisation of aromatic olefins. Styrene can be inserted into a Pd-

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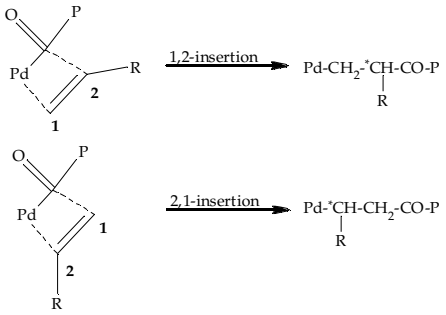
acyl bond either in primary (1,2-insertion) or secondary (2,1-insertion) modes (Scheme 16). Three different arrangements in the polymer structure are possible: tail-to-tail, head-to-head or head-to-tail. When bisnitrogen ligands are used, the styrene has only one possible insertion (secondary mode), and the head-to-tail polymers are obtained [1c,62]. The primary mode takes place when (R, S)-BINAPHOS is used as a ligand. This mode prevents β-H elimination and could explain the activity of this ligand [84]. When P-N-donor ligands are used, a mixture of both insertion modes was observed [70].



Scheme 16. 1,2 and 2,1-insertion of styrene in Pd-acyl intermediate.

In 2006, the CO/tert-butylstyrene copolymerisation was approached in other media or other catalytic systems. For instance, the reaction was performed with a cationic palladium system with N,N'-iminopyridine ligand linked to a carbosilane dendrimer, affording productivities up to 2.64 Kg CP· gPd^{-1} · h^{-1} and molecular weights of 80000 g/mol [85].

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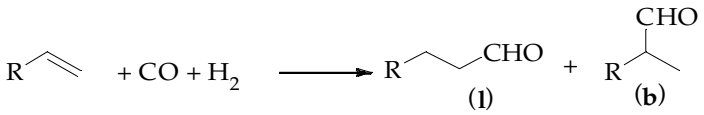
1.6. Hydroformylation

Hydroformylation involves the addition of CO and H_2 to a carbon-carbon double bond, forming an aldehyde containing one more carbon than the starting olefin (Scheme 17). The major products formed are the linear (l) and the branched (b) aldehydes, but hydrogenation of the double bond can also compete with the desired hydroformylation reaction. Isomerisation of the terminal olefins to the internal olefin and, although more difficult, hydroformylation of these internal olefins can also occur.



Scheme 17. Hydroformylation of 1-alkenes.

This reaction, also called "oxo synthesis", was discovered by Otto Roelen in 1938 [86]. In the 1960's, Wilkinson began investigating phosphorus modified rhodium catalyst, which improved the regioselectivity towards the formation of the linear product and was very active in mild conditions [87]. After this approach, different industries began with this line of investigation: Celanese in 1974, Union Carbide Corporation in 1976 and Mitsubishi Chemical Corporation in 1978 all used triphenylphosphine. The hydroformylation of alkenes is the major commercial process used for the production of oxygenated organic compounds. The primary products are used for the production of alcohols, acids, aldol products, diols, acetals, ethers, acroleins and

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esters [88]. Linear aldehydes are used in the manufacture of plasticizers and detergents, while branched aldehydes can be used in the pharmaceutical and agrochemical industries.

Scheme 18 presents the dissociative mechanism of alkene hydroformylation with Rh/PPh_3 systems as proposed by Heck [89]. To begin the catalytic cycle complex $[Rh(CO)H(PPh_3)_3]$ (**39**) is formed. Under 1 atm of carbon monoxide, the isomers of $[Rh(CO)_2H(PPh_3)_2]$ (**40ee** and **40ea**) are formed. The posterior dissociation of CO in **40** isomers or the ligand dissociation of species **39** leads to obtaining square-planar hydride intermediates (**41**) in which the alkene is coordinated (**42**) to form the linear (**43l**) or branched (**43b**) alkyl complexes by migratory insertion. This step determines the regioselectivity of the reaction. A β-elimination of the hydride in isomer **43b** leads to isomerisation. Further reaction with another mole of CO to form **44l** or **44b**, and the subsequent migratory insertion of CO into the rhodium-alkyl bond yield the acyl intermediated **45l** and **45b**. When these species react with hydrogen, they produce aldehyde products and regenerate the square-planar hydride **41**. The dirhodium species **46** can be formed at low hydrogen and high rhodium concentration. This was observed previously by different authors under conditions similar to these [90-93].

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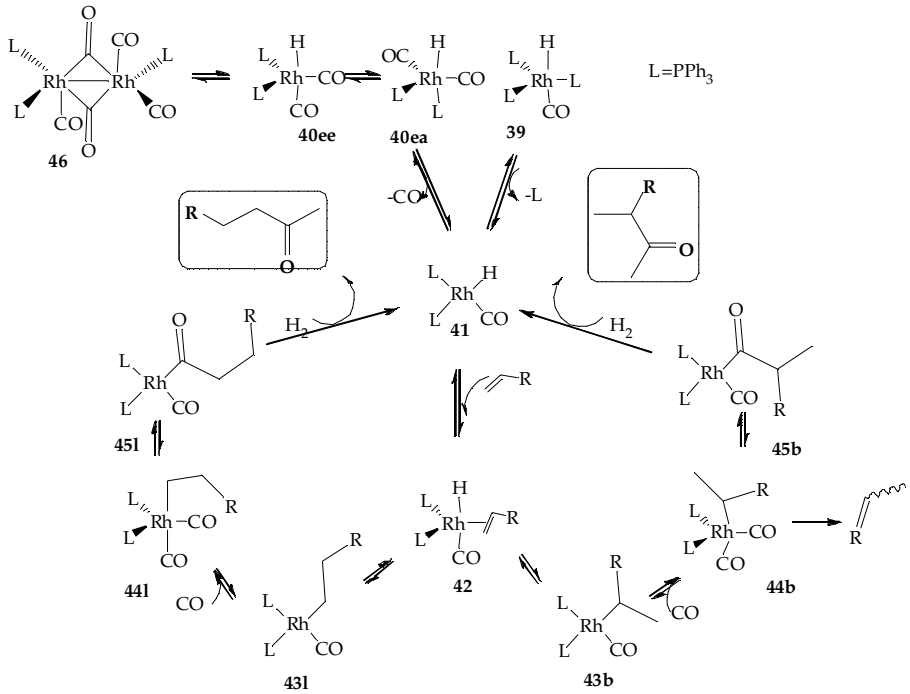

Scheme 18. Hydroformylation mechanism for alkenes.

The regioselectivity of this reaction has been extensively studied [88,12,1a]. It has been demonstrated that the number of phosphines coordinated to rhodium determines the regioselectivity. At high concentrations of PPh_3, the resting state of the catalyst is **39**, which undergoes dissociation to form square-planar *trans*-**41** intermediate. At moderate PPh_3 concentrations, the resting state is an equilibrium between **40ee** and **40ea**. Many authors suggest that the species *trans*-**41** give high linear to branched ratios (20:1), while square-planar intermediates $[Rh(CO)_2H(PPh_3)]$ (**47**) and *cis*-**41,** would lead to a low linear to branched ratio (4:1) [87].

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In the hydroformylation of linear alkenes catalysed by rhodium with monophosphines, it was observed that increasing the cone Tolman angle, the linear aldehyde is favoured. Otherwise, if the cone angle is very large, species with only one ligand are preferentially formed and then the regioselectivity to the linear product decreases. For diphosphine ligands, the control on the regioselectivity is easier. This is because the stability of the bidentate coordination leads to the formation of fewer species than with monophosphine [1c]. Another important parameter that can determine the regioselectivity in Rh-diphosphine ligand systems is the bite angle. Casey *et al.* studied the effect of this in the 1-hexene hydroformylation using different diphosphines (Figure 10) [16]. When BISBI (bite angle = 113º) was used as a ligand, coordinated in bis-equatorial fashion, the l:b ratio obtained was 66, while using dppe (bite angle = 90º), which coordinates in axial-equatorial, gave a l:b ratio of 2.1. This was primarily attributed to steric effects [17].

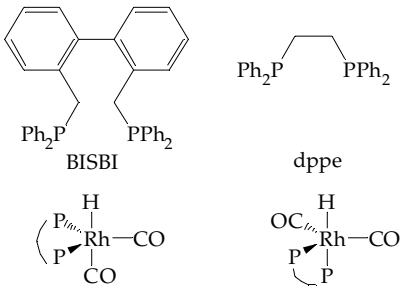

Figure 10. Diphosphines which lead to different l:b ratio.

As was described above, phosphite ligands have different properties than the phosphines. They have been considered the best ligands for

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hydroformylation in the past. The first example of the use of phosphite ligands in rhodium-catalysed hydroformylation of 1-alkenes was reported by Pruett and Smith in Union Carbide Corporation [94]. The general trend of these ligands is to favour the linear aldehyde when the electron withdrawing properties of the ligand increase [88]. In the 1980's, van Leeuwen *et al.* reported a study with a bulky monophosphite that was active in the reaction at very high rates [95,96]. Also in the 1980's, Trzeciak *et al.* studied the hydroformylation of alkenes using rhodium catalyst associated to triphenylphosphite ligand [97]. The facile dissociation of CO and strong alkene association is favoured by the electron-withdrawing properties of the phosphite ligands, and play an important role in the activity and regioselectivity. Furthermore, phosphites have higher χ value than phosphines, therefore this ligand has a preferred bisequatorial coordination which increases formation of the linear aldehyde. The steric hindrance also has an important role in the regioselectivity. Bulky phosphites, with a large cone angle as tris(*o-tert*-butylphenyl)phosphite, tend to form species $[Rh(CO)_3H\{P(O\text{-}^tBuC_6H_5)_3\}]$ under the reaction conditions [89]. This species is electronically poor and easily loses CO forming the square-planar dicarbonyl species *cis*-$[Rh(CO)_2H\{P(O\text{-}^tBuC_6H_5)_3\}]$, which begin the catalytic cycle with the insertion of the alkene. The hydride migration leads to the linear or branched alkyl. In the branched alkyl isomer, the β-hydride elimination is faster for the secondary alkyl intermediates than primary alkyl. Therefore, high isomerisation rates will reduce the formation of branched aldehydes but not the linear acyl intermediate.

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As a consequence, the ratio of linear/branched increases when the isomerisation rate increases [89].

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1.7. Supercritical fluids

A supercritical fluid (SCF) is any compound above the critical point, which is the maximum value of temperature and pressure at which a gas and a liquid can coexist [98]. In the supercritical region there is only one phase, which has properties between gas and liquid (Figure 11).

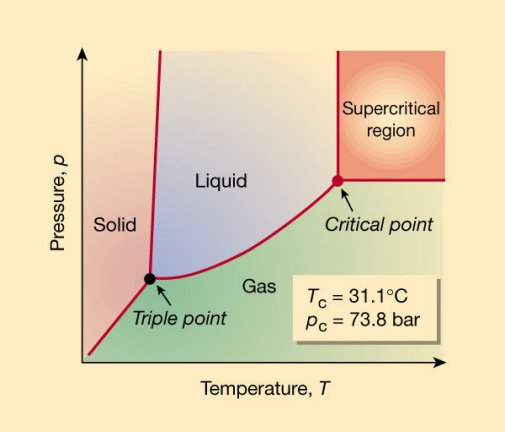

Figure 11. Schematic phase diagram of CO_2.

Carbon dioxide is the most commonly employed substance by far in supercritical fluid processes due to its mild critical constants (31ºC and 73.75 atm), non-toxicity, non-flammability and inexpensive cost. Supercritical carbon dioxide ($scCO_2$) is the only SCF that combine health and safety properties with low cost and availability. Water would be the one exception, but its critical point is very high (374ºC and 221 atm) [99].

The most important industrial processes using $scCO_2$ are extraction plants for the food and pharmaceutical industries. The oldest and the

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most profitable extraction process is the decaffeination of coffee beans by $scCO_2$ [100,101]. More recently, $scCO_2$ has been used in other commercial applications such as impregnations of wood, metal degreasing, polymer processing, synthesis and impregnation and dry cleaning, among others [102-104].

The application of SCFs as reaction media in homogeneous catalyst has been investigated on a laboratory scale by a number of research groups in recent years. Supercritical fluids offer a range of potential reaction advantages for application in homogeneous catalysis (Table 1) [2]. The most important is the high miscibility of $scCO_2$ with gases compared with a limited solubility of gases in organic solvents [105]. This is of interest for homogeneous catalysis where gases are first order in the rate reaction. The possibility of significantly altering solvent properties through relatively small changes in pressure adds an additional parameter for control of rate and selectivity (Figure 12). Thus, it allows, for instance, the separation of transition metal complexes from the reaction products, which solve the problem of recovering the catalyst at the end of the reaction. For example, a reduced controlled pressure can lead to a selectively precipitation of the catalyst, assuming the solubility of the catalyst in less density CO_2 is different than the reaction products.

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Table 1. Potential reaction benefits and corresponding physico-chemical properties for compressed CO_2 as reaction media in transition metals catalyzed organic synthesis.

Potential benefit	Physico-chemical property
Higher rates	Miscibility with gases, rapid mass transfer.
Different selectivities	Weak coordination, pressure tuning
Additional safety	No toxicity, inertness, good heat transfer
Enhanced separation	Tunable solvent properties, multiphase
Continuous flow	Multiphase systems, mass transfer

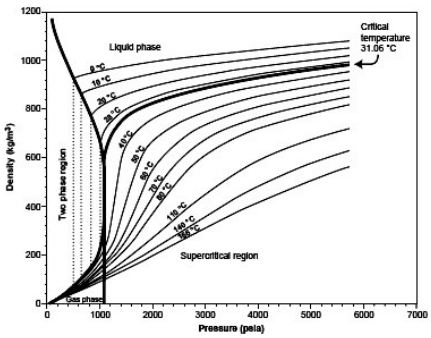

Figure 12. Density *vs*. pressure isotherms for liquid and supercritical carbon dioxide.

Generally, viscosity is also strongly influenced by pressure at low reduced temperatures. Under the most common conditions for supercritical processes, viscosity can generally be expected to decrease with temperature. The diffusion coefficient and viscosity represent transport properties that affect rates of mass transfer. In general these properties are at least one order of magnitude higher (diffusion coefficient), and lower (viscosity) in SCFs compared with liquid solvents. The diffusion of compounds in SCFs will occur at faster rates

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than in liquid solvents. However, this does not mean that all limitations of mass transfer will be absent in all SCF applications.

One property of carbon dioxide potentially limiting its use is its low polarity, and therefore the low solubility of conventional, generally polar homogeneous catalysts. This limitation can be counteracted by using surfactants, co-solvents or other reagents, which increase the solubility of the system in $scCO_2$ [105].

The solubility of a solute in $scCO_2$ is extremely dependent on its structure, with three features of paramount importance:

- Low polarity compounds are more soluble than highly polar substances or salts;
- Solubility increases with increasing vapour pressure of the solute;
- Functional groups, so called *$scCO_2$-philic*, like perfluoroalkyl, polysiloxane substituents or polyether/polycarbonate copolymers give enhanced CO_2 solubility.

The factors which lead to enhanced CO_2 solubility are still not fully understood, but the most important appear to be:

- Weak self-interaction;
- Specific interaction with CO_2;
- Flexible, high free-volume molecules.

The organometallic catalysts, which are very poorly soluble in $scCO_2$, become soluble by introduction of the *$scCO_2$-philic* groups. Thus, ligands with perfluoroalkyl [106,107], polyether, silicone and acetate groups also improve the CO_2-philicity to otherwise insoluble materials

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[108,109]. Alkyl phosphines with low molecular weight (PMe_3, PEt_3) form catalytic systems that are soluble in this medium and provide activity in the hydroformylation reaction [110]. Branched alkylic chains were inserted into surfactants and it has shown that at high degree of chain methylation increased the solubility in the medium [111].

The most successful approach is to insert perfluorinated chains into aryl phosphines (Figure 13). Leitner and co-workers introduced perfluoroalkyl chains into the aryl ring separated with two methylene groups (ponytail) to reduce the strong electron-withdrawing effect of the perfluoroalkyl chain [107,10]. Other groups have studied the use of perfluorinated alkyl chains [112-118].

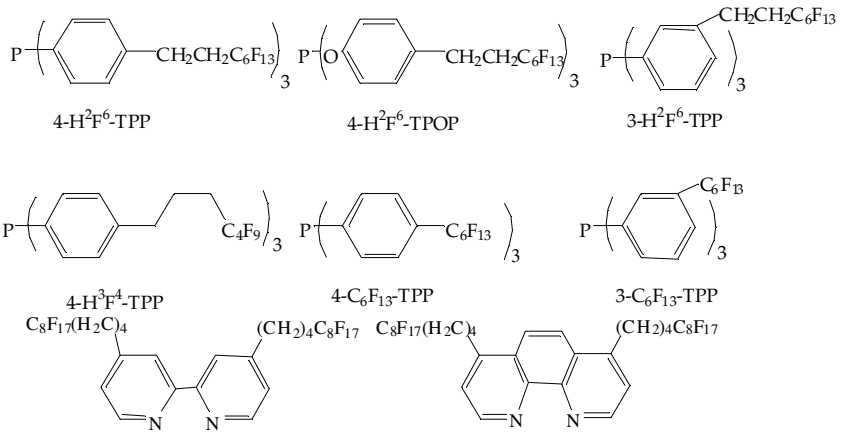

Figure 13. Perfluorinated ligands.

The use of surfactants that contain a polar hydrophilic tail and a CO_2-philic head such fluorinated or siloxane groups increase the solubility in $scCO_2$ [119]. Beckman *et al.* used the first effective fluoro-surfactant in CO_2 [120]. Later, Harrison *et al.* reported the first water-in-

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carbon dioxide (w/c) microemulsion used to solubilize water in $scCO_2$ using $C_7F_{15}CH(OSO_3^-Na^+)C_7H_{15}$ as surfactant [121].

Perfluoropolyethers (PFPE) are also soluble in liquid CO_2 [122,123]. Johnston *et al.* formed w/c microemulsions with an ammonium carboxylate PFPE (PFPE-COO^-NH_4) surfactant of 740 g/mol molecular weight. Success with this class of surfactants was attributed to the chemical structure itself. PFPE constitutes an extremely CO_2- philic tail group, accentuated by the presence of pendant fluoromethyl groups, which tend to increase the volume at the interface on the CO_2 side and thus favour curvature around the water (Figure 14). This kind of surfactant has been used in organic synthesis and also in rhodium-catalysed hydrogenation of alkenes [124,125].

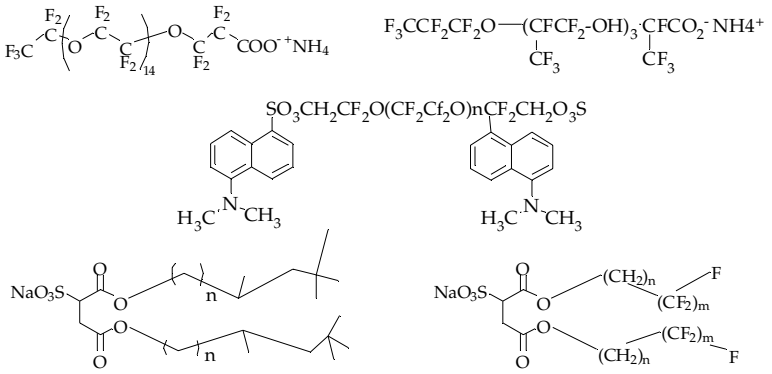

Figure 14. Surfactant used in water/carbon dioxide microemulsions.

Recently, the use of $scCO_2$ has been combined with other phases in multiphasic systems such as ionic liquids/$scCO_2$, water/$scCO_2$ or liquid polymer/ $scCO_2$, which have been applied in different fields, including

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extraction of metal ions, the preparation of nanoparticles or as media for chemical reactions [126-128].

1.7.1. Carbonylation reactions in $scCO_2$

Unlike other carbonylation reactions, hydroformylation of 1-alkenes and vinyl arenes has been deeply studied in $scCO_2$ [129,130]. Rahtke *et al.* performed the first cobalt carbonyl catalyzed hydroformylation of propene in $scCO_2$ [131]. Later, Jessop *et al.* demonstrated the activity of a $[MnH(CO)_5]$ precursor for 3,3-dimethyl-1,2-diphenylcyclopropene hydroformylation in $scCO_2$, obtaining similar chemoselectivity as in organic solvent [132]. In 1997, Guo and Akgerman completed the studies of propene hydroformylation using a cobalt precursor $[Co_2(CO)_8]$ [133]. Koch and Leitner reported the hydroformylation of 1-octene using a perfluoroalkyl-substituted arylphosphine, obtaining a 92% conversion and a regioselectivity of 4.6 (l:b) [10]. An interesting part of this paper is the use of [Rh(cod)(hfacac)] (hfacac = hexafluoroacetyl-acetonate, cod= cyclooctadiene) with non-modified phosphines to perform the reaction in $scCO_2$.

Many authors have reported hydrofomylation in $scCO_2$ using rhodium complexes modified with arylphosphines or phosphite-phosphine ligands [134,112,135,136]. Palo and Erkey performed the 1-octene hydroformylation (100% of conversion in 27h) with *trans*-$[Rh(CO)Cl\{P(p\text{-}CF_3C_6H_4)_3\}_2]$ [116]. Later, they demonstrated the total conversion in 3.5 h with the catalytic precursor [Rh(CO)H{P(*p*-

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$CF_3C_6H_4)_3\}_3$] or [Rh(CO)H{P(*3,5*-$(CF_3)_2C_6H_3)_3\}_3$] [117,113]. The same authors continued studying the influence of fluorinated phosphines. They completed the study with the phosphine $P(C_6F_5)_3$, although this very weakly basic phosphine was not coordinated to the [Rh(acac)$(CO)_2$] because of its low basicity and its large cone angle (184ºC) [115].

Cole-Hamilton *et al.* have reported in different papers the use of soluble rhodium catalytic systems with ligands such as triethylphosphine, low soluble rhodium catalytic systems with ligands trioctylphosphine or non-soluble rhodium catalytic systems with ligands such as tris(*p*-C_9H_{19}-phenyl)phosphite and triphenylphosphite. These systems provide activity in the hydroformylation of long chain alkenes in $scCO_2$ obtaining improved results compared to toluene [137, 138,139]. Recently, Giménez *et al.* has studied the Rh-catalysed hydroformylation of 1-octene with branched alkylic phosphite, phosphonite and phosphinite (Figure 15). All of them were actives in both toluene and $scCO_2$, although the systems with rhodium were not soluble in the reaction conditions [140].

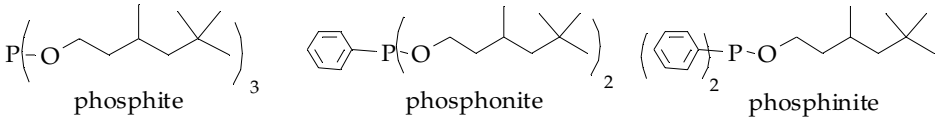

Figure 15. Branched alkylic ligands for hydroformylation of 1-octene.

Even though fluorinated ligands are efficient in providing solubility in $scCO_2$, Hu *et al.* reported the use of carbonylated phosphines as alternatives to fluoroalkylated ligands. For 1-decene

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hydroformylation, the TOF increased from 174 to 535 mol aldehyde· mol catalyst^{-1}·h^{-1} using Rh complexes with carboxylated phosphines [141].

Apart from hydroformylation, very few carbonylation reactions have been studied in $scCO_2$. The alcoxycarbonylation of allyl bromides and the hydroesterification of norbornene using a palladium(II) chloride catalytic precursor were studied by Song *et al*. and Jia *et al.* They optimised the reaction conditions obtaining a clean alcoxycarbonylation of allyl bromides using a lower concentration of carbon monoxide compared with an organic solvent and recycling the catalyst at the end of the reaction [142,143]. Carbonylation of amines to carbamates also using palladium chloride and copper chloride as catalyst has been also studied [144,145]. Photochemical carbonylation of ethane and methane to obtain the corresponding aldehydes using the rhodium catalytic system $[RhCl(L)(PMe_3)_2]$ (L= CO or PR_3) has been also studied [146,147]. The intramolecular carbonylation of benzylalcohol iodide catalysed by palladium complexes with phosphine, phosphonite, phosphinite and phosphite ligands was studied by Ikariya *et al.* affording comparable yields with ones attained in benzene, showing that $scCO_2$ could replace the hazardous organic solvent [148,149]. In 2000, Klaüi *et al.* studied the first example of CO/ethene copolymerisation in supercritical carbon dioxide. They used a catalytic system with nickel(II) associated to N,O-donor bidentates ligands (Figure 16). The nickel catalytic system with perfluorinated C_7F_{15} ligands was tested in $scCO_2$ affording alternated copolymers in a yield of 1898 g CP·g Ni^{-1}.

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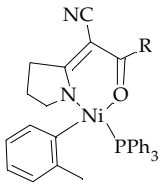
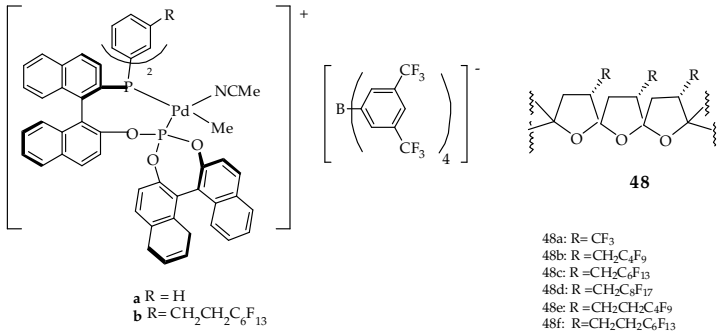


R = Me, Ph, CF_3, C_3F_7, C_7F_{15}, OMe

Figure 16. Nickel catalytic system for CO/ethene copolymerisation in $scCO_2$ [150].

Later, Nozaki *et al.* studied the copolymerisation of CO and ω-perfluoroalkyl-1-alkenes with a palladium(II) complex with (R,S)-BINAPHOS (Figure 17) in Ch_2Cl_2 and in $scCO_2$ [151]. They observed a 3% yield in perfluorinated copolymer (**48,** Figure 17) using the palladium catalytic system (**b**, Figure 17) in $scCO_2$.



a R = H
b R= $CH_2CH_2C_6F_{13}$

48

48a: R= CF_3
48b: R = $CH_2C_4F_9$
48c: R = $CH_2C_6F_{13}$
48d: R = $CH_2C_8F_{17}$
48e: R = $CH_2CH_2C_4F_9$
48f: R= $CH_2CH_2C_6F_{13}$

Figure 17. Palladium catalytic system with BINAPHOS used in CO/perfluoralkyl –1- alkenes copolymerisation.

There is one example of CO/tert-butylstyrene copolymerisation in supercritical carbon dioxide. Giménez *et al.* studied the reaction using perfluorinated bipyridines and phenantrolines as a ligand with a

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palladium system [PdMe(MeCN)(N-N)]BARF (Figure 18). They obtained better polydispersities than in the organic solvent, with productivities up to 15 g CP· gPd^{-1}· h^{-1} and 90000 g/mol of molecular weight [118].

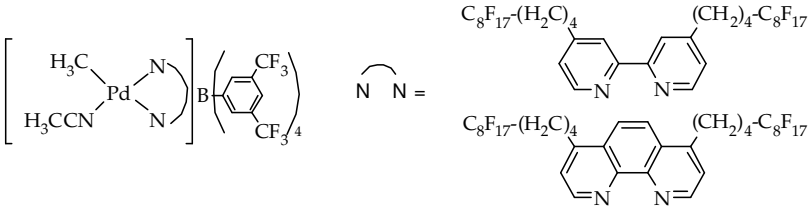

Figure 18. Palladium catalytic system for CO/TBS copolymerisation.

In this context, we found interesting the development of new carbonylation catalysts adapted to be used in supercritical carbon dioxide.

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Chapter 2

Aim and scope

The aim of the present thesis is to use supercritical carbon dioxide as alternative solvent for different catalytic carbonylation reactions such as hydroformylation, hydrocarboxylation, hydroesterification of long chain alkenes and copolimerisation of carbon monoxide and tert-butylstyrene. To afford solubility in that system, different attempts have been used: synthesis of perfluorinated phosphorus or nitrogen donor ligand or the use of acetylated cyclodextrin or perfluoropolyether molecules as solubilizer agents.

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The objectives in the topic of hydrocarboxylation and hydroesterification of terminal alkenes in supercritical carbon dioxide (**Chapter 3**) are:

- To optimise the catalytic conditions of the hydrocarboxylation of linear alkenes in supercritical carbon dioxide medium using palladium complexes associated with perfluorinated phosphines such as tris-(*4*-trifluoromethylphenyl)phosphine, tris-(*3,5*-trifluoromethylphenyl)phosphine, perfluorotriphenylphosphine and tris-(*4*-tridecafluorohexylphenyl)phosphine.
- To study the intermediate species by high pressure NMR(HPNMR) in an organic solvent and in supercritical carbon dioxide.
- To study the effect on activity and selectivity of the addition to the catalytic system a perfluorinated polyether as surfactants in order to improve the solubility of the water in the reaction media.
- To study the hydroesterification of linear alkenes in supercritical carbon dioxide.

The topic CO/ 4-tert-butylstyrene copolymerisation in supercritical carbon dioxide (**Chapter4**) focuses on:

- The synthesis and characterization of different bischelated palladium complexes with nitrogen fluorinated ligands.

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- The study of the coordination chemistry of the perfluorinated ligands to rhodium precursors and the study of the electronic properties by IR.
- The application of palladium bischelated nitrogen catalyst on carbon monoxide/4-*tert*-butylstyrene copolymerisation using supercritical carbon dioxide as a reaction media.

The objectives of the study of the hydroformylation of 1-octene in supercritical carbon dioxide (**Chapter 5**) focuses in:

- The synthesis and characterization of four new modified phosphites ligands with simple CF_3-groups.
- The application of the rhodium catalytic system with thus ligands in hydroformylation of 1-octene in supercritical carbon dioxide.
- The study of the reactivity of rhodium complexes with these ligands with CO and H_2 by HPNMR and HPIR (high pressure IR).
- The study of the ability of the peracetylated cyclodextrin to solubilize in $scCO_2$ insoluble rhodium complexes with alkyl-branched phosphite ligands. The influence in the hydroformylation of 1-octene of the addition of peracetylated cyclodextrin in $scCO_2$.

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Chapter 3

Hydrocarboxylation of terminal alkenes in supercritical carbon dioxide using perfluorinated surfactants

Part 1

Clara Tortosa, Núria Ruiz, Anna Maria Masdeu-Bultó, *Chemical Communications*. **2006**, 2789.

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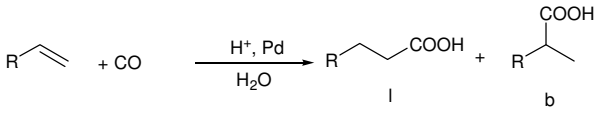
Abstract

High selectivity in acids is obtained in the first example of hydrocarboxylation of 1-octene in supercritical carbon dioxide using a Pd/P(4-C_6H_4-CF_3)$_3$ catalyst system and a perfluorinated surfactant.

Introduction

Palladium-catalysed hydrocarboxylation of alkenes (Scheme 1) is a straightforward and environmentally friendly method for obtaining carboxylic acids with an atom selectivity of 100 %.[1] Carboxylic acids have important industrial applications. For instance, 2-arylproprionic acids are the most important class of non-steroidal anti-inflammatory drugs, and can be obtained by hydrocarboxylation of styrene.[2]



Scheme 1

This reaction has been studied, reviewed and understood in organic solvents in the last decade.[3] One of the most important advances was the discovery that it can be performed in aqueous solutions using the water soluble Pd/TPPTS catalyst system (TPPTS = P(3-C_6H_4-SO_3Na)$_3$).[4,5] Other water-soluble catalyst systems have been studied since then.[6] Water is undoubtedly the greenest solvent for any chemical reaction. In aqueous

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systems, styrene and low terminal aliphatic olefins have been transformed with high conversion to the corresponding acids (TOF of up to 25 h^{-1} and 2500 h^{-1} were reported for styrene and 1-propene respectively).[4,5] However, when higher α-olefins such as 1-hexene or 1-decene were hydrocarboxylated, the low mass transfer between the aqueous and organic phase, and double bond isomerisation dramatically decrease the acid yield.[4] In these cases, mass transfer promoters such as cyclodextrines must be added to obtain selectivities up to 90 %.[7]

Supercritical carbon dioxide ($scCO_2$) is an environmentally friendly substitute for organic solvents in metal-catalysed reactions,[8,9] not only because of its benign character, but also because it often provides higher activities and selectivities[10] than organic or biphasic systems. Examples of this can be found in oxidation,[11] hydrogenation[12] or hydroformylation[13] reactions. Unfortunately, ionic and polar reagents are generally not very soluble in $scCO_2$, which restricts the application of $scCO_2$ in catalytic processes.[14] For example, water/$scCO_2$ multiphasic systems have been successfully used in the hydrogenation of cinnamaldehyde[15] or itaconic acid,[16] which have partial solubility in water, but these systems fail with low water-soluble substrates.

To overcome this limitation, modified ligands such as perfluorinated phosphines or/and soluble surfactants, which induce the formation of micelles with a high-density fluid phase, have been employed.[14] Perfluorinated surfactants are widely known for their ability to reduce interfacial tension and their high thermal and chemical stability. Water-in-carbon dioxide microemulsions (W/C) have been formed using

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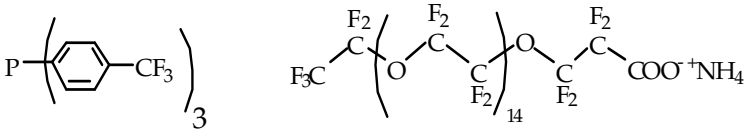
ammonium carboxylate perfluoropolyether surfactants.[17] These dispersions have been used to solubilize hydrophilic substances into CO_2 and applied to organic reactions,[18] and to perform aqueous/$scCO_2$ biphasic metal-catalysed reactions with water-soluble catalysts.[19]

Here we present the first example of the hydrocarboxylation of a terminal alkene (1-octene) in $scCO_2$. We used the $scCO_2$ soluble catalyst precursor $[PdCl_2(NCPh)_2]$[20] associated with phosphine $P(4\text{-}C_6H_4CF_3)_3$ (**1**, Figure 1) and a perfluorinated surfactant ammonium derivated of Krytox® (**2,** Figure 1, M_w = 1937 g/mol) as a stabilizer of the W/C dispersions. The catalyst will be at the $scCO_2$ phase and the water dispersion will facilitate the contact between the hydrophobic substrate and water.



1 **2**

Figure 1

Results and discussion

First, we examined the solubility of the Pd/**1** catalyst precursor in $scCO_2$. To do so, 0.1 mmol of $[PdCl_2(NCPh)_2]$ and 0.4 mmol of **1** were placed in a 100 ml autoclave equipped with sapphire windows, and the system was pressurised up to 30 atm of CO. Then, the pressure and temperature were

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gradually increased. At 180 atm and 70 ºC a single yellow phase was formed.

Once the conditions in which the system became soluble had been determined, we performed the catalytic experiments using the *in situ* formed catalyst precursor $[PdCl_2(NCPh)_2]$/**1** (P/Pd = 4) in the presence of oxalic acid and added water. The results are summarised in Table 1.

Conversion was very low (6 %) at 90 ºC and 200 atm of total pressure, although the system was soluble in these conditions (entry 1, Table 1). The chemoselectivity was also low and only 74 % of the products were acids, the remaining products being the result of isomerisation (2- and 3- octene). Increases in conversion (up to 55 %), selectivity (up to 90 %) and regioselectivity in the linear isomer were observed when the total pressure was decreased to 150 atm (entry 2, Table 1). In these conditions visual inspection through the sapphire windows shows a suspension. When these results are compared with those obtained with $[PdCl_2(NCPh)_2]/PPh_3$ in the same conditions (entry 3, Table 1), it can be observed that there is a clear improvement in the selectivity if $scCO_2$ is used although the conversion is lower. The selectivity obtained with our Pd/**1** system is better than the selectivity reported for aqueous biphasic catalysis with Pd/TPPTS. For instance, for 1-hexene 40 % of isomerisation was reported in the biphasic aqueous system.[4]

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Table 1. Hydrocarboxylation of 1-octene using [Pd(NCPh)$_2$Cl$_2$] / **1** / **2** in scCO_2[a]

Entry	P_T(atm)	H_2O/2	%Conv	%S_a	l/b
1	200	0	6	74	60/40
2	150	0	55	90	75/25
3[b]	30	0	78	63	68/32
4	150	28	80	80	80/20
5	150	14	93	77	82/18
6	150	7	79	81	89/11
7	165	14	44	80	78/22

[a]Reaction conditions: 1mM Pd (0.025 mmol), P/Pd: 4, 12 h, P_{CO}: 30 atm, T: 90ºC, acid: oxalic acid (1.56 mmols); H_2O (12.5mmol); Substrate: 1-octene (1.56 mmol); Phosphine: 0.1mmol; Conv: conversion; Sa: acid selectivity; l: linear acid, b: branched acid. [b] solvent: dimethoxyethane; ligand: PPh_3.

The fact that the conversion obtained was low was attributed to a mass transfer problem of the water to the scCO_2 phase. Thus, we decided to add an ammonium salt of perfluoropolyether carboxylic acid **2**[21] (Krytox®). We first examined the solubility of the [$PdCl_2$(NCPh)$_2$]/**1/2** system under scCO_2 (Figure 2). To do so, 0.05 mmol of [$PdCl_2$(NCPh)$_2$], 0.20 mmol of **1**, 3.13 mmol of oxalic acid, 18.75 mmol of water and 1.78 mmol of **2** were placed in a 100 ml autoclave equipped with sapphire windows, and then the same method as for [$PdCl_2$(NCPh)$_2$]/**1** was followed. At 70 ºC and below 100 atm, the scCO_2 phase was colorless and transparent (Figure 2a). When the temperature and pressure were increased to 90 ºC and 120 atm, respectively, we observed the formation

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of a suspension (Figure 2b) that was white up to 165 atm and then turned yellow up to 180 atm (Figure 2c).

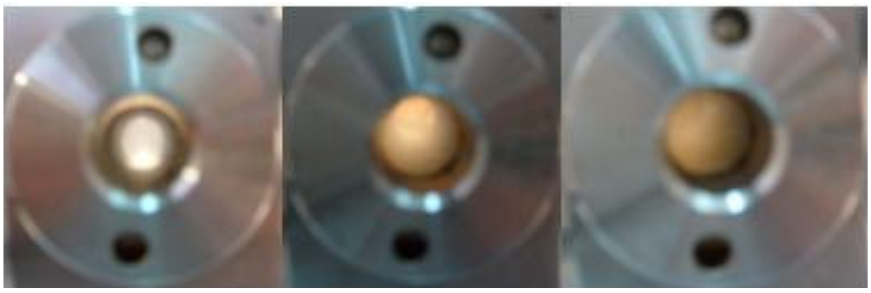

Figure 2. Water-surfactant emulsion in supercritical conditions: a) P < 100 atm, T = 70 ºC; b) 120 atm < P < 150 atm, T = 90 ºC; c) P > 165 atm, T = 90 ºC.

The addition of surfactant **2** (H_2O/**2** = 28) to the Pd/**1** system increased both the conversion (entry 4, Table 1) and the regioselectivity to the linear acid to 80 %. When the amount of **2** was increased, the conversion reached a maximum of 93 % at an H_2O/**2** of 14 (entry 5, Table 1). In all these cases the selectivity in acids remained at 80 % which is a better result than the one obtained with the organic and aqueous systems.[4] At higher pressure, when the system is soluble in $scCO_2$, the conversion decreased (44 % conversion in entry 7, Table 1) as happened without the addition of surfactant.

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Conclusions

In summary, we present the first example of the hydrocarboxylation of 1-octene in $scCO_2$ using the Pd/**1** catalyst precursor. The use of $scCO_2$ means that the selectivity in acids is higher than for the organic and aqueous systems. The addition of a perfluorinated surfactant enhances the activity and the regioselectivity to the linear acid although the selectivity decreases.

Experimental

Catalysis: $[PdCl_2(NCPh)_2]$ (0.025mmol) was mixed with 1.56 mmol of $H_2C_2O_4 \cdot 2H_2O$, 0.1 mmol of **1** and **2** when used (mmol depending on the experiment according to Table 1). The mixture was loaded into a 25ml stainless steel reactor vessel and the system was purged. Degassed water (0.23 ml), 1-octene (1.56 mmol) and undecane (0.13 ml) as GC internal standard were mixed and charged in vacuum. Then the CO gas was charged, the reactor pressurised to 30 atm, and the liquid carbon dioxide introduced. The contents were heated to 90ºC. The compressed carbon dioxide was introduced to attain the desired reaction pressure and magnetically stirred (750 rpm). After the reaction, the vessel was cooled with ice water to 0ºC and slowly depressurised to atmospheric pressure through a cold trap. The reaction mixture was extracted with diethylether and analysed by gas chromatography.

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Acknowledgment

We gratefully acknowledge the Generalitat de Catalunya (DURSI and Fons Social Europeu) for a Fellowship (FI) to C. T. and the Ministerio de Educacion y Ciencia (CTQ2004-03831/PPQ) for financial support. We also thank Brugarolas, S.A. for supplying the Krytox® FS-L 57. Krytox® is a trade mark of DuPont.

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Hydrocarboxylation of terminal alkenes in supercritical carbon dioxide

Part 2

Clara Tortosa Estorach, Arantxa Orejón, Núria Ruiz, Anna M. Masdeu-Bultó and Gábor Laurenczy, *Journal Molecular Catalysis*, submitted.

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Abstract

The catalytic hydrocarboxylation of linear alkenes to obtain carboxylic acids using supercritical carbon dioxide as a solvent was studied. High selectivities in acids have been obtained. The best results were achieved by adding a perfluorinated surfactant to the reaction mixture (93 % conversions and *ca* 80 % selectivity). Comparative multinuclear high pressure NMR studies in THF-d_8 and in supercritical CO_2 show the formation of Pd(0) species.

1. Introduction

Carbon dioxide in its liquid or supercritical state ($scCO_2$) has a great potential as an environmentally benign reaction medium for chemical synthesis [1]. Since the mid-1990s, rapid increasing research efforts have shown that $scCO_2$ can replace conventional solvents in a wide range of processes [2]. Replacing or reducing toxic solvents is also one of the postulates of Green Chemistry [3]. There is also increasing evidence that the application of $scCO_2$ can broaden the scope of catalytic synthetic methodologies. Carbon dioxide becomes supercritical at T_c = 31.1 ºC and P_c= 73.8 bar. Beyond this point there is no distinction between liquid or gas phase and the new supercritical phase presents properties of both states, it means higher solubility of gases than with organic solvents [1]. So it can improve the yield of homogeneous catalysis, particularly for those reactions which are first order in the concentration of the gaseous reagent. In addition, it is known that the

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Clara Tortosa Estorach
ISBN: 978-84-691-0991-5/DL: T.2294-2007

density of CO_2 changes dramatically in the near-critical regime, therefore the reagents solubility suffer the same effect. Small changes in temperature or pressure cause dramatic changes in the density, viscosity and dielectric constant of supercritical CO_2, making it tuneable solvent.

The mild critical data and the low cost of the material itself make carbon dioxide attractive over other solvents, such hydrocarbons or hydrofluorocarbons. Since $scCO_2$ is a nonpolar medium, the best solubility is observed for non polar solutes. Organic fluorocarbons show a high solubility in $scCO_2$. Therefore, many works report that perfluorochains have been used to solubilize substrates, reagents or catalysts [1,4]. The solubility of polar substances can be substantially increased by adding polar cosolvents or surfactants to form microemulsions [5].

Palladium-catalysed hydrocarboxylation of alkenes [6] (Scheme 1) is a straightforward and environmentally friendly method for obtaining carboxylic acids with an atom selectivity of 100 % [7]. Carboxylic acids have important industrial applications as large volume products and chemical intermediates such as acrylic or adipic acid derivatives [6]. Other products of interest are 2-arylproprionic acids, which are the most important class of non-steroidal anti-inflammatory drugs [8], and can be obtained by hydrocarboxylation of styrene. In this reaction (Scheme 1) two regioisomers can be formed: the branched (b) and the linear (l). By-products of this reaction are the isomerization products (isom) and internal carboxylic acids (int).

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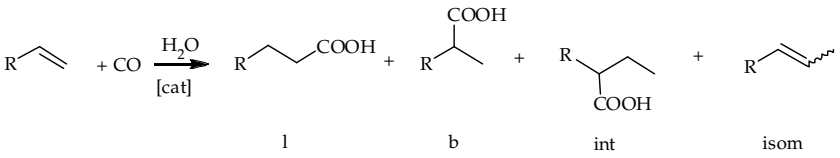

Scheme 1

The carbonylation of alkenes have been extensively studied in the last decade in organic solvents. There are many papers studying the effect of ligand, solvent, temperature and pressure [6,9]. Water has been used as a solvent but when the solubility of the substrates is low the conversion decreases drastically [10]. One efficient way to increase the affinity of water to the $scCO_2$ is to generate water-in-CO_2 (W/C) microemulsions, which can be formed using ammonium carboxylate perfluoropolyether surfactants [5c,11]. These dispersions have been used to solubilize hydrophilic substances into CO_2, applied to organic reactions [11], and to perform aqueous/$scCO_2$ biphasic metal-catalysed reactions with water-soluble catalysts [12]. In part 3.1., it has been explained that the use of perfluoropolyether surfactant enhances the activity and the regioselectivity to the linear acid although the selectivity decreases [13]. In the literature there are different works of carbonylation reaction using $scCO_2$ [14,15], but not in hydrocarboxylation.

Here, we present different aspects of the hydrocarboxylation of linear alkenes in supercritical carbon dioxide media using the catalytic precursor formed with $[PdCl_2(NCPh)_2]$ and phosphine ligands

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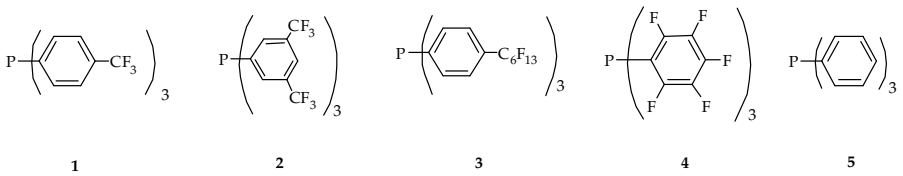
containing fluorinated groups (**1-4**, Figure 1) and triphenylphosphine (**5**, Figure 1) as reference ligand. Ligand **1** forms the rhodium CO_2 soluble complex *trans*-[Rh(CO)Cl(**1**)$_2$] (solubility of at least 5.5 mM in $scCO_2$ at 343K and 273 atm) which was reported to be active in the hydroformylation of 1-octene in $scCO_2$ [16]. We also analysed the ability of perfluorinated surfactants to increase the solubility of water in $scCO_2$. A study of the species formed under CO pressure by HPNMR is also presented.



1 2 3 4 5

Figure 1

2. Experimental

2.1. General remarks

Compounds **1-5** are commercially available and were used without purification. The synthesis of the palladium complex [$PdCl_2$(NCPh)$_2$] was performed according to literature procedures [17]. All olefins used as substrates were filtered over alumina before used. All these material were from Aldrich and Fluorochem. Carbon dioxide (SCF Grade, 99.999 %) was supplied by Air Products and Linde and carbon monoxide 99.99% was supplied by Air Liquid.

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Safety warning. Experiments involving pressurised gases can be hazardous and must be conducted with suitable equipment and following appropriate safety conditions only.

2.2. Solubility and catalytic studies

The solubility studies in supercritical carbon dioxide were performed in a stainless steel Thar reactor (volume 100 ml) containing sapphire windows. The palladium precursor $[PdCl_2(NCPh)_2]$ (0.1 mmols) and the corresponding phosphine (0.4 mmols) were placed in the autoclave, the system was purged with nitrogen/vacuum and it was charged with liquid CO_2. Then, the pressure and temperature were gradually increased and the solubility was examined by ocular inspection through the sapphire windows.

For catalytic experiments, the palladium precursor $[PdCl_2(NCPh)_2]$ (0.025 mmol) with the acid (1.562 mmol), the phosphine (0.1 mmol), the corresponding amount of surfactant when used were loaded into a 25 ml stainless steel reactor vessel. The system was purged with nitrogen/vacumm. The corresponding amount of degassed water, substrate (1.562 mmol) and undecane (97.5 mg) as GC internal standard were mixed and charged in vacuum. Then the CO gas was charged, the reactor pressurised to the desired pressure and the liquid carbon dioxide introduced, and the reactor were heated to the desired temperature. The compressed carbon dioxide was introduced to attain the desired reaction pressure, adjusted by software controlling the syringe pump, and magnetically stirred (750 rpm). After the reaction, the vessel was cooled

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with ice water to 0ºC and slowly depressurised to atmospheric pressure through a cold trap. The reaction mixture was extracted with diethylether and analysed by gas chromatography.

Dimethoxy ethane (DME) was used as organic solvent in the comparative experiments. These were conducted with a 100 ml autoclave following the preceding procedure without the CO_2 charge.

2.3. HPNMR experiments in THF-d_8.

The high pressure nuclear magnetic resonance spectra were performed in a 10 mm sapphire tube [18]. The tube allows work until 100 bar pressure with gas, liquid or supercritical fluid samples. The palladium precursor $[PdCl_2(NCPh)_2]$ (7.7 mg, 0.02 mmol) and phosphine (0.08 mmol) were introduced into the tube under inert atmosphere. Then degassed THF-d_8 (2 ml) was introduced, the tube was charged with ^{13}CO (1-5 atm) and with CO up to 30 atm pressure. The other reagents were introduced stepwise following the same procedure. Measurements were done on a Bruker DRX 400 MHz and Varian 300 MHz NMR spectrometers.

2.4. HPNMR experiments in $scCO_2$.

The same tube was used to carry out these experiments. The corresponding amount of palladium precursor $[PdCl_2(NCPh)_2]$ (31.7 mg, 0.08 mmol) and phosphine (0.33 mmol) were introduced into the tube under inert atmosphere. Then the tube was charged with ^{13}CO (1-5 atm) and with CO up to 30 atm pressure. The tube was cooled with a dry

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ice/acetone bath and liquid CO_2 was introduced up to ¼ of the total volume. The tube was heated up to achieve 100 atm of pressure. The total pressure was measured by a digital manometer connected directly to the NMR tube. The other reagents were introduced stepwise following the same procedure. Measurements were carried out on a Bruker DRX 400 MHz NMR spectrometer.

3. Resultat and discussion

The hydrocarboxylation of alkenes **6a-g** (Scheme 2) in the presence of water was studied using supercritical carbon dioxide as solvent and a catalyst precursor prepared *in situ* by addition of the complex $[PdCl_2(NCPh)_2]$, the corresponding ligand **1-5** (Pd/**1-5** systems) and an acid. The products obtained were the corresponding linear acids (**7a-g**) and branched acids (**8a-f**). Internal alkenes (**9a-e**) formed by isomerisation were also detected in the case of 1-alkenes. For comparative purposes the reactions were also studied using a standard catalyst precursor $[PdCl_2(PPh_3)_2]$ in an organic solvent and at reaction conditions selected in previous literature studies [19].

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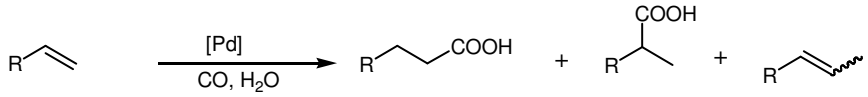

6a = 1-hexene	**7a**	**8a**	**9a**
6b = 1-octene	**7b**	**8b**	**9b**
6c = 1-decene	**7c**	**8c**	**9c**
6d = 1-dodecene	**7d**	**8d**	**9d**
6e = 1-hexadecene	**7e**	**8e**	**9e**
6f = styrene	**7f**	**8f**	**-**
6g = cyclohexene	**7g**	**-**	**-**

Scheme 2

3.1. Hydrocarboxylation in $scCO_2$

First we examined the solubility in $scCO_2$ of the Pd/**1-5** catalyst precursor systems at the reaction conditions To do so, 0.1 mmols of $[PdCl_2(NCPh)_2]$ and 0.4 mmols of the corresponding phosphine were placed in a 100 ml autoclave with sapphire windows, and the system was charged with liquid CO_2. Then, the pressure and temperature were gradually increased in the ranges used in the catalytic experiments. The conditions of solubility of at least 1mM (the concentration used in the reactions) are summarised in Table 1. We observe that the palladium system with the 3,5-CF_3 substituted phosphine **2** is soluble at milder conditions than the systems with the 4-substituted ones, **1** and **3**, regardless of the perfluorinated chain length. The palladium system with phosphine **4** requires higher pressure and temperature to be solubilised and the palladium system with PPh_3 was not apparently soluble up to 250 atm and 100 ºC.

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Table 1. Solubility conditions of $[PdCl_2(NCPh)_2]$ / PR_3[a]

PR_3	P_{Total} (atm)	T (ºC)
1	175	75
2	150	65
3[b]	160	90
4[b]	180	90
5	Not soluble up to 250	Not soluble up to 100

[a] $[PdCl_2(NCPh)_2] = 1.10^{-3}$M, molar ratio $Pd/PR_3 = 1/4$. [b] 30 atm of CO was charged.

Once the initial conditions in which the catalyst precursors showed solubility in $scCO_2$ were established, we proceeded with the catalytic studies analysing the influence of different parameters in the conversion and selectivity of the hydrocarboxylation reaction.

We studied the hydrocarboxylation reaction initially at standard conditions (P/Pd = 4, CO pressure 30 atm) and then we studied different pressures and temperatures. With the system $[PdCl_2(NCPh)_2]$/**1** (Pd/**1**) we observed that at 120 atm total pressure the conversion and selectivity in acid was low (entry 1, Table 2). Increasing the total pressure up to 150 atm, when the system is not soluble, the conversion and selectivity increased up to 55 % and 90 % respectively (entry 2, Table 2). By increasing the total pressure up to 200 atm the catalytic system becomes soluble but the conversion dropped to 6 % (entry 3, Table 2) and no acids were detected at 250 atm (entry 4, Table 2). Apparently, as the solubility in $scCO_2$ of the catalytic precursor increases, the reaction with a polar reagent, such as water, becomes less favourable. The same behaviour in the conversion was observed for the

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catalytic systems Pd/**2** (entries 5 and 6, Table 2) and Pd/**3** (entries 7 and 8, Table 2). Palladium catalytic system with phosphine **4** was not active at the conditions studied (entries 9 and 10, Table 2). At similar conditions of solubility the conversion decreased in the order Pd/**1** ≈ Pd/**2** > Pd/**3** > Pd/**4**. This is in agreement with the observation reported in the literature for the hydrocarboxylation of acenaphthylene in organic solvent, that Pd/**1** system gave higher conversion than Pd/**4** at similar conditions [20].

Regarding the regioselectivity, the systems with the 4-substituted phosphines **1** and **3** gave the linear product as the major product, however with the Pd/**2** system the major product is the branched acid. In all the cases the competitive reaction is the isomerisation to internal alkenes. The isomerisation products are formed from the branched alkylic intermediate. Thus, when isomerisation is important, the ratio of branched acid decreases. The change of regioselectivity between Pd/**1** and Pd/**2** systems does not seem to be related to the isomerisation side reaction since the results are similar in both cases (entries 2 and 5, Table 2). In the styrene hydrocarboxylation, it has been reported that Pd systems with PPh_3 gives mainly the branched isomer, while systems with *cis*-chelated diphosphines favour the formation of the linear isomers. This has been related to the formation of the *trans*-species with the monophosphine ligands favouring the branched product and the palladium with *cis*-chelated diphosphines favouring the linear species [19b]. It has been reported that the formation of *cis* or *trans* palladium phosphine species depends on the steric requirements of the phosphine

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[21]. Thus, phosphines with Tolman angles θ > 140 favour the *trans* species while phosphines with smaller θ can give also *cis* species. So, phosphine **2** (θ = 160º) [22] would favour the formation of *trans* intermediate species in the catalytic cycle and therefore favours the formation of the branched acid.

The effect of the temperature has been studied with the Pd/**1** catalytic system. In Table 2 it can be observed at 150 atm of total pressure, when the system is not soluble, that increasing the temperature, the conversion and the selectivity decrease drastically (entry 11 *versus* entry 2, Table 2). At 200 atm, when the system is soluble the conversion is better but still very low and the selectivity in the linear isomer decreases (entry 12, Table 2). An increase in the branched isomer was also reported for the hydrocarboxylation of alkenes using Pd(II)/PPh_3 as catalytic system when the temperature was increased [23]. The increase of isomerisation products observed in entry 11 (Table 2) could be related to an increase of β-elimination with the temperature [9b].

Regarding the effect of partial pressure, at higher pressure of carbon monoxide (50 atm) the Pd/**1** system is not active probably because competition for coordination to the palladium centre promotes the formation of Pd(0) inactive species [24]. At lower pressure of carbon monoxide (15 atm) no acids were detected. A decrease in the reaction conversion was also reported when the CO pressure decreased for the hydrocarboxylation of 1-octene using $PdCl_2$/PPh_3 as catalytic system [23].

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Table 2. Effect of the temperature in the hydrocarboxylation of 1-octene with $[PdCl_2(NCPh)_2]$/L.[a]

Entry	L	P_{Total} (atm)	P_{CO} (atm)	T (°C)	% C [b]	% $S_{7,8}$ [c]	7/8 (%)	S_9 [d]
1	**1**	120	30	90	10	61	55/45	39
2	**1**	150	30	90	55	90	75/25	10
3	**1**	200	30	90	6	75	60/40	25
4	**1**	250	30	90	0	-	-	-
5	**2**	120	30	90	57	85	41/59	15
6	**2**	150	30	90	2	77	34/66	-
7	**3**	150	30	90	11	55	73/27	45
8	**3**	200	30	90	1	-	-	100
9	**4**	120	30	90	0	-	-	-
10	**4**	150	30	90	0	-	-	-
11	**1**	150	30	120	16	18	58/42	82
12	**1**	200	30	120	26	83	33/67	17
13	**5**	150	30	90	29	33	55/45	67
14[e]	**5**	-	30	90	89	86[f]	51/49	8

[a] Reaction conditions: time = 12h, $[PdCl_2(NCPh)_2]$ = 1.10^{-3}M, molar ratio $Pd/L/H_2C_2O_4 \cdot 2H_2O$/1-octene/$H_2O$ = 1/4/62.5/62.5/500. [b] Total conversion. [c] Selectivity in acids. [d] Selectivity in internal alkenes. [e] $[PdCl_2(PPh_3)_2]/4PPh_3$ as catalyst in dimethoxyethane as solvent. [f] 6 % of oligomers also formed.

These initial experiments lead us to conclude that the best conditions of pressure and temperature for hydrocarboxylation of 1-octene were 30 atm of carbon monoxide pressure, 90 ºC and 150 atm of total pressure for system Pd/**1** and 120 atm of total pressure for catalytic

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system Pd/**2**. In both cases, the results obtained are better than the results obtained with the palladium catalytic system with PPh_3 (**5**) in $scCO_2$ (entry 13, Table 2) but the conversion is lower than the one obtained in an organic solvent (dimethoxyethane) at similar conditions with $[PdCl_2(PPh_3)_2]/4PPh_3$ catalytic system (entry 14, Table 2).

The acid used had also an important effect on the results. The first evidence is that with only water, without added acid, the hydrocarboxylation of 1-octene does not take place in $scCO_2$ using the catalyst precursor Pd/**1** (entry 1, Table 3). Presumably the palladium hydride species is not formed in the absence of a stronger acid. Oxalic acid provided the best conversion while hydrochloric acid or a more CO_2-soluble acid such trifluoroacetic acid gave lower conversion and selectivity (entries 3 and 4, Table 3). Stronger acids may favour the protonation of the phosphine decreasing the formation of actives species.

Table 3. Effect of the acid used in the hydrocarboxylation of 1-octene with Pd/**1**.[a]

Entry	Acid	%C[b]	$\%S_{7,8}$[c]	7/8 (%)
1	-	0	-	-
2	$H_2C_2O_4.2H_2O$	55	90	75/25
3	HCl (aq)[d]	18	76	73/27
4	CF_3COOH	3	35	75/25

[a] Reaction conditions: P_{CO} = 30 atm. P_T = 150 atm, T = 90 ºC, time = 12h, $[PdCl_2(NCPh)_2]$ = 1.10^{-3}M, molar ratio Pd/L/acid/1-octene/H_2O = 1/4/ 62.5/ 62.5/ 500; [b] Total conversion; [c] Selectivity in acids; [d] 35 %.

Finally, we studied the influence on the conversion of the amount of added water to the Pd/**1** system at 200 atm total pressure, 30 atm of CO pressure and at 90 ºC (Table 4) when the catalytic system was

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soluble in $scCO_2$. At a molar ratio H_2O/Pd of 125 the selectivity was very low and the main products were internal octenes, and also other by-products such as aldehydes and oligomers were detected (entry 1, Table 4). Increasing the molar ratio H_2O/Pd the selectivity improves significantly but the conversion at this conditions remains low. With a Pd(II)/PPh_3 system reported in the literature, by increasing the concentration of water the conversion reached a maximum, but higher addition of water lead to a competition for coordination vacant and decreased the conversion [23]. In our case, since it is a two phase reaction, water could not take part in the coordination and no decreasing of conversion was observed up to a molar ratio of H_2O/Pd = 825.

Table 4. Effect of the amount of water used in hydrocarboxylation of 1-octene with Pd/**1**.[a]

Entry	*H_2O/Pd*	%C[b]	%$S_{7,8}$[c]	7/8(%)
1	125	8	8 [d]	62/38
2	500	6	75	60/40
3	825	26	96	67/33

[a] Reaction conditions: P_{CO} = 30 atm. P_T = 200 atm, T = 90 ºC, time = 12h, [$PdCl_2(NCPh)_2$] = 1.10^{-3} M, molar ratio Pd/L/acid/1-octene = 1/4/62.5/62.5. [b] Total conversion. [c] Selectivity in acids. [d] 50 % isomerisation and 42 % aldehydes/oligomers.

Once the reaction conditions were optimised, we concluded that the low solubility of water in $scCO_2$ was the main problem to overcome in order to achieve higher conversion. Therefore we considered the addition of a surfactant as a mass transfer agent.

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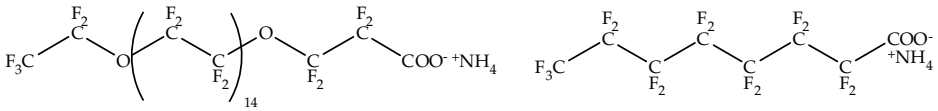
3.2. Addition of a surfactant

We used the ammonium salt of a perfluoropolyether (PFPE), Krytox® [25] (**11**, Figure 2) as surfactant. The synthesis were performed according to literature procedures [26]. The commercial available surfactant ammonium pentadecafluorooctanoate (**12**, Figure 2) was also employed for comparative purposes.



11 **12**

Figure 2

The results obtained using the catalyst precursor Pd/**1** are shown in Table 5. The addition of **11** in a H_2O/**11** molar ratio of 14 promoted an increase of conversion up to 93 % (entry 1, Table 5) working at a molar ratio H_2O/Pd of 500. The selectivity in acids was *ca* 10 % lower than when no surfactant was used (entry 1 in Table 5 *versus* entry 2 in Table 2). Furthermore, when the reactor was vented at pressure and temperature above critical point of pure CO_2, the cold trap contained detectable amounts of the acids. This indicates that, at optimised conditions, extraction of the acids from the reaction mixture would be possible. At a lower H_2O/Pd molar ratio (250) the conversion was also high (83 %). A general increase of the regioselectivity in the linear acid

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up to *ca* 80 % is observed in all the cases at 90 ºC. This increase of linear acid could be related with the higher amount of isomerisation products that are formed from the branched alkylic intermediate. Also the bulkier structure of the water/$scCO_2$ emulsion formed with the surfactant could increase the steric effect and favour the nucleophilic attack to the linear isomer.

Table 5. Hydrocarboxylation of 1-octene using surfactants (surf.) **11** and **12** and system Pd/**1** as catalyst precursor. [a]

Entry	T (ºC)	P_{Total} (atm)	H_2O/Pd (molar ratio)	Surf.	H_2O/Surf. (molar ratio)	%C[b]	$\%S_{7,8}$[c]	7/8 (%)
1	90	150	500	**11**	14	93	77	82/18
2	90	150	250	**11**	14	83	78	83/17
3	120	150	250	**11**	14	11	10	66/44
4	90	150	250	**11**	28	67	78	82/18
5	90	150	500	**11**	28	80	80	80/20
6	90	200	500	**11**	14	26	42	76/24
7[d]	90	150	500	**11**	28	0	-	-
8[e]	90	150	500	**11**	14	0	-	-
9	90	150	500	**12**	14	37	45	80/20

[a] Reaction conditions: P_{CO} = 30 atm, time = 12h, $[PdCl_2(NCPh)_2]$ = $1 \cdot 10^{-3}$M, molar ratio Pd/L/acid/1-octene = 1/4/62.5/62.5. [b] Total conversion. [c] Selectivity in acids. [d] No PR_3 addition, [e] No oxalic acid addition

The addition of surfactant **11** did not improve the results working at 120 ºC (entry 3, Table 5). At lower surfactant concentration, the conversion decreased to 67 % (entry 4 *vs* 2 and entry 5 *vs* 1, Table 5).

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As observed without surfactant, increasing the amount of water increases the conversion (entry 5 *vs* 4, table 5). At the conditions in which the catalyst precursor is soluble in $scCO_2$ (200 atm, 90 ºC) the addition of surfactant promoted a higher conversion but the value was still low (entry 6, Table 5). In the presence of the surfactant, the palladium complex $[PdCl_2(NCPh)_2]$ without ligand **1** was not an active catalyst (entry 7, Table 5). Without the acid the system Pd/**1** with the surfactant was also not active (entry 8, Table 5). Using a surfactant with a shorter perfluorinated chain **12** the results did not improve (entry 9, Table 5).

3.3. Other substrates

The system Pd/**1** with the surfactant **11** at the best conditions obtained for the hydrocarboxylation of 1-octene was studied as catalysts for substrates **6a-6g**. The results obtained are shown in Table 6. With the exception of 1-decene, the total conversions obtained using $scCO_2$ as solvent are high even for the long chain alkenes 1-dodecene and 1-hexadecene (up to *ca* 90 %). The selectivities in acids are in the range of 80 %, the rest being isomerisation products. The regioselectivities in the linear acid for substrates **6b** and **6d** are in the range of 80 %, in the case of **6a** and **6e** are lower and internal alkenes are formed (entry 1 and 5, Table 6). When no isomerisation is possible, as in the case of styrene, no other byproducts were detected (entry 6, Table 6). In the case of styrene,

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the preferred product is the branched acid, but since the addition of **11** favours the formation of the linear product, it results in a low regioselectivity in the branched isomer (56 %). For the hindered substrate cyclohexene only 9 % of conversion was achieved (entry 7, Table 6).

Table 6. Hydrocarboxylation with Pd/**1**/**11** of different substrates in $scCO_2$.[a]

Entry	Substrate	%C [b]	$\%S_{7,8}$ [c]	7/8	$\%S_9$ [d]
1	**6a**	60	76	64/36	24
2	**6b**	93	77	82/18	23
3	**6c**	16	75	63/37	25
4	**6d**	88	86	80/20	14
5	**6e**	95	83	64/25[e]	17
6	**6f**	99	> 99	44/56	-
7	**6g**	9	-	-	-

[a] Reaction conditions: P_{CO} = 30 atm, time = 12h, total pressure = 150 atm, $[PdCl_2(NCPh)_2]$ = 1.10^{-3} M, molar ratio $Pd/L/H_2C_2O_4/H_2O$/substrate = 1/4/62.5/500/62.5, H_2O/11 = 14. [b] Total conversion. [c] Selectivity in acids. [d] Selectivity in internal alkenes. [e] 11 % of internal acids also formed

3.4. Multinuclear high pressure NMR experiments

In order to gain an insight into the species formed during the reaction, we have performed an *in situ* high-pressure NMR (HPNMR) study of the hydrocarboxylation of 1-octene with palladium precursors for both systems, in organic solvent and in supercritical carbon dioxide. In this study the HPNMR spectra were carried out using a palladium precursor $[PdCl_2(NCPh)_2]$ modified with the fluorinated phosphines **1-4**. Oxalic

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acid was used as the acid, under CO pressure in THF-d_8 or supercritical carbon dioxide as a solvent. Due to the detection limits in ^{13}C experiments of the HPNMR, the concentration used to record these spectra was higher than the ones used in the catalytic experiments.

3.4.1. HPNMR in organic solvent

The $^{31}P\{^1H\}$ NMR spectrum of the palladium precursor $[PdCl_2(NCPh)_2]$ ($1 \cdot 10^{-2}$ M) and the phosphine **1** (molar ratio P/Pd = 4/1) in THF-d_8 at room temperature (Figure 3a) shows a singlet signal at δ 23.5 ppm, which corresponds to the complex *trans*-$[PdCl_2(\mathbf{1})_2]$, synthesised and characterised previously [27], and the signal corresponding to free phosphine (δ -5.6 ppm). To this solution, oxalic acid (ratio $H_2C_2O_4 \cdot 2H_2O$/Pd = 62.5) and deuterium oxide (0.1 ml) and 30 atm of CO were added and heated at 90ºC for 1.5 h. The $^{31}P\{^1H\}$ NMR spectrum at room temperature showed a broad signal centred at δ 18 ppm, a singlet at δ 24.4 ppm attributed to the Pd(II) *trans*-$[PdCl_2(\mathbf{1})_2]$ and at δ 19.7 ppm appeared a singlet corresponding to Pd(0) species $Pd(\mathbf{1})_3$. The palladium (0) species were formed by oxidation of the phosphine to the corresponding oxide, which appeared at δ 25.6. ppm (Figure 3b). Pd(0) species with PPh_3 reported in the literature present signals at δ 22.6 ppm at – 70 ºC [28] and 21.48 ppm at room temperature [29].

Upon cooling to -50 ºC (Figure 3c) the broad signal splits into one at δ -6.4 ppm corresponding to free ligand **1** and a signal at δ 22.7, 25.1 and 77.6, which may correspond to Pd(0) carbonyl species in equilibrium $Pd(CO)(\mathbf{1})_x$ (x = 2, 3). A similar behaviour was reported for

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the PPh_3 system [30]. The Pd/**1** systems generate under the conditions studied the expected Pd(0) species.

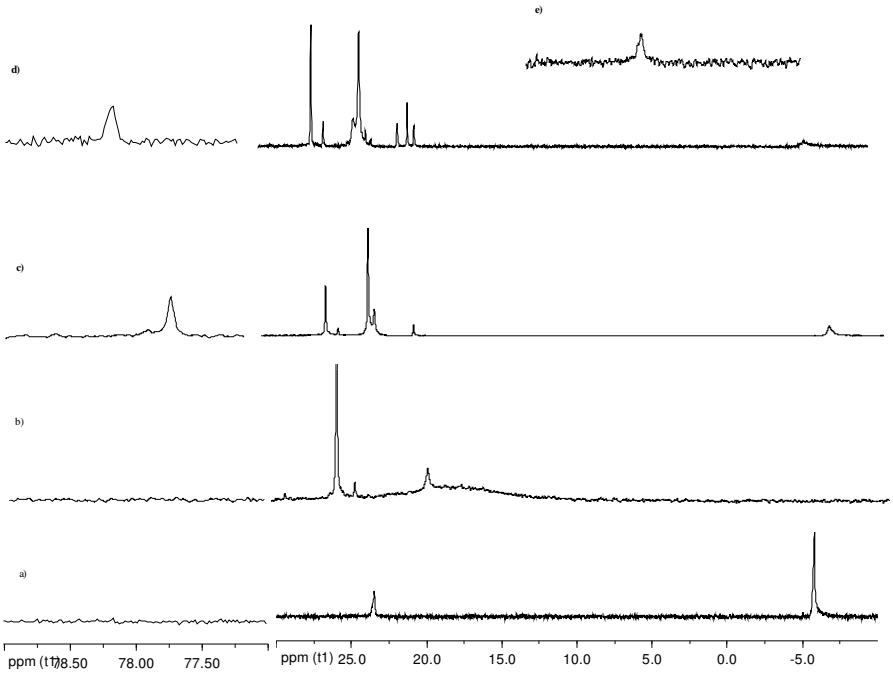

Figure 3. $^{31}P\{^1H\}$ NMR of $[PdCl_2(PhCN)_2]$/1 system in d_8-THF. a) Pd/**1** at r.t. b) Pd/**1**/$H_2C_2O_4.2H_2O$/D_2O/CO at r.t. c) Pd/**1**/acid/D_2O/CO at -50ºC d) Pd/**1**/acid/D_2O/1-octene/CO at -50ºC e) $^{13}C\{^1H\}$ NMR of Pd/**1**/acid/D_2O/1-octene/CO.

Finally, the substrate 1-octene was added (molar ratio 1-octene/Pd = 62.5) and pressurised again at 30 atm of CO. The $^{31}P\{^1H\}$ NMR spectrum at -70ºC of this solution showed the same signals as without the substrate, except that two more peaks at δ 19.6 and 19.1 ppm were observed with a ratio 62/38 (Figure 3d). In the $^{13}C\{^1H\}$ NMR spectra a signal at δ 233.7 ppm appeared (Figure 3e). Comparing with literature data, these new signals are attributed to the acyl isomeric

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species [Pd{C(O)C_8H_{17}}Cl(**1**)$_2$] and [Pd{C(O)(CH_3)C_7H_{15}}Cl(**1**)$_2$] [9,31]. After the reaction was completed the peaks of the acyl species disappeared and only the acid signals remained.

The same study were carried out with the catalytic systems [$PdCl_2$(NCPh)$_2$]/**2** and **3**. The $^{31}P\{^1H\}$ NMR spectra of the solution of the palladium precursor [$PdCl_2$(NCPh)$_2$] with the phosphines **2** or **3** in THF-d_8 at room temperature exhibit a major narrow singlet signal at δ 26.2 which correspond to the complex *trans*-[$PdCl_2$(**2**)$_2$] [22] and a broad siganal at δ 23 ppm corresponding to *trans*-[$PdCl_2$(**3**)$_2$] [32]. For the system [$PdCl_2$(NCPh)$_2$]/**2** appear two minor signals at δ 20.2 and 35.5 ppm which were attributed to cationic species resulting from the chloride exchange with the solvent [PdCl(**2**)$_2$(Solvent)]$^+$ or [Pd(**2**)$_2$(Solvent)$_2$]$^{2+}$ [33]. When the acid, D_2O and 30 atm of CO were added. The $^{31}P\{^1H\}$ NMR spectra of the solution at room temperature show the signals corresponding to palladium (0) species as Pd(**2**)$_3$ at δ 19.7 and other minor signals at 12.6, 7.2 and -4.2 ppm. When 1-octene was added to this solution no substantially changes were observed for both systems.

For all the catalytic systems studied, Pd/**1-3**, the $^{13}C\{^1H\}$ NMR spectra show the corresponding singlets of the carboxilic acids, CH_3-$CH(CH_3)(CH_2)_5$-COOH and CH_3-$(CH_2)_7$-COOH, at δ 178.5 and 174.4 ppm confirming that the hydrocarboxylation took place.

For the palladium system [$PdCl_2$(NCPh)$_2$]/**3** there was not detected signals that could be attributed to Pd(0) species which may

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account for the low activity of Pd/**3** system in hydrocarboxylation catalytic experiments.

3.4.2. HPNMR in $scCO_2$

Having the reference HPNMR experiments in THF-d_8, the same experiments were carried out using supercritical carbon dioxide as a solvent. For this, the 0.083 mmols of the complex were placed in the sapphire tube (8.2 mL) in order to have also 1.10^{-2} M concentration. The different components for each experiment were also placed in the tube. Then, liquid CO_2 was introduced to ¼ of the total volume and the system was heated until the total pressure achieved 100 bar. The total pressure was measures by a digital manometer connected directly to the NMR tube. Due to the CO_2 solidification no experiments at low temperature were performed. For this reason very broad signals were observed.

The $^{31}P\{^1H\}$ NMR spectrum of the palladium precursor $[PdCl_2(NCPh)_2]$ with phosphine **1** (molar ratio P/Pd = 4/1) showed the signal of the free phosphine at -5.8 ppm and the *trans*-$[PdCl_2(\mathbf{1})_2]$ at 23.2 ppm (Figure 4a). After addition of oxalic acid, D_2O and pressurizing the system with CO the formation of the $Pd(\mathbf{1})_3$ and phosphine oxide took place as indicated by the signals at δ 19.9 ppm and 26.6 ppm respectively in the $^{31}P\{^1H\}$ NMR spectra (Figure 4b). When 1-octene was added no substantial changes were observed in the ^{31}P NMR spectra although the ^{13}C NMR showed the formation of the acids. The ratio linear/branched acid was *ca* 65/35 which is close to the catalytic results (Entry 2, Table 2).

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In the ^{13}C NMR spectra the signal corresponding to free CO can be observed at 182 ppm and a small signal at 181 ppm could indicate the presence of species with coordinated CO, which could not be differentiated in the ^{31}P NMR due to the broad signals.

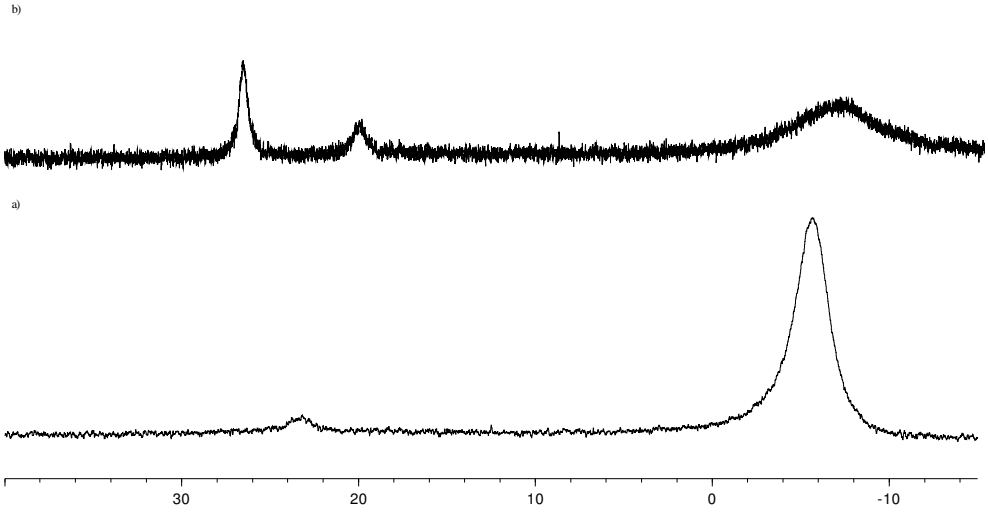

Figure 4. $^{31}P\{^{1}H\}$ NMR of $[PdCl_2(PhCN)_2]$/**1** system in $scCO_2$ at 90 ºC a) Pd/**1**; b) Pd/**1**/$H_2C_2O_4 \cdot 2H_2O/D_2O$/CO.

When the $^{13}C\{^{1}H\}$ NMR spectrum of $[PdCl_2(NCPh)_2]$/**1**/$H_2C_2O_4.2H_2O/D_2O$/CO/1-octene was performed in the presence of the surfactant **11** the signals of the linear and branched acids growing up at 177.6 ppm and 181 ppm respectively, with a ratio of 90/10 were observed. This is a similar ratio than the one observed in the catalytic reaction (entry 1, Table 5). Unfortunately, the $^{31}P\{^{1}H\}$ NMR spectrum at 90ºC showed broad signals and no conclusions could be inferred about the species formed.

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For the $[PdCl_2(NCPh)_2]$/**2** and **3** systems in $scCO_2$ the $^{31}P\{^1H\}$ NMR spectrum showed the signals of the *trans*-$[PdCl_2(\mathbf{1\text{-}2})_2]$ and the ones corresponding to Pd(0) species in the range of 20-21 ppm. The signals of free ligand and the phosphine oxide were also observed. After 1-octene was added the $^{13}C\{^1H\}$ NMR confirms the formation of the acids but the $^{31}P\{^1H\}$ NMR showed no significant changes.

The $^{31}P\{^1H\}$ NMR spectrum of the system $[PdCl_2(NCPh)_2]$/**4** shows a broad small signal at δ -31.2 ppm corresponding to *trans*-$[PdCl_2(\mathbf{4})_2]$ [21] together with the signal of the free phosphine. After the acid addition no significant changes were observed and neither no acid formation was detected in the $^{13}C\{^1H\}$ NMR spectrum. The fact that formation of Pd(0) species was not detected, could explain the low catalytic activity of this system.

For all the systems, the major species formed by reaction of $[PdCl_2(NCPh)_2]$ with **1-4**, was the *trans*-$[PdCl_2(\mathbf{1\text{-}4})_2]$ after the reagents and CO were added, palladium (0) species were formed except with ligand **4**. According to the proposed mechanism for this reaction [9], these Pd(0) species will react with the acid to form a Pd-H species, which has not been detected. At the end of the experiment the formation of the acids was confirmed by ^{13}C NMR.

Conclusion

In conclusion, hydrocarboxylation reactions can be performed in supercritical carbon dioxide as a solvent using palladium catalysts with

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phosphines containing $-CF_3$ groups. Using $[PdCl_2(NCPh)_2]$ and phosphines as catalyst precursors, the conversion in the carbonylation of 1-octene is better when the catalyst is not soluble in $scCO_2$. With these systems the best conversions were up to 60 % with selectivities in the acid up to 90 %. The conversion in the hydrocarboxylation of 1-octene improved up to 93 % by adding a perfluorinated surfactant with a selectivity in acids of 77 %. The regioselectivity in the linear acid increased with the use of the surfactant. Additionally this catalytic system was satisfactorily applied to the hydrocarboxylation of other long chain alkenes. The high pressure multinuclear NMR spectroscopy allowed to follow the formation of Pd(0) species under CO pressure in THF-d_8 and in $scCO_2$.

Acknowledgment

We gratefully acknowledge the Generalitat de Catalunya (DURSI and Fons Social Europeu) for a Fellowship (FI) to C. T. and 2005SGR00777, the Ministerio de Educacion y Ciencia (CTQ2004-03831/PPQ, CSD2006-0003), Swiss State Secretariat for Education and Research (Grant SER C03.0020) and COST D30 Action (European Science Foundation) for financial support. We also thank Brugarolas, S.A. for supplying the Krytox® FS-L 57, and Prof. J. Iggo for helpful discussion.

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Hydroesterification of 1-alkenes in supercritical carbon dioxide

Part 3

Clara Tortosa, Anna Maria Masdeu-Bultó, Catalysis Letters, submitted.

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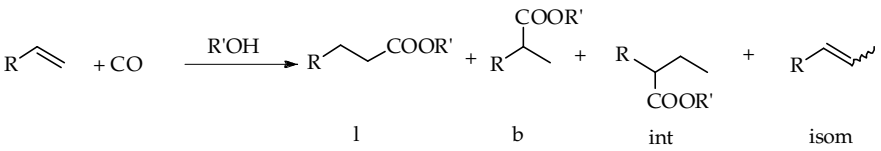
Abstract

The palladium catalysed hydroesterification of linear alkenes to obtain carboxylic esters in supercritical carbon dioxide is studied for the first time. Palladium complexes with phosphines containing -CF_3 groups are used as catalyst precursors. For 1-hexene, conversions into the corresponding methyl esters up to 67 % were obtained using $[PdCl_2(NCPh)_2]/P(3,5\text{-}CF_3C_6H_4)_3$.

1. Introduction

Palladium-catalysed hydroesterification of alkenes (Scheme 1) is a straightforward and environmentally friendly method for obtaining carboxylic esters with a selectivity of 100% [1, 2]. In this reaction (Scheme 1), two regioisomers can be formed: the branched (b) and the linear (l). Carboxylic esters have important industrial applications as large volume products, and chemical intermediates such as methylpropanoate, are used in the methyl metacrylate synthesis. Linear esters are used to synthesize detergents and nylons. Other products of interest include 2-arylpropranoate derivatives, which are transformed to the most important classes of non-steroidal anti-inflammatory drugs [3].



Scheme 1.

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This reaction has been studied in depth in organic solvents. Two mechanisms were proposed for the catalytic cycle (Figure 1). The first one is the alcoxy-mechanism, in which the initial species is an alcoxy intermediate $[Pd\text{-}OR']^+$; it was proposed for the first time by Milstein, in 1988 [4] (Figure 1a). The second mechanism is the hydride-mechanism, in which the active species is the hydride intermediate $[Pd\text{-}H]^+$; this was proposed by Knifton, in 1976 (Figure 1b) [5,6,7]. Furthermore, the regiocontrol depends on the ligand used. It was determined that chelated diphosphine ligand leads to a stabilization of the *cis* intermediate to yield the linear ester as a major product [8]. On the other hand, the monophosphine ligand favors the *trans* intermediate species, leading to the formation of branched esters.

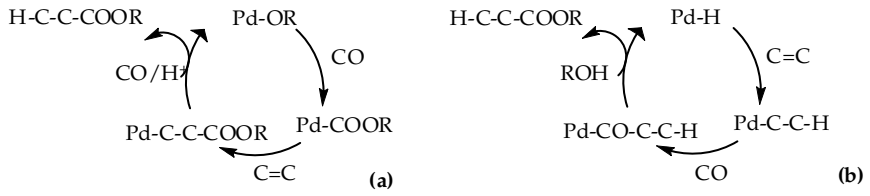

Figure 1.

The use of supercritical fluid (SCF) is attracting considerable attention as an alternative reaction medium to environmentally hazardous organic solvents in green chemistry and catalysis. SCFs with characteristic properties of both liquid- and gas-phase offer a great opportunity to tune the chemical reactivity and to attain the desired selectivity [9-12]. The supercritical carbon dioxide ($scCO_2$) has been used in a growing number of applications by the end of the last decade [13-

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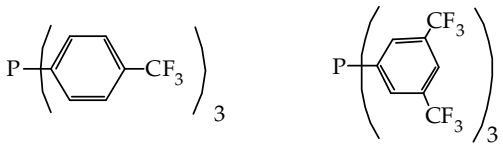
15]. Several features of $scCO_2$ make it an interesting solvent. The critical point of CO_2 is easily accessible at a T_c of 31ºC and a P_c of 73 atm. In addition, carbon dioxide is non-toxic, chemically inert towards many substances, non-flammable; furthermore, simple depressurisation results in its removal and by changing pressure and temperature, it can be easily recovered [16,9,17].

Nowadays, few examples of hydroesterification of alkenes are known in multiphasic systems [18] and only one example of hydroestericationof norbornene in supercritical carbon dioxide has been described in the literature [19].

Here, we present the first example of hydroesterification of linear alkenes in supercritical carbon dioxide media using the catalytic precursor formed with $[PdCl_2(NCPh)_2]$ and phosphine ligands containing fluorinated groups (**1-2**, Figure 1). In chapter 3.2., it has been studied the solubility of the systems $[PdCl_2(NCPh)_2]$/**1-2** and the analogous hydrocarboxylation reaction. It has been observed that the palladium-phosphine **2** system (150 atm, 65ºC) was soluble at milder conditions than was the palladium-phosphine **1** system (175 atm, 75 ºC).



1 **2**

Figure 2.

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2. Experimental

2.1. General remarks

Compounds **1-2** are commercially available and were used without purification. The syntheses of the palladium complex $[PdCl_2(NCPh)_2]$ was performed according to previously described procedures [20]. All olefins used as substrates were filtered over alumina before being used. All materials were obtained from Aldrich and Fluorochem. Carbon dioxide (SCF Grade, 99.999 %) was obtained from Air Products and Linde) and carbon monoxide (99.99%) was supplied by Air Liquid.

Safety warning. Experiments involving pressurised gases can be hazardous and must be conducted with suitable equipment and only following appropriate safety conditions.

2.2. Hydroesterification reaction

For the catalytic experiments, the palladium precursor $[PdCl_2(NCPh)_2]$ (0.025 mmol) with the phosphine (0.1 mmol) were loaded into a 25 ml stainless steel reactor vessel. The system was purged with nitrogen/vacuum. The corresponding amount of degassed alcohol, substrate (1.562 mmol), chlorhidric acid (0.0077 mmol) and undecane (97.5 mg), used as the GC internal standard, were mixed and charged in vacuum. The CO gas was then charged, the reactor pressurised to the desired pressure and the liquid carbon dioxide introduced. The contents were then heated. The compressed carbon dioxide was introduced to attain the desired reaction pressure and magnetically stirred (750 rpm). After the reaction, the vessel was cooled with ice water to 0ºC and

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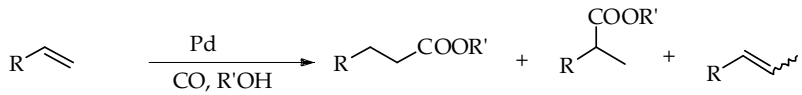
slowly depressurised to atmospheric pressure through a cold trap. The reaction mixture was extracted with diethylether and analysed by gas chromatography.

Dimethoxy ethane (DME) was used as organic solvent in the comparative experiments, which were conducted with a 100 mL autoclave following the preceding procedure, without the CO_2 charge.

3. Results and discussion

The hydroesterification of higher alkenes **6a-d** (Scheme 2) in the presence of an alcohol was studied using a catalyst precursor prepared *in situ* by the addition of the complex $[PdCl_2(NCPh)_2]$, the corresponding ligand **1-2** (Pd/**1-2** systems), an alcohol and using supercritical carbon dioxide as solvent. The products obtained were the corresponding linear esters (**7a-d**) and branched esters (**8a-d**). The corresponding isomerised alkenes (**9a-d**) were the main by-products of the reaction. For comparative purposes, reactions were also studied using a standard catalyst precursor $[PdCl_2(PPh_3)_2]$ in an organic solvent and using reaction conditions selected based on previous studies [21].



6a = 1-hexene	**7a**	**8a**	**9a**
6b = 1-octene	**7b**	**8b**	**9b**
6c= 1-dodecene	**7c**	**8c**	**9c**
6d = 1-hexadecene	**7d**	**8d**	**9d**

Scheme 2.

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The hydroesterification of 1-hexene was first studied using the Pd/**1** and Pd/**2** catalyst precursors in $scCO_2$ at 200 atm and at 150 atm of total pressure. Under these conditions, in which the catalytic systems are soluble, low conversion and selectivity in esters were obtained (entries 1 and 2, Table 1). The main by-products were isomerisation products.

Upon decreasing the total pressure to values in which the catalytic systems were not soluble in the reaction media (150 for Pd/**1** and 120 atm for Pd/**2**), the conversion and selectivity improved. The best results were obtained using the Pd/**2** catalytic system, which provided a 67% of conversion and a 64% of selectivity in esters (entry 4, Table 1). The increase of conversion and selectivity when the catalytic system was not soluble was also observed in the analogous hydrocarboxylation of 1-octene in $scCO_2$ (see part 3.2.). In fact, in the literature there are many reports on catalytic systems which are insoluble under the conditions used for the carbonylation of alkenes in $scCO_2$. The advantage of these systems is the possibility of recycling of the catalysts after product extraction with $scCO_2$ [22]. A moderated regioselectivity to the branched esters was observed in our case. This was also reported by Guiu *et al.* in the hydroesterification of styrene using diphosphine modified with CF_3-groups catalyst precursors [23].

The presence of $scCO_2$ was necessary to have catalytic activity of the catalyst since when we performed the reaction in net 1-hexene, no esters were detected and considerable amount of Pd(0) at the end of the reaction was observed.

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The alcohol plays an important role in this reaction because it determines the termination step to obtain the carboxylic ester. Thus, the amount and nature of the alcohol was changed to study this effect. Upon increasing the amount of alcohol, the conversion and the selectivity dropped off, regardless of whether the catalytic system was soluble or not (entries 5 and 6, Table 1). This could be because the higher concentration of alcohol might lead to a competition for coordination vacant at the catalyst centre and decreased the conversion. A similar inhibiting effect of water was observed in the hydrocarboxylation of alkenes [24].

Using other alcohols, we observed the formation of oligomers and a low conversion to esters. Using trifluoroethanol, only oligomers were obtained (entry 7, Table 1). Using t-BuOH and EtOH, a decrease in conversion was observed (entries 8 and 9, Table 1), probably due to the higher steric hindrance of these alcohols, which decreases the rate of the nucleophilic attack step, as previously reported [25,26]. This also agrees with the results reported for monophosphine PPh_3 complexes, in which the chemoselectivity of the reaction was observed to depend on the alcohol used. The relative growth rate versus termination rates was reported to increase in the order CF_3CH_2OH > t-BuOH > EtOH > MeOH [27, 28, 29].

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Table 1. Hydroesterification of 1-hexene (**6a**) with Pd/L systems. [a]

Entry	L	Substrate	P_T[b]	ROH	ROH/Pd	%C[c]	$S_{7,8}$[d]	7/8	S_9[e]
1	**1**	**6a**	200	MeOH	375	69	0 [f]	0	44
2	**2**	**6a**	150	MeOH	375	44	20	45/55	80
3	**1**	**6a**	150	MeOH	375	40	18[f]	51/49	8
4	**2**	**6a**	120	MeOH	375	67	64[g]	45/46[h]	4
5	**2**	**6a**	120	MeOH	2470	14	26	50/50	19
6	**2**	**6a**	150	MeOH	2470	34	14	33/66	86
7	**2**	**6a**	150	TFE	375	0[f]	-	-	-
8	**2**	**6a**	120	t-BuOH	375	28	100	69/31	-
9	**2**	**6a**	120	EtOH	375	0	-	-	-
10	PPh_3	**6a**	120	MeOH	375	0	-	-	-
11[j]	PPh_3	**6a**	30	MeOH	375	82	99	46/52[i]	-
12	**2**	**6b**	120	MeOH	375	25	35[k]	86/14	36
13	**2**	**6c**	120	MeOH	375	5	98	15/85	2
14	**2**	**6d**	120	MeOH	375	12	8	42/58	92

[a]Pd/L/substrate/HCl(0.1N) = 1/4/62.5/0.31; $[PdCl_2(PhCN)_2]$ = 1.10^{-3}M; P_{CO}: 30atm; time: 12h; T^o = 90ºC; [b] Total pressure; [c] Total conversion; [d] Selectivity in carboxylic esters; [e] Selectivity in internal alkenes; [f] oligomers are also formed; [g] oligomers and acids were also formed, [h] 9 % of methyl-3-ethylpentanoate; [i] 1 % of methyl-3-ethylpentanoate; [j] dimethoxyethane used as a solvent, [k] 29% of aldehydes were also formed.

These experiments lead us to conclude that the best conditions of pressure and temperature for hydroesterification of 1-hexene were 30 atm of carbon monoxide pressure, 90 ºC and 120 atm of total pressure using Pd/**2** catalytic system. This result was better than the results obtained with the palladium catalytic system with PPh_3 in $scCO_2$ (entry 10, Table 1); however, the conversion and selectivity were lower than obtained in an organic solvent (dimethoxyethane) under conditions similar to $[PdCl_2(PPh_3)_2]/4PPh_3$ catalytic system (entry 11, Table 1). The conversion obtained with other long chain substrates **6b-6d** in $scCO_2$

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with the best conditions found for 1-hexene decreased as the chain length increased.

In conclusion, hydroesterification reactions can be performed with supercritical carbon dioxide as a solvent and using palladium catalysts with phosphines containing $–CF_3$ groups. Using $[PdCl_2(PhCN)_2]$ and phosphines as catalyst precursors, the conversion in the carbonylation of 1-hexene was better when the catalyst was not soluble in $scCO_2$. Using these systems, the best conversions were up to 67 %, with selectivities in the ester up to 64 %. The regioselectivity in the branched ester was moderate, but in the expected range. The conversions obtained for higher alkenes were lower.

Acknowledgment

We gratefully acknowledge the Generalitat de Catalunya (DURSI and Fons Social Europeu) for a Fellowship (FI) to C. T. and 2005SGR00777 and the Ministerio de Educacion y Ciencia (CTQ2004-03831/PPQ, CSD2006-0003).

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Chapter 4

Dicationic palladium(II) complexes with nitrogen-donor chelating ligands as efficient catalyst precursors for the co/styrene copolymerization reaction in supercritical carbon dioxide

Clara Tortosa-Estorach, Amaia Bastero, Anna M. Masdeu-Bultó, Giancarlo Franció and Walter Leitner.

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Abstract

New dicationic palladium complexes with different perfluorinated N-donor ligands are used as catalytic systems in CO/4-tert-butylstyrene copolymerisation in supercritical carbon dioxide. Polyketones with high molecular weights and low polydispersities are obtained.

Introduction

The alternating copolymerisation reaction of α-olefins and carbon monoxide yielding polyketones has become a very attractive field of research [1-5]. Interest in these polymers stem from their unusual properties as a thermal plastics, the low cost of monomers, the presence of carbonyl functionality, and the potential for further functionalisation along the backbone [6]. The properties of the polyketones obtained by Pd-catalysed copolymerisation depend on diverse structures of the α-olefins.

Over the past years, there has been much development in the application of homogeneous catalysis of transition metal complexes with heterocyclic nitrogen donor chelating ligands [7,8]. Among them, bipyridines and phenantroline have drawn particular attention. The use of 2,2′-bipyridine and 1,10-phenantroline was reported for the first time by Shell, using palladium catalytic system for CO/styrene [9]. Later, Consiglio *et al.* showed the necessary use of nitrogen-donor ligand to promote the synthesis of polyketones from aromatic olefins [10]. The

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first well-defined precatalyst was reported by Brookhart *et al.* in 1992 that was a monocationic, organometallic complex [Pd(Me)(MeCN)(N-N)][BArF] (BArF = B[3,5-$(CF_3)_2C_6H_3]_4$) [11]. Two years later, Milani *et al.* found that dicationic bischelated complexes of general formula [Pd(N-$N)_2$][$X]_2$ efficiently catalysed the CO/aromatic styrene polymerisation in methanol with no addition of any acid or co-catalyst and in the presence of benzoquinone, despite they decomposed easily to palladium metal [12]. Changing the reaction medium from methanol to trifluoroethanol (TFE), the decomposition to inactive palladium was avoided and high productivity and high molecular weight were obtained with the system [PdMe(MeCN)(N-N)](PF_6) and [Pd(N-$N)_2$]($PF_6)_2$ [13,14]. The ability of the TFE to stabilize the active species due to its lower nucleophilicity allows the synthesis of polyketones in high yield. The use of non-coordinating anions, which do not block any coordination position of the palladium precursor, leads to a better catalytic activity.[2,3] In particular, the use of the $[BArF]^-$ anion in different precursors has shown excellent results in copolymerisation CO/ 4-*tert*-butylstyrene [15].

During the last years, supercritical carbon dioxide ($scCO_2$) has emerged as an alternative solvent for polymerisation reactions [16-18]. The use of supercritical carbon dioxide, as substitutive medium for catalysed reactions, represents friendly environmentally alternative to traditional solvents and it is inexpensive, non-toxic and non-flammable [19].

Last year, we reported the first example of active catalytic systems for the CO/*tert*-butylstyrene copolymerisation in $scCO_2$ based on a

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monocationic palladium complex with perfluorinated bipyridine and phenantroline ligands (**1** and **2**, Figure 1) [Pd(Me)(MeCN)(**1/2**)][BArF] obtaining higher molecular weights and better polydispersities than in an organic solvents [20].

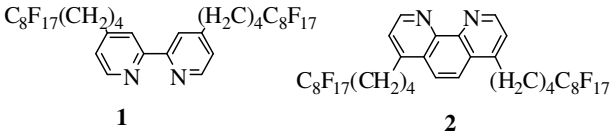
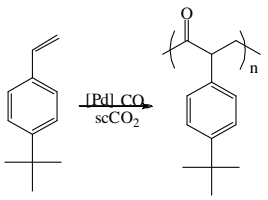


Figure 1.

Since bischelated catalyst precursor $[Pd(N\text{-}N)_2]X_2$ provide much better productivity and molecular weight in organic solvents than the monocationic systems, we though about preparing analogous bischelated complexes with perfluorinated ligands, which could be soluble in $scCO_2$ and studing their activity in CO/4-*tert*-butylstyrene copolymerisation.

Therefore, we report here the synthesis and use of new dicationic palladium (II) complexes with ligands **1** and **2** (Figure 1) and the study of the catalytic activity in the copolymerisation of 4-*tert*-butylstyrene (TBS) with CO in supercritical carbon dioxide (Scheme 1).



Scheme 1.

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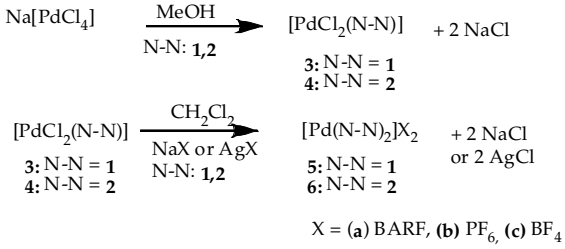
Results and discussion

Preparation of catalysts precursors. The fluorinated N,N-donor ligands **1-2** were obtained according to a published method [20,21] The dicationic bischelated palladium complexes $[Pd(\mathbf{1\text{-}2})_2]X_2$ (**5** and **6**, scheme 2) with different counteranions X (BArF (a), PF_6 (b), BF_4 (c)) were synthesised following a two-steps procedure starting from $Na_2[PdCl_4]$ reacting with one equivalent of the corresponding ligand to get the neutral complexes $[PdCl_2(\mathbf{1\text{-}2})]$ (**3** and **4**, scheme 2) [15b,22,23]. This complex handles with the corresponding salt and another equivalent of the ligand to obtain the dicationic complexes. The driving force for the last step is the formation of NaCl or AgCl which are insoluble in dichloromethane while the complexes **5a-c** and **6a-c** are soluble in the reaction medium.



Scheme 2. Synthesis of the dicationic palladium complexes.

Complexes **3** and **4** were isolated in good yield as light brown solids. They were not soluble in common organic solvents, and were characterised by elemental analysis and mass spectrometry (MALDI-TOF) which confirmed the formation of mononuclear species.

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Complexes **5a-c** and **6a-c** were isolated as pale yellow solids and fully characterised by elemental analysis, mass spectrometry and NMR. The NMR spectra of the complexes show three different broad signals at the aromatic region (7.2-9.4 ppm) corresponding to the two equivalent C_2 symmetric ligands. The ^1H signals of the methylenic protons appear in the region 1.7-3.4 ppm and the signals corresponding to the fluoruous chain can be observed at the ^{19}F NMR spectra in the region from -81 to –126 ppm. The signals corresponding to the coordinated ligand appeared shifted respect to the free ligand [20].

Rhodium carbonyl complexes were synthesised in order to study the coordination ability of the ligand to rhodium and the electronic properties through the variation of the stretching frequency ν(CO). The carbonyl species were obtained in two-steps reaction (Scheme 3) [15d,24]. First the rhodium cyclooctadiene (cod) complex $[Rh(cod)_2]PF_6$ was treated with the corresponding ligand (**1-2**) to obtain the cationic complexes [Rh(cod)(**1-2**)]PF_6 (**7-8**, Scheme 3) which were isolated and characterised by NMR spectroscopy and mass spectrometry. The ^1H NMR spectra show the signals corresponding to coordinated ligands **1-2**. The signals corresponding to the CH_2 of the cyclooctadiene appear as a two broad signals at δ 2.62 and δ 2.15 ppm and the signals corresponding to the olefinic protons were observed around δ 4.51 ppm. In the second step, bubbling carbon monoxide through dichloromethane solutions of **7-8**, the corresponding dicarbonyl species (**9-10**) were formed and were analysed *in situ* by IR spectroscopy.

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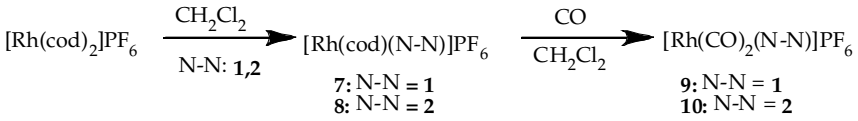
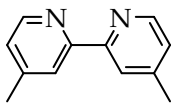


Scheme 3. Synthesis of rhodium complexes **7-10.**

For comparison purposes, analogous Rh-complexes with non fluorinated ligand **11** and **12** (Figure 2) were also prepared following the described method [25-27]. All these complexes show two stretching frequencies ν(CO), typical of cis arrangement of the two-coordinated carbonyl groups [24]. There was no any significant difference between complexes with perfluorinated and non-fluorinated ligands (ν(CO) ≅ 2098, 2040 cm^{-1}, see experimental section), probably due to the ponytail methylenic fragments, which inhibit the electron-withdrawing effect. The difference between different kind of ligand bipyridines and phenantroline were neither significant. Thus, the new dicationic palladium complexes with perfluorinated ligands have similar electronic properties than the non fluorinated ones.



11

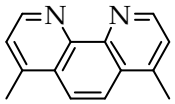


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Figure 2.

CO/tertbutylstyrene copolymerisation. The new dicationic Pd(II) complexes **5a-c** and **6a** were tested as catalyst for alternating CO/4-*tert*-butylstyrene copolymerisation in expanded liquid and supercritical

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carbon dioxide. These complexes were soluble in liquid carbon dioxide at room temperature forming yellow and brown solutions. To perform the catalytic reactions, 0.0022 mmol of the dicationic palladium complex was placed into 10 mL autoclave, after purged with vacuum, the TBS and trifluoroethanol (TFE) as initiator were introduced. After all, the system was pressurised with CO and carbon dioxide and was heated up to the desired temperature. After reaction, the system was depressurised and the polymers were isolated by precipitation with methanol.

In the literature it has been reported that high activities and molecular weights were obtained using palladium complexes with substituted phenantroline ligands although they are less active than the corresponding bipyridines derivatives[13,23,28,29]. The catalytic system with the perfluorinated phenantroline **6a** was tested as catalyst precursor in supercritical carbon dioxide, but considerable amounts of *tert*butylpolystyrene were detected at the $^{13}C\{^{1}H\}$ NMR. The complex **6a** produced also homopolymer using dichloromethane as a solvent. A similar catalyst with methyl substituted groups $[Pd(\mathbf{12})_2](BARF)_2$ (**13a**) was prepared in order to compare the reactivity in supercritical carbon dioxide [13,23]. The system was not selective because there was a 33% of the homopolymer product in both, supercritical carbon dioxide and dichloromethane.

In contrast, using the bipyridine complex **6a**, we obtained polyketones with a productivity of 0.26 Kg of CP ·g Pd^{-1} (Kg CP ·g Pd^{-1}: kilogram of copolymer *per* gram of palladium) in $scCO_2$ (δ = 0.85g/ml)

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and a molecular weight of 96200 g/mol without the addition of oxidant (Figure 3). The productivity increased up to more than 4 times going from supercritical (δ 0.85 and 0.76 g/ml) to liquid expanded phase (δ 0.69 to 0.11 g/ml) (Figure 3). The molecular weight of the polymer (M_w), determined by GPC, also increased in the range from 80000 to 167000 g/mol. It was observed through the autoclave window that between 0.11 to 0.76 g/mL of CO_2 density, the system consisted of two phases. The high productivity obtained in expanded liquid system could be explained because the concentration of the substrate and the catalyst were higher compared with one-phase CO_2 [30]. Nevertheless, when the reaction was performed in net ^{t}Bu-styrene without CO_2, the molecular weight was very high but the productivity was lower and the polydispersity increased up to 2.3 (Figure 3). This may indicate that a chain transfer process takes place favoured by the increase of the substrate concentration. All the polymers obtained have alternated head to tail structure, which is indicative of a chain-end stereocontrol mechanism [2]. Analysis of the decoupled ^{13}C NMR spectra by integration of the signals of the methylene carbon atom indicated a substantial degree of stereoregularity (90%) in the syndiotactic copolymers [31,32].

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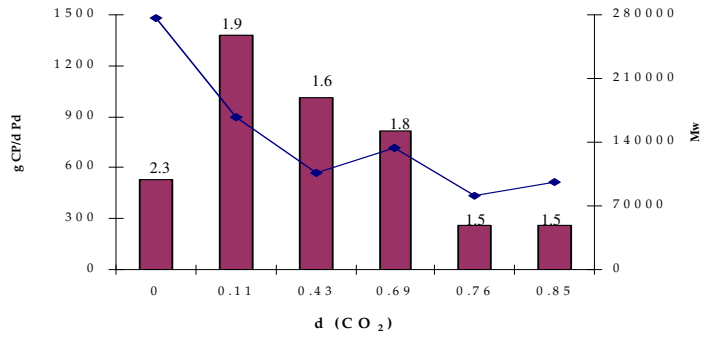

Figure 3. Effect of the CO_2 density in CO/4-^{t}Bu-styrene copolymerisation. Catalytic conditions: 0.0022 mmol catalyst **5a**, TBS/Pd = 4843, TFE/Pd = 300, P(CO)= 30 atm, T(ºC) = 60 ºC, time = 24h; M_w determined by GPC; M_w/M_n on the columns**.**

In an attempt to optimise the results obtained at supercritical conditions, the effect of the reaction conditions were studied (Table 1). Decreasing the CO pressure to 10 atm, the productivity and molecular weight decreased (entry 1, Table 1). At higher CO pressure, the productivity and molecular weight improved (entry 2, Table 1). Increasing the partial pressure of CO, due to total miscibility of it in $scCO_2$, increases the CO concentration and therefore the formation of the polyketones. Durand *et al.* studied the effect of the CO pressure in CO/styrene copolymerisation using different phenantrolines ligands. They observed that for electron-withdrawing substituents, the CO does not play any inhibiting effect in the reaction. While for electron-donor substituents, the competition with the *tert*butylstyrene for the fourth coordination site increases. For phenantrolines without substituents or

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basicity properties in between, like **5a**, the role was not clearly established [29]. Concerning the temperature, low temperature (45 ºC) leads to lower productivity and slightly lower molecular weight (entry 3, Table 1). At higher temperature (80 ºC) results did not improve (entry 4, Table 1) and it was observed decomposition of the catalyst.

Table 1. Copolymerisation CO/*4*-^{t}Bu-styrene[a].

Entry	*Cat.*	P_{CO} *(atm)*	PCO_2 *(atm)*	$\delta(CO_2)$ *(g/mL)*	*ROH/Pd*	*Productivity (g CP/gPd)*	*Mw (Mw/Mn)* [b]
1	**5a**	10	187	0.73	300	120	68237 (1.9)
2	**5a**	50	240	0.73	300	360	134900 (1.4)
3[c]	**5a**	30	200	0.71	300	408	122400 (1.2)
4[d]	**5a**	30	200	0.68	300	192	38500 (1.7)
5	**5a**	30	180	0.70	0	69	137000 (1.9)
6	**5a**	30	115	0.43	300	1008	106800(1.6)
7	**5a**	30	120	0.39	1800	628	112000(1.7)
8[e,f]	**5a**	30	173	0.66	300	150	83400 (1.6)
9[e]	**5a**	30	200	0.74	300	468	108000(1.6)
10[g]	**5a**	30	200	0.70	300	192	83800 (1.6)
11	**5b**	30	126	0.60	300	77	81600 (2.3)
12	**5c**	30	280	0.80	300	243	308140 (3.3)
13	**14a**	30	69	0.11	300	820	117250 (1.7)

[a] Catalytic conditions: 0.0022 mmol catalyst, TBS/Pd = 4843, TFE/Pd = 300, T(ºC) = 60 ºC, time = 24h; [b] determined by GPC; [c] T(ºC) = 45ºC; [d] T(ºC) = 80ºC, 12h. [e] time = 12h; [f] H_2O/ Pd = 300, [g] MeOH as an alcohol.

The role of the alcohol has been reported to be the formation of the carboalcoxy species which initiates the catalytic cycle [13]. When TFE is

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used, the proposed initiation species could be a palladium hydride formed by reaction of the initial precursor with CO and H_2O [4]. In CO_2 as a solvent, without the addition of TFE, low activity was observed and only poly(*tert*-butylstyrene) was formed and considerable amount of Pd(0) was detected at the end of the reaction (entry 5, Table 1). At high TFE/Pd ratio (1800), the productivity was moderate but not better than the productivity obtained in TFE/Pd ratio of 300 at the same conditions (entry 6 and 7, Table 1). The addition of water did not improve the productivity neither the molecular weight (entry 8 *vs.* 9, Table 1). This may indicate that a different initiation step takes place under CO_2 [4]. The use of MeOH instead of TFE produced less productivity and a considerable amounts of Pd (0) was detected at the end (entry 10, Table 1). This is in agreement with the results reported without $scCO_2$ using organic solvents [13].

In order to study the effect of the counteranion we carried out the copolymerisation reaction with catalyst **5b-c**. The complex **5b** with counteranion PF_6 leads to the lowest productivity (entry 11, Table 1), probably because it is strong coordinating anion and the interionic interactions are stronger than with BArF [15a]. The complex **5c**, with the anion BF_4, leads to obtain the highest molecular weight, although the polydispersity was also high and 16% of poly(*tert*-butylstyrene) was also formed (entry 12, Table 5).

The fact that the best activities were obtained using expanded liquid CO_2 prompted us to investigate the activity of the non-fluorinated

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derivative [Pd(**11**)$_2$](BArF)$_2$ **14a** which was also soluble in liquid carbon dioxide. It was prepared following the described method [13,23]. The productivity obtained with **14a** at low CO_2 density was 0.82 Kg CP·g Pd^{-1} and the molecular weight was 117000 (entry 13, Table 1). Comparing both, **14a** and **5a**, we can conclude that at expanded liquide carbon dioxide conditions, although both systems are active producing polyketones with similar tacticity (90%) and polydispersity, **5a** provides higher productivity and molecular weight.

In general, traces of Pd(0) were detected at the end of the reaction. To study the lifetime of the catalyst **5a** we performed the catalytic reaction at different times. The results are showed in Figure 4. The productivity and molecular weight increased up to 48h reaction time, that means that the catalyst is still active in this period. The tendency of the system on time seems to be a living behaviour.

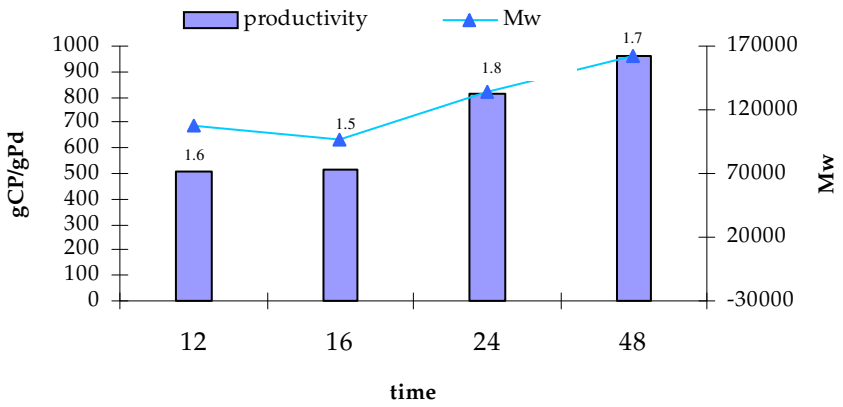

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Figure 4. Effect of the time in the CO/*p*-^{t}Bu-styrene copolymerisation. [a] Catalytic conditions (see Figure 3). (M_w/ M_n) on the columns.

Conclusion

We have synthesised palladium (II) dicationic complexes with perfluorinated phenantroline and bipyridines ligands **3-6** and they have been characterised. The rhodium (I) complexes with these nitrogen ligands have been prepared and characterised by NMR and IR. The IR spectroscopy studies of the Rh-carbonyl derivatives show that the perfluorinated ligands have similar electronic properties than the non perfluorinated ones. Finally the carbon monoxide/4-*tert*-butylstyrene copolymerisation has been studied using palladium dicationic complexes with perfluorinated ligands, affording 1.4 Kg CP·g Pd^{-1}, 167000 of molecular weight and 90% of stereoregularity with catalyst precursor **5a**.

Experimental section

General Comments. Commercial $Na_2[PdCl_4]$ was purchased from Johnson Matthey and used as received. Ligands **11** and **12** were commercial available (Aldrich) and were used without further purification for synthetic and spectroscopic purposes. The methanol (Merck) used to precipitate the polymers was used as received. The 2,2,2-trifluoroethanol (Alfa-Aesar) for the catalytic reactions was purified by distillation with CaH_2. Dichloromethane used for the

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synthesis of complexes was purified through distillation over Na and stored under inert atmosphere. Carbon monoxide (CP grade, 99.0%) was supplied by Westfalen. Carbon dioxide (CO_2, CP grade 4.5) was supplied by Praxair. IR spectra (range 4000-400 cm^{-1}) were recorded on a Midac Grams/386 spectrometer in KBr pellets or dichloromethane solution (when indicated). NMR spectra were recorded at 400 MHz Varian, with tetramethylsilane (^1H NMR) and fluoroform (^{19}F) as the internal standards. MALDI-TOF measurements of complexes: Voyager-DE-STR (Applied Biosystems, Franingham, MA) instrument equipped with a 337 nm nitrogen laser. All spectra were acquired in the positive ion reflector mode. 2,5-dihydroxybenzoic acid (DHB) was used as matrix. The matrix was dissolved in MeOH at a concentration of 10 $mg \cdot mL^{-1}$. The complex was dissolved in CH_2Cl_2 (50 $mg \cdot L^{-1}$). The matrix and the samples were premixed in the ratio 2:1 (Matrix : sample) and then the mixture was deposited (1 μL) on the target. For each spectrum 100 laser shots were accumulated. Molecular weight measurements of polyketones: The molecular weights (Mw) of copolymers and the molecular weight distributions (Mw/Mn) were determined by gel permeation chromatography versus polystyrene standards. Measurements were made in THF on a Millipore-Waters 510 HPLC Pump device using three-serial column system (MZ-Gel 100Å, MZ-Gel 1000 Å, MZ-Gel 10000 Å linear columns) with UV-Detector (ERC-7215) and IR- Detector (ERC-7515a). The software used to get the data was NTeqGPC 5.1. Samples were prepared as follow: 10 mg of the copolymer was solubilised with 2

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mL of tetrahidrofurane (HPLC grade) stabilised with 2,6-Di-tert-4-methylphenol.

Copolymerisation reactions The catalytic experiments were performed in a 10 ml stainless steel autoclave. The catalyst was weight and introduced into the purged autoclave. Then a solution of substrate and the alcohol was added under argon atmosphere. The autoclave was pressurised with CO and CO_2 and heated to the temperature desired. After reaction time, the autoclave was depressurised and the product was redissolved in 5 mL of CH_2Cl_2. The copolymer was precipitated by pouring the reaction solution into rapidly stirred methanol (70 ml). The polymer was filtered, washed with methanol and dried.

[$PdCl_2$(1)] (3). A solution of 4,4′-bis[4′′-(F-octyl)-butyl]-2,2′-bipyridyl (250 mg, 0.22 mmol) in 4ml of tetrahydrofuran was added to a solution of $Na_2[PdCl_4]$ (46.1 mg, 0.17 mmol) in 4ml of methanol. The orange solution was stirred for 1h and a light brown solid was formed. The complex was filtered off and washed with water, methanol and diethyl ether. The complex was dried at reduced pressure. 195 mg, (Yield= 90%). EIMS m/z: 1281 [M^+]. The complex was not soluble enough in common deuterated solvent to allow its NMR spectra to be recorded.

[$PdCl_2$(2)] (4). A solution of 4,7′-bis[4′′-(F-octyl)-butyl]-1,10′-phenantroline (248.6 mg, 0.22 mmol) in 4ml of tetrahydrofuran was

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added to a solution of $Na_2[PdCl_4]$ (46.1 mg, 0.17 mmol) in 4ml of methanol. The orange solution was stirred for 1h and a light brown solid was formed. The complex was filtered off and washed with water, methanol and diethyl ether. The complex was dried at reduced pressure. 172.6 mg, (Yield = 78%). MALDI-TOF m/z: 1305.64 [M^+], 1328.64 [M^++Na], 1270.65 [M^+-Cl]. The complex was not soluble enough in common deuterated solvent to allow its NMR spectra to be recorded.

[Pd(1)$_2$](BARF)$_2$ (5a). To a suspension of **3** (93mg, 0.072mmol) in 20ml dichloromethane, a solution of **1** (84.6 mg, 0.076 mmol) and sodium tetrakis 3,5-(trifluoromethyl)phenyl borate (128.4 mg, 0.145 mmol) in 10ml of dichloromethane were added slowly. The mixture was heated for 1h at 40ºC. The product was filtered off over celite and the solvent was removed under reduced pressure. The product is an oil that was triturated in pentane to obtain pale yellow solid. 101.5mg, (Yield= 34.5%). EIMS m/z: 4084.4 [M^+], 2314.4 [M^+-2·BARF]. ^{1}H NMR (400MHz, $(CD_3)_2CO$): δ 1.77 (m, 8H; $(CH_2)_{4''}$), 2.04 (m, 8H; $(CH_2)_{3''}$), 2.32 (m, 8H, $(CH_2)_{2''}$), 3.14 (t, 8H, $(CH_2)_{1''}$, *J* = 7.2 Hz); 7.66 (s, 8H, BAr'), 7.79 (d, 16H, BAr'), 8.04 (d, 4H, $H_{5,5'}$), 8.82 (s, 4H, $H_{3,3'}$), 9.18 (d, 4H, $H_{6,6'}$, *J* =5.6Hz); ^{19}F NMR ($(CD_3)_2CO$) : δ -63.73 (CF_3,BARF), -81.17 (CF_3), -114.15 (CF_2), -122.39 (CF_2), -123.17 (CF_2), -123.85 (CF_2), -126.57 (CF_2).

[Pd(1)$_2$](PF$_6$)$_2$ (5b). To a suspension of **3** (39mg, 0.030 mmol) in 10ml dichloromethane, a solution of **1** (35.2 mg, 0.0318 mmol) and silver hexafluorophosphate (15.6 mg, 0.0618mmol) in 5ml of dichloromethane

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were added slowly. The mixture was heated for 1h at 40ºC. The product was filtered off over celite and the solvent was removed under reduced pressure. The product is an oil that was triturated in pentane to obtain pale yellow solid. 23 mg, (Yield= 30%). EIMS m/z: 2606 [M^+] . ^{1}H NMR (400MHz, ($CDCl_3$): δ 1.70 (m, 8H; $(CH_2)_{4''}$), 1.81 (m, 8H; $(CH_2)_{3''}$), 2.10 (m, 8H, $(CH_2)_{2''}$), 2.76 (t, 8H, $(CH_2)_{1''}$, *J* = 7.2 Hz); 7.16 (d, 4H, $H_{5,5'}$), 8.26 (s, 4H, $H_{3,3'}$), 8.59 (d, 4H, $H_{6,6'}$, *J* =4.4Hz); ^{19}F NMR (($CDCl_3$) : δ -72.05 (CF_3,PF_6), -81.17 (CF_3), -114.15 (CF_2), -122.15 (CF_2), -122.35 (CF_2), -123.15 (CF_2), -123.95 (CF_2), -126.6(CF_2).

[Pd(1)$_2$](BF$_4$)$_2$ (5c). To a suspension of **3** (39mg, 0.030 mmol) in 10ml dichloromethane, a solution of **1** (35.2 mg, 0.0318 mmol) and silver tetrafluoroborate (12.0 mg, 0.0618 mmol) in 5ml of dichloromethane were added slowly. The mixture was heated for 1h at 40ºC. The product was filtered off over celite and the solvent was removed under reduced pressure. The product obtained as an oil was triturated in pentane and a pale yellow solid was obtained. 8 mg, (Yield= 10%). EIMS m/z: 2488.02 [M^+], 2313.9 [M^+-2·BF_4]. ^{1}H NMR (400MHz, ($CDCl_3$): δ 1.70 (m, 8H; $(CH_2)_{4''}$), 1.83 (m, 8H; $(CH_2)_{3''}$), 2.14 (m, 8H, $(CH_2)_{2''}$), 2.79 (t, 8H, $(CH_2)_{1''}$, *J* = 7.2 Hz); 7.22 (d, 4H, $H_{5,5'}$), 8.22 (s, 4H, $H_{3,3'}$), 8.56 (d, 4H, $H_{6,6'}$, *J* = 4.8Hz); ^{19}F NMR (($CDCl_3$) : δ -28.05 (CF_3,BF_4), -81.17 (CF_3), -114.15 (CF_2), -122.15 (CF_2), -122.35 (CF_2), -123.15 (CF_2), -123.95 (CF_2), -126.6(CF_2).

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[Pd(2)$_2$](BARF)$_2$ (6a). To a suspension of **4** (33.3mg, 0.025mmol) in 10ml dichloromethane, a solution of **2** (29.8 mg, 0.026 mmol) and sodium tetrakis 3,5-(trifluoromethyl)phenyl borate (45.95 mg, 0.0519 mmol) in 5ml of dichloromethane were added slowly. The mixture was heated for 1h at 40ºC. The product was filtered off over celite and the solvent was removed under reduced pressure. The product obtained as a brown oil was triturated in pentane and a pale yellow solid was obtained. 11 mg, (Yield=11%). MALDI-TOF: 2361.77 [M$^+$-2 BARF]. ^{1}H NMR (400MHz, ($CDCl_3$): δ 1.80 (m, 8H; $(CH_2)_{4''}$), 1.9 (m, 16H; $(CH_2)_{3'', 2''}$, 3.25 (t, 8H, $(CH_2)_{1''}$); 7.50 (overlapped, $H_{3,8,3',8'}$), 8.19 (s, 4H, $H_{5,6,5',6'}$), 8.63 (d, 4H, $H_{2,9,2', 9'}$); ^{19}F NMR (($CDCl_3$) : δ -62.05 (CF_3,BARF), -81.17 (CF_3), -114.77 (CF_2), -122.18 (CF_2), -122.40 (CF_2), -123.19 (CF_2), -123.98 (CF_2), -126.6 (CF_2).

[Pd(2)$_2$](PF$_6$)$_2$ (6b). To a suspension of **4** (33.3 mg, 0.025 mmol) in 10ml dichloromethane, a solution of **2** (29.8 mg, 0.026 mmol) and silver hexafluorophosphate (11.9 mg, 0.0519 mmol) in 5ml of dichloromethane were added slowly. The mixture was heated for 1h at 40ºC. The product was filtered off over celite and the solvent was removed under reduced pressure. The product is an oil that was triturated in pentane to obtain pale yellow solid. 13 mg, (Yield=20%). MALDI-TOF: m/z: 2651.81 [M$^+$], 2361.61 [M$^+$-PF_6]. ^{1}H NMR (400MHz, ($CDCl_3$): δ 1.80 (m, 8H; $(CH_2)_{4''}$), 1.9 (m, 16H, $(CH_2)_{3'', 2''}$, 3.36 (t, 8H, $(CH_2)_{1''}$); 7.87 (d, 4H, $H_{3,8,3',8'}$, J = 4.8Hz), 8.27 (s,4H, $H_{5,6,5',6'}$), 9.39 (d, 4H, $H_{2,9,2', 9'}$); ^{19}F NMR (($CDCl_3$) : δ -

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72.05 (CF_3,PF_6), -81.15 (CF_3), -114.68 (CF_2), -122.13 (CF_2), -122.38 (CF_2), -123.14 (CF_2), -123.88 (CF_2), -126.56(CF_2).

[Pd(2)$_2$](BF$_4$)$_2$ (6c). To a suspension of **4** (33.3 mg, 0.025 mmol) in 10ml dichloromethane, a solution of **2** (29.8 mg, 0.026 mmol) and silver tetrafluoroborate (10.1 mg, 0.0519 mmol) in 5ml of dichloromethane were added slowly. The mixture was heated for 1h at 40ºC. The product was filtered off over celite and the solvent was removed under reduced pressure. The product is an oil that was triturated in pentane to obtain pale yellow solid. 4.6 mg, (Yield= 7 %). MALDI-TOF: m/z: 2651.81 [M^+], 2361.61 [M^+-BF_4]. ^{1}H NMR (400MHz, ($CDCl_3$): δ 1.80 (m, 8H; $(CH_2)_{4''}$), 1.97 (m, 16H, $(CH_2)_{3'', 2''}$, 3.35 (t, 8H, $(CH_2)_{1''}$); 7.85 (d, 4H, $H_{3,8,3',8'}$, *J* = 4.8Hz), 8.26 (s, 4H, $H_{5,6,5',6'}$), 9.44 (d, 4H, $H_{2,9,2', 9'}$); ^{19}F NMR (($CDCl_3$) : δ -28 (CF_3, BF_4), -81.15 (CF_3), -114.65 (CF_2), -122.10 (CF_2), -122.34 (CF_2), -123.16 (CF_2), -123.87 (CF_2), -126.54(CF_2).

[Rh(1)(cod)](PF$_6$) (7). Ligand **1** (33 mg, 0.03 mmol) was added to a solution of the complex [Rh(cod)$_2$]PF_6 (13.9 mg, 0.03 mmol) in 2ml of anhydrous dichloromethane. The solution changed from burgundy to orange. Then it was stirred for 5 minutes. Diethyl ether was added to the solution to afford a brown solid. 16.5 mg, (Yield=38%). MALDI-TOF (m/z): 1564.5 [M^+ +Ag], 1330.69 [M^+-PF_6 +H_2O]$^+$. ^{1}H NMR (400MHz, ($CDCl_3$): δ ^{1}H NMR (400 MHz, ($CDCl_3$): δ 1.70 (m, 8H; $(CH_2)_{4''}$), 1.83 (m, 8H; $(CH_2)_{3''}$), 2.14 (m, 8H, $(CH_2)_{2''}$), 2.15 (m, 4H, (CH_2) cod), 2.61 (m 4H,

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(CH_2) cod), 2.79 (t, 8H, $(CH_2)_{1''}$, J = 7.2 Hz); 4.51 (m, 4H, (CH) cod), 7.33 (dd, 2H, $H_{5,5'}$), 7.59 (dd, 2H, $H_{6,6'}$), 8.42 (d, 2H, $H_{3,3'}$). ^{19}F NMR (($CDCl_3$) : δ -71.45 (CF_3,PF_6), -81.15 (CF_3), -114.76 (CF_2), -122.16 (CF_2), -122.39 (CF_2), -123.17 (CF_2), -123.91 (CF_2), -126.58 (CF_2).

[Rh(2)(cod)](PF_6) (8). Ligand **2** (33.9 mg, 0.03 mmol) was added to a solution of the complex [Rh(cod)$_2$]PF_6 (13.9 mg, 0.03 mmol) in 2ml of anhydrous dichloromethane. The solution changed from burgundy to dark brown. Then it was stirred for 5 minutes. Diethyl ether was added to the solution to afford a brown solid. (12 mg, 27%). MALDI-TOF: m/z: 1354 [M^+-PF_6]. ^{1}H NMR (400MHz, ($(CD_3)_2CO$): δ ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 1.70 (m, 8H; $(CH_2)_{4''}$), 1.83 (m, 8H; $(CH_2)_{3''}$), 2.14 (m, 8H, $(CH_2)_{2''}$), 2.32 (m, 4H, (CH_2) cod), 2.65 (m 4H, (CH_2) cod), 2.79 (t, 8H, $(CH_2)_{1''}$, J = 7.2 Hz); 4.76 (m, 4H, (CH) cod), 7.99 (dd, 2H, $H_{5,6,5',6'}$), 8.44 (dd, 2H, $H_{2,9,2',9'}$), 8.54 (d, 2H, $H_{3,8,3',8'}$). ^{19}F NMR ($(CD_3)_2CO$) : δ -72.11 (CF_3,PF_6), -82.05 (CF_3), -115.07 (CF_2), -122.70 (CF_2), -122.87 (CF_2), -123.67 (CF_2), -124.40 (CF_2), -127.17(CF_2).

Reaction of 7 and 8 with CO

To a solution of of [Rh(cod)(**1,2,11,12**)]PF_6 in dichloromethane was bubbled CO during 5 minutes. The solution changed from orange to yellow indicating the formation of carbonyl species.

For ligand **1** ν(CO): 2097.5, 2039.1; **2** ν(CO): 2098.6, 2040.7; **11** ν CO): 2097.4, 2038.5; **12** ν(CO): 2099.5, 2042.5

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Acknowledgment

We gratefully acknowledge the Generalitat de Catalunya (DURSI and Fons Social Europeu) for a Fellowship (FI anb BE2007) to C. T. and 2005SGR00777, the Ministerio de Educacion y Ciencia (CTQ2004-03831/PPQ, CSD2006-0003). Macromolecular chemie (ITMC) of Aachen and the group of polymers (URV) for measuring the molecular weight of the polyketones.

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Chapter 5

New rhodium catalytic systems with trifluoromethyl phosphite derivatives for the hydroformylation of 1-octene in supercritical carbon dioxide

Part 1

Clara Tortosa-Estorach, Arantxa Orejón, Anna M. Masdeu-Bultó, *Green Chemistry*, submitted.

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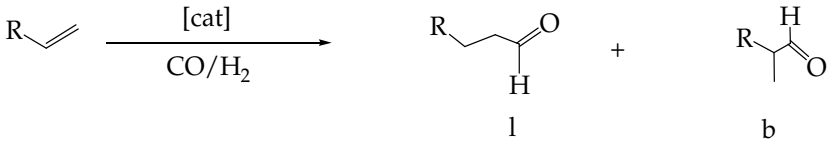
Abstract

Hydroformylation of 1-octene in supercritical carbon dioxide was performed using new soluble rhodium-phosphite catalytic systems. A high conversion and selectivity in the corresponding aldehydes were obtained. The ligands were synthesised and its coordination to Rh(I) complexes was studied. The reactivity of rhodium precursors with these ligands towards CO and H_2 was analysed by high pressure IR and NMR spectroscopies.

Introduction

Catalytic hydroformylation is an interesting reaction used to transform alkenes into aldehydes using carbon monoxide and hydrogen (Scheme 1). The linear aldehydes (l) thus obtained are important in industrial applications because they can be converted into plasticizer alcohols and biodegradable detergents. Additionally, the branched aldehydes (b) are used to promote asymmetric intermediates for the synthesis of arylpropionic acids, which are subsequently used in anti-inflammatory drugs such as ibuprofen or naproxen.[1]



Scheme 1.

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Supercritical carbon dioxide ($scCO_2$) is an environmental benign solvent that can be used in homogeneous catalysis to replace the organic solvents usually employed. The use of $scCO_2$ in homogeneous hydroformylation affords control of the phase behaviour, allows dissolution of the catalyst precursors and recovery of catalyst by precipitation, and has the potential for precise tuning of solvent properties through small changes in temperature and pressure.[2] Water has also been used in hydroformylation as a green solvent, although the low solubility of the organic reactants in this media has restricted its application to the hydroformylation of low alkenes.[3]

P-donor ligands, specifically phosphines and phosphites, with rhodium complexes are the most successful systems in the hydroformylation reactions.[4] The primary advantage for using phosphite ligands rather than phosphines is the higher reactivity of the corresponding rhodium catalysts, which lead to very highly active systems.[5] The first example of the use of phosphite ligands in rhodium-catalysed hydroformylation of 1-alkenes was reported by Pruett and Smith of Union Carbide Corporation.[6] Generally, using these kinds of ligands results in an increase in the linear aldehyde when the electron withdrawing properties of the ligand increase.[1c] In the 1980's, Trzeciak *et al.* studied the hydroformylation of alkenes using rhodium catalyst associated with several phosphite ligands.[7] Van Leeuwen *et al.* studied the hydroformylation of alkenes using rhodium complexes with tris(*o*-tert-butylphenyl)phosphite[8] and bulky ligands as tris(2-tert-butyl-4-methylphenyl)phosphite as catalysts, and obtained high rates in the

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hydroformylation of 1-octene.[9] Also, van Leeuwen studied ligands with a high electron withdrawing effect such as tris(2,2,2-trifluoroethyl)phosphite.[10]

The rhodium-catalysed hydroformylation of alkenes in $scCO_2$ has been extensively studied,[2,11] although the majority of the catalytic systems contain phosphine ligands. To increase the solubility in $scCO_2$ of the low soluble catalysts, *CO_2-philic* groups must be introduced in the ligands. The most efficient groups are the perfluorinated long chains, which have been introduced in aryl phosphines.[12] Simple low molecular weight trialkylphosphines such as PEt_3 have been used as ligands in phosphine-modified homogeneous rhodium-catalysed 1-hexene hydroformylation in supercritical carbon dioxide, but as the alkylic chain grows the solubility and catalytic activity decreases.[13] Erkey and Palo demonstrated that simple CF_3- groups introduced in triphenylphosphine form $scCO_2$ soluble systems with rhodium, which are active in the hydroformylation of 1-octene in $scCO_2$.[14] Very few examples of phosphite-based catalytic systems using $scCO_2$ can be found in the literature.[15]

Taking into account the above-mentioned considerations, we have prepared new rhodium catalytic systems containing easy-to-prepare aryl phosphite ligands with $–CF_3$ groups in order to study their catalytic activity in the rhodium-catalysed hydroformylation of 1-octene. The introduction of a trifluoromethyl group increases the π-acceptor ability of the phosphite. To control the electronic properties of these ligands, the fluorous group was also introduced as trifluoromethoxy

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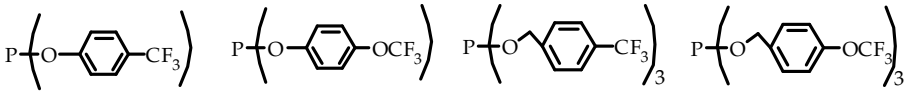
and a methylene was located between the aryl and the oxygen atom of the phosphite. Thus, we have prepared a family of phosphites with different donor and steric properties ligands **1-4** (Figure 1), and we have studied their coordination chemistry to rhodium complexes and the catalytic activity of the [Rh(acac)$(CO)_2$]/**1-4** systems in the hydroformylation of 1-octene in supercritical carbon dioxide.



1 **2** **3** **4**

Figure 1.

Results and discussion

Synthesis of ligands

Ligands **1–4** were prepared from the commercially available corresponding alcohol by reaction with phosphorus trichloride in diethyl ether in the presence of pyridine (Scheme 2). The ligands were purified by flash chromatography on basic alumina and eluted with hexane under an inert gas and obtained as air- and moisture-sensitive colourless oils or white solid in good yields (53-67%). The synthesis of ligand **1** using the lithium phenoxide derivative was previously described by Pringle *et al*.[16] The ^{1}H NMR spectra of ligands **1-4** show two doublets in the aromatic region between δ 7.13 and 7.62 ppm and signals

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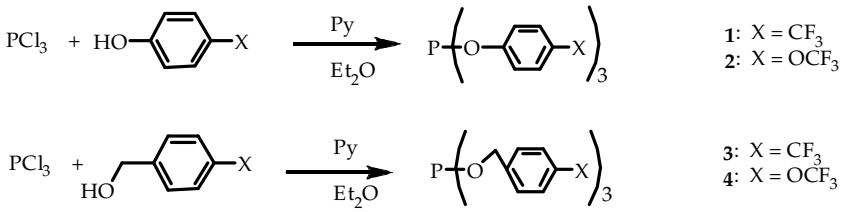
of the $–CF_3$ at δ -62.0 to -63.0 ppm and $–OCF_3$ at -58.7 to -59.0 ppm in the ^{19}F NMR spectra. The ^1H NMR spectra of the benzilic derivatives **3** and **4** contain a doublet for the methylene resonances at δ 4.85 and 4.93 ppm, respectively. The singlet signals at the ^{31}P $\{^1H\}$ NMR spectra appear at δ 126.5, 140.1, 140.6 ppm for **2-4,** respectively, which are typical values for these kinds of aryl phosphite compounds.[17]



Scheme 2.

Synthesis of Complexes

In order to study the coordination chemistry of **1-4**, we explored their reactivity with a model cationic rhodium (I) complex $[Rh(cod)_2]PF_6$ (cod = 1,5-ciclooctadiene). When 2 equivalents of the ligands **1-4** were added to a solution of $[Rh(cod)_2]PF_6$ in anhydrous dichloromethane at room temperature, the $^{31}P\{^1H\}$ NMR showed different signals depending on the ligand. For the less π-acceptor and bulkier ligands **3** and **4**, the ^{31}P $\{^1H\}$NMR spectra show only one doublet at δ 118.5 ppm ($J_{P,Rh}$= 246 Hz) and 117.2 ppm ($J_{P,Rh}$= 246 Hz) respectively, which correspond to the coordinated phosphite ligand in a rhodium complexes [Rh(cod)(**3-4**)$_2$]PF_6 (Scheme 3). The ^1H NMR signals corresponding to the

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coordinated ligands are shifted slightly downfield with respect to the free ligand. The presence of coordinated cyclooctadiene was confirmed by ^{1}H NMR spectrum with signals at δ 4.60 ppm (CH=CH), 2.57 and 2.37 ppm (-CH_2-). The mass spectra confirmed the formation of the complexes that were obtained as orange oils in good yields.

However, in the case of **1** and **2**, the ^{31}P {^{1}H}NMR spectra show two doublets in the region of coordinated phosphorus at δ 108.2 (J_{PRh}= 214 Hz) and 118.4 (J_{PRh} = 312 Hz) for phosphite **1** and δ 104.74 (J_{PRh}= 266.6 Hz) and 117.8 ppm (J_{PRh} = 320.3 Hz) for phosphite **2**, indicating that there may be a mixture of the rhodium complexes [Rh(cod)(**1-2**)$_2$]PF_6 and [Rh(**1-2**)$_4$]PF_6. In the case of ligand **2**, when the synthesis was performed with a P/Rh molar ratio of 4:1, the ^{31}P {^{1}H}NMR spectrum only shows the signal at δ 108.7 ppm, while there was no evidence of the signals corresponding to coordinated cyclooctadiene in the ^{1}H NMR what indicates that [Rh(**2**)$_4$]PF_6 was formed. The complex was isolated by recrystallisation with CH_2Cl_2 and hexane and fully characterised. In the case of the rhodium complex with ligand **1**, when the synthesis was performed at P/Rh molar ratio of 4:1, a mixture of two doublets at the $^{31}P\{^{1}H\}$ NMR persisted. Attempts to separate the complexes by recrystallisation were unsuccessful. The formation of species with more ligands coordinated per rhodium is favoured for the strong π-acceptor and less sterically demanding ligands **1** and **2**. Similar complexes [Rh(ligand)$_4$]X have been prepared with phosphites.[18,15b]

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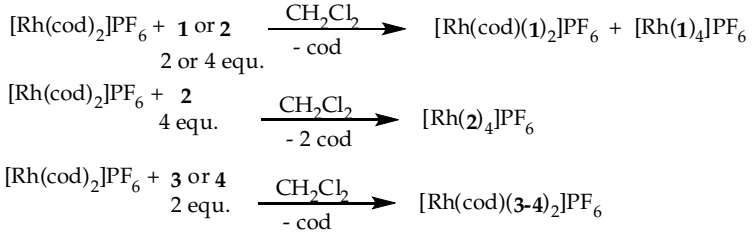

Scheme 3.

Reactivity of [Rh(acac)(CO)$_2$] /1-4 with CO and H_2

In order to determinate which species are formed in conditions similar to those used in hydroformylation, the reactivity of **1-4** with [Rh(acac)(CO)$_2$] in the presence of CO and H_2 was analysed by high pressure NMR (HPNMR) and IR (HPIR) spectroscopies.

The $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded for the complex [Rh(acac)(CO)$_2$] in the presence of 6 equiv. of ligand **1**–**4** in toluene-d_8 ([Rh] = 2×10^{-2} M) after the addition of H_2 and CO. As the IR technique is more sensitive than NMR, the IR spectra could be recorded at concentrations closer to the catalytic value (2.4×10^{-3} M) in methyltetrahydrofurane under the same conditions. A list of identified species is given in Table 1.

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Table 1. Identified species for $[Rh(acac)(CO)_2]$ /**1-4** with CO/H_2 after 1h at 70ºC.

Complex	δ(^{31}P) [ppm] ($J_{Rh,P}$ [Hz])	δ(^{1}H) (hydride) [ppm] ($J_{P,H}$, $J_{Rh,H}$ [Hz])	ν(CO) [cm^{-1}]
$[Rh(CO)H(\mathbf{1})_3]$	135.9 d (239.8)	-10.7 b	2078
$[Rh(CO)H(\mathbf{2})_3]$	138.2 d (238)	-10.7 d (3.6)	2072
$[RhH(\mathbf{2})_4]$	143.9 d (237)	-10.9 dquint (1.6, 4.7)	-
$[Rh(CO)H(\mathbf{3})_3]$	156.8 d (214.5)	-10.5 dq (7.5, 14.5)	2040
$[RhH(\mathbf{3})_4]$	154.6 d (210)	-11.4 dquint (10.5, 36.6)	-
$[Rh(CO)H(\mathbf{4})_3]$	156.5 d (213.5)	-10.5 dq (7.3, 14.5)	2052
$[RhH(\mathbf{4})_4]$	154.6 d (206.1)	-11.4 dquint (10.0, 35.5)	-

[a] Reaction conditions: **1-4/** $[Rh(acac)(CO)_2]$= 6, after 1h at 70ºC with $CO:H_2$(1:1) = 20 atm; n.d. = non determined; d = doublet, t = triplet, dq = double quadruplet, quint = quintuplet, dquint = double quintuplet.

The ^{31}P $\{^{1}H\}$NMR spectrum of the solution containing the system $[Rh(acac)(CO)_2]$/**1** at room temperature consists of a major doublet of doublets at δ 108.4 ppm (J_{PP} = 54; J_{PRh} = 222 Hz) and a doublet of triplets at δ 116.9 ppm (J_{PP} = 53; J_{PRh} = 280 Hz) attributed to $[RhX(\mathbf{1})_3]^+$ (X = CO, solvent, acac) in comparison with reported data.[19] A small broad signal also appeared at δ 114.7 ppm that can be related to species $[Rh(acac)(CO)_n(\mathbf{1})_{2-n}]$ formed by substitution of the CO by **1** at the starting material (Scheme 4).[17c,20] The signal corresponding to free phosphite **1** was also observed and decomposition of the ligand was detected (signals at δ 0 ppm).

$$[Rh(acac)(CO)_2] \underset{CO}{\overset{\mathbf{1}}{\rightleftharpoons}} [Rh(acac)(CO)(\mathbf{1})] \underset{CO}{\overset{\mathbf{1}}{\rightleftharpoons}} [Rh(acac)(\mathbf{1})_2] \overset{\mathbf{1}}{\rightleftharpoons} [RhX(\mathbf{1})_3]$$

X=CO, solvent, acac

Scheme 4. Species formed by reaction of $[Rh(acac)(CO)_2]$ + **1**

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After addition of 20 atm of H_2:CO (1:1) and heating the solution at 70ºC for 1h, the $^{31}P\{^1H\}$NMR showed a major doublet at δ 135.9 ppm and in the ^1H NMR spectrum a broad signal at the hydride region (δ -10.70 ppm), which were assigned to the species [Rh(CO)H(**1**)$_3$] by comparison with published data for the analogous species [Rh(CO)H{P(OPh$_3$}$_3$].[7d] A minor doublet of doublets at 123.9 (J = 292.6, J = 180.0 Hz), related with a double triplet at 63.0 (J = 295.6, J = 101.0 Hz) was attributed to rhodium species with mixed phosphite-phosphonate ligands. Similar species were observed with alkylic phosphites.[15] Resonances corresponding to the free and decomposed ligand **1** were also observed (Figure 2).

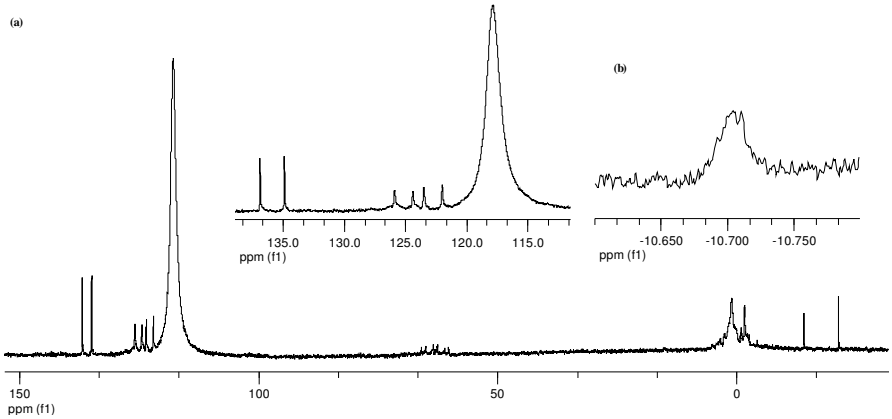

Figure 2. NMR spectra at 20ºC of [Rh(acac)(CO)$_2$] / **1** (P/Rh = 6) in toluene-d$_8$: a) $^{31}P\{^1H\}$ NMR under 20 atm of CO/H_2 (1:1); b) hydride region of ^1H NMR.

The HPIR of the system [Rh(acac)(CO)$_2$]/**1** at 20 atm CO/H_2 (1:1) after 1h stirring at 70ºC, showed in the υ(CO) region signals at 2078, 2018, 1994, 1968 and 1945 cm^{-1}. By comparison with reported data for

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[Rh(CO)H{P(OPh_3}$_3$][21] we assigned the band at 2078 cm^{-1} to [Rh(CO)H(**1**)$_3$]. The other signals are in the range of the ones reported in the literature for dicarbonyl species [$Rh(CO)_2H${P(OPh_3}$_2$][17c,22], therefore could be attributed to the isomers of [$Rh(CO)_2H$(**1**)$_2$]. These species were not detected at the HPNMR but the lower concentration used for the HPIR solution may favour the formation of them. Nevertheless, they could correspond also to carbonyl species with the phosphonate ligands formed by decomposition of **1** observed at the HPNMR.

The ^{31}P {^1H} NMR and ^1H NMR spectra of [Rh(acac)$(CO)_2$]/**2** system (P/Rh = 6) in d_8-toluene under 20 atm of CO/H_2 (1:1), after heating at 70ºC for 1h (Figure 3), showed a major doblet at ^{31}P {^1H} at 138.2 ppm. In the hydride region of ^1H NMR spectrum appeared a doublet at δ -10.70 ppm. For comparison with the above described complexes, these two signals are assigned to the specie [Rh(CO)H(**2**)$_3$]. The doublet corresponds to a Rh-H coupling and the P-H coupling constant was not observed.[23] An small doublet at δ 143.9 ppm and a quintuplet signal in the ^1H NMR at δ -10.93 ppm was assigned to the [RhH(**2**)$_4$]. The resonances of rhodium carbonyl species with phosphonate/phosphite mixed ligands and free phosphite were also observed.

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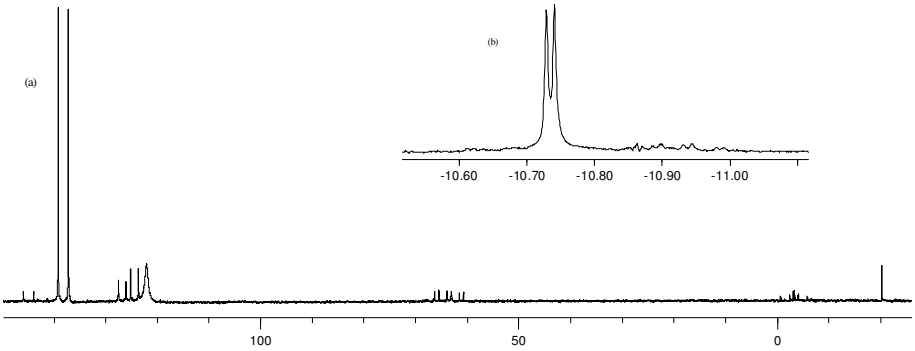

Figure 3. NMR spectra at 20ºC of [Rh(acac)(CO)$_2$] / **2** (P/Rh = 6) in toluene-d$_8$: a) ^{31}P{^{1}H} NMR under 20 atm of CO/H$_2$ (1:1); b) hydride region of ^{1}H NMR.

The signals ν(CO) of the carbonylic rhodium species formed with ligand **2** could be observed at the IR spectrum. The HPIR spectrum, after 1h under reaction conditions, showed the absorption corresponding to [RhH(CO)(**2**)$_3$] at 2072 cm^{-1}, the other small bands at 2051, 2024, 1985 and 1941 cm^{-1}, like in phosphite **1**, could correspond to the minority carbonyl species.

The ^{31}P {^{1}H}NMR and ^{1}H NMR spectra of [Rh(acac)(CO)$_2$]/**3** system (P/Rh = 6) in d$_8$-toluene under 20 atm of CO/H$_2$ (1:1), after heating 70ºC for 1h, showed a major doublet at δ 156.8 ppm corresponding to [Rh(CO)H(**3**)$_3$] together with the doublet of quadruplets at δ -10.50 ppm in the ^{1}H NMR. An small doublet at δ 154.6 ppm together with a doublet of quintuplets in the hydride region at δ -11.80 ppm in the ^{1}H NMR were assigned to [RhH(**3**)$_4$]. At δ 137.3 ppm was the singlet corresponding to the free phosphite (Figure 4).

The HPIR spectrum of the [Rh(acac)(CO)$_2$]/**3** system with 20 atm of CO/H$_2$ (1:1) after 1h at 70ºC, showed a band at 2040 cm^{-1} assigned to

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[Rh(CO)H(**3**)$_3$], the ones at 1986, 1918 and 1968, could correspond to the dicarbonyl isomer species of [Rh(CO)$_2$H(**3**)$_2$]

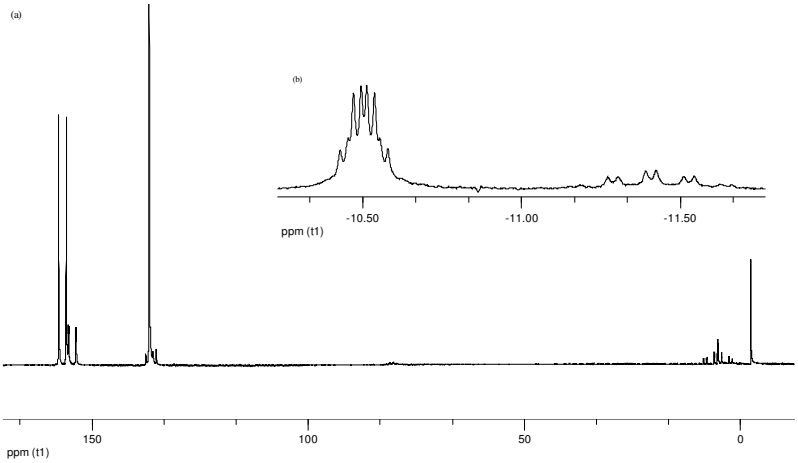

Figure 4. NMR spectra at 20ºC of [Rh(acac)(CO)$_2$] / **3** (P/Rh = 6) in toluene-d$_8$

The ^{31}P {^{1}H}NMR and ^{1}H NMR spectra of [Rh(acac)(CO)$_2$]/**4** system (P/Rh = 6) in d$_8$-toluene under 20 atm of CO/H$_2$ (1:1), after heating 1h at 70ºC were recorded. The major doublet at δ 156.5 ppm showed in the ^{31}P{^{1}H} NMR and the corresponding doublet of quadruplets in the ^{1}H NMR at δ -10.47 ppm were assigned to [RhH(CO)(**4**)$_3$]. An small doublet appeared in the ^{31}P {^{1}H}NMR at 154.6 ppm and the doublet of quintuplets appeared in the ^{1}H NMR at δ -11.39 ppm were assigned to [RhH(**4**)$_4$]. At δ 136.0 ppm was remaining the singlet corresponding to the free phosphite and also other signals near to the free phosphite which corresponded to [Rh(acac)(**4**)$_2$] and [Rh(acac)(CO)(**4**)]. Finally, resonances at δ 80 and 0 ppm correspond to species with decomposed ligand (Figure 5).

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In the HPIR experiment of $Rh(acac)(CO)_2$/**4** system with 20 atm of CO/H_2 (1:1) at 70ºC for 1h was observed 2053 cm^{-1} a band corresponding to the $[Rh(CO)H(\mathbf{4})_3]$, the absorptions at 2021 and 1938 cm^{-1} and the ones at 1990 and 1930 cm^{-1} could be assigned to the $[Rh(CO)_2H(\mathbf{4})_2]$. A band at 1881 cm^{-1} could correspond to rhodium species with bridging carbonyl ligands.

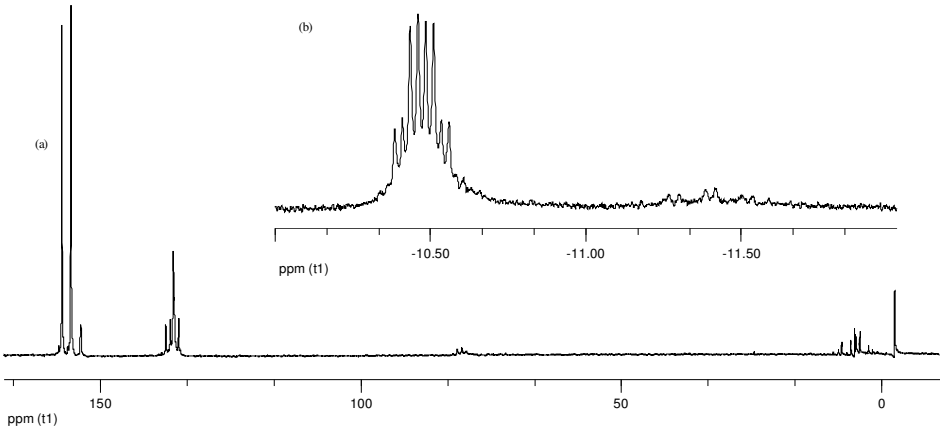

Figure 5. NMR spectra at 20ºC of $[Rh(acac)(CO)_2]$ / **4** (P/Rh = 6) in toluene-d_8: a) $^{31}P\{^1H\}$ NMR under 20 atm of CO/H_2 (1:1); b) hydride region of ^1H NMR.

In summary, for all these phosphites, the major rhodium species formed under CO/H_2 pressure were the expected carbonyls $[Rh(CO)H(\mathbf{1\text{-}4})_3]$, which are the precursors for the active hydroformylation catalysts. The values of the streching ν(CO) bands confirm that the ligands **1** and **2** are stronger π-acceptors than ligands **3** and **4**. The species lacking the carbonyl $[RhH(\mathbf{2\text{-}4})_4]$ were also detected. The analogous species $[Rh(CO)H\{P(OPh)_3\}_3]$ and $[RhH\{P(OPh)_3\}_4]$ also

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exists in equilibrium when [Rh(acac){P(OPh)$_3$}$_2$] reacts with CO and H_2 in the presence of free phosphite.[7d] To determine which type of species are formed is important to understand the catalytic behaviour since it has been shown that [Rh(CO)H{P(OPh)$_3$}$_3$] is active in hydroformylation while [RhH{P(OPh)$_3$}$_4$] produces isomerisation by-products.[7d,24] In the case of phenol-derived phosphites (**1** and **2**), mixed phosphite/phosphonate carbonyl rhodium species were formed during the experiment. It is likely that dicarbonyl species such as [Rh(CO)$_2$H(**1-4**)$_2$] were formed in the HPIR solution conditions, due to its low concentration.

Hydroformylation of 1-octene

We studied the hydroformylation of 1-octene with the catalytic precursors system [Rh(acac)(CO)$_2$]/**1-4**, in supercritical carbon dioxide ($scCO_2$) and in toluene as a model solvent.

Initially, the solubility in $scCO_2$ of the catalysts precursors at catalytic concentration in the presence of CO and H_2 was evaluated. To do this, a 100 ml Thar autoclave equipped with sapphire windows was used. The purged autoclave was charged with 0.06 mmol of [Rh(acac)(CO)$_2$] and the corresponding ligand **1-4** (P/Rh = 6), filled with CO/H_2 at 20 atm (CO/H_2 = 1/1), and pressurised with CO_2 up to 250 atm at 70ºC. The solubility was determined by visual inspection through the windows which showed the coloured supercritical phase at different conditions depending on the ligand used. Catalytic systems with

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phenol-derived phosphites **1** and **2** were soluble at milder conditions (175 atm) compared to the benzyl derivates **3** and **4**, which were soluble at 210 atm. There were no apparent differences between the solubility in $scCO_2$ of the systems containing the ligands with trifluoromethyl or trifluoromethoxi groups.

For comparative purposes and as a reference organic medium, we performed the hydroformylation of 1-octene in toluene at 100ºC, 20 atm of total pressure and at a phosphite /rhodium ratio of 6. The results are shown in Figure 6.

Catalytic systems with ligands containing the $–OCF_3$ groups **2** and **4** show total conversion and very high selectivity in the aldehydes. Lower conversions and chemoselectivities were obtained with the catalytic systems with the ligands **1** and **3**. The by-products were 2-octenes, which can be formed through isomerisation due to the presence of [RhH(**1-4**)$_4$]. The l/b ratio for all the systems was high (2.5-5.2), as was similarly observed for other rhodium-phosphite systems.[7a,24] Nevertheless, the cases with the higher values of l/b can be related with high isomerisation, which transforms the branched Rh-alkyl intermediate in the product of isomerisation.

The catalytic experiments using $scCO_2$ as solvent with the catalytic systems [Rh(acac)$(CO)_2$]/**1-4** are summarised in Figure 6 and Table 2. The hydroformylation of 1-octene was performed at 250 atm of total pressure and 100ºC to ensure the solubility of the catalytic systems. The catalytic systems with the phenol CF_3-phosphites **1** and **2** resulted in very high conversions. In the case of [Rh(acac)$(CO)_2$]/**1,** the conversion

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was higher than that obtained in toluene. Nevertheless, the selectivities in aldehydes for $scCO_2$ systems were lower than the ones obtained in toluene. However, the catalytic systems with ligands **3** and **4** $scCO_2$ resulted in high selectivities in aldehydes, which were only slightly lower than the ones obtained in toluene (Figure 6). To improve the selectivity of the Rh/**1-2** catalytic systems, the reaction conditions were optimised with the catalytic system [Rh(acac)$(CO)_2$]/**1** (Table 2).

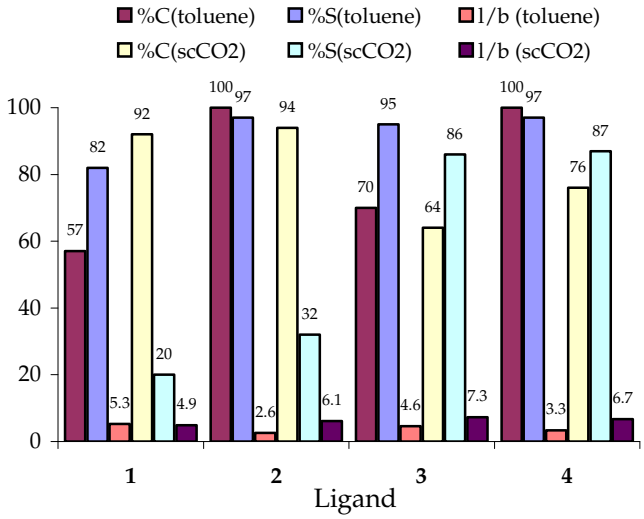

Figure 6. Hydroformylation of 1-octene in $scCO_2$ and in toluene. [Rh(acac)$(CO)_2$] = $2.4 \cdot 10^{-3}$ M, 1-octene/Rh = 200, $P_{CO} = P_{H2}$ = 10 atm, T(ºC) = 100, t = 3 h; for toluene: V = 10 mL; for $scCO_2$: V = 25 mL, P_{TOT} = 250 atm. %C : Total conversion measured by GC. %S: Selectivity in aldehydes.

Decreasing the concentration of rhodium leads to less conversion of products, although the selectivity in aldehydes increased from 20% to

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40% (entry 1, Table 2). In this case the internal aldehyde, 3-ethyl-heptanal, was also detected.

Since the isomerisation process involves β-hydride elimination which requires the creation of a vacant site,[25,26] it can be suppressed by low temperatures. Decreasing the temperature from 100ºC to 70ºC leads to an increase in the selectivity in aldehydes from 20 to 40%, as well as a higher regioselectivity to the linear product (entry 2, Table 2).

Table 2. Hydroformylation of 1-octene using $Rh(acac)(CO)_2$/**1** catalytic system in $scCO_2$.

Entry	T(ºC)	P_{CO}/P_{H2} (atm)	P_{TOT} (atm)[b]	%C[c]	$\%S_a$[d]	l/b/int[e]	$\%S_i$ [f]
1[g]	100	10/10	250	53	40	70/20/10	60
2	70	10/10	250	99	40	86/11/3	60
3	70	10/10	180	99	60	87/12/1	40
4	70	5/5	180	86	20	90/10/-	80
5	70	10/10	180	71	49	86/14/-	51

[a] Reaction conditions: $[Rh(acac)(CO)_2]$ = 0.06 mmol, [Rh]= $2.4 \cdot 10^{-3}$ M, 1-octene = 12 mmol, 1-octene/Rh = 200, L/Rh = 6, *V* = 25 mL, *t* = 3 h. [b] Total pressure. [c] Total conversion measured by GC. [d] Selectivity for aldehydes.[e] int = internal aldehydes: 2-ethylheptanal. [f] Selectivity in isomerised products (internal octenes). [g] $[Rh(acac)(CO)_2]$ = 0.03 mmol, [Rh]= $1 \cdot 10^{-3}$ M. [h] L/Rh =10.

Decreasing the total pressure to the limit conditions of solubility (180 atm, 70ºC) increased the selectivity to 60% and the conversion remained high (entry 3, Table 2). When the partial pressure of carbon monoxide and hydrogen was decreased to 10 atm (CO/H_2 = 5/5) at 70ºC, the selectivity in aldehydes dropped to 20% and the conversion decreased to 86% (entry 4, Table 2). To avoid the effect of a possible decomposition of the ligand, the ligand/rhodium ratio was increased to

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10, although no improvement of the results was obtained (entry 5, Table 2), indicating that this decomposition is not produced to a large extent in catalytic conditions.

These experiments lead us to conclude that the best conditions for hydroformylation of 1-octene is 70ºC, 20 atm of partial pressure, a phosphite/rhodium ratio of 6 and a total pressure close to the solubility conditions. At these conditions, we performed the hydroformylation of 1-octene with the other phosphite ligands (Table 3).

Table 3. Hydroformylation of 1-octene with system [Rh(acac)$(CO)_2$]/**2-4** at soluble and non soluble conditions.[a]

Entry	Ligand	T(°C)	P_{TOT} (atm)[b]	%Conv[c]	$\%S_a$[d]	l/b/int[e]	$\%S_i$[f]
1	**2**	100	250	94	32	86/14/-	68
2	**3**	100	250	64	86	88/12/-	14
3	**4**	100	250	76	28	83/17/-	72
4	**2**	70	180	99	37	61/21/11	63
5	**3**	70	210	50	94	80/20/-	6
6	**4**	70	210	93	62	77/22/1	38

[a] Reaction conditions: [Rh(acac)$(CO)_2$] = 0.06 mmol, [Rh]= $2.4 \cdot 10^{-3}$ M, 1-octene = 12 mmol, 1-octene/Rh = 200, V = 25 mL, $P_{CO} = P_{H2}$ = 10 atm, t = 3 h. [b] Total pressure. [c] Total conversion measured by GC. [d] Selectivity for aldehydes.[e] int = internal aldehydes: 2-ethylheptanal. [f] Selectivity in isomerised products (internal octenes).

For the [Rh(acac)$(CO)_2$]/**2** catalytic system, the conversion and the selectivity increased up to 99% and 37% respectively, although the regioselectivity to the linear aldehyde decreased to 61% (entries 1 *vs.* 4, Table 3). For [Rh(acac)$(CO)_2$]/**3,** the reaction was performed at 210 atm

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and we observed an increase in the regioselectivity to 94%, although the conversion dropped to 50% (entries 2 *vs.* 5, Table 3). Finally, for the catalytic system [Rh(acac)$(CO)_2$]/**4** at 210 atm, the conversion increased from 76% to 93% and the selectivity from 28 to 62% respectively (entries 3 *vs.* 6, Table 3).

In summary, the catalyst precursor [Rh(acac)$(CO)_2$]/**1-4** were active in the hydroformylation of 1-octene in $scCO_2$. Changing the solvent from toluene to a more environmentally friendly $scCO_2$ resulted in higher or similar conversions and regioselectivities for systems [Rh(acac)$(CO)_2$]/**1,2,4** although the selectivity was lower. With catalytic system [Rh(acac)$(CO)_2$]/**3** the selectivity obtained in $scCO_2$ was higher than the one in toluene and the conversion was 20% lower.

Conclusions

Here, we have synthesised new P-donor ligands **2-4** with CF_3 and $-OCF_3$ groups and studied their coordination with rhodium (I). The reactivity of Rh(acac)$(CO)_2$/ **1-4** with CO/H_2 at 20 atm and 70ºC, studied by HPNMR and HPIR, showed [RhH(CO)(**1-4**)$_3$] as the main specie formed in solution. The solubility conditions of the systems were similar for phenol derivates phosphites (180 atm) and for benzyl derivates phosphites (210 am). All of them were active in the hydroformylation of 1-octene in $scCO_2$, affording conversions up to 93-99% for the systems

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[Rh(acac)$(CO)_2$]/**1,2,4** and selectivities up to 94% for the system [Rh(acac)$(CO)_2$]/**3**.

Experimental

All reactions were performed under nitrogen using standard Schlenk techniques. Solvents were distilled and degassed prior to use. ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F and $^{31}P\{^{1}H\}$ NMR spectra were recorded with Varian Gemini spectrometers operating at 300 or 400 MHz (^{1}H), 75.43 or 100.57 MHz (^{13}C), 376.3 MHz (^{19}F) or 121.4 or 161.9 MHz (^{31}P). Chemical shifts are reported relative to tetramethylsilane for ^{1}H and $^{13}C\{^{1}H\}$ as internal reference, 85 % H_3PO_4 for $^{31}P\{^{1}H\}$. Mass spectrometry was performed with Voyager-DE-STR (Applied Biosystems, MDS SCIEX) instrument equipped with a 337 nm nitrogen laser). All spectra were acquired in the positive ion reflector mode 2,5-Dihydroxybenzoic acid (DHB) was used as the matrix. The matrix was dissolved in MeOH at a concentration of 10 mg/mL. The sample was dissolved in CH_2Cl_2 (5 mg/mL) and was deposited (0.5 mL) prior to the matrix on the target. For each spectrum, 100 laser shots were accumulated. In a typical MALDI experiment, the matrix and the salt solutions were premixed in the ratio 1 mL matrix: 0.5 mL sample. Approximately 1 µl of the obtained mixture was hand spotted on the target plate. High-pressure NMR experiments (HPNMR) were carried out in a 10-mm-diameter sapphire tube with a titanium cap equipped with a Teflon/polycarbonate protection.[27] High-pressure IR experiments were performed *in situ* with an infrared autoclave.[28] Gas

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chromatography analyses were performed with a Hewlett-Packard 5890A apparatus in an HP-5 (5% diphenylsilicone/95% dimethylsilicone) column (25 m × 0.2 mm) for the separation of the products and undecane as internal standard.

Preparation of tris(4-Trifluoromethyphenyl)phosphite (1)

To a solution of 4-(trifluoromethyl)fenol (1 g, 5.98 mmol) and pyridine (0.58 ml, 7.18 mmol, 1.2 eq) in 15 ml diethylether at 0ºC, a solution of PCl_3 (0.21 ml, 2.39 mmol, 1.2 eq) in 3 ml of diethyl ether was added drop wise. The solution was stirred at room temperature under inert atmosphere for 2h. The formation of a salt was observed immediately. After 2h, the solvent was removed under reduced pressure. The resulting colourless solid was redissolved in hexane and purified by flash chromatography on basic alumina eluting with hexane to give **1** (0.619 g, 60%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.23 (d, 6H, CH, J_{HH} = 8.4 Hz), 7.62 (d, 6H, CH, J_{HH} = 8.4 Hz). $^{13}C\{^{1}H\}$ NMR (100.57 MHz, $CDCl_3$) δ (ppm) 121.2 (d, CH, J_{CP} = 6.8 Hz), 124.4 (q, CF_3, J_{CF} = 271.5 Hz), 127.4 (s, C), 127.9 (q, CH, J_{CF} = 3.8 Hz), 154.1 (s, C). $^{31}P\{^{1}H\}$ NMR (161.9 MHz, $CDCl_3$) δ (ppm) 126.1 (in accordance with ref.[16]). ^{19}F NMR (376.3 MHz, $CDCl_3$) δ (ppm) -62.5. EIMS m/z: 515.2 $(M+H)^+$.

Preparation of tris(4-trifluoromethoxyphenyl)phosphite (2)

To a solution of 4-(trifluoromethoxy)fenol (1 ml, 7.56 mmol) and pyridine (0.73 ml, 9.08 mmol, 1.2 eq) in 10 ml diethyl ether at 0ºC, a

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solution of PCl_3 (0.27 ml, 3.03 mmol, 1.2 eq) in 3 ml of diethyl ether was added drop wise. The solution was stirred at room temperature under inert atmosphere for 2h. The formation of a salt was observed immediately. After 2h, the solvent was removed under reduced pressure. The resulting colourless solid was redissolved in hexane and purified by flash chromatography on basic alumina eluting with hexane to give **2** (0.543 g, 53%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.13 (d, 6H, CH, J_{HH} = 9 Hz); 7.19 (d, 6H, CH, J_{HH} = 9 Hz). $^{13}C\{^{1}H\}$ NMR (75.43 MHz, $CDCl_3$) δ (ppm) 120.7 (q, CF_3, J_{CF} = 257.2 Hz), 121.9 (d, CH, J_{CP} = 6.7 Hz), 122.8 (s, CH), 145.9 (s, C), 149.8 (s, C). $^{31}P\{^{1}H\}$ NMR (161.9 MHz, $CDCl_3$) δ (ppm) 126.5. ^{19}F NMR (376.3 MHz, $CDCl_3$) δ (ppm) -58.7. EIMS m/z: 563.2 $(MH)^+$.

Preparation of tris(4-trifluoromethylbenzyl)phosphite (3)

To a solution of 4-(trifluoromethyl)benzylalcohol (1 ml, 7.06 mmol) and pyridine (0.7 ml, 8.59 mmol, 1.2 eq) in 15 ml diethyl ether at 0ºC, a solution of PCl_3 (0.25 ml, 2.86 mmol, 1.2 eq) in 3 ml of diethyl ether was added drop wise. The solution was stirred at room temperature under inert atmosphere for 2h. The formation of a salt was observed immediately. After 2h, the solvent was removed under reduced pressure. The resulting colourless solid was redissolved in hexane and purified by flash chromatography on basic alumina eluting with hexane to give **3** (0.896 g, 67%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.93 (d, 6H, CH_2, J_{HP} = 8Hz), 7.38 (d, 6H, CH, J_{HH} = 8 Hz), 7.56 (d, 6H, CH, J_{HH} = 8 Hz). $^{13}C\{^{1}H\}$ NMR (100.57 MHz, $CDCl_3$) δ (ppm) 64.0 (d,

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CH_2, J_{CP} = 11.4 Hz), 125.6 (q, CH, J_{CF} = 3.7 Hz), 127.6 (s, CH), 130.5 (q, C, J_{CF} = 32 Hz), 124.3 (q, CF_3, J_{CF} = 277.6 Hz), 142.0 (d, C, J_{CP} = 4.5 Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ (ppm) 140.1. ^{19}F NMR (376.3 MHz, $CDCl_3$) δ (ppm) -63.0. EIMS m/z: 553.2 $(M-3H)^+$; 175.0 $(C_8H_6F_3O)^+$.

Preparation of tris(4-trifluoromethoxybenzyl)phosphite (4)

To a solution of 4-(trifluoromethoxy)benzylalcohol (1 ml, 6.70 mmol) and pyridine (0.6 ml, 8.03 mmol, 1.2 eq) in 15 ml diethyl ether at 0ºC, a solution of PCl_3 (0.2 ml, 2.68 mmol, 1.2 eq) in 3 ml of diethyl ether was added drop-wise. The solution was stirred at room temperature under inert atmosphere for 2 h. The formation of a salt was observed immediately. After 2 h, the solvent was removed under reduced pressure. The resulting colourless solid was redissolved in hexane and purified by flash chromatography on basic alumina eluting with hexane to produce **4** (0.780 g, 58%) as a colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.86 (d, 6H, CH_2, J_{HP} = 8Hz), 7.17 (d, 6H, CH, J_{HH} = 8.4 Hz), 7.31 (d, 6H, CH, J_{HH} = 8.4 Hz). $^{13}C\{^1H\}$ NMR (100.57 MHz, $CDCl_3$) δ (ppm) 63.9 (d, CH_2, J_{CP} = 11.3 Hz), 121.2 (s, CH), 129.0 (s, CH), 136.9 (d, C, J_{CP} = 4.5 Hz), 149.0 (s, C), 120.7 (q, C, J_{CF} = 256.3 Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ (ppm) 140.6. ^{19}F NMR (376.3 MHz, $CDCl_3$) δ (ppm) -58.4. EIMS m/z: 605.2 $(MH)^+$.

Reaction of $[Rh(cod)_2]BF_4$ with 1

Ligand **1** (154 mg, 0.30 mmol or 308 mg, 0.60 mmol) was added to a solution of $[Rh(cod)_2]BF_4$ (30.4 mg, 0.07 mmol) in 2 mL of anhydrous

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dichloromethane. The solution turned yellow immediately and was stirred for 1 h. The solvent was then evaporated in a vacuum to obtain a yellow solid containing a mixture of $[Rh(\mathbf{1})_4]BF_4$ and $[Rh(cod)(\mathbf{1})_2]BF_4$. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$) δ (ppm) 108.2 (d, J = 216.9 Hz) corresponding to $[Rh(\mathbf{1})_4]BF_4$; 118.4 (d, J = 316.9 Hz) corresponding to $[Rh(cod)(\mathbf{1})_2]BF_4$.

Preparation of $[Rh(\mathbf{2})_4]BF_4$

Ligand **2** (168 mg, 0.32 mmol) was added to a solution of $[Rh(cod)_2]BF_4$ (30.4 mg, 0.08 mmol) in 2 mL of anhydrous dichloromethane. The solution turned yellow immediately and was stirred for 1 h. The solvent was then evaporated in a vacuum and was dried under vacuum overnight. The product was obtained as a yellow solid. (125.6 mg, 69%).

^1H NMR (300 MHz, $(CD_3)_2CO$) δ(ppm) 6.9 (d, 24H, CH, J_{HH} = 9 Hz), 7.15 (d, 24H, CH, J_{HH} = 9 Hz). $^{13}C\{^1H\}$ NMR (75.43 MHz, $(CD_3)_2CO$) δ(ppm) 117.4 (*br q*, CF_3), 123.8 (d, CH), 123.5 (q, CH, J = 25 Hz), 147.5 (s, C), 150.7 (s, C). $^{31}P\{^1H\}$ NMR (121.4 MHz, $(CD_3)_2CO$) δ(ppm) 108.7 (d, J_{PRh}= 216 Hz). ^{19}F NMR (376.3 MHz, $(CD_3)_2CO$) δ (ppm) -63.4. MALDI-TOF m/z: 2442 $(M)^+$, 2354 (M^+-BF_4).

Preparation of $[Rh(C_8H_{12})(\mathbf{3})_2]BF_4$

Ligand **3** (63 mg, 0.11 mmol) was added to a solution of $[Rh(cod)_2]BF_4$ (19 mg, 0.05 mmol) in 2 mL of anhydrous dichloromethane. The solution turned yellow immediately and was

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stirred for 1 h. The solvent was then evaporated in a vacuum and was dried under vacuum overnight. The product was obtained as an orange solid. (20 mg, 30%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.37 (m, 4H, CH_2 cod), 2.58 (m, 4H, CH_2 cod), 4.67 (m, 4H, CH cod), 5.15 (d, 12H, CH_2, J_{HP} = 9Hz), 7.31 (d, 12H, CH, J_{HH} = 8.7 Hz), 7.54 (d, 12H, CH, J_{HH} = 8 Hz. ^{13}C{^{1}H} NMR (100.57 MHz, $CDCl_3$) δ (ppm) 29.7 (s, CH_2 cod), 68.5 (d, CH_2, J_{CP} = 5.3 Hz), 113.8 (s, CH cod), 126.4 (q, CF_3, J_{CF} = 271.6 Hz), 125.6 (q, CH, J = 3.8 Hz), 127.8 (s, CH), 131.0 (s, C), 139.3 (s, C). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$) δ (ppm) 118.5 (d, J_{PRh}= 246.6 Hz). ^{19}F NMR (376.3 MHz, $CDCl_3$) δ (ppm) -63.1. MALDI-TOF m/z: 1351 (M^{+}-BF_4).

Preparation of $[Rh(C_8H_{12})(4)_2]PF_6$

Ligand **4** (109 mg, 0.18 mmol) was added to a solution of $[Rh(cod)_2]PF_6$ (35 mg, 0.08 mmol) in 2 mL of anhydrous dichloromethane. The solution turned yellow immediately and was stirred for 1 h. The solvent was then evaporated in a vacuum and was dried under vacuum overnight. The product $[Rh(C_8H_{12})(\mathbf{4})_2]PF_6$ was obtained as a orange oil (105 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.54 (m, 8H, CH_2 cod), 4.56 (b, 4H, CH cod), 5.02 (d, 12H, CH_2), 7.14 (d, 12H, CH, J_{HH} = 8.4 Hz), 7.22 (d, 12H, CH, J_{HH} = 8.4 Hz. ^{13}C{^{1}H} NMR (100.57 MHz, $CDCl_3$) δ (ppm) 29.7 (s, CH_2 cod), 68.5 (d, CH_2, J_{CP} = 5.5 Hz), 127.7 (q, C, J_{CF} = 237 Hz), 121.1 (s, CH), 129.4 (s, CH), 134.1 (s, C,), 142.5 (s, C). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$) δ (ppm) 117.2 (d, J_{PRh}=

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246.1 Hz). ^{19}F NMR (376.3 MHz, $CDCl_3$) δ (ppm) -58.3. MALDI-TOF m/z: 1419.7 $(M\text{-}PF_6)^+$ required for 1419.14.

Catalysis

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

Standard hydroformylation experiment in toluene

The reactions in toluene were performed in the same Parr autoclave as above. The complex $[Rh(acac)(CO)_2]$ (0.02 mmol) and the ligand (0.10 mmol) in toluene (10 mL) were stirred at room temperature for 1 h. The substrate (4.80 mmol) and undecane as GC internal standard were then added and the resulting solution was introduced into the evacuated autoclave. The system was pressurised and heated. When thermal equilibrium was reached, additional gas mixture was introduced until the desired pressure was attained. After the required reaction time, the autoclave was cooled to room temperature and depressurised. The products were identified by GC/MS.

Standard hydroformylation experiment in $scCO_2$.

The complex $[Rh(acac)(CO)_2]$ (0.06 mmol) was introduced into the evacuated autoclave, after which the autoclave was purged with nitrogen/vacuum cycles. Next, 1-octene (12 mmol), the ligand (0.36

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mmol) and undecane (1.11g) as GC internal standard were added. The system was pressurised with 20 atm of CO/H_2 (1:1), and liquid CO_2 was introduced until a total pressure of 60 bar was reached. The autoclave was heated to the desired temperature. When thermal equilibrium was reached, the total pressure was adjusted with a Thar syringe pump. After the reaction time, the autoclave was cooled down to 0°C and depressurised. The final mixture was analysed by GC. The products were identified by GC/MS.

Solubility studies.

The solubility studies were carried out in a Thar reactor (100 mL) equipped with sapphire windows and magnetic stirring. The autoclave was charged with a solution of the ligand (0.22 mmol) and $[Rh(acac)(CO)_2]$ (0.06 mmol) in diethyl ether. The solvent was removed in vacuum, the reactor was pressurised with syn-gas and CO_2, the system was heated to 80°C, and the total pressure was adjusted to 250 atm. Solubility was monitored by visual inspection through the sapphire windows with a mirror due to safety requirements.

HPNMR.

In a typical experiment, the NMR tube was filled under N_2 with a solution of $[Rh(acac)(CO)_2]$ (0.04 mmol), the ligand **1-4** (0.24 mmol) and toluene-d_8 (2 mL). The tube was pressurised to 20 atm of CO/H_2 (1:1) and left at 70°C for 1 h. The NMR spectra were then recorded.

HPIR.

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In a typical experiment, the HPIR cell was filled under N_2 with a solution of [Rh(acac)$(CO)_2$] (0.04 mmol), the ligand **1-4** (0.22 mmol) and methyltetrahydrofuran (15 mL). The cell was pressurised to 20 atm of CO/H_2 (1:1) and left at 70°C for 1 h. The IR spectra were then recorded.

Acknowledgements

We gratefully acknowledge the Generalitat de Catalunya (DURSI and Fons Social Europeu) for a Fellowship (FI) to C. T. and 2005SGR00777 and the Ministerio de Educacion y Ciencia (CTQ2004-03831/PPQ, CSD2006-0003).

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Hydroformylation of 1-Octene in Supercritical Carbon Dioxide with Rhodium Alkyl P-donor Ligands Using a Peracetylated β-Cyclodextrin as Solubiliser

Part 2

Clara Tortosa-Estorach, Marta Giménez-Pedrós, Arantxa Orejón, Anna M. Masdeu-Bultó, Adlane D. Sayede, Eric Monflier, *Dalton Transition,* submitted.

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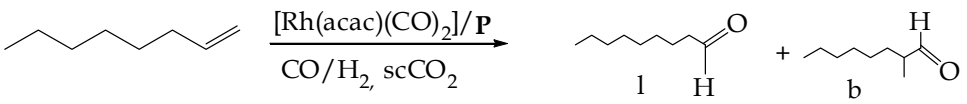
Abstract

The ability of peracetylated β-cyclodextrin to solubilize in supercritical carbon dioxide rhodium species modified by alkyl P-donor ligand was investigated. The addition of the peracetylated β-cyclodextrin allowed to increase the conversions in the hydroformylation of 1-octene but had a detrimental effect on the aldehydes selectivity. The results were explained by considering an interaction between the peracetylated β-cyclodextrin and the P-donor ligand.

Introduction

Hydroformylation involves the addition of carbon monoxide and hydrogen to a carbon-carbon double bond, forming the corresponding linear and branched aldehydes. The reaction (Scheme 1) is mostly accomplished with a rhodium or cobalt based catalyst.[1] The main products are used for the production of alcohols, carboxylic acids, aldol products, diols, acetals, ethers, acroleins and esters.[2] Specifically, hydroformylation of 1-octene is performed to the production of plasticizer alcohols and biodegradable detergents.[1]



Scheme 1.

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The application of supercritical carbon dioxide ($scCO_2$) as reaction media in homogeneous catalysis has been investigated by a number of research groups in recent years since it is inert, non toxic, non flammable, cheap, readily available and environmentally acceptable.[3] In addition, gases are completely miscible with $scCO_2$; therefore, gas-phase reactants concentrations would be higher than in organic solvents.[4]

Unfortunately, ionic and polar reagents are generally not very soluble in $scCO_2$, which restricts its application in catalytic processes.[4] To overcome this limitation, modified ligands by incorporation of perfluorinated chains,[5] polysilanes[6] and carbonyl groups[7] have been employed. Other possibilities include the use of soluble surfactants or mass transfer agents, which induce the formation of micelles with a high-density fluid phase,[8,9] increasing the solubility of the catalyst in the $scCO_2$.

It has been recently reported that peracetylated cyclodextrin exhibits a high degree of miscibility with dense CO_2 over a broad range of concentration.[10] Interestingly, Monflier *et al.* have recently demonstrated that peracetylated β-cyclodextrin has a great ability to form inclusion complexes with various arylphosphines in $scCO_2$ medium.[11] A similar phenomenon had also been observed with sulfonated arylphosphines in water by using hydrosoluble cyclodextrins.[12]

In a previous work Giménez *et al.* reported the use of new P-donor ligands (**1**-**3**, Figure 1) containing branched alkylic chain to performed hydroformylation of 1-octene in supercritical carbon dioxide.

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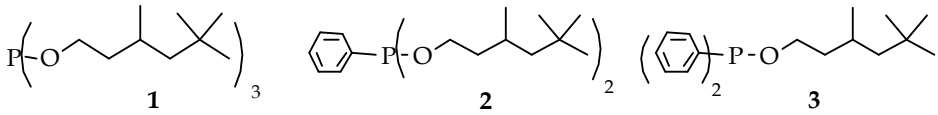
The rhodium catalytic systems formed with these ligands formed non soluble systems in $scCO_2$. Despite they were not soluble in the reaction condition media, activities up to 82 % and selectivities up to 94 % were achieved using this phosphite, phosphonite and phosphinite ligands in the hydroformylation of 1-octene in $scCO_2$.[13] Therefore, we consider the possibility of increasing the solubility in $scCO_2$ of these catalytic systems by forming inclusion complexes between the peracetylated cyclodextrin and the ligand.

Here we present the hydroformylation of 1-octene with the catalytic system $[Rh(acac)(CO)_2]$ associated to a branched alkyl phosphite, phosphonite and phosphinite ligands (**1-3**, Figure 1) in supercritical carbon dioxide, using a peracetylated cyclodextrin as a mass transfer promoter (Figure 2).



1 **2** **3**

Figure 1.

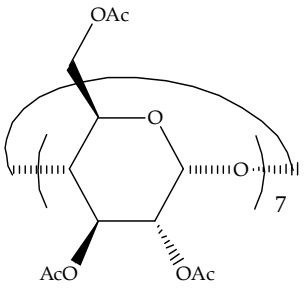


Figure 2.

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Results and discussion

Ligands **1-3** were synthesised as was previously reported by Giménez *et al.* from the commercial available 3,5,5-trimethylhexanol by reaction with the phosphorus trichloride or the corresponding chlorophenylphosphane in diethylether in the presence of pyridine.[13] Peracetylated β-cyclodextrin were purchased from Aldrich Chemicals and used without further purification. This CD is a cyclic oligosaccharide composed of seven D-glucopyranose residues linked by α-(1,4) bonds. Each glucopyranose unit was fully acetylated.

Inclusion studies

As the formation of inclusion complexes is difficult to prove experimentally in supercritical conditions, some attempts to observe the interaction between ligand **1** and Per-Ac-β–CD were performed by using toluene as solvent instead of supercritical CO_2. Unfortunately, the formation of inclusion species in toluene was rejected by analyzing the reactivity of the system $[Rh(acac)(CO)_2]$/**1** in the presence of Per-Ac-β–CD with CO and H_2 under pressure NMR spectroscopy. Indeed, the detected species at these conditions were comparable with the ones reported by Giménez *et al.* without the cyclodextrin.[13] So, the major species observed in the $^{31}P\{^1H\}$ and ^1H NMR spectra were $[Rh(CO)H(\mathbf{1})_3]$ and $[Rh(CO)_2H(\mathbf{1})_2]$. It must be noticed that this result is not surprising as formation of inclusion complexes in organic medium is seldom

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observed with cyclodextrin derivatives due to the disappearance of hydrophobic forces.

In this context, the ability of Per–Ac-β–CD to form inclusion complexes with ligands **1-3** was investigated by performing quantum chemical calculations on the Per–Ac-β–CD/ligand systems.

For the Per–Ac-β–CD/**1** system, the inclusion complex was constructed from separately optimised Per-Ac-β-CD and **1** geometries. The glycosidic oxygen atoms of Per-Ac-β-CD were placed onto the *XY* plane and their centre was defined as the centre of the coordination system. The complexation of **1** was then investigated by moving one of its alkylic chains along the *Z*-axis at fixed increment of 0.2 Å. All energy minimizations were performed without any geometry constraint. Two different inclusion orientations were considered: the orientation in which **1** points toward the narrower native β-CD ring (containing 7 acetyl-groups) and the other in which **1** points toward wider native β-CD rim (containing 14 acetyl-groups). For simplicity, we keep the same rim designation as in the native β-CD, i.e. primary and secondary rim. Figure 3 depicts the stabilization energy variation of the inclusion processes of **1** into Per-Ac-β-CD at different distances and orientations.

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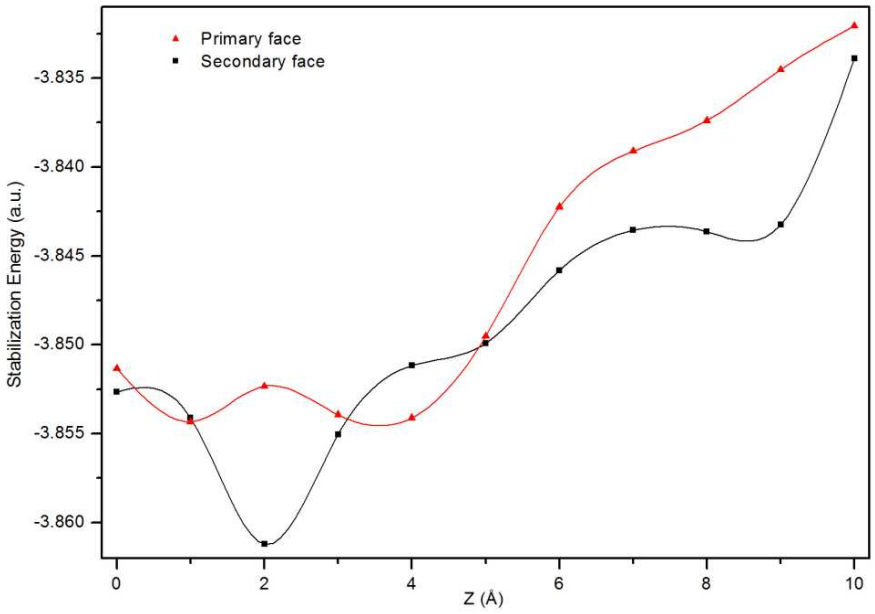

Figure 3. Graphic diagram for the inclusion process of the phosphite **1** into Per-Ac-β-CD thought primary and secondary face.

In both cases, favorable interactions take place between the two species. The energy of the complex decreases as the alkylic chain enters into the Per-Ac-β-CD cavity, and again increases because of crowding (i.e. steric hinders) between the alkylic chains remaining outside the cavity and the acetyl groups of the Per-Ac-β-CD rims. However, we notice that the more favorable energy minimum structure of Per–Ac-β–CD/**1** complex occurred via the secondary rim. Figure 4 (a) displays the computer-generated structure of this complex.

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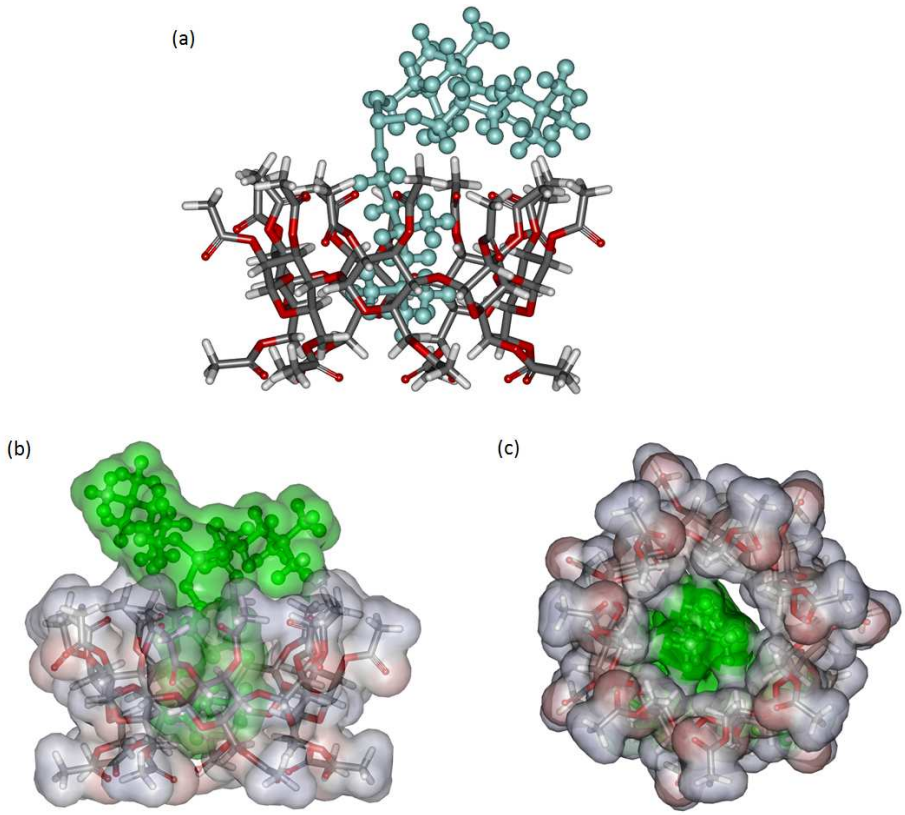

Figure 4. (a) Side view of the computer-generated structure of the Per-Ac-β-CD/**1** inclusion complex. (b) Side view and (c) bottom view of van der Waals surfaces of the Per-Ac-β-CD/**1** inclusion complex.

The energy variation involved in the inclusion emulsion indicates that the complexes prefer to adopt inclusion geometry with the alkyl chain inside the host cavity in order to increase the van der Waals attraction between the host and guest. This is supported by the van der Waals surfaces of Per–Ac-β–CD/**1** complex, see Figure 4 (b and c), where one can clearly see that the alkylic chains of the phosphite **1** fits

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tightly in the Per-Ac-β-CD cavity, leading to the formation of stable inclusion complexes.

For ligands **2** and **3**, calculations confirm also that Per-Ac-β-CD can include in its cavity an alkylic chain of the ligand. The figure 5 shows the most stable computer-generated structure of Per–Ac-β–CD/**2** and Per–Ac-β–CD/**3** inclusion complexes.

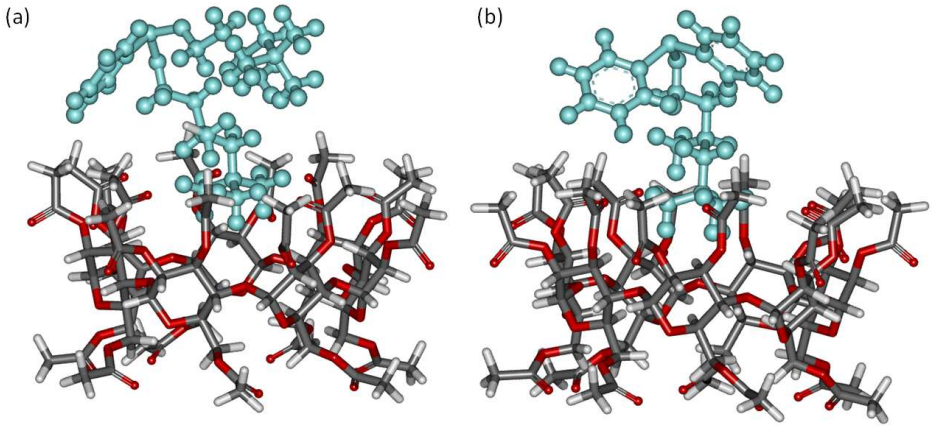

Figure 5. Side view of the computer-generated structure of the (a) Per–Ac-β–CD/**2** and (b) Per–Ac-β–CD/**3** inclusion complexes

Possibility to include an aromatic ring of the ligand into the Per–Ac-β–CD cavity was also investigated. In this case, calculations indicate that inclusion into the Per-Ac-β-CD cavity can hardly occur by the aromatic ring

By comparing figure 4 and 5, it appears clearly that ligand **1** is more deeply included into Per-Ac-β-CD cavity than ligands **2** and **3**, strongly suggesting that the Per-Ac-β-CD/**1** inclusion complex was

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more stable than the two others. The less deep penetration of ligands **2** and **3** into the CD cavity is likely a consequence of the steric hindrance between the external aromatic ring and the β-CD border.

Solubility studies

As the ligand **1** has the greater ability to interaction the Per-Ac-β-CD, solubility studies were performed with this ligand. The solubility of the new catalytic system [Rh(acac)$(CO)_2$]/**1**/Per-Ac-β–CD was studied in an autoclave equipped with a view windows. In a previous work, we observed by visual inspection through the windows of the autoclave that the [Rh(acac)$(CO)_2$]/**1-3** catalytic systems had no apparent solubility in $scCO_2$ up to 240 atm and 80 ^oC.[13] When similar solubility studies were performed with [Rh(acac)$(CO)_2$] (6.10^{-3} M) , the ligand **1** (P/Rh = 6) and the Per–Ac-β –*CD* (*per*-Ac-β–CD/Rh = 6) in the autoclave with CO/H_2 at 20 atm and 80 ^oC, we observed at 140 atm the formation of a initial suspension, which at 250 atm turned to a orange coloured solution (Figure 6). The presence of the Per-Ac-β–CD favored the solubility in $scCO_2$ of the species formed under hydroformylation conditions.

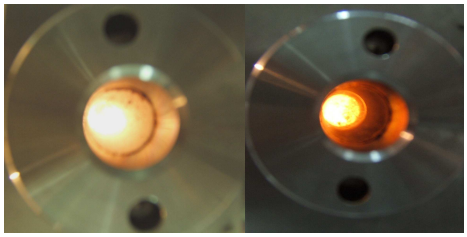

Figure 6. Soluble catalyst one-phase system of [Rh(acac)$(CO)_2$]/**1**/Per-Ac-β–CD at 80^{o}C and 250 atm.

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Hydroformylation of 1-octene

We performed the catalytic hydroformylation of 1-octene using the in situ formed catalyst precursor $[Rh(acac)(CO)_2]$/**1-3** with the addition of peracetylated β–cyclodextrin. The results are summarised in Table 1.

Table 1. Hydroformylation of 1-octene with using $[Rh(acac)(CO)_2]$/ **L**(**1-3**)/ Per-Ac-β–CD in $scCO_2$.

Entry	L	CD /Rh	T (°C)	P_{CO}/ P_{H2} (atm)	P_{TOT}[b] (atm)	%C[c]	%S_a[d]	l/b/int[e]	%S_i[f]
1	**1**	6	100	10/10	167	96	77	45/33/22	22
2[g]	**1**	0	100	10/10	167	49	90	80/20/-	10
3	**1**	6	100	10/10	250	71	71	80/17/3	29
4[g]	**1**	0	100	10/10	250	82	89	78/22/-	11
5	**1**	6	80	10/10	250	87	84	75/24/1	16
6	**1**	6	80	2.5/2.5	250	25	64	70/12/18	36
7	**1**	3	80	10/10	250	99	55	49/34/17	45
8	**1**	12	80	10/10	250	39	20	67/33/-	80
9[h]	**1**	6	80	10/10	250	23	80	26/48/26	20
10	**2**	6	80	10/10	250	65	75	44/40/16	25
11	**3**	6	80	10/10	250	98	54	48/37/15	46

[a] Reaction condition: $scCO_2$: $[Rh(acac)(CO)_2]$ = 0.06 mmol; Rh/L = 6, L = 0.36 mmol; 1-octene = 12 mmol; 1-octene/Rh = 200; V = 25 ml; t = 3 h; [b]Total pressure; [c] Total conversion by GC; [d] Selectivity to aldehydes; [e] int = 3-ethylheptanal and 4-propylhexanal; [f] Selectivity to internal octenes; [g] reference [13]; [h] substrate = trans-2-octene

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The addition of the Per-Ac-β–CD increases the total conversion of the reaction when the reaction is performed at 167 bar of total pressure (from 49 % t entry 2 to 96 % in entry 1, Table 1). The chemoselectivity in aldehydes decreases to 77% and an increase in the amount of internal aldehydes associated to olefin isomerisation was clearly observed (entry 1, Table 1). This could be attributed to the formation of inclusion complexes between the ligand **1** and the Per-Ac-β–CD. Indeed, as observed in the aqueous/organic biphasic hydroformylation reaction promoted by methylated β-cyclodextrins, [14] Per-Ac-β–CD may favour the dissociation of the ligand **1** from the catalytic species. In the $scCO_2$ medium, this dissociation could be very high and would lead to free ligand catalytic species which favour the isomerisation.

When the reaction is performed at higher total pressure (250 atm) the addition of Per-Ac-β–CD has no positive effect at 100 ^oC ,the conversion and the selectivity decreased in contrast with no cyclodextrin was added (entries 4 and 3, Table 1). At this pressure the selectivity in aldehydes could be increased up to 84 %, decreasing the temperature to 80^oC (entry 5, Table 1). The total conversion was also better (87 %) and the regioselectivity (l/b = 3.5) was in the order for this kind of P-donor ligands.[1b] Decreasing the partial pressure to 5 atm ($CO:H_2$ = 1:1) the conversion drops to 25% and the selectivity decrease to 64% (entry 6, Table 1).

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Once we optimised the catalytic conditions, we studied the effect of the cyclodextrin/ligand ratio. Decreasing the Per-Ac-β–CD /**1** ratio to 3, the conversion increased (99%) but the selectivity decreased (55%), with the concomitant formation of internal aldehydes (entry 7, Table 1). Increasing the Per-Ac-β–CD /**1** ratio to 12, the conversion and selectivity decreased to 39 and 20% respectively (entry 8, Table 1), what confirm that species without coordinated ligand could be formed due to the formation of inclusion complex between the ligand and Per-Ac-β–CD. In fact, it is reasonable to assume that the included ligand is not capable to complex rhodium metallic center owing to the steric congestion generated by the presence of the cyclodextrin.

Since we observed an important amount of isomerisation, we used [Rh(acac)$(CO)_2$]/**1**/ Per-Ac-β–CD under the same conditions in the hydroformylation of trans-2-octene. In this experiment the distribution of aldehydes (entry 9, Table 1) indicates that isomerisation rate is slower than the hydroformylation rate for this system.

When the systems [Rh(acac)$(CO)_2$]/**2** or **3**/Per-Ac-β–CD were used, the conversion obtained was better in the case of **2** or in the same order for catalytic system with ligand **3** although the selectivity in aldehydes was not improved respect the one obtained with the analogous system without the cyclodextrin (entries 10 and 11, Table 1).[13]

Conclusion

Peracetylated β-cyclodextrin affects greatly the catalytic behavior of rhodium complexes modified by branched alkylic phosphite ligands

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in $scCO_2$. Addition of Peracetylated β-cylcodextrin allowed to increase the conversion but has a negative effect in the selectivity in aldehydes. The selectivity decrease was attributed to the formation of catalytic species without coordinated ligand. This phenomenon was explained by inclusion of the ligand into the Per-Ac-β-CD cavity. Indeed, it was postulated that the ligand is not capable to stabilize rhodium species when it is included into the cavity due to the steric constraint generated by cyclodextrin around the phosphorus atom.

Experimental part

General. The material were purchased from Aldrich and Fluorochem and used without further purification. 1-octene used as substrate was filtered over alumina before to use it. Carbon dioxide (SCF Grade, 99.999 %, Air Products), carbon monoxide 99.99% was supplied by Air Liquid and hydrogen C-50 was supplied by Carburos Metalicos.

Safety warning. Experiments involving pressurised gases can be hazardous and must be conducted with suitable equipment and following appropriate safety conditions only.

High-pressure NMR experiments (HPNMR) were carried out in a 10-mm-diameter sapphire tube with a titanium cap equipped with a Teflon/polycarbonate protection.[15]

Gas chromatography analyses were performed with a Hewlett-Packard 5890A apparatus in an HP-5 (5 % diphenylsilicone/95 %

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dimethylsilicone) column (25 m × 0.2 mm) for the separation of the products and undecane as internal standard added after reaction.

Calculations. The calculations have been performed at the PM3 level of theory using the GAUSSIAN 03 program.[16] The initial geometries were constructed, with the help of Molden program,[17] as already reported.[18]

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

Standard Hydroformylation Experiment in $scCO_2$. The complex $[Rh(acac)(CO)_2]$ (0.06 mmol) and the peracetylated cyclodextrine (Per-Ac-β–CD) (0.36 mmol) were introduced into the evacuated autoclave. Then the autoclave was purged with nitrogen/vacuum cycles. After that, 1-octene (12 mmol) and the ligand (0.36 mmol) were added. The system was pressurised with 20 atm of CO/H_2 (1:1), and liquid CO_2 was introduced until a total pressure of 60 bar was reached. The autoclave was heated to the desired temperature. When thermal equilibrium was reached, the total pressure was adjusted with a Thar syringe pump. After the reaction time, the autoclave was cooled down to 0 °C and depressurised. Undecane was added to the final mixture and was analysed by GC. The products were identified by GC/MS.

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Solubility Studies. The solubility studies were carried out in a Thar reactor (100 mL) equipped with sapphire windows and magnetic stirring. The autoclave was charged with the ligand (0.33 mmol), the [Rh(acac)(CO)$_2$] (0.055 mmol) and the Per-Ac-β–CD. The autoclave was purged with nitrogen/vacuum. Then, the reactor was pressurised with syn-gas and CO_2, the system was heated to 80 °C, and the total pressure was increased gradually up to 250 atm. Solubility was monitored by visual inspection through the sapphire windows with a mirror due to safety requirements.

HPNMR. In a typical experiment, the NMR tube was filled under N_2 with a solution of [Rh(acac)(CO)$_2$] (0.04 mmol), the ligand **1** (0.24 mmol), the Per-Ac-β–CD (0.24 mmol) and [d_8]toluene (2 mL). The tube was pressurised to 20 atm of CO/H_2 (1:1) and left at 70 °C for 1 h. The NMR spectra were then recorded.

Acknowledgment

We gratefully acknowledge the Generalitat de Catalunya (DURSI and Fons Social Europeu) for a Fellowship (FI) to C. T. and 2005SGR00777, the Ministerio de Educacion y Ciencia (CTQ2004-03831/PPQ, CSD2006-0003) for financial support.

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Chapter 6

Concluding remarks

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Concluding remarks

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

For the palladium hydrocarboxylation of linear alkenes the following conclusions were drawn:

- The reaction has been performed for the first time in supercritical carbon dioxide, using a palladium(II) precursor associated with phosphines with CF_3-groups.
- The best catalytic conditions were obtained with Pd/P(4-$CF_3C_6H_4)_3$/oxalic acid system, 30 atm of CO, 90ºC, and 150 atm of total pressure, when the system was not soluble. At this conditions, the best result was 55% conversion, 90% selectivity in acids and l/b=3.
- Adding a perfluoropolyether as a surfactant the conversion increases up to 93%.
- The HPNMR studies lead to conclude that Pd(0) species were formed in both $scCO_2$ and THF for the systems $[PdCl_2(PhCN)_2]$ / P(4-$CF_3C_6H_4)_3$ – P(3,5-$(CF_3)_2C_6H_3)_3$.
- The reaction could be extrapolated to higher alkenes as 1-dodecene and 1-hexadecene, for which the conversions were up to 95% and selectivity in acids up to 86%.

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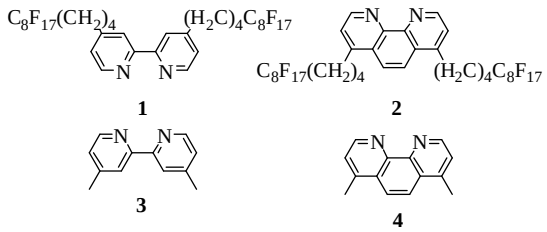
For the hydroesterification of 1-octene in supercritical carbon dioxide the general conclusions drawn are presented as follows:

- Hydroesterification of 1-octene can be performed in supercritical carbon dioxide as a solvent using palladium catalysts with phosphines containing $-CF_3$ groups.
- The best conditions were obtained when the catalytic system was not soluble. The best catalytic system was $[PdCl_2(NCPh)_2]$/ $P(3,5\text{-}(CF_3)_2C_6H_3)_3$ which provide 67% of total conversion and 64% in esters selectivity.

Regarding the CO/*tert*-butylstyrene copolymerisation in expanded-liquid and supercritical carbon dioxide, the experiments performed lead to conclude:

- Palladium(II) dicationic complexes with perfluorinated and non-perfluorinated bipyridines and phenantrolines (**1, 2, 3, 4**) have been synthesised and characterised.



- The HPIR spectra of the rhodium (I) complexes associated with this nitrogen ligands show that there was no significant difference in the electronic properties of the different ligands used.

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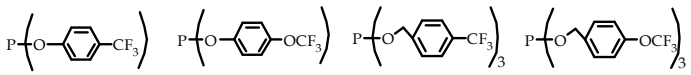
- The CO/4-tert-butylstyrene copolymerisation was performed for the first time by dicationic palladium(II) complexes in expanded-liquid carbon dioxide obtaining better polydispersities than when an organic solvent was used.
- Using a perfluorinated phenantroline as a ligand the palladium system was not active.
- The best result (1.4 Kg CP ·g Pd^{-1}, 167000 of molecular weight and 90% of stereoregularity) was obtained using perfluorinated bipyridine **1** as a ligand, with low carbon dioxide density.

Regarding the hydroformylation of alkenes using $scCO_2$, the studies are divided in two parts. For the first part the conclusions drawn are:

- New phosphites **6-8** with CF_3 and $-OCF_3$ groups were synthesised and characterised.



5 **6** **7** **8**

- When these ligands were coordinated to rhodium precursors, two kinds of complexes were formed. For phenol derivates phosphites, which had less steric hindrance and less donor ability, $[Rh(\mathbf{5\text{-}6})_4]BF_4$ were formed although $[Rh(\mathbf{5})_4]BF_4$ could not be obtained in pure form. For benzyl derivated phosphites, $[Rh(cod)(\mathbf{7\text{-}8})_2]PF_6$ (cod= 1,5-cyclooctadiene) were obtained.
- The reactivity with CO/H_2 of rhodium complexes with these ligands were studied by HPNMR and HPIR showing that at similar reaction conditions, the major species formed for all the

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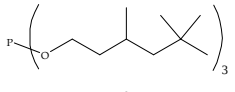
catalytic systems was [Rh(CO)H(**5-8**)$_3$] and also the minor species [Rh(CO)$_2$H(**5-8**)$_2$] were detected.

- The activity obtained with supercritical carbon dioxide, was similar or higher for the Rh/**5,6,8** systems than the ones obtained in toluene, although the selectivity was lower. For the system Rh/**7**, the selectivity obtained in scCO_2 was higher than the one obtained in toluene, although the conversion was lower. The l/b ratio for Rh/**6-8** phosphite systems were higher in scCO_2 conditions than in toluene.
- For rhodium systems with phenol derivatives **5-6** the results improved using low CO_2 density. For the benzylic derivates phosphites, **7** P(OCH$_2$C$_6$H$_4$CF$_3$)$_3$ and **8** P(OCH$_2$C$_6$H$_4$OCF$_3$)$_3$ an increase in the selectivity on aldehydes was observed.
- The best result was obtained with Rh/**5** P(OC$_6$H$_4$CF$_3$)$_3$, which provided 99% conversion, 60% aldehydes selectivity and l/b ratio of 7.3 and for Rh/**8** P(OCH$_2$C$_6$H$_4$OCF$_3$)$_3$, which provided 93% conversion, 62% selectivity and 4 of l/b ratio.

For the second part of this chapter, the conclusions drawn are:

- The addition of the peracetylated cyclodextrin (**10**) to the [Rh(acac)(CO)$_2$] / P(O(CH$_2$)$_2$CH(CH$_3$)CH$_2$C(CH$_3$)$_3$)$_3$ increases the solubility of the system in scCO_2.



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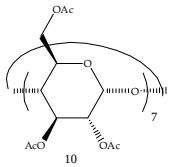

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- The activity increased when the cyclodextrin was used as a mass transfer agent although the selectivity in aldehydes decreased.

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Resum

En les darreres dècades, la catàlisis homogènia ha aconseguit un paper destacat dintre de la indústria química. També ha tingut un gran impacte en els últims anys l'ús de dissolvents alternatius com a medis de reacció per evitar l'ús de dissolvents orgànics que són tòxics i tenen un impacte mediambiental molt elevat. L'ús del diòxid de carboni supercrític ($scCO_2$) com a medi de reacció, a part de ser de baix cost, no ser tòxic, no ser inflamable, presenta les avantatges de permetre reciclar fàcilment el catalitzador, tenir una elevada solubilitat amb els gasos i permetre modular les seves propietats fàcilment canviant la pressió i temperatura. Una de les propietats d'aquest solvent és la baixa polaritat del medi, això fa que la solubilitat dels sistemes catalítics es vegi afectada en funció dels reactius utilitzats.

En aquest context, l'objectiu principal d'aquesta tesis és la realització de reaccions de carbonilació, com hidroformilació, hidrocarboxilació, hidroesterificació i copolimerització, utilitzant com a medi de reacció el diòxid de carboni supercrític. Per duu a terme aquestes reaccions en $scCO_2$ s'han utilitzat sistemes catalítics modificats, és a dir, s'han sintetitzat lligands P- o N- donadors amb cadenes alquíliques perfluorades o s'han incorporat al sistema surfactants com perfluoropolièters o ciclodextrines amb grups acetats, que fan que el sistema es solubilitzi més fàcilment en el medi.

En la introducció s'ha fet un recull bibliogràfic de les reaccions de carbonilació en dissolvents orgànics, dels lligands més utilitzats en aquests tipus de reaccions i dels cicles catalítics que tenen lloc. També

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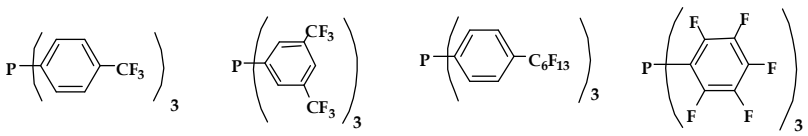
s'ha fet una introducció de les propietats i l'ús del diòxid de carboni en estat supercrític i de la seva aplicació en les reaccions de carbonilació.

S'ha estudiat la reacció d'hidrocarboxilació d'alquens lineals en diòxid de carboni supercrític. Com a sistema catalític s'ha utilitzat un precursor de pal·ladi(II) $[PdCl_2(PhCN)_2]$, associat amb fosfines perfluorades (Figura 1).



1 2 3 4

Figura 1

S'ha realitzat un estudi de solubilitat i de l'activitat catalítica en $scCO_2$ dels diferents sistemes catalítics. El millor sistema catalític ha estat $[PdCl_2(PhCN)_2]$/**1** quan es duia la reaccions en sistemes no solubles. En aquest sistema s'ha obtingut 55% de conversió, 90% de selectivitat amb àcids i l/b=3 a 150 atm de pressió total i 90ºC. També s'ha estudiat l'activitat de la reacció amb el mateix sistema però addicionant un perfluoropolièter (sal d'amoni de Krytox) com a surfactà, millorant així els resultats obtinguts (93% de conversió, 77% de selectivitat en àcids i l/b de 4.5). També s'ha estudiat mitjançant tècniques d'alta pressió de ressonància magnètica nuclear(HPNMR) les espècies formades *in situ* en condicions similars a les de reacció.

També ha estat estudiada la reacció d'hidroesterificació d'1-hexè en $scCO_2$ utilitzant els mateixos sistemes. El millor resultat però, ha estat

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amb el sistema $[PdCl_2(PhCN)_2]$/**2** amb el que s'han obtingut 67% de conversió i 64% de selectivitat amb èsters.

Referent a la reacció de copolimerització amb CO i tert-butilestirè en $scCO_2$. Per duu a terme la reacció s'han utilitzat lligands nitrogen-donadors amb cadenes perfluorades (Figura 2) amb els que s'han sintetitzat complexos dicatiònics de pal·ladi(II) $[Pd(\mathbf{5,6,7,8})_2]X_2$.

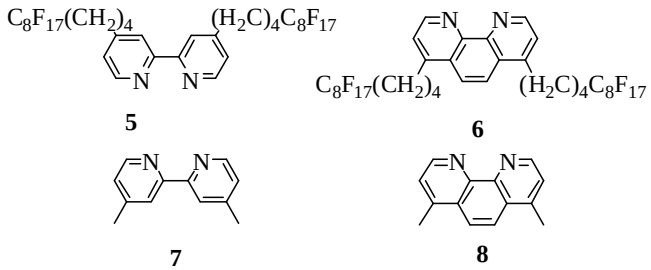

Figura 2

S'ha estudiat la solubilitat de tots els complexos en $scCO_2$ i s'ha vist que tots ells són solubles en aquest medi. S'ha estudiat l'activitat catalítica dels diferents lligands a diferents pressions de CO_2, observant que la selectivitat de la reacció canvia en funció del lligand. Els millors resultats s'han obtingut amb el complex $[Pd(\mathbf{5})_2](BArF)_2$, a baixes pressions de CO_2, amb el que s'han obtingut 1.4 Kg de copolímer gPd^{-1}, amb un pes molecular de 167000 i una estereoregularitat del 90%.

Finalment, s'ha estudiat la hidroformilació d'1-octè en $scCO_2$. S'han sintetitzat quatre fosfits, dos derivats del fenol (**9-10**) i dos derivats del benzil alcohol (**11-12**), amb grups $-CF_3$ (Figura 3).

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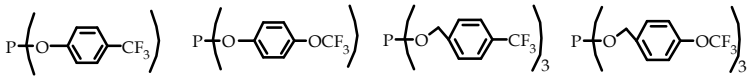

9 **10** **11** **12**

Figura 3

S'ha estudiat la coordinació d'aquests lligands en complexos catiònics de rodi(I) observant que els lligands amb menys impediments estèrics (**9-10**) es coordinen formant complexos [Rh(**9-10**)$_4$]X, mentre que els lligands **11-12** formen complexos [Rh(cod)(**11-12**)$_2$]X. S'ha estudiat la reactivitat amb CO i H_2 dels sistemes de rodi [Rh(CO)(acac)] amb els lligands **9-12** per RMN i IR d'alta pressió (HPNMR, HPIR) en condicions similars a les catalítiques. També s'ha estudiat la reactivitat catalítica dels quatre sistemes en diferents pressions de CO_2 i amb toluè per poder comparar el sistema en un solvent orgànic. L'activitat obtinguda en la reacció en scCO_2 per als sistemes Rh/**9,10,12** és similar o superior a l'obtinguda amb toluè, encara que la selectivitat va ser més baixa. En canvi, per al sistema Rh/**3**, la selectivitat obtinguda amb scCO_2 va ser major que l'obtinguda amb toluè. La relació n/iso obtinguda per al sistemes Rh/**10-12** va ser superior amb scCO_2.

Els millors resultats s'obtenen amb el sistema [Rh(CO)(acac)]/**9**, que proporciona 99% de conversió, 60% de selectivitat i una relació n/iso de 7.3; i amb el sistema [Rh(CO)(acac)]/ **12** amb el que s'ha obtingut 93% de conversió, 62% de selectivitat i una relació n/iso de 4.

Dins d'aquest tema també s'ha estudiat la hidroformilació d'1-octè en scCO_2 utilitzant un sistema inicialment insoluble, del qual amb l'addició d'una ciclodextrina amb grups acetats (**16,** Figura 4) s'ha

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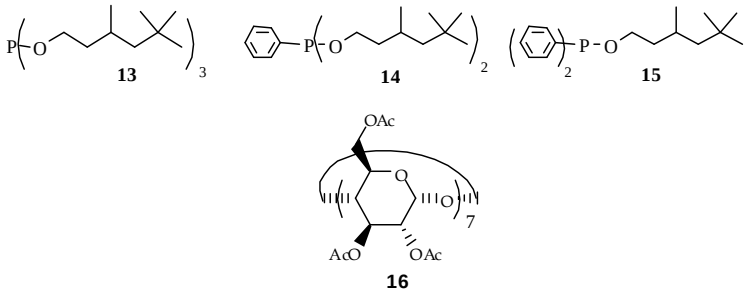
aconseguit augmentar-ne la solubilitat. El sistema insoluble està format per $[Rh(CO)_2(acac)]$ amb lligands P-donadors amb cadenes alquíliques ramificades (**13-15**).



13 **14** **15** **16**

Figura 4

L'activitat catalítica dels sistemes $[Rh(CO)_2(acac)]$/**13-15** (Figura 4) es millora afegint la ciclodextrina. Malauradament, la selectivitat en aldehids disminueix, possiblement degut a la descoordinació del lligand (**13**) al introduir-se a la cavitat de la ciclodextrina.

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Scientific contributions:

Publications:

- M. Giménez-Pedrós, C. Tortosa-Estorach, A. Bastero, A. M. Masdeu-Bultó, M. Solinas, W. Leitner. "New palladium complexes for alternating CO/tert-butylstyrene copolymerisation in supercritical carbon dioxide". *Green Chemistry,* **2006,** *8*, 875.
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- C. Tortosa-Estorach, A. Orejón, A. M. Masdeu-Bultó. "New rhodium catalytic systems with trifluoromethyl phosphite derivatives for the hydroformylation of 1-octene in supercritical carbon dioxide". *Green Chemistry,* **2007**, submitted.
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- C. Tortosa, M. Gimenez, A. Bastero, A. M. Masdeu, W. Leitner. "New palladium complexes for CO/tertbuthylstyrene copolymerization in supercritical carbon dioxide". 15th International Symposium on Homogeneous Catalysis. **Poster contribution**. Sun City, South Africa. August 2006.
- C. Tortosa, M. Gimenez, A. Bastero, A. M. Masdeu, W. Leitner. "New palladium complexes for CO/tertbuthylstyrene copolymerization in supercritical carbon dioxide". **Poster contribution**. XXII International Conference on Organometallic Chemistry (ICOMC), Zaragoza, Spain. July 2006.
- C. Tortosa, A. M. Masdeu, N. Ruiz. "Hidrocarboxilació d'1-octè en diòxid de carboni supercrític". **Poster contribution**. "Catàlisis

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- C. Tortosa, A. M. Masdeu, N. Ruiz. "Hydroxycarbonylation of 1-octene in supercritical carbon dioxide". **Poster contribution**. Summer School on *Catalysis, Fundamental and practice*. Liverpool, September 2005.
- C. Tortosa, A. M. Masdeu, N. Ruiz. "Carbonylation in supercritical carbon dioxide". **Oral Contribution**. COST D30 group meeting, Tarragona, Spain. November 21st 2004.
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