UNIVERSITAT ROVIRA I VIRGILI
PALLADIUM COMPLEXES CONTAINING DIPHOSPHINE AND SULFONATED PHOSPHINE LIGANDS FOR C-C BOND FORMING REACTIONS. CATALYTIC AND MECHANISTIC STUDIES
Eduardo José García Suárez
ISBN:978-84-691-0369-2/DL: T.2187-2007

Agradecimientos

Después de poco más de tres años de trabajo ha llegado el momento de escribir esta tesis, con su escritura el mejor momento para agradecer a todas las personas que de una manera directa o indirecta han hecho posible la realización de este trabajo del que me siento muy orgulloso.

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Una vez conseguida mí licenciatura en química por la Universidad de Oviedo, la primera oportunidad de adentrarme en el mundo de la investigación me la dieron en Oviedo en el Instituto del Carbón (INCAR) de la mano de la Dra. Ana Beatriz García, en cuyo grupo estuve unos 10 meses, por eso mi primer agradecimiento va para ella, ya que si ahora mismo estoy a punto de presentar mi tesis en buena medida es gracias a esa primera oportunidad. Durante mi estancia en el INCAR solo puedo decir que me encontré con gente magnífica, para todos ellos un gran abrazo en especial para Miguelín y Davicín (ellos saben porque, ¡no! no es por lo que me habéis hecho tamizar).

Después de este primer contacto con la investigación y el laboratorio me decidí a irme unos meses fuera de España (por saber si había algo más del otro lado de la frontera de mi Asturias, simple curiosidad) por ello me decidí a solicitar una beca Marie Curie, con tan buena suerte que fui aceptado en el grupo del Dr. Claudio Bianchini en el “Istituto di Chimica dei Composti Organometallici” de Florencia (ICCOM), para trabajar durante 9 meses en el proyecto “POLYCAT”. Mis primeros días en Florencia, no lo puedo negar, fueron duros, una ciudad distinta, unas costumbres distintas, una lengua distinta, a mas de 1800 Km de

casa, además llegué justo en el momento que el grupo del Dr. Claudio Bianchini se mudaba de edificio, y lógicamente en ese momento la gente estaba inmersa en la mudanza. Pero bueno, pasados esos primeros días, frenéticos para todos, tuve una muy buena acogida y empecé a trabajar bajo la tutela del Dr. Werner Oberhauser al que debo agradecer la paciencia que tuvo conmigo en un primer momento para enseñarme las técnicas básicas de trabajo en el laboratorio pues la química organometálica para mi era una gran desconocida.

Después de 6 meses de trabajo en el ICCOM, en todo ese tiempo ya me desenvolvía en el laboratorio e incluso había aprendido Italiano, hablando con el Dr. Claudio Bianchini surgió la posibilidad de realizar la tesis doctoral, en un principio tuve mis dudas pero dada la excelente experiencia vivida hasta ese momento no tarde mucho en aceptar la propuesta y enseguida el Dr. Claudio Bianchini me puso en contacto con la Prof. Camen Claver de la URV de Tarragona, puesto que la idea de realizar la tesis era a través de una colaboración entre el ICCOM y el grupo OMICH de la Prof. Carmen Claver. Después de intercambiar varios e-mail con la Prof. Carmen Claver, se decidió que empezaría ha hacer esta tesis doctoral que ahora presento como una colaboración entre el ICCOM donde pasaría los dos primeros años y el grupo OMICH donde actualmente me encuentro realizando mi tesis. Aunque la decisión de realizar la tesis no fue fácil, me iba a Italia solo 9 meses!!!!, no me arrepiento en absoluto de tomar la decisión de hacerla, gracias a ello he conocido a gente que verdaderamente vale la pena.

Ahora os preguntareis ¿todo este rollo para qué? Pues todo este rollo para decir que todo en la vida tiene sentido y a veces un simple gesto o una simple acción trae consigo desenlaces tan gratos e inesperados como éste. Además me sirve para agradecer todo lo que ha hecho en mi favor el Dr. Claudio Bianchini, director del ICCOM-CNR Firenze y excelente persona, dándome la

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Ramírez, Olga Begardá por estar siempre dispuestos a echar una mano y ayudar en todo lo posible y sobre todo por haber sido tan buenos compañeros, ánimos chicos ya estáis en la recta final. A los futuros Doctores/as Vanesa Lillo (este año el Nástic lo tiene difícil, espero que el año que viene sea mejor, incluso para el Sporting), Eva Raluy, Isabel Vicente, me lo he pasado muy bien con todos vosotros. No puedo olvidar a todos los chicos/as nuevos/as que acaban de llegar muy ilusionados/as con el trabajo que empiezan, la verdad ahora que lo pienso son todo chicas, Verónica, Angélica, Carolina, Martha y Ariadna disfrutar del grupo, es fantástico.

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International congress:

September 2004

European Network PALLADIUM Mid-Term Meeting, Amsterdam (Holland).

Oral presentation: **"Synthesis and characterisation of chelating diphosphines bearing the bis(dianisylphosphino) moiety; their palladium complexes as catalysts precursors in the CO/ethene copolymerisation"**

July 2005

ISHHC-10: 10th International Symposium on Relations between Homogeneous and Heterogeneous Catalysis, Florence (Italy), **poster contribution**

September 2005

FECHEM XVI conference on Organometallic Chemistry, Budapest (Hungary), **poster contribution**

September 2005

COST D17 Meeting, Budapest (Hungria)

Oral presentation: **"The role of the *ortho*-methoxy group in Pd(II) diphosphines complexes applied in the copolymerisation of CO and ethene"**

October 2005

European Network PALLADIUM Meeting, Florence (Italy)

Oral presentation: **"The role of the *ortho*-methoxy group in Pd(II) diphosphines complexes. A catalytic and mechanistic study"**

June 2006

European Network PALLADIUM Final Meeting, Grado-Trieste (Italy)

Oral presentation: **"Palladium (II) catalyst based on new phosphine sulfonated ligands for the non-alternating copolymerisation of ethene with CO"**

July 2006

ICOMC-2006 XXII-International Conference on Organometallic Chemistry, Zaragoza (Spain), **poster contribution**

Publications

1. M. Cabielles, E. García-Suárez and A. B. García, **"Unburned carbon from coal combustion fly ashes as precursor for graphite materials"**, proceeding of Carbon **2003**, Oviedo, Spain. Ed. Spanish Carbon Group.

2. C. Bianchini, P. Brüggeller, C. Claver, G. Czermak, A. Dumfort, A. Meli, W. Oberhauser and E. J. Garcia Suarez, **" Synthesis and characterization of palladium (II) complexes with new diphosphonium-diphosphine and diphosphine ligands. Production of low-molecular-weight alternating polyketones via catalytic CO/ethene copolymerisation"** *Dalton Trans*., **2006**, 2964.

3. C. Bianchini, A. Meli, W. Oberhauser, A. M. Segarra, C. Claver and E. J. Garcia Suarez, **"The effect of the *ortho*-methoxy group in the Pd(II) diphosphine complexes, catalysing the CO-ethene copolymerisation reaction in different reaction mediums"** *J. Mol. Catal. A: Chemical* **2006**, accepted.

4. C. Bianchini, A. Meli, W. Oberhauser, C. Claver and E. J. Garcia Suarez, **"Unraveling the *o*-methoxy effect in the CO/ethene copolymerisation reaction by palladium(II)-diphosphine catalysts"**, *Eur. J. Inorg. Chem.*, accepted.

5. E. J. García Suárez, C. Godard, A. Ruiz and C. Claver **"Alternating and non-alternating Pd-catalysed co- and terpolymerisation of carbon monoxide and alkenes"** *Eur. J. Inorg. Chem.*, accepted.

6. E. J. García Suárez, A. Ruiz, S. Castillón, W. Oberhauser, C. Bianchini, and C. Claver **"New alkyl derivates phosphine sulfonate (P-O) ligands. Catalytic activity in Pd-catalysed Suzuki-Miyaura reaction in water"** *Dalton Trans., **2007***, accepted.

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1. Introduction and scope

1.1. Organometallic chemistry and homogeneous catalysis

The term catalysis was coined by Berzelius around 1850 after observing changes in substances when they came into contact with small amounts of species called “ferments”. Many years later in 1895 Ostwald came up with a definition “*A catalyst is a substance that changes the rate of a chemical reaction without itself appearing into the products*” according to which a catalyst could also slow down a reaction. Nowadays, the definition in use is “*A catalyst is a substance which increases the rate at which a chemical reaction approaches equilibrium without becoming itself permanently involved*”

The effect of the catalyst is purely kinetic; catalysts work by providing an alternative mechanism that involves a different transition state and lower activation energy (**Figure 1**). The effect is that more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can perform reactions that, albeit thermodynamically feasible, would not take place without the presence of a catalyst, or which take place much faster, more specifically, or at lower temperatures. However, a catalyst can catalyse competitive reactions at different rates, thus affecting the distribution of the products. Catalysts do not affect the Gibbs free energy of the overall reaction. The net free energy change of a reaction is the same whether a catalyst is used or not; the catalyst just makes it easier to activate.

A very important property of the catalyst is its activity which can be express in terms of TON (turnover number) or TOF (turnover frequency). An active catalyst presents both high TON and high TOF.

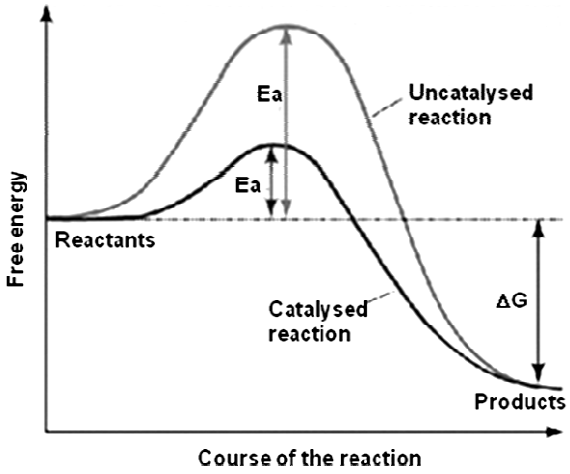

Figure 1. Effect of the catalysts in a thermodynamically favourable reaction

Catalysts can be either, homogeneous if they are in the same phase as the reactants and products, normally the liquid one[1] and heterogeneous if they are in different phases. In this latter case the catalytic reaction takes place in the interphase.

The advantages of the homogeneous catalysis over heterogeneous catalysis are its high activity, its selectivity and its mild reaction conditions. Its major problem is its industrial application regarding principally the separation of the catalyst from the products.

Catalysis plays a key role in the industrial production of liquid fuels and bulk chemicals as well as most in the processes for the production of fine chemicals. One interesting application of homogeneous catalysis is asymmetric catalysis. It focuses in the synthesis of enantiopure compounds, which are active ingredients of pharmaceuticals, agricultural products, flavours, fragrances and some advanced materials.[2]

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Organometallic catalysts are formed by a central metal surrounded by organic and/or inorganic ligands. Organometallic complexes act in different ways within the catalytic reaction, bringing the substrates together, activating the substrates by coordinating to the metal and lowering the activation energy of the reaction. The properties of the catalyst are due to both the metal and the ligand.

The success of organometallic catalysts is due to the fact that they can be modified relatively easily by changing the ligand environment. The effect of these modifications on the catalytic reaction can then be studied by such techniques HP-NMR or HP-IR *in situ* and *operando* measurements, because organometallic catalysts are soluble in organic solvents. The information provided by these studies can help to improve the efficiency of catalytic system.

One important aspect in homogeneous catalysis is the elucidation of changes in the reactivity of a catalyst which are caused by subtle modification in the ligand environment of the metal centre. It is interesting to know how a change in the ligand environment affects the reactivity of the metal system bound to it. Ligand exchange can modify such crucial properties of the catalytic reaction as the rate of the reaction and the selectivity.

Palladium is one of the most extensively studied metals in organometallic chemistry because it is versatile and catalyses numerous organic reactions. Palladium is commonly used to catalyse reactions involving the formation of C-C bond such as oligomerisation, copolymerisation or carbonylation of alkenes, Wacker oxidation of alkenes, cross-coupling reactions, etc.[3]

The main steps in the mechanism reactions catalysed by palladium complexes are: oxidative addition, reductive elimination, transmetallation and migratory insertion.

In this work we shall focus on the palladium-catalysed CO/ethene copolymerisation reaction as well as the Suzuki-Miyaura cross-coupling reaction. Particular attention will be paid to the modification of diphosphine and phosphine sulfonated ligands and their effect on the activity and on the reaction mechanism.

1.2. Alternating copolymerisation of CO and ethene

1.2.1. General aspects

Over the last decades the catalytic conversion of accessible alkenes into high molecular weight polymers using transition metal catalysts has become an interesting industrial process. Polyketones obtained by alternating copolymerisation of carbon monoxide with other unsaturated monomers such as olefins represent a class of low-cost thermoplastics whose synthesis, properties and applications are object of fundamental and applied research.

Since the discovery of the first copolymerisation of CO and ethene in 1941 by Farbenfabriken Bayer,[4] the synthetic routes leading to polyketones have undergone constant improvement in terms of selectivity, productivity, environmental impact and economy.[5] The catalytic systems using nickel for the CO/ethene copolymerisation which require high temperatures (around 200 ^{o}C) and high pressures (around 200 bar), were improved by replacing the nickel with palladium. Temperature and pressure were decreased to 80 ^{o}C and 20bar of CO/ethene respectively. Methanol or water have replaced environmentally incompatible solvents, such as chlorinated ones.[6]

Polyketones are featured by a unique web of chemical and physical properties, which include photo- and biodegradability, good chemical resistance to acids, bases and solvents, easy functionalisation, impermeability to hydrocarbons, and

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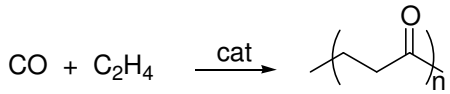
strong rigidity and impact strength.[5c,7] These properties can be modified and improved by changing the number or the nature of the co monomers and tuning the structure of the metal catalyst. The diversity of properties makes polyketones superior to polyolefines, polyamides and polyacetals.[8] The simplest polyketone is the CO/ethene copolymer (**Scheme 1**).



Scheme 1. Polyketone formation by alternating CO/ethene copolymerisation

The perfectly alternating CO/ethene copolymerisation is efficiently carried out in methanol at moderate temperature (about 80 °C) in the presence of a catalyst system comprising, as essential components, a Pd(II) salt with a weakly coordinating counteranion and a chelating diphosphine (**Figure 2**).[5b,9]

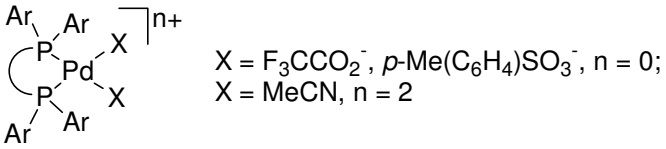


Figure 2. Pd(P-P) based precatalysts

1,3-bis(diphenylphosphino)propane (dppp) was the ligand that opened the way to the efficient synthesis of polyketones.[10] The perfect alternation of CO/ethene seems to be independent of the CO pressure. Generally, pressures between 30-60 bar of CO/ethene are used but perfect alternation can also be maintained at lower CO pressure. Only when the entire CO has been consumed does the catalyst promote the dimerisation of ethene to butenes.[11] In methanol polyketones with different combinations of diketone, keto-ester and diester end groups can be obtained (**Figure 3**).

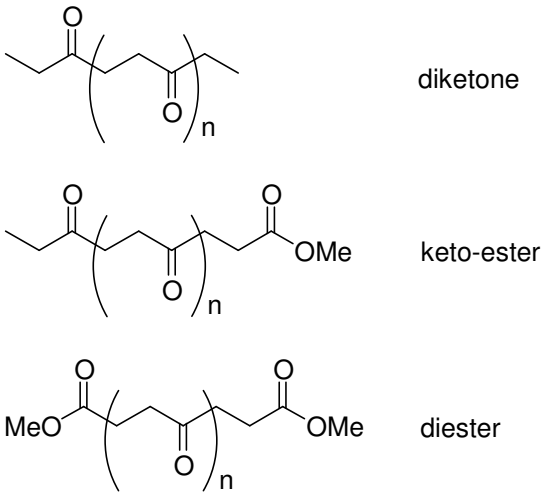
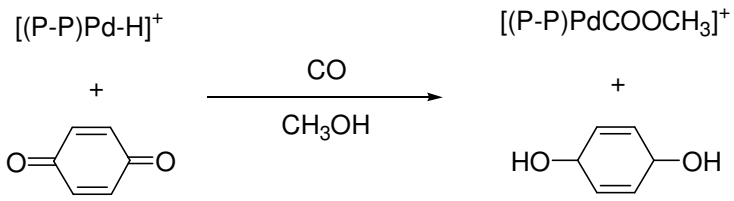


Figure 3. Polyketone structures obtained by CO/ethene copolymerisation in methanol

Optimal reaction conditions in methanol require the presence of both a strong oxidant with $E^0 \geq 0$ and a protic acid with $pK_a \leq 4$ whose conjugate base must have a low binding affinity for Pd(II). 1,4-benzoquinone (BQ, $E^º$ = 0.7v) and *p*-toluenesulfonic acid (TsOH, pK_a = -2.7) are two examples that amply fulfil these requirements and are indeed the stabilising compounds of the most productive catalytic systems. In these experimental conditions, productivities as high as 11 Kg polyketone/(g Pd*h) can be obtained.[5b,9] The main role of the 1,4-benzoquinone is to oxidise the Pd(0) or Pd(I) species that have been formed in the catalytic process to Pd(II). Another important role of the oxidant is to convert Pd-H into Pd-OMe (**Scheme 2**).[10b] While the main role of the protic acid is to prevent the deactivation of the palladium(II) catalyst into inactive (P-P)Pd(0), by protonation of the latter to yield catalytically active $[(P\text{-}P)PdH]^+$ species.



Scheme 2. Role of BQ in the conversion of Pd-H into Pd-C(O)OMe

1.2.2. Ligands used in the CO/ethene Pd catalysed copolymerisation reaction

Drent et al.[5b,10b] were the first to investigated the influence of the diphosphine ligand structure on the activity of the Pd(II) catalyst. They showed that the catalytic activity strongly depended on the chain length of the carbon backbone between the two phosphorus donor atoms (**Table 1**).

Table 1. Effect of the ligand backbone chain length on the CO/ethene copolymerisation activity[a]

Ligand	$H(CH_2CH_2CO)_n$-$(OCH_3)_n$[b]	Productivity (g polymer/g Pd*h)
$Ph_2P(CH_2)PPh_2$ (dppm)	2	1
$Ph_2P(CH_2)_2PPh_2$ (dppe)	100	1000
$Ph_2P(CH_2)_3PPh_2$ (dppp)	180	6000
$Ph_2P(CH_2)_4PPh_2$ (dppb)	45	2300
$Ph_2P(CH_2)_5PPh_2$ (dpppe)	6	1800
$Ph_2P(CH_2)_6PPh_2$ (dppph)	2	5

[a]Copolymerisation carried out in 150 mL of MeOH with $Pd(NCMe)_2(TsO)_2$ (0.1 mmol), C_2H_4/CO = 1, temperature = 84 °C, pressure = 45 bar. [b]Average degree of polymerisation determined by end-group analysis from $^{13}C\{^1H\}$ NMR spectra

Since the discovery of the effectiveness of palladium catalysts containing dppp ligand by Shell Research in 1984, various dppp-like ligands have been designed and successfully used to catalyse the CO/ethene copolymerisation in

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combination with palladium (II) salts. Ligand variations have often involved substitutions in either phenyl groups or the carbon backbone. It has been found that the introduction of alkyl groups in the 2-position of the carbon backbone of dppp does not improve the catalytic activity of the corresponding palladium (II) precursors.[12] On the other hand a considerable increase of the productivity, more than 50%, was obtained when alkyl groups were introduced in both 1- and 3-position of the dppp backbone, to yield both the *meso* and the *rac* 2,4-bis(diphenylphosphino)pentane (bdpp)[12] (**Figure 4**).

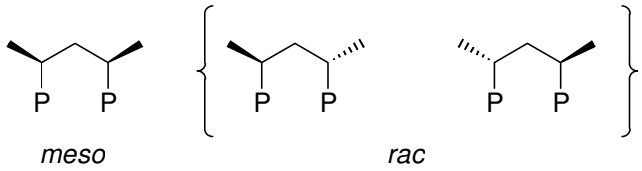

Figure 4. *Meso*- and *rac*-2,4-bis(diphenylphosphino)pentane

Under comparable experimental conditions, *meso*-bdpp has been reported to be more active in the palladium-catalysed CO/ethene copolymerisation than dppp or *rac*-bdpp. In this case, it has been suggested that both electronic and steric factors explain the remarkable activity of the *meso*-bdpp catalyst. In particular, *meso*-bdpp was found to undergo in methanol a quasireversible one-electron reduction, whereas both dppp and *rac*-dppp were irreversibly reduced. It was therefore proposed that the increased activity of Pd(*meso*-bdpp) might also be due to the more facile re-oxidation of the one-electron reduced species by both 1,4-benzoquinone or H^+, which ultimately results in a large number of active Pd centres in the catalytic mixture.[12]

The *R,S* (*S,R*) stereochemistry of the methyl groups makes a six-membered Pd(*meso*-bdpp) ring preferentially adopting a chair conformation with equatorial methyl groups and with one equatorial and one axial phenyl group on each phosphorus atom (**Figure 5**(**A**)).[13] In contrast, in solution the *rac* isomer adopts

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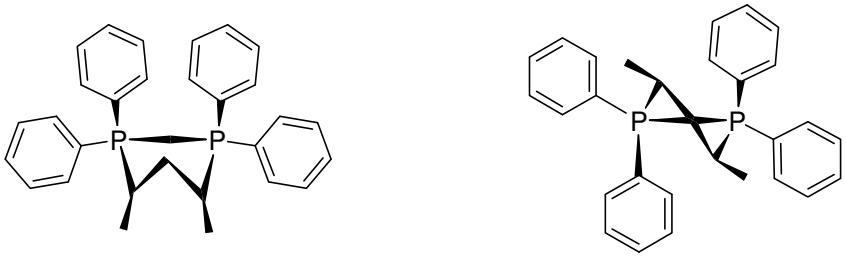
the δ-skew conformation in which the steric hindrance due to the phenyl rings is diagonally placed with respect to the P-Pd-P plane (**Figure 5**(**B**)).[13]



A **B**

Figure 5. Preferred conformations adopted by the six-membered chelate rings with *meso*-bdpp (chair, **A**) and *rac*-bdpp (δ-skew, **B**)

It has been suggested that steric factors together with the chair conformation of the metallaring play a major role in enhancing the activity of the *meso*-bdpp precursors. This *meso effect* has also been observed by Consiglio et al. in the copolymerisation reaction of propene with CO catalysed by cationic palladium complexes.[14]

Excellent results in terms of productivity and catalyst stability have been obtained by introducing an *ortho*-methoxy group at each phenyl unit in dppp in order to obtain 1,3-bis(di(2-methoxyphenyl)phosphino)propane (*o*-MeO-dppp)[15] (**Figure 6**).

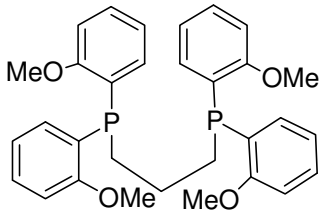
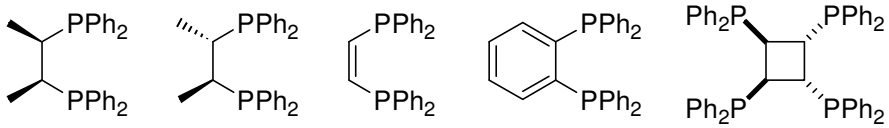


Figure 6. *o*-MeO-dppp used in both fluid and slurry CO/ethene palladium catalysed copolymerisation

A study with a water-soluble version of *o*-MeO-dppp containing *m*-sodium sulfonatophenyl groups has confirmed that the *o*-MeO moiety can exert both steric and electronic influence on the palladium centre.[15b] Similar studies, modifying the ligand backbone of dppe-based ligands have also been performed. Indeed, the chelate ring size is not the only parameter that controls the copolymerisation activity of Pd(diphosphine) catalysts. The backbone rigidity and the overall steric crowding at the Pd centre seem to be more important than the chelate ring size in the determination of the catalytic activity.[16] This is the case for the diphosphine ligands with two carbon atoms in between the phosphorous donor atoms (**Figure 7**).



meso-dppb *rac*-dppb *cis*-dppen *o*-dppbe *cyclo*-tetraphos

Figure 7. Rigid diphosphine ligands forming five membered metallarings

The beneficial effect of the ligand rigidity on copolymerisation reactions has also been confirmed by Doherty, in bis-phospholyl substituted carbon backbones. Some bis-phospholyl ligands are presented in **Figure 8**.[17]

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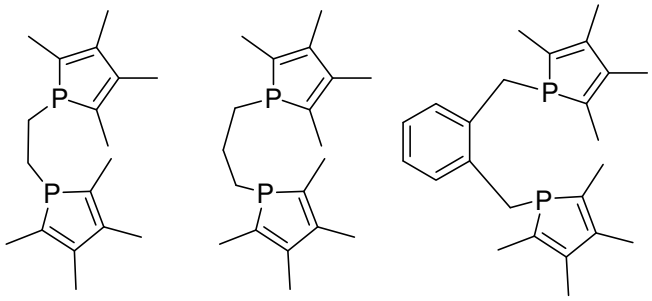
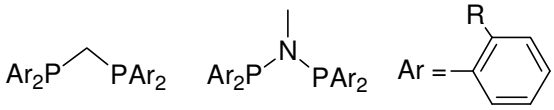


Figure 8. Bis-phospholyl ligands used in CO/ethene palladium-catalysed copolymerisation

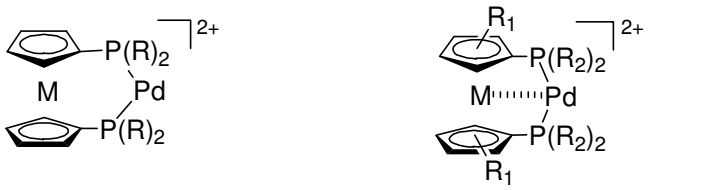
Dossett et al. provided experimental evidence that four-membered ring systems with *i*-propyl substituted phenyl rings exhibit high catalytic activity (**Figure 9**).[18]



R = H, OMe, Me, Et or ^{i}Pr

Figure 9. Ligands which form four membered metallarings

Recently, metallocene-based ligands have been tested in the copolymerisation reaction of CO/ethene. From these studies it turned out, that both, the catalytic activity and the chemoselectivity of the copolymerisation reaction depend on the sandwiched metal centre, on the substituents of the cyclopentadienyl ring and the substituents of the phosphorous donor atoms. Since metallocene-based ligands can be considered to be both bidentate (κ^2-P,P) and terdentate (κ^3-P,M,P) coordinating ligands, the formation of copolymers in methanol was observed only in those cases, in which the ligand coordinated strictly in a κ^2-P,P mode. In all other cases only low weight oxygenates or methyl propionate were obtained (**Figure 10**).[19]



M = Fe; R = Me, Et, Ph
M = Ru; R = Ph

M = Fe; R_1 = Me; R_2 = Ph
R_1 = H; R_2 = ^{i}Pr
M = Os; R_1 = H; R_2 = Ph

Figure 10. Bis-(diphosphino) metallocene palladium catalytic precursors

Hemilable phosphine ligands containing oxygen, nitrogen or sulfur functions have been used in the palladium-catalysed CO/ethene copolymerisation reaction. However their catalytic activity is lower than that of dinitrogen and diphosphine ligands. Some of the P-O, P-N and P-S ligands that have been studied to obtain efficient palladium catalyst for the CO/ethene copolymerisation are presented in **Figure 11**.[20]

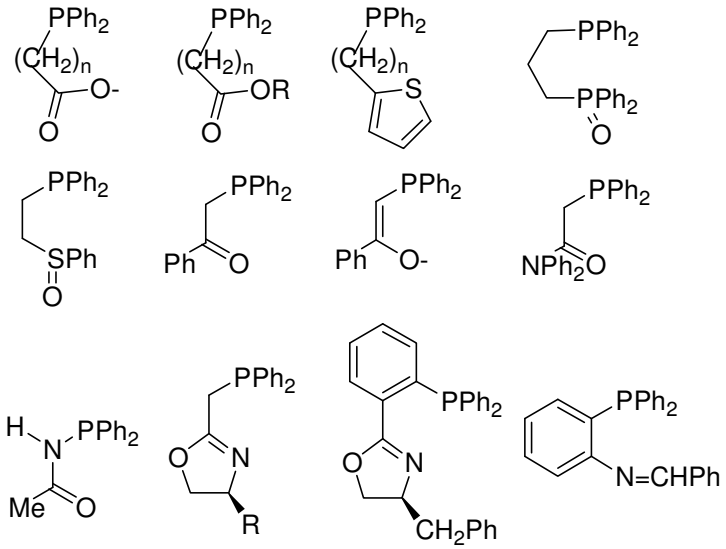


Figure 11. Hemilable P-O, P-N and P-S ligands

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Sterically rigid dinitrogen ligands such as bipyridine (bipy), phenanthroline (phen) and their alkyl-subtituted derivates are used to form efficient palladium catalysts for alternating CO/ethene copolymerisation in both homogeneous and heterogeneous conditions (**Figure 12**).[21]

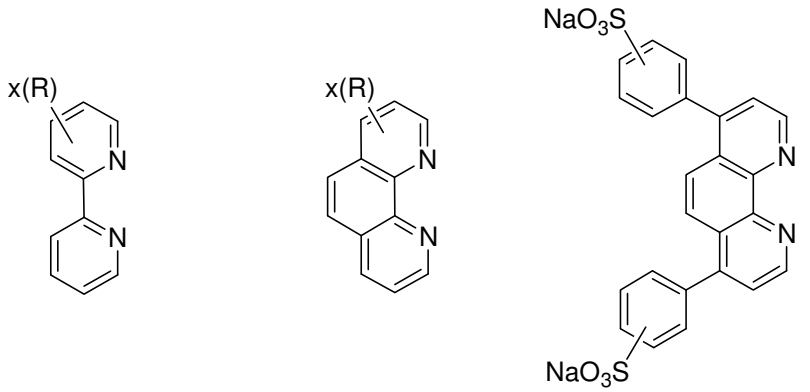

Figure 12. Dinitrogen ligands used in CO/ethene palladium-catalysed copolymerisation

1.2.3. Mechanism of the CO/ethene copolymerisation catalysed by palladium (II) catalysts with bidentate ligands

In 1991, Drent et al. reported on the basis of end-group analysis of the polyketone material, the first mechanism for the CO/ethene copolymerisation using cationic palladium complexes with chelating diphosphine ligands in alcoholic solvents.[10b] After this first mechanism several *in situ* studies were carried out and numerous model studies have been proposed on the bases of different experimental and theoretical approaches. All these studies have contributed to a better understanding of the initiation, propagation and termination steps. Most of these studies have been reviewed by Sen in 1993[5a] by Drent and Budzelar in 1996[5b] by Sommazzi and Garbassi in 1997[5c] and by C. Bianchini et al. in 2002[9] , and 2005[5e]

The mechanism reported in **Scheme 3** summarises all the principal steps of the alternating CO/ethene copolymerisation in MeOH catalysed by palladium(II) complexes stabilised by bidentate ligands. The catalytic process comprises two competing cycles, connected by two cross termination steps. The prevalence of both cycles depends on the experimental conditions. Cycle **B** initiates (***I***) with the insertion of ethene into a Pd-H bond that can be generated in the catalytic mixture in a variety of ways, in particular when the methanol solvent contains traces of water (Water Gas Shift reaction).[22] Insertion of CO into the resulting ethyl complex is reversible and faster than ethene insertion, while CO insertion into the Pd-acyl is thermodynamically disfavoured. Since ethene insertion into the Pd-acyl is rapid and irreversible, the propagation (***P***) can occur by alternately inserting CO and ethene. The copolymer produced by this cycle shows either keto-ester or diketone end groups depending on the termination path: the keto-ester is obtained by methanolysis (***M***) of the Pd-acyl bond, while the diketone is obtained by protonolysis (***H***) of a Pd-alkyl intermediate.

A copolymer with keto-ester end groups is also produced by methanolysis of a Pd-alkyl bond formed during the propagation in the alternative cycle **A**, which starts with the insertion of CO into a Pd-OMe bond giving a palladium carbomethoxy (Pd-C(O)OMe) complex. The copolymer with diester end groups is obtained by a methanolysis reaction of the Pd-acyl species derived from cycle **A**. In the following sections, the single steps of the copolymerisation process, which comprise initiation, propagation and chain-transfer will be discussed separately.

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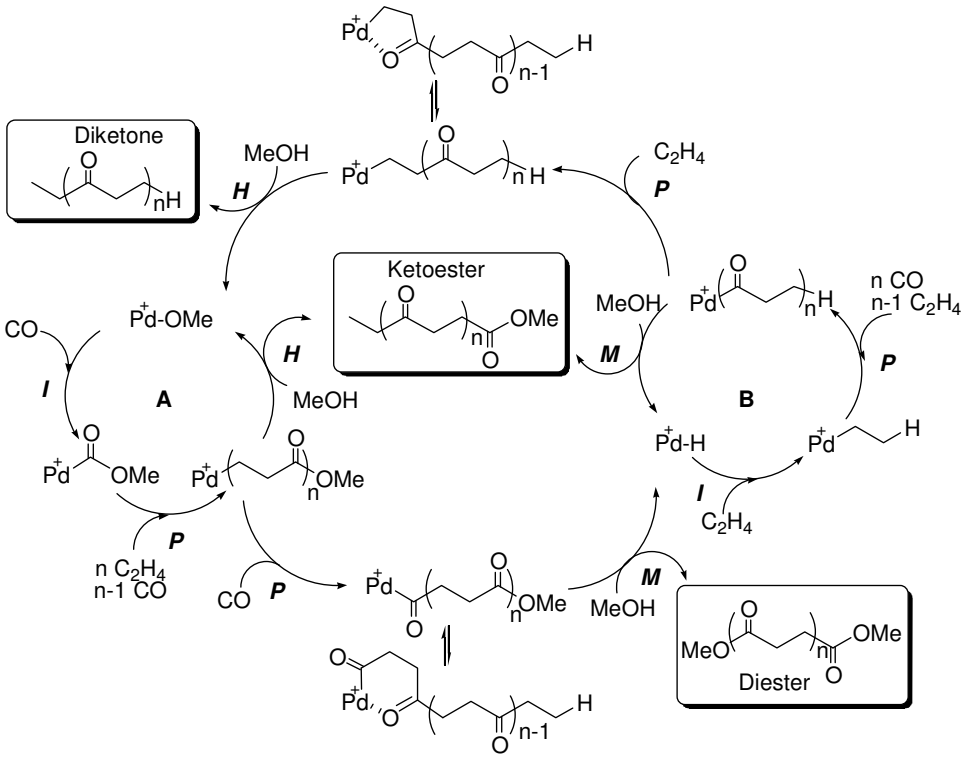

Scheme 3. Proposed mechanism of CO/ethene copolymerisation catalysed by diphosphine palladium(II) catalysts

Initiation

The catalytic active species in the alternating CO/ethene copolymerisation in methanol are generally square-planar Pd(II) complexes of the general formula [Pd(II)(Pk)(S)(P-P)]X where (P-P) is a chelating diphophine, Pk is the growing polyketone chain and S may be MeOH, water, a comonomer or a keto group from the chain. X is the counteranion of weak nucleophilicity in order to avoid competition with the comonomer for coordination to palladium. These active species are formed by appropriate neutral $Pd(X)_2(P\text{-}P)$ or cationic $[Pd(S)_2(P\text{-}$

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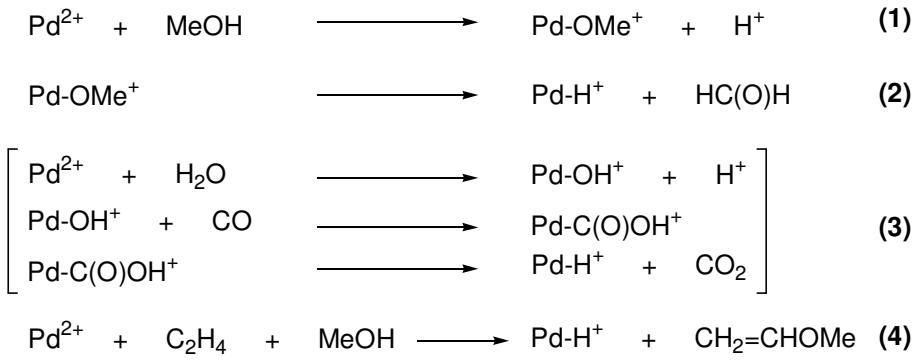
P)]X_2 precursors that can also be formed *in situ* by reaction of a palladium(II) salt (commonly $Pd(OAc)_2$ or $[Pd(NCMe)_4](BF_4)_2$) with a diphosphine ligand.
In both cases, a slight excess of strong protic acid (commonly *p*-toluenesulfonic acid) must be added to the reaction mixture in order to stabilise the Pd-H species. The role of this acid is also to neutralise anionic nucleophiles (e. g., acetate ions) that can compete with methanol in the activation of the precursor and with the comonomers in the coordination on palladium(II), thus retarding the propagation step. Some studies have shown that depending on the chelating diphosphine, *in situ* preparation of the catalyst precursor may give much lower productivities as compared to reactions where a preformed palladium(II) complex is used.[23]

The palladium (II) precursor needs to be activated to generate the Pd-H and Pd-OMe species that will initiate the copolymer propagation (**Scheme 4)**[5,9,10,24] In the absence of specific reagents, the promoter is activated by the formation of a Pd(II)-OMe complex (**Scheme 4**, eq. **1**) that generates a Pd(II)-H species through a β-hydride elimination (**Scheme 4**, eq. **2**).[25] Furthermore Pd(II)-H species can also be generated by both the Water-Gas Shift reaction (**Scheme 4**, eq. **3**) or a Wacker-type reaction (**Scheme 4**, eq. **4**)[5,9,10,24]



Scheme 4. Reaction path for the synthesis of Pd-OMe and Pd-H species

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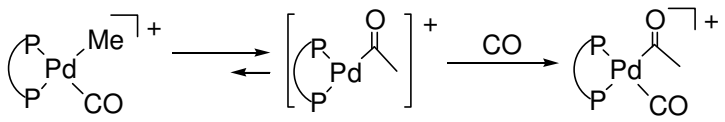
The spectroscopic detection of Pd-OMe as well as Pd-H species is rather seldom, as both of them constitute highly active intermediates.[26] However, indirect methods such as end group analysis of the polyketone, isotopic labeling and model compounds have provided experimental evidence for the proposed mechanism.[5,9,10,24]

Chain propagation

Two alternating migratory insertion steps, involving Pd(alkyl)(CO) and Pd(acyl)(ethene) moieties comprise the chain propagation. Pd(alkyl)(ethene) insertions are virtually excluded, because the CO insertion into the Pd-alkyl bond is 10^5 faster than ethene insertion, which avoids the double ethene insertion.[27a] Early studies under actual copolymerisation conditions have shown that the copolymerisation rate depends on the ethene pressure.[5b] High pressure NMR experiments with model compounds in aprotic solvents (CD_2Cl_2) have provided interesting information on the energy barriers associated with the migratory insertion of CO and ethene occurring during the propagation step. It has been proved that the migratory insertion reaction of CO in $[Pd(R)(CO)(P\text{-}P)]^+$ complexes (R = Me, Et) is reversible, following first-order kinetics and it is therefore independent of the CO concentration in solution (**Scheme 5**).[27]

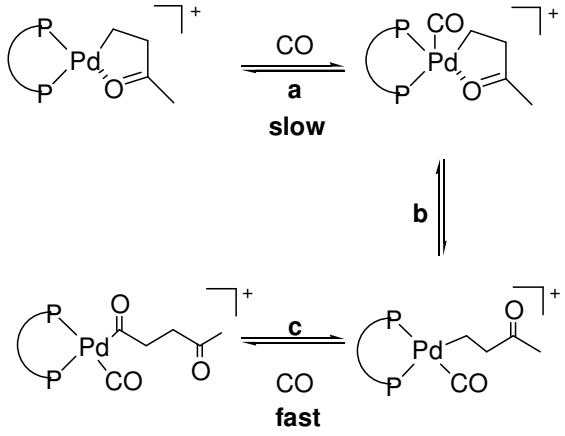


Scheme 5. Migratory insertion of CO into a Pd methyl bond

The free energies of CO insertion into a Pd-alkyl bond can be calculated from the half-life times ($t_{1/2}$) obtained by integrating the corresponding $^{31}P\{^1H\}$NMR signals. $\Delta G^{\ddagger}$ values for the migratory insertions reactions of palladium(II) methyl carbonyl complexes with chelating diphosphines in range from 14 to 18 Kcal

mol^{-1}.[27a,27b,27c] The energy barriers for the migratory insertions seem to decrease with both, the increasing P-Pd-P bite angle and the steric bulk of the diphosphine ligand.[27e]

The displacement of the coordinating carbonyl group from palladium in β-keto chelates by ethene has never been observed. Carbon monoxide is much smaller than ethene and exhibits a greater binding affinity for palladium than ethene. In the active catalytic systems, the β-keto chelates generally react with CO to give Pd acyl(carbonyl) complexes at very low temperature (**Scheme 6**).



Scheme 6. Reaction of the Pd β-keto-chelate with CO

For the systems investigated the rates of conversion of the β-keto chelates into the corresponding Pd acyl(carbonyl) complexes were evaluated by the half-life times obtained from the decay and increase of the corresponding $^{31}P\{^{1}H\}$NMR resonances at the appropriate temperatures. The results obtained show that the energy barriers for the opening of the β-keto chelates decrease by increasing the number of carbon atom spacers in between the phosphorous atoms and thus with increasing P-Pd-P bond angle.[27b,27c]

On the basis of the CO pressure dependence of the transformation of the β-keto chelates into the Pd acyl(carbonyl) complexes, it has been proposed that the rate limiting step for this conversion is related to the opening of the metallacycle by CO (**Scheme 6**, steps **a** and **b**) rather than the following migratory insertion of CO into the Pd alkyl carbonyl compound, which follows first order kinetics (**Scheme 6**, step **c**).[27b,27c]

A PM-RAIRS (Polarization Modulation Reflection Absortion Infrared Spectroscopy) study (**Figure 13**) clearly evidenced, that the β- and γ- keto chelates $[(dppp)Pd\{CH_2CH_2C(O)CH_3\}]^+$ and $[(dppp)Pd\{C(O)CH_2CH_2C(O)CH_3\}]^+$ complexes are resting-states in equilibrium with each other under catalytic conditions. This study also revealed that at least in solid-gas copolymerisation reactions ethene insertion into the Pd-acyl bond of the γ-keto chelate complex $[(dppp)Pd\{C(O)CH_2CH_2C(O)CH_3\}]^+$ occurs only in the presence of CO (**Scheme 7**).[28]

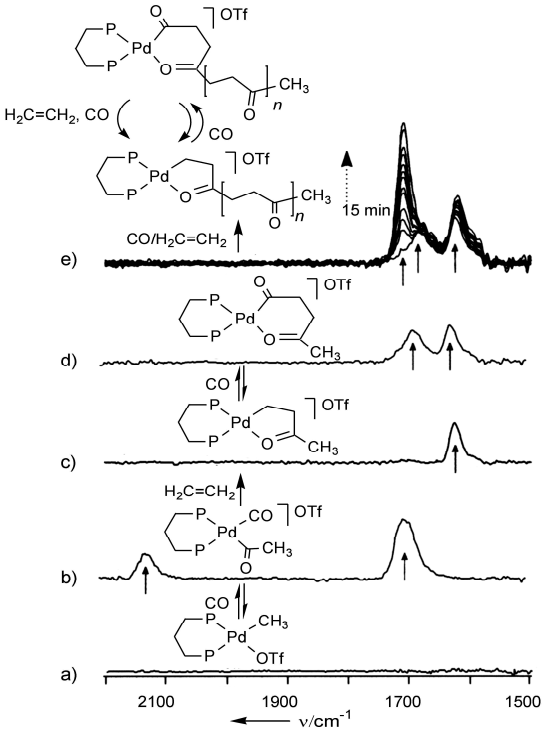


Figure 13. In situ PM-RAIRS spectra of a microcrystalline sample of [(dppp)Pd(CH_3)(OTf)]. (**a**) At room temperature, (**b**) under 500 mbar of CO, (**c**) under 2 mbar of CO and 333 mbar of ethene, (**d**) under subsequent exposure to 750 mbar CO, (**e**) during subsequent polymerisation under 666 mbar of CO/ethene (evolution of the spectrum at 15 min intervals)

The importance of β- and γ- keto chelates in controlling both the selectivity and the propagation rate of the CO/ethene copolymerisation has been confirmed by several *in situ* and model studies.[27b,28,29]

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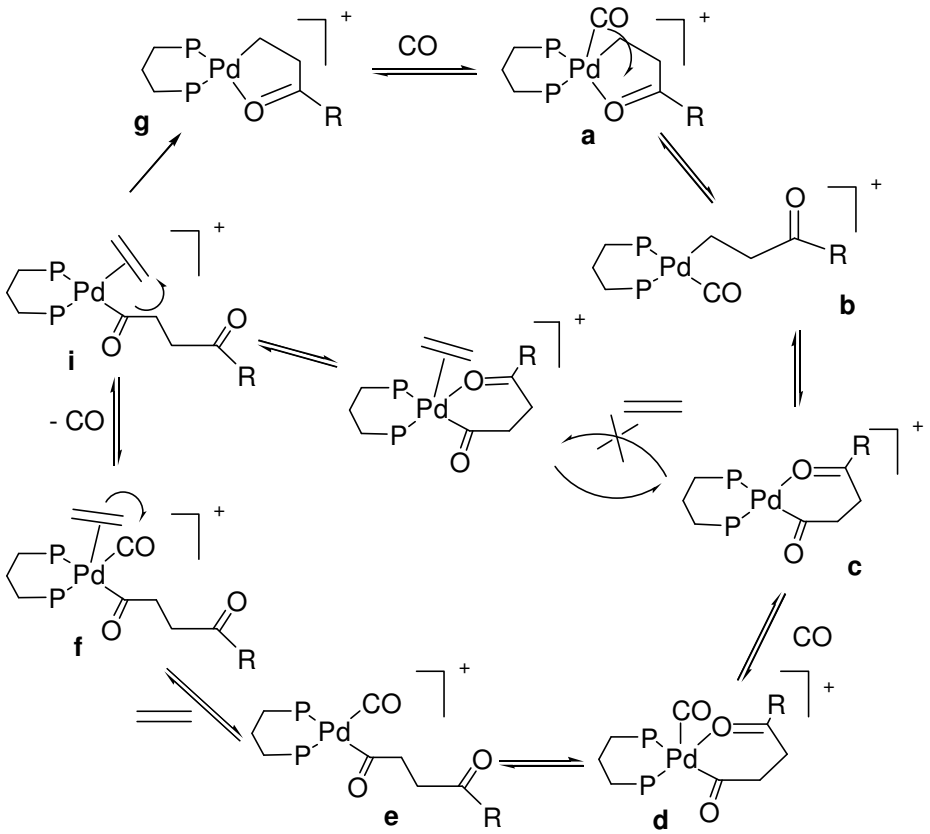
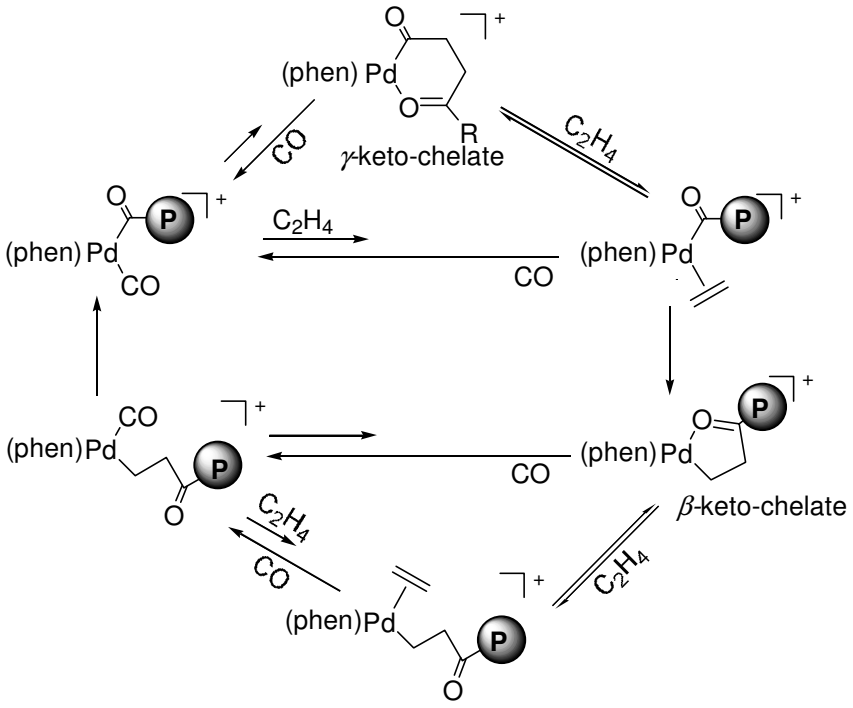


Scheme 7. Mechanism of the heterogeneous CO/ethene copolymerisation proposed on the basis of a PM-RAIRS study

Unlike diphosphine ligands, rigid dinitrogen ligands such as bipyridin (bipy), phenathrolin (phen) and bis(arylimino)acenaphthene (Ar-BIAN) also exhibit the formation of γ-keto chelates by a successive insertion of CO and ethene (**Scheme 8**).[29]



Scheme 8. Proposed mechanistic cycle of the chain-propagation of the CO/ethene copolymerisation catalysed by the phenanthrolyne-based palladium catalysts

A similar mechanism has been observed by Braunstein et al. with a hemilable P-O ligand $Ph_2PNH(CO)Me$. The stepwise reaction of the palladium(II) precursor with CO and ethene allowed the authors to isolate the four intermediates shown in **Scheme 9** and to identify the reversible and irreversible steps.[20a]

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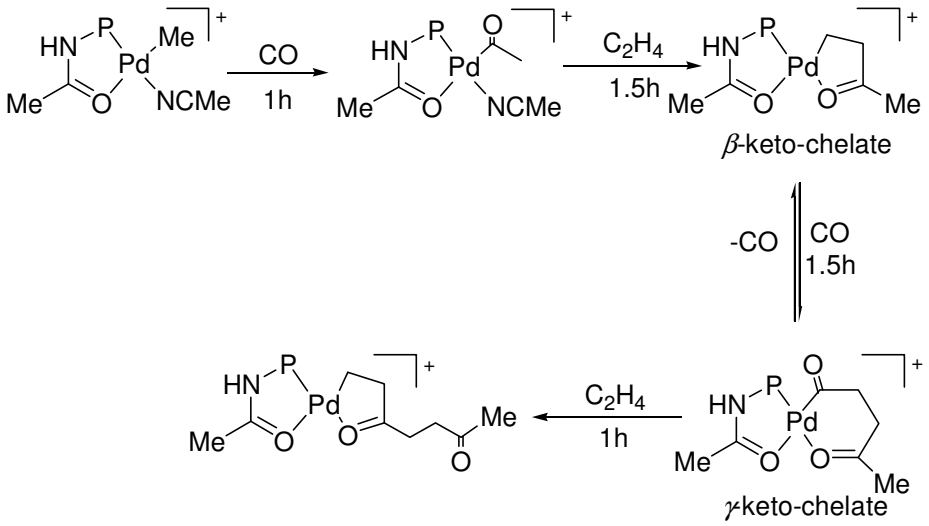


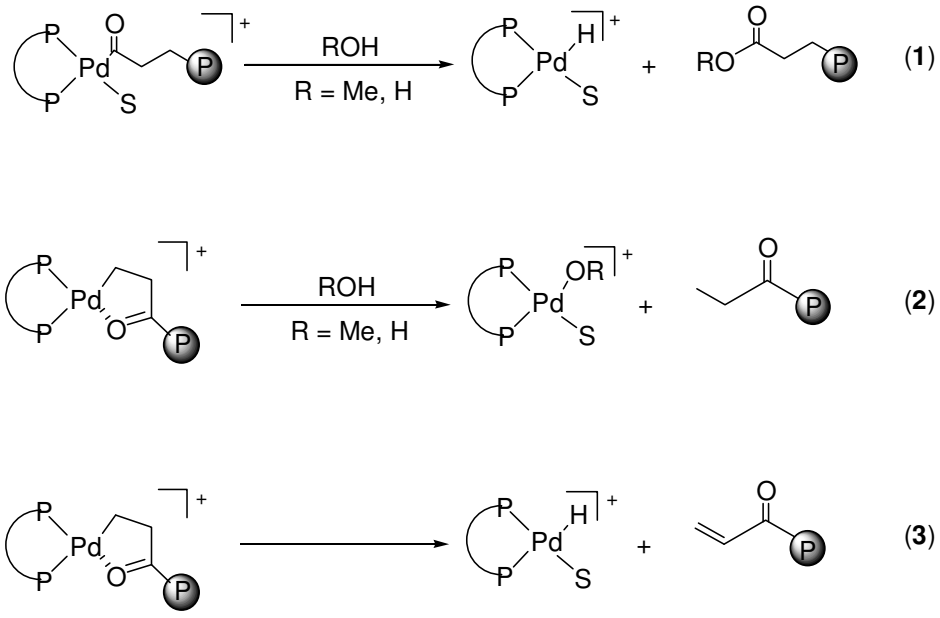
Scheme 9. Model study of the chain propagation step with a Pd(P-O)-based catalyst

In summary both the β-keto chelates and the much more favourable coordination of CO over ethene avoids a thermodynamically favourable double insertion of ethene. On the other hand the double insertion of CO is thermodynamically much less favourable than the alternating insertion of CO and ethene.

Chain-transfer

High molecular weight polyketones are obtained when the propagation rate prevails over the chain-transfer process. If both rates are similar, oligomers are obtained. If the chain-transfer is prevalent only methyl propionate is formed. The chain-transfer mechanism depends on the solvent in which the CO/ethene copolymerisation is carried out. For instance in protic solvents like MeOH, two chain-transfer mechanism occur simultaneously, namely the methanolysis reaction of Pd-acyl species (**Scheme 10**, eq. **1**) and the protonolysis reaction of

Pd-alkyl species (**Scheme 10**, eq. **2**).[5b] This is shown by NMR analysis of the polyketone end groups and the oligomeric fractions, while the mechanism of chain-transfer in aprotic solvents is accomplished by β-hydride elimination (**Scheme 10**, eq. **3**).



Scheme 10. Chain- transfer mechanism in protic and aprotic solvents

Depending on the chain-transfer mechanism, the termination metal product may contain Pd-OR, Pd-OH or Pd-H moieties, al of which can re-initiate the catalytic cycle by inserting CO or ethene, respectively. In principle, the rate of chain-transfer should not affect the overall productivity rather it influences the molecular weight of the polyketone product. When the termination processes **1** and **2** (**Scheme 10**) occur at comparable rates, the copolymers have diester, keto-ester and diketone end groups in a 1:2:1 ratio, respectively.[10]

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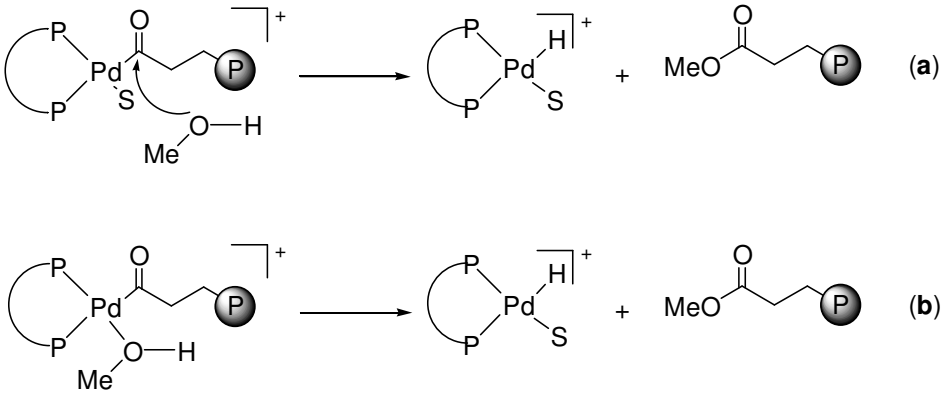
The relative occurrence of protonolysis and methanolysis depends on many factors. When the growing copolymer chain reaches a length of about 13-20 – CH_2CH_2-C(O)- units, and the copolymerisation assumes heterogeneous character, chain termination can equally proceed by protonolysis and methanolysis, while protonolysis predominates over the methanolysis in the homogeneous phase.[30] Furthermore the protic acids, which are commonly used to maintain a high number of catalytically centre palladium(II) species during the catalysis, can also influence the methanolysis rate.[24a]

Chain-transfer by methanolysis

Chain-transfer by methanolysis involves the attack of a MeOH molecule on a propagating Pd-acyl species, which yields an ester-end group, and a Pd(II)-H species which re-initiates the chain growth by inserting of ethene (**Scheme 11**). The use of other alcohols as solvents in the CO/ethene copolymerisation can dramatically affect the termination rate and the molecular weight of the polyketone.[31] Normally, the alcolysis rate decreases by both increasing the steric bulk of the alcohol or decreasing its nucleophilicity.[31c]

Remaining to the exclusive use of methanol, it has been found that the chain-transfer rate depends on the nature of the chelating diphosphine and on the concentration of protic acid added in the reaction media. Some studies on model palladium acyl complexes show that the methanolysis rate increases considerably with the steric bulk of the chelating diphosphine ligand.[32]

Two mechanism may take part in chain-transfer through methanolysis namely, the intermolecular (**Scheme 11, a**) or intramolecular (**Scheme 11, b**) attack of Pd-acyl intermediates.



Scheme 11. Intermolecular (**a**) and intramolecular (**b**) mechanism of the methanolysis reaction

The intermolecular mechanism, which has been studied by van Leeuwen et al. seems to be less probable than the intramolecular mechanism, although it cannot be excluded.[31c] The *cis*-coordination of the ligand is required to force the coordination of methanol *cis* to the acyl group. This intramolecular nucleophilic attack of the oxygen atom of methanol at the palladium acyl species can occur *via* a concomitant formation of Pd-H or a reductive elimination of the Pd(acyl)(methoxy) species followed by a protonation of the Pd(0) centre.[33]

Chain-transfer by protonolysis

The chain-transfer by protonolysis represents the predominant termination step in homogeneous CO/ethene copolymerisation. It involves the reaction between a propagating Pd-alkyl species and MeOH or water. The propagation is terminated with the formation of a polymeric chain with a ketone end group and Pd-OMe (or Pd-OH) species. These species can re-enter the catalytic cycle by CO insertion. The protonolysis process has been elucidated by van Leeuwen et al. by means of deuterium incorporation experiments[29c] which showed that the β-keto chelates are in equilibrium with their enolates formed by a β–hydride

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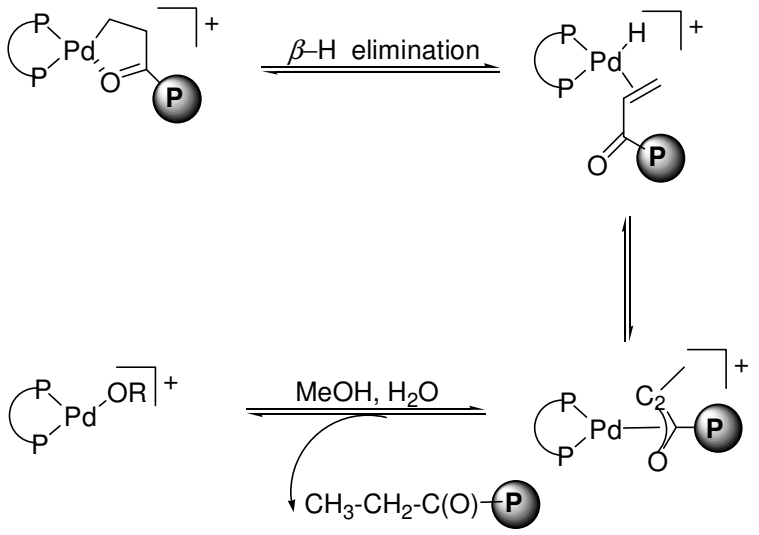
elimination/hydride migration process (**Scheme 12**). The coordinated enolate is then regioselectively protonated at the C_2 carbon atom by either MeOH or H_2O. Furthermore from detailed studies of the protonolysis reaction, van Leeuwen et al. inferred a dependence of the protonolysis rate on the diphosphine bite angle. Indeed, a slight increase of the protonolysis rate with increasing bite angles of the diphosphine ligand was found.[34]



Scheme 12. Chain termination mechanism by protonolysis

When dppf[19b] was used as ligand β-keto chelate was observed in high pressure NMR experiments in MeOD-d_4, which contrasts with the model studies carried out by van Leeuwen et al., as dppf has a wider bite angle than dppe or dppp. In the latter cases no β-keto chelate was observed in identical high pressure NMR experiments. These evidences suggest that also other parameters in the catalytic system may also affect the protonolysis rate.

Deactivation paths in the copolymerisation process

Under the conditions, used for the CO/ethene copolymerisation, the propagation rate decreases with time, and no catalytic activity is normally observed after 8-10 hours. **Scheme 13** gives an overview of the different deactivation processes known to date involving chelating diphosphine ligands.

The deactivation process of palladium diphosphine catalysed copolymerisation reactions generally comprises five different compounds namely, the palladium bis-chelate compound **A** (**Scheme 13**), the dimeric Pd μ-OH compound **B**, the dimeric Pd(I) μ-H, μ-CO compound **C** and the less common dimeric compounds **D** and **E**. Compound **A** is formed from Pd-H species, which slowly degrade under the concomitant formation of inactive Pd(0) and free ligand, which can react with active palladium (II) species to generate bis-chelate complexes. Not all species represent the dead end of the copolymerisation, rather some of them may be defined as robust resting states. Indeed, bis-chelates containing diphosphine ligands with a C_2 backbone are inactive,[27b] but those with dppp-like ligands have an appreciable activity, due to the destabilisation of the six membered ring systems by steric interactions between the phenyl groups of each ligand **Scheme 14** shows how Pd bis-chelate complexes can re-enter the catalytic cycle.[35] It is important to emphasise, that they can be formed in both protic and aprotic media.

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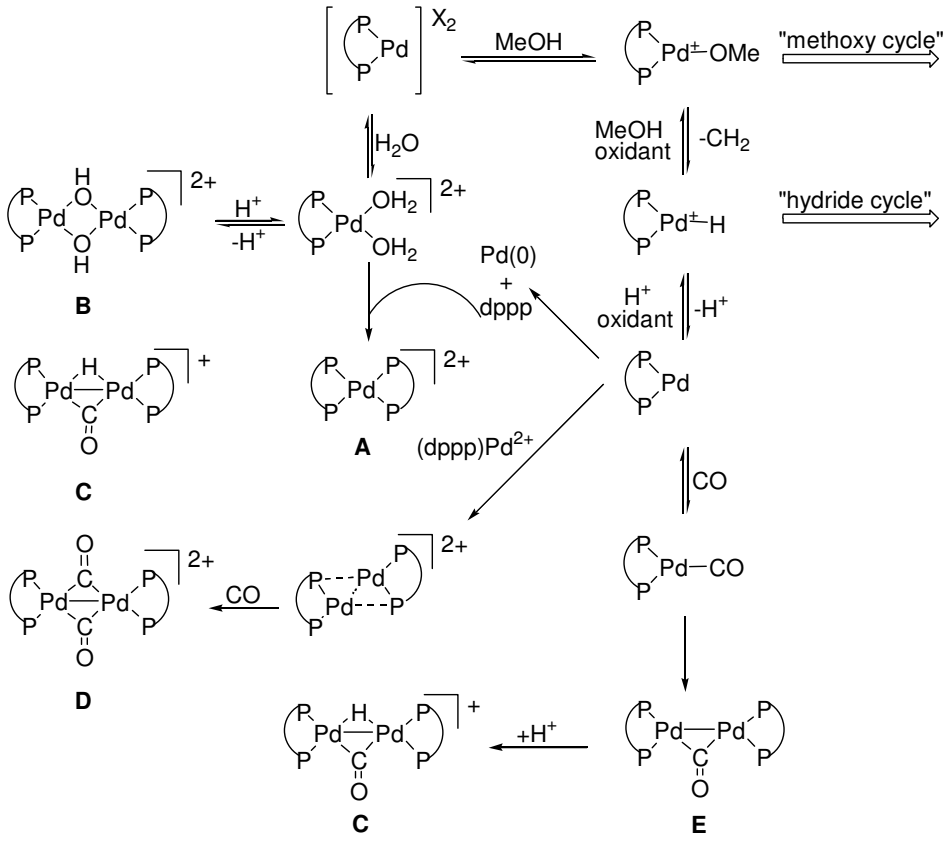
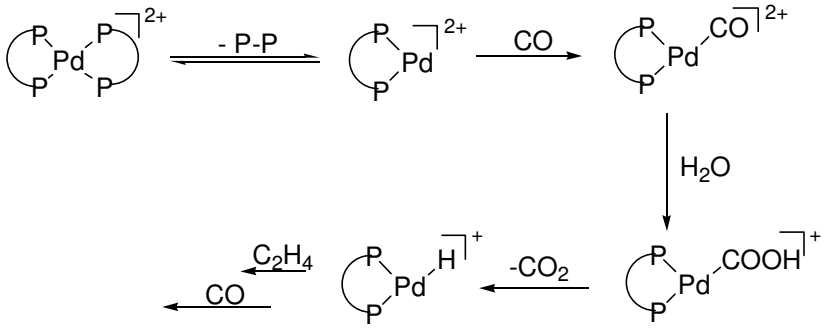


Scheme 13. Possible deactivation paths of Pd(II)(P-P) catalyst under CO/ethene copolymerisation conditions



Scheme 14. Contribution of Pd bis-chelate complexes to the catalytic process

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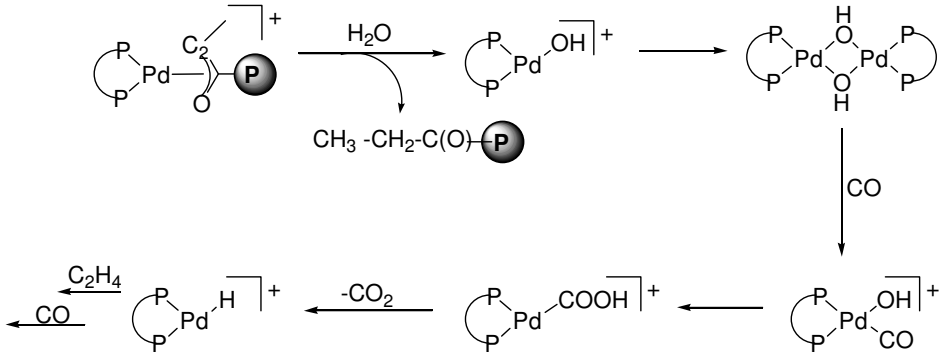
The μ-hydroxo complexes **B** can be formed in protic systems from bis-acquo complexes as presented in **Scheme 13** They are also formed from the protonolysis reaction, if no additional Broensted acid is present. Under real catalytic conditions the dimeric form is in equilibrium with a monomeric species, which can insert CO into the Pd-OH bond to yield Pd-C(O)OH, which in turn inserts ethene or eliminates CO_2 to form a Pd-H species (**Scheme 15**).[36] The contribution of the dimeric Pd μ-hydroxo complexes to the overall productivity of the catalytic system is generally higher than that of the Pd bis-chelate compounds. In general, the steric rigidity of the ligand backbone destabilises the dimeric Pd μ-hydroxo species.[27c]



Scheme 15. Reaction of dimeric μ-hydroxo complexes under copolymerisation conditions

The dimeric palladium(I) μ-H, μ-CO compound **C** (**Scheme 13**), which results from the formal reaction of a Pd(0)-CO complex with a Pd(II)-H intermediate has been observed during high pressure NMR experiments in MeOH as solvent.[19b] Its formation is strongly related to the methanolysis reaction of an Pd-acyl intermediate in the presence of excess CO.[19b] Furthermore such compounds have been obtained by independent synthesis, upon reaction of dimeric Pd μ-hydroxo compounds with CO,[37a] or by oxidative addition of an acid at a dimeric Pd(0) monocarbonyl intermediate (**Scheme 13**).[37b]

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The dimeric compounds **D** and **E** (**Scheme 13**) have also be obtained under reductive conditions and in the presence of CO. Both of these compounds have been synthesised but never observed under real catalytic conditions.[37c,37d]

1.3. Non-alternating CO/ethene copolymerisation

The development of novel late transition-metal catalysts for the synthesis of new copolymers containing non-polar backbone and a controlled amount of a polar monomer is of considerable interest to both academia and industry.[11] However, the design of metal-catalysed for such copolymerisation reactions is not a trivial task and many attempts have been made in this area. So far, however, very few new materials have been obtained.[38]

In previous sections, we have dealt with the palladium-catalysed perfectly alternating copolymerisation reaction of carbon monoxide and ethene and its mechanism. It is well known that the double insertion of carbon monoxide in this reaction does not occur for thermodynamic reasons. However, the double insertion of ethene is kinetically disfavoured. The formation of a stable five-membered cationic palladium metallacycle **(A)** (**Figure 14**) *via* an electrostatic interaction between the oxygen of the carbonyl and the cationic palladium centre, which is called “back-biting”, kinetically favours the insertion of carbon monoxide over ethene insertion.[29a,39,40]

In over two decades of research in the area of late transition metal catalysed polymerisation of carbon monoxide and ethene, no extra insertions of ethene or carbon monoxide have ever been reported; even high ethene/carbon monoxide ratios produce exclusively error-free polyketone until all carbon monoxide is consumed.[10b,41] Nevertheless, the double insertion of ethene should be possible, as the same cationic palladium species that is used for the copolymerisation has been shown to efficiently dimerise ethene into butanes.[11]

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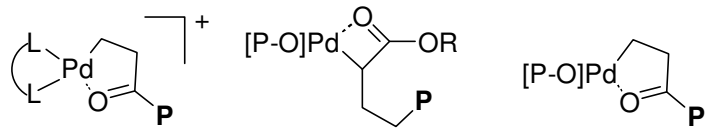
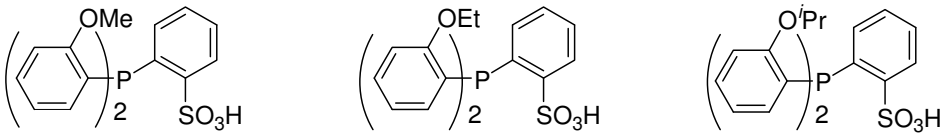


A **B** **C**

Figure 14. Chelates formed during the copolymerisation reaction

The production of non-perfectly alternating carbon monoxide and ethene copolymers is one of the aims in polyketone research in order to obtain new materials with desirable properties and that could be further functionalised.

In 2002, Drent et al. reported the first example of palladium-catalysed non-perfectly alternating copolymerisation of carbon monoxide and ethene. The palladium precursors bearing alkoxy-aryl-phosphine ligands containing sulfonic acid groups (**Figure 15**) as catalysts were formed *in situ* by mixing palladium acetate and the ligand in a near stoichiometric ratio. Double, triple and quadruple extra insertions of ethene in the growing polyketone chain were observed. These extra insertions were attributed to the destabilisation of the neutral chelate **C** (**Figure 14**) to the extent that ethene effectively competes with carbon monoxide for the next insertion.[42]



1a **1b** **1c**

Figure 15. (P-O) ligands derivates diphenylphosphinobenzene sulfonic acid, used in the non-alternating copolymerisation of CO and ethene

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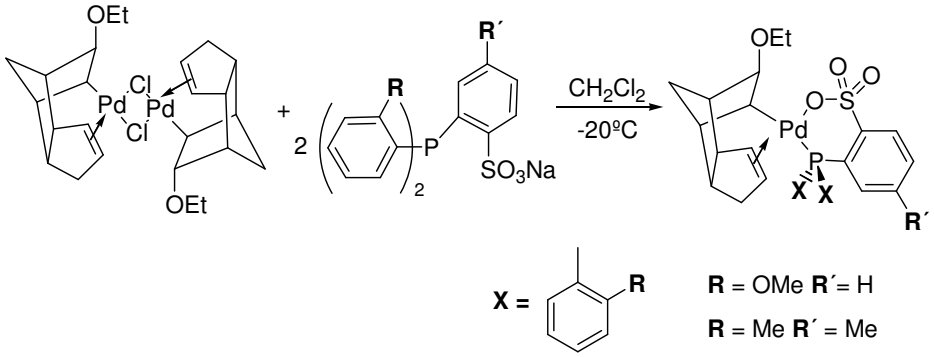
Table 2 shows the results that Drent et al. have obtained using the phosphine sulfonated ligands **1a-c** (entries 1-7). Activities were best with ligand **1a** (entry 1) while the extra insertion of ethene (up to 18%) was highest with the palladium system containing phosphine sulfonated ligand **1c** (entry 7).

Table 2. Pd catalysed non-alternating copolymerisation of CO and ethene[a]

Entry	[P-O]	T (°C)	P_{ethene} (bar)	P_{CO} (bar)	Activity[b] ($gmmol^{-1}h^{-1}$)	Extra insertion of ethene (%)[c]
1	**1a**	110	20	30	190	2.4
2	**1a**	110	30	20	123	7.3
3	**1a**	110	30	10	49	15.2
4	**1a**	100	30	20	86	4.7
5	**1a**	120	30	20	108	11.0
6	**1b**	110	30	20	103	11.9
7	**1c**	110	30	20	108	18.3

[a]Reaction conditions: catalyst, 0.04 mmol $Pd(OAc)_2$, solvent, MeOH. [b]Based on Pd over experiment run time (2.0-2.2 h).[c]Total mol% ethene of copolymer involved in non-alternation, calculated from $^{13}C\{^1H\}$ NMR spectra (measured in 1,1,1,3,3,3-hexafluoropropan-2-ol-C_6D_6).

More recently, Rieger et al. reported the first examples of neutral palladium(II) complexes bearing sulfonated phosphine ligands (**Scheme 16**). Higher activities and higher insertion of extra amounts of ethene (up to 30%) into the copolymeric chain were achieved[43] when compared to the previously reported in *in situ* copolymerisation reactions.[42]



Scheme 16. Neutral Pd(II) complexes bearing sulfonated phosphine ligands used as precatalyst for non alternating CO/ethene copolymerisation

The mechanism of the perfectly alternating copolymerisation of carbon monoxide and ethene by palladium(II) catalysts based on diphosphine ligands has been extensively studied and is now well known[5a,5b,5c,5e,9] However, few studies have reported the mechanism for the non-alternating copolymerisation of carbon monoxide and ethene.[42,43,44]

Rieger et al. proposed that this new polymerisation proceeds *via* two intertwined pathways (**Scheme 17**), where the same active species may switch between the production of alternating and non-alternating blocks in the same polymer chain.[43] This mechanism is based on a stereoelectronic destabilisation of the neutral chelate, which enables ethene to compete with carbon monoxide and to open the five-membered metallacycle, as previously proposed by Drent et al.[42] On the bases of Drent´s report, it was assumed that the neutral nature of the CO-inserted 6-membered chelate could lead to a decarbonylation reaction yielding the five-membered ring complex that could therefore react with ethene to form a seven-membered chelate, which is proposed to open more easily and therefore facilitates the incorporation of further ethene units. Furthermore, increasing of the pressure of ethene at high CO/ethene ratios (1:20) provides higher probability of ethene insertion over carbon monoxide insertion.

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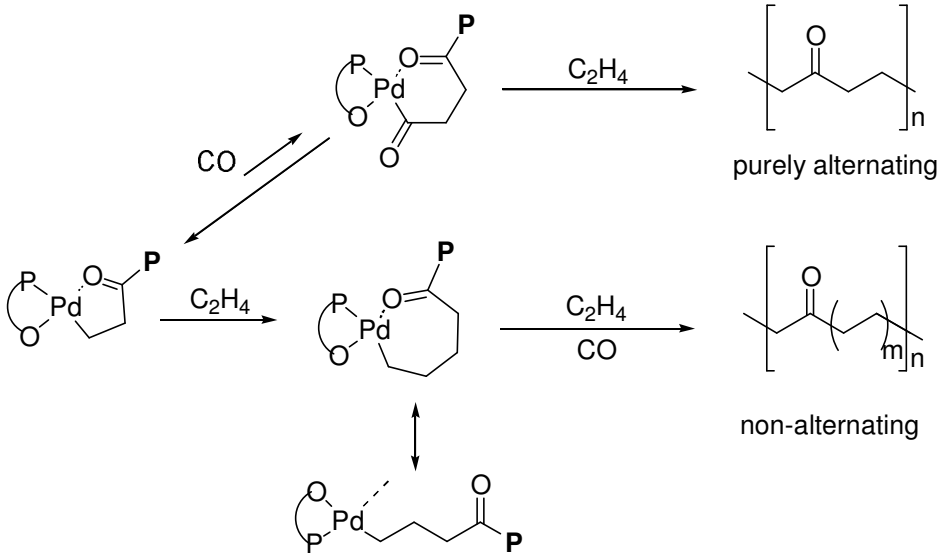
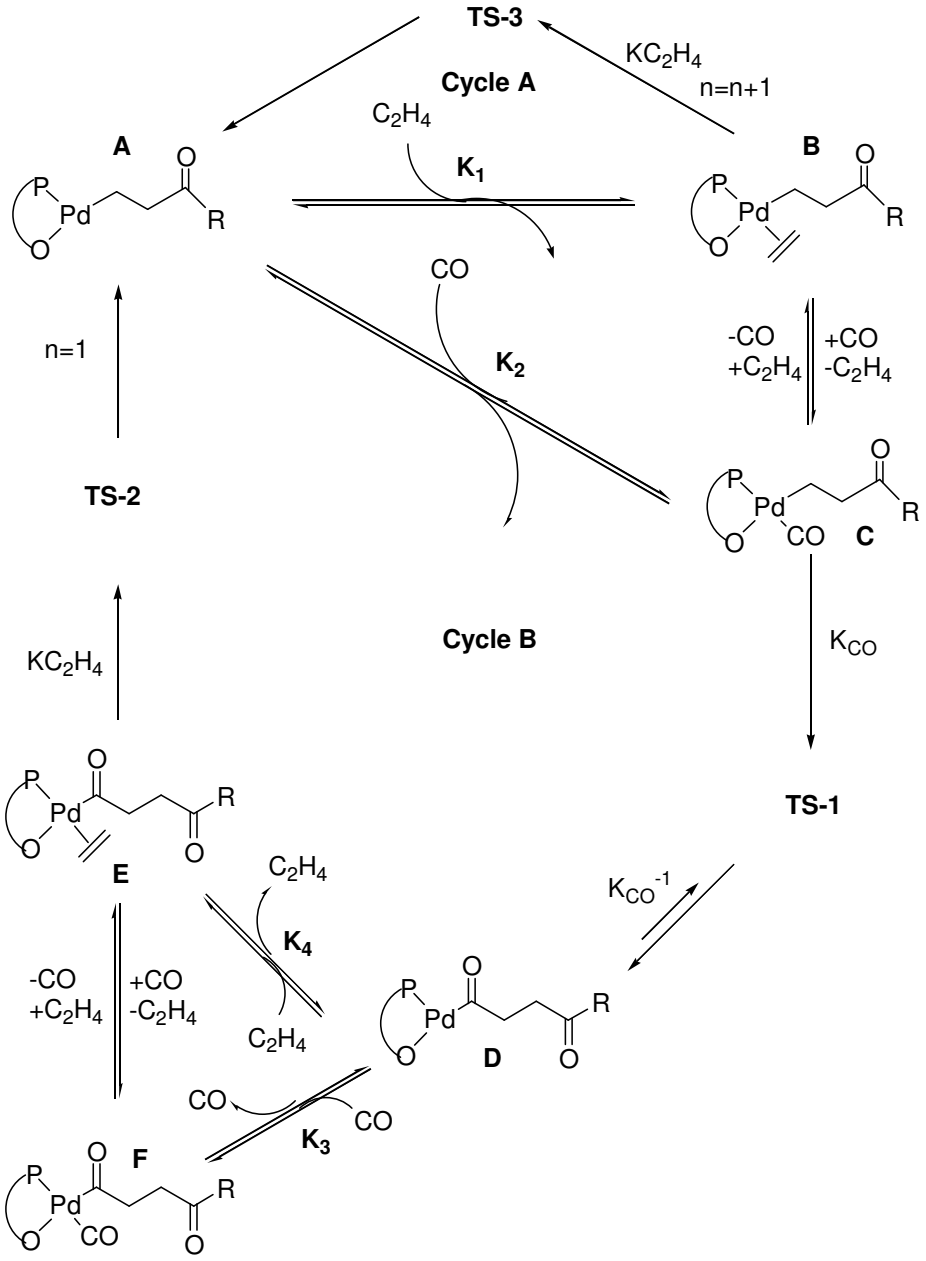


Scheme 17. Mechanism for non-perfectly alternating carbon monoxide and ethene copolymerisation

Ziegler et al. have proposed a mechanism in which they compared catalytic systems containing ligands **1a** and **1c**, previously described by Drent et al., with the catalytic systems containing dppp ligand which produces always perfectly alternating polyketones. They explained the formation of a non-perfectly alternating copolymer in terms of the decarbonylation of the palladium-acyl complexes formed during the catalytic process.[44] The mechanism proposed by Ziegler et al. for the carbon monoxide and ethene non alternating copolymerisation is shown in **Scheme 18**.



Scheme 18. Chain propagation mechanism for the CO/ethene copolymerisation reaction

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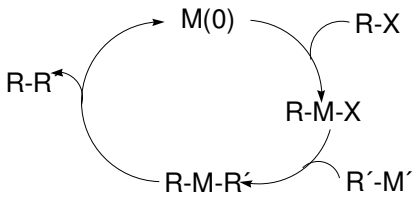
The mechanism involves two main competing cycles: cycle **A** (A → B → TS-3) corresponds to the non alternating and cycle **B** (A → C → TS-1 → D → E → TS-2) to the strictly alternating. Both cycles **A** and **B** start with the formation of carbon monoxide and ethene species with the Pd-alkyl complexes in a pre-equilibrium step (A ←→ B) for cycle **A** and (A ←→ C) for cycle **B**. The next step is that the complexes generated undergo migratory insertion into the Pd-alkyl bond, which leads to the formation of Pd-alkyl species (B → TS-3 → A) for cycle **A** or Pd-acyl complexes (C → TS-1 → D) for cycle **B**. On the basis of theoretical and experimental studies, the ethene insertion is assumed to be irreversible.[45,46] The CO insertion into the Pd-alkyl bond (C → TS-1 → D) was thought to be irreversible. However, recent studies[47] have shown that decarbonylation is also important. The decarbonylation process is shown in **Scheme 18** (D → TS-1 → C). To complete the alternating cycle **B**, the Pd-acyl complex interatcs with both carbon monoxide and ethene, which leads to the formation of Pd acyl carbonyl (D → F) or Pd-acyl-ethene (D → E) species. The Pd-acyl-ethene complex is a precursor specie for the migratory insertion of the ethene molecule into the Pd-acyl bond (E → TS-2 → A), which yields strictly alternating polyketone.[47]

1.4. Suzuki-Miyaura cross-coupling reaction

1.4.1. General aspects

Homogeneous palladium catalysts have acquired enormous importance in such coupling reactions as Heck,[48] Suzuki,[49] Sonogashira[50] and Stille.[51] Many products can be synthesised by this methodology for the first time or in much more efficiently way than before. Palladium catalysts have emerged as extremely powerful tools for the construction of carbon-carbon and carbon-heteroatom bonds.[52] The properties of the palladium catalysts can be modified by changing the ligands. For instance, phosphines, amines, carbenes, dibenzylidenacetone (dba), etc are used to tune the catalysts. Furthermore, subtle modifications in the substitute groups can provide fine tuning of the catalysts.

Ligand design provides catalysts that tolerate weak leaving groups, have high TON and reaction rates and improve lifetimes. Appropriate ligands make it possible to carry out reactions in water and at room temperature. **Scheme 19** shows a general catalytic cycle for cross-coupling of organic halides and organometallics.



Scheme 19. Catalytic cycle for cross-coupling of organic halides and organometallics

Of the palladium-catalysed cross-coupling reactions, the Suzuki-Miyaura cross-coupling reaction is one of the most versatile and widely used reactions for the

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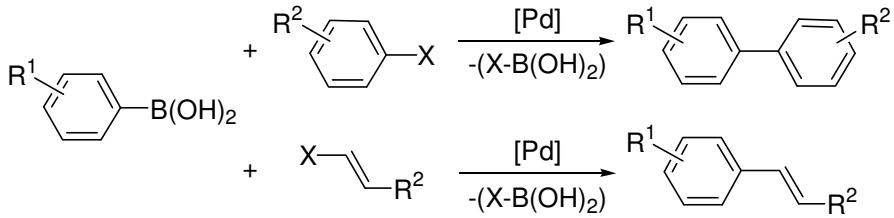
selective construction of C-C bonds, and in particular for the formation of unsymmetrical biaryls. Since this reaction has been used in numerous synthetic processes[53] and it has been applied industrially to the production of compounds such as losartan, a Merck antihypertensive drug,[54] developments to improve the conditions for the Suzuki-Miyaura reaction have received much attention. Indeed, in the last 10 years, over 700 publications have been published in the area of aryl-aryl bond formation. This reaction has gained prominence in the last few years because the conditions developed for the Suzuki reaction have many desirable features for large-scale synthesis and are amenable to industrial synthesis of pharmaceuticals and fine chemicals.

Suzuki-Miyaura cross-coupling reactions generally use organic solvents such as THF and diethyl ether in the presence of Pd(II) or Pd(0) catalyst which are soluble in these solvents. This reaction comprises the coupling of aryl- or vinyl-halides with arylboronic acids (**Scheme 20)**.

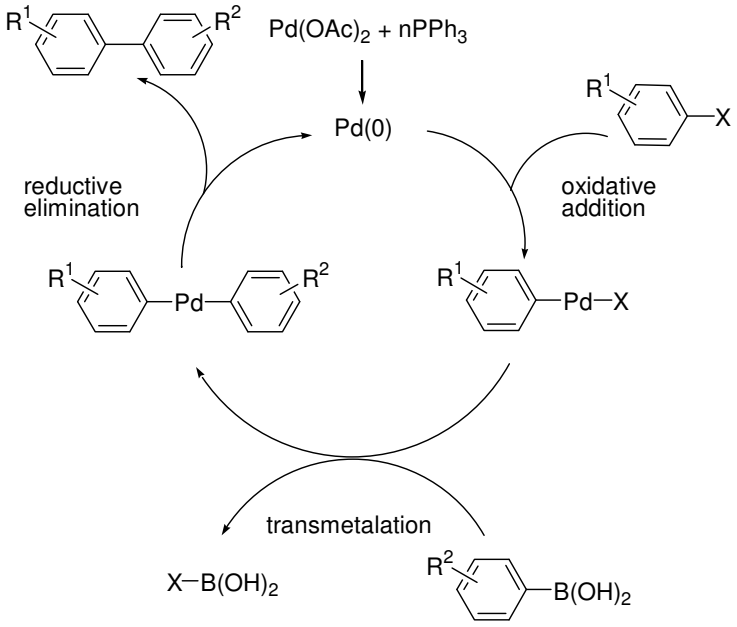


Scheme 20. Suzuki-Miyaura reaction of aryl- or vinyl-halides with arylboronic acids

This reaction is popular because of a variety of factors: a large number of boronic acids are commercially available, they are non toxic, they are stable to heat, air, and moisture. Furthermore, the boron-containing by-product of the Suzuki-Miyaura cross-coupling reaction can be easily separated from the desired product of the reaction.

1.4.2. Mechanism of the S-M cross-coupling reaction

The classical catalytic cycle described for both Heck and Suzuki reactions in most organic chemistry textbooks involves an homogeneous palladium catalyst that cycles between the Pd(0) and Pd(II) oxidation states during the course of the catalytic reaction. Normally, a Pd(II) precatalyst is used for this reaction, the catalytic cycle stars with the *in situ* reduction of the Pd(II) precatalyst to Pd(0), followied by the oxidative addition of the aryl halide to form a palladium(II) intermediate as shown in **Scheme 21**. Then the transmetallation from the arylboronic acid takes place. The last step is the reductive elimination to yield the biaryl product and the Pd(0) specie, which stars the cycle again.



Scheme 21. Typical mechanism for S-M cross-coupling reaction

Unlike other cross-coupling reactions involving the transmetallation step, the Suzuki-Miyaura reaction requires the use of a base for this transmetallation

step. The role of the base is to form a more electron-rich intermediate with the boronic acid resulting more reactive than the original boronic acid towards attack of the palladium(II) complexes making easier the transmetallation step. Normally, mineral bases such as alkali metal carbonates are used. The use of water either as a solvent or additive helps with the solvation of these organic-insoluble materials.

The possibility that palladium(IV) species were involved as intermediates was considered[55] but seems to be unlikely in the light of later results.[56] Each of the steps in the catalytic cycle can be rate-determining, depending on the type of substrate and catalyst.

Mechanistic studies published by Fu and co-workers in 2002 showed that the Pd:P ratio played a major role in the catalytic performance of the complexes formed *in situ*.[57] Whereas activity was high at a Pd:P ratio of 1:1 or 1:1.5, a ratio of 1:2, gave only lethargic reactions. In NMR studies, the only identified species observed at a Pd:P ratio of 2:1 to 1: 1.5 was the species containing two phosphines, $Pd[P(t\text{-}Bu)_3]_2$ In a further NMR studies of the reaction between an aryl chloride and a boronic acid at a Pd:P ratio of 1:1, the only species observed was $Pd[P(t\text{-}Bu)_3]_2$. Since the Pd:P ratio was 1:1, this suggested that half of the Pd contained two ligands and the other half contained no phosphine ligand. As the complex containing two phosphine ligands did not seem to be active under the condition used, the authors concluded that small amounts of the palladium-monophosphine adduct may represent the true catalytic species.[57]

Recently, a mechanistic study on Suzuki cross-coupling reaction has been reported by J. M. Brown et al. In their report they compared aryl bromides with ary trifaltes as substrates for the Suzuki reaction, and observe a different behavior in the catalytic cycle. Their observations showed that the Suzuki

coupling reaction was out of line with all other common cross-coupling reactions when aryl triflates derivates are used.[58]

1.4.3. Palladium catalytic systems in Suzuki-Miyaura cross-coupling reaction

Palladium catalysts containing phosphorous ligands

The triphenyphosphine ligand was one of the first ligands to be used for the earliest catalytic precursors in Suzuki and Heck cross-coupling reactions.[59] Indeed, this pre-catalyst with triphenylphosphine as the ligand was use in most coupling protocols until the mid 1990's despite the fact that other ligands such as tri(*o*-tolyl)phosphine gave better results.[60] Nowadays these well-known pre-catalysts are still being studied and basic trends such as the effect of the solvent or the palladium:phosphorous ratio are being tested.[61]

In 1997 Shen showed that aryl chlorides could be activated in Suzuki reaction by using $P(Cy)_3$, (tricyclohexylphosphine) and dppb, (diphenylphosphinobutane) as phosphorous ligands.[62] Interestingly, the activity of phosphorous ligands that are sterically and electronically similar to $P(Cy)_3$, namely tricyclopentylphosphine and triisopropylphosphine were found to be poor in the Suzuki-Miyaura reaction of alkyl chlorides.[63]

Although, it had been shown that bulky ligands facilitate cross-coupling reactions,[64] the use of bulky diphosphine ligand in the Suzuki reaction was not widespread until the late 1990's when numerous authors including van Leeuwen, Beller, Buchwald, Fu and others published accounts of bulky, monodentate phosphine ligands as effective components for palladium Suzuki-Miyaura and Heck coupling catalysts.[65] The use of a bulky trialkylphosphine P(*t*-

$Bu)_3$ as ligand in the Pd-catalysed Suzuki coupling reaction of a great number of aryl halides was described by Fu and co-workers.[66]

In 1990 Buchwald reported a very important class of monodentate, bulky phosphines based on functionalised biphenyls (ligands **1**-**4**) (**Figure 16**).[67] These ligands combined *in situ* with a palladium source proved to be effective catalysts for a variety of cross-coupling reactions. The outstanding catalytic performance of these ligands in conjunction with a palladium source has been attributed to a combination of both electronic properties, which facilitates the oxidative addition, and steric hindrance, which favours the reductive elimination steps in the catalytic cycle.[68] Other authors have suggested that biphenyl-based phosphines can contribute to the stabilization of the Pd(0) intermediates though the formation of π interactions with the aryl ring.[17,69] Detailed proof of this was given in a later study with ligand **6**, SPhos by Buchwald et al..[70]

The bulky monodentate phosphine ligand **7**, diadamantyl-*n*-butyl phosphine was used in 2000 by Beller et al. for the Suzuki-Miyaura coupling of aryl chlorides.[71] Later they describe monophosphine-Pd(0) complexes based on other bulky ligands and they used them as pre-catalysts in Suzuki-Miyaura coupling reactions.[72]

Beller et al. also described N-arylpyrroles (ligand **8**) and N-aryl-2-(dialkylphosphino)imidazoles (ligand **9**) as effective ligands for activating aryl chlorides in the Suzuki coupling reaction.[73]

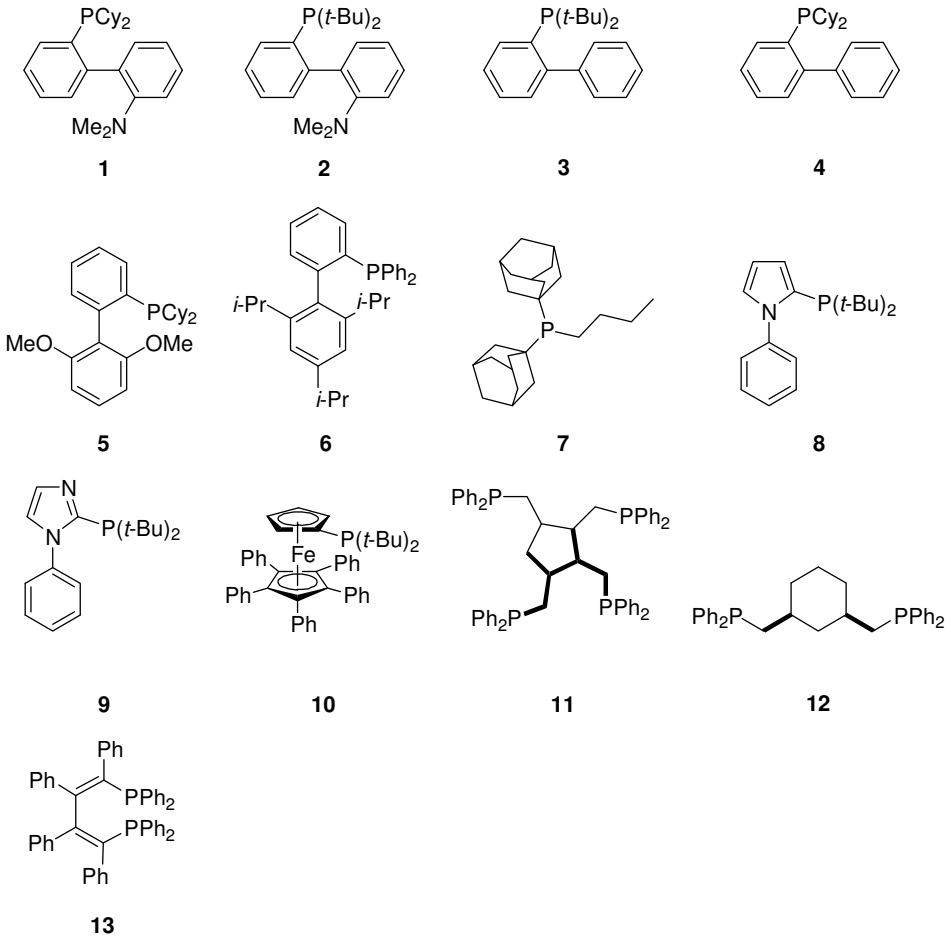


Figure 16. A variety of monodetante, bidentate, and tetradentate phosphine ligands used in palladium-catalysed Heck and Suzuki coupling reactions

Several groups have reported the use of ferrocene-based ligands for instance, Fu et al. reported a bulky, ferrocene-based triarylphosphine, ligand **10** that proved to be active in Suzuki coupling of aryl chlorides.[74]

A variety of ligands containing P-O bonds have been successfully tested in Heck and Suzuki coupling reactions. Indeed, palladium(II)-phosphate

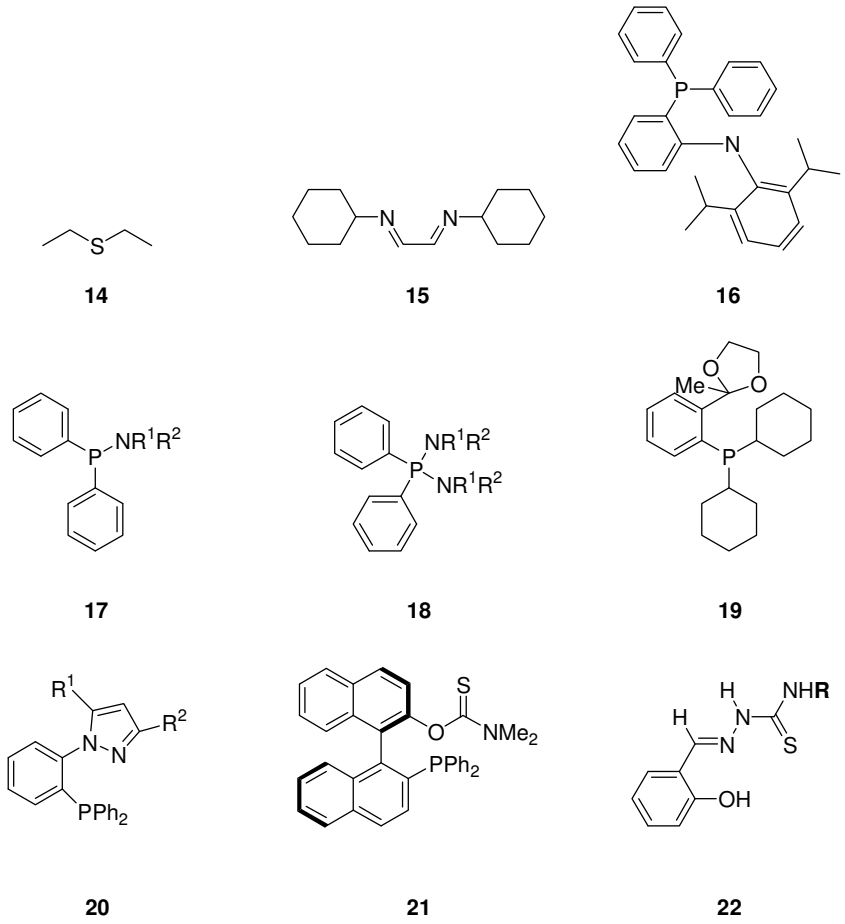
complexes and phosphates were found to be excellent complexes and ligands for the Suzuki coupling of aryl chlorides and bromides. [75]

Doucet and Santelli showed that tetradentate phosphine ligand, **11** was able to activate aryl chlorides or bromides in the Suzuki coupling reaction.[76] Diphosphine ligand, **12** was reported by Anderson et al. and seemed to give stable palladium catalysts for Suzuki couplings.[77] Bidentate ligand NUPHOS, **13** was also shown to be useful in Suzuki couplings of bromoarenes with phenylboronic acid.[78]

Palladium catalytic systems containing non-phosphorous or mixed phosphorous ligands

Although the most commonly studied ligands are phosphorous-based, recently interest in the use of ligands with other donor atoms has increased (**Figure 17**). Dupont et al. have reported that palladium complexes with thioether donor ligands, **14** lead effective palladium precursors in Suzuki coupling reaction.[79]

Nolan et al. reported excellent results for the coupling reaction of various aryl bromides and activated aryl chlorides with arylboronic acids using palladium (II) complexes of bidentate diazabutadiene (DAB) ligands, **15**.[80] Liang et al. showed that for amido-phosphine P-N ligand, **16** the palladium complexes of which were extremely stables in the Suzuki coupling reactions, palladium black did no form during the catalytic process.[81] A wide variety of amino-phosphine ligands, **17** and **18**, also proved to be highly effective in Suzuki reactions under mild conditions.[82]



14 **15** **16**

17 **18** **19**

20 **21** **22**

Figure 17. A variety of monodentate, bidentate, and tridentate with non-phosphorous or mixed phosphorous ligands used in conjunction with palladium source in Suzuki coupling reactions

Chelating P-O ligand, **19** has also been used in the Suzuki reaction of both aryl chlorides and bromides. The reason for the excellent catalytic properties of the palladium complexes containing ligand **19** can be ascribed to both the overall structure ligand and the presence of the "PCy_2" unit. The rigid backbone favours the generation and stability of the chelating (P-O)-Pd intermediates which

appear to be most suitable for catalysis,[83] while the "PCy_2" unit makes the Pd center sufficiently electron-rich to promote oxidative addition of the usually unreactive aryl chlorides.[84]

Welton en al. reported the use of some commercially available imidazoles ligands for the Suzuki reaction, although in almost all cases catalyst decomposition was observed.[85] Sarkar et al. described the use of pyrazole-tethered arylphosphine, **20** as ligands for the Suzuki coupling of aryl chlorides, suggesting that palladium chelation could play an important role in stabilizing the catalyst. It has been suggested that the steric crowding in the metal complex would increase the catalytic activity of such complexes.[86]

Binaphthyl-based P-S bidentate ligand, **21** was used by Shi et al. as an effective promoter in the palladium(0)-catalysed Suzuki cross-coupling of aryl bromides and Iodides.[87] Kostas et al. used palladium complexes with thiosemicarbazone ligands, **22** for the first time as precatalysts in the Suzuki coupling reaction of aryl bromides and chlorides.[88]

1.4.4. Suzuki-Miyaura cross-coupling reaction in aqueous media

Due to the high solubility of arylboronic acids in water and the low toxicity of both reagents and by-products compared to other reactions.[89,90] It is particulary interesting to perform the Suzuki coupling reaction in water. The fact that organoboron compounds are quite stable to protolytic decomposition by water means that methodologies using water or aqueous media as solvents have considerable potential. When neat water is used as a solvent, the reactions can be performed using simple palladium salts such as $PdCl_2$ or $Pd(OAc)_2$ in air.

Several reports have appeared in recent years on water soluble Pd-systems.[91,92] Beletskaya et al. proved that the reaction of arylboronic acids with

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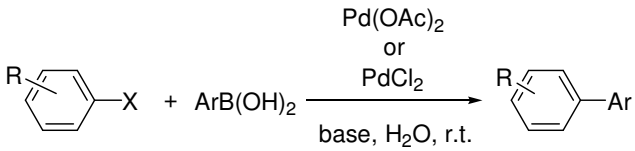
water-soluble aryl halides can be performed at room temperature in the presence of a palladium salt and an inorganic base (**Scheme 22**).[93]



X = I, Br
R = *m*-, *p*-OH, *o*-, *m*-, *p*-COOH

Scheme 22. Suzuki-Miyaura cross-coupling reaction performed in water

Water soluble phosphines have been used as ligands for Suzuki-Miyaura reactions in aqueous media (**Figure 18**).[94] One of the best known phosphine for its application in water is tri-(3-sulfonatophenyl)phosphine, **23** (TPPTS). The Suzuki coupling of unactivated aryl bromides has been reported using high catalyst loadings of Pd/TPPTS in the aqueous phase but modest activity was achieved.[91a]

The related tri(4,6-dimethyl-3-sulfonatophenyl) phosphine trisodium **24** (TXPTS) and tri(4-methoxy-6-methyl-3-sulfonatophenyl) phosphine trisodium salt **25** (TMAPTS) provide active catalysts for Suzuki couplings in aqueous media of aryl bromides at 50°C.[91b] Water-soluble phosphines TPPTS (**23**) and TXPTS (**24**) in combination with $Pd(OAc)_2$ have also been applied for the efficient synthesis of aryl-modified nucleosides, which can be obtained in a single step and without protecting the halogenated nucleoside.[91c]

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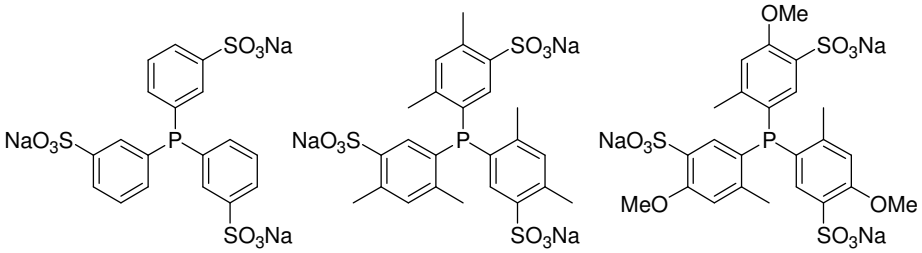
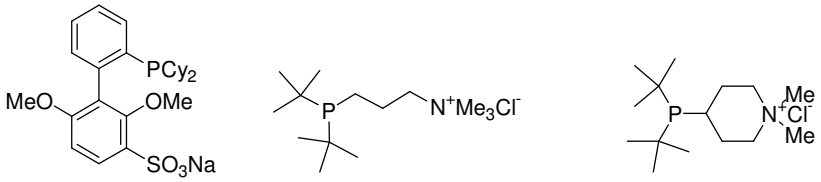


23 **24** **25**



26 **27** **28**

Figure 18. Some phosphine water-soluble ligands used recently in the Suzuki-Miyaura reaction performed in aqueous or neat water media

Buchwald et al. have recently reported the application of an electron-rich sulfonate ligand **26** with excellent yields and wide scope for the Suzuki coupling of highly functionalised aryl chlorides or heterocyclic chlorides/bromides and aryl or alkyl boronic acids in aqueous media.[91d]

Shaughnessy and Booth[95] prepared two sterically demanding, water-soluble alkylphosphines **27** and **28**, which produce highly active palladium catalysts for Suzuki-Miyaura couplings of aryl bromides or chlorides with arylboronic acids in aqueous solvents. They also found that the more sterically demanding ligand **28** lead catalysts with higher activity toward aryl chlorides than the catalysts obtained with ligand **27.**

Other systems containing water-soluble Pd ligand-free systems or ligands other than sulfonated phosphines ones:[92] for instance, the catalytic system formed by

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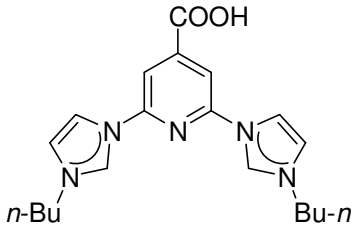
$Pd(OAc)_2$/DABCO with PEG-400 as the phase-transfer catalyst,[92c] $Pd(OAc)_2$/PEG-2000/H_2O under ligand-free conditions[92d] or amphiphilic water-soluble diblock copolymers based on 2-oxazoline derivatives with pendant N-heterocyclic carbene/palladium catalysts.[92b]

Recently, SanMartín et al. reported a palladium catalyst with a CNC pincer ligand **29** (**Figure 19**) that is soluble in water due to the *p*-carboxy group of the ligand. This system provides high turnover frequencies combined with effective catalyst reuse.[92d]



29

Figure 19. CNC pincer water-soluble ligand prepared by R. SanMartín et al.

1.4.5. Microwave techniques as a tool for synthetic chemistry

Microwave-promoted synthesis is an area of increasing interest in both academic and industrial laboratories; it provides a very efficient way of heating reaction mixtures. In 1986 the first reports of microwave-heating in organic synthesis appeared in the literature.[96]

Microwave-promoted chemistry is founded on the fact that materials can absorb microwave energy and convert it to heat.[97] It is possible to control the temperature, the microwave power and the reaction time very easily and perform reactions reproducibly. The concept of efficient and selective synthesis in water has been exemplified as the rates, yields and selectivity observed for

may reactions in water have begun to match or in many cases, surpass those in organic solvents.[98]

The effect of microwave irradiation has not yet been fully elucidated; however, it is significant that many metal-catalysed reactions are completed within a few minutes. Since polar solvents efficiently absorb microwaves, reactions have been carried out in water, ethylene glycol of DMF. The use of microwaves was first reported in 1996 for both homogeneous[99] and solid-phase coupling reactions of arylboronic acids.[100] Microwave irradiation significantly increases the efficiency of ligandless palladium acetate.

Water as solvent offers practical advantages over organic solvents, it is readily available, cheap, non-toxic and non-flammable. It also provides a medium for solution chemistry but also often takes part in elementary chemical events on a molecular scale. As well as water is used for chemistry at ambient pressure there has been increasing interest in high-temperature water,[101] superheated water[102] and supercritical water.[103]

Because of its properties, water is an excellent solvent for microwave-promoted synthesis. For the Suzuki reaction, the solubility in water of arylboronic acids provides an interesting possibility to perform this coupling reaction in aqueous media under microwave conditions.

1.5. Scope and objectives of the thesis

The interest in the palladium(II)-catalysed copolymerisation reaction of carbon monoxide and ethene as well as other reactions involving the formation of the C-C bond is increasing because of the possibilities of application in synthesis of new products and materials. This interest is reflected in the large number of reports published in recent years

Since catalyst degradation to inactive species, is the major cause of the low productivity, considerable research effort is being made to design diphosphine ligands that can prevent them from degrading. Many papers have shown that the introduction of an *o*-methoxy substituent on the P-aryl rings of the diphosphine enhances the productivity in comparison with the unsubstituted ligands. It has been suggested that both steric and electronic factors are responsible for the positive effect of the *o*-methoxy groups on catalyst activity.

This thesis focuses on elucidating the effect of the *o*-methoxy group introduced on the P-aryl rings of the diphosphine ligands in the copolymerization reaction of carbon monoxide and ethene from a catalytic and a mechanistic point of view.

In the second part, the thesis focuses on the synthesis of new phosphine sulfonated ligands for the less well known reaction of non-alternating copolymerisation of CO and ethene and the applications of the later ligands in the Suzuki-Miyaura cross-coupling reaction in aqueous media.

To achieve these objectives, new ligands and neutral, cationic as well as anionic palladium complexes have been synthesised. New alternative synthetic protocols have been developed to: 1) introduce the –OMe group on the P-aryl

rings of known and new diphosphine ligands, 2) synthesise new phosphine sulfonated ligands.

Catalytic reactions are carried out in different media as well as high pressure NMR experiments in an attempt to better understand the beneficial effect of *o*-methoxy groups and the less well known mechanism of the non-alternating copolymerisation of CO and ethene.

Chapter 1 covers the basic literature and most recent development in the alternating copolymerisation of carbon monoxide and ethene, non-alternating copolymerisation of carbon monoxide and ethene and Suzuki-Miyaura cross-coupling reaction.

Chapter 2 discusses the effect of the *o*-methoxy group on the alternating copolymerisation reaction of carbon monoxide and ethene. Diphosphine ligands 1,2-bis(di(2-methoxyphenyl)phosphino)ethane,1,3-bis(di(2-methoxyphenyl)phosphino)propane are synthesised by an alternative synthetic protocol. Both ligands and their phenyl counterparts for comparative purpose, are used to synthesise neutral and cationic palladium(II) complexes. The complexes are used to catalyse the CO-ethene copolymerisation reaction in either protic or aprotic solvents. *In situ* and *operando* high-pressure NMR experiments provide valuable information on catalysis resting states and intermediates. In addition, important steps in the CO/ethene copolymerisation reaction are studied by *in situ* high-pressure NMR spectroscopy, which helps rationalise the effect of the *o*-methoxy group.

In *Chapter 3*, the new diphosphine (*o*-MeO-bdpp) *rac*-2,4-bis(di(2-methoxyphenyl)phosphino)pentane is synthesised. This ligand is used to synthesise new neutral palladium(II) complexes. The ligand and complexes are fully characterised in solution by multinuclear NMR spectroscopy. This C_2-

bridged ligand is compared with the C_3-bridged ligand and the more rigid ligand bis-cationic diphosphonium-diphosphine 6,7-di(di-2-methoxyphenyl)phosphinyl-2,2,4,4-tetra(di-2-methoxyphenyl)-2λ^4,4λ^4-diphosphoniumbicyclo[3.1.1]heptane-bis(PF_6) (*o*-MeO-PCP)(PF_6)$_2$) in the copolymerisation of CO with ethene in different reaction media in order to compare the effect of backbone rigidity.

Chaper 4 deals with the synthesis of new phosphine sulfonated ligands. The ligands are prepared through a new and sustainable synthetic route and used to synthesise new palladium(II) anionic complexes. The later anionic complexes are used in the less well known non-alternating copolymerisation reaction of carbon monoxide and ethene and compared with other phosphine sulfonate ligands that have been applied in this kind of catalysis. In addition, high pressure NMR experiments are carried out in order to go further into the mechanism of this polymerisation reaction.

Furthermore, taking advantage of the fact that the new phosphine sulfonated ligands are both water-soluble and air stable, they are successfully applied in palladium-catalysed Suzuki-Miyaura cross-coupling reactions in neat water in conjunction with microwave heating.

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1.6. References

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UNIVERSITAT ROVIRA I VIRGILI
PALLADIUM COMPLEXES CONTAINING DIPHOSPHINE AND SULFONATED PHOSPHINE LIGANDS FOR C-C BOND FORMING REACTIONS. CATALYTIC AND MECHANISTIC STUDIES
Eduardo José García Suárez
ISBN:978-84-691-0369-2/DL: T.2187-2007

The *o*-methoxy groups on the P-aryl rings effect in the carbon monoxide and ethene copolymerisation reaction by palladium(II)-diphosphine catalysts. A catalytic study in different reaction media

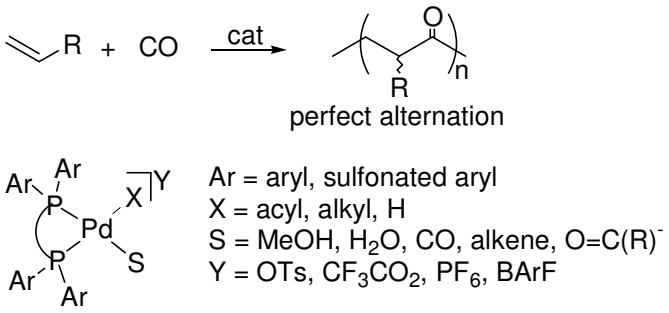
Abstract

Neutral and bis-cationic palladium(II) complexes with 1,2-bis(di(2-methoxyphenyl)phosphino)ethane (*o*-MeO-dppe) and 1,3-bis(di(2-methoxyphenyl)phosphino)propane (*o*-MeO-dppp) have been synthesised and employed to catalyse the CO-ethene copolymerisation reaction in either protic or aprotic solvents. A comparison of the catalytic performance of these complexes with that of analogous precursors stabilised by 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) ligands have shown significant differences in terms of catalytic productivity and molecular weight. *In situ* and *operando* high-pressure NMR experiments have provided valuable information on catalysis resting states and intermediates and have contributed to rationalise the observed productivity as well.

2.1.1. Introduction

As previous mentioned in *chapter 1*, polyketones are a family of high-performance thermoplastics featured by excellent resistance to solvents as well as good mechanical properties. Unlike many other engineering plastics, perfectly alternating polyketones such as Shell's Carilon are relatively easy to synthesise and are derived from inexpensive monomers such as ethene and CO.[1] A small fraction of the ethene can be replaced with propene to reduce the melting point and improve the stability and rheology of the materials. Low molecular weight Carilon is known with the name Carilite and is currently used as wood-binding adhesive.[2]

Polyketones (alt-ethene-CO) are made with palladium(II) catalysts modified with chelating diphosphines bearing various substituents on the phosphorus aryl rings (**Scheme 1**). Either protic (alcohols, preferentially methanol) or aprotic (toluene, dichloromethane, THF (tetrahydrofurane)) solvents can be used depending on the structure of the metal precursors that can generate the catalysts by a number of pathways. Sulfonation of the aryl rings is a common procedure to have water soluble catalysts.



Scheme 1. Copolymerisation reaction with palladium(II)(P-P) complexes

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A major drawback to the large scale commercialisation of alt-ethene-CO materials is provided by the low catalytic productivity which seldom exceeds 20-30 kg polyketone (g Pd x h)$^{-1}$. The productivity is particularly low for low molecular weight materials such as Carilite. Studies aimed at improving the performance of the palladium catalysts are therefore under way in many laboratories. Since catalyst degradation to inactive species, including black palladium, is the major cause of the low productivity, much research efforts are being directed to design both diphosphine ligands and reaction media capable of stabilising mononuclear palladium(II) under the copolymerisation conditions.

It is now established that the introduction of an *ortho*-methoxy substituent on the P-aryl rings of the diphosphine greatly enhances the productivity as compared to the unsubstituted ligands.[3] Two such ligands are shown in **Figure 1** together with their unsubstituted counterparts.

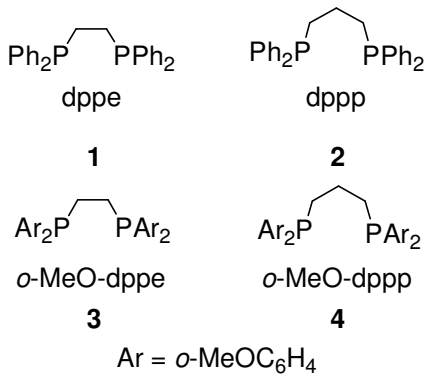

Figure 1

Both steric and electronic factors have been proposed to be responsible for the positive effect of the *ortho*-methoxy groups on catalyst activity: lower tendency to form inactive bis-chelates and dimers, reduced tendency to phosphine oxidation,[4a] a increased basicity of the metal center,[4b] reduced stability of relevant catalyst resting states such as β-keto alkyl chelates.[4c]

Besides the P-aryl substituents, the productivity of palladium(II) copolymerisation catalysts is affected remarkably by the reaction media as well as by added co-reagents. The latter include protic acid and organic oxidants,[1] while protic solvents such as alcohols and water are much better media than aprotic organic solvents. As a matter of fact, the highest productivities of both Carilon and Carilite have been obtained in water in the presence of added protic acid by means of water-soluble diphosphines bearing *o*-methoxy groups.[2]

Despite the undoubted qualities of *o*-methoxy substituted diphosphines and the many papers assessing these qualities, we are not aware of a study where such ligands are employed, in conjunction with palladium(II) salts, to copolymerise ethene and CO in reaction media other than MeOH or water.

In this chapter, we report a new synthetic protocol for the synthesis of 1,2-bis(di(2-methoxyphenyl)phosphino)ethane (*o*-MeO-dppe) (**3**) (**Figure 1**) and 1,3-bis(di(2-methoxyphenyl)phosphino)propane (*o*-MeO-dppp) (**4**) (**Figure 1**) the synthesis and characterisation of various palladium(II) neutral and cationic catalyst precursors and their use to catalyse the CO/C_2H_4 copolymerisation in different solvents such as MeOH, 2,2,2-Trifluoroethanol (TFE), water-AcOH (acetic acid) mixtures, CH_2Cl_2, and toluene. For comparative purposes all catalytic reactions have also been performed with the classical ligands 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(diphenylphosphino)propane (dppp).

In situ and *operando* high-pressure NMR experiments carried out on selected reactions have provided valuable information on catalysis resting states and intermediates as well as have contributed to rationalise the observed productivity.

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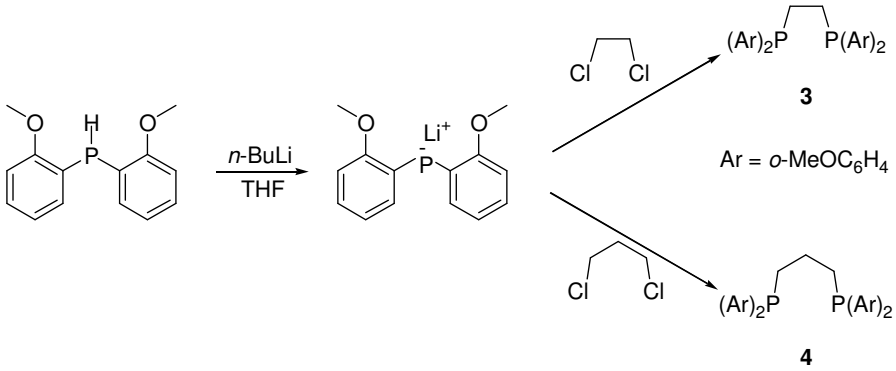
2.1.2. Results and discussion

Synthesis of ligands and complexes

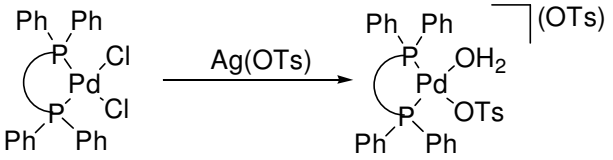
The known diphosphines *o*-MeO-dppe[5a,5b] and *o*-MeO-dppp[5c] were synthesised by a new synthetic route, illustrated in **Scheme 2**, which is simpler and more efficient as compared with the procedures reported in the literature.



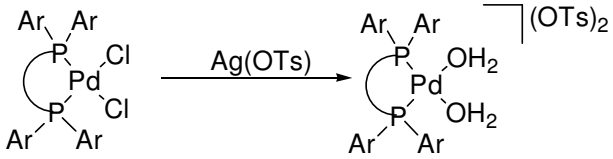
Scheme 2. New synthetic route for the synthesis of *o*-MeO-dppe and *o*-MeO-dppp

The new synthetic protocol involves the deprotonation of the stable and isolable secondary phosphine bis(2-methoxyphenyl)phosphine[6a] with *n*-BuLi in THF, followed by addition of the corresponding dichloride reagent. Both ligands were isolated as microcrystalline solids in good yields (78% *o*-MeO-dppe; 68% *o*-MeO-dppp). The reaction of either ligand with $PdCl_2(COD)$ in CH_2Cl_2 gave the complexes $PdCl_2$(*o*-MeO-dppe) (**3a**) and $PdCl_2$(*o*-MeO-dppp) (**4a**) as yellow crystalline compounds, which were characterised in solution by multinuclear NMR spectroscopy and in the solid state by single crystal X-ray structure analyses.

The reaction of **3a** or **4a** with AgOTs led to the formation of the bis-cationic tosylate derivatives $[Pd(H_2O)_2(o\text{-MeO-dppe})](OTs)_2$ (**3b**) and $[Pd(H_2O)_2(o\text{-MeO-dppp})](OTs)_2$ (**4b**) (**Scheme 3**). The authentication of these complexes was achieved in solution by multinuclear NMR spectroscopy where both complexes behave as 1:2 electrolytes (conductivity measurements in nitroethane). Notably, the known and isostructural compounds $[Pd(OTs)(H_2O)(dppe)]OTs$ (**1b**) and $[Pd(OTs)(H_2O)(dppp)]OTs$ (**2b**) (**Scheme 3**) behave as 1:1 electrolytes in the same solvent, which is consistent with the coordination of a tosylate ion to palladium.



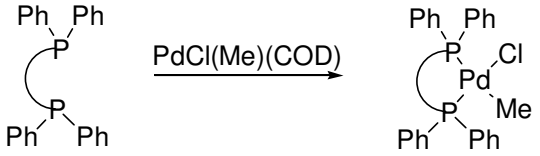
1a, 2a **1b, 2b**



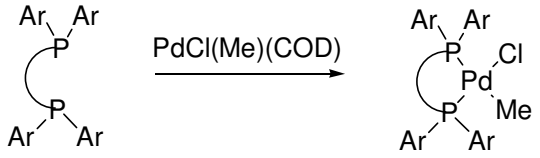
3a, 4a Ar = *o*- $MeOC_6H_4$ **3b, 4b**

Scheme 3

The neutral complexes PdCl(Me)(P-P) (P-P = *o*-MeO-dppe, **3c**; *o*-MeO-dppp, **4c**) were prepared by reaction of the appropriate ligand with PdCl(Me)(COD) in CH_2Cl_2 in good yield (78%, **3c**; 68%, **4c**) (**Scheme 4**).



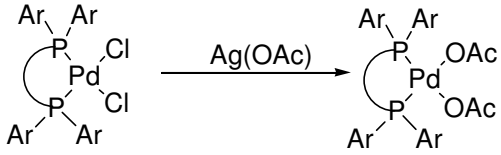
1c, 2c



Ar = *o*-$MeOC_6H_4$ **3c, 4c**

Scheme 4

The reaction of complexes **3a** and **4a** with Ag(OAc) in dichloromethane brought about the formation of the neutral palladium(II)-acetate complexes **3d** or **4d**, which were isolated as yellow microcrystalline compounds in good yield (62%, **3d**; 71%, **4d**) (**Scheme 5**). Both latter complexes were characterised in solution by multinuclear NMR spectroscopy and in the solid state by single crystal X-ray structure analyses.



3a, 4a Ar =*o*- $MeOC_6H_4$ **3d, 4d**

Scheme 5

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Crystal structure determination of 3a·2.3 CH_2Cl_2, 4a, 3d and 4d

Single crystals of **3a**·2.3 CH_2Cl_2 and **4a** were obtained by slow diffusion of *n*-hexane into CH_2Cl_2 solutions of **3a** and **4a**, while suitable single crystals of compounds **3d** and **4d** were obtained by a slow diffusion of toluene into a dichloromethane solution of the corresponding compounds. Crystallographic details for **3a**·2.3 CH_2Cl_2, **4a** are reported in **Table 1**, while those for **3d** and **4d** are shown in **Table 3**. Selected bond distances and angles are reported for the Pd-dichloride complexes in **Table 2** and for the Pd-acetate complexes in **Table 4**. An ORTEP drawing of **3a**·2.3 CH_2Cl_2, **4a**, **3d** and **4d** is shown in **Figures 2**, **3**, **4** and **5**, respectively.

Table 1. Summary of crystallographic data

Compound	**3a**·2.3 CH_2Cl_2	**4a**
Empirical formula	$C_{32.20}H_{36.60}Cl_{6.60}O_4P_2Pd$	$C_{31}H_{34}Cl_2O_4P_2Pd$
Formula weight	891.13	709.82
Temperature (K)	203(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	*C2/c*	*Pcca*
a (Å)	19.386(5)	23.432(5)
b (Å)	12.616(5)	9.059(2)
c (Å)	16.485(5)	14.876(5)
α °	90.00	90.00
β °	97.655(5)	90.00
γ °	90.00	90.00
Volume ($Å^3$)	3996(2)	3157.7(14)
Z	4	4
ρ_{calc} (gcm^{-3})	1.481	1.493
μ(Mo Kα) (mm^{-1})	1.019	0.892
Diffractometer radiation (Å)	$\lambda(Mo_{K\alpha})$= 0.71069	
F(000)	1802.4	1448
Crystal size (mm)	0.22 × 0.05 × 0.02	0.25 × 0.20 × 0.18
Θ range (°)	4.10-25.00	2.77-25.00

	-23<=*h*<=23	0<=*h*<=27
Index ranges	14<=*k*<=14	0<=*k*<=10
	19<=*l* = 19	0 <= *l* <= 17
Reflections collected	3464	2759
Independent reflections	2912	2759
Refined parameters	212	186
R1 (2σ(*I*))	0.0688	0.0274
R1 (all data)	0.0875	0.0384
wR2 (all data)	0.1518	0.0789
Goodness-of-fit on F^2	1.167	1.015
Largest diff.peak and hole ($eÅ^{-3}$)	1.005/-0.834	0.414/-0.480

The crystal structure of **3a**·2.3 CH_2Cl_2 shows half molecule of **3a** and 1.15 molecules of disordered CH_2Cl_2 per asymmetric unit. The palladium centre is square planar coordinated with *cis* phosphorus atoms.

Table 2. Selected bond lengths (Å), bond angles (°), and intramolecular Pd-O and Pd-H distances (Å)

Complex	**3a** 2.3 CH_2Cl_2	**4a**
Pd(1)-P(1)	2.239(2)	2.250(1)
Pd(1)-Cl(1)	2.366(2)	2.362(1)
P(1)-Pd(1)-P(1)#1[a]	86.55(8)	90.09(4)
P(1)-Pd(1)-Cl(1)	174.43(5)	88.88(3)
Cl(1)-Pd(1)-Cl(1)#1[a]	93.00(8)	92.70(4)
Pd(1)…O(1)	5.173(4)	3.435(2)
Pd(1)…O(2)	3.482(4)	5.193(2)
Pd(1)...H(2)	2.877	
Pd(1)...H(9)		2.871

[a] Symmetry transformation used to generate equivalent atoms: -x+1, y, -z+1/2

The Pd-P bond length of 2.239(2) Å and the P-Pd-P bite angle of 86.55(8)° are comparable to the values found for the dppe analogue **1a**.[7] The four *o*-methoxy

oxygen atoms are disposed around the palladium centre in such a way that two of them occupy a *pseudo*-apical position of the metal coordination sphere (Pd…O distance of 3.482(4) Å) while the other two symmetry-related *o*-methoxy oxygen atoms are close to *pseudo*-equatorial positions (Pd…O distance of 5.173(4) Å). However, all of these Pd…O distances are too large to consider an electrostatic interaction between the palladium and the *o*-methoxy groups. In contrast, the *o*-hydrogen atoms of two axial aryl ring groups interact with the palladium centre (Pd(1)...H(2) distance of 2.877 Å). Very similar structure features were already observed for the related complex NiI_2(*o*-MeO-dppe).[4a]

The asymmetric unit of **4a** contains half molecule and the coordination geometry about the palladium centre is square planar. The P-Pd-P angle of 90.09(4)° is comparable to that found for the related dppp complex **2a** of 90.58(5)°.[7] Likewise, the Pd-P bond distance of 2.250(1) Å is very close to those observed in **2a** of 2.244(1) and 2.249(2) Å.[7] The major difference between **4a** and **2a** is provided by the conformation of the six-member PdP_2C_3 ring. Indeed, in **2a** the three bridging carbon atoms are located at the same side of the coordination plane, while **4a** exhibits a symmetrical twisting of the ligand with a deviation of C(15) of 0.878(2) Å in direction of O(1) from the coordination plane defined by the atoms Pd(1), Cl(1), and P(1). Like **3a**·2.3 CH_2Cl_2, **4a** exhibits two rather long Pd...O distances of 3.435(2) and 5.193(2) Å and one short intramolecular Pd(1)…H(9) distance of 2.871 Å per asymmetric unit, which was already observed in the structure of the nickel complex $NiCl_2$(*o*-MeO-dppp).[8] The short Pd…H intramolecular interactions observed in the structures of both **3a**·2.3 CH_2Cl_2 and **4a** have been found to persist in solution as shown by ^{1}H NMR spectroscopy.

UNIVERSITAT ROVIRA I VIRGILI
PALLADIUM COMPLEXES CONTAINING DIPHOSPHINE AND SULFONATED PHOSPHINE LIGANDS FOR C-C BOND FORMING REACTIONS. CATALYTIC AND MECHANISTIC STUDIES
Eduardo José García Suárez
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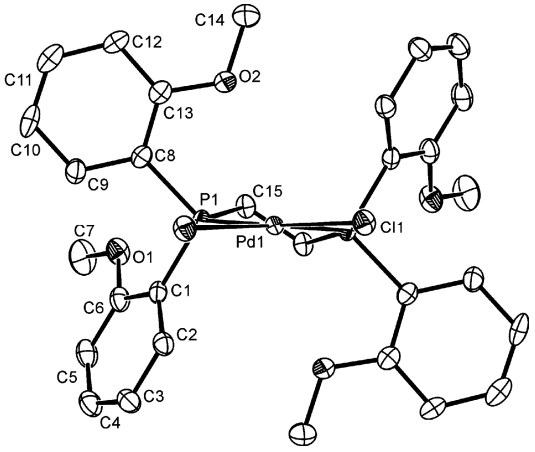


Figure 2. ORTEP plot of **3a**·2.3·CH_2Cl_2. Solvent molecules and hydrogen atoms are omitted for clarity. Only the asymmetric unit of the molecule is labelled. Thermal ellipsoids are shown at the 30% probability level

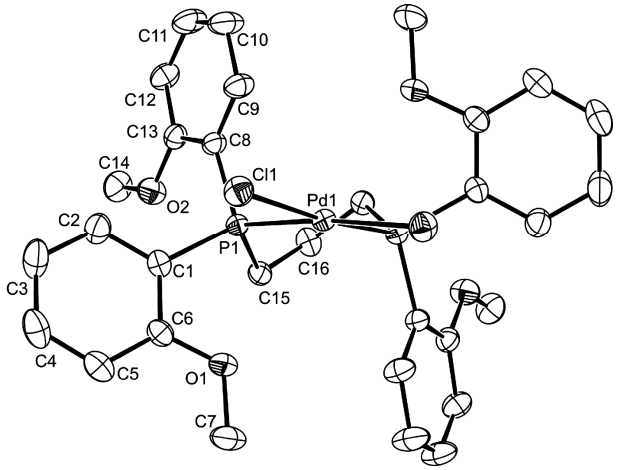


Figure 3. ORTEP plot of **4a**. Solvent molecules and hydrogen atoms are omitted for clarity. Only the asymmetric unit of the molecule is labelled. Thermal ellipsoids are shown at the 30% probability level

Table 3. Summary of crystallographic data for **3d** and **4d**

Complex	**3d**	**4d**
empirical formula	$C_{34}H_{38}O_8P_2Pd$	$C_{35}H_{40}O_8P_2Pd$
Fw	742.98	757.01
Cryst. size (mm)	0.30 x 0.30 x 0.20	0.30 x 0.30 x 0.20
Cryst. system	triclinic	monoclinic
Space group	*P*-1	$P2_1/n$
a (Å)	10.430(5)	14.065(3)
b (Å)	10.536(5)	16.297(2)
c (Å)	18.933(5)	15.385(2)
α^{o}	78.820(5)	90.00
β^{o}	81.260(5)	92.420(15)
γ^{o}	77.060(5)	90.00
V ($Å^3$)	1976.4(14)	3523.4(10)
D_{calcd} (Mg/m^3)	1.248	1.427
Z	2	4
μ(Mo Kα) (mm^{-1})		0.666
μ(Cu Kα) (mm^{-1})	4.905	
Diffractometer radiation (Å)	$\lambda(Cu_{K\alpha})$= 1.54180	$\lambda(Mo_{K\alpha})$= 0.71069
F(000)	764	1560
temp (K)	293(2)	293(2)
Θ range for data collecn (deg)	4.37-55.0	2.00-22.97
index range	-1<= *h* <= 11 -10 <= *k* <= 11 -19 <= *l* <= 20	-15 <= *h* <= 15 0 <= *k* <= 17 0 <= *l* <= 16
Nº. of reflns collected	4913	5102
Nº. of independent reflns	4576	4896
Nº. of refined params	412	421
R1 (2σ(*I*))	0.0369	0.0331
R1 (all data)	0.0402	0.0617
wR2 (all data)	0.0955	0.0805
goodness of fit on F^2	1.053	0.998
Largest diff peak and hole (e/ $Å^3$)	0.063/-0.890	0.372/-0.448

Table 4. Selected Bond lengths (Å), bond angles (°) and intra-molecular Pd-O and P-H distances(Å) for **3d** and **4d**

Complex	**3d**	**4d**
Pd(1)-P(1)	2.229(1)	2.223(1)
Pd(1)-P(2)	2.221(1)	2.226(1)
Pd(1)-O(5)	2.108(3)	2.092(2)
Pd(1)-O(7)	2.104(3)	2.109(3)
P(1)-Pd(1)-P(2)	85.42(4)	95.30(4)
O(5)-Pd(1)-O(7)	92.83(11)	87.00(10)
P(1)-Pd(1)-O(5)	174.56(8)	174.31(7)
P(2)-Pd(1)-O(7)	176.86(8)	172.18(7)
Intramolecular Pd-oxygen distances in (Å)		
Pd(1)…O(1)	3.732(3)	5.144(3)
Pd(1)…O(2)	5.163(3)	3.564(3)
Pd(1)…O(3)	5.102(4)	3.699(3)
Pd(1)…O(4)	3.604(3)	5.106(3)
Pd(1)…H(2)		2.716
Pd(1)…H(23)		2.695
Pd(1)…H(9)	2.855	
Pd(1)…H(16)	2.778	

The crystal structure of **3d** shows a square planar coordination geometry for palladium with a slight displacement of the Pd(1) from its coordination plane, defined by P(1), P(2), O(5) and O(7), by 0.035(2) Å in direction of O(2). The conformation of the five membered ring is puckered, as typically found in complexes bearing dppe as ligand. The P(1)-Pd(1)-P(2) bite angle is 85.42(4)°, is comparable with that observed in $Pd(OAc)_2$(dppe).[11a] The same is valid for the Pd-P bond length of 2.229(1) and 2.221(1) Å in **3d** and of 2.218(2) and 2.225(2) Å in the analogous dppe complex.

The crystal structure of **4d** shows a typical square planar coordination geometry. The Pd-P bond distances of 2.223(1) and 2.226(1) Å are significantly shorter than those of the analogous $PdCl_2$ compound (**4a**) of 2.250(1) and

2.244(1) Å, due to the weaker *trans* influence of actetae compared to chloride. Compound 4d shows thus a significantly larger P(1)-Pd(1)-P(2) bite angle of 95.30(4)^{o} compared to that of **4a**.is significantly larger than that found for **4a** of 90.09(4)^{o}.

Like the crystal structures of both $PdCl_2$ complexes **3a** 2.3 CH_2Cl_2 and **4a**, also the crystal structures of the Pd-acetate complexes **3d** and **4d** show intra-molecular palladium methoxy-oxygen distances, which range from 3.604(3) to 5.163(3) for **3d** and 3.699 (3) to 5.144(3) Å for **4d** and palladium *ortho*-hydrogen atom interactions of less than 3.0 Å. The intra-molecular distances are reported in **Table 4**. This typical pair-wise orientation of the *o*-methoxy groups around the metal centre has been observed also by Bouwman in comparable nickel complexes.[8]

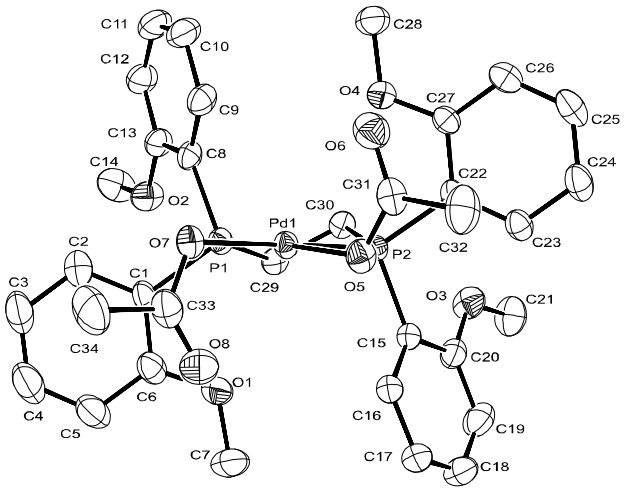


Figure 4. ORTEP plot of **3d**. Solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level

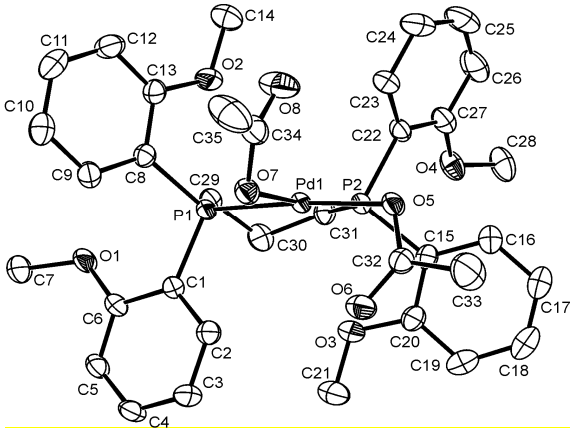


Figure 5. ORTEP plot of **4d**. Solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level

Variable-temperature NMR studies of 3a, 4a, and 4b in CD_2Cl_2

In an attempt of elucidating the solution structure of the palladium(II) complexes with the *o*-methoxy ligands, (*o*-MeO-dppe and *o*-MeO-dppp) $^{31}P\{^1H\}$ and ^1H NMR studies were carried out on CD_2Cl_2 solutions of **3a**, **4a**, and **4b** in the temperature range from 20 to -80 °C. Complexes **3a** and **4a** exhibit fluxional behaviour on the NMR time-scale. The ^1H NMR spectrum at 20 °C of either complex displayed one set of resonances for the aryl hydrogen (δ 6.96-7.95 and 6.97-7.60, respectively) and one singlet for the *o*-methoxy groups (δ 3.61 and 3.75, respectively), which indicates the equivalence of all four aryl groups in the *o*-MeO-ligands. Decreasing the temperature led to a progressive broadening of all resonances. At -80 °C, the ^1H NMR spectra of **3a** and **4a** contained a couple of singlets at δ 3.75 and 3.42 and δ 3.73 and 3.68 for the *o*-methoxy groups, respectively. This pattern can be safely attributed to the formation of couples of axially and equatorially oriented methoxy groups as shown also by the crystal structures of **3a**·2.3·CH_2Cl_2 and **4a**. Notably, the ^1H NMR spectra of **3a** and **4a** at -80 °C showed a significant downfield shift of the resonances of two aryl

hydrogen (δ 8.85 and 8.95, respectively), which suggests that the interactions between the *o*-hydrogen atoms of the aryl groups and the metal centre, observed in the crystal structures of **3a**·2.3·CH_2Cl_2 and **4a**, are maintained in solution.[9] An analogous fluxional behaviour has been reported for $NiCl_2$(*o*-MeO-dppp) whose crystal structure closely resembles those of **3a**·2.3·CH_2Cl_2 and **4a**.[8]

Like the bis-chloride complexes **3a** and **4a**, the tosylate complex **4b** is fluxional in CD_2Cl_2 solution at room temperature due to the exchange of equatorial and axial aryl groups. The temperature-dependent ^{1}H NMR spectra of **4b** are reported in **Figure 6**. Analogously to **3a** and **4a**, the spectrum at 20 ^{o}C (trace **a**) showed a singlet at δ 4.05 which resolved at -80 ^{o}C into two singlets at δ3.97 (equatorial) and 4.32 (axial) (trace **c**). Unlike **3a** and **4a**, the ^{1}H NMR spectrum of **4b** at -80 ^{o}C contained no downfield shifted resonance, consistent with no interaction between the metal centre and the *o*-hydrogen atoms of the aryl groups.

The NMR pattern observed for **4b** is in perfect agreement with that exhibited by the nickel derivative [Ni(H_2O)$_2$(*o*-MeO-dppp)](PF_6)$_2$ whose X-ray crystal structure analysis revealed the absence of any interaction between nickel and the *o*-hydrogen with all four *o*-methoxy groups pointing towards palladium.[8] It is therefore most likely that **4b** and [Ni(H_2O)$_2$(*o*-MeO-dppp)](PF_6)$_2$ adopt the same structure in both the solid state and solution.

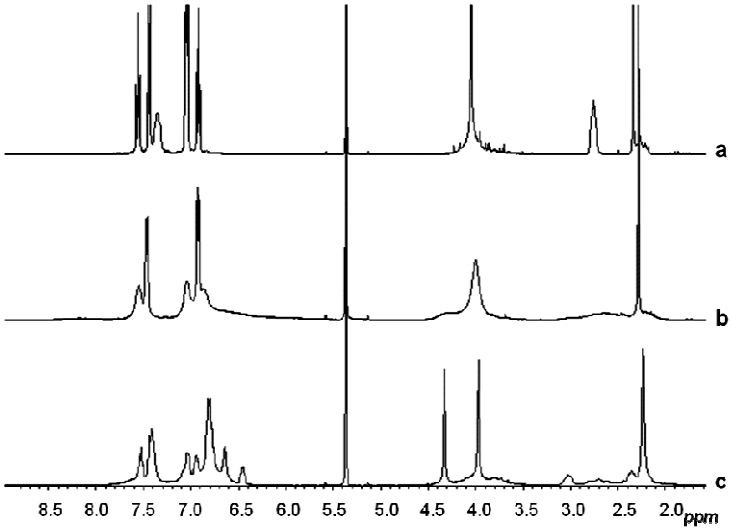


Figure 6. Variable-temperature ^{1}H NMR study of **4b** (CD_2Cl_2, 400.13 MHz): (**a**) 20 ^{o}C; (**b**) -40 ^{o}C; (**c**) -80 ^{o}C.

The $^{31}P\{^{1}H\}$ NMR spectra of **3a**, **4a**, and **4b** at 20 ^{o}C consist of a single relatively sharp resonance at δ 69.02, 16.30, and 13.72, respectively. A sharp resonance was also observed at -80 ^{o}C for **3a** (δ 68.97) and **4a** (δ 17.63), while the spectrum of **4b** showed a quite different behaviour with the temperature (**Figure 7**). At -80 ^{o}C the initial $^{31}P\{^{1}H\}$ NMR singlet was split into two resonances at δ -4.46 and 22.78 in a 5:1 ratio (trace **c**). The chemical shifts of these two resonances as well as their line-shape do not appear to be consistent with a slow exchange regime of a unique fluxional species: It is much more likely that new species are formed at low temperature where tosylate ions may compete with water molecules for coordination.

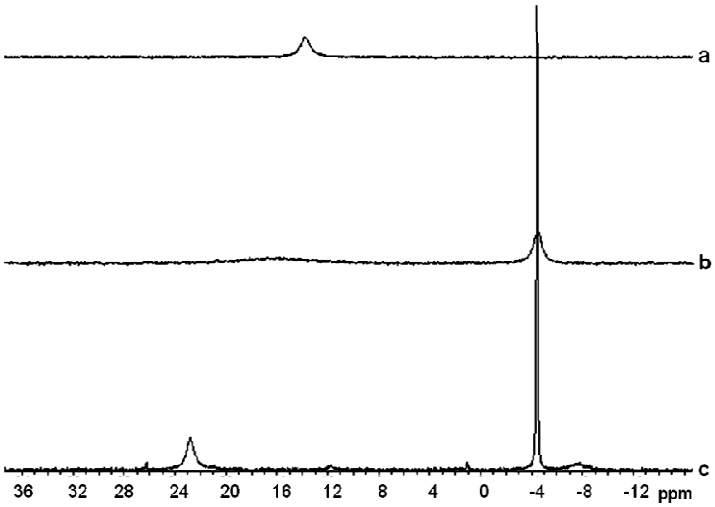


Figure 7. Variable temperature $^{31}P\{^{1}H\}$ NMR study of **4b** (CD_2Cl_2, 400.13 MHz): (**a**) 20 °C; (**b**) -40 °C; (**c**) -80 °C.

Catalytic copolymerisation of CO and ethene

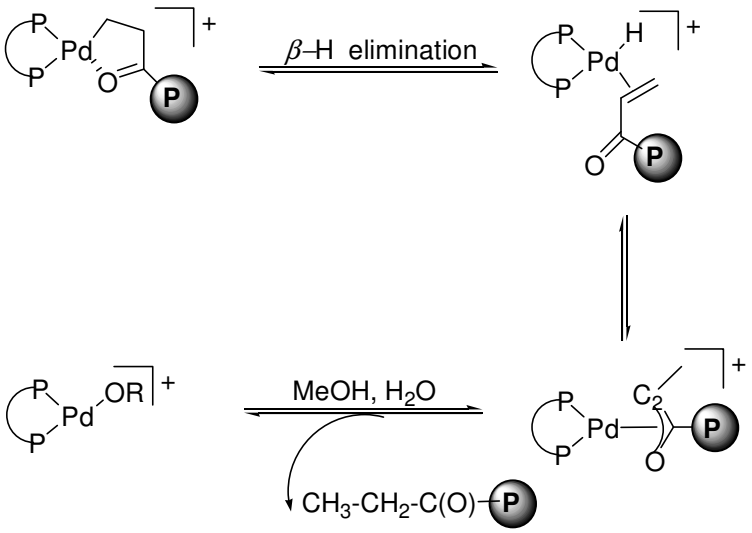
Both neutral and cationic Pd(II) complexes, with either *ortho*-methoxy modified ligands *o*-MeO-dppe and *o*-MeO-dppp or with the unmodified dppe and dppp ligands, were employed to catalyse CO-ethene copolymerisation reactions in five different solvents: MeOH, TFE, water-AcOH mixtures, CH_2Cl_2 and toluene. All reactions in protic solvents were performed at 85 °C and with a 1:1 CO/C_2H_4 pressure of 40 bar. Lower temperatures (50-60 °C) were used for the reactions in aprotic solvents. No optimisation of the catalytic activity was attempted. The results obtained are summarised in **Table 5-8**.

Prior to the presentation and discussion of the catalytic results, it may be useful to anticipate that, with the only exception of the reactions carried out in TFE, higher productivities as well as higher molecular weights of the polyketone products were observed both for the dppp-like catalysts in comparison with the

corresponding dppe-like catalysts (i.e., dppp > dppe and *o*-MeO-dppp > *o*-MeO-dppe) as well as for the ortho-methoxy modified catalysts as compared to the corresponding unmodified catalysts (i.e., *o*-MeO-dppp > dppp and *o*-MeO-dppe > dppe).[10]

The different catalytic activities exhibited by the palladium precursors with diphosphine chelating ligands bearing CH_2 spacers between the phosphorus donor atoms have been subject of many studies.[11,12] According to several authors, the Pd(P-P) chelate ring is the main factor that effectively controls the catalytic activity.[1] In particular, the formation of a more stable β-keto alkyl metallacycle, involving intramolecular interaction between the β-carbonyl group of the propagating chain and the palladium centre (**Scheme 6**) has been suggested to account for the lower activity of the dppe-like catalysts as compared to the dppp-like ones.[11a] In a similar way, the higher productivity exhibited in most solvents by the catalysts with the *ortho*-methoxy substituted ligands can be related to the capability of such nucleophlic groups to stabilise, by virtue of the oxygen donor atoms, coordinatively unsaturated intermediates as well as destabilise the β-keto alkyl metallaring favouring its opening by CO and thus speeding up the propagation process.[3]

Protonolysis and/or β-hydride elimination are the unique or largely prevailing chain termination processes operative in the copolymerization reactions investigated in this work. **Scheme 6** illustrates the generally accepted mechanism by which diphosphine palladium(II) propagating species undergo chain transfer mechanism.[13] This mechanism, experimentally demonstrated by van Leeuwen et al.,[13] involves equilibrium between the β-keto alkyl metallacycle and its enolate. However, since the overall protonolysis rate depends on the rate of the β-hydride elimination,[13] the polyketone molecular weight is determined by the kinetics of the β-hydride elimination step: the lower the rate of the β-H elimination, the higher the molecular weight.



Scheme 6

β-H elimination reactions involving organometallic complexes are steered by both electronic and steric factors.[14] In particular, it is agreed that the agostic interaction between the metal and a *β*-hydrogen (precursor to hydrogen transfer) is disfavoured both by a high electron density at the metal centre and by the presence of groups on the supporting ligand which can compete with the *β*-hydrogen for interaction with the metal center.[14] Within this picture, it is apparent that highly basic phosphines bearing also two potential donor atoms such as *o*-MeO-dppe and *o*-MeO-dppp are more appropriately design suited than their unsubstituted counterparts dppe and dppp to retard *β*-H elimination paths.

Catalytic reactions with the tosylate complexes 1b-4b as catalyst precursors in either MeOH or TFE

The bis-cationic complexes **3b** and **4b** and the mono-cationic complexes **1b** and **2b** were employed to catalyse the CO-ethene copolymerisation in MeOH

with or without added *p*-toluensulfonic acid (TsOH) and/or 1,4-benzoquinone (BQ) (**Table 5**). The latter oxidant is commonly used for the re-generation of the catalytically active palladium(II) species by oxidation of catalytically inactive Pd(I) and Pd(0) species, that may form under the reducing conditions of the copolymerisation reactions. In turn, the protic acid serves to generate Pd-H moieties by oxidative addition to Pd(0) species as well as to convert catalytically inactive μ-OH dimers (generated by adventitious moisture) into active mononuclear species.[11] Irrespective of the catalyst precursor employed, the alt-ethene-CO copolymers obtained in MeOH were featured by ketone and ester end groups in a 1:1 ratio, which is typical for CO-ethene copolymerisation in MeOH where initiation involves both Pd-OMe or Pd-H species and termination, may occur *via* either protonolysis or methanolysis.[1]

The highest productivities (up to 17-18 kg alt-ethene-CO (g Pd x h)-1) were obtained with the *o*-MeO catalyst precursors **3b** ([Pd(H_2O)$_2$(*o*-MeO-dppe)](OTs)$_2$) and **4b** ([Pd(H_2O)$_2$(*o*-MeO-dppp)](OTs)$_2$) without any acid co-catalyst and, under these conditions, the productivity gap between the *o*-MeO substituted catalysts and the unsubstituted congeners reached its maximum. Irrespective of catalyst and acidity of the reaction medium, a beneficial effect on the polymerisation rate was produced by the addition of 80 equiv of BQ. As an example, productivities of 18.1 vs 13.6 and 11.2 vs 9.1 were obtained for the **4b**-derived catalyst with or without BQ. Notably, the addition of increasing amounts of TsOH produced a significant increase in the productivity and stability of the unsubstituted catalysts (for **2b**, 3.5 / 4.2 / 4.4), whereas a negative effect was observed for the *o*-MeO-substituted ones (for **4b**, 13.6 / 11.0 / 9.1).

Table 5. Productivities (Kg alt-ethene-CO(g Pd x h)$^{-1}$) and M_n (Kg mol^{-1}) of $[Pd(H_2O)_{2-x}(OTs)_x(\mathbf{P\text{-}P})](OTs)_{2-x}$ precursors in the CO/ethene copolymerisation reactions catalysed by Pd(II)-diphosphine precursor in MeOH.[a]

Entry	(**P-P**)	BQ(equiv.)	TsOH(equiv.)	Productivity 1h/3h	M_n
1	dppe			0.3/0.2	
2[b]	*o*-OMe-dppe			12.4/9.6	14.2
3	dppp			3.5/2.5	
4[b]	*o*-OMe-dppp			13.6/13.2	
5	dppe	80		0.4/-	
6[b]	*o*-OMe-dppe	80		17.4/-	
7	dppp	80		4.1/-	
8[b]	*o*-OMe-dppp	80		18.1/-	
9	dppe		2	0.8/0.3	
10	*o*-OMe-dppe		2	10.8/8.2	
11	dppp		2	4.2/4.0	
12	*o*-OMe-dppp		2	11.0/7.8	
13	dppe		20	1.9/1.7	4.3
14	*o*-OMe-dppe		20	8.9/7.2	16.2
15	dppp		20	4.4/4.4	14.9
16	*o*-OMe-dppp		20	9.1/6.6	>35
17	dppp	80	20	6.2/-	
18	*o*-OMe-dppp	80	20	11.2/-	

[a]Reaction conditions: catalyst 0.0048 mmol, MeOH 100 mL, P(CO/C_2H_4) 40 bar at 85 °C, 1 h and 3 h, 1200 rpm. [b]Catalyst 0.0024 mmol..

The decrease in productivity exhibited by the *o*-MeO catalysts upon increasing the acid concentration may be explained in the light of previous studies of palladium complexes with phosphine ligands bearing *o*-MeO substituted aryl rings.[15] Indeed, it has been reported that the *o*-MeO oxygen atoms act as effective H-bond acceptors, which, in an environment rich of H-bond donors, creates a web of interactions involving the complex, protons, solvent, and counteranions.[16] This would ultimately results in an increase of the steric congestion at the metal centre with negative effects on the monomers uptake and thus on the propagation rate. The substitution of MeOH (pk_a = 16) by the

stronger Broensted acid TFE (pk_a = 12.4) was found to affect the catalytic productivity, M_n as well as the nature of the end groups (**Table 6**).

The data reported in **Table 6** shows, as already anticipated, that TFE depresses the productivity of the *o*-MeO catalysts **3b** and **4b** as compared to MeOH, while it enhances the activity of the catalysts derived from the unsubstituted precursors **1b** and **2b** up to ca. 16 kg alt-ethene-CO (g Pd x h)$^{-1}$.

Table 6. Productivities (Kg alt-ethene-CO(g Pd x h)$^{-1}$) and M_n (Kg mol^{-1}) of $[Pd(H_2O)_{2-x}(OTs)_x(\mathbf{P\text{-}P})](OTs)_{2-x}$ precursors in the CO/ethene copolymerisation reactions catalysed by Pd(II)-diphosphine precursor in TFE.[a]

Entry	(**P-P**)	BQ (equiv.)	Productivity 1h/3h	M_n
1	dppe		3.5/2.8	4.9
2	*o*-OMe-dppe		2.1/1.9	6.0
3	dppp		15.9/13.6	23.5
4	*o*-OMe-dppp		3.0/2.6	29.4
5	dppe	80	3.3/-	4.7
6	*o*-OMe-dppe	80	2.7/-	
7	dppp	80	15.6/-	
8	*o*-OMe-dppp	80	2.0/-	

[a]Reaction conditions: catalyst 0.0048 mmol, CF_3CH_2OH 100 mL, $P(CO/C_2H_4)$ 40 bar at 85 °C, 1 h and 3 h, 1200 rpm.

A $^{13}C\{^1H\}$ and ^1H NMR analysis in 1,1,1,3,3,3-hexafluoroisopropanol-d_2/C_6H_6-d_6 of the products obtained with the catalysts based on C_2-bridged ligands showed the alt-ethene-CO materials obtained in TFE to have ketone, ester, and vinyl end groups. Since alcoholysis as chain transfer reaction in TFE can be ruled out due to the low nucleophilicity of this alcohol,[17] the only effective termination reactions in this solvent are β-hydride elimination and protonolysis.[1] Accordingly, polymeric materials with keto-ester (**KE**), vinyl-ester (**VE**), vinyl-ketone (**VK**) and diketone (**KK**) end groups may form. On the basis of the ^1H

NMR integration of the corresponding signals, the ratios between vinyl, ester and ketone end groups have been found to be 5:42:53 and <1:46:54 for **1b** and **3b**, respectively. The addition of BQ had no significant influence either on the ratio between the end groups or on the M_n values of the copolymers. The copolymers obtained with **1b** in the presence of BQ showed a vinyl:ester:ketone end group ratio of 7:40:53 and a M_n value of 4.7 kg mol^{-1}.

Based on the end groups analysis of the polyketone products as well as previous literature reports,[17] a general catalytic mechanism for the CO/ethene copolymerisation in TFE is proposed in **Scheme 7**. Since the keto-ester copolymers are the dominant products, the most frequent initiator (> 85%) should be Pd-OCH_2CF_3 and protonolysis the most effective termination path.

Operando and *in situ* HP-NMR experiments were carried out using either **2b** or **4b** as catalyst precursor and ^{13}C labelled CO as reagent in a 1:1 (v:v) mixture of CD_2Cl_2 and TFE. While details of this study will be provided in a following section, it is useful to anticipate here that **4b** was converted under catalytic conditions into at least three dynamic species, likely alkoxycarbonyl and/or carbonyl, whereas no intermediate species was intercepted with **2b**, only a very fluxional species being observed even at low temperature.[18] Although no clear-cut experimental evidence was actually obtained, the ^{13}C labelling HP-NMR experiments suggest that the *o*-OMe-dppp ligand favour the formation of more stable carbonyl or ester species as compared to dppp, which may account for the lower activity of the catalysts with the former ligand. A largely positive influence of TFE on the CO/styrene copolymerisation by palladium(II) catalysts has been previously demonstrated by Milani et al. and has been attributed to the stabilising effect of TFE on important catalytic intermediates, such as Pd-H species.[17]

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Eduardo José García Suárez
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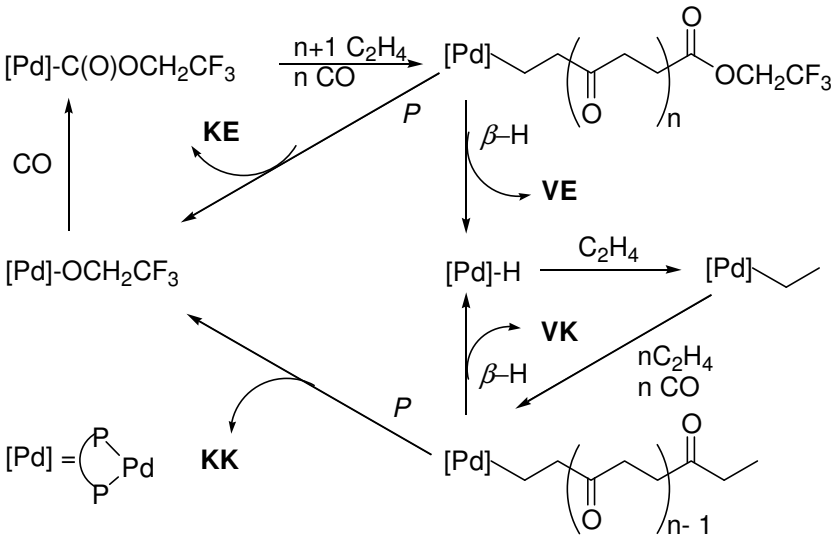
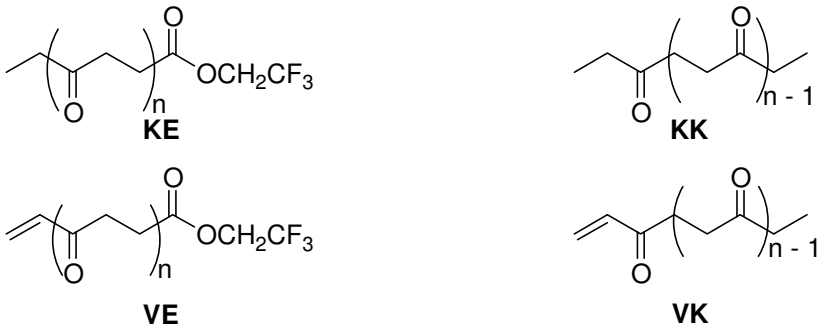


P = protonolysis; *β*-H = hydride elimination



Scheme 7

Another positive effect on the catalytic activity is likely provided by the increased diffusion of the monomers in reactions performed in TFE due to capability of this alcohol to dissolve perfectly alternating polyketones as well as propagating Pd-polyketone chains.[19] Since there is no reason to think that these two positive effects are influenced by the presence of *o*-MeO substituted aryl rings in the catalysts precursors as is the case of **3b** and **4b**, the dramatic decrease in productivity observed with these catalysts in TFE must have a specific reason.

We do think that the low catalytic productivity exhibited by the *o*-MeO systems is due to the excellent H-bond donor and poor H-bond acceptor properties of TFE. Indeed, evidence has been provided according to which a web of strong H-bond interactions may be built up on the side of the metal coordination sphere where the *o*-MeO oxygen atoms can act as H-bond acceptors from TFE.[19] As a consequence, the steric congestion around the metal centre would be drastically increased, resulting in a slow diffusion of the monomers towards the metal centre and, hence, in the stabilisation of intermediates, for example alkoxycarbonyl species.

CO-ethene copolymerisation reactions with the bis-chloride complexes 1a-4a as catalyst precursors in water-AcOH mixtures

The bis-chloride complexes **1a**-**4a** were employed as catalyst precursors for the CO-ethene copolymerisation in mixtures of water and AcOH with a water content ranging from 55 to 85 mol% (**Table 7**). Irrespective of the catalyst precursor, the maximum of catalytic productivity was found using a water-AcOH mixture containing 75 mol% water.

Table 7. Productivities (Kg alt-ethene-CO(gPdxh)$^{-1}$) and M_n (Kg mol^{-1}) of $PdCl_2$(**P-P**) (**1a**-**4a**) precursors in the CO/ethene copolymerisation reactions catalysed by Pd(II)-diphosphine precursor in AcOH/H_2O.[a]

Entry	(**P-P**)	Productivity 1h/2h	M_n
1	dppe	0.8/0.4	3.3
2	*o*-OMe-dppe	8.9/5.5	5.7
3	dppp	5.6/4.5	14.5
4	*o*-OMe-dppp	9.1/6.0	> 40

[a]Reaction conditions: catalyst 0.0048 mmol, AcOH/H_2O 75% mol 100 mL, P(CO/C_2H_4) 40 bar at 85 °C, 1 h and 2 h, 1200 rpm.

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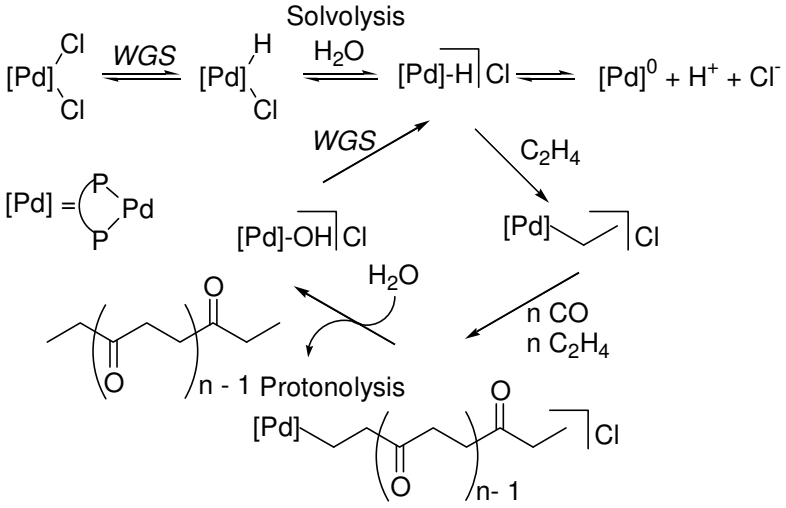
All of the alt-ethene-CO products obtained were exclusively featured by ketone end groups, which is consistent with the mechanism proposed for CO/ethene copolymerisations catalysed by $PdCl_2$(diphosphine) complexes in acidic aqueous media involving Pd-H initiators and chain termination by protonolysis (**Scheme 8**).[15,20]



Scheme 8

The neutral palladium(II)-H complexes shown in **Scheme 8** are believed to be generated from the bis-chloride precursors by water gas shift reaction (WGS), and then converted into the catalytically active cationic palladium(II)-H species by a water-controlled solvolysis process.[20a] It has been also demonstrated by Toniolo and Zudin that increasing the water proportion in the water/AcOH mixture increases the concentration of the cationic Pd(II)-H species by speeding up the solvolysis process.[20]

On the other hand, a too large proportion of water has been found to have a detrimental effect on the solubility of CO and C_2H_4.[20] In the case at hand, 75 mo% in water seems to be the best compromise between an efficient solvolysis

process rate and acceptable co monomer solubility. The chain-transfer reaction of CO/ethene copolymerisation performed in acidic aqueous media has been demonstrated to occur exclusively *via* protonolysis by water with formation of a Pd-OH unit that re-generates a Pd-H initiator by WGS.[20]

CO-ethene copolymerisation reactions with the methyl complexes 1c-4c as catalyst precursors in both CH_2Cl_2 and toluene

A few examples of palladium-catalysed CO-ethene copolymerisation in aprotic solvents such as dichloromethane, THF or acetone have been reported so far.[21] Herrmann has reported the performance of monocationic palladacycles stabilised by dppe and dppp, while Barron has studied the influence of *tert*-butylaluminoxane co-catalysts on dppp modified catalysts.[22] Under these conditions, the only effective chain termination mechanism is β-H elimination to give high molecular weight copolymers with vinyl end groups. The neutral methyl complexes PdCl(Me)(P-P) **1c**-**4c** were scrutinised in either CH_2Cl_2 with NaBArF (ArF = 3,5-$(CF_3)_2$-C_6H_3) as activator at 50 ^oC or in toluene in the presence of MAO at 60 ^oC (**Table 8**). No end-group could be seen by ^1H and ^{13}C NMR analysis of the copolymers obtained, which indicates the exclusive formation of very high molecular weight copolymers. However, ketone and vinyl end groups were detected in the copolymer samples obtained in CH_2Cl_2 at higher temperature (85 ^oC), which is consistent with the formation of Pd-H initiators and β-H transfer as termination path.

Table 8. Productivities (Kg alt-ethene-CO(gPdxh)$^{-1}$) of PdCl(Me)(**P-P**) (**1c**-**4c**) precursors in the CO/ethene copolymerisation reactions catalysed by Pd(II)-diphosphine precursor in CH_2Cl_2[a] and Toluene.[b]

Entry	(**P-P**)	BQ (equiv.)	NaBArF (equiv.)	Productivity
1[a]	dppe	80	1.5	0.4
2[a]	*o*-MeO-dppe	80	1.5	2.9
3[a]	dppp	80	1.5	2.8
4[a]	*o*-MeO-dppp	80	1.5	5.1
5[b]	dppe			-
6[b]	*o*-MeO-dppe			0.4
7[b]	dppp			0.1
8[b]	*o*-MeO-dppp			0.5

[a]Reaction conditions: catalyst 0.01 mmol, CH_2Cl_2 75 mL, P(CO/C_2H_4) 40 bar at 50 °C, 20 min., 1200 rpm. [b]Reaction conditions: catalyst 0.01 mmol, MAO 100 equiv., Toluene 75 mL, P(CO/C_2H_4) 40 bar at 60 °C, 2 h, 1200 rpm.

Irrespective of the catalyst precursor, the productivities were generally much lower than those in protic solvents, which may be due to the minor stability of the Pd-H initiator to reduction to Pd(0) and H^+ in aprotic solvents. The catalytic data of **1c** and **2c** in CH_2Cl_2 are comparable with those reported by Herrmann.[21]

Operando and *in situ* HP-NMR studies of the CO-ethene copolymerisation with 2b and 4b

In an attempt to find out a reliable explanation for the low productivity exhibited by the *ortho*-methoxy modified catalysts in TFE, *operando* HP-NMR experiments were carried out in a 1:1 (v:v) mixture of CD_2Cl_2/TFE employing **4b** as catalyst precursor. Selected $^{31}P\{^1H\}$ NMR spectra are reported in **Figure 8**. Pressurising the NMR tube with 20 bar CO converted **4b** (δ 19.0 in trace **a**) into a species featured by a broad signal centred at δ 16.5 (trace **b**). The line-shape of the latter resonance suggests that the carbonylation of **4b** is accompanied by fluxional processes. Pressurising the tube with ethene to 40 bar led to the

formation of polyketone product while the broad signal moved to ca. δ 14 (trace **c**). Upon heating, first to 50 °C and then to 85 °C, the signal narrowed and shifted to ca. δ 19.0 (traces **d** and **e**). After the tube was cooled to 20 °C, the $^{31}P\{^{1}H\}$ NMR spectrum became similar to that observed before heating (compare traces **f** and **c**).

In line with previously reported studies of CO-ethene copolymerisation by palladium complexes stabilised by dppp-like diphosphines, the resonances shown in traces **C**-**F** are attributed to a catalyst resting state containing "Pd(P-P)$^{2+}$" moieties stabilised by OTs^- ligands, eventually in rapid exchange with solvent molecules and/or monomers.[1,12a] In analogous *operando* HP-NMR experiments carried either in CD_2Cl_2/TFE with the catalyst precursor **2b** or in MeOD-d_4 with the catalyst precursors **2b** and **4b**, the $^{31}P\{^{1}H\}$ NMR spectra showed a single relatively sharp resonance at the chemical shift of the starting complex during all experiments. This evidence suggests that the fluxional species observed in trace **b** of **Figure 8** forms only when the reaction is performed in TFE and the catalyst is modified with a diphosphine ligand containing *o*-OMe-aryl substituents.

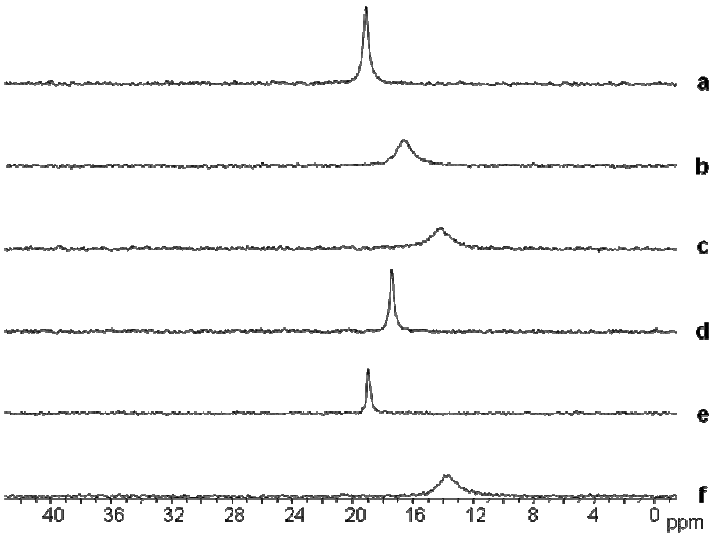


Figure 8. *Operando* $^{31}P\{^{1}H\}$ HP-NMR study (sapphire tube, 1:1 (v:v) CD_2Cl_2/TFE, 81.01 MHz) of the CO-ethene copolymerisation catalysed by 4b: (**a**) under nitrogen at room temperature; (**b**) under 20 bar of CO at room temperature; (**c**) under 40 bar of 1:1 CO/ethene at room temperature; (**d**) at 50 ^{o}C; (**e**) at 85 ^{o}C; (**f**) after the sapphire tube was cooled to room temperature

In an attempt of elucidating the structure of the species formed by carbonylation of **4b** (trace **b** in **Figure 8**), a variable-temperature $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR study was performed in a 1:1 (v:v) mixture of CH_2Cl_2/TFE, using ^{13}C labeled CO. A selected sequence of $^{31}P\{^{1}H\}$NMR spectra is presented in **Figure 9.** Traces (**a**) (singlet at δ 19.0) and (**b**) (broad resonance at ca. δ 3.0) are consistent with **4b** being in axial/equatorial aryl conformational exchange (see **Figure 6** and **Figure 7**). Upon pressurization to 20 bar with 1:19 $^{13}CO/^{12}CO$, the $^{31}P\{^{1}H\}$NMR spectrum displayed a hump centred at δ 16.5 at 20 ^{o}C, analogous to that reported in trace (**b**) of **Figure 9**, which resolved at -40 ^{o}C into at least three broad resonances at ca. δ 7, -16, and -20. (trace **c**). A quite similar NMR picture was observed at -40 ^{o}C when the tube was pressurised with 20 bar ethene (trace **d**).

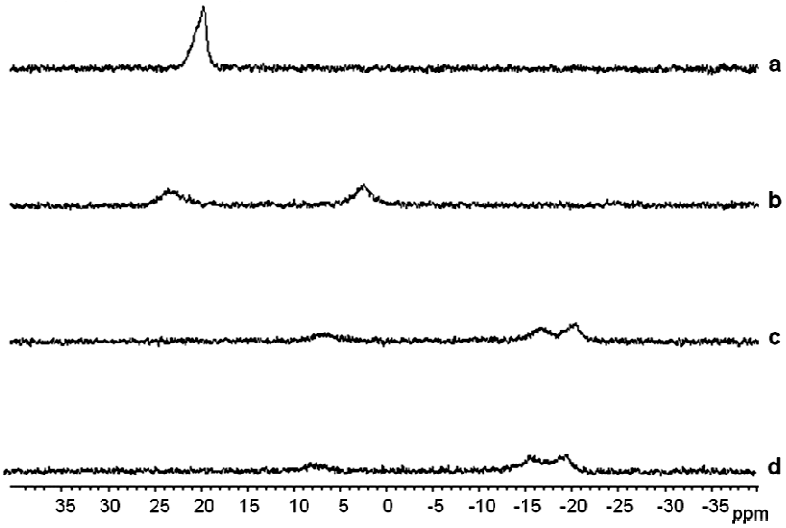


Figure 9. *In situ* $^{31}P\{^{1}H\}$ NMR study (sapphire tube, 1:1 (v:v) CD_2Cl_2/TFE, 81.01 MHz) of the CO/ethene copolymerisation catalysed by 4b: (**a**) under nitrogen at room temperature; (**b**) under nitrogen at -40 °C; (**c**) under 20 bar of 1:19 $^{13}CO/^{12}CO$ at -40 °C; (**d**) under 20 bar of 1:19 $^{13}CO/^{12}CO$ and 20 bar of ethene at -40 °C

$^{13}C\{^{1}H\}$ NMR spectra of the latter reaction mixture were acquired at different temperatures. At room temperature, a rather broad resonance centered at ca δ 186 was observed, which resolved at low temperature into several resonances between δ 187 and 185. The spectrum at -80 °C is shown in **Figure 10**. Apart from the sharp signal at δ 186.7 of free CO, no clear cut assignment of the other resonances was possible due to the broadness of the signals as well as the absence of any well defined multiplicity. The only reliable assumption is that signals in this spectral region are typical of linearly bonded CO as well as other keto ligands such as (alkoxy)carbonyls. It is worth reporting that no copolymer was produced along the whole experiments with **4b**, whereas the formation of polyketone bearing $-C(O)OCH_2CF_3$ end groups was observed using **2b** under comparable experimental conditions. On the other hand, there was no NMR

evidence whatsoever of the formation of carbonyl or alkoxycarbonyl species[18a] with the dppp-modified catalysts, which is consistent with its much higher activity.

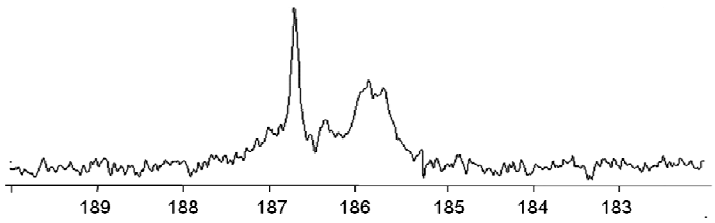


Figure 10. High pressure $^{13}C\{^{1}H\}$ NMR spectrum of **4b** under 20 bar of 1:19 $^{13}CO/^{12}CO$ at -80 ^{o}C

2.1.3. Conclusions

The results obtained in this work confirm that, irrespective of the reaction medium, the palladium(II) catalysts supported by the dppp-like chelating diphosphines give higher productivities as well as higher molecular weight polyketones as compared to the dppe-like counterparts (i.e., dppp > dppe and *o*-MeO-dppp > *o*-MeO-dppe). Except for the reactions performed in TFE, the *ortho*-methoxy modified catalysts are by far more productive than their unmodified catalysts (*o*-MeO-dppp > *o*-MeO-dppe > dppp > dppe) and also provide higher molecular weight materials.

In TFE, the *ortho*-methoxy oxygen atoms of either *o*-MeO-dppp or *o*-MeO-dppe form an effective web of hydrogen bonding interactions with solvent molecules. As a result of the increased congestion at the metal centre, a slower diffusion of the monomers would take place with a retardant effect on the propagation rate. Organic solvents such as CH_2Cl_2 and toluene promote the formation of very high molecular weight materials, yet in unsatisfactory yields.

2.1.4. Experimental section

General considerations

All reactions and manipulations were carried out under a nitrogen atmosphere by using Schlenk-type techniques. The solvents were generally distilled over dehydrating reagents and were deoxygenated before use. 2,2,2-Trifluoroethanol (TFE) was used as purchased from Aldrich. The reagents were used as purchased from Aldrich or Fluka, unless stated otherwise. $PdCl_2(COD)$[23a] PdCl(Me)(COD) (COD = cycloocta-1,5-diene),[23b] $PdCl_2$(dppe) (**1a**),[7] $PdCl_2$(dppp) (**2a**),[7] $[Pd(H_2O)(dppp)](OTs)_2$ (OTs = *p*-toluenesulfonate, **2b**),[24] PdCl(Me)(dppe) (**1c**),[11a] PdCl(Me)(dppp) (**2**),[11b] and NaBArF (ArF = 3,5-$(CF_3)_2$-C_6H_3)[25] were prepared according to literature methods. Solid MAO (methylaluminoxane) for the copolymerisation reaction was prepared by removing toluene and $AlMe_3$ under vacuum from a commercially available MAO solution (10 wt.% in toluene, Crompton Corp.).[26] All the isolated solid samples were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Copolymerisation reactions were performed with a 250 mL stainless steel autoclave, constructed at the ICCOM-CNR (Florence, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure during the catalytic reactions. GC/MS analyses of the solutions were performed on a Shimadzu QP2100S apparatus equipped with a SPB-1 Supelco fused silica capillary column (30m, 0.25 mm i.d., 0.25µm film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra were obtained on either a Bruker ACP 200 (200.13, 50.32 and 81.01 MHz, respectively) or a Bruker Avance DRX-400 spectrometer (400.13, 100.62 and 161.98 MHz), respectively. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvents resonances (^1H

and ^{13}C NMR) or 85% H_3PO_4 (^{31}P NMR). High pressure NMR (HP-NMR) experiments were carried out on Bruker ACP 200 spectrometer using a 10 mm HP-NMR tube (Saphikon (Milford, NH) sapphire tube; titanium high-pressure charging head constructed at the ICCOM-CNR).[27] The conductivity of ionic compounds was measured with an Orion model 990101 conductance cell connected to a model 101 conductivity meter. The conductivity data were obtained at a sample concentration of ca. 10^{-3} M in nitroethane solutions.[28] Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyser. Infrared spectra were recorded on a FT-IR Spectrum GX instrument (Perkin Elmer).

Syntheses

Preparation of 1,2-bis(di(2-methoxyphenyl)phosphino)ethane (*o*-MeO-dppe) and 1,3-bis(di(2-methoxyphenyl)phosphino)propane (*o*-MeO-dppp)

n-BuLi1.6 M in n-hexane (6.80 mL, 10.80 mmol) was slowly added to a stirred solution of bis(2-methoxyphenyl)phosphine[6a] (2.00 g, 8.31 mmol) in THF (150 mL) at 0 ^{o}C. The resulting suspension was allowed to warm to room temperature and stirred for further 2 h. A solution of 1,2-dichloroethane or 1,3-dichloropropane, (4.10 mmol) in THF (20 mL) was added drop wise to this suspension that became almost colourless. Afterwards, the reaction mixture was quenched with water (3 mL) and concentrated to dryness under reduced pressure. Treating the residue with a 1:3 (v:v) mixture of water/ethanol (50 mL) under vigorous stirring gave a white solid. Recrystallisation from CH_2Cl_2/ethanol led to the precipitation of *o*-MeO-dppe (or *o*-MeO-dppp) as an off-white powder, which was filtered off, washed with ethanol, and dried under a stream of nitrogen.

***o*-MeO-dppe**: 1.66 g (78%). $C_{30}H_{32}O_4P_2$ (518.52 g/mol): calc. C 69.49, H 6.22; found: C 69.46, H 6.24. $^{31}P\{^1H\}$ NMR (δ, 81.01 MHz, $CDCl_3$, 21 ^oC) -30.80 (s); ^1H NMR (δ, 200.13 MHz, $CDCl_3$, 21 ^oC) 2.20 (t, $^2J_{HP}$ = 3.7 Hz, 4H, PCH_2), 3.75 (s, 12H, OCH_3), 6.80-7.35 (m, 16H, Ar)

***o*-MeO-dppp**: 1.48 g (68%). $C_{31}H_{34}O_4P_2$ (532.54 g/mol): calc. C 69.92, H 6.44; found: C 69.94, H 6.47. $^{31}P\{^1H\}$ NMR (δ, 81.01 MHz, $CDCl_3$, 21 ^oC) -36.7 (s); ^1H NMR (δ, 200.13 MHz, $CDCl_3$, 21 ^oC) 1.73 (br s, 2H, CH_2), 2.23 (m, 4H, PCH_2), 3.80 (m, 12H, OCH_3), 6.79-7.05 (m, 16H, Ar)

Preparation of $PdCl_2$(*o*-MeO-dppe) (3a) and $PdCl_2$(*o*-MeO-dppp) (4a)

A solid sample of $PdCl_2$(COD) (57.1 mg, 0.20 mmol) was added to a stirred solution of the appropriate diphosphine ligand (0.20 mmol) in CH_2Cl_2 (20 mL) at room temperature. After 1 h, the reaction mixture was concentrated to ca. 5 mL under reduced pressure. Addition of a 1:1 (v:v) mixture of *n*-pentane/diethylether (20 mL) led to the precipitation of **3a** or **4a** as a yellow solid, which was filtered off, washed with n-pentane, and dried under a stream of nitrogen.

Complex 3a: 102.9 mg (74%). $C_{30}H_{32}Cl_2O_4P_2Pd$ (695.84 g/mol): calc. C 51.78, H 4.64; found: C 51.65, H 4.60. $^{31}P\{^1H\}$ NMR (δ, 81.01 MHz, CD_2Cl_2, 21 ^oC) 69.02 (s); ^1H NMR (δ, 200.13 MHz, CD_2Cl_2, 21 ^oC) 2.78 (m, 4H, PCH_2), 3.61 (s, 12H, OCH_3), 6.96-7.95 (m, 16H, Ar); $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, -80 ^oC) 68.97 (s); ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, -80 ^oC) 3.00 (m, 4H, PCH_2), 3.42 (s, 6H, Ar_{ax}-*o*-OCH_3), 3.75 (s, 6H, Ar_{eq}-*o*-OCH_3), 6.81-8.81 (m, 14H, Ar), 8.85 (m, 2H, Ar_{eq}-*o*-*H*)

Complex 4a: 116.4 mg (82%). $C_{31}H_{34}Cl_2O_4P_2Pd$ (709.86 g/mol): calc. C 52.45, H 4.83; found: C 52.48, H 4.86. $^{31}P\{^1H\}$ NMR (δ, 81.01 MHz, CD_2Cl_2, 21 ^oC) 16.30 (s); ^1H NMR (δ, 200.13 MHz, CD_2Cl_2, 21 ^oC) 1.90 (m, 2H, CH_2), 2.50 (m, 4H, PCH_2), 3.75 (s, 12H, OCH_3), 6.97-7.60 (m, 16H, Ar); $^{31}P\{^1H\}$ NMR (δ,

161.98 MHz, CD_2Cl_2, -80 °C) 17.63 (s); ^{1}H NMR (δ, 400.13 MHz, CD_2Cl_2, -80 °C) 1.92 (m, 2H, CH_2), 2.45 (m, 4H, PCH_2), 3.68 (s, 6H, Ar_{ax}-*o*-OCH_3), 3.73 (s, 6H, Ar_{eq}-*o*-OCH_3), 6.82-8.92 (m, 14H, Ar), 8.95 (dd, $^3J_{HP}$ = 16 Hz, $^3J_{HH}$ = 7 Hz, 2H, Ar_{ax}-*o*-*H*)

Preparation of [Pd(OTs)(H_2O)(dppe)]OTs (1b)

A solid sample of AgOTs (136.70 mg, 0.49 mmol) was added to a stirred solution of **1a** (138.12 mg, 0.24 mmol) in CH_2Cl_2 (40 mL) at room temperature. After 3 h, the precipitated AgCl was removed by filtration of the suspension through a celite column and the clear filtrate was concentrated to ca. 3 mL. Addition of a 1:1 (v:v) mixture of *n*-pentane/diethylether (15 mL) led to the precipitation of **1b** as a yellow microcrystalline solid, which was filtered off, washed with *n*-pentane, and dried under a stream of nitrogen.

Complex 1b: 145.4 mg (70%). $C_{40}H_{40}O_7P_2S_2Pd$ (865.23 g/mol): calc. C 55.55, H 4.62; found: C 55.40, H 4.53. ΛM (nitroethane, 26 °C): 65 $\Omega^{-1}cm^2m\tilde{o}l^{-1}$. $^{31}P\{^1H\}$ NMR (δ, 81.01 MHz, $CDCl_3$, 21 °C) 71.01 (s); ^{1}H NMR (δ, 200.13 MHz, $CDCl_3$, 21 °C) 2.27 (s, 6H, OTs-CH_3), 2.69 (m, 4H, CH_2), 5.15 (br s, 2H, H_2O), 6.90-7.79 (m, 28H, Ar)

Preparation of [Pd(H_2O)$_2$(*o*-MeO-dppe)](OTs)$_2$ (3b) and [Pd(H_2O)$_2$(*o*-MeO-dppp)](OTs)$_2$ (4b)

A solid sample of AgOTs (125.54 mg, 0.45 mmol) was added to a stirred solution of **3a** or **4a**, (0.22 mmol) in CH_2Cl_2 (40 mL) at room temperature. After 3 h, the precipitated AgCl was removed by filtration of the suspension through a celite column and the clear filtrate was concentrated to ca. 3 mL. Addition of a 1:1 (v:v) mixture of *n*-pentane/diethylether (15 mL) led to the precipitation of **3b**

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or **4b** as a yellow microcrystalline solid, which was filtered off, washed with *n*-pentane, and dried under a stream of nitrogen.

Complex 3b: 145.7 mg (66%). $C_{44}H_{50}O_{12}P_2S_2Pd$ (1003.32 g/mol): calc. C 52.70, H 4.98; found: C 52.50, H 4.60. ΛM (nitroethane, 26 °C): 98 $\Omega^{-1}cm^2mol^{-1}$. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, 21 °C) 69.73 (s), ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 °C) 2.29 (s, 6H, OTs-CH_3), 2.78 (m, 4H, PCH_2), 3.66 (s, 12H, OCH_3), 4.43 (br s, 4H, H_2O), 6.97-7.59 (m, 24H, Ar)

Complex 4b: 190.3 mg (85%). $C_{45}H_{52}O_{12}P_2S_2Pd$ (1017.35 g/mol): calc. C 53.12, H 5.15; found: C 53.14, H 5.18. ΛM (nitroethane, 26 °C): 100 $\Omega^{-1}cm^2mol^{-1}$. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, 21 °C) 13.72 (s); ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 °C) 2.27 (m, 2H, CH_2), 2.34 (s, 6H, OTs-CH_3), 2.75 (m, 4H, PCH_2), 4.05 (s, 16H, OCH_3 + H_2O), 6.90-7.60 (m, 24H, Ar); $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, -80 °C) -4.46 (s); ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, -80 °C) 2.31 (s, 6H, OTs-CH_3), 2.35 (m, 2H, CH_2), 3.02 (m, 4H, PCH_2), 3.97 (s, 6H, Ar_{ax}-*o*-OCH_3), 4.33 (s, 6H, Ar_{eq}-*o*-OCH_3), 6.4-7.8 (m, 24H, Ar), the water resonance was not detected at -80 °C

Preparation of PdCl(Me)(*o*-MeO-dppe) (3c) and PdCl(Me)(*o*-MeO-dppp) (4c)

A solid sample of PdCl(Me)(COD) (52.99 mg, 0.20 mmol) was added to a stirred solution of the appropriate diphosphine ligand *o*-MeO-dppe or *o*-MeO-dppp (0.20 mmol) in CH_2Cl_2 (20 mL) at room temperature. After 1 h, the resulting colourless solution was concentrated to ca. 5 mL under reduced pressure. Addition of a 1:1 (v:v) mixture of *n*-pentane/diethylether (20 mL) led to the complete precipitation of **3c** or **4c** as an off-white solid, which was filtered off, washed with *n*-pentane, and dried under a stream of nitrogen.

Complex 3c: 105.4 mg (78%). $C_{31}H_{35}ClO_4P_2Pd$ (675.43 g/mol): calc. C 55.13, H 5.22; found: C 55.09, H 5.24. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, $CDCl_3$, 21 ^oC) 61.09 (d, $^2J_{PP}$ = 22.0 Hz), 39.07 (d); ^1H NMR (δ, 200.13 MHz, $CDCl_3$, 21 ^oC) 0.40 (dd, $^3J_{HPtrans}$ = 8.0 Hz, $^3J_{HPcis}$ = 3.2 Hz, 3H, PdC*H*$_3$), 2.19-2.93 (m, 4H, C*H*2), 3.59 (s, 6H, OC*H*$_3$), 3.60 (s, 6H, OC*H*$_3$), 6.87-7.91 (m, 16H, Ar); $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, -70 ^oC) 60.70 (d, $^2J_{PP}$ = 23.2 Hz, P_A), 38.32 (d, P_M); ^1H NMR (δ, 400.16 MHz, CD_2Cl_2, -70 ^oC) 0.40 (dd, $^3J_{HPM}$ = 8.0 Hz, $^3J_{HPA}$ = 3.0 Hz, 3H, PdC*H*$_3$), 2.08 (m, 1H, PCH*H*), 2.38 (m, 1H, P'CH*H*), 2.91 (dt, $^2J_{HP}$ = 56.0 Hz, $^3J_{HH}$ = 13.6 Hz, 1H, PC*H*H), 3.08 (dt, $^2J_{HP}$ = 56.0 Hz, $^3J_{HH}$ = 13.6 Hz, 1H, P'C*H*H), 3.42 (s, 3H, OC*H*$_3$), 3.44 (s, 3H, OC*H*$_3$), 3.76 (s, 6H, OC*H*$_3$), 6.72-7.73 (m, 14H, Ar), 8.45 (dd, $^2J_{HP}$ = 15.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1H, *o-H*-Ar$_{ax.}$(P_A)), 8.61 (dd, $^2J_{HP}$ = 15.1 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, *o-H*-Ar$_{ax.}$(P_M))

Complex 4c: 92.4 mg (67%). $C_{32}H_{37}ClO_4P_2Pd$ (689.46 g/mol): calc. C 55.75, H 5.41; found: C 55.74, H 5.43. $^{31}P\{^1H\}$ NMR (δ, 81.01 MHz, $CDCl_3$, 21 ^oC) 30.80 (d, $^2J_{PP}$ = 52.5 Hz), -0.56 (d); ^1H NMR (δ, 200.13 MHz, $CDCl_3$, 21 ^oC) 0.32 (dd, $^3J_{HPtrans}$ = 7.9 Hz, $^3J_{HPcis}$ = 3.5 Hz, PdC*H*$_3$), 1.92 (m, 2H, C*H*$_2$), 2.43 (m, 2H, PC*H*$_2$), 2.57 (m, 2H, PC*H*$_2$), 3.66 (s, 6H, OC*H*$_3$), 3.76 (s, 6H, OC*H*$_3$), 6.87-7.58 (m, 16H, Ar); $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, -70 ^oC) 30.88 (d, $^2J_{PP}$ = 51.4 Hz, P_A), -2.42 (d, P_M); ^1H NMR (δ, 400.16 MHz, CD_2Cl_2, -70 ^oC) -0.89 (dd, $^3J_{HPM}$ = 7.7 Hz, $^3J_{HPA}$ = 3.2 Hz, PdC*H*$_3$), 1.70 (m, 1H, CH*H*)), 1.92 (m, 1H, C*H*H), 2.20 (m, 1H, PCH*H*), 2.30 (m, 1H, P'CH*H*), 2.48 (m, 1H, PC*H*H), 2.79 (m, 1H, P'C*H*H), 3.56 (s, 3H, OC*H*$_3$), 3.67 (s, 3H, OC*H*$_3$), 3.69 (s, 3H, OC*H*$_3$), 3.72 (s, 3H, OC*H*$_3$), 6.67-7.71 (m, 14H, Ar), 8.55 (dd, $^2J_{HP}$ = 16.4 Hz, $^3J_{HH}$ = 7.3 Hz, 1H, *o-H*-Ar$_{ax.}$(P_A)), 8.74 (dd, $^2J_{HP}$ = 14.7 Hz, $^3J_{HH}$ = 7.1 Hz, 1H, *o-H*-Ar$_{ax.}$(P_M))

Preparation of Pd(OAc)$_2$(*o*-MeO-dppe) (3d) and Pd(OAc)$_2$(*o*-MeO-dppp) (4d)

In a Schlenk flask silver acetate (128.5 mg, 0.77 mmol) was added to a solution of complex **3a** or **4a**, (0.35 mmol) in dichloromethane (20 mL). The solution was allowed to stir for half an hour at room temperature. Afterwards AgCl was

removed by filtration of the suspension through a plug of celite. The clear filtrate was concentrated to ca. 3 mL and a solvent mixture of *n*-hexane and diethylether (1:1) (v:v) (20 mL) was added under nitrogen in order to precipitate the product as a yellow solid, which was filtered off and dried under a stream of nitrogen.

Complex 3d: 161.1 mg (62%). $C_{34}H_{38}O_8P_2Pd$ (742.42 g/mol): calc. C 54.96, H 5.15; found: C 54.94, H 5.18. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, 21 ^oC) 61.94 (s); ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 ^oC) 1.30 (s, 6H, CH_3COO), 2.77 (m, 4H, CH_2), 3.73 (s, 12H, OCH_3), 6.95-8.04 (m, 16H, Ar)
Complex 4d: 187.9 mg (71%). $C_{35}H_{40}O_8P_2Pd$ (756.42 g/mol): calc. C 55.53, H 5.33; found: C 55.49, H 5.35. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, 21 ^oC) 14.40 (s); ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 ^oC) 1.25 (br s, 6H, CH_3COO), 1.98 (m, 2H, CH_2), 2.40 (m, 4H, CH_2-P), 3.70 (s, 12H, OCH_3), 6.90-7.60 (m, 16H, Ar)

NMR studies

Variable-temperature ^1H and $^{31}P\{^1H\}$ NMR studies of 3a, 4a, and 4b in CD_2Cl_2

A solution of the appropriate complex (0.015 mmol) in CD_2Cl_2 (0.8 mL) was transferred under nitrogen into a 5 mm NMR tube, which was placed into a NMR probe at 20 °C. ^1H and $^{31}P\{^1H\}$ NMR spectra were acquired every 10 ^oC in the temperature range from 20 to -80 ^oC.

***In situ* HP-NMR studies of the CO-ethene copolymerisation with 2b and 4b as catalyst precursors in CD_2Cl_2/TFE**

A 10 mm sapphire NMR tube was charged with a solution of **2b** or **4b**, (0.02 mmol) in a 1:1 (v:v) mixture of CD_2Cl_2/TFE (2 mL) under nitrogen at room temperature and then placed into a NMR probe at 20 ^oC. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded at this temperature and then at -40 ^oC. Analogous spectra were recorded at the same temperatures after the sapphire tube was charged first with a 1:19 mixture of $^{13}CO/^{12}CO$ to 20 bar and then with ethene to 40 bar.

***Operando* HP-NMR studies of the CO-ethene copolymerisation with 2b and 4b as catalyst precursors in either CD_2Cl_2/TFE or MeOD-d_4**

A 10 mm sapphire NMR tube was charged with a solution of **2b** or **4b**, (0.02 mmol) in either a 1:1 (v:v) mixture of CD_2Cl_2/TFE or MeOD-d_4 (2 mL) under nitrogen at room temperature and then placed into a NMR probe at 20 ^oC. After $^{31}P\{^1H\}$ and ^1H (only for the study in MeOD-d_4) NMR spectra were recorded, the sapphire tube was removed from the NMR probe, charged with CO to 20 bar, and placed again into the NMR probe at 20 ^oC. After the spectra were recorded, the sapphire tube was removed from the NMR probe, charged with ethylene to 40 bar, and placed again into the NMR probe at 20 ^oC. The reaction was followed by variable-temperature NMR spectroscopy in the temperature range from 20 to 85 ^oC. After 1 h at 85 ^oC, the tube was cooled to 20 ^oC, which was followed by the acquisition of the last spectra. Once the tube was removed from the probe head, the copolymer appeared as a off-white solid layer over a colourless solution.

Catalytic reactions

Catalytic reactions in MeOH or TFE with 1b-4b as catalyst precursors

Typically, MeOH or TFE, (100 mL), was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.0048 mmol). When the catalytic reactions were performed with additives such as *p*-toluenesulphonic acid monohydrate (*p*-TsOH) and 1,4-benzoquinone (BQ), they were added together with the catalyst precursor into the autoclave. The autoclave was charged with a 1:1 CO/C_2H_4 mixture to 30 bar at room temperature and then heated. As soon as the temperature reached 85 ^oC and the pressure was equilibrated to 40 bar, stirring (1200 rpm) was started. After the desired time (1 or 3 h), the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. Due to the much higher solubility capacity of TFE for the alt-ethene-CO materials as compared to MeOH, two different procedures were employed to collect the polymer produced in the two solvents. For the experiments in MeOH, the insoluble copolymer was filtered off, washed with MeOH, and dried under vacuum at 60 ^oC to constant weight. For the experiments in TFE, the catalysis mixture, extremely viscous for the dissolved polymer, was concentrated to dryness under vacuum and the residue was then washed and dried as above. In all of the experiments the solutions were analysed by GC/MS.

Catalytic reactions in water-acetic acid with 1a-4a as catalyst precursors

A mixture of acetic acid (AcOH) and distilled water (100 mL) was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing 0.0048 mmol of catalyst precursor. The autoclave was charged with a 1:1 CO/C_2H_4 mixture to 30 bar at room temperature and then heated. As soon as the temperature reached 85 ^oC and the pressure was equilibrated to 40 bar,

stirring (1200 rpm) was started. After the desired time(1 or 2 h), the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. The insoluble copolymer was filtered off, washed with water, and dried under vacuum at 60 °C to constant weight. Experiments were carried out in water-AcOH mixtures with water in the range from 55 to 85 mol%.

Catalytic reactions in CH_2Cl_2 with 1c-4c as catalyst precursors

CH_2Cl_2 (75 mL), saturated with CO at room temperature, was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.010 mmol) and NaBArF (0.012 mmol). The autoclave was charged with a 1:1 CO/C_2H_4 mixture to 30 bar at room temperature and then heated. As soon as the temperature reached 50 °C and the pressure was equilibrated to 40 bar, stirring (1200 rpm) was started. After 20 min, the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. The insoluble copolymer was filtered off, washed with CH_2Cl_2, and dried under vacuum at 60 °C to constant weight.

Catalytic reactions in toluene with 1c-4c as catalyst precursors

A solution of solid MAO (58.02 mg, 1.0 mmol) in toluene (75 mL), saturated with CO at room temperature, was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.010 mmol). The autoclave was charged with a 1:1 CO/C_2H_4 mixture to 30 bar at room temperature and then heated. As soon as the temperature reached 60 °C and the pressure was equilibrated to 40 bar, stirring (1200 rpm) was started. After 2 h, the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. The reaction mixture was treated with MeOH acidified with dilute HCl. The insoluble copolymer was filtered off, washed with MeOH, and dried under vacuum at 60 °C to constant weight.

Characterisation of the alt-ethene-CO copolymers obtained in TFE

Polyketone products were analysed by IR, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopies. The NMR measurements were performed in a 1:1 (v:v) mixture of 1,1,1,3,3,3-hexafluoroisopropanol-d_2/C_6H_6-d_6 showing a perfectly alternating structure. The entire polymer samples were featured by the presence of four different combinations of end groups in the following order of abundance: keto-ester (**KE**) > diketone (**KK**) >> vinyl-ester (**VE**) > vinyl-ketone (**VK**). The number-average molecular weight (M_n) of the copolymers was determined by ^{1}H NMR spectroscopy. NMR and IR data for a representative example are reported below: ^{1}H NMR (δ, 400.13 MHz, 21 ^{o}C) 0.93 (t, $^{3}J_{HH}$ = 7.4 Hz, C(O)CH_2CH_3), 2.17 (q, $^{3}J_{HH}$ = 7.4 Hz, C(O)CH_2CH_3), 2.51 (br s, $CH_2C(O)CH_2$), 4.25 (q, $^{3}J_{HF}$ = 8.0 Hz, C(O)OCH_2CF_3), 5.68 (m, C(O)CH=CH_2), 6.06 (m, C(O)CH=CHH'), 6.15 (m, C(O)CH=CHH'); $^{13}C\{^{1}H\}$ NMR (δ, 100.62 MHz, 21 ^{o}C) 6.94 (C(O)CH_2CH_3), 26.80 ($CH_2C(O)OCH_2CF_3$), 35.04 ($CH_2C(O)CH_2$), 60.27 ($^{2}J_{CF}$ = 35.9 Hz, C(O)OCH_2CF_3), 124.10 ($^{1}J_{CF}$ = 283.6 Hz, C(O)OCH_2CF_3), 172.14 (C(O)OCH_2CF_3), 209.85 (C(O)$CH_2CH_2C(O)OCH_2CF_3$), 210.90 (CH_2C(O)CH_2), 214.32 (C(O)CH_2CH_3). The vinyl resonances were not assigned as obscured by other carbons. IR (KBr pellets, cm^{-1}): 3392 (w), 2912 (m), 1695 (vs), 1407 (s), 1332 (s), 1259 (m), 1165 (m), 1055 (s), 809 (m), 592 (m)

X-Ray crystallography

Suitable crystals of **3a**·2.3 CH_2Cl_2 and **4a** for single crystal X-ray structure analysis were obtained by slow diffusion of *n*-hexane into a saturated CH_2Cl_2 solution of either **3a** or **4a**, while crystal of compounds **3d** and **4d** were obtained by diffusion of toluene into a saturated dichloromethane solution of **3d** and **4d**. X-ray diffraction intensity data were collected on Oxford Diffraction diffractometers, equipped with a graphite monocromator and a CCD area detector. While for **3a**·2.3 CH_2Cl_2, **4a** and **4d** $Mo_{K\alpha}$ radiation (λ= 0.71073 Å) was

employed, for **3d** $Cu_{K\alpha}$ radiation (λ= 1.54180 Å) was employed. Cell refinement, data reduction and empirical absorption correction were carried out with the Oxford diffraction software and SADABS.[29a] All structure determination calculations were performed with the WINGX package[29b] with SIR-97,[29c] SHELXL-97[29d] and ORTEP-3 programs.[29e] Final refinements based on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms, which were included using a riding model with isotropic U values depending on the Ueq of the adjacent carbon atoms.

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2.1.5. References

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The *o*-methoxy groups on the P-aryl rings effect in the carbon monoxide and ethene copolymerisation reaction by palladium(II)-diphosphine catalysts. A mechanistic study

Abstract

In this chapter, relevant steps in the CO/ethene copolymerisation reaction, such as the migratory insertion of [Pd(Me)(CO)(P-P)]BArF (ArF = 3,5-$(CF_3)_2$-C_6H_3) and the carbonylation of the β-keto chelates [Pd(CH_2CH_2C(O)Me)(P-P)]BArF have been studied by *in situ* HP-NMR spectroscopy. The (P-P) ligands used in this study were the 1,2-bis(di(2-methoxyphenyl)phosphino)ethane (MeO-dppe) and the 1,3-bis(di(2-methoxyphenyl)phosphino)propane) (MeO-dppp).

This study contributes to rationalise the higher catalytic activity of palladium(II) catalysts modified with *o*-methoxy substituted diphosphine ligands as compared to analogous palladium(II) catalysts with 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) ligands.

NMR studies have shown that the presence of *o*-MeO substituents on the P-aryl rings affects the kinetics of the CO/ethene copolymerisation. Unlike the catalysts with the dppe and dppp ligands, the rate of carbonylation of the *o*-MeO-modified β-keto chelates is limited by the Pd(alkyl)(CO) migratory insertion, which makes the overall copolymerisation process independent of the CO pressure.

2.2.1. Introduction

As described in *chapter 1*, perfectly alternating polyketones are high-performance thermoplastics obtainable by copolymerisation of carbon monoxide and alkenes, generally ethene, in the presence of Pd(II) catalysts modified with chelating diphosphines (**Scheme 1,** *chapter 2*, section 2.1, pag. 66).[1] The copolymerisation reactions are commonly performed in protic solvents (alcohols, preferentially methanol), yet aprotic solvents such as CH_2Cl_2 are used in reactions catalysed by palladium(II) alkyl precursors as well as in model mechanistic studies.[2]

In section 2.1 (pag. 67) we presented that the introduction of one *o*-methoxy substituent on each P-aryl ring of the ligand greatly enhances the productivity as compared to reactions promoted by catalysts with unsubstituted diphosphines.[3,2d] Both steric and electronic factors have been invoked to account for the positive effect of the *o*-methoxy groups on the catalyst activity, yet no clear-cut explanation has been put forward so far. Indeed, most of the previous hypotheses are based on indirect observations such as the decreased formation of catalytically inactive bis-chelates or binuclear species;[4] the reduced tendency to phosphine oxidation;[5a] the increased basicity of the metal center;[5b] and the reduced stability of catalyst resting states.[5c]

Intrigued by the possibility of elucidating the *o*-methoxy effect, it was decided to look at two well-known reactions occurring during the propagation step of the alternating CO/C_2H_4 copolymerisation: i) the migratory insertion of $[Pd(Me)(CO)(P\text{-}P)]^+$ complexes and ii) the carbonylation of the β-keto chelates $[Pd(CH_2CH_2C(O)Me)(P\text{-}P)]^+$ (**Scheme 1**).[5b,5c]

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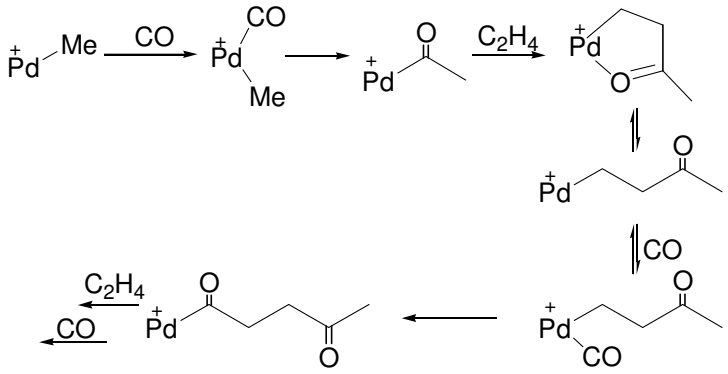


Scheme 1

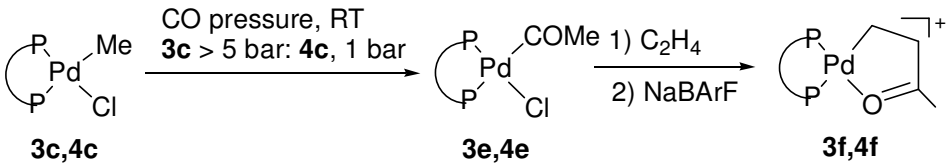
To this purpose, palladium complexes stabilised by the two couples of ligands shown in **Figure 1,** *chapter 2*, section 2.1, pag. 67 were employed as model compounds.[5b,5c]

In situ high-pressure NMR (HP-NMR) and IR techniques have been employed to determine kinetic and thermodynamic parameters, while batch catalytic reactions in different experimental conditions have provided information on the dependence of the reaction rate on CO and ethene pressures. Incorporation of the results obtained unambiguously show that the *o*-methoxy groups can interact with the metal centre, leading to a mechanism where the opening of the *β*-keto chelates and the overall copolymerisation rate as well are zero-order with respect to the CO pressure.

2.2.2. Results and Discussion

Generation of the β-Keto chelates [Pd(CH$_2$CH$_2$C(O)Me)(P-P)]BArF

The synthetic procedure to prepare the β-keto chelate complexes [Pd(CH$_2$CH$_2$C(O)Me)(P-P)]BArF (P-P = *o*-MeO-dppe, **3f**; *o*-MeO-dppp, **4f**; **(**ArF = 3,5-(CF$_3$)$_2$-C$_6$H$_3$) is illustrated in
Scheme 2.



3c,4c **3e,4e** **3f,4f**

Scheme 2. *In situ* synthesis of palladium(II) β-Keto chelates **3f** and **4f**

The methyl chloride precursors PdCl(Me)(P-P) (P-P = *o*-MeO-dppe, **3c**; *o*-MeO-dppp, **4c**) were conveniently prepared by reaction of PdCl(Me)(COD) (COD = cycloocta-1,5-diene) with the appropriate diphosphine and isolated as off-white crystalline solids in 78% and 67% yield, respectively.[2d]

Unambiguous characterisation of **3c** and **4c** in solution was achieved by variable-temperature ^{1}H and ^{31}P{^{1}H} NMR spectroscopy in CD_2Cl_2 (*chapter 2*, section 2.1, pag. 102).[2d] Complexes **3c** and **4c** exhibit fluxional behavior on the NMR time-scale due to the exchange of equatorial and axial aryl groups. The ^{1}H NMR spectrum at 21 °C of either complex displayed one set of resonances for the aryl hydrogens (δ 6.87-7.91 and 6.87-7.58, respectively) and two singlets for the methoxy groups (δ 3.59/3.60 and 3.66/3.76, respectively),[2d] which is consistent with the presence of two couples of equivalent aryl groups in the *o*-MeO-ligands. Decreasing the temperature led to a progressive broadening of all resonances. At -70 °C, the ^{1}H NMR spectra of **3c** and **4c** showed four singlets

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for the methoxy groups at δ 3.42, 3.44, 3.75, and 3.76 and δ 3.56, 3.67, 3.69, and 3.72, respectively. This pattern can be safely attributed to the formation of equatorially and axially oriented methoxy groups as illustrated in the sketch reported in **Figure 1**.[2d,6]

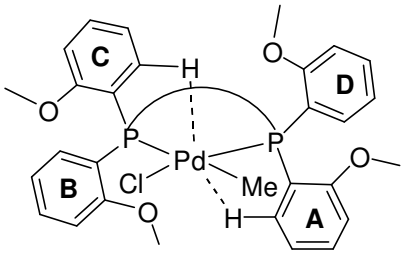

Figure 1. Low temperature conformation of **3c** and **4c**

The ^{1}H NMR spectra at -70 ^{o}C showed a significant downfield shift of the resonances of two aryl hydrogens (δ 8.450/8.61 and 8.55/8.8.74, respectively), which, on the basis of ^{1}H-^{31}P COSY experiments, can be assigned to the *o*-H atoms of the axial aryl rings **A** and **C** interacting with the metal centre. Analogous fluxional behavior has been previously reported for the X-ray authenticated complexes $PdCl_2$(P-P) (P-P = *o*-MeO-dppe, *o*-MeO-dppp).[2d] Further spectroscopic evidence in support of the conformation proposed in **Figure 1** was provided by a ^{1}H ROESY experiment at -70 ^{o}C of **3c**, indicating two significant correlations between the hydrogen atoms of the Pd methyl group and the *o*-H atoms of the aryl rings **A** and **D**. Based on this NMR study, it is highly probable that the slow-exchange conformation of PdCl(Me)(P-P) is stabilised by two *o*-methoxy oxygen atoms (from the equatorial aryl rings **B** and **D**) and by two *o*-H atoms (from the axial rings **A** and **C**), all pointing towards the palladium centre.

A single-crystal X-ray analysis of **3c**·$CHCl_3$ has confirmed the structure proposed in solution. Suitable crystals were obtained by slow diffusion of toluene into a $CHCl_3$ solution of **3c**. An ORTEP drawing of **3c**·$CHCl_3$ is shown in **Figure 2**, while crystal data and selected distances and angles are reported in **Table 1** and **Table 2**, respectively.

Table 1. Crystal Data and Structure Refinement Details for **3c**·$CHCl_3$

Empirical formula	$C_{32}H_{36}Cl_4O_4P_2Pd$
Molecular mass [g mol^{-1}]	794.75
Crystal color, shape	white, plate
Crystal size [mm]	0.2 × 0.1 × 0.05
Temperature [K]	223
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	9.294(6)
b [Å]	23.054(10)
c [Å]	22.295(11)
β [°]	94.75(5)
V [$Å^3$]	4761(4)
Z	4
Density (calculated), [g cm^{-3}]	1.109
F(000)	1616
θ range [°]	3.98-23.27
Radiation-wavelength [Å]	MoKα/0.71073
Absorption coefficient [mm^{-1}]	0.707
Reflections collected	18877
Independent reflections	6802
Data/restraints/parameters	5200/0/390
Gof on F^2	1.111
R1, wR2 ($I > 2\sigma(I)$)	0.1038, 0.2801
R1, wR2 (all data)	0.1190, 0.2970
Largest diff peak/hole [e $Å^{-3}$]	1.915/-2.054

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Table 2. Selected Bond Length [Å] and Bond Angles [°] for **3c**·$CHCl_3$

Pd(1)-P(1)	2.221(2)
Pd(1)-P(2)	2.343(2)
Pd(1)-Cl(1)	2.389(2)
Pd(1)-C(31)	2.095(8)
P(1)-Pd(1)-P(2)	86.27(9)
C(31)-Pd(1)-Cl(1)	89.30(20)
Intramolecular Distances [Å]	
Pd(1)-O(1)	3.573(6)
Pd(1)-O(2)	5.181(6)
Pd(1)-O(3)	5.271(7)
Pd(1)-O(4)	3.870(6)
Pd(1)-H(9)	2.809
Pd(1)-H(16)	2.855

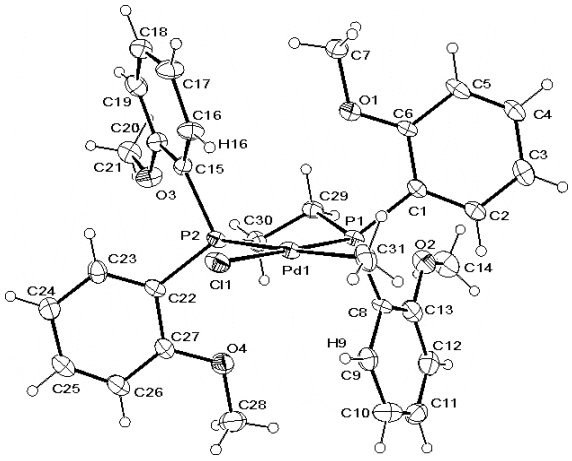

Figure 2. ORTEP plot of **3c**·$CHCl_3$. The solvent molecule was omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

The crystal structure shows a square-planar palladium centre coordinated by *cis* phosphorus atoms. The Pd-P bond lengths of 2.221(2) Å (*trans* to chloride) and 2.343(2) Å (*trans* to methyl) are in line with the greater *trans*-influence of the methyl group as compared to chloride. The four *o*-methoxy oxygen atoms are

arranged around the palladium centre in such a way that two of them, O(1) and O(4), occupy a *pseudo*-apical position of the metal coordination sphere (Pd…O distances of 3.573(6) and 3.870(6) Å), while the other two, O(2) and O(3), are close to pseudo-equatorial positions (Pd…O distances of 5.181(6) and 5.271(7) Å). All of these Pd…O distances are too large for an effective electrostatic interaction between palladium and the *o*-methoxy groups. In contrast, the *o*-H atoms H(9) and H(16) show short intramolecular Pd…H distances of 2.809 and 2.855 Å, respectively, which are comparable to those found in the crystal structure of $PdCl_2$(*o*-MeO-dppe).[2d]

Pressurising a CH_2Cl_2 solution of **3c** with >5 bar CO in a 10 mm-OD HP-NMR tube at room temperature led to the immediate formation of the acetyl complex PdCl(COMe)(*o*-MeO-dppe) (**3e**). In contrast, the formation of the complex PdCl(COMe)(*o*-MeO-dppp) (**4e**) from **4c** required no pressurisation as it was quantitatively obtained by bubbling CO into a CH_2Cl_2 solution of the methyl complex at room temperature (**Scheme 2**). Once formed, the acetyl complexes were stable in solution even in the absence of CO. Ethene bubbling into CH_2Cl_2 solutions of the acyl complexes **3e** and **4e** for 2 min, followed by the addition of stoichiometric NaBArF, gave the β-keto chelates **3f** and **4f** (**Scheme 2**). Compounds **3e**, **3f, 4e,** and **4f** have been unambiguously characterised by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Selected NMR data are reported in **Table 3** and **Table 4**, respectively.

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Table 3. $^{31}P\{^{1}H\}$NMR chemical shifts in ppm, (multiplicity), and [PP coupling constant in (Hz)] for the palladium complexes $[Pd(X)(Y)(P\text{-}P)]^{0/+}$ in CD_2Cl_2 solutions at {T in (^{o}C)}

P-P	X= COMe Y= Cl	X= $(CH_2)_2$COMe Y= $(CH_2)_2$COMe	X= $(CH_2)_2$COMe Y= CO	X= CO$(CH_2)_2$COMe Y= CO
o-MeO-dppe	37.50(d) [48.7] 27.80(d) **{22}**	58.00(d) [26.0] 26.77(d) **{-50}**	57.55(d) [29.5] 25.80(d) **{-50}**	36.02(d) [49.6] 16.74(d) **{-30}**
o-MeO-dppp	15.40(d) [75.9] -3.20(d) **{22}**	33.90(d) [57.6] -12.00(br.s)**{-90}**	21.30(d) [67.1] -30.50(br s) **{-90}**	8.86(d) [86.9] -29.16(d) **{-30}**

Table 4. ^{1}H NMR chemical shifts in ppm, (multiplicity) for the palladium complexes $[Pd(X)(Y)(P\text{-}P)]^{0/+}$ in CD_2Cl_2 solutions at {T in (^{o}C)}

P-P	X= COMe Y= Cl	X= $(CH_2)_2$COMe Y= $(CH_2)_2$COMe	X= $(CH_2)_2$COMe Y= CO	X= CO$(CH_2)_2$COMe Y= CO
o-MeO-dppe	1.79(s) CO*Me***{22}**	0.82(br m) PdCH_2 2.40(s) CO*Me* 3.13(m) CH_2COMe**{-50}**	0.30(br m) PdCH_2 2.10(s) CO*Me* 2.65(m) CH_2COMe**{-50}**	1.88(s) CO*Me* 3.10(m) CH_2COMe 2.25(m) PdCOCH_2 **{-30}**
o-MeO-dppp	1.73(s) CO*Me***{22}**	0.84(br m) PdCH_2 2.17(s) CO*Me* 2.89(m)CH_2COMe**{-90}**	0.37(br m) PdCH_2 1.51(s) CO*Me* 2.42(m) CH_2COMe**{-90}**	1.92(s) CO*Me* 2.52(m) CH_2COMe 2.08(m) PdCOCH_2 **{-30}**

Like the methyl chloride precursors **3c** and **4c**, the β-keto chelates **3f** and **4f** exhibit fluxional behavior in CD_2Cl_2 solution at room temperature, due to the exchange of equatorial and axial aryl groups. At -70 ^{o}C both compounds adopt the conformation shown in **Figure 3**.

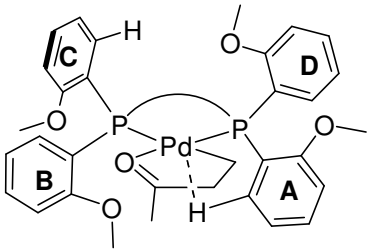

Figure 3. Low temperature conformation of **3f** and **4f**

The ^{1}H NMR spectra of **3f** and **4f** at -70 ^{o}C showed a multiplet at δ 8.48 and 8.28, respectively, which, on the basis of ^{1}H-^{31}P COSY experiments, was assigned to the *o*-H atom of ring **A**. At the same temperature, a ^{1}H-ROESY experiment of **3f** revealed the existence of significant correlations between the Pd-CH_2 unit and the *o*-H atoms of the aryl rings **A** and **D** and between the *o*-methoxy hydrogen atoms from the equatorial aryl ring **B** and the hydrogen atoms of the COMe unit. The stereochemical position of the aryl ring **C** could not be unambiguously determined, yet, due to the lack of the down-field shifted multiplet of the *o*-H atom of ring **C** in the ^{1}H NMR spectrum. It is very likely that ring **C** is turned around in such a way that the corresponding *o*-methoxy group points towards the metal centre. The β-keto chelates **3f** and **4f** and the corresponding derivatives with dppe (**1f**) and dppp (**2f**) were also characterised by *in situ* IR spectroscopy in CH_2Cl_2 at room temperature (**Table 5**). The spectra were scarcely informative except for showing a blue shift of ca. 6 cm^{-1} of the C=O stretching band for the *o*-methoxy-susbstituted complexes, which is consistent with the higher σ-donor ability of *o*-MeO-dppe and *o*-MeO-dppp as compared to dppe and dppp.

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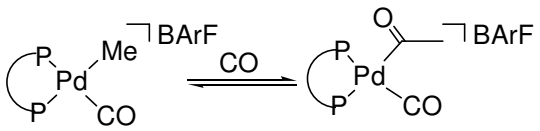
Table 5. Selected IR absorption bands in CH_2Cl_2 of selected complexes

(P-P)	[Pd($CH_2CH_2C(O)Me$)(P-P)]BArF ν(C=O)(cm^{-1})	[Pd(CO)(COMe)(P-P)]BArF ν(CO)/ν(C=O) (cm^{-1})
o-MeO-dppe	1636	2122/1696
dppe	1629	2130/1693
o-MeO-dppp	1636	2122/1700
dppp	1630	2129/1694

Generation and migratory insertion barriers of [PdMe(CO)(P-P)]BArF

The methyl carbonyl complexes [PdMe(CO)(P-P)]BArF (P-P = *o*-MeO-dppe, **3g**; *o*-MeO-dppp, **4g**) were selectively generated *in situ* by bubbling CO into a HP-NMR tube containing a CD_2Cl_2 solution of the corresponding chloride methyl complex at -100 °C. The kinetics of conversion of the methyl carbonyl complexes to the acetyl carbonyl products [Pd(CO)(COMe)(P-P)]BArF (P-P = *o*-MeO-dppe, **3h**; *o*-MeO-dppp, **4h**) (**Scheme 3**) were conveniently followed by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy in CD_2Cl_2. $^{31}P\{^1H\}$ and ^1H NMR data for **3g, 4g, 3h** and **4h** are given in **Table 6** and **Table 7**, respectively.



3g, 4g **3h, 4h**

Scheme 3. Migratory insertion of **3g** and **4g**

Table 6. $^{31}P\{^{1}H\}$ NMR chemical shifts in ppm, (multiplicity), and [PP coupling constant in Hz] for the palladium complexes [Pd(**X**)(**Y**)(P-P)]BArF in CD_2Cl_2 solutions at {T in ^{o}C}.

P-P	X= Me,Y= CO	X= COMe, Y= CO
o-MeO-dppe	57.59(d) [31.0] 24.34(d) **{-50}**	35.75(d) [48.7] 16.55(d) **{-40}**
o-MeO-dppp	22.40(d) [62.8] -29.9(br s) **{-90}**	8.00(d) [88.7] -28.5(d) **{-40}**

Table 7. ^{1}H NMR chemical shifts in ppm and (multiplicity) for the palladium complexes [Pd(**X**)(**Y**)(P-P)]BArF in CD_2Cl_2 solutions at {T in ^{o}C}.

P-P	X= Me, Y= CO	X= COMe, Y= CO
o-MeO-dppe	0.43(m) **{-50}**	1.65(s)**{-40}**
o-MeO-dppp	0.08(m) **{-90}**	1.88(s)**{-40}**

Consistent with the greater σ-donor ability of *o*-MeO-dppe and *o*-MeO-dppp vs. dppe and dppp, the IR spectra of the carbonyl acyl complexes **3h** and **4h** in CH_2Cl_2 (**Table 5**) showed a blue shift of the COMe absorption band (3-6 cm^{-1}) and a red shift of the CO absorption band (7-8 cm^{-1}) as compared to the analogue derivatives [Pd(CO)(COMe)(P-P)]BArF with dppe (**1h**) and dppp (**2h**).[2b,2c]

The study of the migratory insertion of the methyl(carbonyl) complexes was carried out at different CO pressures (5-20 bar), showing the reaction rate to be independent of the CO concentration. According to first-order kinetics, the free energy of activation for the migration insertion process was calculated applying the equation: $\Delta G^{\ddagger} = RT(\ln kT/h - \ln k_r)$ with $k_r = \ln 2/t_{1/2}$ (T = temperature during the conversion; $t_{1/2}$ = half-life time in sec).[2b,2c] The values of the activation energies for the migratory insertion in **3g** and **4g** are given in **Table 8** that also reports data previously reported for the dppe and dppp analogues [PdMe(CO)(P-P)]BArF (P-P = dppe, **1g**; dppp, **2g**).[2b,2c]

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Table 8. Experimental activation barriers and temperatures for migratory insertions.

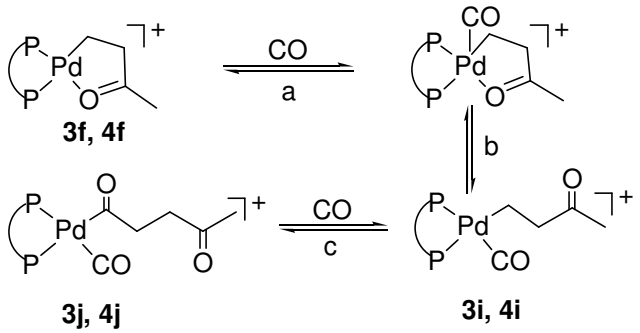
	$[Pd(Me)(CO)(\mathbf{L})]^+$			$[Pd(CH_2CH_2C(O)Me)(\mathbf{L})]^+$		$[Pd(CH_2CH_2C(O)Me)(CO)(\mathbf{L})]^+$			
L = P-P	**T (°C)**	**$t_{1/2}$ (min)**	**$\Delta G^{\ddagger}$ (kcal/mol)**	**T (°C)**	**$t_{1/2}$ (min)**	**p(CO) (bar)**	**T (°C)**	**$t_{1/2}$ (min)**	**$\Delta G^{\ddagger}$ (kcal/mol)**
o-MeO-dppe	-40	52	17.4(1)	-60	25	20	-40	100	17.7(1)
dppe[2b]	-40	12	16.9(1)	-20	15	20			
o-MeO-dppp	-80	105	14.6(1)	-90	6	20	-60	10	15.2(1)
dppp[2c]	-60	10	15.2(1)	-70	84	20			

The results obtained showed the migratory insertion of PdMe(CO) to be a low-energy process for all complexes, yet lower for the dppp complexes than for the dppe ones and, in particular, for the *o*-MeO-dppp complex **4g**, which is known to generate most active catalysts in several reaction media.[2d]

Carbonylation reactions of the *β*-Keto chelates

The reactions of the *β*-keto chelates **3f** and **4f** with 20 bar CO in CD_2Cl_2 were studied *in situ* by ^1H and $^{31}P\{^1H\}$ HPNMR spectroscopy at low temperature. HP-NMR tubes containing CD_2Cl_2 solutions of these complexes under nitrogen were cooled to ca. -100 °C, pressurised with 20 bar CO and then inserted into the NMR probe-head pre-cooled at -90 °C. The conversion of the *β*-keto chelates into the carbonyl acyl complexes $[Pd(CO)(COCH_2CH_2C(O)Me)(P\text{-}P)]BArF$ (P-P = *o*-MeO-dppe, **3j**; *o*-MeO-dppp, **4j**) was found to involve alkyl carbonyl intermediates of the formula $[Pd(CO)(CH_2CH_2C(O)Me)(P\text{-}P)]BArF$ (P-P = *o*-MeO-dppe, **3i**; *o*-MeO-dppp, **4i**) (**Scheme 4**). Selected $^{31}P\{^1H\}$ and ^1H NMR data of final products and intermediates are reported in **Table 3** and **Table 4**, respectively, while sequences of $^{31}P\{^1H\}$ NMR spectra acquired during the

carbonylation of either **3f** or **4f** with 20 bar CO are reported in **Figure 4** and **Figure 5**, respectively.



Scheme 4. Carbonylation of **3f** and **4f**

Compound **3f** started to convert into the alkyl carbonyl complex **3i** at -60 °C with a $t_{1/2}$ value of 25 min (**Figure 4**, trace **b**). Increasing the temperature to -40 °C led to the quantitative formation of **3i** already after recording the first $^{31}P\{^{1}H\}$ NMR spectrum (trace **c**). At this temperature, **3i** slowly converted into the acyl carbonyl complex **3j** (trace **d**), which was the only phosphorus-containing species at room temperature (trace **e**).

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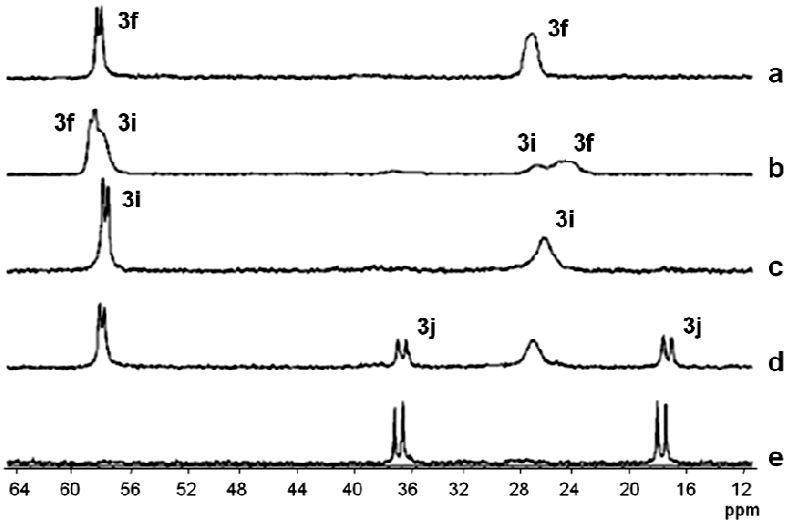

Figure 4. Variable-temperature $^{31}P\{^{1}H\}$ NMR study (sapphire tube, CD_2Cl_2, 81.01 MHz) of the carbonylation reaction of **3f**: (**a**) under nitrogen at -90 ^{o}C; (**b**) under CO (20 bar) after 40 minutes at -60 ^{o}C; (**c**) after 5 minutes at -40 ^{o}C; (**d**) after 80 minutes at -40 ^{o}C; (**e**) at room temperature

In an analogous experiment, **4f** was found to convert already at -90 ^{o}C into the alkyl carbonyl complex **4i** (**Figure 5**, trace **b**), which, in turn, started to transform into the final acyl carbonyl product **4j** (**Scheme 4**) at -80 ^{o}C. Due to the slow conversion rate at this temperature, the migratory insertion of **4i** was more conveniently evaluated at -60 ^{o}C (trace **d**).

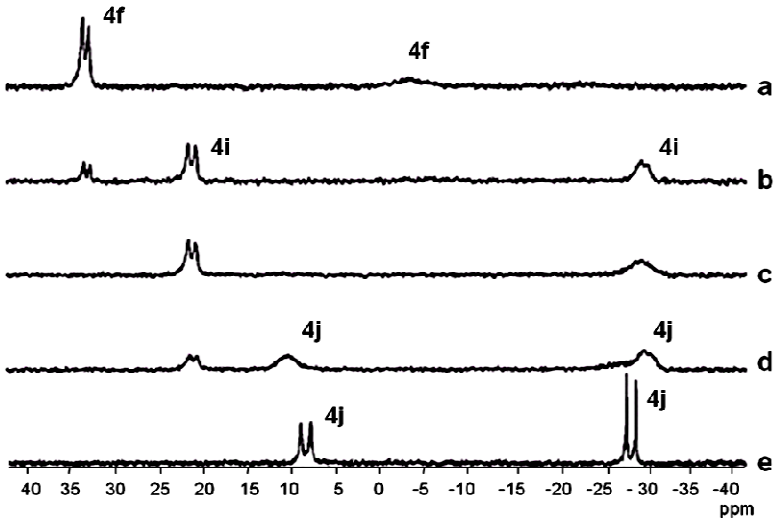

Figure 5. Variable-temperature $^{31}P\{^{1}H\}$ NMR study (sapphire tube, CD_2Cl_2, 81.01 MHz) of the carbonylation reaction of **4f**: (**a**) under nitrogen at -90 °C; (**b**) under CO (20 bar) after 30 min at -90 °C; (**c**) after 30 min at -80 °C; (**d**) after 10 min at -60 °C; (**e**) at room temperature

To the best of our knowledge, so far alkyl carbonyl compounds such as **3i** and **4i** have never been intercepted along the carbonylation of diphosphine-modified palladium alkyl complexes. For the other new products obtained *in situ*, unambiguous characterisation of the alkyl carbonyl complexes was achieved by NMR spectroscopy as well as by comparison with the spectra of similar or related complexes (i.e., γ-keto acyl chelates)[7] described in the literature (**Table 3** and **Table 4**). Experimental evidence supporting the alkyl carbonyl structure of **3i** and **4i** was provided by the ^{31}P chemical shifts and the $^{2}J_{PP}$ coupling constants that were practically identical to those of the methyl carbonyl complexes **3g** and **4g**. Moreover, the ^{1}H NMR shifts of the $PdCH_2CH_2C(O)Me$ units were significantly upfield shifted with respect to the values observed for the β-keto chelates (**3f** vs **3i**: C(O)CH_3, δ 2.40 vs 2.10; PdCH_2, δ 0.82 vs 0.30. **4f** vs **4i**: C(O)CH_3, δ 2.17 vs 1.51; PdCH_2, δ 0.84 vs 0.37). In particular, the high-

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field shift of the C(O)Me singlets agrees well with the de-coordination of the carbonyl-oxygen atom from the metal centre.[7g]

Temperatures and $t_{1/2}$ values for the conversion of the β-keto-chelates **3f** and **4f** into the corresponding alkyl carbonyl product and the activation energies of the migratory insertions of the latter compounds are reported in **Table 8**. The opening of the β-keto-chelate ring by CO is apparently easier for the *o*-MeO-susbstituted complexes than for the PPh_2-ones, which might well account for the greater catalytic activity of the former complexes in batch reactions.[2d,3,4,5]

On the basis of these data, one may safely conclude that the alkyl migration to CO (step **c** of **Scheme 4**) limits the rate of carbonylation of the β-keto-chelates **3f** and **4f**, which is a relevant step in the propagation mechanism of the CO/ethene copolymerisation by palladium(II)-diphoshine catalysis.[1] Accordingly, since the Pd(CO)alkyl migratory insertion is independent of the CO pressure, the overall copolymerisation process would be independent of the CO pressure, at least under a gas pressure of 20 bar. This result dramatically differs from the previously reported studies of CO/ethene copolymerisation by the PPh_2-precursors **1f** and **2f** where the actual copolymerisation rate depends on both CO and C_2H_4 pressure[8] and the opening of the β-keto-chelates by CO is the rate limiting step in the propagation step involving CO insertion (**Table 8**).[2b,2c]

Catalytic CO/ethene copolymerisation reactions

In an attempt of determining the dependence of the copolymerisation rate on CO and ethene pressures in actual catalytic conditions, several batch reactions were carried out using either the *o*-MeO-modified chloride methyl complex **4c** or the analogous dppp derivative **2c** in CH_2Cl_2 at 50 °C.[2d] The results of this study are summarised in **Table 9** that also reports data obtained in MeOH with the known catalyst $[Pd(H_2O)_2(o\text{-MeO-dppp})](OTs)_2$.[2d] In excellent accord with the

present kinetic study, the catalytic activity of **4c** did not vary with the CO pressure in the range from 5 to 30 bar (entries 1,2,4), whereas an increase in activity occurred on increasing the C_2H_4 pressure (entry 3 vs. 2). In contrast, the productivity of the dppp precursor **2c** showed a clear dependence on the CO pressure (entries 5-6), which is in accord with a previous kinetic study by Toniolo and Chaudhari for reactions carried out in MeOH.[8] The latter solvent was therefore used in reactions catalysed by the $[Pd(H_2O)_2$(*o*-MeO-dppp)$](OTs)_2$[2d] precursor (entries 7-9) that showed no dependence on the CO pressure above 10 bar, thus confirming and generalising the results of the present kinetic study in CH_2Cl_2. Noteworthy, a zero-order dependence on the CO pressure has been also reported for the CO/ethene/propene terpolymerisation catalysed by the water-soluble system palladium acetate/sulfonated *o*-MeO-dppp.[9]

Table 9. Ethene/CO copolymerisation reactions catalysed by palladium diphosphine precursors in different solvents

Entry[a]	Precursor	P(CO)	$P(C_2H_4)$	Productivity[b]
1	PdCl(Me)(*o*-MeO-dppp)	5	20	5.0
2	PdCl(Me)(*o*-MeO-dppp)	20	20	5.1
3	PdCl(Me)(*o*-MeO-dppp)	20	40	7.4
4	PdCl(Me)(*o*-MeO-dppp)	30	20	4.9
5	PdCl(Me)(dppp)	5	20	0.6
6	PdCl(Me)(dppp)	20	20	2.8
7[c]	$[Pd(H_2O)_2$(*o*-MeO-dppp)$](OTs)_2$	10	20	17.0
8[c]	$[Pd(H_2O)_2$(*o*-MeO-dppp)$](OTs)_2$	15	20	16.8
9[c]	$[Pd(H_2O)_2$(*o*-MeO-dppp)$](OTs)_2$	20	20	18.1

[a]Reaction conditions: precursor (0.010 mmol), CH_2Cl_2 (75 ml), NaBArF (1.5 equiv.), BQ (80 equiv.), 20 min., 50 °C, 1200 rpm; [b]Productivity: kg alt-E-CO (g Pd x h)$^{-1}$; [c]Reaction conditions: precursor (0.0024 mmol), MeOH (100 ml), 1 h, 85 °C, 1200 rpm.

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2.2.3. Conclusions

In situ high-pressure NMR studies supported by batch catalytic reactions have unambiguously shown that the presence of *o*-MeO substituents on the P-aryl rings affects the kinetics of the CO/ethene copolymerisation by palladium(II)-chelating diphosphine catalysis. Unlike analogous catalysts without *o*-methoxy-substituted ligands, the rate of carbonylation of the β-keto chelates is limited by the palladium(alkyl)(CO) migratory insertion, which makes the overall copolymerisation process independent of the CO pressure, at least in the range of the partial CO pressures investigated (5-30 bar).

No direct evidence for the coordination of the *o*-MeO group to palladium has been observed in the course of either migratory insertion or carbonylation reactions, yet NMR spectroscopy shows the aryl rings to adopt a conformation which favors the interaction between the *o*-MeO oxygen atoms and the metal centre.

2.2.4. Experimental Section

General Procedures

All reactions and manipulations were carried out under a nitrogen atmosphere by using Schlenk-type techniques. The solvents were generally distilled over dehydrating reagents and were deoxygenated before use. The reagents were used as purchased from Aldrich or Fluka, unless stated otherwise. PdCl(Me)(COD)[10], [PdCl(Me)(P-P)] ((P-P) = *o*-MeO-dppe (**3c**), *o*-MeO-dppp (**4c**))[2d], [Pd(CH_2CH_2C(O)Me)(dppe)]BArF (**1f**),[2b] (COD = cycloocta-1,5-diene; BArF = tetrakis 3,5-bis(trifluoromethyl)phenyl borate), [Pd(CH_2CH_2C(O)Me)(dppp)]BArF (**2f**),[2c] [Pd(CO)(C(O)Me)(dppe)]BArF (**1h**),[2b] [Pd(CO)(C(O)Me)(dppp)]BArF (**2h**)[2c] and NaBArF[11] were prepared according to

literature methods. All the isolated solid samples were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Copolymerisation reactions were performed with a 250 mL stainless steel autoclave, constructed at the ICCOM-CNR (Florence, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure during the catalytic reactions. GC/MS analyses of the solutions were performed on a Shimadzu QP2100S apparatus equipped with a SPB-1 Supelco fused silica capillary column (30m, 0.25 mm i.d., 0.25μm film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectra were obtained on either a Bruker ACP 200 (200.13, 50.32 and 81.01 MHz, respectively) or a Bruker Avance DRX-400 spectrometer (400.13, 100.62 and 161.98 MHz), respectively. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvents resonances (^{1}H and ^{13}C NMR) or 85% H_3PO_4 (^{31}P NMR). ^{1}H-^{31}P COSY spectra and ^{1}H ROESY were recorded on a Bruker Avance DRX-400 spectrometer. High pressure NMR experiments were carried out on Bruker ACP 200 using a 10mm sapphire NMR tube, which was purchased from Saphikon (Milford, NH), while the titanium high-pressure charging head was constructed at the ISSECC-CNR (Florence-Italy).[12] Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyser. Infrared spectra were recorded on a FT-IR Spectrum GX instrument (Perkin Elmer).

Syntheses

In situ Synthesis of the acetyl chloride complexes PdCl(COMe)(P-P)

In a typical experiment, a solid sample of the methyl chloride complex PdCl(Me)(P-P) (0.03 mmol) was dissolved in a Schlenk tube containing CD_2Cl_2 (2 mL) under nitrogen at room temperature. The resulting solution was first transferred into a 10 mm sapphire tube and then pressurised to >5 bar of CO at room temperature. Irrespective of the diphosphine the quantitative formation of the corresponding acetyl chloride complex PdCl(COMe)(P-P) (P-P = *o*-MeO-dppe, **3e**; *o*-MeO-dppp, **4e**). occurred at room temperature. The most relevant $^{31}P\{^1H\}$ and ^1H NMR chemical shifts and coupling constants for **3e** and **4e** are reported in **Table 3** and **Table 4**, respectively. The excess CO was released and nitrogen was gently bubbled through the solution previously cooled to -30 ^oC for 2 min to eliminate any trace of CO. Both complexes were found to be stable also in the absence of CO. Unlike **3e**, **4e** was generated even by bubbling CO through **4c** solutions for 5 minutes at room temperature. A procedure analogous to that described above was applied to prepare CH_2Cl_2 solutions of **3e** and **4e** for the IR characterisation: ν(C=O) 1669 cm^{-1} (**3e**), 1674 cm^{-1} (**4e)**

In situ Synthesis of the β-Keto chelates [Pd($CH_2CH_2C(O)Me$)(P-P)]BArF

In a typical experiment, a solution of PdCl(COMe)(P-P) (0.03 mmol) in CD_2Cl_2 (2 mL) was prepared as above in a Schlenk tube at -30 ^oC under nitrogen. Ethene was bubbled through the solution maintained at -30 ^oC for 2 min and then a solid sample of NaBArF (26,59 mg, 0.03 mmol) was added to the solution to scavenge the chloride ligand from Pd. The resulting solution was transferred into a 10 mm sapphire tube. $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired in the temperature range from 20 to -90 ^oC. Irrespective of the

diphosphine ligand, the $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of this sample showed the quantitative conversion of the chloride acyl complex into the corresponding β-keto chelate complex [Pd($CH_2CH_2C(O)Me$)(P-P)]BArF (P-P = *o*-MeO-dppe, **3f**; *o*-MeO-dppp, **4f**). IR spectra of **3f** and **4f** were acquired from CH_2Cl_2 solutions of these compounds prepared by applying the same synthetic protocol as described above, using CH_2Cl_2 instead of CD_2Cl_2. The IR values of the CO stretching frequencies are reported in **Table 5**.

Compound 3c: $^{31}P\{^{1}H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, -70 °C) 57.36 (d, $^{2}J_{PP}$ = 26.9 Hz, P_A), 25.43 (br, P_M); ^{1}H NMR (δ, 400.13 MHz, CD_2Cl_2, -70 °C) 0.82 (m, 1H, PdCH*H*), 1.21 (m, 1H, PdC*H*H), 2.05 (m, 2H, PCH_2), 2.42 (m, 3H, COCH_3), 2.58 (m, 2H, P'CH_2), 2.80 (m, 1H, COCH*H*), 3.08 (m, 4H, COC*H*H + OCH_3), 3.51 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.72-7.82 (m, 27H, Ar), 8.48 (dd, $^{2}J_{HP}$ = 17.0 Hz, $^{3}J_{HH}$ = 7.3 Hz, 1H, *o-H*-$Ar_{ax.}(P_A)$)
Compound 4c: $^{31}P\{^{1}H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, -70 °C) 33.51 (d, $^{2}J_{PP}$ = 57.9 Hz, P_A), -12.4 (br, P_M); ^{1}H NMR (δ, 400.13 MHz, CD_2Cl_2, -70 °C) 0.95 (m, 2H, PdCH_2), 2.21 (s, 3H, COCH_3), 2.31 (m, 3H, PC*H*H + CH_2), 2.51 (m, 2H, PCH*H* + P'CH*H*), 2.92 (m, 3H, $COCH_2$ + P'C*H*H), 3.59 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.62-7.83 (m, 27H, Ar), 8.28 (dd, $^{2}J_{HP}$ = 17.0 Hz, $^{3}J_{HH}$ = 7.1 Hz, 1H, *o-H*-$Ar_{ax.}(P_A)$)

In situ generation and migratory insertion barriers of [PdMe(CO)(P-P)]BArF. HP-NMR experiments

In a typical experiment, the methyl chloride complex PdCl(Me)(P-P) (0.03 mmol) was dissolved in deoxygenated CD_2Cl_2 (2 mL)and the resulting solution was then transferred into a 10 mm sapphire tube, which was cooled to -100 °C by means of an ethanol/liquid nitrogen bath. CO was bubbled through this solution for 2 min at this temperature, followed by the addition of NaBArF (26.59 mg, 0.03 mmol). The CO pressure was adjusted to the desired value (5-20 bar). The

solution was shaken for 2 min at -100 °C, followed by the introduction of the sapphire tube into the probe-head previously cooled to -90 °C. Irrespective of the diphosphine ligand, the $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra showed the quantitative conversion of the starting methyl chloride complex into the corresponding methyl carbonyl complexes [PdMe(CO)(P-P)]BArF (P-P = *o*-MeO-dppe, **3g;** *o*-MeO-dppp, **4g**) (selected $^{31}P\{^{1}H\}$ and ^{1}H NMR data of the methyl carbonyl complexes are reported in **Table 6** and **Table 7**, respectively). Afterwards the probe temperature was gradually increased and $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra were recorded at each intermediate temperature. Increasing the temperature converted each methyl carbonyl complex into the corresponding carbonyl acyl derivative [Pd(COMe)(CO)(P-P)]BArF (P-P= *o*-MeO-dppe, **3h**; *o*-MeO-dppp, **4h**) (selected $^{31}P\{^{1}H\}$ and ^{1}H NMR data of the carbonyl acyl complexes are reported in **Table 6** and **Table 7**, respectively). At the conversion temperature, the decrease in concentration of the methyl carbonyl complex was followed by $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra were taken at intervals of 5-10 min, depending on conditions. The reaction was followed for 2-3 half-lives. IR spectra of **3h** and **4h** were acquired from CH_2Cl_2 solutions of these compounds prepared by applying the same synthetic protocol as described above, using CH_2Cl_2 instead of CD_2Cl_2. The IR values of the CO stretching frequencies are reported in **Table 5**.

Carbonylation of the *β*-Keto chelates [Pd($CH_2CH_2C(O)Me$)(P-P)]BArF. HP-NMR experiments

CD_2Cl_2 (2 mL) solutions of the *β*-keto chelates [Pd($CH_2CH_2C(O)Me$)(P-P)]BArF (P-P = *o*-MeO-dppe, **3f**; *o*-MeO-dppp, **4f**) (0.03 mmol) were synthesised *in situ* in a Schlenk tube at -30 °C, as described above. Nitrogen was bubbled through the solution to eliminate any trace of ethene. The solutions were transferred into a 10 mm sapphire tube at room temperature. Then the sapphire tube was introduced in a pre-cooled NMR probe (-90 °C) and $^{31}P\{^{1}H\}$ and ^{1}H NMR

spectra were acquired at this temperature. The sapphire tube was then removed from the probe and immersed into an ethanol/liquid nitrogen thermostat bath (ca. -100 °C) before to be charged with CO (5-20 bar). Afterwards the sapphire tube was introduced again into the NMR probe head at -90 °C. $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra showed that the β-keto-chelate complexes were still present. Afterwards the probe temperature was gradually increased and $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra were recorded at each intermediate temperature. Increasing the temperature caused the conversion of the β-keto-chelate complex into the corresponding carbonyl acyl derivative [Pd(CO)($COCH_2CH_2C(O)Me$)(P-P)]BArF (P-P = *o*-MeO-dppe, **3j**; *o*-MeO-dppp, **4j**) *via* the alkyl carbonyl complexes [Pd(CO)($CH_2CH_2C(O)Me$)(P-P)]BArF (P-P = *o*-MeO-dppe, **3i**; *o*-MeO-dppp, **4i**). Selected high pressure $^{31}P\{^{1}H\}$ NMR spectra of the carbonylation of either **3f** or **4f** under 20 bar of CO are shown in **Figure 4** and **Figure 5**, respectively. Selected $^{31}P\{^{1}H\}$ and ^{1}H NMR data of the complexes **3i**, **4i**, **3j**, and **4j** are reported in **Table 3** and **Table 4**, respectively. At the conversion temperature the decrease in concentration of the β-keto chelates was followed by $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra were taken at intervals of 5-10 min, depending on conditions. The reaction was followed for 2-3 half-lives.

[Pd($CH_2CH_2C(O)Me$)(P-P)]BArF/[Pd($COCH_2CH_2C(O)Me$)(CO)(P-P)]BArF equilibria

Solutions of the carbonyl acyl complexes **3j** and **4j,** prepared as reported above in HPNMR tubes, were immersed in a thermostat bath at -20 °C. CO was released and then couples of vacuum-nitrogen cycles were applied. $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of these samples acquired at -20 °C let us to follow the transformation of the carbonyl acyl complexes into the corresponding β-chelates **3f** and **4f**.

Catalytic copolymerisation reactions in CH_2Cl_2

CH_2Cl_2 (75 mL), saturated with CO at room temperature, was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.010 mmol) and NaBArF (0.012 mmol). The autoclave was charged with the required pressures of CO and C_2H_4 at room temperature and then heated. As soon as the temperature reached 50 ^oC, stirring (1200 rpm) was started and the catalytic reaction was conducted under constant pressure. After 20 min, the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. The insoluble copolymer was filtered off, washed with CH_2Cl_2, and dried under vacuum at 60 ^oC to constant weight.

Catalytic copolymerisation reactions in MeOH

Typically, MeOH (100 mL), was introduced by suction into an autoclave (250 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.0024 mmol) and 1,4-benzoquinone (BQ, 0.192 mmol). The autoclave was charged with the desired pressure of CO and C_2H_4 at room temperature and then heated. As soon as the temperature reached 85 ^oC, stirring (1200 rpm) was started and the catalytic reaction was conducted under constant pressure for 1 h. Afterwards the autoclave was cooled by means of an ice-water bath and the unreacted gases were released. The insoluble copolymer was was filtered off, washed with MeOH, and dried under vacuum at 60 ^oC to constant weight.

Crystal structure determination of 3c·$CHCl_3$

Several crystallisation attempts with different solvents were performed and only by the diffusion of toluene into a $CHCl_3$ solution of **3c** gave single crystal, although of poor quality. X-ray diffraction intensity data were collected at 223 K on an Oxford Diffraction CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) using ω-scans. Cell refinement, data reduction and empirical absorption correction were carried out with the Oxford diffraction software and SADABS.[13a] All structure determination calculations were performed with the WINGX package[13b] with SIR-97,[13c] SHELXL-97[13d] and ORTEP-3 programs[13e] Final refinements based on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms, which were included using a riding model with isotropic *U* values depending on the *U*eq of the adjacent carbon atoms.

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Synthesis and characterisation of palladium(II) complexes with new diphosphine ligands. Application in the alternating copolymerisation of carbon monoxide and ethene.

Abstract

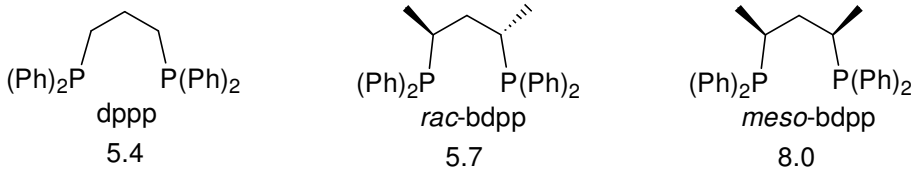
The diphosphine *rac*-2,4-bis(di(2-methoxyphenyl)phosphino)pentane (*rac*-*o*-MeO-bdpp) has been synthesised. The last ligand has been employed to synthesised new neutral palladium(II) complexes. Ligand and complexes have been fully characterised in solution by multinuclear NMR spectroscopy.

This C_2-briged ligand is compared with the C_3-briged and more rigid ligand bis-cationic diphosphonium-diphosphine 6,7-bis(di(2-methoxyphenyl)phosphinyl-2,2,4,4-tetra(di-2-methoxyphenyl)-2λ^4,4λ^4-diphosphoniumbicyclo[3.1.1]heptane-bis(PF_6) (*o*-MeO-PCP)(PF_6)$_2$) in the copolymerisation of CO with ethene in different reaction media in order to compare the effect of the backbone rigidity.

Irrespective of the reaction media, perfectly alternating polyketones were obtained in excellent yields and with number-average molecular weights ranging from 7.1 to 13.9 kg mol^{-1} with the diphosphonium-diphosphine catalysts and from 37.2 to 48.2 kg mol^{-1} with the diphosphine catalysts.

3.1. Introduction

As previous mentioned in *chapter 1*, the design of conformationally rigid polyphosphine ligands for the coordination of late transition metals is a subject of much interest in organometallic chemistry and homogeneous catalysis.[1] Indeed, decreasing the flexibility of the supporting ligand decreases the number of the possible conformations of the metal-ligand assembly, thus leading to improved selectivity. Unlike selectivity, the effect of the skeletal rigidity on the activity is unpredictable as it mainly depends on the reaction under investigation rather than on the structural and conformational properties of the metal-diphosphine precursor. In the particular case of the copolymerisation of CO with ethene by palladium(II) catalysis[2], a direct correlation between catalytic productivity and structural rigidity of the chelating diphosphine has been unambiguously observed for a number of ligands, including C_2-bridged[3] and C_3-bridged[4] diphosphines, 1,1'-bis(diorganylphosphino)ferrocenes,[5] and bis(phosphino)ferrocenophanes.[6] **Figure 1** shows the molecular sketches of two 1,3-diphosphine ligands bearing backbone substituents that decrease the ligand flexibility (*rac*-bdpp and *meso*-bdpp; bdpp = 2,4-bis(diphenylphosphino)pentane). Below each sketch is reported the productivity as kg(polyketone) (g(Pd) × h)$^{-1}$ exhibited by the corresponding palladium(II) catalysts under comparable reaction conditions. For comparative purposes, it is also reported the palladium(II) catalyst with the commonly used 1,3-bis(diphenylphosphino)propane (dppp) ligand.



dppp 5.4 | *rac*-bdpp 5.7 | *meso*-bdpp 8.0

Figure 1

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PALLADIUM COMPLEXES CONTAINING DIPHOSPHINE AND SULFONATED PHOSPHINE LIGANDS FOR C-C BOND FORMING REACTIONS. CATALYTIC AND MECHANISTIC STUDIES
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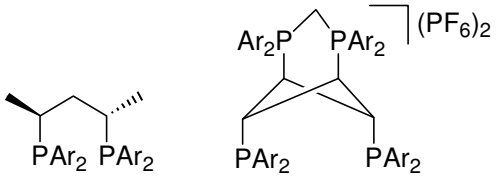
ISBN:978-84-691-0369-2/DL: T.2187-2007

In this work is reported the synthesis of the new diphosphine *rac*-2,4-bis(di(2-methoxyphenyl)phosphino)pentane (*rac*-*o*-MeO-bdpp) (**a**) (**Figure**)as well as its $PdCl_2$ and $Pd(OAc)_2$ complexes $PdCl_2$(*rac*-*o*-MeO-bdpp) (**1a**) and $Pd(OAc)_2$(*rac*-*o*-MeO-bdpp) (**2a**). All these palladium(II) complexes have been tested as catalyst precursors for the copolymerisation of CO and ethene in different solvents and compared with $PdCl_2$((*o*-MeO-PCP)$(PF_6)_2$) (**1b**) and $Pd(OAc)_2$((*o*-MeO-PCP)$(PF_6)_2$) (**2b**) containing the ligand bis-cationic diphosphonium-diphosphine 6,7-bis(di(2-methoxyphenyl)phosphinyl-2,2,4,4-tetra(di-2-methoxyphenyl)-2λ^4,4λ^4-diphosphoniumbicyclo[3.1.1]heptane-bis(PF_6) ((*o*-MeO-PCP)$(PF_6)_2$) (**b**) (**Figure 2**) respectively in order to study the effect of the backbone rigidity. All complexes have shown high activity and a remarkable control on the molecular weight of the alternating polyketone products.



rac-*o*-MeO-bdpp (*o*-MeO-PCP)$(PF_6)_2$

a **b**

Ar = 2-methoxyphenyl

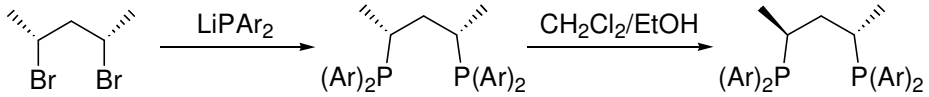
Figure 2

3.2. Results and discussion

Syntheses

Synthesis of the ligand

The diphosphine *rac-o*-MeO-bdpp was synthesised by the reaction of $LiPAr_2$ (Ar = 2-methoxyphenyl)[7] with a 26/74 *meso/rac* mixture of 2,4-dibromopentane in THF (**Scheme 1**). Only the *rac* isomer of *o*-MeO-bdpp could be isolated in a pure form (36% yield) as an white off solid by recrystallisation of the stereoisomeric mixture from CH_2Cl_2/ethanol.



meso/rac-o-MeO-bdpp *rac-o*-MeO-bdpp

Ar = 2-methoxyphenyl

Scheme 1

Synthesis and characterisation of the catalytic precursors

The reaction of *rac-o*-MeO-bdpp with $PdCl_2(COD)$ in CH_2Cl_2 gave $PdCl_2$(*rac-o*-MeO-bdpp) (**1a**), while the analogous reaction with $Pd(OAc)_2$ yielded $Pd(OAc)_2$(*rac-o*-MeO-bdpp) (**2a**) as an impure product. However, the reaction of **1a** with Ag(OAc) in CH_2Cl_2 gave **2a** in a pure form. **1a** and **2a** were obtained in 70% and 60% yield, respectively (**Scheme 2**). The diphosphine *rac-o*-MeO-bdpp is just the *o*-methoxy derivative of the well-known ligand *skew*phos ligand.[8]

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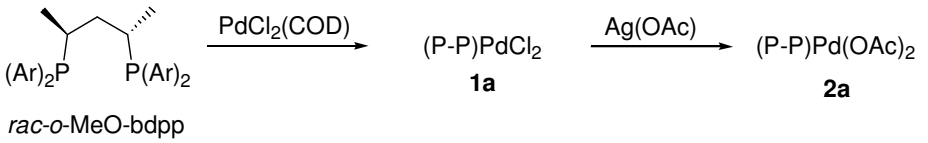

Scheme 2. Synthesis of the neutral palladium(II) complexes **1a** and **2a**

The crystal structure of **1a** shows the *S,S* stereoisomer (*S,S*-**1a**), which crystallises in the chiral space group $P2_1$. A selected ORTEP plot of *S,S*-**1a** is reported in **Figure 3**. Crystallographic data and selected bond distances and angles for (*S,S*)-**1a** are reported in **Table 1** and **Table 2**, respectively.

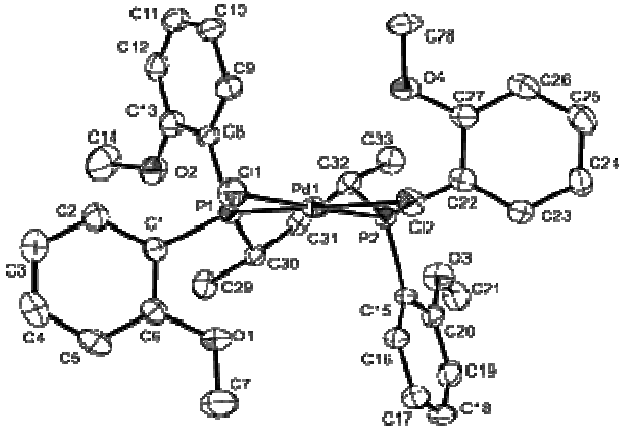

Figure 3. ORTEP plot of **1a**. Thermal ellipsoids are shown at the 30% probability level

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Table 1. Crystalographic data for (*S*,*S*) **1a**

Empirical formula	$C_{33}H_{38}Cl_2O_4P_2Pd$
Formula weight	737.87
T/K	293(2)
λ/Å	0.71073
Crystal system, space group	Monoclinic, $P2_1$
a/Å	10.6259(7)
b/Å	13.6492(11)
c/Å	11.9265(9)
α/°	90.0
β/°	107.937(7)
γ/°	90.0
V/ Å^3, Z	1645.7(2), 2
D_c/Mgm^{-3}	1.489
μ/mm^{-1}	0.859
F(000)	756
Crystal size/mm	0.40 × 0.20 × 0.10
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameter	10051/1/391
Goodness-of-fit on F^2	0.855
Final *R* indices	[$I > 2\sigma(I)$] $R1$ = 0.0451, w$R2$ = 0.0808
R indices (all data)	$R1$ = 0.1015, w$R2$ = 0.0949
Largest diff. Peak, hole/e Å^3	1.122, -0.375

Table 2. Selected bond distances (Å) and angles (°) for and (*S,S*)-**1a**

Pd(1)-P(1)	2.2671(11)
Pd(1)-P(2)	2.2757(11)
Pd(1)-Cl(1)	2.3620(11)
Pd(1)-Cl(2)	2.3608(10)
P(1)-Pd(1)-P(2)	90.11(4)
Cl(1)-Pd(1)-Cl(2)	91.53(4)
Cl(1)-Pd(1)-P(2)	177.98(4)
Cl(2)-Pd(1)-P(1)	179.62(5)
Intramolecular distances in (Å)	
Pd(1)-O(1)	3.5077(36)
Pd(1)-O(2)	5.1814(31)
Pd(1)-O(3)	5.1989(31)
Pd(1)-O(4)	3.4846(35)

The palladium centre is square-planar coordinated by two phosphorus and two chloride atoms. The deviation of the metal centre from the coordination plane, defined by the atoms P(1), P(2), Cl(1) and Cl(2), is 0.0192(7) Å in direction of C(1). (*S,S*)-**1a** exhibits a typical P(1)-Pd(1)-P(2) bite angle of 90.11(4)°, which is comparable to that of many other six-membered palladium diphosphine complexes.[9] The Pd(1)-P(1) and Pd(1)-P(2) bond lengths in (*S,S*)-**1a** are of 2.2671(11) and 2.2757(11) Å, respectively. Like in other *S,S-skew*phos metal complexes, the carbon backbone of the ligand in (*S*,*S*)-**1a** exhibits a diagonal disposition with respect to the coordination plane, which is the most common conformation for skewphos metal complexes.[8] Strictly related to the diagonal disposition of the C5 carbon backbone, the four 2-methoxyphenyl groups are disposed diagonally with respect to the palladium coordination plane, which is shown by the deviation of the four *ipso* carbon atoms from the coordination plane (C(1) 0.9327(51) Å, C(8) -1,7077(45) Å, C(15) 1.6957(43) Å and C(22) -0.8764 Å). Furthermore, two *o*-methoxy oxygen atoms, namely O(1) and O(4) show shorter intramolecular distances to Pd(1) (3.5077(36) Å and 3.4846(35) Å, respectively), while O(2) and O(3) show by far a higher intramolecular distance to Pd(1) of 5.1814(31) and 5.1989(31) Å, respectively.

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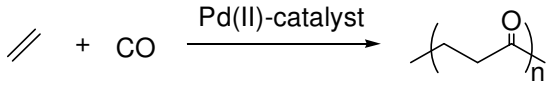
Catalytic copolymerisation of CO and ethene

The solvent of choice of most CO/C_2H_4 copolymerisation reactions by PdX_2(diphosphine) catalysis (**Scheme 3**) is either MeOH or water.



Scheme 3

This implies the use of weakly coordinating co-ligands (X = TsO^-, $CF_3CO_2^-$) to allow for the activation of either solvent to give Pd-H, Pd-OMe or Pd-OH initiators.[2] Recently, however, Toniolo et al. have shown that the bis-chloride and bis-acetate complexes PdX_2(diphosphine) (diphosphine = dppe, dppp, dppb) (X = Cl^-, OAc^-) can generate very active catalysts in water/AcOH mixtures.[10] Therefore, the bis-chloride complexes **1a** and **1b** were tested in different mixtures of water/AcOH under standard experimental conditions (40 bar 1/1 CO/ethene, 85ºC). The results obtained are reported in **Table 3**. Irrespective of catalyst and solvent composition, perfectly alternating polyketone products were obtained with exclusively ketone end-groups.

A maximum catalytic activity for **1a** was observed with the use of a 75/25 mol% mixture of water/AcOH (entry 3), while a mixture containing 65 mol% water was the optimum value for **1b** (entry 7). In reactions lasting 1 and 2 h, **1a** was slightly more active than **1b** but appreciably less stable with time (entries 3 and 4 vs. 7 and 8). However, the most striking catalytic difference between **1a** and **1b** was the M_n of the polyketone products: around 37 kg mol^{-1} with **1a** and 7 kg mol^{-1} with **1b** (**Table 3**). These results indicate that the chain-transfer rate is significantly faster in the reactions catalysed by **1b** than for the reactions catalysed by **1a**.

Table 3. Alternating copolymerisation of CO with ethene catalysed by $PdCl_2$(**a**), (**1a)** and $PdCl_2$(**b**), (**1b**) in water/AcOH[a]

Entry	Precatalyst	Water (mol%)	Time (h)	Polymer (g)	Productivity[b]	M_n (kg mol^{-1})
1	**1a**	55	1	4.12	7.74	
2	**1a**	65	1	4.75	8.93	37.4
3	**1a**	75	1	5.28	9.92	37.2
4	**1a**	75	2	7.84	7.37	
5	**1a**	85	1	3.91	7.35	
6	**1b**	55	1	3.10	5.83	
7	**1b**	65	1	3.70	6.95	7.3
8	**1b**	65	2	6.46	6.07	
9	**1b**	75	1	3.18	5.98	7.1
10	**1b**	85	1	2.19	4.11	

[a]Catalytic conditions: catalyst precursor, 0.005 mmol; $p(CO)/p(C_2H_4)$, 20/20 bar; water/AcOH, 100 ml; temperature, 85 °C; stirring rate, 1100 rpm. [b]Expressed as kg(polyketone) $(g(Pd) \times h)^{-1}$.

The mechanism of the CO/C_2H_4 copolymerisation by palladium(II)-diphosphine catalysis has been intensely studied over the last years and most of the elementary steps involved, especially chain-transfer and propagation, have been clarified.[2] **Scheme 4** provides a brief summary of the mechanism proposed for CO/ethene copolymerisation catalysed by $PdCl_2$(diphosphine) complexes in acidic aqueous media.[11]

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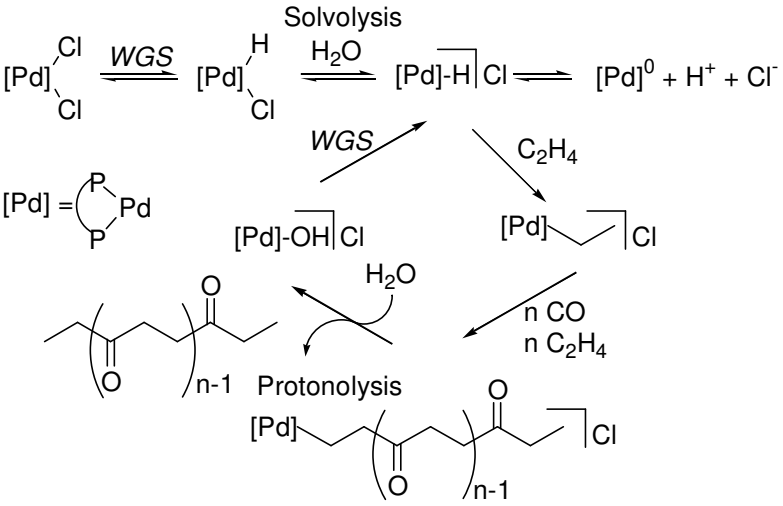

Scheme 4

It is agreed that the neutral palladium(II)-H complexes are generated from the bis-chloride precursors by a water gas shift reaction (WGS),[11] and then converted into the catalytically active cationic palladium(II) hydride species by a water-controlled solvolysis process.[11a] Toniolo[10] and Zudin[11] have also demonstrated that increasing the water proportion in the water/AcOH mixture increases the concentration of the cationic palladium(II)-H species by speeding up the solvolysis process. On the other hand, a too large proportion of water has been found to have a detrimental effect on the solubility of CO and C_2H_4.[10] This may account for the significant decrease in productivity (from 6.95 to 4.11 kg (g (Pd) x h)$^{-1}$) by increasing the water proportion from 65 to 85 mol% (Table 3, entries 7,9,10).

The chain-transfer reaction of CO/ethene copolymerisation performed in acidic aqueous media has been demonstrated to occur exclusively *via* protonolysis by water with formation of a Pd-OH unit that re-generates a Pd-H initiator by WGS.[12] In these conditions, the intimate mechanism of chain transfer involves β-hydride elimination in a β-keto alkyl chelate, followed by hydride migration to

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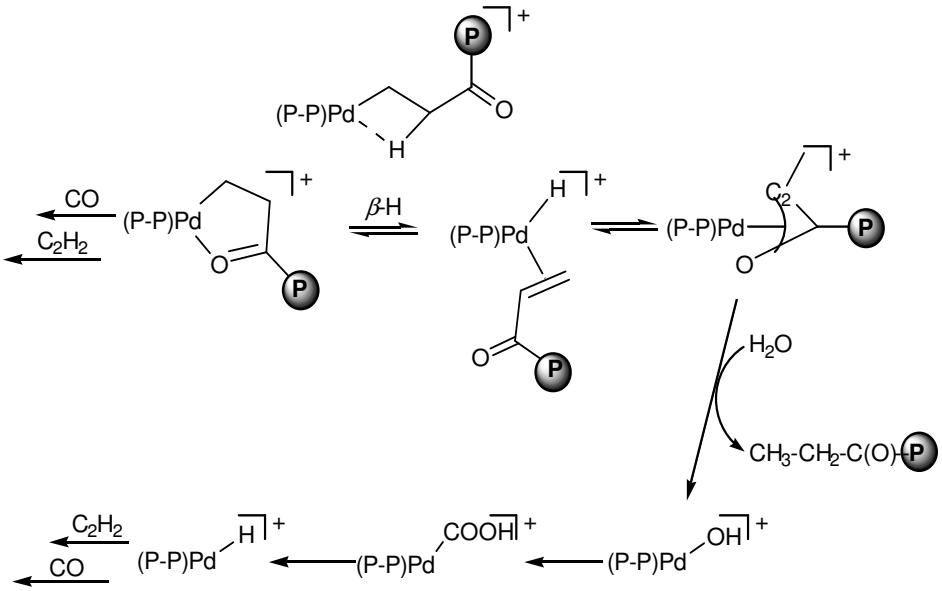
give an enolate whose regioselective protonation terminates the chain growth (**Scheme 5**).[13] The rate of the β-H elimination determines the overall chain transfer rate, hence it controls the molecular weight of the polyketone produced.[2] β-H elimination reactions in organometallics are steered by both electronic and steric factors.[14] In particular, it is agreed that the agostic interaction between the metal and β-hydrogens (precursor to hydrogentransfer to the metal) is favoured by a low electron density at the metal centre.



Scheme 5

In complexes of the same metal ion, the electron density at the metal depends on the electronic and steric characteristics of the supporting ligands as well as on the overall charge of the complex. In the present case, a lower electron-donating ability of (*o*-MeO-PCP)$(PF_6)_2$ (**b**) as compared to *rac*-*o*-MeO-bdpp (**a**) is indicated by the significantly shorter Pd-P bond distances in **1b**[15] as compared to **1a** (2.2546(13) and 2.2403(13) Å *vs*. 2.2671(11) and 2.2757(11)

Å). As a further, indirect proof of the lower metal basicity of complexes with (*o*-MeO-PCP)$(PF_6)_2$ vs. complexes with *rac*-*o*-MeO-bdpp, we have found that the IR spectrum of the bis-carbonyl complex *cis*-[Rh$(CO)_2$(*o*-MeO-PCP)]$(PF_6)_3$ shows, in CH_2Cl_2, ν(CO) bands at 2097 and 2052 cm^{-1},[15] while *cis*-[Rh$(CO)_2$(*rac*-*o*-MeO-bdpp)](PF_6) exhibits red-shifted bands at 2086 and 2036 cm^{-1}.

Besides metal basicity, the β-H elimination rate in the propagating palladium-alkyl (**Scheme 5**) might be influenced by the interaction of the metal centre with the oxygen atoms from the *o*-methoxy substituents. Indeed, evidence has been reported in the literature for the coordinative interaction of this oxygen to metal centres.[16] In the eventuality of an analogous interaction in the propagating alkyls generated by **1a** and **1b**, the oxygen atoms would compete with the β-hydrogens for coordination, with a retarding effect on the β-H elimination rate. In this mechanistic picture, the stereochemical rigidity of (*o*-MeO-PCP)$(PF_6)_2$ (**b**) would disfavour the interaction of the *o*-methoxy units with the palladium centre, whereas a simple twisting of the C_5 backbone of *rac*-*o*-MeO-bdpp would allow for an axial interaction between the *o*-methoxy groups and the metal centre.

In an attempt of gaining further information on the present copolymerisation reactions in water/AcOH, a catalytic run was performed in a HP-NMR tube containing D_2O/AcOH (45 mol% D_2O) and catalyst precursor $PdCl_2$(**a**) (**1a**). A selected sequence of $^{31}P\{^1H\}$ HP-NMR spectra is presented in **Figure 4**.

A 10 mm sapphire tube was charged with $PdCl_2$(**a**) (**1a**) (14.8 mg, 0.02 mmol) in a solvent mixture D_2O/AcOH (45 mol% D_2O) (2 ml). A $^{31}P\{^1H\}$ NMR spectrum acquired at 20 ^oC showed a broad resonance centred at 28.00 ppm (trace **a**).[17] The HP-NMR tube was then pressurised with a 1/1 mixture of CO/C_2H_4 to a total pressure of 40 bar and a $^{31}P\{^1H\}$ NMR spectrum was acquired at 20 ^oC (trace **b**), which showed no substantial change. The probe-head was heated to

85 °C for 1 h during which time $^{31}P\{^{1}H\}$ NMR spectra were acquired every 20 min. Since the first spectrum, a quite sharp singlet appeared at 25.5 ppm. The $^{31}P\{^{1}H\}$ spectrum acquired after 1 h at 85 °C is reported in **Figure 4** as trace **c**. When the probe-head was cooled to 20 °C, the $^{31}P\{^{1}H\}$ NMR spectrum showed the same broad hump (trace **d**) as in the initial spectrum (trace **a**). The tube was removed from the NMR probe showing formation of the copolymer as a white off powder.

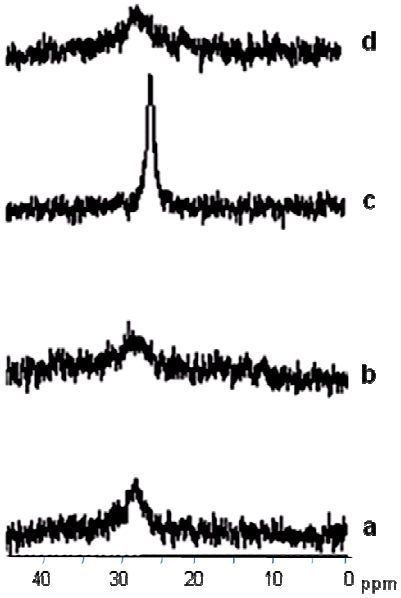


Figure 4. Selected $^{31}P\{^{1}H\}$ HPNMR spectra (sapphire tube, D_2O/AcOH, 20-85 °C, 81.01 MHz) recorded during a CO/C_2H_4 copolymerisation reaction catalysed by 1a: (**a**) **1a** suspended in D_2O/AcOH (45 mol% D_2O) at 20 °C; (**b**) after pressurisation of the tube with a 1/1 mixture of CO/C_2H_4 (40 bar total pressure) at 20 °C; (**c**) spectrum taken after 1 h at 85 °C); (**d**) after cooling to 20 °C

A very similar sequence of $^{31}P\{^{1}H\}$ HPNMR spectra has been observed for the CO/ethene copolymerisation catalysed by $Pd(CF_3CO_2)_2$(NaDPPPDS) in water.[12b] It was suggested, and the same can be said for the present case, that most of the palladium remains incorporated into the precursor from which a small and undetectable aliquot is delivered into the catalysis cycle.

The catalytic activity of the neutral bis-acetate complexes **2a** and **2b** was tested in MeOH in the presence of 2 or 20 equiv. of TsOH, which serves both as scavenger of the acetate ion and oxidising agent for Pd(0) species eventually formed by palladium(II) reduction (**Scheme 4**).[2] The results of this study are reported in **Table 4**.

Table 4. Alternating copolymerisation of CO with ethene catalysed by $Pd(OAc)_2$(**a**), (**2a**) and $Pd(OAc)_2$(**b**), (**2b**) in MeOH in the presence of TsOH[a]

Entry	Precatalyst	TsOH (equiv.)	Time (h)	Polymer (g)	Productivity[b]	M_n (kg mol^{-1})
1	**2a**	2	1	3.94	7.41	47.0
2	**2a**	2	3	11.54	7.23	
3	**2a**	20	1	2.90	5.45	48.2
4	**2a**	20	3	6.45	4.04	
5	**2b**	2	1	4.00	7.52	7.7
6	**2b**	2	3	4.50	2.82	
7	**2b**	20	1	5.21	9.79	13.9
8	**2b**	20	3	13.48	8.45	

[a]Catalytic conditions: catalyst precursor, 0.005 mmol; $p(CO)/p(C_2H_4)$, 20/20 bar; MeOH, 100 ml, temperature, 85 °C; stirring rate, 1100 rpm. [b]Expressed as kg(polyketone) (g(Pd) x h)$^{-1}$.

With either catalyst precursor, the copolymer contained keto and ester end-groups in a 1/1 ratio. As observed in water/AcOH as solvent, the *rac-o*-MeO-bdpp precursor, **2a**, gave higher-molecular-weight products (47.0-48.2 kg mol^{-1}) as compared to the (*o*-MeO-PCP)$(PF_6)_2$ one, **2b** (7.7-13.9 kg mol^{-1}). However,

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with either catalyst the copolymers exhibited larger M_n values as compared to the products obtained in water/AcOH, which is consistent with a slower chain transfer rate in MeOH than in water/AcOH. Increasing the concentration of TsOH had a detrimental effect on that of **2a** (entries 1 *vs* 3 and 2 *vs* 4) and a beneficial effect on the productivity of **2b** (entries 5 *vs* 7 and 6 *vs* 8). The lower activity in the presence of 2 equiv. of TsOH and the much higher M_n of the polyketones obtained with 20 equiv. of acid in the reactions with **2b** suggest that the acid concentration is important not only for decreasing the extent of palladium(II) reduction but also for stabilising the overall metal-ligand assembly, likely by inhibiting the deprotonation of the diphosphonium-diphosphine ligand with formation of ylide species.

The reverse dependence of the productivity on the acid concentration for the reactions catalysed by the *rac-o*-MeO-bdpp precursor **2a** (**Table 4**, entries 1-4) is quite surprising as the opposite trend is generally observed for CO/ethene copolymerization in MeOH by palladium(II)-diphosphine catalysis.[2] This effect could be a direct consequence of the presence of the *o*-methoxy substituents on the phenyl rings. Indeed, a large excess of TsOH, containing one water molecule of crystallisation, would promote the creation of a web of hydrogen-bonding interactions around the metal centre, involving not only the coordinated solvent molecules but also the four oxygen atoms of the *o*-methoxyphenyl groups. As a result, the palladium(II) centre would become less accessible to the incoming monomers,[18,19] and contemporaneously the beneficial effect of the *o*-methoxy groups on the propagation rate would be diminished and even lost.[2d,16,20]

Support to the hydrogen-bonding interactions around the palladium centre in *rac-o*-MeO-bdpp catalysis intermediates is provided by several molecular structures of palladium(II)-aquo complexes with tosylate anions, which show the presence of hydrogen bonds between the coordinated water molecules and the

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oxygen atoms of both tosylate ligands and counter-anions.[5c,18] Moreover, DFT calculations performed on cationic $[L_3Pd(H_2O)]^+$ compounds have confirmed that the stability of such compounds is due to an efficient interaction of the counter-anions with the coordinated water molecule.[21]

3.3. Conclusions

The pool of available chelating diphosphine ligands has been enriched by a new member. A standard procedure has been employed to prepare the *rac*-*o*-MeO-bdpp. The ligand has been used to coordinate $PdCl_2$ and $Pd(OAc)_2$ yielding square-planar complexes that generate active catalysts for the copolymerisation of CO and ethene in either water/AcOH mixtures or MeOH/TsOH. The synthesised complexes have been compared with $PdCl_2$ and $Pd(OAc)_2$ complexes with (*o*-MeO-PCP)$(PF_6)_2$ ligand in the CO ethene copolymerisation reaction using both, water/AcOH mixture in the case of neutral palladium dichloride complexes or MeOH in the case of palladium diacetate complexes, as solvent media. The perfectly alternating polyketones bear either exclusively ketone or 1:1 ketone:ester end groups depending on the reaction solvent. The polyketone products produced with the phosphine catalysts show number-average molecular weights up to five times bigger than those obtained with the diphosphonium-diphosphine catalysts. These results have been interpreted in terms of faster chain-transfer rate due to the electronic and steric properties of the diphosphonium diphosphine ligand.

3.4. Experimental Section

General procedures

All reactions and manipulations were carried out under a nitrogen atmosphere by using Schlenk-type techniques. The solvents were generally distilled over dehydrating reagents and were deoxygenated before use. The reagents were used as purchased from Aldrich or Fluka, unless stated otherwise. $PdCl_2$(COD) (COD = 1,5-cyclooctadiene)[22], bis(*o*-methoxyphenyl)phosphine[23] and *meso*/*rac*-2,4-pentanediol dimesylate[7] were prepared according to literature methods. $PdCl_2$((*o*-MeO-PCP)$(PF_6)_2$) and $Pd(OAc)_2$((*o*-MeO-PCP)$(PF_6)_2$) complexes were synthesised by Peter Brüeggeller et al..[15] All the isolated solid samples were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Copolymerisation reactions were performed with a 250 ml stainless steel autoclave, constructed at the ICCOM-CNR (Florence, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure over the catalytic reactions. GC/MS analyses of the solutions were performed on a Shimadzu QP 5000 apparatus equipped with a SPB-1 Supelco fused silica capillary column (30m, 0.25 mm i.d., 0.25μm film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectra were obtained on either a Bruker ACP 200 (200.13, 50.32 and 81.01 MHz, respectively) or a Bruker Avance DRX-400 spectrometer (400.13, 100.62 and 161.98 MHz), respectively. Chemical shifts are reported in ppm (δ) with reference to either TMS as an internal standard (^{1}H and ^{13}C NMR) or 85% H_3PO_4 as an external standard (^{31}P NMR). High-pressure NMR (HP-NMR) experiments were carried out on the Bruker ACP 200 spectrometer, using a 10 mm HPNMR tube (Saphikon sapphire tube; titanium high-pressure charging head constructed at the ICCOM-CNR).[24] Elemental analyses were performed

using a Carlo Erba Model 1106 elemental analyser. Infrared spectra were recorded on a FT-IR Spectrum GX instrument (Perkin Elmer). The conductivity of ionic compounds was measured with an Orion model 990101 conductance cell connected to a model 101 conductivity meter. The conductivity data were obtained at a sample concentration of *ca.* 10^{-3} M in nitroethane solutions.[25] Polyketone products were analysed by IR, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. The NMR measurements were performed in a solvent mixture of 1,1,1,3,3,3-hexafluoroisopropanol-d_2/C_6H_6-d_6 (5/1, v/v) showing a perfectly alternating structure with ketone or ketone/ester end groups. The number-average molecular weight (M_n) of the copolymers was determined by ^{1}H NMR spectroscopy.

Syntheses

***Synthesis of the meso/rac*-2,4-dibromopentane**

This mixture of stereoisomers was synthesised using a modified version of the synthetic protocol reported by Wiberg et al.[26] LiBr (7.33 g, 84.4 mmol) was added to an acetone solution of *meso*/*rac*-2,4-pentanediol dimesylate (5.50 g, 21.1 mmol). The mixture was refluxed for 20 h, then it was cooled to room temperature. The solvent was removed by distillation and the crude residue was suspended in a solvent mixture of water/Et_2O/*n*-pentane (60 ml) (30/15/15, v/v/v). The organic layer was separated and the solvent was removed under reduced pressure to give a yellow liquid residue.

(*meso*/*rac*)-2,4-dibromopentane (26/74): 3.19 g (65.7%). $C_5H_{10}Br_2$ (229.85 g/mol): calc. C 26.13, H 4.35; found C 26.40, H 4.55%. ^{1}H NMR (δ, 200.13 MHz, $CDCl_3$, 21 ^{o}C) 1.73 (d, $^{3}J_{HH}$ = 6.72 Hz, 6H, CH_3), 1.77 (d, $^{3}J_{HH}$ = 6.60 Hz 6H, CH_3), 2.15 (m, 3H, *meso*-C*H*H, *rac*-CH_2), 2.47 (dt, $^{2}J_{HH}$ 14.2 Hz, $^{3}J_{HH}$ 8.0 Hz, 1H, *meso*-CH*H*), 4.21 (m, 1H, Br-C*H*), 4.38 (m, 1H, Br-C*H*)

Synthesis of the ligand (*rac-o*-MeO-bdpp) (a)

n-BuLi (6.80 ml, 10.8 mmol) was slowly added to bis(*o*-methoxyphenyl)phosphine (2.00 g, 8.13 mmol) dissolved in anhydrous and degassed THF (150 ml) at 0 °C. After the yellow Li salt precipitated, the suspension was stirred for 1 h at room temperature. A 26/74 mixture of *meso*/*rac*-2,4-dibromopentane (0.92 g, 4.02 mmol) was added dropwise to this suspension at room temperature, then the yellow solution was stirred overnight. Afterwards, the reaction was quenched with water (3 ml), concentrated to dryness, and washed with water and ethanol. Yield of *meso*/*rac-o*-MeO-bdpp 71.0% (1.60 g, 2.86 mmol). Recrystallisation of the mixture from CH_2Cl_2/EtOH led to the precipitation of a pure sample of *rac-o*-MeO-bdpp as a off white powder.

***rac-o*-MeO-bdpp**: 817.9 mg (36.0%). $C_{33}H_{38}O_4P_2$ (560.26 g/mol): calc. C 70.70, H 6.83; found C 70.65, H 6.85%. $^{31}P\{^1H\}$ NMR (δ, 81.01 MHz, $CDCl_3$, 21 °C) -23.8 (s); ^1H NMR (δ, 200.13 MHz, $CDCl_3$, 21 °C) δ 1.06 (dd, $^3J_{HP}$ = 15.8 Hz, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3), 1.53 (m, 2H, CH_2), 2.75 (m, 2H, P-CH), 3.63 (s, 6H, OCH_3), 3.69 (s, 6H, OCH_3), 6.72-7.83 (m, 16H, Ar-H). All attempts to isolate the *meso* ligand in a pure form were unsuccessful

Syntheses of the neutral complexes

Synthesis of $PdCl_2$(*rac-o*-MeO-bdpp) (1a)

Rac-o-MeO-bdpp (112.1 mg, 0.20 mmol) was dissolved in degassed CH_2Cl_2 (20 ml) under nitrogen. To this colourless solution was added $PdCl_2$(COD) (57.1 mg, 0.20 mmol). The resultant suspension was stirred for 1 h, and then it was concentrated to half volume. The addition of a 1/1 (v/v) mixture of *n*-pentane and diethyl ether (20 ml) completed the precipitation of **1a** as a white off

microcrystalline solid, which was filtered off and dried in a stream of nitrogen. Crystals of **1a** suitable for X-ray analysis were obtained by slow diffusion of toluene into a saturated CH_2Cl_2 solution at room temperature.

Complex 1a: 102.9 mg (69.8%). $C_{33}H_{38}Cl_2O_4P_2Pd$ (737.58 g/mol): calc. C 53.71, H 5.19; found C 53.69, H 5.20%. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, 21 ^oC) 34.50 (s); ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 ^oC) 0.86 (dd, $^3J_{HP}$ = 15.9 Hz, $^3J_{HH}$ = 6.7 Hz, 6H, C*H*$_3$), 1.82 (m, 2H, C*H*$_2$), 3.24 (m, 2H, P-C*H*), 3.72 (s, 6H, OC*H*$_3$), 3.90 (s, 6H, OC*H*$_3$), 6.80-7.70 (m, 16H, Ar-*H*)

Synthesis of Pd(OAc)$_2$(*rac*-*o*-MeO-bdpp) (2a)

Compound **1a** (258.2 mg, 0.35 mmol) was dissolved in degassed CH_2Cl_2 (30 ml) under nitrogen. To this solution was added Ag(OAc) (128.5 mg, 0.77 mmol) and the resultant suspension was stirred for 30 min. The precipitated AgCl was removed by filtration through a column of Celite and the clear solution was concentrated to *ca.* 5 ml. The addition of a 1/1 (v/v) mixture of *n*-hexane and diethyl ether (20 ml) completed the precipitation of **2a** as yellow microcrystals which were filtered off, and dried in a stream of nitrogen.

Complex 2a: 164.8 mg (60%). $C_{37}H_{44}O_8P_2Pd$ (784.69 g/mol): calc. C 56.60, H 5.65; found C 56.63, H 5.66%. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_2Cl_2, 21 ^oC) 31.78 (s); ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 ^oC) 1.01 (dd, $^3J_{HP}$ = 16.0 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, C*H*$_3$), 1.10 (s, 6H, OAc-C*H*$_3$), 1.88 (m, 2H, C*H*$_2$), 3.12 (m, 2H, P-C*H*), 3.68 (s, 6H, OC*H*$_3$), 3.93 (s, 6H, OC*H*$_3$), 6.95-7.68 (m, 16H, Ar-*H*)

UNIVERSITAT ROVIRA I VIRGILI
PALLADIUM COMPLEXES CONTAINING DIPHOSPHINE AND SULFONATED PHOSPHINE LIGANDS FOR C-C BOND FORMING REACTIONS. CATALYTIC AND MECHANISTIC STUDIES
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Catalytic copolymerisation of CO and ethane

HP-NMR experiment in water/AcOH with 1a as catalyst precursor

A 10 mm sapphire HP-NMR tube was charged with a suspension of **1a** (14.8 mg, 0.02 mmol) in a mixture of D_2O and AcOH (0.4 ml/1.6 ml) under nitrogen and then placed into the NMR probe maintained at 20 ^oC. After a $^{31}P\{^1H\}$ NMR spectrum was acquired, the sapphire tube was removed from the NMR probe and pressurised with a 1/1 mixture of CO/C_2H_4 to a total pressure of 40 bar at room temperature. A $^{31}P\{^1H\}$ NMR spectrum was recorded at 20 ^oC and then the probe-head was heated to 80 ^oC. This temperature was maintained for 1 h, during which time $^{31}P\{^1H\}$ NMR spectra were acquired every 20 min. The tube was then allowed to cool to 20 ^oC and a final $^{31}P\{^1H\}$ NMR spectrum was acquired. The formation of copolymer was observed.

Autoclave experiments in water/AcOH with 1a and 1b as catalyst precursors

A deoxygenated mixture of distilled water and AcOH (100 ml) was introduced by suction into an autoclave (250 ml), previously evacuated by a vacuum pump, containing the catalyst precursor **1a** or **1b** (0.005 mmol). The autoclave was charged with a 1/1 CO/C_2H_4 mixture to 30 bar at room temperature. The temperature was increased to 85 ^oC while the pressure inside the autoclave was maintained at 40 bar. The autoclave was stirred (1100 rpm) for the desired time. Then it was cooled with an ice-water bath. The unreacted gases were released and the insoluble copolymer was filtered off, washed with water, and dried under vacuum at 60 ^oC to constant weight.

Autoclave experiments in MeOH with 2a and 2b as catalyst precursors

MeOH (reagent grade from Aldrich, 100 ml) was introduced under a nitrogen into an autoclave (250 ml) containing the catalytic precursor **2a** or **2b** (0.005 mmol) and the desired amount of *p*-toluenesulphonic acid monohydrate (TsOH). The autoclave was pressurised with a 1/1 CO/C_2H_4 mixture to 30 bar at room temperature. The temperature was increased to 85 ^oC while the pressure inside the autoclave was maintained at 40 bar. The autoclave was stirred (1100 rpm) for the desired time. Then it was cooled with an ice-water bath. The unreacted gases were released and the insoluble copolymer was filtered off, washed with water, and dried under vacuum at 60 ^oC to constant weight. The filtered solutions were analysed by GC/MS.

X-ray crystallographic data collection and refinement of the structures

The crystallographic data for (*S,S*)-**1a** are summarised in **Table 1**. Graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) was used. The data collection was performed on a Oxford Diffraction CCD diffractometer using ω-scans for (*S,S*)-**1a**, respectively. Cell refinement, data reduction and empirical absorption correction were carried out with the Oxford diffraction software and SADABS[27a] for (*S,S*)-**1a**. All structure determination calculations for (*S,S*)-**1b**. were performed with WINGX package[27b] with SIR-97,[27c] SHELXL-97 and ORTEP-3 programs.[27d] Final refinements on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were included using a riding model with isotropic U values depending on the Ueq of the adjacent carbon atoms. CCDC reference number 293489 for (*S,S*)-**1a**

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Ligand effects in the non-alternating CO/ethene copolymerisation reaction

Abstract

This chapter describes the synthesis of two novel bis(*o*-methoxyphenyl) phosphinoalkylsulfonate (P-O) ligands through a new and sustainable synthetic route as well as the synthesis of new neutral and anionic palladium (II) complexes. Furthermore, it deals with the effects of the rigidity of the anionic phosphine sulfonate ligands in neutral palladium(II) complexes on the catalytic outcome of the non-alternating CO-ethene copolymerisation in terms of catalytic productivity and the extra-ethene insertion into the polymeric chain. To this purpose neutral palladium(II) complexes bearing P-O ligands containing a 2-phenylidene and an ethylidene back-bone are compared from both a catalytic and a mechanistic point of view.

4.1.1. Introduction

The development of novel late transition metal catalysts for the synthesis of new copolymers containing a controlled amount of polar monomer is of considerable interest to both academia and industry.[1]

As it has been discussed in *chapter 1*, chelating anionic P-O ligands constitute a class of ligands that has much less been studied in catalytic reactions than their diphoshine counterparts. Apart from oligomerisation and polymerisation reactions,[2] very few homogeneous processes are efficiently catalysed by metal complexes with anionic P-O ligands. One of these is the palladium catalysed copolymerisation of carbon monoxide and ethene that gives perfectly alternating polyketones with diphosphine ligands and non-alternating polyketones with P-O ligands.[3]

Within the field of polar copolymers, the carbon monoxide and ethene copolymerisation, catalysed by cationic palladium (II) complexes bearing chelating diphosphine ligands is one of the most studied reaction.[4] These catalytic CO-ethene copolymerisation reactions are known to provide polyketones with strictly alternating CO and ethene units, due to the lack of the double CO insertion (thermodynamic control) and the difference in binding affinity of CO and ethene to cationic palladium centres (kinetic control). Furthermore coordination of an oxygen atom from the growing polymeric chain to the palladium centre takes place, increasing the activation barrier for the ethene incorporation into a metal-alkyl bond.[5]

The production of non-perfectly alternating carbon monoxide and ethene copolymers is one of the aims in polyketone research in order to obtain new materials with desirable properties. The architecture of randomly extra-ethene

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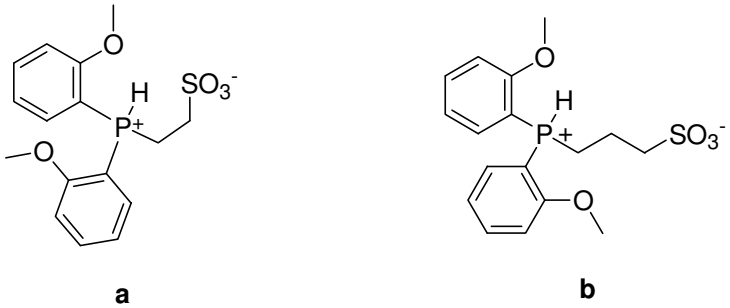
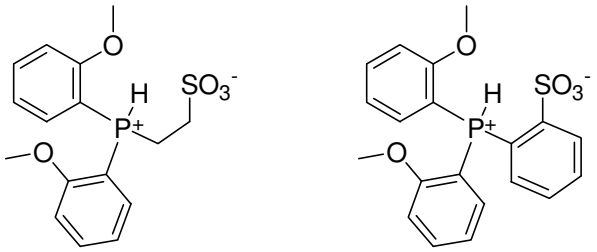
incorporated into a linear CO-ethene copolymer is obtained by employing neutral Pd(P-O) complexes (P-O = anionic chelating ligand) as precatalysts.[6]
Since the non-alternating polyketones might exhibit improved thermal stability, while retaining the excellent engineering properties of the strictly alternating polyketones, the development of highly efficient catalytic systems for the non-alternating CO-ethene copolymerisation, based on the knowledge of the key-steps of the catalytic copolymerisation cycle, are subject of experimental[6a,6b,6c] and theoretical[6d,6e] studies.

This chapter is focused on an alternative synthesis of two new phosphine-sulfonate ligands **a** and **b** (**Figure 1**) and on the comparison of neutral palladium(II)(P-O) complexes bearing the two phosphine sulfonate ligands **a** and **c**[6a] featured by a different rigidity of the carbon-backbone (**Figure 2**) in the non-alternating CO-ethene copolymerisation reaction from a catalytic and a mechanistic point of view.



a **b**

Figure 1. New phosphine sulfonate ligands



a **c**

Figure 2. Phosphine sulfonate ligands used for comparative purposes in the CO-ethene copolymerisation reaction

4.1.2. Results and discussion

Syntheses of the phosphine sulfonated ligands

The synthesis of two novel diaryl alkyl phosphine sulfonate ligands was carried out applying a modified synthetic protocol.

Synthetic routes for related phenyl derivates reported in the literature involve the use of ammonia as solvent[7] or sultones as reactants.[8] Indeed, all attempts to synthesise phosphinoalkylsulfonate ligands without either ammonia or sultones reported so far were unsuccessful.[9]

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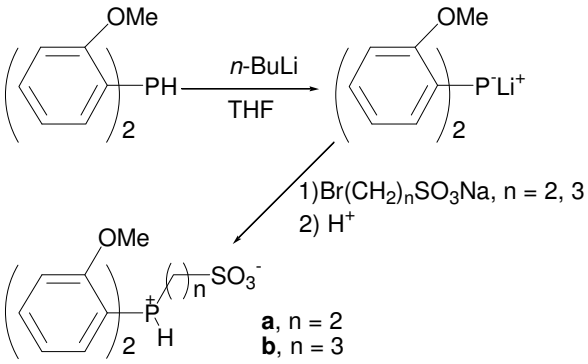

Scheme 1. Synthetic route for the syntheses of ligands **a** and **b**

Ligands **a** and **b** were synthesised by a new synthetic route that involves the reaction of *n*-butyllithium with bis(*o*-mehoxyphenyl)phosphine in THF[10] in order to obtain the corresponding lithium salt, followed by the reaction of the latter salt with the appropriate bromoalkylsulfonate derivate as shown in **Scheme 1**. Both ligands were isolated as zwitterions in 54% and 43% yield, respectively and characterised in solution by multinuclear NMR spectroscopy and in addition ligand **b** was also characterised in the solid state by a single crystal X-ray structure analysis. Both ligands resulted to be water soluble as well as air stable.

Single crystals of ligand **b** were obtained by diffusion of diethyl-ether into a $CHCl_3$ solution of **b**. An ORTEP drawing of ligand **b** is shown in **Figure 3**. The crystal structure of **b**.H_2O shows one molecule of **b** along and one molecule of H_2O per asymmetric unit. Crystallographic data and selected bond distances and angles for **b**.H_2O are reported in **Table 1** and **Table 2,** respectively.

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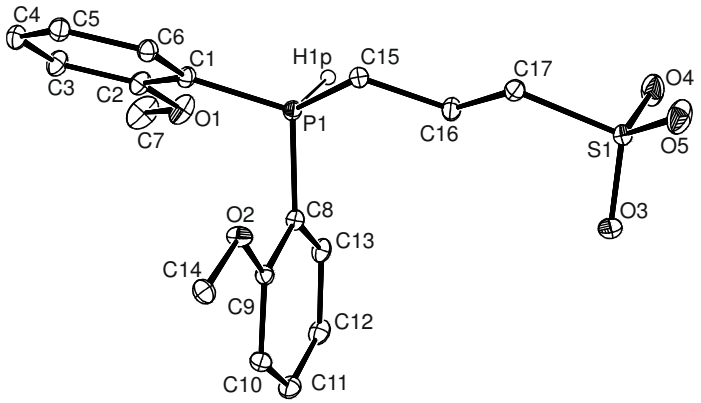


Figure 3. ORTEP drawing of ligand **b**. The solvent molecule as well as the hydrogen-atoms, except the one attached to P(1) have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level

Table 1. Summary of crystallographic data for ligand **b**.H_2O

Empirical formula	$C_{17}\ H_{21}\ O_5\ PS.H_2O$
Formula weight	386.38
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P*2(1)/c
a	10.717(2) Å
b	15.216(3) Å
c	12.173(2) Å
α	90^o
β	112.803(4)°
γ	90^o
Volume	1829.8(5) $Å^3$
Z	4
Density (calculated)	1.403 Mg/m^3
Absorption coefficient	0.294 mm^{-1}
F(000)	816
Crystal size	0.20 x 0.10 x 0.02 mm^3
Theta range for data collection	3.44 to 39.58°.

Index ranges	-18<=h<=19 -26<=k<=23 -19<=l<=21
Reflections collected	36864
Independent reflections	10350 [R(int) = 0.0318]
Completeness to theta = 39.55°	93.9 %
Absorption correction	SADABS (Bruker-Nonius)
Max. and min. transmission	0.9941 and 0.9435
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10350 / 0 / 240
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.1115
R indices (all data)	R1 = 0.0442, wR2 = 0.1165
Largest diff. peak and hole	1.417 and -0.512 e.Å^{-3}

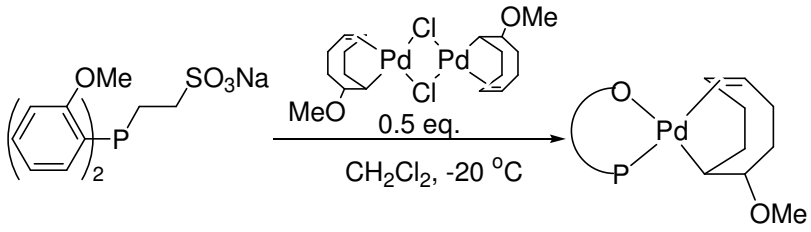
Table 2. Selected bond distances (Å) and angles (^{o}) for ligand **b**.H_2O

P(1)-C(1)	1.7813(8)
P(1)-C(8)	2.7853(8)
P(1)-C(15)	1.7980(8)
S(1)-C(17)	1.7865(8)
S(1)-O(3)	1.4534(7)
S(1)-O(4)	1.4566(8)
S(1)-O(5)	1.4537(8)
C(1)-P(1)-C(8)	109.42(4)
C(1)-P(1)-C(15)	112.60(4)
C(8)-P(1)-C(15)	110.99(4)
C(16)-C(17)-S(1)	112.24(6)

The zwitterionic structure of ligands **a** and **b** was unambiguously determined by low temperature ^{31}P NMR spectroscopy, showing in the corresponding ^{31}P NMR spectra a characteristic $^1J_{PH}$ coupling constants of 545 Hz, respectively. In the case of ligand **b** the presence of the P-H bond was also confirmed by its X-ray structure (**Figure 3**).

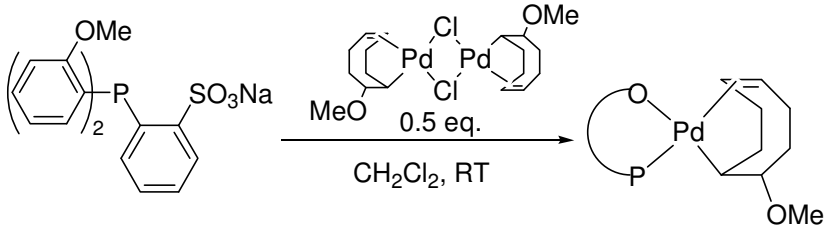
Syntheses of the neutral complexes

The neutral palladium(II) complex Pd(COD-OMe)((*o*-MeO-C_6H_4)$_2$$PC_2H_4SO_3$) (COD-OMe = 2-methoxycyclooct-5-enyl) (**1a**) containing the more flexible zwitterionic P-O ligand {bis-(2-methoxyphenyl)phosphonium}ethanesulfonate (**a**) was obtained upon reaction of the dimeric palladium (II) complex [Pd_2(μ-Cl)$_2${η^1,η^2-C_8H_{12}OMe}$_2$][11] with the sodium salt of ligand **a** at -20 ^oC, which was formed by the reaction of ligand **a** with NaH in CH_2Cl_2 (**Scheme 2**).



Scheme 2. Synthesis of the palladium(II) complex **1a**

Analogously, Pd(COD-OMe)((*o*-MeO-C_6H_4)$_2$$PC_6H_4SO_3$) (**1c**) was obtained upon reaction of the dimeric palladium (II) complex [Pd(μ-Cl){η^1,η^2-C_8H_{12}OMe}$_2$][11] with the Na-salt of the zwitterionic P-O ligand {bis-(2-methoxyphenyl)phosphonium}benezenesulfonate (**c**)[6a] in CH_2Cl_2 at room temperature (**Scheme 3**).



Scheme 3. Synthesis of the palladium(II) complex **1c**

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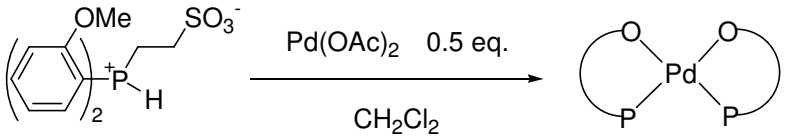
Both complexes were characterised in solution by multinuclear NMR spectroscopy and in the solid state by elemental analysis. Unlike compound **1c**, **1a** shows a much lower stability in most organic solvents. Indeed, a methanol solution of **1a** decomposes within one day at room temperature to yield the neutral bis-chelate complex Pd(**a**)$_2$ (**2a**), which was also obtained upon reaction of a CH_2Cl_2 solution of $Pd(OAc)_2$ with ligand **a** in a 1:2 molar ratio (**Scheme 4**). This latter complex is almost insoluble in most common organic solvents as reported for the analogous palladium compound with ligand **c**.[6b] Nevertheless the latter complex has been characterised in solution by ^1H and $^{31}P\{^1H\}$NMR spectroscopy and in the solid state by elemental analysis and a single X-ray structure analysis.



Scheme 4. Synthesis of complex **2a**

The reaction of the triethylammonium salt of ligands **a** and **c** with the neutral palladium(II) complex PdClMe(COD) (COD = cycloocta-1,5-diene) yields the anionic palladium complexes of the type [PdClMe(**L**)](NHEt$_3$) (**L** = **a** (**3a)**, **c** (**3c**)[12]). Both complexes were prepared following the synthetic procedure reported by Nozaki et al.,[12] which comprises the deprotonation of the zwitterionic P-O ligand with triethylamine in CH_2Cl_2, followed by the reaction of the obtained ammonium-salt with PdClMe(COD) in the same solvent (**Scheme 5**).

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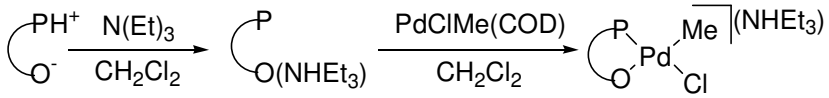
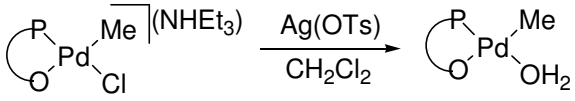


a, c **3a, 3c**

Scheme 5. General procedure for the syntheses of the anionic palladium complexes **3a** and **3c**

In both cases an off-white semi-crystalline powder was obtained, which was analysed in solution by multinuclear NMR spectroscopy and in the solid state by elemental analysis. The reaction of these latter palladium complexes with Ag(OTs) (OTs = *p*-toluenesulfonate) in CH_2Cl_2 yields the corresponding neutral palladium complexes PdMe(**L**)(H_2O) (**L** = **a** (**4a**), **c** (**4c**)) (**Scheme 6**), which were separated from the inorganic salt upon a CH_2Cl_2/water extraction. Since both latter complexes are slightly soluble in water, the yield of both complexes were rather low (around 38% in both cases).



3a, 3c **4a, 4c**

Scheme 6. Syntheses of the neutral complexes **4a** and **4c**

It is important to stress at this point that the low Lewis-acidity of the neutral palladium complexes brings about a weak coordination of the solvent molecule to the metal centre. Thus, the complete evaporation of a CH_2Cl_2 solution of **4a** and **4c** yields probably dimeric pallladium species, featured by intra-molecular palladium-oxygen (sulfonate) interactions (**Figure 4**). This latter dimeric species are not soluble in CH_2Cl_2 but show and excellent solubility in methanol. The formation of similar dimeric complexes has also been described for neutral Ni(P-O) complexes.[13]

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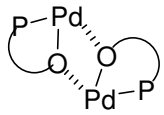


Figure 4

X-ray structures of compounds 1a and 2a

Suitable crystals of compound **1a** were obtained by a slow diffusion of diethyl-ether into a chloroform solution of compound **1a**, while crystals of complex **2a** were obtained by diffusion of a methanol solution of $Pd(OAc)_2$ into a dichloromethane solution of ligand **a**. Experimental X-ray diffraction parameters and selected bond length and angles for both complexes are reported in **Table 3** and **Table 4,** respectively. An ORTEP drawing of compounds **1a** and **2a** is shown in **Figure 5** and **Figure 6**, respectively.

Table 3. Experimental X-ray diffraction parameters and crystal data for compounds **1a** and **2a**

Compound	**1a**	**2a**
Empirical formula	$C_{25}H_{33}O_6PPdS$	$C_{32}H_{36}O_{10}P_2PdS_2$
Formula weight	598.94	813.07
Temperature	100(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$
a	9.4428(3) Å	9.403(5) Å
b	14.8530(5) Å	19.844(5) Å
c	17.7593(6) Å	10.566(5) Å
α	90°	90°
β	100.5950(10)º.	114.647(5)º
γ	90°	90°
Volume	2448.35(14) $Å^3$	1791.9(14) $Å^3$
Z	4	2
Density (calculated)	1.625 Mg/m^3	1.507 Mg/m^3

Absorption coefficient	0.948 mm^{-1}	0.777 mm^{-1}
F(000)	1232	832
Crystal size	0.20 x 0.10 x 0.10 mm^3	0.40 x 0.30 x 0.25 mm^3
Theta range for data collection	3.75 to 25.00°	2.36 to 24.97°
Index ranges	-11<=h<=11 0<=k<=17 0<=l<=21	-11<=h<=10 0<=k<=23 0<=l<=9
Reflections collected	4275	2982
Independent reflections	4275	2803
Data / restraints /	4275 / 0 / 310	2803 / 0 / 428
Goodness-of-fit on F^2	1.100	1.081
R indices (all data)	R1 = 0.0297, wR2 = 0.0701	R1 = 0.0306, wR2 = 0.0832
Largest diff. peak and hole	1.755 and -1.447 e/$Å^{-3}$	0.086 and -0.417 $Å^{-3}$

Table 4. Selected Bond length (Å) and angles (°) of compounds **1a** and **2a**

Compound	**1a**	**2a**
Pd(1)-P(1)	2.2836(7)	2.241(1)
Pd(1)-P(2)		2.340(1)
Pd(1)-O(4)	2.161(2)	
Pd(1)-O(5)		2.105(4)
Pd(1)-O(8)		2.103(4)
Pd(1)-C(15)	2.044(3)	
Pd(1)-C(18)	2.274(3)	
Pd(1)-C(19)	2.276(3)	
P(1)-Pd(1)-P(2)		102.97(6)
P(1)-Pd(1)-O(4)	96.78(6)	
P(1)-Pd(1)-C(15)	89.87(8)	
C(15)-Pd(1)-C(18)	80.98(11)	
C(15)-Pd(1)-C(19)	88.93(11)	
O(5)-Pd(1)-O(8)		87.29(17)
P(1)-Pd(1)-O(5)		85.30(12)
P(2)-Pd(1)-O(8)		84.44(13)

Intramolecular distances (Å)		
Pd(1)-O(1)	3.829(2)	5.083(5)
Pd(1)-O(2)	5.207(2)	3.679(4)
Pd(1)-O(3)		3.783(5)
Pd(1)-O(4)		5.018(4)
Pd(1)-H(9)	2.935	2.720
Pd(1)-H(25)		2.756

Complex **1a** (**Figure 5**) exhibits a distorted square-planar coordination geometry with the phosphine sulfonate ligand coordinating to the palladium atom in a bidentate fashion. Very few examples of metal complexes containing a direct M-oxygen (SO_3) bond are reported in the literature, due to the poor coordination properties of this latter group. The Pd(1)-O(4) bond length of 2.161(2) Å and the P(1)-Pd(1)-O(4) bite angle of 96.78(6)^o are comparable to related palladium structures.[12,6b]

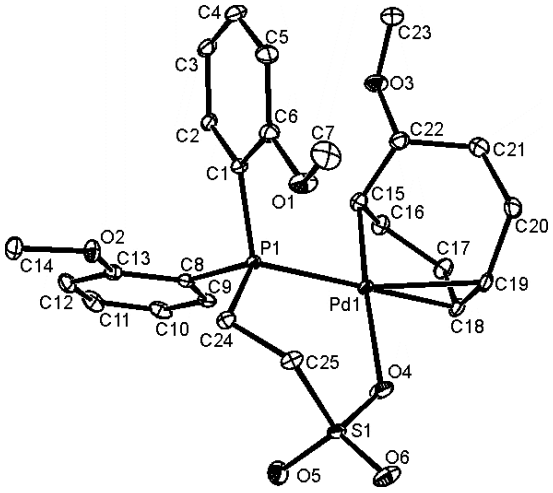


Figure 5. ORTEP drawing of compound **1a**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are shown at a 30% probability level

The crystal structure of the neutral palladium(II) bis-chelate complex **2a** (**Figure 6**) shows a square planar coordination sphere with a *cis* coordination of the

phosphorus atoms belonging to two different P-O ligands.[6b,14] The two remaining coordination sites are occupied by two oxygen atoms stemming from sulfonate units. The palladium atom shows no significant deviation from the best coordination plane, which is defined by the atoms P(1), P(2), O(5) and O(8). The molecule shows almost C_2-symmetry, with the C_2 axis bisecting the P(1)-Pd(1)-P(2) angle of 102.97(6)°. The bite angles of the two coordinating P-O ligands of 85.30(12)° (P(1)-Pd(1)-O(5)) and of 84.44(13)° (P(2)-Pd(1)-O(8)) are only slightly different from each other. While both Pd-O bonds of 2.105(4) Å (Pd(1)-O(5)) and of 2.103(4) Å (Pd(1)-O(8)) are identical, the Pd-P bond lengths of 2.241(1) Å (Pd(1)-P(1)) and of 2.340(1) Å (Pd(1)-P(2)) are significantly different, which may be accounted for by the steric pressure, which exert the two equatorial 2-methoxyphenyl units on each other. The intra-molecular palladium methoxy-oxygen distances range from 3.679(4) Å to 5.083(5) Å and are thus far from being bonding interactions.[15] Unlike the intra-molecular palladium methoxy-oxygen distances, the intra-molecular palladium-hydrogen distances of 2.720 Å (Pd(1)-H(9)) and of 2.756 Å (Pd(1)-H(25)) evidence interactions between the palladium atom and two *ortho*-hydrogen atoms, which belong to the axial 2-methoxyphenyl units of both P-O ligands. These latter interactions are retained also in solution at room temperature, which is evidenced by ^{1}H-NMR spectroscopy, showing a broad singlet centred at 9.10 ppm in the corresponding ^{1}H NMR spectrum. Such down-field shifts of ^{1}H-NMR signals of *ortho*- phenyl hydrogen atoms, due to interactions with the palladium atom has also been observed in 2-methoxy modified Pd(P-P) complexes (see *chapter 2*, sections 2.1 and 2.2).[15]

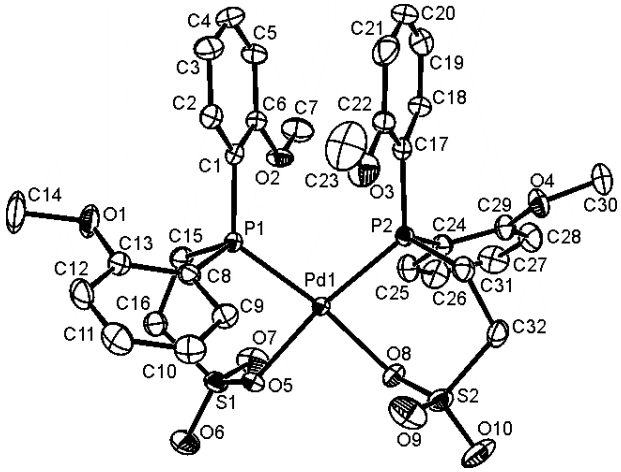


Figure 6. ORTEP drawing of compound **2a**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at a 30% probability level

Catalytic study

Non-alternating CO-ethene copolymerisation reactions, catalysed by the neutral Pd(P-O) complexes **1a**, **1c**, **4a** and **4c** were carried in methanol and 2,2,2-trifluoroethanol at 110 and 120 ^{o}C in the presence of different CO-ethene gas ratios. The results of the catalytic study are reported in **Table 5**.

A perusal of **Table 5** shows that irrespective of the catalytic conditions chosen, the precatalysts bearing the more rigid ligand **c** are much more productive than those bearing the flexible counterpart. A comparable trend has been observed in oligo-and polymerisation reactions, catalysed by neutral Ni(P-O) complexes.[13] Performing the catalytic reactions in the presence of 1,4-benzoquinone (BQ) leads to an increase of the catalytic productivity, being more pronounced in those catalytic reactions, performed with the rigid pre-catalysts.

The addition of Broensted-acid to the catalytic system has an enhancing effect on the productivity of those pre-catalyst, which bear the flexible ligand **a**, which

might be explained by the lower stability of the corresponding Pd-H species formed during the catalytic process, while for the rigid pre-catalyst, the opposite applies. Indeed, a negative acid effect on the catalytic productivity has already been observed in CO-ethene copolymerisation reactions, catalysed by Pd-diphosphine complexes, bearing 2-methoxyphenyl groups at the phosphorus donor atoms (see *chapter 2*, section 2.1).[15a] This latter phenomenon has been rationalised by the formation of a net of strong hydrogen-bond interactions between the acid and the *ortho*-methoxy-oxygen atoms.

Irrespective of the pre-catalyst employed, the CO-ethene gas-ratio steers the catalytic productivity significantly. In fact, on increasing the partial pressure of ethene going from a 1/3 to a 1/20 CO-ethene gas-ratio, the catalytic productivity decreases significantly (entries 31 *vs* 39, 32 *vs* 40 and 33 *vs* 38), which might be accounted for by the CO assisted insertion of ethene into Pd-γ-chelate complexes, which was postulated as the rate determining step in the propagation of the CO-ethene copolymerisation reaction.[16]

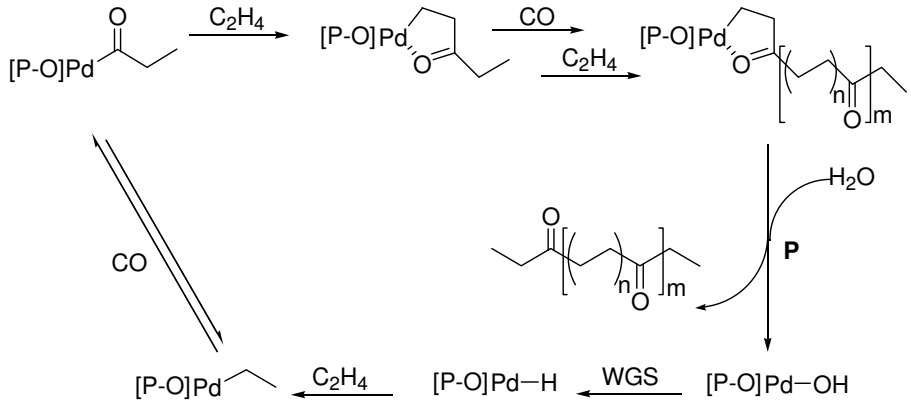
Performing analogous catalytic reactions in 2,2,2-trifluoroethanol shows with both types of pre-catalysts a positive effect on the catalytic productivity, being more pronounced in those cases were high molecular weight non-alternating copolymers were obtained, thus indicating the importance of the reaction to be carried out in a homogeneous phase, which is provided by the excellent solubilising properties of fluorinated solvents for polymeric materials.[17] As far as the molecular weight of the copolymers is concerned, two different ranges of average molecular weight were observed. While the pre-catalysts bearing the rigid ligand **c** produce high molecular weight copolymers (>300.000),[6b] the flexible counterparts produce low molecular weight non-alternating copolymers (**Table 5**), indicating the prevalence of the termination over the propagation reactions in the latter case.

Table 5. Non-alternating copolymerisation of CO and ethene, catalysed by the neutral Pd(P-O) complexes **1a**, **1c**, **4a** and **4c**[a]

Entry	Precat	t(h)	T (°C)	p(CO)/ $p(C_2H_4)$	Acid/BQ	Productivity[b]	M_n[c]	Extra-C_2H_4 (%)
1	**1a**	6	100	1/3	80/0	1.3		
2	**1a**	6	110	1/1	20/0	4		
3	**1a**	3	110	1/3		0.6		
4	**1a**	6	110	1/3		0.4	5.3	0.3
5	**4a**	6	110	1/3		0.4		
6	**1a**	12	110	1/3		0.1		
7[†]	**1a**	6	110	1/3		0.6	4.3	0.5
8	**1a**	6	110	1/3	0/80	1.3		
9	**1a**	6	110	1/3	20/0	1.9	5.2	3.0
10	**1a**	6	110	1/3	80/0	5.4	5.4	6.6
11[e]	**1a**	6	110	1/3	80/0	0.7	8.0	3.2
12	**1a**	12	110	1/3	80/0	2.5		
13	**1a**	6	110	1/3	160/0	1.8	8.4	23.2
14[e]	**1a**	6	110	1/3	160/0	0.7		
15	**1a**	6	110	1/6	20/0	0.6	2.3	8.2
16	**1a**	6	120	1/3	20/0	0.6	5.6	9.9
17	**1a**	6	120	1/3	80/0	1.3	4.8	13.7
18	**1c**	1	110	1/3		153	n.d.	3.2
19[d]	**1c**	1	110	1/3	0/80	210		
20	**4c**	1	110	1/3		150		
21[d,f]	**1c**	1	110	1/3		390	n.d.	2.5
22	**1c**	1	110	1/3	20/0	58	n.d.	3.2
23	**1c**	1	110	1/6		92	n.d.	5.4
24[d]	**1c**	1	110	1/6	0/80	133		
25	**1c**	1	110	1/20		44	n.d.	22.2
26[d]	**1c**	1	110	1/20	0/80	83		
27[g]	**1c**	1	110	0/1		340		
28	**1c**	1	120	1/1		254	n.d.	1.5
29[d]	**1c**	1	120	1/1	0/80	490	n.d.	1.1
30	**1c**	1	120	1/3		175	n.d.	6.0
31[d,f]	**1c**	1	120	1/3		337		3.4
32[d,f]	**1c**	1	120	1/3	0/80	607		
33[d]	**1c**	1	120	1/3	0/80	337		
34	**1c**	1	120	1/6		125	n.d.	9.9
35[d]	**1c**	1	120	1/6	0/80	190		
36	**1c**	1	120	1/20		40.8		27.8
37[d]	**1c**	1	120	1/20	0/80	133		
38[d]	**1c**	2	120	1/20	0/80	95		
39[d,f]	**1c**	1	120	1/20		77	n.d.	23.8
40[d,f]	**1c**	1	120	1/20	0/80	130		

[a]Catalytic conditions: pre-catalyst (0.012 mmol), p(total) (800psi), MeOH (50 mL), [b]Productivity expressed as g × (mmol (Pd) × h)$^{-1}$, [c]M_n (kg × mol^{-1}), [d]precatalyst (0.003 mmol), [e] HBF_4, [f]CF_3CH_2OH (50 mL), [g]ethene (600 psi).

End-group analyses of the non-alternating CO-ethene copolymers, which were carried out in a 1:3 (v:v) mixture of hexafluoropropan-2-ol-d_2 and C_6D_6 by means of ^{1}H NMR spectroscopy show in the case of the low-weight copolymers, which were obtained in the absence of any additives, three types of end-groups, namely ester (E), ketone (K) and vinyl (V) end-groups in a 10:10:1 ratio, while those produced in the presence of acid exhibited only ketone end groups, stemming from protonolysis reaction of Pd-alkyl species.[4] A possible catalytic cycle operative in acidic methanol solution is shown in **Scheme 7**.



P = Protonolysis reaction, WGS = Water Gas Shift reaction

Scheme 7. Proposed catalytic cycle operative in acidic methanol solution

The protonolysis reaction of Pd-alkyl species with water in conjunction with the water gas shift reaction (WGS) generates the Pd-H species, which inserting ethene starts the propagation of a new polymeric chain. The fast protonolysis reaction of Pd-alkyl species bearing the flexible Pd(P-O) moiety, might be rationalised by a fast coordination-de-coordination equilibrium of the sulfonate group to and from the palladium centre, increasing thus the Lewis acidity of the metal centre upon de-coordination of the sulfonate unit from the metal centre and therefore accelerating the β-hydride elimination reaction, which is followed by a protonation step. The extra-ethene insertion into the growing polymeric

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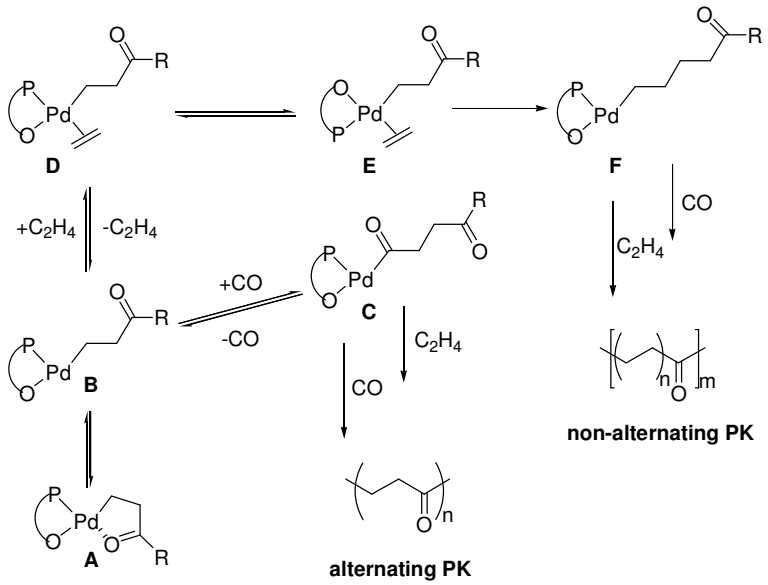
chain is mainly influenced by the coordinating P-O ligand, by the reaction temperature, by the CO-ethene gas-pressure ratio.

Theoretical studies of the catalytic cycle concerning the non-alternating CO-ethene copolymerisation reaction, catalysed by neutral Pd(P-O) complexes, revealed that the rate controlling step of the chain-propagation is the insertion of ethene into a palladium-alkyl bond (**Scheme 8**, **E**-**F**).[6d,6e] The Pd(ethene)-alkyl species (**E**) shows the migrating alkyl group in *trans*-position to the phosphine unit lowering the activation energy for the migration step significantly, due to the higher trans influence of the phosphorus donor atom compared to the oxygen atom, favour the extra-ethene insertion into the growing polymeric chain.[6d,6e]



Scheme 8. Proposed mechanism for the production of non-alternating CO-ethene copolymers

The concentration of latter compound **E** increases with **a**) the temperature, due to the decarbonylation of the palladium acyl complex **C** (**Scheme 8**), shifting the

equilibrium versus the open form of the Pd-β-chelate (**B**); **b**) the ethene partial pressure, shifting the equilibrium between compound **B** and **D** versus the latter compound on increasing the ethene partial pressure; **c**) the bulkiness of the phosphorus-substitutens of the P-O ligand, shifting the isomerisation equilibrium between the two Pd(ethene)-alkyl species **D** and **E**, versus the latter one on increasing the steric congestion at the phosphorus donor atom of the ligand.[6d,6e]

Indeed, the catalytic study shows very clearly an increase of the extra-ethene insertion on increasing the temperature and the ethene partial pressure. Furthermore catalytic reactions under identical conditions for both types of precatalysts show, that an increase of the ligand rigidity brings about a higher degree of extra-ethene incorporation into the polymeric chain (**Table 5**, entry 4 vs entry 18). While the presence of 1,4-benozquinone in catalytic non-alternating copolymerisation reactions showed no effect on the extra-ethene incorporation, an increase of the amount of *p*-toluenesulfonic acid show only in those copolymerisation reactions, catalysed by the flexible pre-catalysts a significant increase of extra-ethene incorporation. This positive effect on the extra-ethene incorporation vanishes on employing HBF_4 instead of *p*-toluenesulfonic acid (**Table 5**, entry 10 *vs* 11), evidencing, that the coordination of the tosylate plays a crucial role in the overall mechanism of extra-ethene incorporation.

Irrespective of the pre-catalyst and catalytic conditions employed for the copolymerization reactions, all non-alternating CO-ethene copolymers exhibit a linear structure, which was confirmed by $^{13}C\{^1H\}$NMR spectroscopy, evidencing a step-wise ethene insertion into the growing polymeric chain and thus excluding the incorporation of ethene-oligomers, stemming from a parallel ethene-oligomerisation reaction.[6a] Reactions, catalysed by the pre-catalysts containing the rigid ligand **c** employing only ethene, brings about the formation

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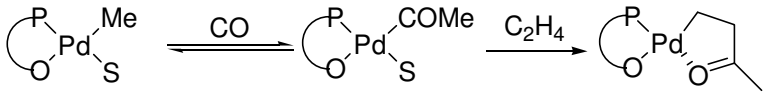
of polyethylene, while analogous reactions, catalysed by the flexible pre-catalysts containing ligans **a** leads to the formation of traces butenes and hexenes, evidencing a fast β-hydride-elimination reaction in the latter case.

NMR Model study

In order to identify metallorganic species, which might be formed during the catalytic non-alternating CO-ethene copolymerisation reaction in MeOH, catalysed by neutral palladium complexes, the neutral Pd-Me complexes **4a** and **4c** were used as starting compounds for the step-wise insertion of CO and ethene, which was carried out in CD_3OD as outlined in **Scheme 9**.



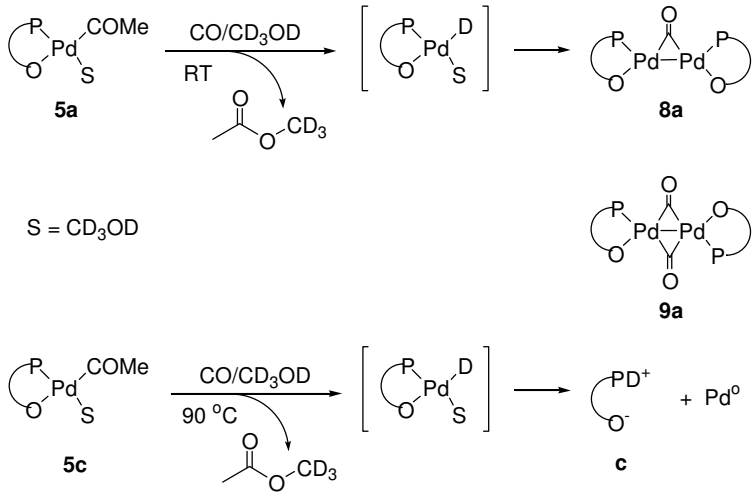
4a, 4c **5a, 5c** **6a, 6c**

S = CD_3OD

Scheme 9. Step-wise insertion of CO and ethene into Pd-alkyl and Pd-acyl bonds, respectively

On bubbling CO through a CD_3OD solution of the neutral Pd-Me complexes **4a** and **4c**, the corresponding Pd-acyl complexes **5a** and **5c** were formed. Like the former complexes, the Pd-acyl complexes **5a** and **5c** exhibit a *cis* coordination of the coordinating carbon atom with respect to the phosphine moiety, which is evidenced by $^{13}C\{^1H\}$NMR spectra, showing a singlet centred at 223.34 ppm and a doublet centred at 222.58 ppm ($^2J_{PC}$ = 8.0 Hz) for **5a** and **5c**, respectively. Interestingly, even in the presence of a (1:9) $^{13}CO/^{12}CO$ gas-mixture (total pressure (200 psi)), no $^{13}C\{^1H\}$ NMR signal, due to CO coordination to the palladium centre was observed. While compound **5c** undergoes methanolysis reaction at 90 ^oC, yielding methyl-acetate and the zwitterionic ligand **c**, which is

evidenced by a $^{31}P\{^{1}H\}$ NMR spectra, showing in CD_3OD a broad hump centred at -9.20 ppm at 90° C and in CD_2Cl_2 a 1:1:1 triplet centred at -10.80 ppm with a $^{1}J_{PD}$ of 92.0 Hz, **5a** undergoes methanolysis reaction already at room temperature yielding methyl-acetate and dimeric CO-bridged palladium(I) complexes. Based on $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra, structures as shown in **Scheme 10** are assigned to compounds **8a** and **9a**, respectively.

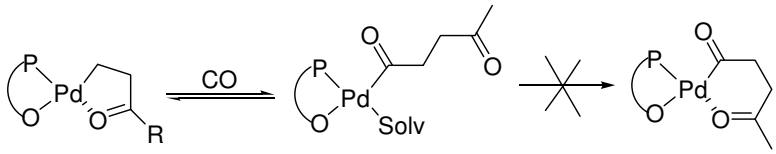


Scheme 10. Methanolysis reaction of compounds **5a** and **5c**

Once the CD_3OD solution of compound **5c** was obtained, excess CO was eliminated upon bubbling nitrogen through the solution, followed by bubbling ethene through the same solution for 10 minutes at room temperature yielding the first-generation Pd-β-chelate (**6c**) quantitatively as the only phosphorus containing compound (**Scheme 9**). The same synthetic procedure was employed for the 2:1:1 mixture of **5a**/**8a**/**9a** yielding a 1:1 mixture of **6a**/**8a**.

The NMR-spectroscopic data for both Pd-β-chelate complexes **6a** and **6c**, are in line with a *trans*-coordination of the carbonyl oxygen atom to the phosphorus

atom of the ligand, as shown in **Scheme 9**. The coordination of the carbonyl unit to the palladium atom is clearly evidenced by singlets in the $^{13}C\{^1H\}$ NMR spectra centred at 230.86 and 231.59 ppm for **6a** and **6c**, respectively. Furthermore concentrating the CD_3OD solution of both Pd-β-chelate complexes to dryness and acquiring IR spectra in CH_2Cl_2 shows in both cases a carbonyl stretching band at 1641 cm^{-1}, which clearly underscores the formation of Pd-β-chelates. Complex **6c** was then further converted into the second-generation Pd-acyl complex **7c** on successively bubbling nitrogen and CO through a CD_3OD solution of **6c** (**Scheme 11**).



6c **7c**

Solv = CD_3OD

Scheme 11. *in situ* synthesis of the second generation Pd-acyl complex **7c**

Compound **7c** is characterised by a singlet in the $^{31}P\{^1H\}$NMR spectrum, centred at 14.53 ppm, which is similar to the ^{31}P chemical shift obtained for the Pd-acyl complex **5c** at 13.60 ppm. The $^{13}C\{^1H\}$NMR spectrum shows for compound **7c** two signals, namely a doublet centred at 221.44 ppm with a $^2J_{PC}$ of 7.5 Hz, which corresponds to the carbonyl-unit directly bond to palladium and a singlet centred at 210.18 ppm, which corresponds to the carbonyl-unit, which is not directly bond to palladium, evidencing the lack of Pd-γ-chelate formation, due to the low Lewis acidity of the palladium centre in neutral Pd(P-O) complexes. As a consequence the de-carbonylation of Pd-acyl complexes yielding Pd-alkyl complexes is facilitated **Scheme 8** (**C**-**B**).[6d,6e]

Operando HP-NMR study

In an attempt of intercepting metallorganic species formed during the non-alternating CO-ethene copolymerisation reaction, catalysed by neutral Pd(P-O) complexes, *operando* HP-NMR experiments were carried out, employing the Pd-Me complexes **4a** and **4c** in the presence of a CO-ethene gas-ratio of 1:3. While a HPNMR experiment with pre-catalyst **4a** was carried out in CD_3OD, an analogous experiment was performed with pre-catalyst **4c** in the presence of a 3:1 (v:v) solvent-mixture of CF_3CH_2OH and C_6D_6 in order to avoid the precipitation of the polymeric material during the NMR experiment. A sequence of selected $^{31}P\{^1H\}$ NMR spectra for both studies are shown in **Figure 7** (for **4a**) and **Figure 8** (for **4c**).

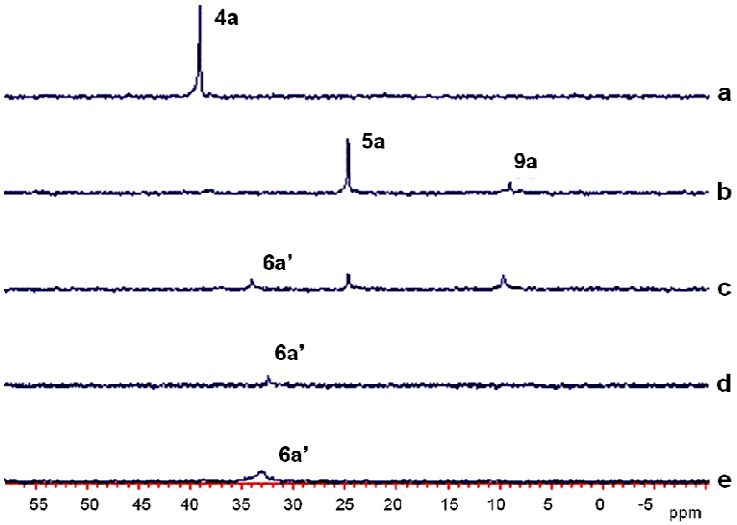


Figure 7. Variable–temperature $^{31}P\{^1H\}$ NMR study (sapphire tube, CD_3OD, 81.01 MHz) of the non-alternating CO-ethene copolymerisation reaction catalysed by pre-catalyst **4a**: (**a**) compound **4a** under nitrogen at RT; (**b**) under CO (200 psi) at RT.; (**c**) under CO (200 psi) and C_2H_4 (600 psi) at RT; (**d**) after 10 min at 110 ^oC; (**e**) after cooling to RT.

The $^{31}P\{^{1}H\}$ HP-NMR experiment carried out in CD_3OD with the neutral complex **4a** (**Figure 7**) shows for the latter complex a singlet, centred at 38.00 ppm at room temperature (**Figure 7**, trace **a**). On pressurising the solution with 200 psi of CO leads after 15 min at room temperature to a complete conversion of **4a** into the Pd-acyl complex **5a** and the dimeric palladium(I) complex **9a** (**Scheme 10)**. This latter complex stems from the methanolysis reaction of the Pd-acyl complex **5a**. Charging the sapphire tube with 600 psi of ethene at room temperature brings about the conversion of the Pd-acyl compound **5a** into Pd-β-chelates (**6a'**), featured by polymeric chains of different length, showing in the $^{31}P\{^{1}H\}$NMR spectrum a singlet, centred at 34.00 ppm (**Figure 7**, trace **c**), which resembles that found for the first-generation Pd-β-chelate (**6a**) (**Scheme 9**). Heating the NMR solution to 110 ^{o}C, shows the complete conversion of **5a** and **9a** into **6a'** (**Figure 7**, trace **d**), indicating that the dimeric Pd(I) complex is not a dead end of the CO-ethene copolymerisation reaction.[18] On cooling the NMR solution to room temperature the $^{31}P\{^{1}H\}$ NMR spectrum shows **6a'** as the only phosphorus containing compound. Performing an identical HP-NMR experiment in the presence of 20 equivalents of *p*-toluenesulfonic acid, shows the same sequence of metallorganic species during the HP-NMR study as in the absent of it.

An analogous HP-NMR experiment carried out with compound **4c** in a 3:1 solvent mixture of CF_3CH_2OH/C_6D_6 shows in the $^{31}P\{^{1}H\}$ NMR spectrum for **4c** a singlet centred at 27.9 ppm (**Figure 8**, trace **a**) at room temperature. On charging the sapphire tube with CO (200 psi) at room temperature brings about the complete conversion of the latter compound into the Pd-acyl complex **5c** (**Figure 8**, trace **b**),which shows a $^{31}P\{^{1}H\}$NMR signal centred at 0.20 ppm. At this point it is important to emphasis the fact that both the $^{31}P\{^{1}H\}$ and the $^{13}C\{^{1}H\}$NMR (Pd-*C*OCH_3) signal for the latter complex are shifted up-filed in this solvent mixture compared to the analogous chemical shifts observed in CD_3OD (TFE/C_6D_6: $^{31}P\{^{1}H\}$NMR: δ 0.2 ppm (s), $^{13}C\{^{1}H\}$NMR: δ 211.49 ppm (d),

^{2}J(PC) of 8.0 Hz; CD_3OD: $^{31}P\{^{1}H\}$NMR: δ 13.60 ppm (s), $^{13}C\{^{1}H\}$NMR: δ 222.58 ppm (d), ^{2}J(PC) of 8.0 Hz. Furthermore a parallel HPNMR experiment in the same solvent mixture employing a (1:10) gas-ratio between ^{13}CO and ^{12}CO at a total pressure of 200 psi, gives no hint for CO coordination to the metal centre of complex **5c**. Once compound **5c** was formed, the sapphire tube was pressurised with 600 psi of ethene, which brings about the conversion of the latter compound into Pd-β-chelates (**6c'**), featured in the $^{31}P\{^{1}H\}$NMR spectrum by a singlet, centred at 21.50 ppm (**Figure 8**, trace **c**). The $^{31}P\{^{1}H\}$NMR chemical shift of these latter species is almost identical to that observed for the first generation Pd-β-chelate (**6c**) (**Scheme 9**) in CD_3OD. Heating the solvent mixture to 110 ^{o}C (**Figure 8**, trace **d**) and then cooling it to room temperature (**Figure 8**, trace **e**) shows the Pd-β-chelates (**6c'**) as the only phosphorus containing species.

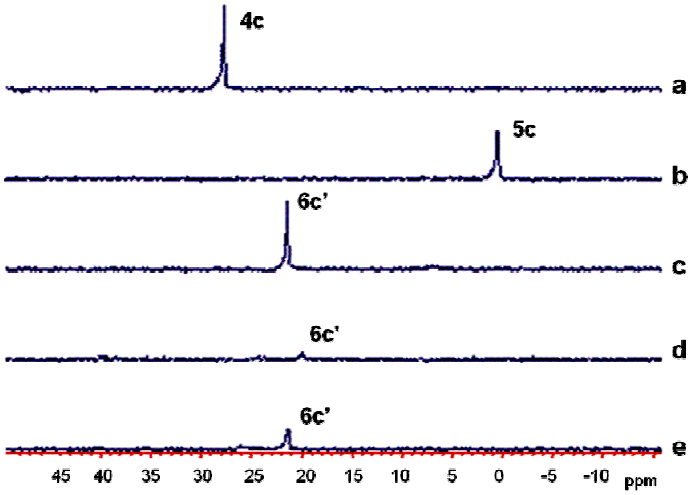


Figure 8. Variable–temperature $^{31}P\{^{1}H\}$ NMR study (sapphire tube, CF_3CH_2OH/C_6D_6 (v:v) (3:1), 81.01 MHz) of the non-alternating CO-ethene copolymerisation reaction catalysed by pre-catalyst **4c**: (**a**) compound **4c** under nitrogen at RT; (**b**) under CO (200 psi) at RT; (**c**) under CO (200 psi) and C_2H_4 (600 psi) at RT; (**d**) after 10 min at 110 ^{o}C; (**e**) after cooling to RT.

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4.1.3. Conclusions

The zwitterionic phosphine sufonate ligands 2-{bis(*o*-methoxyphenyl)phosphino}ethanesulfonic acid (**a**) and 3-{bis(*o*-methoxyphenyl)phosphino}propanesulfonic acid (**b**) were prepared using a simple synthetic procedure.

A comparison of the catalytic CO-ethene copolymerisation reactions, catalysed by neutral Pd(P-O) complexes bearing the flexible 2-{bis(*o*-methoxyphenyl)phosphino}ethanesulfonate and the rigid 2-{bis(*o*-methoxyphenyl)phosphino}benzenesulfonate, show that the former complexes lead to the formation of low-molecular weight copolymers, due to fast chain-transfer reactions, with an extra-ethene content in the polymeric chain up to 23.2 % on addition of *p*-toluensulfonic acid to the catalytic system, while the latter complexes are orders of magnitude more active yielding non-alternating CO-ethene copolymers with an extra-ethene incorporation up to 27.8 %.

Operando HP-NMR experiments of the copolymerisation reactions, catalysed by neutral Pd(P-O) complexes show the corresponding Pd-β-chelates as resting state of the copolymerisation reaction. Since Pd-γ-chelates are not formed in methanol with neutral Pd(P-O) complexes and CO does not coordinate to the palladium centre of Pd-acyl complexes, the decarbonylation reaction of the latter complexes increases with temperature favouring extra-ethene insertion into the growing polymeric chain and thus yielding non-strictly alternating polyketones.

4.1.4. Experimental section

General considerations

All reactions and manipulations were carried out under a nitrogen atmosphere by using Schlenk-type techniques. The solvents were generally distilled over dehydrating reagents and were deareated before use. The reagents were used as purchased from Aldrich or Fluka, unless stated otherwise. Ligand **c**[6a], PdCl(Me)(COD)[19] (COD = cycloocta-1,5-diene), [Pd(μ-Cl){η^1,η^2-C_8H_{12}OMe}$_2$][11] and **3c**[12] were prepared according to literature methods. All isolated solid samples were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Copolymerisation reactions were performed with a 200 mL stainless steel autoclave, constructed at the ICCOM-CNR (Florence, Italy), equipped with a magnetic drive stirrer and a home made temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure during the catalytic reactions. GC/MS analyses of the solutions were performed on a Shimadzu QP2010S apparatus equipped with a SPB-1 Supelco fused silica capillary column (30m, 0.25 mm i.d., 0.25 μm film thickness). Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{31}P NMR spectra were obtained on a Bruker ACP 200 and a Bruker Avance DRX-400 spectrometers or on a Varian Mercury VX 400 MHz and Varian Gemini 300 MHz spectrometers. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvents resonances (^{1}H and ^{13}C NMR) or 85% H_3PO_4 (^{31}P NMR). High pressure NMR experiments (HP-NMR) were carried out on Bruker ACP 200 using a 10mm sapphire NMR tube, which was purchased from Saphikon (Milford, NH), while the titanium high-pressure charging head was constructed at the ISSECC-CNR (Florence-Italy).[20] Elemental analyses were performed using either a Carlo Erba

Model 1106 or Model 1108 elemental analyser. Infrared spectra were recorded on a FT-IR Spectrum GX instrument (Perkin Elmer).

Syntheses

Synthesis of 2-{bis(*o*-methoxyphenyl)phosphino}ethanesulfonic acid (a)

To a solution of bis(*o*-methoxy)phenylphosphine[10] (1.00 g, 4.07 mmol) in deareated THF (50 ml) was added dropwise *n*-BuLi (3.1 mL, 4.9 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and was further stirred for 1 h in order to form the corresponding lithium salt. Afterwards the THF solution of the lithium salt was added to a flask containing the sodium salt of 2-bromoethane sulfonic acid (0.83 g, 3.9 mmol). The mixture was then allowed to stir for 1.5 h at room temperature. The reaction was quenched with water and the solvent evaporated to yield a slightly yellow solid, which was dissolved in water (20 ml) and then acidified with HCl (37% in water) to pH 2. The acqueous phase was extracted with dichloromethane (3 x 80 mL). Afterwards the combined organic phases were dried over $MgSO_4$ and the solvent was evaporated to yield a white powder.

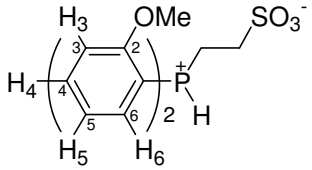

Figure 9. Ligand **a**

Ligand a: 746.3 mg (54%). $C_{16}H_{19}O_5PS.H_2O$ (372.35 g/mol): calc. C 51.61, H 5.68, S 8.61; found: C 52.11, H 5.42, S 8.49. $^{31}P\{^1H\}$ NMR (δ, 121.50 MHz, CD_2Cl_2, 21 °C) 0.5 (br s); ^{31}P NMR (δ, 121.5 MHz, CD_2Cl_2, -60 °C) 2.86 (d, $^1J_{PH}$ = 544,9 Hz); ^1H NMR (δ, 300.13 MHz, CD_2Cl_2, 21 °C) 2.96 (m, 1H, SCH_2), 3.04

(m, 1H, SCH_2), 3.17 (m, 2H, PCH_2), 3.90 (s, 6H, OCH_3), 7.08 (m, 2H, *H*-3), 7.19 (m, 2H, *H*-5), 7.60 (m, 2H, *H*-6), 7.72 (m, 2H, *H*-4); $^{13}C\{^1H\}$ NMR (δ, 75.00 MHz, $CDCl_3$, 21º C)16.7 (d, $^1J_{PC}$ = 56.1Hz, P*C*H_2), 44.2 (d, $^2J_{PC}$ = 3.9Hz, S*C*H_2), 56.7 (s, O*C*H_3), 104.4 (d, $^1J_{PC}$ = 90.25 Hz, *ipso*-*C*), 111.9 (d, $^3J_{PC}$ = 6.1Hz, *C*-3), 122.5 (d, $^3J_{PC}$ = 12.9Hz, *C*-5), 135.3 (d, $^2J_{PC}$ = 7.6Hz, *C*-6), 137.2 (s, *C*-4), 161.7 (s, *C*-2). See **Figure 9**

Synthesis of 3-{bis(*o*-methoxyphenyl)phosphino}propanesulfonic acid (b)

To a solution of bis(*o*-methoxy)phenylphosphine[10] (1.00 g, 4.07 mmol) in THF (50 ml) was added dropwise *n*-BuLi (3.1 mL, 4.9 mmol) at 0 ^oC. The reaction mixture was allowed to warm to room temperature and was further stirred for 1h in order to form the corresponding lithium salt. The THF solution of the latter salt was added to a flask containing the sodium salt fo 3-bromopropane sulfonic acid (0.88 g, 3.9 mmol).The mixture was then allowed to stir for 1.5 h at room temperature. The reaction was quenched with water and the solvent evaporated to yield a slightly yellow solid, which was dissolved in water (20 ml). The obtained solution was then acidified with HCl (37% in water) to pH 2 and extracted with dichloromethane (3 x 80 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated to yield a white powder, which was recrystallised from MeOH.

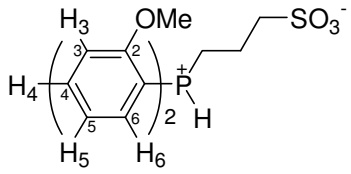

Figure 10. Ligand **b**

Ligand b: 589.1 mg (41%). $C_{17}H_{21}O_5PS$ (368.39 g/mol): calc. C 55.43, H 5.75, S 8.70; found: C 55.67, H 5.22, S 8.56. $^{31}P\{^1H\}$ NMR (δ, 121.5 MHz, $CDCl_3$, 21

^{o}C) -3.94 (br s); ^{31}P NMR (δ, 121.5 MHz, $CDCl_3$, -60 ^{o}C) -2.73 (d, $^{1}J_{PH}$ = 532.89 Hz); ^{1}H NMR (δ, 300.13 MHz, $CDCl_3$, 21 ^{o}C) 2.14 (m, 2H, PCH_2CH_2), 2.99 (t, $^{3}J_{HH}$ = 6.3 Hz, 2H, SCH_2), 3.10 (m, 2H, PCH_2), 3.87 (s, 6H, OCH_3), 7.00 (m, 2H, *H*-3), 7.10 (m, 2H, *H*-5), 7.59 (m, 2H, *H*-4), 7.79 (m, 2H, *H*-6); $^{13}C\{^{1}H\}$ NMR (δ, 75.00 MHz, $CDCl_3$, 21 ^{o}C) 17.94 (d, $^{1}J_{PC}$ = 49 Hz, PCH_2), 19.6 (s, PCH_2CH_2) 50.6 (d, $^{3}J_{PC}$ = 15.9, SCH_2), 56.9 (s, OCH_3), 105.2 (d, $^{1}J_{PC}$ = 83.4 Hz, *ipso-C*), 112.0 (d, $^{3}J_{PC}$ = 5.9 Hz, *C*-3), 122.3 (d, $^{3}J_{PC}$ = 12.9 Hz, *C*-5), 135.3 (d, $^{2}J_{PC}$ = 8.4 Hz, *C*-6), 135.8 (s, *C*-4), 161.9 (s, *C*-2). See **Figure 10**

Synthesis of Pd(COD-OMe)((*o*-MeO-C_6H_4)$_2$$PC_2H_4SO_3$) (1a)

NaH (3.6 mg, 0.15 mmol) was added to a Schlenk flask containing a solution of ligand **a** (49.6 mg, 0.14 mmol) in deareated dichloromethane (5 ml). After this solution had been stirred for 30 minutes [$Pd_2(\mu$-$Cl)_2\{\eta^1,\eta^2$-$C_8H_{12}OMe\}_2$] (39.2 mg, 0.07 mmol) was added under stirring at -20 ^{o}C. The reaction mixture was allowed to stir for 1h at RT, followed by concentration of the solution to a small volume (2 ml) and on addition of diethyl-ether (10 mL) compound **1a** precipitated as yellow solid, which was filtered off and dried under a flow of nitrogen.

Complex 1a: 51.2 mg (57%). $C_{25}H_{33}O_6PdPS$ (598.9 g/mol): calc. C 50.09, H 5.51, S 5.34; found: C 50.27, H 5.22, S 5.23. $^{31}P\{^{1}H\}$ NMR (δ, 121.5 MHz, $CDCl_3$, 21 ^{o}C) 20.3 (s); ^{1}H NMR (δ, 300.13 MHz, CD_2Cl_2, 21 ^{o}C) 1.79-2.82 (m, 10H, (COD)), 2.37 (s, 3H, OCH_3, (COD)), 3.01-3.12 (m, 4H, PCH_2CH_2S), 3.76 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 6.20 (m, 1H, PdC*H*), 6.45 (m, 1H, C*H,* (COD*)*), 6.92 (m, 2H, Ar-H), 7.15 (m, 2H, Ar-H), 7.42 (m, 2H, Ar-H), 7.62 (m, 2H, Ar-H); $^{13}C\{^{1}H\}$ NMR (δ, 75.00 MHz, $CDCl_3$, 21 ^{o}C) 23.50 (d, $^{1}J_{PC}$ = 29.6Hz, PCH_2), 25.25 (s, CH_2(COD)), 29.07 (s, CH_2(COD)), 31.58 (s, CH_2(COD)), 35.41 (s, CH_2(COD)), 41.4 (s, *C*H(COD)), 46.92 (s, SCH_2), 55.61 (s, OCH_3), 55.72 (s, OCH_3), 55.81 (s, OCH_3), 82.06 (s, Pd*C*H), 111.5 (d, $^{1}J_{PC}$ = 19.5Hz, *C*-ipso, Ar),

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120.30 (*C*, Ar), 121.24 (d, $^2J_{PC}$ = 7.95Hz, *C*, Ar), 121.63 (d, $^2J_{PC}$ = 10.8Hz, *C*, Ar), 122.20 (d, $^2J_{PC}$ = 7.35Hz, *C*, Ar), 133.25 (s, *C*, Ar), 134.57 (s, *C*, Ar), 161.9 (s, *C*, Ar)

Synthesis of Pd[(*o*-MeO-C_6H_4)$_2$$PC_2H_4SO_3$]$_2$ (2a)

In a Schlenk tube was dissolved $Pd(OAc)_2$ (11.3 mg, 0.05 mmol) in deareated MeOH (2 mL). To this solution was added ligand **a** (35.4 mg, 0.10 mmol) and the solution was then stirred at room temperature for 3 hours, during which the product precipitated as yellow powder, which was filtered off, washed with diethyl-ether (5 mL) and dried in a stream of nitrogen. The product was insoluble in common organic solvents. Even in DMSO a very low solubility of the compound was obtained.

Complex 2a: 26.4 mg (65%). $C_{32}H_{36}O_{10}P_2PdS_2$ (813.08 g/mol): cal. C 49.16, H 4.60; found: C 49.01, H, 4.58. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, $(CD_3)_2SO$, 21 ^oC) 32.28 (br s); ^1H NMR (δ, 400.13 MHz, $(CD_3)_2SO$, 21 ^oC) 2.80 (br m, 4H, CH_2P), 3.10 (br s, 4H, CH_2SO_3), 3.55-4.09 (br s, 12H, OCH_3), 6.15-7.74 (m, 14H, Ar-H), 9.10 (br. s, 2H, *o-H*)

Synthesis of Pd(COD-OMe)((*o*-MeO-C_6H_4)$_2$$PC_6H_4SO_3$) (1c)

NaH (8.9 mg, 0.37 mmol) was added to a Schlenk flask containing a solution of ligand **c** (148.9 mg, 0.37 mmol) in deareated dichloromethane (5 ml). After stirring the reaction solution for 30 minutes [$Pd_2(\mu$-Cl)$_2${η^1,η^2-C_8H_{12}OMe}$_2$] (100.8 mg, 0.18 mmol) was added at RT. The reaction mixture was allowed to stir for 1h at RT, followed by concentration of the solution to a small volume (2 ml) and addition of *n*-pentane (10 mL) in order to precipitate the product, which was filtered off, washed with *n*-pentane and dried under a flow of nitrogen, yielding complex **1c** as a pale yellow semi-crystalline solid.

Complex 1c: 162.9 mg (67%). $C_{29}H_{33}O_6PPdS$ (657.02 g/mol): calc. C 53.86, H 5.10; found: C 53.42, H, 5.01. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, $CDCl_3$, 21 °C) 8.20 (s); ^1H NMR (δ, 400.13 MHz, $CDCl_3$, 21 °C) 1.70-2.72 (m, 13H, (COD) + OC*H*$_3$), 2.42 (s, overlapped), 3.59 (s, 3H, OC*H*$_3$), 3.65 (s, 3H, OC*H*$_3$), 6.04 (m, 1H, (COD)), 6.72 (m, 1H, (COD)), 6.92-7.51 (m, 10H, Ar) 8.07 (dd, $^3J_{PH}$ = 12.4 Hz, $^3J_{HH}$ = 10.0 Hz, 1H, *o-H*), 8.16 (dd, $^3J_{PH}$ = 20.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, *o-H*); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, $CDCl_3$, 21 °C) 25.37 (s, *C*H$_2$(COD)), 28.62 (s, *C*H$_2$(COD)), 30.72 (s, *C*H$_2$(COD)), 35.26 (s, *C*H$_2$(COD)), 40.72 (s, *C*H(COD)), 54.82 (s, O*C*H$_3$), 55.27 (s, O*C*H$_3$), 55.54 (s, O*C*H$_3$), 81.55 (s, Pd*C*H), 111.24 (s, *C*, Ar), 114.70 (d, $^1J_{PC}$ = 52.0 Hz, *ipso-C*), 115.37 (d, $^1J_{PC}$ = 52.0 Hz, *ipso-C*), 117.08 (d, $^3J_{PC}$ = 9.2 Hz, *C*H), 120.85 (s, *C*, Ar), 121.14 (s, *C*, Ar), 121.42 (d, $^2J_{PC}$ = 12.1 Hz, *C*H), 127.85 (d, $^2J_{PC}$ = 10.62 Hz, *C*, Ar), 128.45 (s, *C*, Ar), 130.27 (s, *C*, Ar), 132.93 (s, *C*,Ar), 134.27 (s, *C*, Ar), 134.90 (s, *C*, Ar), 140.47 (d, $^2J_{PC}$ = 27.8 Hz, *C*, Ar), 147.90 (s, *C*, Ar), 160.04 (s, *C*, Ar), 161.06 (s, *C*, Ar).

Synthesis of [PdClMe(*o*-MeO-C$_6$H$_4$)$_2$PC$_2$H$_4$SO$_3$)](NHEt$_3$) (**3a**)

In a Schlenk flask containing deareated CH_2Cl_2 was added triethylamine (97.6 µL, 0.70 mmol) and ligand **a** (49.6 mg, 0.14 mmol). This solution was stirred for 15 min. at room temperature, followed by the addition of PdClMe(COD) (37.1 mg, 0.14 mmol). The reaction solution was allowed to stir for one hour at room temperature. Then the solution was filtered through a plug of celite, followed by the addition of *n*-hexane (20 mL) to cause the precipitation of the product, which was filtered off, washed with *n*-hexane and dried in a flow of nitrogen, yielding an off-white semi-crystalline product.

Complex 3a: 59.4 mg (73%). $C_{23}H_{37}ClNO_5PdPS$ (581.50 g/mol): cal. C 45.13, H 6.04: found: C 45.01, H 5.97. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 °C) 31.44 (s); ^1H NMR (δ, 400.13 MHz, CD_3OD, 21 °C) 0.37 (d, $^3J_{PH}$ = 2.2 Hz, 3H, PdC*H*$_3$), 1.33 (t, $^3J_{HH}$ = 7.2 Hz, 9H, NCH$_2$C*H*$_3$), 3.02 (m, 2H, SC*H*$_2$), 3.12 (m, 2H,

PCH_2), 3.22 (q, $^3J_{HH}$ = 7.2 Hz, 6H, NCH_2), 3.91 (s, 6H, OCH_3), 7.05 (m, 2H, Ar), 7.15 (m, 2H, Ar), 7.57 (m, 2H, Ar), 7.68 (m, 2H, Ar); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 °C) -0.20 (br s, PdCH$_3$), 7.87 (s, CH_2CH_3), 22.32 (d, $^1J_{PC}$ = 33.7 Hz, CH_2P), 46.48 (s, CH_2N), (SCH_2, overlapped signal), 55.12 (s, OCH$_3$), 111.31 (d, $^3J_{PC}$ = 4.3 Hz, *m-C*, Ar), 111.59 (d, $^1J_{PC}$ = 53.7 Hz, *ipso-C*, Ar),120.55 (d, $^3J_{PC}$ = 11.2 Hz, *m-C*, Ar), 133.25 (s, *o-C*, Ar), 135.81 (s, *p-C*, Ar); 160.62 (s, *C*, Ar).

Synthesis of [PdMe(L)]$_2$ (L = a, (4a); c, (4c))

In a Schlenk flask compounds (**3a**) or (**3c**) (0.20 mmol) were dissolved in deareated CH_2Cl_2 (5mL), followed by the addition of Ag(OTs) (OTs = *p*-toluenesulfonate) (58.6 mg, 0.21 mmol) at room temperature. The suspension was allowed to stir for half an hour and was then filtered through celite. The CH_2Cl_2 solution was washed with deareated water (3×5 mL) and then the organic phase separated, dried over Mg_2SO_4 and concentrated to dryness by means of a vacuum pump, obtaining an off-white solid in both cases. Both complexes were characterised in CD_3OD, were both of them a monomeric complexes, best described as PdMe(L)(CD_3OD).

Complex 4a: 37.9 mg (40%). $C_{34}H_{42}O_{10}Pd_2P_2S_2$ (949.58 g/mol): calc. C 43.02, H 4.42; found: C 42.91, H 4.37%. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 °C) 37.67 (s); ^1H NMR (δ, 400.13 MHz, CD_3OD, 21 °C) 0.11 (d, $^3J_{PH}$ = 1.2 Hz, 3H, PdCH_3), 3.06 (m, 2H, CH_2S), 3.12 (m, 2H, CH_2P), 3.90 (s, 6H, OCH_3), 7.04-7.65 (m, 8H, Ar); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 °C) -2.22 (s, PdCH$_3$), 22.99 (d, $^1J_{PC}$ = 35.2 Hz, PCH$_2$), 46.84(s, CH_2S), 54.78 (s, OCH$_3$), 111.31 (d, $^3J_{PC}$ = 4.3 Hz, *m-C*, Ar), 115.32 (d, $^1J_{PC}$ = 53.7 Hz, *ipso*-C, Ar),120.55 (d, $^3J_{PC}$ = 11.2 Hz, *m-C*, Ar), 133.25 (s, *o-C*, Ar), 136.91 (s, *p-C*, Ar), 160.36 (s, *C*, Ar)

Complex 4c: 36.6 mg (35%). $C_{42}H_{42}O_{10}Pd_2P_2S_2$ (1045.66 g/mol): calc. C 48.26, H 4.02; found: C 48.15, H 3.90%. $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 °C)

26.98 (s); ^{1}H NMR (δ, 400.13 MHz, CD_3OD, 21 ^{o}C) 0.18 (d, $^{3}J_{PH}$ = 0.8 Hz, 3H, PdCH_3), 3.69 (s, 6H, OCH_3), 7.05-7.61 (m, 11H, Ar), 8.02 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{PH}$ = 4.8 Hz, 1H, *o-H*); ^{13}C{^{1}H}NMR (δ, 100.62 MHz, CD_3OD, 21 ^{o}C) -0.63 (s, PdCH_3), 54.31 (s, OCH_3), 111.33 (d, $^{3}J_{PC}$ = 4.3 Hz, *m-C*, Ar), 115.37 (d, $^{1}J_{PC}$ = 61.4 Hz, *ipso-C*, Ar), 120.20 (d, $^{3}J_{PC}$ = 12.5 Hz, *m-C*, Ar), 126.80 (d, $^{3}J_{PC}$ = 8.3 Hz, *C*, Ar), 127.84 (d, $^{1}J_{PC}$ = 53.0 Hz, *ipso-C*, Ar), 128.74 (d, $^{3}J_{PC}$ = 8.2 Hz, *C*, Ar), 129.99 (s, *C*, Ar), 133.56 (s, *o-C*, Ar), 134.92 (s, *C*, Ar), 137.40 (s, *p-C*, Ar), 146.87 (d, $^{2}J_{PC}$ = 14 Hz, *C*, Ar), 160.44 (s, *C*, Ar)

***In situ* synthesis of Pd(COMe)(L)(CD_3OD) (L = a, (5a); b, (5c))**

In a Schlenk tube compounds **4a** and **4c** (0.05 mmol) were dissolved in deareated CD_3OD (1.5 mL). These solutions were transferred into a 5 mm NMR tube followed by bubbling CO through the solution at room temperature. In the case of **4a**, complete transformation into compound **5a** was achieved after 40 minutes under a concomitant formation of two palladium(I) complexes (**8a**/**9a**), while the analogous procedure applied to **4c**, yielded **5c** quantitatively after 10 minutes.

Selected spectroscopic data for 5a: ^{31}P{^{1}H} NMR (δ, 161.98 MHz, CD_3OD, 21º C) 23.66 (s); ^{1}H NMR (δ, 400.13 MHz, CD_3OD, 21 ^{o}C) 1.84 (d, $^{4}J_{PH}$ = 0.4 Hz, 3H, COCH_3); ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_3OD, 21 ^{o}C) 32.38 (d, $^{3}J_{PC}$ = 28.1 Hz, CO*C*H_3), 223.34 (s, *C*OCH_3).
Selected spectroscopic data for 8a: ^{31}P{^{1}H} NMR (δ, 161.98 MHz, CD_3OD, 21 ^{o}C) 8.09 (s); ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_3OD, 21 ^{o}C) 227.60 (s, *C*O).
Selected spectroscopic data for 9a: ^{31}P{^{1}H} NMR (δ, 161.98 MHz, CD_3OD, 21 ^{o}C) 8.55 (s); ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_3OD, 21 ^{o}C) 225.36 (s, *C*O).
Selected spectroscopic data for 5c: ^{31}P{^{1}H} NMR (δ, 161.98 MHz, CD_3OD, 21 ^{o}C) 13.60 (s); ^{1}H NMR (δ, 400.13 MHz, CD_3OD, 21 ^{o}C) 1.85 (d, $^{4}J_{PH}$ = 0.4 Hz,

3H, COCH_3); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 °C) 34.24 (d, $^3J_{PC}$ = 29.2 Hz, CO*C*H_3), 222.58 (d, $^2J_{PC}$ = 8.0 Hz, *C*OCH_3).

***In situ* syntheses of PdCH$_2$CH$_2$COMe(L) (L = a, (6a); b, (6c))**

In a Schlenk tube compound **4a** and **4c** (0.05 mmol) were dissolved in deareated CD_3OD (1.5 mL). These solutions were transferred into 5 mm NMR tubes. While the CD_3OD solution of ob **4a** was bubbled successively with CO for 40 min, with nitrogen for 2 min. and then with ethene for 20 min. obtaining a 1:1 mixture of **6a** and **8a**, the solution of **4c** was successively bubbled with CO for 10 min., with nitrogen for 2 min. and then with ethene for 2 min. to quantitatively transform the latter compound into **6c**. IR-spectroscopic data for **6a** and **6c** were obtained by evaporating the CD_3OD solutions of **6a**/**8a** and **6c** to dryness and dissolving the residuals in CH_2Cl_2.

Selected spectroscopic data for 6a: $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 °C) 32.80 (s); ^1H NMR (δ, 400.13 MHz, CD_3OD, 21 °C) 1.21 (td, $^3J_{HH}$ = 6.2 Hz, $^3J_{PH}$ = 2.4 Hz, 2H, PdCH_2), 2.30 (s, 3H, COCH_3), 2.81 (t, $^3J_{HH}$ = 6.2 Hz, 2H, COCH_2); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 °C) 19.80 (s, PdCH_2), 26.02 (s, CO*C*H_3), 49.47 (s, CO*C*H_2), 230.86 (s, *C*OCH_3); IR (CH_2Cl_2): ν(CO) = 1641 cm^{-1}.

Selected spectroscopic data for 6c: $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 °C) 21.73 (s); ^1H NMR (δ, 400.13 MHz, CD_3OD, 21 °C) 1.33 (td, $^3J_{HH}$ = 6.2 Hz, $^3J_{PH}$ = 2.6 Hz, 2H, PdCH_2), 2.36 (s, 3H, COCH_3), 2.84 (t, $^3J_{HH}$= 6.2 Hz, 2H, COCH_2); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 °C) 20.63 (s, PdCH_2), 26.34 (s, CO*C*H3), 49.80 (s, CO*C*H_2), 231.59 (s, *C*OCH_3); IR (CH_2Cl_2): ν(CO) = 1641 cm^{-1}.

***In situ* synthesis of $PdCOCH_2CH_2COMe(L)(CD_3OD)$ (L = c, (7c))**

A CD_3OD solution (1.5 mL) of compound **6c**, which was obtained as described above, was transferred into a 5 mm NMR tube. The solution was bubbled successively with nitrogen for 2 min. and CO for 10 minutes.

Selected spectroscopic data for 7c: $^{31}P\{^1H\}$ NMR (δ, 161.98 MHz, CD_3OD, 21 ^oC) 14.53 (s); ^1H NMR (δ, 400.13 MHz, CD_3OD, 21 ^oC) 2.02 (s, 3H, $COCH_3$), 2.18 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2CO), 2.61 (t, $^3J_{HH}$ = 6.6 Hz, 2H, $COCH_2$); $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_3OD, 21 ^oC) 28.28 (s, $COCH_3$), 36.97 (s, CH_2CO), 39.92 (d, $^3J_{PC}$ = 26.3 Hz, $PdCOCH_2$), 210.18 (s, $COCH_3$), 221.44 (d, $^2J_{PC}$ = 7.5 Hz, $COCH_2$)

Catalytic reactions

Catalytic reactions in MeOH or 2,2,2-trifluoroethanol (TFE) employing 1a, 1c, 4a and 4c as pre-catalysts

Typically, MeOH (50 mL) or TFE (50 mL), was introduced by suction into an autoclave (200 mL), previously evacuated by a vacuum pump, containing the catalyst precursor (0.012 mmol). When the catalytic reaction was performed in the presence of 1,4-benzoquinone (BQ) or *p*-toluenesulfonic acid, these latter compounds and the catalytic precursors were added together in the autoclave. The autoclave was then charged with the desired CO/C_2H_4 mixture to 600 psi at room temperature followed by heating to the desired temperature. Once the desired temperature was reached the total pressure of the gas mixture was equilibrated to 800 psi and stirring (1300 rpm) was started. After the desired reaction time, the autoclave was cooled by means of an ice-water bath and the gases released. Due to the much higher solubility of the copolymers in TFE compared to MeOH, two different work-up procedures were employed. While for

the catalytic experiments carried out in MeOH, the insoluble copolymer was filtered off, washed with MeOH, and dried under vacuum at 60 °C to constant weight, for the catalytic experiments carried out in TFE, the catalysis mixture was poured into a flask containing 100 mL of MeOH, followed by stirring the suspension for half an hour. Then the solid polymeric material was filtered off and dried under vacuum at 60 °C to constant weight.

Characterisation of the non-alternating CO-ethene copolymer

While the low-molecular weight copolymers were characterised by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy in a 1:3 (v:v) solvent mixture of 1,1,1,3,3,3-hexafluoroisopropanol-d_2 and C_6D_6, the high molecular weight non-alternating copolymers were analysed only by $^{13}C\{^{1}H\}$ NMR spectroscopy in a 1:3 (v:v) solvent mixture of 1,1,1,3,3,3-hexafluoroisopropanol and C_6D_6. The assignment of $^{1}H$and ^{13}C chemical shifts were based on literature reports.[6a]

NMR studies

***Operando* HP-NMR studies of 4a and 4c in CD_3OD and TFE/C_6D_6, respectively**

A 10 mm sapphire tube was charged with a solution of compound **4a** (**4c**) (0.03 mmol) in CD_3OD (2.0 mL) or a 3:1(v:v) mixture of TFE/C_6D_6 under nitrogen at room temperature and placed into a NMR probe at 20 °C. After $^{31}P\{^{1}H\}$ and ^{1}H (only for the study in CD_3OD) NMR spectra had been recorded, the sapphire tube was removed from the NMR probe, charged with CO to 200 psi, and then placed again into the NMR probe at 20 °C. After the NMR spectra had been recorded, the sapphire tube was removed from the NMR probe and charged with ethene to 800 psi, and placed again into the NMR probe at 20 °C. The reaction was followed by variable-temperature NMR spectroscopy in the

temperature range from 20 to 110 °C. After heating the NMR solution for 10 min at 110 °C, the sapphire was cooled to 20 °C, followed by the acquisition of NMR spectra. Once the sapphire tube was removed from the NMR probe, in the case of **4a** a layer of grey copolymer and a dark solution was observed while in the case of the NMR study employing **4c** as pre-catalyst an off-white layer of copolymer over a yellow solution was observed.

X-Ray crystallography

While suitable crystals of ligand **b** and compound **1a** were obtained by diffusion of diethylether in a saturated CH_3Cl solution of the corresponding compounds, crystals of compound **2a** were obtained by a slow diffusion of a methanol solution of $Pd(OAC)_2$ (0.05 mmol) into a CH_2Cl_2 solution of ligand **a** (0.1 mmol) at room temperature. Diffraction data of compounds **b** and **1a** were collected on a Bruker-Nonius diffractometer equipped with APPEX 2 4K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = 100 K), while for the collection of diffraction data for compound **2a** an Enraf Nonius CAD4 diffractometer with $Mo_{K\alpha}$ radiation and graphite monochromator was employed. The absorption correction was carried out for compounds **b** and **1a** were carried out using SADABS v.2.10 (2003) while for compound **2a** *psi*-scans were applied. The structures were solved by direct methods and refined by full-matrix F^2 refinement. Anisotropic thermal parameters were assigned to all non-hydrogen atoms, while hydrogen atoms were introduced in their calculated positions. All calculations were performed on a PC using SIR97[21a], SHELXL-97[21b] and ORTEP-3[21]

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New alkyl derivates phosphine sulfonate (P-O) ligands. Catalytic activity in Pd-catalysed Suzuki-Miyaura reaction in water

Abstract

In this chapter two novel bis(*o*-methoxyphenyl) phosphinoalkylsulfonate (P-O) ligands are applied in palladium-catalysed Suzuki-Miyaura cross-coupling reactions in neat water in conjunction with microwave heating. These ligands in combination with a palladium source yield efficient catalyst for the Suzuki-Miyaura reaction.

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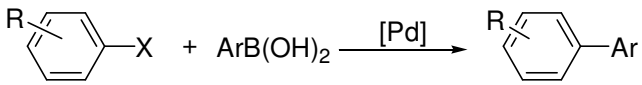
4.2.1. Introduction

The Suzuki-Miyaura coupling (**Scheme 1**) is one of the most useful methods for the formation of C-C bonds.[1] Due to the high solubility of arylboronic acids in water and the low toxicity of reagents and by-products as compared to other protocols,[1,2] the Suzuki coupling is an ideal reaction to be performed in water. Over the last years, several reports have appeared describing Suzuki coupling reactions catalysed by water-soluble Pd systems.[1a,3,4]

The fact that the ligands 2-{bis(o-methoxyphenyl)phosphino}ethanesulfonic acid (**a**) and 3-{bis(o-methoxyphenyl)phosphino}propanesulfonic acid (**b**) (section 4.1, **Figure 1**, pag. 171) are water-soluble and air stable, makes these ligands promising candidates to be use in the Suzuki-Miyaura cross-coupling reaction performed in non-deareated water



X=I, Br, Cl

Scheme 1. Suzuki-Miyaura cross-coupling reaction

4.2.2. Results and Discussion

Catalytic Suzuki-Miyaura cross-coupling experiments

The properties of these new ligands **a** and **b** makes water the solvent of choice for the performance of the catalytic Suzuki-Miyaura cross-coupling reaction. To the best of our knowledge, no diaryl alkyl phosphine sulfonate anionic ligand has ever been employed in such reaction in neat water.

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In **Table 1** are reported the results obtained for the Suzuki-Miyaura reaction between aryl bromides and aryl boronic acids in neat water and in open atmosphere.

Irrespective of the ligand employed, quantitative conversions were achieved when either 4-bromoacetophenone or bromobenzene were used for the catalytic cross-coupling reaction (entries 1-6), using only 0.05 mol% of palladium. On using the less reactive 4-bromoanisole, the catalytic conversions decrease slightly (entries 7-8) but they are still high.

Table 1. Palladium-catalysed S-M cross-coupling of aryl bromides R^1-Br and boronic acids R^2-$B(OH)_2$[a]

Entry	R^1	R^2	Conversion[b](%) [P-O] **a**	Conversion[b](%) [P-O] **b**
1	4-AcC_6H_4	Ph	>99	>99
2	4-AcC_6H_4	1-naphthyl	>99	>99
3	4-AcC_6H_4	4-FC_6H_4	>99	>99
4	4-AcC_6H_4	4-$MeOC_6H_4$	>99	>99
5	C_6H_4	4-FC_6H_4	>99	>99
6	C_6H_4	4-$MeOC_6H_4$	>99	>99
7	4-$MeOC_6H_4$	4-FC_6H_4	60	71
8	4-$MeOC_6H_4$	4-$MeOC_6H_4$	90	90

[a]Conditions: 0.05 mol% $Pd(OAc)_2$, T = 80 °C, t = 2 h, Solvent H_2O (3 ml), R^1-Br (1.5 mmol, R^2-$B(OH)_2$ (1.72 mmol), L/Pd (1/1), K_2CO_3 (3 mmol). [b]Conversion determined by GC and ^{1}H-NMR spectroscopy in $CDCl_3$

It is well known that microwave technology may be a successful technique for chemical syntheses.[5] Since this technique may shorten the reaction times of catalytic Suzuki-Miyaura couplings, especially in water,[6] some experiments with the present catalysts were performed in conjunction with microwave heating. The catalytic results of this study are summarised in **Table 2**. Under the catalytic conditions reported in **Table 2**, high conversions were obtained even in a very short time. When electron-poor aryl bromides were used as reagents,

conversions up to 96% were obtained in a reaction time of only 5 minutes (**Table 2**, entries 1-2 and entries 5-6) irrespective of the ligand used. Similar conversions were achieved with electron-rich aryl bromides prolonging the reaction time (10 min.) (**Table 2**, entries 3-4). As already shown (**Table 1**, entries 7-8), ligand **b**, containing a larger akyl chain, is slighty more active than ligand **a** (**Table 2**, entries 3-4). This ligand effect is put in evidence in entry 6 that shows how high conversions can be obtained even with a very small amounts of Pd complex (0.025 mol%).

Table 2. Palladium-catalysed S-M cross-coupling of aryl bromides R^1-Br and boronic acids R^2-$B(OH)_2$ promoted by microwave heating[a]

Entry	[P-O]	t (min.)	mol% Pd	R^1	R^2	Conv.(%)[b]
1	**a**	5	0.05	4-AcC_6H_4	1-naphthyl	87
2	**a**	5	0.05	4-AcC_6H_4	F-C_6H_4	96
3	**a**	10	0.05	4-$MeOC_6H_4$	1-naphthyl	72
4	**b**	10	0.05	4-$MeOC_6H_4$	1-naphthyl	86
5	**b**	5	0.05	4-AcC_6H_4	Ph	90
6	**b**	5	0.025	4-AcC_6H_4	Ph	90

[a]Conditions: microwave heating with cooling, cat. $Pd(OAc)_2$/[P-O], L/Pd (1/1), T = 150 °C, (300 w), Solvent H_2O (3 ml), R^1-Br (1.5 mmol), R^2-$B(OH)_2$ (1.72 mmol), K_2CO_3 (3 mmol). [b]Conversion determined by GC.

In the light of the results obtained with aryl bromides, ligands **a** and **b** were tested with the much less reactive and less expensive 4-chloroacetophenone substrate. The results obtained are shown in **Table 3**.

Table 3. Palladium-catalysed S-M cross-coupling of aryl chlorides R^1-Cl and boronic acids R^2-$B(OH)_2$ promoted by microwave heating[a]

Entry	[P-O]	mol% Pd	R^1	R^2	Conv.(%)[b]
1	**a**	1.0	4-AcC_6H_4	Ph	45
2	**a**	2.0	4-AcC_6H_4	1-naphthyl	60
3	**a**	1.0	4-AcC_6H_4	4-$MeOC_6H_4$	45
4	**b**	0.2	4-AcC_6H_4	Ph	30
5	**b**	0.2	4-AcC_6H_4	2-formylphenyl	56

[a]Conditions: microwave heating with cooling, cat. $Pd(OAc)_2$/[P-O], L/Pd (1/1), T = 150 °C, (300 w), Solvent H_2O (3 ml), t = 10 min., R^1-Cl (1.5 mmol), R^2-$B(OH)_2$ (1.72 mmol), L/Pd (1/1), K_2CO_3 (3 mmol). [b]Conversion determined by GC.

Conversions up to 60 % were achieved using ligand **a** (**Table 3**, entry 2) with 2 mol% of Pd complex, while for ligand **b** conversions up to 56 % were obtained with 0.2 mol% of Pd complex (entry 5).

4.2.3. Conclusions

Both ligands **a** and **b** have been succcesfully used in conjuntion with $Pd(OAc)_2$ in the Suzuki-Miyaura cross-coupling reaction of aryl bromides as well as aryl chlorides in neat and non-deareated water under either, conventional and microwave heating.

4.2.4. Experimental Section

General Considerations

Deuterated solvents (dichloromethane-d_2 or chloroform-d_1) were used as purchased from Sigma-Aldrich. Commercial reagents were used as supplied, unless otherwise stated. ^{1}H-NMR spectra (chemical shifts relative to residual solvent), were recorded on a Varian Mercury VX 400 MHz or Varian Gemini 300

MHz spectrometer. Gas cromatografy analyses were run on a Hewlett-Packard HP 5890A instrument equipped with a Hewlett-Packard HP 366 series II integrator, using an HP-5(25 m x 0.25 mm d. i.). Microwave experiments were performed in a CEM microwave Discover model.

Catalysis

In a 25 mL round botton flask was added ligand **a** or **b** (0.05 mol%) to a solution of K_2CO_3 (3 mmol) in 3 mL of non-deareated water. This mixure was allowed to stirr for 5 minutes. Afterwards were added successively aryl bromide (1.5 mmol), arylboronic acid (1.72 mmol) and $Pd(OAc)_2$ (0.05 mol%). After stitting the solution at 80 ^oC for 2 h, the reaction was quenched by cooling it by means of an ice-bath. In those reactions were microwave heating was employed, the water solution was heated to 150 ^oC for 5 or 10 minutes, followed by quenching the reaction with an ice-bath. The organic product was extracted with CH_2Cl_2 (3 x 15 mL) and the organic extracts were dried over magnesium sulfate, followed by concentration of the solution to dryness. The catalytic conversion, which is reported as average value of two analyses, was estimated by GC or ^{1}H-NMR spectroscopy.

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Everything is interesting: not everything is important

J.Meurig Thomas

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Concluding remarks

As described in *Chapter 1*, the objectives in the present thesis are: 1) the elucidation of the effect of the *o*-methoxy group introduced on the P-aryl rings of various diphosphine ligands in the palladium catalysed copolymerisation reaction of carbon monoxide and ethene and 2) the synthesis of new phosphine sulfonated ligands and their application in the less well known palladium catalysed non-alternating copolymerisation of carbon monoxide and ethene. Furthermore, the phosphine sulfonated ligands were applied in the palladium catalysed Suzuki-Miyaura cross-coupling reaction.

To reach these objectives, a large number of synthesis, studies of characterisation, catalytic reactions and high pressure NMR experiments were carried out.

In *Chapter 2*, two diphosphine ligands namely, 1,2-bis(di(2-methoxyphenyl)phosphino)ethane (*o*-MeO-dppe) and 1,3-bis(di(2-methoxyphenyl)phosphino)propane (*o*-MeO-dppp) were synthesised trough a new synthetic protocol. Neutral and cationic palladium(II) complexes were synthesised and used as precatalysts in the palladium catalysed copolymerisation reaction of carbon monoxide and ethene in various reaction media. These ligands were compared with their phenyl counterparts in order two know more about the effect of the *o*-methoxy groups in the palladium catalysed CO/ethene. For this purpose, *in situ* HP-NMR experiments were carried out. It was found that irrespective of the reaction medium, the palladium(II) catalysts containing the dppp-like chelating diphosphines provide higher productivities as well as higher molecular weight polyketones as compared to the dppe-like counterparts. In 2,2,2-trifluoroethanol (TFE) was found that the *o*-methoxy oxygen atoms of either *o*-MeO-dppp or *o*-MeO-dppe ligands, produce a retardant effect on the propagation rate. This effect could be

due to the formation of an effective web of hydrogen bonding interactions with solvent molecules. As a result of the increased congestion at the metal centre, a slower diffusion of the monomers would take place. *In situ* high-pressure NMR studies have evidenced that the presence of *o*-MeO substituents on the P-aryl rings affects the kinetics of the CO/ethene copolymerisation. The rate of carbonylation of the β-keto chelates was found to be limited by the palladium(alkyl)(CO) migratory insertion, which makes the overall copolymerisation process independent of the CO pressure, at least in the range of the partial CO pressures investigated (5-30 bar).

In *chapter 3*, the synthesis of a new diphosphine ligands namely, *rac*-2,4-bis(di(2-methoxyphenyl)phosphino)pentane (*rac-o*-MeO-bdpp) as well as the synthesis of the corresponding palladium dichloride and palladium diacetate complexes were carried out. Since the objective of the *chapter 3* was to compare the backbone rigidity in the palladium catalysed copolymerisation reaction of carbon monoxide and ethene, this ligand was compared with the more rigid ligand 6,7–di(di-2-methoxyphenyl)phosphinyl-2,2,4,4-tetra(di-2-methoxyphenyl) $2\lambda^4,4\lambda^4$ diphosphoniumbicyclo[3.1.1]heptane-bis-(PF_6) in different reaction media. It was found that the polyketone products produced with the phosphine catalysts show number-average molecular weights up to five times bigger than those obtained with the diphosphonium-diphosphine catalysts. The results have been interpreted in terms of faster chain-transfer rate due to the electronic and steric properties of the diphosphonium diphosphine ligand.

In *chapter 4*, new phosphine sulfonated ligands and neutral and cationic palladium(II) complexes were synthesised and characterised. These ligans were used for the non-alternating palladium catalysed copolymerization of carbon monoxide and ethene and compared with other more rigid phosphine sulfonated ligands from a mechanistic and catalytic point of view. It shows that

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the complexes with the new phosphine sulfonated and more flexible ligand lead to the formation of low molecular weight copolymers, due to fast chain-transfer reactions, with an extra-ethene insertion in the growing polymer chain up to 23.2 % on addition of *p*-toluensulfonic acid, while the complexes containing the more rigid phosphine sulfonated ligand are orders of magnitude more active yielding non-alternating CO-ethene copolymers with an extra-ethene incorporation up to 27.8 %.

Operando HP-NMR experiments with both types of pre-catalyst have shown the corresponding Pd-*β*-chelates as resting state of the copolymerisation reaction, catalysed by neutral Pd(P-O) complexes.

In addition, due to the properties of these ligands, they were applied successfully in the Suzuki cross-coupling reaction of aryl –bromides and –chlorides under microwave conditions in neat water

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CERTIFICAN:

Que la memoria que lleva por título "PALLADIUM COMPLEXES CONTAINING DIPHOSPHINE AND SULFONATED PHOSPHINE LIGANDS FOR C-C BOND FORMING REACTIONS. CATALYTIC AND MECHANISTIC STUDIES", que presenta Eduardo J. García Suárez para obtener el grado de Doctor en Química, ha sido realizada bajo nuestra dirección en el Departament de Química Física i Inorgànica de la Universitat Rovira i Virgili.

Tarragona, Mayo de 2007

Prof. Dra. Carmen Claver

Dr. Claudio Bianchini

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Una vez conseguida mí licenciatura en química por la Universidad de Oviedo, la primera oportunidad de adentrarme en el mundo de la investigación me la dieron en Oviedo en el Instituto del Carbón (INCAR) de la mano de la Dra. Ana Beatriz García, en cuyo grupo estuve unos 10 meses, por eso mi primer agradecimiento va para ella, ya que si ahora mismo estoy a punto de presentar mi tesis en buena medida es gracias a esa primera oportunidad. Durante mi estancia en el INCAR solo puedo decir que me encontré con gente magnífica, para todos ellos un gran abrazo en especial para Miguelín y Davicín (ellos saben porque, ¡no! no es por lo que me habéis hecho tamizar).

Después de este primer contacto con la investigación y el laboratorio me decidí a irme unos meses fuera de España (por saber si había algo más del otro lado de la frontera de mi Asturias, simple curiosidad) por ello me decidí a solicitar una beca Marie Curie, con tan buena suerte que fui aceptado en el grupo del Dr. Claudio Bianchini en el “Istituto di Chimica dei Composti Organometallici” de Florencia (ICCOM), para trabajar durante 9 meses en el proyecto “POLYCAT”. Mis primeros días en Florencia, no lo puedo negar, fueron duros, una ciudad distinta, unas costumbres distintas, una lengua distinta, a mas de 1800 Km de

casa, además llegué justo en el momento que el grupo del Dr. Claudio Bianchini se mudaba de edificio, y lógicamente en ese momento la gente estaba inmersa en la mudanza. Pero bueno, pasados esos primeros días, frenéticos para todos, tuve una muy buena acogida y empecé a trabajar bajo la tutela del Dr. Werner Oberhauser al que debo agradecer la paciencia que tuvo conmigo en un primer momento para enseñarme las técnicas básicas de trabajo en el laboratorio pues la química organometálica para mi era una gran desconocida.

Después de 6 meses de trabajo en el ICCOM, en todo ese tiempo ya me desenvolvía en el laboratorio e incluso había aprendido Italiano, hablando con el Dr. Claudio Bianchini surgió la posibilidad de realizar la tesis doctoral, en un principio tuve mis dudas pero dada la excelente experiencia vivida hasta ese momento no tarde mucho en aceptar la propuesta y enseguida el Dr. Claudio Bianchini me puso en contacto con la Prof. Carmen Claver de la URV de Tarragona, puesto que la idea de realizar la tesis era a través de una colaboración entre el ICCOM y el grupo OMICH de la Prof. Carmen Claver. Después de intercambiar varios e-mail con la Prof. Carmen Claver, se decidió que empezaría a hacer esta tesis doctoral que ahora presento como una colaboración entre el ICCOM donde pasaría los dos primeros años y el grupo OMICH donde actualmente me encuentro realizando mi tesis. Aunque la decisión de realizar la tesis no fue fácil, me iba a Italia solo 9 meses!!!!, no me arrepiento en absoluto de tomar la decisión de hacerla, gracias a ello he conocido a gente que verdaderamente vale la pena.

Ahora os preguntareis ¿todo este rollo para qué? Pues todo este rollo para decir que todo en la vida tiene sentido y a veces un simple gesto o una simple acción trae consigo desenlaces tan gratos e inesperados como éste. Además me sirve para agradecer todo lo que ha hecho en mi favor el Dr. Claudio Bianchini, director del ICCOM-CNR Firenze y excelente persona, dándome la

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Memoria presentada por

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